

# Palladium(II) and Gold(I) Complexes of a New O-Functionalized N-Heterocyclic Carbene Ligand: Synthesis, Structures, and Catalytic Application

Lipika Ray,<sup>†</sup> Mobin M. Shaikh,<sup>‡</sup> and Prasenjit Ghosh<sup>\*,†</sup>

Department of Chemistry and National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

Received September 12, 2006

Synthetic and structural studies of Pd(II) and Au(I) complexes of a new O-functionalized N-heterocyclic carbene ligand, namely, 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene, are reported. Specifically, the N-heterocyclic carbene precursor 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazolium bromide (**1a**) was synthesized by the reaction of 2-methoxybenzyl bromide and *tert*-butylimidazole in 44% yield. The Au(I) and Pd(II) complexes [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**) and [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]<sub>2</sub>PdCl<sub>2</sub> (**1d**) were prepared in 77% and 89% yields, respectively, by the commonly used silver carbene transfer route from the silver complex {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]<sub>2</sub>Ag}<sup>+</sup>Br<sup>−</sup> (**1b**). The silver complex **1b** was in turn synthesized from the reaction of **1a** with Ag<sub>2</sub>O. The molecular structures of the complexes **1c** and **1d** have been determined by X-ray diffraction studies, which revealed that the gold complex **1c** possessed a linear geometry while the palladium complex **1d** had a trans-square-planar geometry at their respective metal centers. The Pd(II) complex **1d** was found to be an efficient catalyst for Suzuki–Miyaura type cross-coupling reactions of phenylboronic acid and aryl halides (ArX, X = Br, I) in high yields and turnover numbers (up to 109 600).

## Introduction

Being central to many important cross-coupling reactions such as Hiyama,<sup>1</sup> Kumada,<sup>2</sup> Negishi,<sup>3,4</sup> Suzuki,<sup>5</sup> and Stille<sup>6–8</sup> reactions, Pd has revolutionized transition-metal-mediated C–C bond forming reactions in a big way over the last three decades and is now duly recognized for its catalytic utility in synthetic

organic chemistry. Its versatility, ease of use, and efficiency are key factors that have brought such unprecedented success in metal-mediated cross-coupling reactions.<sup>9</sup> Though the frequently used Pd precatalysts are still the phosphine-based ones such as [Pd(PPh<sub>3</sub>)<sub>4</sub>],<sup>10</sup> a growing number of reports of N-heterocyclic carbene based analogues have been emerging lately.<sup>11–14</sup> Despite significant advancements reported for phosphine-based systems,<sup>15,16</sup> there remains a need for more user-friendly precatalysts, as the phosphine-based species are expensive, sensitive to air, and difficult to handle and thus are of limited availability.<sup>9</sup> N-heterocyclic carbenes (NHCs) provide a viable alternative, as they are better  $\sigma$ -donors and yield precatalysts that are more stable to air, moisture, and heat and are more tolerant toward oxidizing conditions than their

\* To whom correspondence should be addressed. E-mail: pghosh@chem.iitb.ac.in. Fax: +91-22-2572-3480.

<sup>†</sup> Department of Chemistry.

<sup>‡</sup> National Single Crystal X-ray Diffraction Facility.

(1) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918–920.  
(2) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374–4376.

(3) (a) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821–1823. (b) King, A. O.; Okukado, N.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1977**, 683–688.

(4) (a) Kondolff, I.; Doucet, H.; Santelli, M. *Organometallics* **2006**, *25*, 5219–5222. (b) Genov, M.; Fuentes, B.; Espinet, P.; Pelaz, B. *Tetrahedron: Asymmetry* **2006**, *17*, 2593–2595. (c) Shimizu, H.; Manabe, K. *Tetrahedron Lett.* **2006**, *47*, 5927–5931.

(5) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437–3440.

(6) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636–3638.

(7) Ozawa, F.; Yoshifuji, M. *Dalton Trans.* **2006**, 4987–4995.

(8) (a) Nakao, Y.; Satoh, J.; Shirakawa, E.; Hiyama, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 2271–2274. (b) Heureux, N.; Marchant, M.; Maulide, N.; Berthon-Gelloz, G.; Hermans, C.; Hermant, S.; Kiss, E.; Leroy, B.; Wasnaire, P.; Markó, I. E. *Tetrahedron Lett.* **2005**, *46*, 79–83. (c) Konno, T.; Takehana, T.; Chae, J.; Ishihara, T.; Yamanaka, H. *J. Org. Chem.* **2004**, *69*, 2188–2190.

(9) (a) César, V.; Bellemin-Lapponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619–636. (b) Cavell, K. J.; McGuinness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671–681. (c) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239–2246. (d) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247–2273. (e) Perry, M. C.; Cui, X.; Burgess, K. *Tetrahedron: Asymmetry* **2002**, *13*, 1969–1972. (f) Herrmann, W. A.; Öfele, K.; Presysing, D. v.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229–248. (g) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309.

(10) Malatesta, L.; Angoletta, M. *J. Chem. Soc.* **1957**, 1186–1188.

(11) Frisch, A. C.; Rataboul, F.; Zapf, A.; Beller, M. *J. Organomet. Chem.* **2003**, *687*, 403–409.

(12) (a) Frey, G. D.; Schütz, J.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2005**, *24*, 4416–4426. (b) Herrmann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93–96.

(13) Gstöttmayr, C. W. K.; Böhm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363–1365.

(14) (a) Navarro, O.; Marion, N.; Scott, N. M.; González, J.; Amoroso, D.; Bell, A.; Nolan, S. P. *Tetrahedron* **2005**, *61*, 9716–9722. (b) Singh, R.; Viciu, M. S.; Kramareva, N.; Navarro, O.; Nolan, S. P. *Org. Lett.* **2005**, *7*, 1829–1832. (c) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046–5047. (d) Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752–3755. (e) Viciu, M. S.; Navarro, O.; Germann, R. F.; Kelly, R. A., III; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629–1635. (f) Viciu, M. S.; Kelly, R. A., III; Stevens, E. D.; Naud, F.; Studer, M.; Nolan, S. P. *Org. Lett.* **2003**, *5*, 1479–1482.

(15) Zapf, A.; Jackstell, R.; Rataboul, F.; Riermeier, T.; Monsees, A.; Fuhrmann, C.; Shaikh, N.; Dingerdissen, U.; Beller, M. *Chem. Commun.* **2004**, 38–39.

(16) (a) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696. (b) Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 13028–13032.

Scheme 1

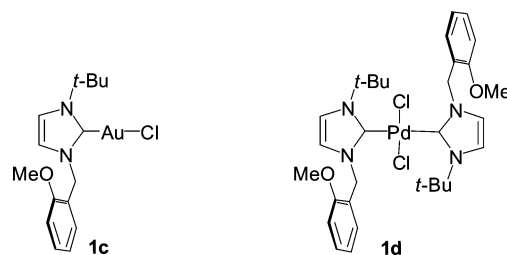
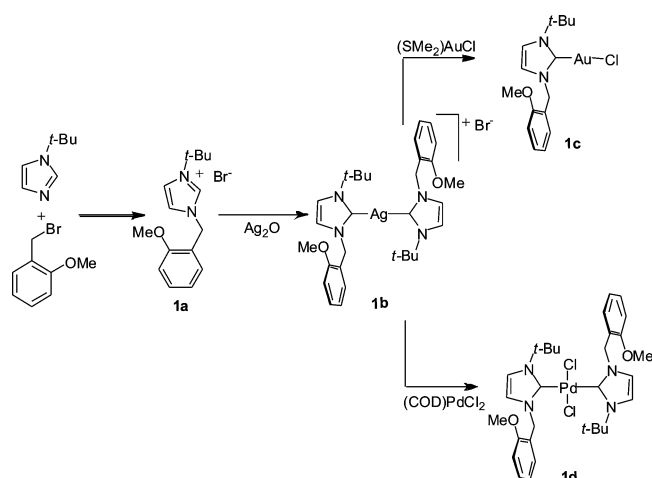


Figure 1.

phosphine counterparts. More importantly, the phosphines, apart from being expensive, are also required in excess quantities, as they often exhibit leaching of bare metals from the soluble precatalysts and also show considerable P–C bond cleavage at elevated temperatures.<sup>14a,17</sup> The N-heterocyclic carbenes, however, do not suffer from such shortcomings and thus are not needed in excess during catalysis. Significant improvements have been reported on the ancillary ligand design front, both for the in situ generation of catalysts<sup>17,18</sup> as well as for the well-defined catalysts.<sup>12–14</sup> As the ligand-assisted catalysis (LAC) involving in situ generation of catalysts suffers from many limitations such as uncertainty in stoichiometry and composition of the active species, difficulty in controlling the catalysis rate and catalyst efficiency, and unnecessary waste of precious Pd and NHC precursors and poses difficulties in the mechanistic understanding of the results, we became interested in designing well-defined precatalysts for our study. Furthermore, well-defined catalysts display shorter reaction times<sup>19</sup> and also reduce unwanted side reactions.<sup>14a</sup>

The Suzuki–Miyaura reaction offers a powerful and general methodology for the construction of C–C bonds and is perhaps the most widely used transition-metal-mediated cross-coupling reaction today.<sup>20</sup> The popularity of the Suzuki–Miyaura reaction is due to the ready availability of reactants that are nontoxic and air- and water-stable, its simplicity of use, ease of waste disposal, and, more importantly, its extreme versatility and high regio- and stereoselectivity.<sup>21</sup> It is worth noting that recently several highly active Pd precatalysts supported over N-heterocyclic carbenes have been reported by Herrmann<sup>13</sup> and Organ.<sup>19</sup>

The central theme of one of our core program revolves around designing N-heterocyclic carbene based complexes of late transition metals for their utility in chemical catalysis. In this regard, we have recently reported several Ag–NHC com-

pounds<sup>22</sup> and the first example of a Au–NHC-based initiator<sup>23</sup> for the bulk ring-opening polymerization of L-lactide. Our motivation in this program is derived from the exceptional success exhibited by N-heterocyclic carbenes in the realm of chemical catalysis, as they have found applications in a wide gamut of important transformations such as olefin metathesis,<sup>24</sup> hydrogenation,<sup>25</sup> hydroformylation,<sup>26</sup> hydrosilylation,<sup>27</sup> hydroboration,<sup>28</sup> carbene-transfer reactions,<sup>29</sup> etc. in addition to the C–C bond forming reactions<sup>12–14</sup> discussed earlier. As the role played by N-heterocyclic carbenes has thus far been very promising in the development of Pd-based precatalysts for cross-coupling reactions,<sup>9</sup> we set out to explore the utility of other new Pd–NHC complexes in the coupling reactions. Specifically, we decided to synthesize Pd complexes supported over new functionalized N-heterocyclic carbenes in order to study their catalytic potential in C–C bond forming reactions.

In this contribution, we report the Pd–NHC complex [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]<sub>2</sub>PdCl<sub>2</sub> (**1d**), which displays high activity toward Suzuki–Miyaura type cross-coupling reactions of phenylboronic acid and aryl halides (ArX,

(22) (a) Samantaray, M. K.; Katiyar, V.; Roy, D.; Pang, K.; Nanavati, H.; Stephen, R.; Sunoj, R. B.; Ghosh, P. *Eur. J. Inorg. Chem.* **2006**, 2975–2984. (b) Samantaray, M. K.; Roy, D.; Patra, A.; Stephen, R.; Saikh, M.; Sunoj, R. B.; Ghosh, P. *J. Organomet. Chem.* **2006**, 691, 3797–3805. (c) Samantaray, M. K.; Katiyar, V.; Pang, K.; Nanavati, H.; Ghosh, P. *J. Organomet. Chem.*, published online Dec. 23, 2006.

(23) Ray, L.; Katiyar, V.; Raihan, M. J.; Nanavati, H.; Shaikh, M. M.; Ghosh, P. *Eur. J. Inorg. Chem.* **2006**, 3724–3730.

(24) (a) Streuff, J.; Mu  iz, K. *J. Organomet. Chem.* **2005**, 690, 5973–5978. (b) Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, 19, 1194–1197.

(25) (a) Messerle, B. A.; Page, M. J.; Turner, P. *Dalton Trans.* **2006**, 3927–3933. (b) Kuhl, S.; Schneider, R.; Fort, Y. *Organometallics* **2003**, 22, 4184–4186. (c) Dioumaev, V. K.; Szalda, D. J.; Hanson, J.; Franz, J. A.; Bullock, R. M. *Chem. Commun.* **2003**, 1670–1671. (d) V  zquez-Serrano, L. D.; Owens, B. T.; Buriak, J. M. *Chem. Commun.* **2002**, 2518–2519. (e) Lee, H. M.; Jiang, T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, 20, 1255–1258. (f) Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, 123, 8878–8879.

(26) (a) Bortenschlager, M.; Sch  tz, J.; von Preysing, D.; Nuyken, O.; Herrmann, W. A.; Weberskirch, R. *J. Organomet. Chem.* **2005**, 690, 6233–6237. (b) van Rensburg, H.; Tooze, R. P.; Foster, D. F.; Slawin, A. M. Z. *Inorg. Chem.* **2004**, 43, 2468–2470.

(27) (a) Mas-Mara, E.; Sana  , M.; Peris, E. *Inorg. Chem.* **2005**, 44, 9961–9967. (b) Thangavelu, G.; Andavan, S.; Bauer, E. B.; Letko, C. S.; Hollis, T. K.; Tham, F. S. *J. Organomet. Chem.* **2005**, 690, 5938–5947. (c) Berthon-Gelloz, G.; Buisine, O.; Bri  re, J.-F.; Michaud, G.; St  rin, S.; Mignani, G.; Tinant, B.; Declercq, J.-P.; Chapon, D.; Mark  , I. E. *J. Organomet. Chem.* **2005**, 690, 6156–6168. (d) Mas-Mara, E.; Poyatos, M.; Sanati, M.; Peris, E. *Inorg. Chem.* **2004**, 43, 2213–2219. (e) Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, 23, 1157–1160. (f) Park, K. H.; Kim, S. Y.; Son, S. U.; Chung, Y. K. *Eur. J. Org. Chem.* **2003**, 22, 4341–4345. (g) Duan, W.-L.; Shi, M.; Rong, G.-B. *Chem. Commun.* **2003**, 2916–2917. (h) Marko, I. E.; St  rin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinanti, B.; Declercq, J.-P. *Science* **2002**, 298, 204–206. (i) Dioumaev, V. K.; Bullock, R. M. *Nature* **2000**, 424, 530–532.

(28) Grasa, G. Moore, Z.; Martin, K. L.; Stevens, E. D.; Nolan, S. P.; Paquet, V.; Lebel, H. *J. Organomet. Chem.* **2002**, 658, 126–131.

(29) Frutos, M. R.; Belderrain, T. R.; Fr  mont, P. de, Scott, N. M.; Nolan, S. P.; D  az-Requejo, M. M.; P  rez, P. *J. Angew. Chem., Int. Ed.* **2005**, 44, 5284–5288.

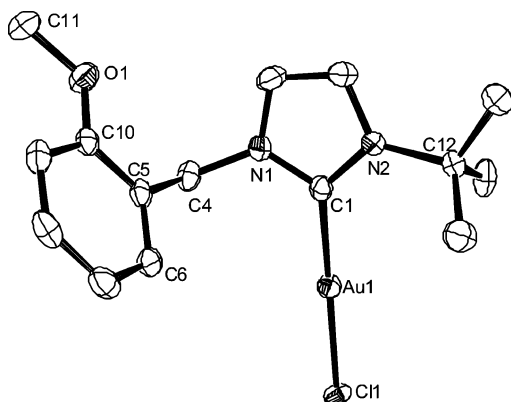
(17) O'Brien, C. J.; Kantachev, E. A. B.; Chass, G. A.; Hadei, N.; Hopkinson, A. C.; Organ, M. G.; Setaidi, D. H.; Tang, T.-H.; Fang, D.-C. *Tetrahedron* **2005**, 61, 9723–9735.

(18) (a) Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, 3, 119–122. (b) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, 3, 1511–1514.

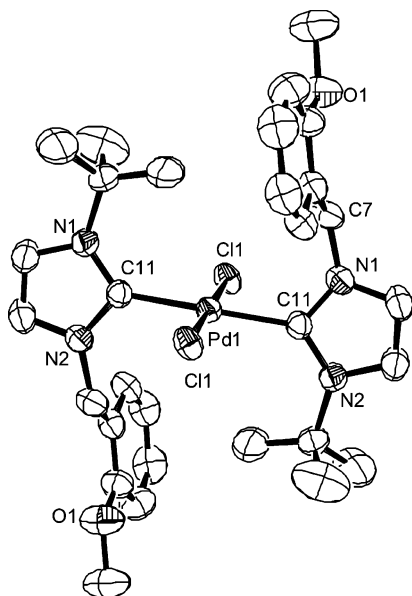
(19) (a) O'Brien, C. J.; Kantachev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. Eur. J.* **2006**, 12, 4743–4748. (b) Organ, M. G.; Avola, S.; Dubovyk, I.; Hadei, N.; Kantchev, A. S. B.; O'Brien, C. J.; Valente, C. *Chem. Eur. J.* **2006**, 12, 4749–4755.

(20) (a) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, 58, 9633–9695. (b) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, 41, 4176–4211.

(21) Suzuki, A. *Chem. Commun.* **2005**, 4759–4763.



**Figure 2.** ORTEP drawing of **1c** with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): N(1)–C(1) = 1.347(5), N(2)–C(1) = 1.347(5), Au(1)–C(1) = 1.979(4), Au(1)–Cl(1) = 2.2872(10); C(1)–Au(1)–Cl(1) = 179.74(11).



**Figure 3.** ORTEP drawing of **1d** with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): N(1)–C(11) = 1.356(7), N(2)–C(11) = 1.364(7), Pd(1)–C(11) = 2.036(5), Pd(1)–Cl(1) = 2.3531(12); Cl(1)–Pd(1)–C(11) = 91.61(15), C(11)–Pd(1)–C(11) = 180.0(4).

X = Br, I). We also report the syntheses and structural characterizations of the Au–NHC complex [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**) and the Pd–NHC complex **1d**, supported over a new O-functionalized N-heterocyclic carbene ligand: namely, 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene.

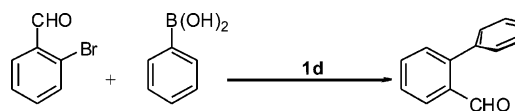
## Results and Discussion

A new neutral O-functionalized N-heterocyclic carbene ligand, namely, 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene, having a methoxy-functionalized sidearm, was designed with the intent of stabilizing metal complexes with enhanced catalytic attributes. In this regard it is noteworthy that a similar anionic aryloxy O-functionalized N-heterocyclic carbene analogue, 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-3-R-imidazol-2-

**Table 1.** X-ray Crystallographic Data for **1c** and **1d**

	<b>1c</b>	<b>1d</b>
lattice	monoclinic	monoclinic
formula	C <sub>15</sub> H <sub>20</sub> AuClN <sub>2</sub> O	C <sub>15</sub> H <sub>20</sub> ClN <sub>2</sub> OPd <sub>0.50</sub>
formula wt	476.75	332.98
space group	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	16.5313(19)	8.740
<i>b</i> (Å)	11.2567(18)	12.687
<i>c</i> (Å)	17.275(7)	14.204
$\alpha$ (deg)	90.00	90.00
$\beta$ (deg)	99.65(2)	104.17
$\gamma$ (deg)	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	3169.1(15)	1527.1
<i>Z</i>	8	4
temp (K)	150(2)	293(2)
radiation ( $\lambda$ , Å)	0.710 73	0.709 30
$\rho$ (calcd) (g cm <sup>−3</sup> )	1.998	1.448
$\mu$ (Mo K $\alpha$ ) (mm <sup>−1</sup> )	9.450	0.816
$\theta_{\max}$ (deg)	24.99	11.4200–13.5600
no. of data	2804	2694
no. of params	185	178
R1	0.0199	0.0492
wR2	0.0429	0.1337
GOF	1.084	1.066

**Table 2.** Selected Results of Suzuki Coupling of *o*-Bromobenzaldehyde with Phenylboronic Acid Catalyzed by **1d**<sup>a</sup>



entry	amt of <b>1d</b> (mmol)	amt of <b>1d</b> (mol %)	time (h)	yield <sup>b</sup> (%)	TON
1	$7.5 \times 10^{-3}$	$3.5 \times 10^{-1}$	12	>99	288
2	$1.9 \times 10^{-3}$	$8.6 \times 10^{-2}$	12	>99	1110
3	$7.5 \times 10^{-4}$	$3.5 \times 10^{-2}$	12	>99	2880
4	$3.7 \times 10^{-4}$	$1.7 \times 10^{-2}$	12	>99	6000
5	$1.8 \times 10^{-4}$	$8.6 \times 10^{-3}$	12	>99	11700
6	$4.3 \times 10^{-5}$	$2.0 \times 10^{-3}$	12	>99	50600
7	$2.0 \times 10^{-5}$	$9.2 \times 10^{-4}$	12	45	49700
8	$2.0 \times 10^{-5}$	$9.2 \times 10^{-4}$	24	>99	109600

<sup>a</sup> Reaction conditions: 2.16 mmol of aryl halide, 2.64 mmol of phenylboronic acid, 3.24 mmol of K<sub>2</sub>CO<sub>3</sub>, complex **1d**, 30 mL of CH<sub>3</sub>CN, 85 °C. <sup>b</sup> Determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard.

ylidene (R = *i*-Pr, benzyl),<sup>30</sup> has been recently reported, and its Fe complex<sup>31</sup> showed activity toward the ring-opening polymerization of  $\epsilon$ -caprolactone. Also worth mentioning is that another class of analogous anionic aryloxy O-functionalized N-heterocyclic carbene ligands, namely, 1-(3-(adamantan-1-yl)-2-hydroxy-5-methylphenyl)-3-(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene and its variants, has been reported by Grubbs<sup>32</sup> and these displayed a novel type of ring-opening reaction of N-heterocyclic carbenes.<sup>33</sup> Specifically, the new O-functionalized imidazolium bromide salt 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazolium bromide (**1a**) was prepared by the direct alkylation of *tert*-butylimidazole with 2-methoxybenzyl

(30) (a) Wang, Z.-G.; Sun, H.-M.; Yao, H.-S.; Yao, Y.-M.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2006**, 691, 3383–3390. (b) Li, W.-F.; Sun, H.-M.; Wang, Z. G.; Chen, M.-Z.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2005**, 690, 6227–6232.

(31) Chen, M.-Z.; Sun, H.-M.; Li, W.-F.; Wang, Z.-G.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2006**, 691, 2489–2494.

(32) Waltman, W. A.; Grubbs, R. H. *Organometallics* **2004**, 23, 3105–3107.

(33) Waltman, W. A.; Ritter, T.; Grubbs, R. H. *Organometallics* **2006**, 25, 4238–4239.



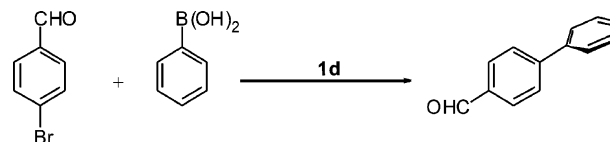
bromide in 44% yield (Scheme 1). The  $^1\text{H}$  NMR spectrum of **1a** showed the diagnostic, highly downfield shifted imidazolium (NCHN) resonance at 10.6 ppm. The bridging methylene ( $\text{CH}_2$ ) moiety appeared as a singlet at 5.64 ppm in the  $^1\text{H}$  NMR spectrum and at 58.4 ppm in the  $^{13}\text{C}$  NMR spectrum. In the electrospray mass spectrum the 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazolium cation appeared as a  $m/z$  245 peak in 100% abundance.

The treatment of the imidazolium bromide salt **1a** with  $\text{Ag}_2\text{O}$  yielded the silver complex **1b** by the procedure reported by Lin.<sup>34</sup> Consistent with the formation of **1b**, the  $^1\text{H}$  NMR spectrum showed the absence of an imidazolium (NCHN) resonance at 10.6 ppm owing to the loss of the acidic imidazolium proton of **1a** as result of the reaction with  $\text{Ag}_2\text{O}$  along with the appearance of a diagnostic silver-bound carbene (NCN–Ag) peak at 178.3 ppm in the  $^{13}\text{C}$  NMR spectrum of **1b**. The HRMS data of **1b** gave a peak at  $m/z$  595.2177 corresponding to the cationic fragment  $\{[1-(o\text{-methoxybenzyl})-3\text{-tert-butylimidazol-2-ylidene}]_2\text{Ag}\}^+$  (calculated  $m/z$  595.2202).

The treatment of the silver complex **1b** with  $(\text{SMe}_2)\text{AuCl}$  yielded the gold complex  $[1-(o\text{-methoxybenzyl})-3\text{-tert-butylimidazol-2-ylidene}]\text{AuCl}$  (**1c**; Figure 1) in 77% yield along with the formation of AgBr precipitate. In this context it is worth mentioning that though several methods have been reported for synthesizing Au–NHC complexes, namely, (i) cleavage of electron-rich olefins,<sup>35</sup> (ii) carbene transfer from group 6 carbonyl complexes,<sup>36</sup> (iii) reactions of azolium salts or free NHCs with Au(I) precursors,<sup>37</sup> (iv) protonation or alkylation of gold azolyl complexes,<sup>38</sup> and (v) transmetalation via the reaction of Ag(I)–NHC complexes with Au(I) precursors,<sup>34</sup> the milder conditions of the transmetalation pathway make it an attractive choice. The  $^1\text{H}$  NMR spectrum of **1c** showed the bridging methylene ( $\text{CH}_2$ ) and the methoxy ( $\text{OCH}_3$ ) resonances appearing as singlets at 5.47 and 3.88 ppm, respectively. The diagnostic gold-bound carbene (NCN–Au) peak appeared at 169.2 ppm in the  $^{13}\text{C}$  NMR spectrum.

The molecular structure of the gold complex **1c** has been determined by X-ray diffraction studies (Figure 2). The X-ray structure of **1c** revealed the formation of a neutral monomeric (NHC)AuCl type complex in which the metal center was bound to a N-heterocyclic carbene ligand on the one side and to a chloride on the other. The geometry around the metal center is linear ( $\angle\text{C}(1)\text{--Au}(1)\text{--Cl}(1) = 179.74(11)^\circ$ ) and is consistent with the  $d^{10}$  configuration of Au(I) in **1c**.<sup>39</sup> The structure of **1c** is analogous to those of other reported neutral monomeric (NHC)AuCl type complexes such as  $[1-(2\text{-hydroxycyclohexyl})-3-(N\text{-tert-butylacetamido})\text{imidazol-2-ylidene}]\text{AuCl}$ , recently reported by us,<sup>23</sup> and  $[1,3\text{-R}_2\text{-imidazol-2-ylidene}]\text{AuCl}$  complexes ( $\text{R} = \text{mesityl}, 2,6\text{-diisopropylphenyl}, \text{cyclohexyl}, \text{adamantyl}$ ), reported by Nolan and co-workers.<sup>40</sup> The bond distances Au–C<sub>carb</sub> (1.979(4) Å) and Au–Cl (2.2872(10) Å) are consistent

**Table 3.** Selected Results of Suzuki Coupling of *p*-Bromobenzaldehyde with Phenylboronic Acid Catalyzed by **1d**<sup>a</sup>



entry	amt of <b>1d</b> (mmol)	amt of <b>1d</b> (mol %)	time (h)	yield <sup>b</sup> (%)	TON
1	$7.5 \times 10^{-3}$	$3.5 \times 10^{-1}$	12	>99	288
2	$2.8 \times 10^{-4}$	$1.3 \times 10^{-2}$	12	>99	7580
3	$2.8 \times 10^{-5}$	$1.3 \times 10^{-3}$	12	51	39200

<sup>a</sup> Reaction conditions: 2.16 mmol of aryl halide, 2.64 mmol of phenylboronic acid, 3.24 mmol of  $\text{K}_2\text{CO}_3$ , complex **1d**, 30 mL of  $\text{CH}_3\text{CN}$ , 85 °C. <sup>b</sup> Determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard.

with single-bond character, as they are marginally shorter than the sum of the individual covalent radii ( $d_{\text{Au–C}} = 2.108$  Å;  $d_{\text{Au–Cl}} = 2.326$  Å).<sup>41,42</sup> Another notable feature of the **1c** structure is that the methoxy O of the functionalized 1-N substituent (*o*-methoxybenzyl) was oriented away from the metal center, with the  $\text{O1}\cdots\text{Au1}$  distance being 6.041 Å.

The palladium complex  $[1-(o\text{-methoxybenzyl})-3\text{-tert-butylimidazol-2-ylidene}]_2\text{PdCl}_2$  (**1d**) was also synthesized via the transmetalation route by the reaction of the silver complex **1b** with  $(\text{COD})\text{PdCl}_2$  in 89% yield, following the procedure reported by Tilset and co-workers.<sup>43,44</sup> In this context it is worth mentioning that several other methods have been reported for synthesizing Pd–NHC complexes. For example, a frequently used pathway involves reaction of imidazolium halide salts with  $\text{Pd}(\text{OAc})_2$ .<sup>45,46</sup> Along the same lines, Organ and co-workers<sup>19</sup> reported a convenient preparation of highly active Pd–NHC precatalysts by the reaction of imidazolium halide salts with  $\text{PdCl}_2$  in air. Another ingenious one-pot synthesis of chiral Pd–NHC complexes by the activation of the C–S bond of methyl levamisole has been recently reported by Cabeza and co-workers.<sup>47</sup> The complex **1d** is sufficiently air-stable and could be purified by column chromatography. In this regard it is worth mentioning that several air-stable  $\text{Pd}^{46,48,49}$  and  $\text{Ir}^{50}$  complexes of N-heterocyclic carbene ligands have been reported that were purified using column chromatography. In the  $^1\text{H}$  NMR

(41) Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 224–228, 256–258.

(42) (a) Frémont, P. de; Stevens, E. D.; Frutos, M. R.; Díaz-Requejo, M. M.; Pérez, P. J.; Nolan, S. P. *Chem. Commun.* **2006**, 2045–2047. (b) Baker, M. V.; Barnard, P. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2005**, 37–43.

(43) Frøseth, M.; Netland, K. A.; Tornroos, K. W.; Dhindsa, A.; Tilset, M. *Dalton Trans.* **2005**, 1664–1674.

(44) Frøseth, M.; Dhindsa, A.; Røise, H.; Tilset, M. *Dalton Trans.* **2003**, 4516–4524.

(45) (a) Miecznikowski, J. R.; Gründemann, S.; Albrecht, M.; Męgret, C.; Clot, E.; Faller, J. W.; Eisenstein, O.; Crabtree, R. H. *Dalton Trans.* **2003**, 831–838. (b) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, 21, 700–706. (c) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201–202.

(46) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, 20, 5485–5488.

(47) Cabeza, J. A.; del Río, I.; Sánchez-Vega, G.; Suárez, M. *Organometallics* **2006**, 25, 1831–1834.

(48) Herrmann, W. A.; Schwarz, J.; Gardiner, M. J. *Organometallics* **1999**, 18, 4082–4089.

(49) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P.; Weskamp, T. *J. Organomet. Chem.* **2001**, 617–618, 616–628.

(50) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, 21, 3596–3604.

(34) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, 17, 972–975. (35) Cetinkaya, B.; Dixneuf, P.; Lappert, M. F. J. *Chem. Soc., Dalton Trans.* **1974**, 1827–1833.

(36) (a) Liu, S.-T.; Reddy, K. R. *Chem. Soc. Rev.* **1999**, 28, 315–322. (b) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Reddy, K. R.; Chen, Y.-C.; Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1999**, 18, 2145–2154.









(37) Lee, K. M.; Lee, C. K.; Lin, I. J. B. *Angew. Chem., Int. Ed.* **1997**, 36, 1850–1852.

(38) Bovio, B.; Calogero, S.; Wagner, F. E.; Burini, A.; Pietroni, B. R. *J. Organomet. Chem.* **1994**, 470, 275–283.

(39) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; pp 1085–1094.

(40) Frémont, P. de.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, 24, 2411–2418.

**Table 4.** Selected Results of Suzuki–Miyaura Cross-coupling Reaction of Aryl Halides (ArX, X = Br, I) Catalyzed by **1d**

Entry	Reagent <sup>a</sup>	Reagent <sup>a</sup>	<b>1d</b> <sup>a</sup> (mol %)	Temp (°C)	Time (hour)	Yield <sup>b</sup> (%)	TON
1			$3.5 \times 10^{-1}$	85	12	>99	288
2			$3.5 \times 10^{-1}$	85	12	>99	288
3			$3.5 \times 10^{-1}$	85	12	41	119
4			$3.5 \times 10^{-1}$	85	12	42	121

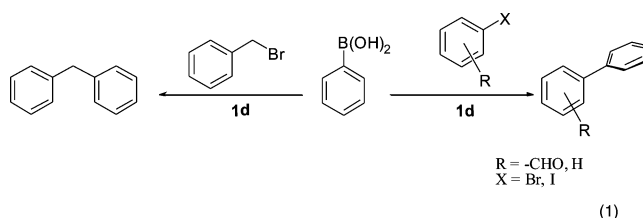
<sup>a</sup> Reaction conditions: 2.16 mmol of aryl halides (ArX, X = Br, I), 2.64 mmol of phenylboronic acid, 3.24 mmol of K<sub>2</sub>CO<sub>3</sub>,  $7.5 \times 10^{-3}$  mmol of catalyst **1d**, and 30 mL of CH<sub>3</sub>CN were taken for each run. <sup>b</sup> Determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard.

spectrum of **1d**, the bridging methylene (CH<sub>2</sub>) and the methoxy (OCH<sub>3</sub>) moieties appeared at 6.18 and 3.87 ppm, respectively. The characteristic palladium-bound carbene (NCN–Pd) peak appeared at 157.2 ppm in the <sup>13</sup>C NMR and falls well within the range, ca. 175–145 ppm, observed for other reported Pd–NHC complexes.<sup>46,49,51</sup>

The definitive proof for the **1d** structure came from X-ray diffraction studies, which showed the formation of a square-planar (NHC)<sub>2</sub>PdCl<sub>2</sub> type complex having the two N-heterocyclic carbene ligands and two chloride ligands disposed trans to each other (Figure 3). As observed in the case of the **1c** structure, the **1d** structure also showed that the methoxy O of the functionalized sidearm (*o*-methoxybenzyl) did not chelate to the palladium center and was found to be disposed away from the metal center (O1···Pd1 = 5.360 Å). The two equivalent Pd–Cl bond distances (2.3531(12) Å) in **1d** are slightly larger than the sum of the individual covalent radii ( $d_{\text{Pd–Cl}}$  = 2.273 Å)<sup>41</sup> but compare well with the range observed for other related Pd complexes such as in *trans*-{3-[2-((2,6-diisopropylphenyl)imino)propyl]-1-methylimidazol-2-ylidene}PdCl<sub>2</sub><sup>43</sup> (2.3070(3) Å) and *trans*-{3-[2-(benzylideneamino)cyclohexyl]-4-phenyl-1-propylimidazol-2-ylidene}PdCl<sub>2</sub><sup>52</sup> (2.359(2) Å). Interestingly enough, the two equivalent Pd–C<sub>carb</sub> bond distances (2.036(5) Å) in **1d** are slightly smaller than the sum of the individual covalent radii ( $d_{\text{Pd–C}}$  = 2.055 Å).<sup>41</sup> In this regard it is worth mentioning that a theoretical study by Cundari<sup>53</sup> and co-workers revealed that up to 4% shortening of a metal–carbene bond can be ascribed to the change in hybridization state of the carbene carbon as a consequence of enhanced s character of the in-plane carbene lone pair σ-bonded to metal in the metal–NHC complexes. Consistent with an almost perfect square-planar geometry in **1d**, the ∠C11–Pd1–C11 angle is 91.61(15)° and the ∠C11–Pd1–Cl1 angle is 180.0(4)°.

The palladium complex **1d** was found to be an efficient catalyst for Suzuki–Miyaura type cross-coupling reactions. Specifically, the coupling of phenylboronic acid and *o*-bromobenzaldehyde to yield biphenyl-2-carbaldehyde was achieved

in high yield and turnover numbers at 85 °C after 12 h of reaction time (eq 1 and Table 2). A study of the variation of



catalyst loading was carried out in order to gauge the upper limit of the catalyst efficiency (Table 2), and in fact, a maximum turnover number of ca. 49 700 and 45% conversion (Table 2, entry 7) were observed by gas chromatography at  $9.2 \times 10^{-4}$  mol % of catalyst loading after 12 h at 85 °C. Further increase in the yield (>99%) and turnover number (to ca. 109 600) were achieved by extending the reaction time to 24 h under the same conditions (Table 2, entry 8). Similar results were obtained for the cross-coupling of phenylboronic acid with *p*-bromobenzaldehyde, which produced biphenyl-4-carbaldehyde (Table 3). High turnover numbers up to ca. 39 200 were observed at 51% conversion by <sup>1</sup>H NMR at  $1.3 \times 10^{-3}$  mol % of catalyst loading after 12 h at 85 °C (Table 3, entry 3). Quite significantly, for the coupling of aryl bromides with phenylboronic acid, the high turnover numbers exhibited by **1d** not only are substantially greater than those reported for the palladium bis-chelating N-heterocyclic carbene complex [methylenebis(*N*-methylimidazol-2-ylidene)]PdI<sub>2</sub> (TON up to 100)<sup>12b</sup> but also are comparable to those reported for a well-known phosphapalladacyclic precatalyst, namely, *trans*-bis(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (TON up to 74 000).<sup>54</sup> It is noteworthy that phosphapalladacyclic complexes are renowned for their proficiencies in cross-coupling reactions, including Suzuki–Miyaura type reactions.<sup>14f,55,56</sup> In this context it is worth mentioning that two highly active Pd–NHC–phosphine cata-

(51) (a) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999**, 575, 80–86. (b) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, 572, 239–247.

(52) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R.; Houghton, J.; Kariuki, B. M.; Simonovic, S. *Dalton Trans.* **2004**, 3528–3535.

(53) Baba, E.; Cundari, T. R.; Firkin, I. *Inorg. Chim. Acta* **2005**, 358, 2867–2875.

(54) (a) Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1848–1849. (b) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.-P.; Priemeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1844–1848.

(55) (a) Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, 248, 2283–2321. (b) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917–1927.

(56) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, 125, 16194–16195.

lysts, namely, *trans*-{[1,3-diisopropyl-1,4,5,6-tetrahydropyrimidine]Pd(PPh<sub>3</sub>)<sub>2</sub>Cl}<sup>+</sup>Cl<sup>−</sup> (TON up to 800 000) and *cis*-[1,3-diisopropyl-1,4,5,6-tetrahydropyrimidine]Pd(PPh<sub>3</sub>)Cl<sub>2</sub> (TON up to 1 000 000), exhibiting ultrahigh turnover numbers, have been recently reported by Herrmann and co-workers.<sup>57</sup> Notably, significant emphasis has been placed in recent years on designing cross-coupling catalysts of low catalyst loadings<sup>58</sup> in order to minimize the cost related to the usage of Pd and the ligand (particularly the phosphines), both considered expensive, alongside achieving large-scale synthesis requiring minimum effort in removal of Pd from the final product.<sup>16a</sup>

The palladium precatalyst **1d** successfully carried out Suzuki–Miyaura cross-coupling of a variety of aryl halides (ArX, X = Br, I) substrates (Table 4). Furthermore, the cross-coupling of an aryl iodide, namely, iodobenzene, with phenylboronic acid to give biphenyl was also achieved under analogous conditions. Quite interestingly, the C–C coupling can be extended from the C<sub>sp</sub><sup>2</sup> carbon center, e.g., in *o*-bromobenzaldehyde, to the C<sub>sp</sub><sup>3</sup> center in benzyl bromide (Table 4). However, much lower yield (42%) and turnover numbers (121) were observed for benzyl bromide compared to those for *o*-bromobenzaldehyde (yield >99%; TON = 288) obtained under the same reaction conditions.

## Conclusion

In summary, two new gold and palladium complexes, namely, [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**) and [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]<sub>2</sub>PdCl<sub>2</sub> (**1d**), supported over a new O-functionalized N-heterocyclic carbene ligand, have been synthesized. Complexes **1c** and **1d** have been structurally characterized by X-ray diffraction studies, which revealed the formation of a neutral monomeric (NHC)–AuCl type complex in **1c** and a *trans*-square-planar (NHC)<sub>2</sub>PdCl<sub>2</sub> type complex in **1d**, in accordance with the preferred geometries of the respective metal ions. Notably, in the structures of **1c** and **1d**, chelation of the O-functionalized sidearm to the metal was not observed. The palladium complex **1d** effectively catalyzed Suzuki–Miyaura type cross-coupling of phenylboronic acid and aryl halides (ArX, X = Br, I) in high yield and high turnover numbers.

## Experimental Section

**General Procedures.** All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. Ag<sub>2</sub>O was purchased from SD-Fine Chemicals (India) and used without any further purification. (COD)PdCl<sub>2</sub><sup>59</sup> and (SMe<sub>2</sub>)AuCl<sup>60</sup> were prepared according to the reported literature procedures, while 2-methoxybenzyl bromide<sup>61</sup> was prepared by a procedure modified from that reported in the literature. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra

were recorded in CDCl<sub>3</sub> on a Varian 400 MHz NMR spectrometer. <sup>1</sup>H NMR peaks are labeled as singlet (s), doublet (d), and multiplet (m). Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Mass spectrometric measurements were done on a Micromass Q-ToF spectrometer. GC spectra were measured on a Shimadzu GC-15A gas chromatograph equipped with an FID detector. X-ray diffraction data for **1c** and **1d** were collected on a NONIUS-MACH3 diffractometer. The crystal data and data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F<sup>2</sup> with SHELXTL (version 6.10).

**Synthesis of 1-(*o*-Methoxybenzyl)-3-*tert*-butylimidazolium Bromide (**1a**).** A mixture of 2-methoxybenzyl bromide (3.00 g, 14.9 mmol) and *tert*-butylimidazole (1.84 g, 14.9 mmol) was dissolved in toluene (ca. 50 mL), and the reaction mixture was refluxed at 110 °C for 12 h, at which point a sticky solid separated out. The solid was isolated by decanting off the solvent and washed with hot hexane (3 × ca. 10 mL) to obtain the product **1a** as a brown solid (2.16 g, 6.65 mmol; 44% with respect to 2-methoxybenzyl bromide). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ 10.6 (s, 1H, NCHN), 7.79 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-C<sub>6</sub>H<sub>4</sub>), 7.47 (br, 1H, NCHCHN), 7.37 (br, 1H, NCHCHN), 7.25 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *p*-C<sub>6</sub>H<sub>4</sub>), 6.98 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-C<sub>6</sub>H<sub>4</sub>), 6.92 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *o*-C<sub>6</sub>H<sub>4</sub>), 5.65 (s, 2H, CH<sub>2</sub>), 3.90 (s, 3H, OCH<sub>3</sub>), 1.72 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C): δ 155.7 (OC<sub>6</sub>H<sub>4</sub>), 133.0 (NCN), 129.8 (*o*-C<sub>6</sub>H<sub>4</sub>), 129.4 (*m*-C<sub>6</sub>H<sub>4</sub>), 120.9 (*ipso*-C<sub>6</sub>H<sub>4</sub>), 120.2 (*p*-C<sub>6</sub>H<sub>4</sub>), 119.2 (NCHCHN), 118.7 (NCHCHN), 109.2 (*m*-C<sub>6</sub>H<sub>4</sub>), 58.4 (CH<sub>2</sub>), 54.0 (OCH<sub>3</sub>), 46.5 (C(CH<sub>3</sub>)<sub>3</sub>), 28.3 (C(CH<sub>3</sub>)<sub>3</sub>). IR (KBr pellet): 3012 (m), 2955 (m), 1431 (s), 1417 (s), 1331 (s), 1253 (s), 1236 (s), 1215 (s), 1190 (s), 1161 (m), 1144 (m), 955 (m), 868 (s), 849 (m), 760 (s), 670 (s), 623 (s), 564 cm<sup>−1</sup> (s). LRMS (ES): *m/z* 245 [(NHC)]<sup>+</sup>. HRMS (ES): *m/z* 245.1662 (NHC-ligand)<sup>+</sup>, calcd 245.1654.

**Synthesis of {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]<sub>2</sub>Ag}<sup>+</sup>Br<sup>−</sup> (**1b**).** A mixture of 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazolium bromide (**1a**; 1.45 g, 4.47 mmol) and Ag<sub>2</sub>O (0.519 g, 2.24 mmol) in dichloromethane (ca. 60 mL) was stirred at room temperature for 6 h. The reaction mixture was filtered, and the solvent was removed under vacuum to give the product **1b** as a brown solid (0.876 g, 1.30 mmol; 58% with respect to Ag<sub>2</sub>O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ 7.33 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *p*-C<sub>6</sub>H<sub>4</sub>), 7.24 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-C<sub>6</sub>H<sub>4</sub>), 7.12 (br, 1H, NCHCHN), 7.02 (br, 1H, NCHCHN), 6.95 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-C<sub>6</sub>H<sub>4</sub>), 6.91 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *o*-C<sub>6</sub>H<sub>4</sub>), 5.33 (s, 2H, CH<sub>2</sub>), 3.88 (s, 3H, OCH<sub>3</sub>), 1.72 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C): δ 178.3 (NCN–Ag), 156.9 (OC<sub>6</sub>H<sub>4</sub>), 130.0 (*o*-C<sub>6</sub>H<sub>4</sub>), 129.7 (*m*-C<sub>6</sub>H<sub>4</sub>), 123.8 (*ipso*-C<sub>6</sub>H<sub>4</sub>), 120.7 (*p*-C<sub>6</sub>H<sub>4</sub>), 119.8 (NCHCHN), 118.6 (NCHCHN), 110.6 (*m*-C<sub>6</sub>H<sub>4</sub>), 57.5 (CH<sub>2</sub>), 55.2 (OCH<sub>3</sub>), 51.7 (C(CH<sub>3</sub>)<sub>3</sub>), 31.6 (C(CH<sub>3</sub>)<sub>3</sub>). IR (KBr pellet): 3089 (w), 2971 (s), 2929 (m), 2339 (s), 1658 (w), 1558 (m), 1456 (m), 1370 (s), 1262 (w), 1229 (m), 1149 (w), 1108 (w), 1025 (w), 796 (w), 737 (s), 573 cm<sup>−1</sup> (w). HRMS (ES): *m/z* 595.2177 [(NHC)<sub>2</sub>Ag]<sup>+</sup>, calcd 595.2202. Anal. Calcd for C<sub>30</sub>H<sub>40</sub>AgBrN<sub>4</sub>O<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 48.90; H, 5.56; N, 7.36. Found: C, 48.07; H, 4.81; N, 8.43.

**Synthesis of [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**).** A mixture of {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]<sub>2</sub>Ag}<sup>+</sup>Br<sup>−</sup> (**1b**; 0.825 g, 1.22 mmol) and (SMe<sub>2</sub>)AuCl (0.720 g, 2.44 mmol) in dichloromethane (ca. 40 mL) was stirred at room temperature for 6 h, at which point the formation of an off-white AgBr precipitate was observed. The reaction mixture was filtered, and the solvent was removed under vacuum to obtain the product **1c** as a brown solid (0.446 g, 0.938 mmol; 77% with respect to **1b**). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ 7.41 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-C<sub>6</sub>H<sub>4</sub>), 7.33 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *p*-C<sub>6</sub>H<sub>4</sub>), 7.03 (br, 1H, NCHCHN), 6.97 (br, 2H, NCHCHN and *o*-C<sub>6</sub>H<sub>4</sub>), 6.92 (t,

(57) Schneider, S. K.; Herrmann, W. A.; Herdtweck, E. *J. Mol. Catal.* **2006**, *245*, 248–254.

(58) (a) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E.; Albisson, D. A.; Draper, S. M.; Scully, P. N.; Coles, S. J.; Hursthouse, M. B. *Chem. Eur. J.* **2003**, *9*, 3216–3227. (b) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E. *Chem. Commun.* **2002**, 2610–2611. (c) Bedford, R. B.; Cazin, C. S. J.; Hazelwood, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 4120–4122. (d) Alonso, D. A.; Najera, C.; Pacheco, M. C. *J. Org. Chem.* **2002**, *67*, 5588–5594. (e) Zapf, A.; Ehrentauf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4153–4155. (f) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550–9561.

(59) Müller, M.; Penk, R.; Rohlfing, E.; Krickemeyer, J. *Inorg. Synth.* **1990**, *28*, 348–349.

(60) Brandys, M.-C.; Jennings, M. C.; Puddephatt, R. J. *Dalton Trans.* **2000**, 4601–4606.

(61) Stern, A. J.; Swenton, J. S. *J. Org. Chem.* **1989**, *54*, 2953–2958.



$^1\text{H}$ ,  $^3J_{\text{HH}} = 8$  Hz,  $m\text{-C}_6\text{H}_4$ ), 5.47 (s, 2H,  $\text{CH}_2$ ), 3.88 (s, 3H,  $\text{OCH}_3$ ), 1.84 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 25 °C):  $\delta$  169.2 (NCN–Au), 157.0 ( $\text{OC}_6\text{H}_4$ ), 130.4 ( $o\text{-C}_6\text{H}_4$ ), 130.1 ( $m\text{-C}_6\text{H}_4$ ), 123.6 ( $ipso\text{-C}_6\text{H}_4$ ), 120.9 (NCHCHN), 119.1 ( $p\text{-C}_6\text{H}_4$ ), 118.2 (NCHCHN), 110.5 ( $m\text{-C}_6\text{H}_4$ ), 58.7 ( $\text{CH}_2$ ), 55.3 ( $\text{OCH}_3$ ), 51.2 ( $\text{C}(\text{CH}_3)_3$ ), 31.6 ( $\text{C}(\text{CH}_3)_3$ ). IR (KBr pellet): 3174 (w), 3145 (w), 3065 (w), 3004 (w), 2971 (m), 2837 (w), 2713 (w), 1601 (m), 1563 (w), 1496 (s), 1464 (s), 1445 (s), 1406 (s), 1367 (m), 1343 (w), 1291 (m), 1253 (s), 1219 (s), 1193 (m), 1162 (w), 1109 (m), 1052 (m), 1024 (s), 936 (w), 868 (w), 834 (w), 765 (s), 750 (s), 728 (m), 703 (w), 687 (m), 643 (w), 595 (w), 556 (w), 538  $\text{cm}^{-1}$  (w). HRMS (ES):  $m/z$  441.1232 [(NHC)Au] $^+$ , calcd 441.1241. Anal. Calcd for  $\text{C}_{15}\text{H}_{20}\text{AuClIN}_2\text{O}$ : C, 37.79; H, 4.23; N, 5.88. Found: C, 38.36; H, 4.51; N, 6.61.

**Synthesis of [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene] $_2$ PdCl $_2$  (**1d**).** A mixture of {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene] $_2$ Ag} $^+$ Br $^-$  (**1b**; 1.00 g, 2.32 mmol) and (COD)PdCl $_2$  (0.331 g, 1.16 mmol) was refluxed in acetonitrile (ca. 30 mL) at 85 °C for 6 h, at which point the formation of an off-white AgBr precipitate was observed. The reaction mixture was filtered, and the solvent was removed under vacuum to obtain a yellow solid, which was purified using column chromatography by eluting it with a mixed solvent (10% MeOH in  $\text{CHCl}_3$ ) to obtain the pure product **1d** as a brown solid (0.857 g, 1.29 mmol; 89% with respect to **1b**).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 25 °C):  $\delta$  7.61 (d, 1H,  $^3J_{\text{HH}} = 8$  Hz,  $o\text{-C}_6\text{H}_4$ ), 7.31 (t, 1H,  $^3J_{\text{HH}} = 8$  Hz,  $p\text{-C}_6\text{H}_4$ ), 7.01 (d, 1H,  $^3J_{\text{HH}} = 3$  Hz, NCHCHN), 6.96 (t, 1H,  $^3J_{\text{HH}} = 8$  Hz,  $m\text{-C}_6\text{H}_4$ ), 6.91 (d, 1H,  $^3J_{\text{HH}} = 8$  Hz,  $m\text{-C}_6\text{H}_4$ ), 6.79 (d, 1H,  $^3J_{\text{HH}} = 3$  Hz, NCHCHN), 6.18 (s, 2H,  $\text{CH}_2$ ), 3.87 (s, 3H,  $\text{OCH}_3$ ), 2.09 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 25 °C):  $\delta$  157.2 (NCN–Pd), 135.9 ( $\text{OC}_6\text{H}_4$ ), 131.9 ( $ipso\text{-C}_6\text{H}_4$ ), 131.0 ( $o\text{-C}_6\text{H}_4$ ), 122.1 ( $p\text{-C}_6\text{H}_4$ ), 121.8 (NCHCHN), 121.2 (NCHCHN), 119.0 ( $m\text{-C}_6\text{H}_4$ ), 110.6 ( $m\text{-C}_6\text{H}_4$ ), 60.0 ( $\text{CH}_2$ ), 55.4 ( $\text{OCH}_3$ ), 48.3 ( $\text{C}(\text{CH}_3)_3$ ),

29.9 ( $\text{C}(\text{CH}_3)_3$ ). IR (KBr pellet): 3138 (w), 2971 (m), 2936 (m), 2837 (w), 1603 (m), 1463 (m), 1440 (m), 1415 (m), 1372 (m), 1290 (w), 1246 (s), 1110 (m), 1049 (w), 1025 (m), 949 (w), 862 (w), 820 (w), 803 (w), 758 (s), 701 (m), 657 (w), 638 (w), 558  $\text{cm}^{-1}$  (w). Anal. Calcd for  $\text{C}_{30}\text{H}_{40}\text{Cl}_2\text{N}_4\text{O}_2\text{Pd}\cdot\text{CHCl}_3$ : C, 47.41; H, 5.26; N, 7.13. Found: C, 47.51; H, 5.07; N, 7.60.

**General Procedure for the Suzuki Coupling Reaction.** In a typical run, a round-bottom flask was charged with a mixture of aryl halides (ArX, X = Br, I), phenylboronic acid,  $\text{K}_2\text{CO}_3$ , and diethylene glycol di-*n*-butyl ether (internal standard) in a molar ratio of 1:1.2:1.5:1 and to this mixture was added [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene] $_2$ PdCl $_2$  (**1d**) at varying mole percent amounts (Tables 2 and 3). Acetonitrile (30 mL) was added to the reaction mixture, and this mixture was refluxed for an appropriate period of time, after which it was filtered and the product was analyzed by gas chromatography using diethylene glycol di-*n*-butyl ether as an internal standard.

**Acknowledgment.** We thank Department of Science and Technology (Grant No: SR/S1/IC-25/2003) for financial support of this research. We are grateful to the National Single Crystal X-ray Diffraction Facility at IIT Bombay, India, for the crystallographic results. L.R. thanks IIT Bombay, India, for research fellowship.

**Supporting Information Available:** CIF files giving crystallographic data for [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**) and [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene] $_2$ PdCl $_2$  (**1d**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM060834B

# First Example of a Gold(I) *N*-Heterocyclic-Carbene-Based Initiator for the Bulk Ring-Opening Polymerization of L-Lactide

Lipika Ray,<sup>[a]</sup> Vimal Katiyar,<sup>[a]</sup> Mustafa J. Raihan,<sup>[a]</sup> Hemant Nanavati,<sup>[a]</sup>  
Mobin M. Shaikh,<sup>[a]</sup> and Prasenjit Ghosh\*<sup>[a]</sup>

**Keywords:** Carbenes / Functionalized NHC / Ring-opening polymerization (ROP) / Organometallic catalysis / Silver–NHC complex / Gold–NHC complex

Synthesis, structure, and catalysis studies of two Au- and Ag-based initiators, namely, [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**) and [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**), for the bulk ring-opening polymerization of L-lactide are reported. Specifically, gold complex **1c** was obtained from silver complex **1b** by the transmetalation reaction with (SMe<sub>2</sub>)AuCl. Silver complex **1b** was synthesized by the treatment of 3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium chloride (**1a**) with Ag<sub>2</sub>O. Compound **1a** was synthesized directly from the reaction of *N*-*tert*-butyl-2-chloroacetamide, cyclohexene oxide, and imidazole. The

molecular structures of **1a**, **1b**, and **1c** have been determined by X-ray diffraction studies. The formation of neutral monomeric complexes with linear geometries at the metal centers was observed for both **1b** and **1c**. The Au and Ag complexes **1c** and **1b** successfully catalyzed the bulk ring-opening polymerization of L-lactide at elevated temperatures under solvent-free melt conditions to produce moderate to low molecular weight polylactide polymers with narrow molecular weight distributions.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

## Introduction

The long-standing notion of gold being an expensive and unreactive coinage metal with limited utility is gradually changing. Various new applications of Au<sup>I</sup> complexes in pharmaceuticals,<sup>[1]</sup> chemical vapor depositions,<sup>[2]</sup> and in homogeneous catalysis<sup>[3]</sup> have been recently reported. Compared to the other coinage metals (i.e. Cu and Ag), Au has seen relatively few applications and poses a formidable challenge in utility-oriented research. Quite significantly, a recent report detailed the use of a Au<sup>I</sup> complex supported over a sterically demanding *N*-heterocyclic carbene (NHC) ligand as a catalyst for the ethyl diazoacetate-assisted carbene-transfer reaction;<sup>[3]</sup> this represents an important breakthrough in this field of chemistry and adds further promise to the use of gold in chemical catalysis. The growing utility of NHCs in homogeneous catalysis is now well-recognized, and a plethora of NHC-based catalysts have been developed in recent years for a wide variety of transformations, such as C–C coupling reactions,<sup>[4,5]</sup> olefin metatheses,<sup>[6]</sup> hydrogenations,<sup>[7,8]</sup> hydroformylations,<sup>[9]</sup> hydrosilylations,<sup>[10]</sup> CO-ethylene copolymerizations,<sup>[11]</sup> hydroboration<sup>[12]</sup> reactions, and so forth. Interestingly enough, despite the numerous NHC-transition metal complexes that

exist, the Au–NHC complexes are surprisingly few in number and have seldomly been employed in catalysis.<sup>[13]</sup>

A growing number of new applications have appeared lately for the Ag<sup>I</sup>–NHC counterparts however, and their catalytic utility has just begun to unfold.<sup>[14,15]</sup> Specifically, the Ag<sup>I</sup>–NHC complexes have been found to be active catalysts for several chemical transformations, such as, ethyl diazoacetate (EDA)-assisted carbene-transfer reactions,<sup>[16]</sup> catalytic preparation of 1,2-bis(boronate) esters,<sup>[17]</sup> transesterification reactions, and ring-opening lactide polymerization reactions.<sup>[18]</sup> It is noteworthy that even though the applications of Ag<sup>I</sup>–NHC complexes in chemical catalysis is a recent phenomenon, they are long-known for their use as transmetalation agents for the synthesis of other transition metal–NHC complexes.<sup>[14,15]</sup> Like its heavier congener, the Au analogue, biomedical applications, particularly with regard to antimicrobial activities, have recently been reported for Ag<sup>I</sup>–NHC complexes.<sup>[19,20]</sup> Thus far, the popularity of Ag–NHC complexes can be ascribed to their broadly based applications, to their synthetic accessibility, and to their air and moisture stabilities, which make them user-friendly and hence convenient to handle.<sup>[14,15]</sup>

As the catalytic utility of Au–NHC complexes remains largely unexplored and that of the Ag–NHC complexes is just beginning to emerge, we became interested in the design of Au and Ag complexes for their potential application in homogeneous catalysis. In particular, we were interested in

[a] Department of Chemistry and Department of Chemical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India  
Fax: +91-22-2572-3480  
E-mail: pghosh@chem.iitb.ac.in



the design of Au–NHC and Ag–NHC based initiators for the ring-opening polymerization (ROP) of L-lactide. In this regard, we have recently reported a Ag–NHC complex as an initiator for the bulk ROP of L-lactide.<sup>[21]</sup> Although there exists a few reports on the use of Ag<sup>I</sup>–NHC complexes for the ROP of L-lactides,<sup>[18,21]</sup> we are unaware of any such report in the case of the Au<sup>I</sup>–NHC complexes.

Of late, the ROP of L-lactide has attracted considerable attention by virtue of its eco-friendliness. Not only is the polylactide polymer (PLA) biodegradable, but the lactide monomer can also be generated from renewable resources by a corn fermentation process or from agricultural starch wastes.<sup>[22,23]</sup> Because of their good mechanical properties and biocompatibility, PLAs have found wide utility in medical and pharmaceutical applications.<sup>[24,25]</sup> Various metals, such as Zn, Al, and Sn, have been extensively utilized for the synthesis of PLAs.<sup>[22a]</sup> The specific objective of our program is centered around the design of novel initiators for the bulk polymerization of L-lactides, which are often used for the large-scale production of PLAs. It is interesting to note that even though PLAs can be synthesized by both solution polymerization<sup>[26]</sup> and bulk polymerization,<sup>[27]</sup> solution polymerization suffers from certain disadvantages such as being susceptible to impurity levels and to various unwanted reactions, namely, racemization and transesterification, and hence is not conducive for the large-scale production of PLAs.<sup>[28]</sup> Our approach towards the design of initiators for bulk polymerization involved the utilization of functionalized NHCs as we rationalized that the presence of functional groups would enhance the solubility of the initiators in the monomer melt.

Here in this contribution, we disclose the first example of Au<sup>I</sup>–NHC-based initiator **1c** along with Ag<sup>I</sup>–NHC-based initiator **1b** for the bulk ROP of L-lactide (Figure 1). Specifically, both the gold and the silver complexes, namely, [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**) and [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**)

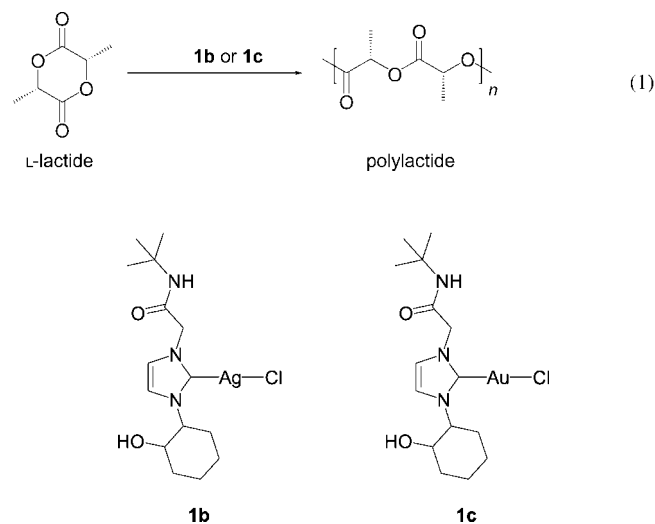
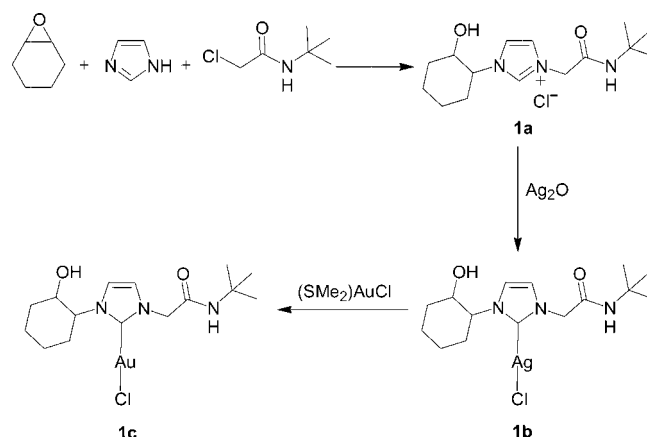


Figure 1. The complexes [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**) and [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**).

(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**), effectively catalyze the ROP of L-lactide at elevated temperatures under solvent-free melt conditions to afford polylactide polymers of moderate to low molecular weights with narrow molecular weight distributions [Equation (1)]. We also disclose the synthesis and structural characterizations of both the Au (**1c**) and Ag (**1b**) complexes supported over a novel difunctionalized *N*-heterocyclic carbene ligand, 3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene.

## Results and Discussion

A difunctionalized *N*-heterocyclic carbene ligand, 3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene, with two functionalized imidazolyl *N*-substituents, a 2-hydroxycyclohexyl moiety and an *N*-*tert*-butylacetamido moiety, was synthesized by a modified procedure reported by Arnold and coworkers.<sup>[29]</sup> Specifically, the NHC precursor, 3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium chloride (**1a**), was obtained from the direct reaction of *N*-*tert*-butyl-2-chloroacetamide, cyclohexene oxide, and imidazole in 96% yield (Scheme 1). The formation of imidazolium salt **1a** was confirmed by the appearance of the diagnostic (NCHN) resonance at  $\delta = 9.31$  ppm in the <sup>1</sup>H NMR spectrum and the corresponding carbon resonance (NCHN) at  $\delta = 136.3$  ppm in the <sup>13</sup>C NMR spectrum. The most interesting aspect of the <sup>1</sup>H NMR spectrum is the diastereotopic nature of the two bridging methylene proton (–CH<sub>2</sub>–) resonances which appear as two doublets at  $\delta = 5.16$  ppm and 4.96 ppm and display a geminal coupling between the two protons (<sup>2</sup>*J*<sub>H,H</sub> = 15 Hz). For example, similar diastereotopic hydrogens for the bridging methylene moiety (–CH<sub>2</sub>–) have been reported for Ir complexes with a 1-*n*-butyl-3-(2-pyridylmethyl)imidazol-2-ylidene ligand.<sup>[30]</sup> The carbonyl moiety (–CONH–) appeared at  $\delta = 163.8$  ppm in the <sup>13</sup>C NMR spectrum and at 1671 cm<sup>–1</sup> ( $\nu_{\text{CO}}$ ) in the infrared spectrum. In the electrospray mass spectrum the 3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium cation appeared as a peak at *m/z* = 280 and was further substantiated by HRMS results.



Scheme 1.

The imidazolium halide salt **1a** has been structurally characterized by X-ray diffraction studies (Figure 2). The N1–C9 and N2–C9 bond lengths are 1.326(6) Å and 1.314(6) Å, respectively, and the N2–C9–N1 angle is 107.9(5)° for **1a** and is comparable with other imidazolium halide salts. For example, in a CN-functionalized imidazolium salt, 1-CH<sub>2</sub>CN-3-methylimidazolium chloride, the C–N bond lengths are 1.348(3) Å and 1.336(3) Å and the N–C–N angle is 107.6°.<sup>[31]</sup>

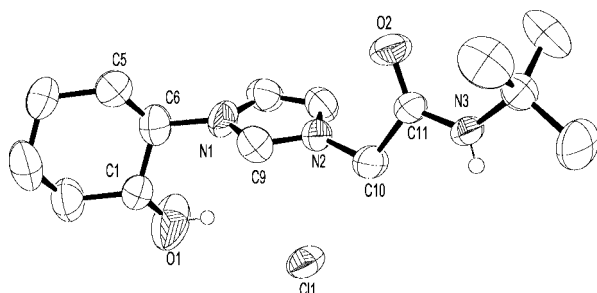


Figure 2. ORTEP drawing of **1a** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: N1–C9 1.326(6), N2–C9 1.314(6), N2–C9–N1 107.9(5).

The silver complex, [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**), was synthesized by the reaction of 3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium chloride (**1a**) with Ag<sub>2</sub>O in dichloromethane at room temperature in 86% yield with the convenient methodology developed by Lin and coworkers.<sup>[32]</sup> The <sup>1</sup>H NMR spectrum of **1b** confirmed the absence of the reactant imidazolium (NCHN) peak in the ca. 9 ppm region. The <sup>13</sup>C NMR spectrum showed a new peak at  $\delta$  = 181.6 ppm, which corresponds to the silver-bound carbene (NCN) resonance; the peak at  $\delta$  = 136.3 ppm attributable to reactant **1a** (NCHN) was absent as a result of its deprotonation by Ag<sub>2</sub>O and is indicative of the formation of **1b**. The two diastereotopic protons of the bridging methylene (–CH<sub>2</sub>–) group appeared shifted as two doublets at  $\delta$  = 4.94 ppm (<sup>2</sup>*J*<sub>H,H</sub> = 15 Hz) and 4.82 ppm (<sup>2</sup>*J*<sub>H,H</sub> = 15 Hz), respectively, compared to that of **1a**. The carbon resonance of the bridging methylene (–CH<sub>2</sub>–) group appeared at  $\delta$  = 54.4 ppm in the <sup>13</sup>C NMR spectrum. In the infrared spectrum, the amide carbonyl (–CONH–) appeared at 1673 cm<sup>–1</sup> while the hydroxy group appeared as a broad peak at 3302 cm<sup>–1</sup>.

The definitive proof for the structure of **1b** came from X-ray diffraction studies (Figure 3), which revealed a neutral monomeric complex bearing a 1:1 (NHC ligand/metal) stoichiometry. The silver center of **1b** was found to be two-coordinate, displays a linear geometry [ $\angle$  C1–Ag1–Cl1 = 172.66(11)°], and is consistent with the most common geometry displayed by *d*<sup>10</sup> silver(I) ions.<sup>[33]</sup> The Ag–C<sub>carb</sub> (Ag1–C1 = 2.066(4) Å) bond length of **1b** is shorter than the sum of the individual covalent radii of Ag and C (2.111 Å),<sup>[34a]</sup> but is comparable to that observed in other related (NHC)AgCl-type complexes. For example, a Ag–C<sub>carb</sub> bond length of 2.056(7) Å was observed in the case of [1,3-*bis*(mesityl)imidazol-2-ylidene]AgCl,<sup>[35]</sup> while that of

2.098(2) Å was observed in another functionalized NHC complex, [1-(2-benzylideneamino-3,5-di-*tert*-butylbenzyl)-3-(*tert*-butyl)imidazol-2-ylidene]AgCl.<sup>[36]</sup> However, it is to be noted that the extent of  $\pi$ -backbonding in Group 11 metal–NHC (Cu, Au, Ag) complexes still remains a matter of debate with independent theoretical calculations carried out by Frenking<sup>[37]</sup> and Meyer,<sup>[38]</sup> who propose opposing views. In addition, a recent study by Cundari<sup>[39]</sup> concluded that a shortening of the metal–carbene bond up to 4% can be attributed to the change in hybridization state of the carbene carbon as a consequence of the enhanced *s*-character of the in-plane carbene lone pair  $\sigma$ -bonded to the metal in the metal–NHC complexes. The Ag1–Cl1 bond length of 2.3264(11) Å in **1b**, however, matches more closely with the sum of individual covalent radii of Ag and Cl (2.329 Å)<sup>[34a]</sup> and is in agreement with a single-bond character.

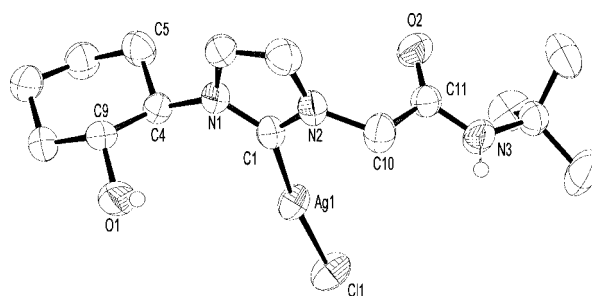


Figure 3. ORTEP drawing of **1b** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Ag–C1 2.066(4), Ag–Cl1 2.3264(11), N1–C1 1.350(4), N2–C1 1.345(5), C1–Ag–Cl1 172.66(11), N2–C1–N1 110.9(3).

Another notable structural feature of **1b** is that both of the *N*-substituents, that is, the 2-hydroxycyclohexyl and the *N*-*tert*-butylacetamido moieties, are disposed *trans* to each other with respect to the plane that contains the central imidazole ring and the silver center. The 2-hydroxy cyclohexyl O atom (O1⋯Ag1 = 4.176 Å) and the *N*-*tert*-butylacetamido O atom (O2⋯Ag1 = 4.199 Å) are located equidistant from the central Ag atom but in approximately diagonally opposite directions (*trans* orientation). Furthermore, the 2-hydroxycyclohexyl and the *N*-*tert*-butylacetamido moieties are perpendicular to the imidazole ring where the dihedral angle is 111.2° (C9–C4–N1–C1) and 85.6° (C1–N2–C10–C11), respectively.

The treatment of silver complex **1b** with (SMe<sub>2</sub>)AuCl yielded the gold complex, [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**), along with the precipitation of off-white AgCl in 77% yield. It is interesting to note that there are several methods available for the synthesis of Au–NHC complexes: (1) cleavage of electron-rich olefins,<sup>[40]</sup> (2) carbene transfer from Group 6 carbonyl complexes,<sup>[41]</sup> (3) reactions of azolium salts or free NHCs with Au<sup>I</sup> precursors,<sup>[42]</sup> (4) protonation or alkylation of gold azolyl complexes,<sup>[43]</sup> and (5) transmetalation by the reaction of Ag<sup>I</sup>–NHC complexes with Au<sup>I</sup> precursors.<sup>[32]</sup> The popularity of the transmetalation method is primarily a result of the fact that the generation of free carbenes from the imidazolium salts with the use of strong bases often

promotes decomposition reactions, and also the generated free carbenes are often difficult to handle because of their air and moisture sensitivities.<sup>[13]</sup> The <sup>1</sup>H NMR spectrum of **1c** shows two diastereotopic bridging methylene protons (-CH<sub>2</sub>-) that appear as two sets of doublets at  $\delta$  = 5.01 ppm (<sup>2</sup>*J*<sub>H,H</sub> = 15 Hz) and 4.40 ppm (<sup>2</sup>*J*<sub>H,H</sub> = 15 Hz). The Au-bound carbene (NCN) peak appears slightly shifted at  $\delta$  = 170.2 ppm compared to the Ag-bound carbene (NCN) resonance at  $\delta$  = 181.6 ppm in the <sup>13</sup>C NMR spectrum. In the infrared spectrum, the carbonyl peak of the amido (-CONH-) moiety appears at 1676 cm<sup>-1</sup> while the cyclohexyl hydroxy peak appears at 3439 cm<sup>-1</sup>.

The X-ray diffraction study revealed that the molecular structure of gold complex **1c** (Figure 4) is isomorphous with silver complex **1b**. The *N*-substituents, 2-hydroxycyclohexyl and *N*-*tert*-butylacetamido, were found to be perpendicular to the imidazole ring, and the dihedral angles between each of these two moieties and the imidazolium ring is 112.1(5)° (C9–C4–N2–C1) and 83.7(6)° (C11–C10–N1–C1), respectively. Notably, the 2-hydroxycyclohexyl O atom and the *N*-*tert*-butylacetamido O atom are disposed *trans* to each other with respect to the central imidazole ring and they also point away from the Au atom in diagonally opposite directions. The O1⋯Au1 (2-hydroxycyclohexyl O atom) and the O2⋯Au1 (*N*-*tert*-butylacetamido O atom) distances are 4.082 Å and 4.109 Å, respectively. Consistent with a shorter covalent radii of Au compared to Ag,<sup>[34]</sup> the Au1–C1 bond [1.969(5) Å] in **1c** was indeed shorter than the corresponding Ag1–C1 bond [2.066(4) Å] in **1b**. Another noticeable difference is that the N1–C1–N2 angle [105.2(4)°] in **1c** is slightly greater than the value seen in **1b** [104.3(3)°].

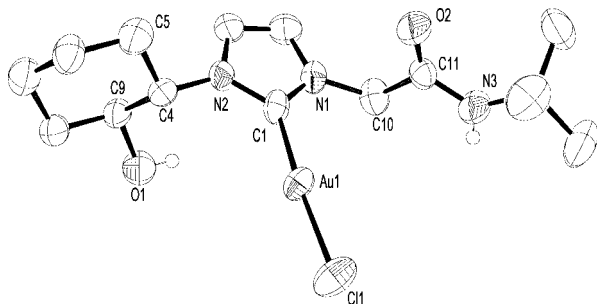


Figure 4. ORTEP drawing of **1c** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Au–C1 1.969(5), Au–C11 2.2845(13), N1–C1 1.332(6), N2–C1 1.355(5), C1–Au–C11 175.30(15), N2–C1–N1 111.3(4).

It is worth noting that compared to the numerous Ag<sup>I</sup>–NHC complexes that are known, the Au<sup>I</sup>–NHC complexes are surprisingly few in number. Correspondingly, the structural diversity exhibited by Ag<sup>I</sup>–NHC complexes are more varied and diverse<sup>[35,36,44,45]</sup> when compared to their gold counterparts,<sup>[46–48]</sup> which commonly exhibit neutral monomeric (NHC)AuX (X = halide) and cationic [(NHC)<sub>2</sub>Au]<sup>+</sup> type structures.<sup>[13]</sup> In this regard, Nolan and coworkers<sup>[49]</sup> have recently reported a series of neutral monomeric gold complexes, [1,3-bis(R)imidazol-2-ylidene]AuCl (R = mesityl, 2,6-di-*i*-propylphenyl, cyclohexyl and adamantyl); the

bond lengths and bond angles of which are comparable to that observed in **1c**.

Because of their synthetic ease and air and moisture stabilities, there is a growing emphasis on the catalytic utility of Au and Ag complexes of the (NHC)MX (M = Au, Ag, X = halide) type. Research in this area may facilitate their use as precursors in the preparation of other important compounds.

Quite significantly, both Au and Ag complexes **1c** and **1b** efficiently catalyze the bulk ROP of L-lactide under solvent-free melt conditions at elevated temperatures. To the best of our knowledge, **1c** represents the first example of a Au<sup>I</sup>–NHC based initiator for the ROP of L-lactide. Even though there exists a report of solution polymerization<sup>[18]</sup> and a report of the bulk polymerization<sup>[21]</sup> of L-lactide by Ag<sup>I</sup>–NHC complexes, we are not aware of any such polymerization by Au<sup>I</sup>–NHC complexes. Bulk polymerization exhibits certain advantages over solution polymerization: (1) no solvent is required, (2) it is less vulnerable to impurity levels and unwanted side reactions, (3) it is often useful for the large-scale production of PLAs.<sup>[28]</sup>

Specifically, a typical polymerization experiment would involve the heating of L-lactide and the catalyst, **1b** or **1c**, for a given monomer to catalyst ratio in a sealed vessel under vacuum at a designated temperature for a specific period of time. Under these conditions, the reaction mixture would form a monomer melt in which the polymerization would occur. The variation of the [M]:[C] ratio (M = monomer, C = catalyst) showed that the maximum molecular weight in the case of **1b** (Entry 2: *M<sub>n</sub>* = 5.1·10<sup>3</sup>, Table 1) as well as in **1c** (Entry 2: *M<sub>n</sub>* = 5.4·10<sup>3</sup>, Table 2) were obtained at [M]:[C] ratio 100:1 for a 4 h run at 160 °C. The molecular weight distributions are almost similar for both catalysts **1b** (PDI = 1.10–1.53) and **1c** (PDI = 1.07–1.35). Interesting would be the comparison of the polymerization results of **1b** and **1c** with that of the other reported Au and Ag–NHC complexes. As we are unaware of any Au–NHC complex known for the ROP of L-lactide, such a comparison can only be drawn for the Ag–NHC complexes.<sup>[18,21]</sup> For example, for a cationic 2:1 (NHC ligand/metal) silver–NHC complex supported over a mono-functionalized NHC ligand re-

Table 1. Melt polymerization of L-lactide by **1b**.

Entry	L-Lactide/ <b>1b</b> ratio	Temp. [°C]	Time [h]	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>	Conversion [%]
1	50	160	4	3.6·10 <sup>3</sup>	1.39	98
2	100	160	4	5.1·10 <sup>3</sup>	1.23	93
3	150	160	4	4.9·10 <sup>3</sup>	1.24	86
4	200	160	4	4.8·10 <sup>3</sup>	1.16	67
5	250	160	4	4.5·10 <sup>3</sup>	1.14	53
6	300	160	4	4.1·10 <sup>3</sup>	1.13	42
7	100	120	4	4.2·10 <sup>3</sup>	1.10	78
8	100	140	4	4.9·10 <sup>3</sup>	1.17	96
9	100	180	4	4.9·10 <sup>3</sup>	1.31	96
10	100	160	1	3.0·10 <sup>3</sup>	1.19	67
11	100	160	2	4.0·10 <sup>3</sup>	1.25	92
12	100	160	3	4.4·10 <sup>3</sup>	1.20	95
13	100	160	6	5.1·10 <sup>3</sup>	1.29	98
14	100	160	8	4.6·10 <sup>3</sup>	1.53	99



cently reported by us<sup>[21]</sup> for the bulk polymerization of L-lactide under analogous melt conditions, higher molecular weight polymers were obtained as compared to that of **1b** and **1c**. However, it should be noted that in the present study neutral monomeric (NHC)MCl (M = Ag and Au) type complexes, supported over a different difunctionalized NHC ligand, were examined as initiators for lactide polymerizations.

Table 2. Melt polymerization of L-lactide by **1c**.

Entry	L-Lactide/ <b>1c</b> ratio	Temp. [°C]	Time [h]	$M_n$	Mw/ $M_n$	Conversion [%]
1	50	160	4	$3.9 \cdot 10^3$	1.23	96
2	100	160	4	$5.4 \cdot 10^3$	1.17	80
3	150	160	4	$5.0 \cdot 10^3$	1.13	56
4	200	160	4	$3.8 \cdot 10^3$	1.22	42
5	250	160	4	$3.6 \cdot 10^3$	1.21	31
6	300	160	4	$3.6 \cdot 10^3$	1.13	29
7	100	120	4	$2.7 \cdot 10^3$	1.13	56
8	100	140	4	$4.3 \cdot 10^3$	1.17	74
9	100	180	4	$4.1 \cdot 10^3$	1.12	97
10	100	160	1	$2.0 \cdot 10^3$	1.07	27
11	100	160	2	$2.8 \cdot 10^3$	1.11	41
12	100	160	3	$3.4 \cdot 10^3$	1.11	61
13	100	160	6	$4.1 \cdot 10^3$	1.22	74
14	100	160	8	$5.1 \cdot 10^3$	1.35	90

The time-dependence study showed that the average molecular weight ( $M_n$ ) of the polymer increased with time for the first 6 h in the case of **1b** and for the first 4 h in the case of **1c**, after which it reached saturation. The temperature-dependence study was carried out in the range 120–180 °C and showed that for both **1b** and **1c** the molecular weight increased steadily with the temperature till 160 °C after which point it started to decrease. The decrease in molecular weight may be attributed to the depolymerization that takes place at higher temperatures. A similar decrease in the molecular weight at higher temperatures has been reported by Liao<sup>[27a]</sup> and by Albertson and Varma.<sup>[24]</sup> Detailed mechanistic studies are underway to establish the nature of the active species responsible for the catalysis. In this regard, it is worth mentioning that there have been reports of both metal-mediated polymerization<sup>[21]</sup> as well as carbene-mediated lactide polymerization.<sup>[52]</sup>

It is interesting to note that despite the fact that the Au–C<sub>carb</sub> bond energy (76.3 kcal/mol) is significantly stronger than the Ag–C<sub>carb</sub> bond energy (53.1 kcal/mol) in (NHC)–MCl (M = Ag and Au) complexes,<sup>[37]</sup> comparable polymer molecular weights were observed in the case of **1b** ( $M_n$  =  $3.0$ – $5.1 \cdot 10^3$ ) and **1c** ( $M_n$  =  $2.0$ – $5.4 \cdot 10^3$ ). At this juncture, it will be worthwhile to compare the activity of **1c**, with representative examples of other metal-based catalysts for the bulk ROP of L-lactide. For example, the zinc complexes of the picolyl carbene ligand, namely, ethyl zinc iodide-1-mesityl-3-picolylimidazol-2-ylidene adduct and its bis-ligand adduct gave PLAs with  $M_n$  =  $(6.1$ – $20) \cdot 10^3$ , when the polymerization was carried out at 140 °C.<sup>[26b]</sup> The molecular weight distributions (PDI = 1.78–2.45) for PLAs obtained from these picolylcarbene-based zinc complexes are, however, higher as compared to that of **1b** or **1c**. Similarly,

the Co, Ni, Cu, and Zn complexes of a Schiff base ligand derived from salicylidene and L-aspartic acid, also yielded PLAs with a viscosity average molecular weight in the order of  $(4.86$ – $11.1) \cdot 10^3$  at 130 °C over a period of 24 h.<sup>[53]</sup> Furthermore, PLAs with a relatively narrow molecular weight distribution (PDI = 1.12–1.32) have been obtained with  $M_n$  =  $(1.93$ – $2.3) \cdot 10^4$  with the use of Red-Al as a catalyst in the temperature range of 110–135 °C.<sup>[27b]</sup> In addition, a series of titanatranes with varying ring sizes have been successfully employed to achieve molecular weights [ $M_n$  =  $(1.6$ – $3.36) \cdot 10^4$ ] with PDI in the range of 1.42–1.97 at 130 °C.<sup>[27c]</sup> Recently, various ferric alkoxides [Fe(OR)<sub>3</sub>; R = Et, Pr, *i*Pr, Bu] have been reported for moderate molecular weight PLAs [ $M_n$  =  $(1.78$ – $13.97) \cdot 10^4$ ] with PDI = 1.60–1.98; however, the polymerization have been carried out up to 72 h at 130–150 °C.<sup>[27a]</sup> We believe that, as a first example of a Au-based initiator for the bulk polymerization of L-lactide, the Au–NHC complex **1c** would encourage further research in the utility of gold in this area.

## Conclusion

In summary, two new silver and gold complexes, namely, [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**) and [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**), supported over a difunctionalized *N*-heterocyclic carbene ligand have been synthesized. The **1a**, **1b**, and **1c** complexes have been structurally characterized by X-ray diffraction studies. The comparison of structures **1b** and **1c** show the formation of neutral monomeric complexes that have a 1:1 (NHC ligand/metal) stoichiometry. Notably, in neither structure **1b** nor structure **1c** was the chelation of the functionalized sidearms to the metals observed. This is in agreement with the two-coordinated *d*<sup>10</sup> configurations of the Au<sup>I</sup> and Ag<sup>I</sup> ions that prefer linear geometries. The gold and silver complexes **1c** and **1b** effectively catalyze the ROP of L-lactide under solvent-free melt conditions to produce the polylactide polymer of moderate to low molecular weight with a narrow molecular weight distribution. Gold complex **1c** represents the first example of a Au<sup>I</sup>–NHC based initiator for the ROP of L-lactide.

## Experimental Section

**General Procedures:** All manipulations were carried out with a glove box and/or standard Schlenk techniques. Solvents were purified and degassed by standard procedures. Ag<sub>2</sub>O was purchased from SD-fine chemicals (India) and used without any further purification. (SMe<sub>2</sub>)AuCl<sup>[50]</sup> and *N*-*tert*-butyl-2-chloroacetamide<sup>[51]</sup> were synthesized according to literature procedures. <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded in CDCl<sub>3</sub> with a Varian 400 MHz NMR spectrometer. <sup>1</sup>H NMR peaks are labeled as singlet (s), doublet (d) and multiplet (m). Infrared spectra were recorded with a Perkin–Elmer Spectrum One FTIR spectrometer. Mass spectrometry measurements were performed with a Micro-mass Q-ToF spectrometer. Polymer molecular weights were determined with a Waters GPC (Waters 2414 RI Detector) and with PL-

gel, 5  $\mu$  Mixed-D (2  $\times$  300 mm) column, with polystyrene standards in chloroform, with a covered molecular weight range of 140 to 4  $\times$  10<sup>5</sup>. X-ray diffraction data for **1b** was collected with a NONIUS-MACH3 diffractometer and that of **1a** and **1c** was collected on Oxford diffraction XCALIBUR-S instrument. The crystal data collection and refinement parameters are summarized in Table 3. The structures were solved by direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on *F*<sup>2</sup> with SHELXTL (Version 6.10). CCDC-606428 (**1a**), CCDC-606429 (**1b**), and CCDC-606427 (**1c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 3. X-ray crystallographic data for **1a**, **1b** and **1c**.

Compound	<b>1a</b>	<b>1b</b>	<b>1c</b>
Lattice	monoclinic	orthorhombic	orthorhombic
Formula	C <sub>15</sub> H <sub>26</sub> ClN <sub>3</sub> O <sub>2</sub>	C <sub>15</sub> H <sub>25</sub> AgClN <sub>3</sub> O <sub>2</sub>	C <sub>15</sub> H <sub>24</sub> AuClN <sub>3</sub> O <sub>2</sub>
Formula weight	315.84	422.70	510.79
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> <i>ab</i> c	<i>P</i> <i>cab</i>
<i>a</i> [Å]	14.799(4)	9.8760(11)	9.879(2)
<i>b</i> [Å]	5.648(5)	19.0390(11)	18.800(2)
<i>c</i> [Å]	21.571(3)	19.2450(12)	19.391(3)
$\alpha$ [°]	90.00	90.00	90.00
$\beta$ [°]	105.802(15)	90.00	90.00
$\gamma$ [°]	90.00	90.00	90.00
<i>V</i> [Å <sup>3</sup> ]	1734.8(16)	3618.6(5)	3601.4(11)
<i>Z</i>	4	8	8
Temperature [K]	293(2)	293(2)	293(2)
Radiation ( $\lambda$ [Å])	0.71073	0.71073	0.71073
$\rho$ (calcd.) [g cm <sup>-3</sup> ]	1.209	1.884	1.884
$\mu$ (Mo- <i>K</i> $\alpha$ ) [mm <sup>-1</sup> ]	0.228	1.271	8.328
$\theta$ max [°]	32.2342	12.2000	2.99–30.16
No. of data	3051	3182	5309
No. of parameters	194	211	203
<i>R</i> <sub>1</sub>	0.0821	0.0320	0.0316
<i>wR</i> <sub>2</sub>	0.2143	0.0708	0.0560
GOF	1.102	0.964	0.827

**Synthesis of 3-(*N*-*tert*-Butylacetamido)-1-(2-hydroxycyclohexyl)-imidazolium Chloride (**1a**):** Cyclohexene oxide (0.656 g, 6.69 mmol) and imidazole (0.455 g, 6.69 mmol) were heated at 60 °C for 12 h and the resulting sticky brown solid was dissolved in acetonitrile (ca. 20 mL). *N*-*tert*-Butyl-2-chloroacetamide (1.00 g, 6.69 mmol) was added to the solution and the reaction mixture was heated at 90 °C for 2 h. A white precipitate was collected by filtration and was recrystallized from acetonitrile (ca. 10 mL) and dried under vacuum to give the product **1a** as a white solid (2.02 g, 96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C):  $\delta$  = 9.31 (s, 1 H, NCHN), 8.19 (br., 1 H, NH), 7.44 (br., 2 H, NCHCHN), 5.16 (d, <sup>2</sup>*J* = 15 Hz, 1 H, CH<sub>2</sub>), 4.96 (d, <sup>2</sup>*J* = 15 Hz, 1 H, CH<sub>2</sub>), 4.12–4.00 (m, 1 H, C<sub>6</sub>H<sub>10</sub>), 3.62–3.56 (m, 1 H, C<sub>6</sub>H<sub>10</sub>), 2.12–1.98 (m, 4 H, C<sub>6</sub>H<sub>10</sub>), 1.78–1.68 (m, 4 H, C<sub>6</sub>H<sub>10</sub>), 1.30 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C):  $\delta$  = 163.8 (CO), 136.3 (NCHN), 123.1 (NCHCHN), 120.1 (NCHCHN), 51.8 (CH<sub>2</sub>), 34.3 (C<sub>6</sub>H<sub>10</sub>), 31.2 (C<sub>6</sub>H<sub>10</sub>), 30.9 [C(CH<sub>3</sub>)<sub>3</sub>], 28.5 [C(CH<sub>3</sub>)<sub>2</sub>], 24.5 (2C, C<sub>6</sub>H<sub>10</sub>), 23.9 (2C, C<sub>6</sub>H<sub>10</sub>) ppm. IR (KBr):  $\tilde{\nu}$  = 3213 (br, OH), 1671 (s, CO) cm<sup>-1</sup>. LRMS (ES): *m/z* (%) = 280 [100, (NHC–Ligand)<sup>+</sup>]. HRMS (ES): calcd. for (NHC–Ligand)<sup>+</sup> 280.2025; found 280.2022.

**Synthesis of [3-(*N*-*tert*-Butylacetamido)-1-(2-hydroxycyclohexyl)-imidazol-2-ylidene]AgCl (**1b**):** A mixture of 3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium chloride **1a** (2.98 g, 9.53 mmol) and Ag<sub>2</sub>O (1.11 g, 4.77 mmol) in dichloromethane (ca. 25 mL) was stirred at room temperature for 6 h. The reaction mixture

was filtered and the solvent was removed under vacuum to give the product **1b** as a white solid (3.46 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C):  $\delta$  = 8.19 (br., 1 H, NH), 7.03 (br., 2 H, NCHCHN), 4.94 (d, <sup>2</sup>*J* = 15 Hz, 1 H, CH<sub>2</sub>), 4.82 (d, <sup>2</sup>*J* = 15 Hz, 1 H, CH<sub>2</sub>), 4.25–4.20 (m, 1 H, C<sub>6</sub>H<sub>10</sub>), 3.68–3.55 (m, 1 H, C<sub>6</sub>H<sub>10</sub>), 2.13–2.04 (m, 4 H, C<sub>6</sub>H<sub>10</sub>), 1.80–1.70 (m, 4 H, C<sub>6</sub>H<sub>10</sub>), 1.34 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C):  $\delta$  = 181.6 (NCN–Ag), 166.6 (CO), 123.0 (NCHCHN), 117.8 (NCHCHN), 54.4 (CH<sub>2</sub>), 34.4 (C<sub>6</sub>H<sub>10</sub>), 32.9 (C<sub>6</sub>H<sub>10</sub>), 32.3 [C(CH<sub>3</sub>)<sub>3</sub>], 28.6 [C(CH<sub>3</sub>)<sub>2</sub>], 24.9 (2 C, C<sub>6</sub>H<sub>10</sub>), 24.4 (2 C, C<sub>6</sub>H<sub>10</sub>) ppm. IR (KBr):  $\tilde{\nu}$  = 3302 (br, OH), 1673 (s, CO) cm<sup>-1</sup>. LRMS (ES): *m/z* = 386 (NHC–Ag)<sup>+</sup>, 667 (NHC)<sub>2</sub>Ag<sup>+</sup>.

**Synthesis of [3-(*N*-*tert*-Butylacetamido)-1-(2-hydroxycyclohexyl)-imidazol-2-ylidene]AuCl (**1c**):** A mixture of [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl **1b** (0.277 g, 0.651 mmol) and (SMe<sub>2</sub>)AuCl (0.193 g, 0.651 mmol) in dichloromethane (ca. 15 mL) was stirred at room temperature for 6 h, when the formation of an off-white AgCl precipitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to obtain the product **1c** as a white solid (0.259 g, 77%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C):  $\delta$  = 9.12 (br., 1 H, NH), 7.12 (br., 1 H, NCHCHN), 6.93 (br., 1 H, NCHCHN), 5.01 (d, <sup>2</sup>*J* = 15 Hz, 1 H, CH<sub>2</sub>), 4.40 (d, <sup>2</sup>*J* = 15 Hz, 1 H, CH<sub>2</sub>), 4.35–4.29 (m, 1 H, C<sub>6</sub>H<sub>10</sub>), 3.76–3.70 (m, 1 H, C<sub>6</sub>H<sub>10</sub>), 2.07–2.01 (m, 4 H, C<sub>6</sub>H<sub>10</sub>), 1.80–1.67 (m, 4 H, C<sub>6</sub>H<sub>10</sub>), 1.30 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C):  $\delta$  = 170.2 (NCN–Au), 165.7 (CO), 123.6 (NCHCHN), 117.7 (NCHCHN), 54.4 (CH<sub>2</sub>), 41.0 (C<sub>6</sub>H<sub>10</sub>), 34.0 (C<sub>6</sub>H<sub>10</sub>), 32.4 [C(CH<sub>3</sub>)<sub>3</sub>], 29.7 [C(CH<sub>3</sub>)<sub>2</sub>], 24.9 (2 C, C<sub>6</sub>H<sub>10</sub>), 24.3 (2 C, C<sub>6</sub>H<sub>10</sub>) ppm. IR (KBr):  $\tilde{\nu}$  = 3439 (br, OH), 1676 (s, CO) cm<sup>-1</sup>.

**Polymerization Experiments:** Bulk polymerizations of L-lactide were carried out in vacuo-sealed glass ampoules. Firstly, the glass ampoule was charged with monomer (L-lactide) and dried for a period of two hours under high vacuum at 50 °C. Subsequently, the catalyst (**1b** or **1c**) was then added with the monomer to catalyst ratio in the range of 50–300. The ampoule was sealed under high vacuum and immersed in an oil bath. Polymerizations were carried out in the temperature range 120–180 °C. After a predetermined time (1–8 h) the glass ampoule was removed and subsequently the molten reactive polymer mixture was cooled while the sealed ampoule was immersed in liquid nitrogen to stop the polymerization, and thereafter the samples were removed for analysis. The analyses were performed on the crude reaction mixture; no precipitation was executed in order to avoid fractionation of the sample.

## Acknowledgments

We thank the Department of Science and Technology (Grant No: SR/S1/IC-25/2003) for financial support of this research. We are grateful to the National Single Crystal X-ray Diffraction Facility at IIT Bombay, India, for the crystallographic results. LR thanks IIT Bombay, Mumbai, for a research fellowship.

- [1] a) F. Caruso, M. Rossi, J. Tanski, C. Pettinari, F. Marchetti, *J. Med. Chem.* **2003**, *46*, 1737–1742; b) K. Nomiya, S. Yamamoto, R. Noguchi, H. Yokoyama, N. C. Kasuga, K. Ohya, C. Kato, *J. Inorg. Biochem.* **2003**, *95*, 208–220; c) K. Nomiya, S. Takahashi, R. Noguchi, *J. Chem. Soc., Dalton Trans.* **2000**, 2091–2097; d) C. F. Shaw III, *Chem. Rev.* **1999**, *99*, 2589–2600.
- [2] Y.-J. Chen, C.-T. Yeh, *J. Catal.* **2001**, *200*, 59–68.
- [3] M. R. Fructos, T. R. Belderrain, P. de Frémont, N. M. Scott, S. P. Nolan, M. M. Díaz-Requejo, P. J. Pérez, *Angew. Chem. Int. Ed.* **2005**, *44*, 5284–5288.

- [4] D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748.
- [5] L. Xu, W. Chen, J. F. Bickley, A. Steiner, J. Xiao, *J. Organomet. Chem.* **2000**, *598*, 409–416.
- [6] J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **2000**, *19*, 1194–1197.
- [7] For representative examples, see a) J. R. Miecznikowski, R. H. Crabtree, *Organometallics* **2004**, *23*, 629–631; b) S. Kuhl, R. Schneider, Y. Fort, *Organometallics* **2003**, *22*, 4184–4186; c) V. K. Dioumaev, D. J. Szalda, J. Hanson, J. A. Franz, R. M. Bullock, *Chem. Commun.* **2003**, 1670–1671; d) L. D. Vázquez-Serrano, B. T. Owens, J. M. Buriak, *Chem. Commun.* **2002**, 2518–2519; e) H. M. Lee, T. Jiang, E. D. Stevens, S. P. Nolan, *Organometallics* **2001**, *20*, 1255–1258; f) M. T. Powell, D.-R. Hou, M. C. Perry, X. Cui, K. Burgess, *J. Am. Chem. Soc.* **2001**, *123*, 8878–8879.
- [8] M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 3596–3604.
- [9] H. Van Rensburg, R. P. Tooze, D. F. Foster, A. M. Z. Slawin, *Inorg. Chem.* **2004**, *43*, 2468–2470.
- [10] For representative examples, see a) E. Mas-Marzá, M. Poyatos, M. Sanaú, E. Peris, *Inorg. Chem.* **2004**, *43*, 2213–2219; b) R. A. Diggle, S. A. Macgregor, M. M. Whittlesey, *Organometallics* **2004**, *23*, 1857–1865; c) H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2004**, *23*, 1157–1160; d) K. H. Park, S. Y. Kim, S. U. Son, Y. K. Chung, *Eur. J. Org. Chem.* **2003**, *22*, 4341–4345; e) W.-L. Duan, M. Shi, G.-B. Rong, *Chem. Commun.* **2003**, 2916–2917; f) I. E. Marko, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, *Science* **2002**, *298*, 204–206; g) V. K. Dioumaev, R. M. Bullock, *Nature* **2003**, *424*, 530–532.
- [11] M. G. Gardiner, W. A. Herrmann, C. P. Reisinger, J. Schwarz, M. Spiegler, *J. Organomet. Chem.* **1999**, *572*, 239–247.
- [12] G. Grasa, Z. Moore, K. L. Martin, E. D. Stevens, S. P. Nolan, V. Paquet, H. Lebel, *J. Organomet. Chem.* **2002**, *658*, 126–131.
- [13] For a recent review on Au–NHC complexes see I. J. B. Lin, C. S. Vasam, *Can. J. Chem.* **2005**, *83*, 812–825.
- [14] J. C. Garrison, W. J. Youngs, *Chem. Rev.* **2005**, *105*, 3978–4008.
- [15] P. L. Arnold, *Heteroat. Chem.* **2002**, *13*, 534–539.
- [16] M. M. Díaz-Requejo, P. J. Pérez, *J. Organomet. Chem.* **2005**, *690*, 5441–5450.
- [17] J. Ramírez, R. Corberán, M. Sanaú, E. Peris, E. Fernandez, *Chem. Commun.* **2005**, 3056–3058.
- [18] A. C. Sentman, S. Csihony, R. M. Waymouth, J. L. Hedrick, *J. Org. Chem.* **2005**, *70*, 2391–2393.
- [19] A. Melaiye, R. S. Simons, A. Milsted, F. Pingitore, C. Wesdemiotis, C. A. Tessier, W. J. Youngs, *J. Med. Chem.* **2004**, *47*, 973–977.
- [20] A. Melaiye, Z. Sun, K. Hindi, A. Milsted, D. Ely, D. H. Reneker, C. A. Tessier, W. J. Youngs, *J. Am. Chem. Soc.* **2005**, *127*, 2285–2291.
- [21] M. K. Samantaray, V. Katiyar, D. Roy, K. Pang, H. Nanavati, R. B. Sunoj, P. Ghosh, *Eur. J. Inorg. Chem.* **2006**, 2975–2984.
- [22] a) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176; b) B. J. O’Keefe, M. A. Hillmyer, W. B. Tolman, *J. Chem. Soc., Dalton Trans.* **2001**, 2215–2224.
- [23] a) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, E. J. Munson, *Macromolecules* **1998**, *31*, 1487–1494; b) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A. Doscotch, J. I. Siepmann, E. J. Munson, *Macromolecules* **1997**, *30*, 2422–2428.
- [24] A.-C. Albertsson, I. K. Varma, *Biomacromolecules* **2003**, *4*, 1466–1486.
- [25] a) M. Okada, *Prog. Polym. Sci.* **2002**, *27*, 87–133; b) H. R. Kricheldorf, *Chemosphere* **2001**, *43*, 49–54.
- [26] a) J. Ejfler, M. Kobylka, L. B. Jerzykiewicz, P. Sobota, *Dalton Trans.* **2005**, 2047–2050; b) T. R. Jensen, C. P. Schaller, M. A. Hillmyer, W. B. Tolman, *J. Organomet. Chem.* **2005**, *690*, 5881–5891; c) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Chem. Commun.* **2003**, 48–49; d) C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young Jr, M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc.* **2003**, *125*, 11350–11359; e) M. Myers, E. F. Connor, T. Glauser, A. Möck, G. Nyce, J. L. Hedrick, *J. Polymer Sci., Part A: Polym. Chem.* **2002**, *40*, 844–851; f) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238; g) Ph. Dubios, N. Ropson, R. Jérôme, Ph. Teyssié, *Macromolecules* **1996**, *29*, 1965–1975.
- [27] a) X. Wang, K. Liao, D. Quan, Q. Wu, *Macromolecules* **2005**, *38*, 4611–4617; b) H. Li, C. Wang, F. Bai, J. Yue, H.-G. Woo, *Organometallics* **2004**, *23*, 1411–1415; c) Y. Kim, J. G. Verkade, *Organometallics* **2002**, *21*, 2395–2399; d) A. J. Nijenhuis, D. W. Grijpma, A. J. Pennings, *Macromolecules* **1992**, *25*, 6419–6424.
- [28] D. Garlotta, *J. Polym. Environ.* **2001**, *9*, 63–84.
- [29] P. L. Arnold, M. Rodden, K. M. Davis, A. C. Scarisbrick, A. J. Blake, C. Wilson, *Chem. Commun.* **2004**, 1612–1613.
- [30] E. Mas-Marzá, M. Sanaú, E. Peris, *Inorg. Chem.* **2005**, *44*, 9961–9967.
- [31] D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2004**, *43*, 2197–2205.
- [32] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975.
- [33] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed. **1999**, p. 1085–1094.
- [34] a) L. Pauling, *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, **1960**; p. 224–228, 256–258; b) U. M. Tripathi, A. Bauer, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1997**, 2865–2868.
- [35] T. Ramnial, C. D. Abernethy, M. D. Spicer, I. D. McKenzie, I. D. Gay, J. A. C. Clyburne, *Inorg. Chem.* **2003**, *42*, 1391–1393.
- [36] A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz, G. Eastham, *J. Chem. Soc., Dalton Trans.* **2000**, 4499–4506.
- [37] D. Nemcsok, K. Wichmann, G. Frenking, *Organometallics* **2004**, *23*, 3640–3646.
- [38] X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, *Organometallics* **2004**, *23*, 755–764.
- [39] E. Baba, T. R. Cundari, I. Firkin, *Inorg. Chim. Acta* **2005**, *358*, 2867–2875.
- [40] B. Cetinkaya, P. Dixneuf, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1974**, 1827–1833.
- [41] a) S.-T. Liu, K. R. Reddy, *Chem. Soc. Rev.* **1999**, *28*, 315–322; b) R.-Z. Ku, J.-C. Huang, J.-Y. Cho, F.-M. Kiang, K. R. Reddy, Y.-C. Chen, Y. K.-J. Lee, J.-H. Lee, G.-H. Lee, S.-M. Peng, S.-T. Liu, *Organometallics* **1999**, *18*, 2145–2154.
- [42] K. M. Lee, C. K. Lee, I. J. B. Lin, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1850–1852.
- [43] B. Bovio, S. Calogero, F. E. Wagner, A. Burini, B. R. Pietroni, *J. Organomet. Chem.* **1994**, *470*, 275–283.
- [44] K. M. Lee, H. M. J. Wang, I. J. B. Lin, *J. Chem. Soc., Dalton Trans.* **2002**, 2852–2856.
- [45] Q.-X. Liu, F.-B. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng, Y. L. Chou, Z.-Z. Zhang, *Organometallics* **2003**, *22*, 309–314.
- [46] V. J. Catalano, A. L. Moore, *Inorg. Chem.* **2005**, *44*, 6558–6566.
- [47] H. M. J. Wang, C. S. Vasam, T. Y. R. Tsai, S.-H. Chen, H. H. Chang, I. J. B. Lin, *Organometallics* **2005**, *24*, 486–493.
- [48] M. V. Baker, P. J. Barnard, S. J. Berners-Price, S. K. Brayshaw, J. L. Hickey, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2005**, *690*, 5625–5635.
- [49] P. de Frémont, N. M. Scott, E. D. Stevens, S. P. Nolan, *Organometallics* **2005**, *24*, 2411–2418.
- [50] M.-C. Brandys, M. C. Jennings, R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.* **2000**, 4601–4606.
- [51] M. P. Dave, J. M. Patel, N. A. Langalia, S. R. Shah, K. A. Thaker, *J. Indian Chem. Soc.* **1985**, *62*, 386–387.
- [52] G. W. Nyce, T. Glauser, E. F. Connor, A. Mock, R. M. Waymouth, J. L. Hedrick, *J. Am. Chem. Soc.* **2003**, *125*, 3046–3056.
- [53] J. Sun, W. Shi, D. Chen, C. Liang, *J. Appl. Polym. Sci.* **2002**, *86*, 3312–3315.

Received: May 3, 2006

Published Online: August 7, 2006



# Air-stable, convenient to handle Pd based PEPPSI (pyridine enhanced precatalyst preparation, stabilization and initiation) themed precatalysts of *N/O*-functionalized N-heterocyclic carbenes and its utility in Suzuki–Miyaura cross-coupling reaction†‡

Lipika Ray,<sup>a</sup> Mobin M. Shaikh<sup>b</sup> and Prasenjit Ghosh<sup>\*a</sup>

Received 1st May 2007, Accepted 6th July 2007

First published as an Advance Article on the web 2nd August 2007

DOI: 10.1039/b706607d

Several new air-stable, convenient to handle and easily synthesized Pd based PEPPSI (Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation) type precatalysts supported over *N/O*-functionalized N-heterocyclic carbenes (NHC) namely, *trans*-[1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]Pd(pyridine)Cl<sub>2</sub> (**2**), *trans*-[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]Pd(pyridine)Cl<sub>2</sub> (**3**) and *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd(pyridine)Br<sub>2</sub> (**4**), have been designed. Specifically, the Pd–NHC complexes, **2**, **3** and **4**, were conveniently synthesized from their respective imidazolium halide salts by the reaction with PdCl<sub>2</sub> in pyridine in presence of K<sub>2</sub>CO<sub>3</sub> as a base. A new imidazolium chloride salt, 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride (**1**) was synthesized by the alkylation reaction of benzyl imidazole with *N*-*t*-butyl-2-chloroacetamide. The molecular structures of the imidazolium chloride salt, **1**, and the Pd–NHC complexes, **2**, **3** and **4**, have been determined by X-ray diffraction studies. The density functional theory studies of the **2**, **3** and **4** complexes were carried out in order to gain insight about their structure, bonding and the electronic properties. The nature of the NHC–metal bond in these complexes was examined using Charge Decomposition Analysis (CDA), which revealed that the N-heterocyclic carbene ligands are effective  $\sigma$ -donors. In addition, the catalysis studies revealed that the Pd–NHC complexes, **2**, **3** and **4**, are effective catalysts for the Suzuki–Miyaura type C–C cross-coupling reactions.

## Introduction

With N-heterocyclic carbenes (NHCs) being extremely successful in homogeneous catalysis<sup>1</sup> and with Pd emerging as an undisputed leader in the catalysis of many important C–C bond forming reactions<sup>2</sup> namely, the Hiyama,<sup>3</sup> Kumada,<sup>4</sup> Negishi,<sup>5</sup> Suzuki,<sup>6</sup> and Stille<sup>7</sup> reactions, rational catalyst designing involving Pd–NHC complexes has thus taken center stage and has brought forth significant advancements in the area of catalyst development in recent years. The focus has mainly been on developing a universal catalyst that would be highly efficient, robust, user-friendly and convenient to synthesize and could be employed for various Pd-mediated cross-coupling reactions.<sup>2</sup> The key to a rational catalyst designing exercise lies in the successful realization of important fundamental concepts<sup>8</sup> and one such instance has been in the introduction of a “throwaway ligand,” intended to give way to the incoming substrate, in the

Grubbs catalyst for olefin metathesis.<sup>9</sup> Specifically, when loosely bound pyridine and its substituted derivatives, acting as the “throwaway” ligands, replaced a more tightly bound tricyclohexylphosphane (PCy<sub>3</sub>) in the Grubbs second-generation catalyst, [(H<sub>2</sub>IMes)(PCy<sub>3</sub>)(Cl)<sub>2</sub>Ru=CHPh], higher activities were observed even for the more challenging acetonitrile Cross-Metathesis (CM) reactions.<sup>9</sup> Along a similar theme, PEPPSI (Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation), a term recently coined and demonstrated by Organ and coworkers,<sup>10,11</sup> also resulted in highly active catalysts for various Pd-mediated C–C cross-coupling reactions.

Our interest lies in designing high performance Pd catalysts stabilized by *N/O*-functionalized N-heterocyclic carbenes (NHCs) for a variety of C–C bond forming reactions particularly, the Suzuki–Miyaura cross-coupling reaction.<sup>12</sup> The growing popularity of the Suzuki–Miyaura cross-coupling reaction can be ascribed to mild reaction conditions (ambient temperature *ca.* 80–100° C in air), commercial availability of diverse boronic acids that are also environmentally safer than many organometallic reagents, the ease of handling and removal of boron by-products and functional group tolerance.<sup>13</sup> The extent of the importance of the Suzuki–Miyaura cross-coupling reaction can be gauged from the diverse range of its applications that span from materials to pharmaceuticals to polymers to ligands in organometallic chemistry to natural product synthesis.<sup>13</sup> For example, many important natural products and pharmaceuticals possessing complex

<sup>a</sup>Department of Chemistry, Powai, Mumbai, 400 076

<sup>b</sup>National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology Bombay, Powai, Mumbai, 400 076. E-mail: pghosh@chem.iitb.ac.in; Fax: +91 22 2572 3480

† CCDC reference numbers 623546 (**1**), 630834 (**2**), 627573 (**3**) and 623095 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706607d

‡ Electronic supplementary information (ESI) available: B3LYP coordinates for geometry optimized calculations and CDA of **2**, **3** and **4**. See DOI: 10.1039/b706607d

architectures like, kendamycin,<sup>14</sup> myxovirescin,<sup>15</sup> marinomycin A,<sup>16</sup> vancomycin<sup>17</sup> etc. have been synthesized employing the Suzuki–Miyaura cross-coupling reaction.

Our intention in using *N/O*-functionalized *N*-heterocyclic carbenes for designing these precatalysts was in enhancing the stability of these precatalysts as the incorporation of polar groups often leads to greater stability of metal–NHC complexes through a variety of intermolecular interactions,<sup>18</sup> chelation to the metal center,<sup>19</sup> etc. For example, higher decomposition temperatures (*ca.* > 180 °C) were observed for the two cationic Ag–NHC complexes, [(1-*i*-propyl-3- $\{N$ -phenylacetamido $\}$ imidazol-2-ylidene)<sub>2</sub>Ag]<sup>+</sup>Cl<sup>–</sup><sup>18</sup> and {[1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazol-2-ylidene]<sub>2</sub>Ag}<sup>+</sup>Cl<sup>–</sup>,<sup>20</sup> bearing *N/O*-functionalized sidearms as *N*-substituents.

Here in this contribution, we report the syntheses and structural characterizations of a series of air-stable, convenient to handle and easily accessible PEPSI styled precatalysts, *trans*-(NHC)Pd(pyridine)X<sub>2</sub> (X = Cl, Br) (Fig. 1), **2**, **3** and **4**, stabilized over *N/O*-functionalized *N*-heterocyclic carbene ligands and containing a “throwaway” pyridine ligand. These **2**, **3** and **4** precatalysts are effective for the Suzuki–Miyaura cross-coupling reactions of phenylboronic acids and aryl halides (X = Br, I). In addition, the synthesis and the structural characterization of a new imidazolium chloride salt, 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride **1** is also described.

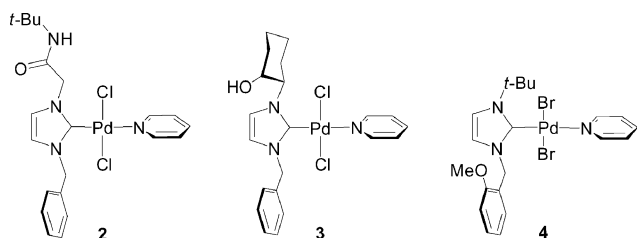
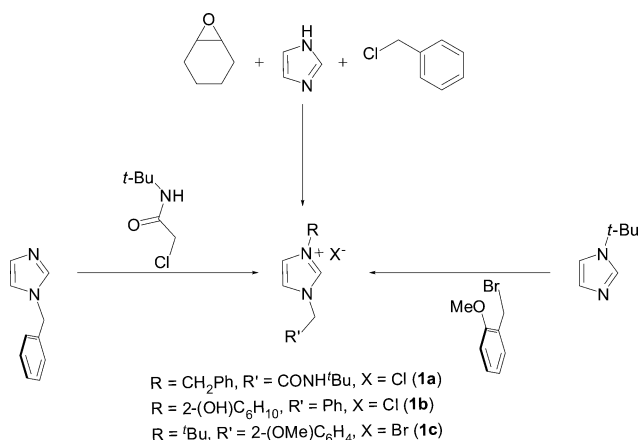


Fig. 1 *trans*-(NHC)Pd(pyridine)X<sub>2</sub> (X = Cl, Br) **2**, **3** and **4**.

## Results and discussion

The *N/O*-functionalized imidazolium halide salts were synthesized as outlined in Scheme 1. While the 1-(2-hydroxycyclohexyl)-3-(benzyl)imidazolium chloride<sup>21</sup> was synthesized by



Scheme 1

following a ring-opening reaction of the cyclohexene oxide with imidazole and benzyl chloride reported earlier by us,<sup>22</sup> the 1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazolium bromide<sup>12</sup> and 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride **1** were synthesized by the direct alkylation reaction of the respective imidazoles with the corresponding alkyl halides. Specifically, the new imidazolium chloride salt, **1**, was synthesized by the alkylation reaction of benzyl imidazole with *N*-*t*-butyl-2-chloroacetamide in 70% yield. The formation of **1** was verified by the appearance of the diagnostic NCHN peak at 10.1 ppm in the <sup>1</sup>H NMR spectrum. The two bridging methylene peaks of the benzyl and the *N*-*t*-butylacetamido moieties appeared at 5.45 ppm and 5.31 ppm in the <sup>1</sup>H NMR spectrum and at 53.0 ppm and 51.8 ppm in the <sup>13</sup>C NMR spectrum. The amide proton of the –CONH– moiety appeared downfield shifted at 8.66 ppm in the <sup>1</sup>H NMR spectrum while the carbonyl band of the –CONH– moiety appeared at 1685 cm<sup>–1</sup> in the infrared spectrum.

The molecular structure of the imidazolium chloride salt, **1**, has been determined by X-ray diffraction studies (Table 1 and Fig. 2). The N–C bond distances of 1.329(3) Å and 1.330(3) Å in the imidazolium ring are consistent with its aromatic nature and are in concurrence with the values reported for other structurally characterized imidazolium halide salts. For example, in closely related imidazolium halide salts the corresponding N–C distances are, 1-(2-hydroxycyclohexyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride<sup>22</sup> [1.326(6) Å, 1.314(6) Å], 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride<sup>23</sup> [1.320(2) Å, 1.323(2) Å] and 1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazolium chloride<sup>20</sup> [1.324(3) Å, 1.322(3) Å]. Similarly, the ∠N–C–N angle of 108.60(17)° of the imidazolium ring in **1** is similar to that of other related imidazolium halide salts.

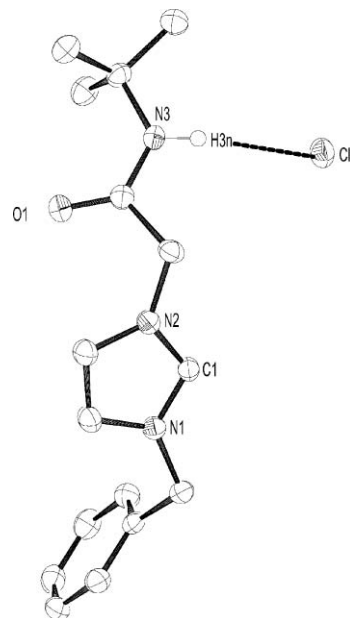


Fig. 2 ORTEP of **1** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.329(3), N(2)–C(1) 1.330(3), N(1)–C(1)–N(2) 108.60(17).

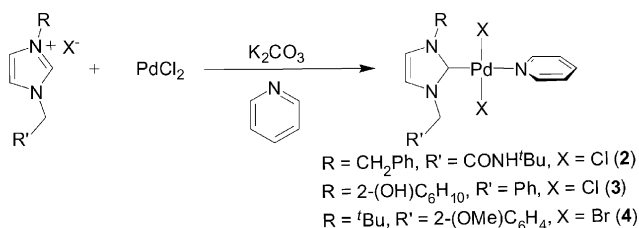
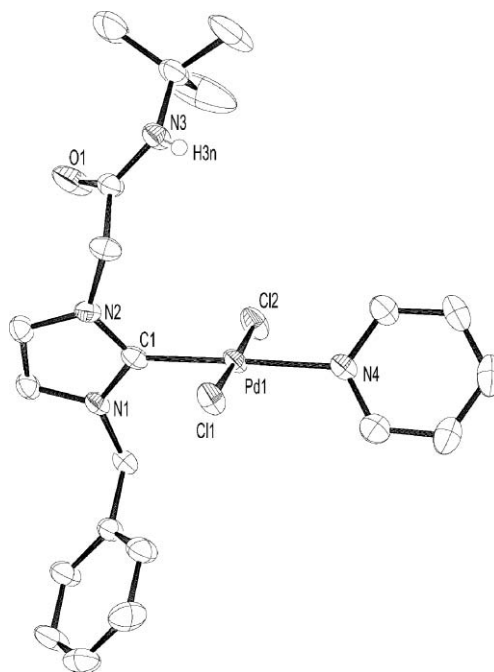
The most important aspect of the imidazolium chloride **1** structure is the presence of [Cl⋯H–N] type H-bonding interaction

**Table 1** X-Ray crystallographic data for **1**, **2**, **3** and **4**

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Lattice	Triclinic	Triclinic	Triclinic	Monoclinic
Formula	C <sub>16</sub> H <sub>22</sub> ClN <sub>3</sub> O	C <sub>21</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>4</sub> OPd	C <sub>21</sub> H <sub>25</sub> Cl <sub>2</sub> N <sub>3</sub> OPd	C <sub>20</sub> H <sub>25</sub> Br <sub>2</sub> N <sub>3</sub> OPd
Formula weight	307.82	527.76	512.74	589.65
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	6.0741(3)	10.829(2)	8.9556(10)	12.9252(3)
<i>b</i> /Å	10.996(3)	11.2668(15)	9.830(2)	10.8313(3)
<i>c</i> /Å	12.313(4)	11.429(2)	14.552(2)	16.0613(4)
<i>a</i> /°	82.75(2)	107.068(14)	71.923(17)	90.00
<i>β</i> /°	83.452(14)	111.852(19)	75.819(10)	102.569(2)
<i>γ</i> /°	81.642(13)	100.997(14)	64.689(16)	90.00
<i>V</i> /Å <sup>3</sup>	803.3(3)	1164.3(4)	1091.5(3)	2194.64(10)
<i>Z</i>	2	2	2	4
Temperature/K	150(2)	150(2)	150(2)	150(2)
Radiation (λ/Å)	0.71073	0.71073	0.71073	0.71073
ρ(calcd.)/g cm <sup>-3</sup>	1.273	1.505	1.560	1.785
μ(Mo-Kα), mm <sup>-1</sup>	0.241	1.045	1.111	4.501
θ/°	25.00–3.35	32.50–3.05	32.17–3.09	32.19–3.20
No. of data	2819	4090	3827	3840
No. of parameters	197	269	253	248
<i>R</i> <sub>1</sub>	0.0411	0.0374	0.0365	0.0682
<i>wR</i> <sub>2</sub>	0.1049	0.0963	0.0834	0.2190
GOF	1.207	1.009	1.088	1.169

between the Cl<sup>−</sup> anion and the amide proton of the –CONH– substituent of the imidazole ring. The [Cl⋯N] distance of 3.267 Å is comparable to the sum of the individual van der Waals radii (Cl–N = 3.30 Å).<sup>24</sup> Quite interestingly, the Cl<sup>−</sup> anion was found to interact with the amide proton of the –CONH– substituent and not with the acidic NCHN proton of the imidazole ring. In this regard, it is worth mentioning that the H-bonding interaction of the halide counter anion with the acidic proton of the functional sidearm (HX<sup>−</sup>; X = O, NR) as well as with that of the acidic NCHN proton have been observed for various imidazolium halide salts. Indeed, examples of imidazolium halide salts exhibiting all three [Cl⋯H–O] [*d*<sub>(Cl⋯O)</sub> = 3.091 Å],<sup>22</sup> [Cl⋯H–N] [*d*<sub>(Cl⋯N)</sub> = 3.244 Å, 3.236 Å]<sup>20</sup> and [Cl⋯H–C] [*d*<sub>(Cl⋯C)</sub> = 3.373 Å]<sup>23</sup> types of H-bonding interactions have been recently reported by us. It is worth mentioning that the H-bonding interaction in imidazolium halide salts has been extensively studied by NMR<sup>25</sup> and X-ray diffraction techniques.<sup>26</sup>

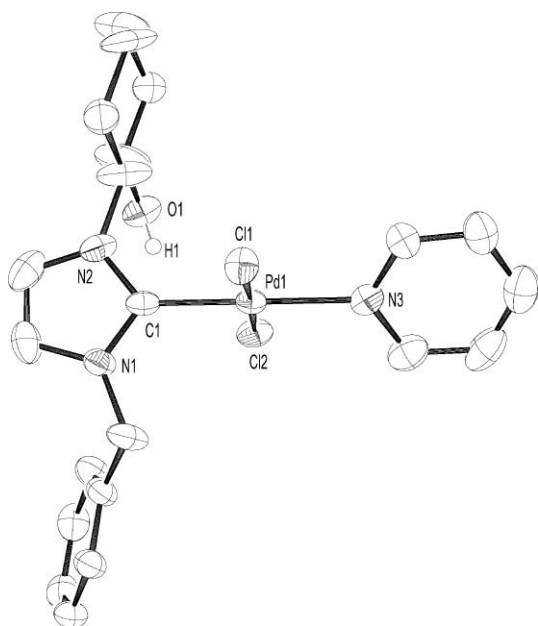
The **2**, **3** and **4** precatalysts were conveniently synthesized by direct reaction of the imidazolium halide salt with PdCl<sub>2</sub> in pyridine (Scheme 2).<sup>11</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR of **2**, **3** and **4** showed the metal bound carbene NCN–Pd resonances appearing at 157–153 ppm and are comparable to that observed in other reported Pd–NHC complexes (175–145 ppm).<sup>27</sup> The **2**, **3** and **4** complexes have been structurally characterized and, as expected, the geometries around the Pd centers were found to be square planar (Table 1 and Fig. 3–5) with the C<sub>carbene</sub>–Pd–Cl angles in

**Scheme 2**

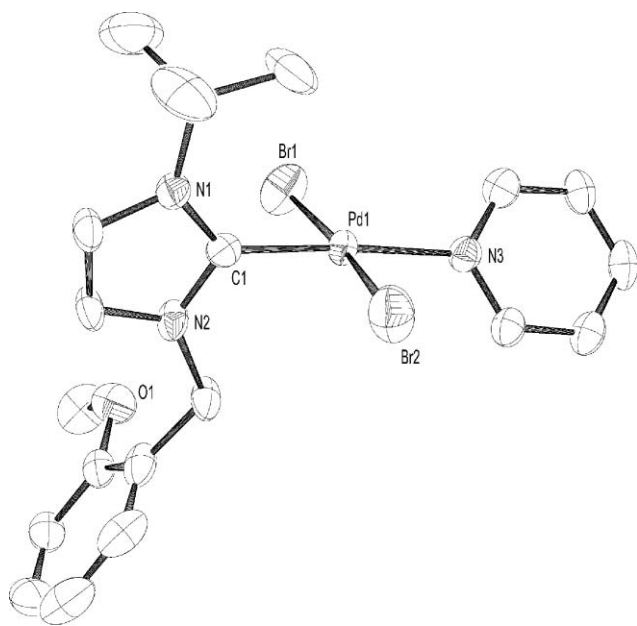
**Fig. 3** ORTEP of **2** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.356(4), N(2)–C(1) 1.337(4), Pd(1)–C(1) 1.957(3), Pd(1)–Cl(1) 2.3026(9), Pd(1)–N(4) 2.089(3), C(1)–Pd(1)–N(4) 178.63(11), C(1)–Pd(1)–Cl(1) 87.62(9).

**2** [C1–Pd1–Cl2 = 91.24(9)°], **3** [C1–Pd1–Cl2 = 88.70(11)°] and **4** [C1–Pd1–Br2 = 86.3(2)°] being closer to *ca.* 90°. While the C<sub>carbene</sub>–Pd–N<sub>pyridine</sub> angles in **2** [C1–Pd1–N4 = 178.63(11)°], **3** [C1–Pd1–N3 = 179.66(14)°] and **4** [C1–Pd1–N3 = 176.0(3)°] are nearly linear. The Pd–C<sub>carbene</sub> bond distances [1.953(8)–1.967(4) Å] in these complexes, **2** [Pd1–C1 = 1.957(3) Å], **3** [Pd1–C1 = 1.967(4) Å] and **4** [Pd1–C1 = 1.953(8) Å], are comparable to that reported for other Pd–NHC complexes.<sup>19,28,29</sup> The two Pd–Cl bond distances in **2** [Pd1–Cl1 = 2.3026(9) Å, Pd1–Cl2 = 2.2913(9) Å] and **3**





**Fig. 4** ORTEP of **3** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.345(5), N(2)–C(1) 1.343(5), Pd(1)–C(1) 1.967(4), Pd(1)–Cl(1) 2.3071(10), Pd(1)–N(3) 2.096(3), C(1)–Pd(1)–N(3) 179.66(14), C(1)–Pd(1)–Cl(1) 89.07(11).



**Fig. 5** ORTEP of **4** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.359(11), N(2)–C(1) 1.341(12), Pd(1)–C(1) 1.953(9), Pd(1)–Br(1) 2.3993(13), Pd(1)–N(3) 2.100(8), C(1)–Pd(1)–N(3) 176.0(3), C(1)–Pd(1)–Br(1) 87.6(2).

[Pd1–Cl1 = 2.3071(10) Å, Pd1–Cl2 = 2.3068(10) Å] and the two Pd–Br bond distances in **4** [Pd1–Br1 = 2.399(2) Å, Pd1–Br2 = 2.393(2) Å] are comparable to the sum of the individual covalent radii (Pd–Cl = 2.273 Å and Pd–Br = 2.423 Å).<sup>30</sup> Quite interestingly, though no chelation of the functionalized sidearms to Pd was observed in any of the **2**, **3** and **4** complexes, a variety

of both intermolecular as well as intramolecular H-bonding interactions involving the functional sidearm substituents were observed in these complexes *e.g.*, **2** (intermolecular [Cl⋯H–N] interaction,  $d_{(\text{Cl}\cdots\text{N})} = 3.306$  Å), **3** (intramolecular [Cl⋯H–O] interaction,  $d_{(\text{Cl}\cdots\text{O})} = 3.316$  Å, intermolecular [Cl⋯H–C] interaction,  $d_{(\text{Cl}\cdots\text{C})} = 3.695$  Å) and **4** (intermolecular [Br⋯H–C] interaction,  $d_{(\text{Br}\cdots\text{C})} = 3.666$  Å, intermolecular [Br⋯H–C] interaction,  $d_{(\text{Br}\cdots\text{C})} = 3.583$  Å).

The role of the metal bound pyridine is vital to the observed high activities of the PEPPSI based precatalysts and thus merits discussion. For the **2**, **3** and **4** complexes, the Pd-bound pyridine appeared as distinct resonances in comparison to the free pyridine in the <sup>1</sup>H NMR spectra of these complexes.<sup>31</sup> However, the definitive proof came from the X-ray diffraction studies that showed the pyridine was, indeed, coordinated to Pd and was tilted by *ca.* 39°–46° relative to the plane containing the imidazolium ring of the NHC ligand.<sup>32</sup> Interestingly, the Pd–N (pyridine) bond distances [2.100(8)–2.089(3) Å] in **2**, **3** and **4** are closer to that in a related complex, [1,3-bis-2,6-di-*i*-propylphenyl-imidazol-2-ylidene]PdCl<sub>2</sub>(3-chloropyridine) [2.137(2) Å],<sup>11</sup> bearing a similar *trans* pyridine ligand, but are longer than that observed [2.017(4) Å] in [{CNC}Pd(pyridine)][BF<sub>4</sub>]<sub>2</sub>, [CNC = (2,6-bis{[N-methyl-*N'*-methylene]imidazol-2-ylidene}pyridine)],<sup>33</sup> in which the metal bound pyridine was not *trans* to the NHC ligand. It is worth noting that owing to the strong *trans*-effect<sup>34</sup> of the N-heterocyclic carbene ligand, the Pd–N (pyridine) bond distance of the *trans*-pyridine is expected to be longer, thereby, resulting in weaker binding of the pyridine and subsequent triggering of the “throwaway” pyridine ligand dissociation in the initiation step of the catalytic cycle.<sup>10,11</sup> Indeed, when the precatalyst **4** was heated at 85 °C with 3 equivalents of phenylboronic acid in the absence of aryl halides, simultaneous formations of pyridine and biphenyl, as verified independently by gas chromatography, were observed. Further support for the relatively weaker Pd–pyridine bond came from the density functional theory studies as the Pd–pyridine bond dissociation energy [ $D_e$  (Pd–pyridine)], computed for the geometry optimized structures of **2**, **3** and **4** respectively designated by **2'**, ( $32.9$  kcal mol<sup>–1</sup>), **3'** ( $32.7$  kcal mol<sup>–1</sup>), and **4'** ( $30.8$  kcal mol<sup>–1</sup>) using B3LYP/SDD, 6-31G(d) level of theory, were found to be significantly lower than the (NHC)–Pd bond dissociation energy [ $D_e$  (Pd–C<sub>carbene</sub>)] in these complexes, **2'** ( $81.9$  kcal mol<sup>–1</sup>), **3'** ( $82.4$  kcal mol<sup>–1</sup>) and **4'** ( $77.6$  kcal mol<sup>–1</sup>) and thus the pyridine moiety in these palladium complexes are more amenable to dissociation.

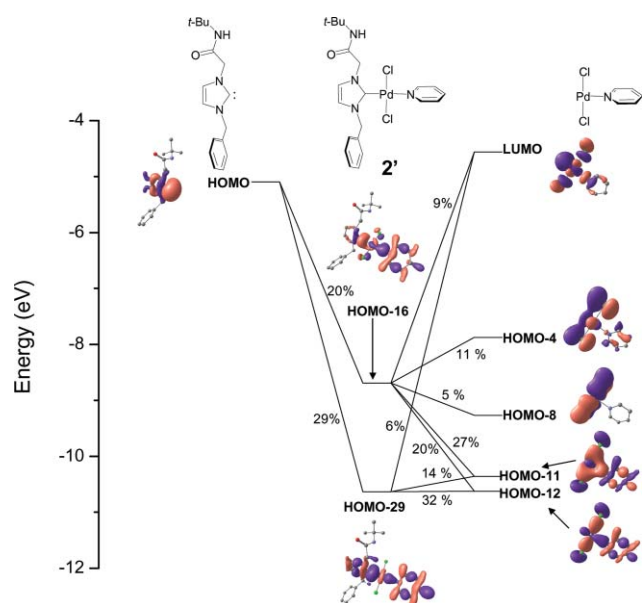
Detailed bonding studies on the geometry optimized structures **2'**, **3'** and **4'** were performed using Charge Decomposition Analysis (CDA) that involved breaking the molecule into two fragments, *i.e.* N-heterocyclic carbene (NHC) (fragment 1) and Pd(pyridine)X<sub>2</sub> (fragment 2) (Table 2). The optimized geometries were obtained from the crystallographic co-ordinates using B3LYP/SDD, 6-31G\* level of theory for the complexes **2**, **3** and **4**. The electron donation from the carbene fragment to the metal center [NHC → Pd(pyridine)X<sub>2</sub>] is denoted as *d* while the electron back donation from the metal center to the carbene moiety [NHC ← Pd(pyridine)X<sub>2</sub>] is represented by *b* and the (*d*/*b*) ratio gives a measure of the forward [NHC → Pd(pyridine)X<sub>2</sub>] and backward [NHC ← Pd(pyridine)X<sub>2</sub>] donations occurring in these complexes. Thus high (*d*/*b*) ratio in **2'** (2.59), **3'** (2.79) and **4'** (3.99) complexes are indicative of the predominantly

**Table 2** Charge decomposition analysis (CDA) results showing the  $[\text{NHC} \rightarrow \sigma \text{ Pd(pyridine)X}_2]$  donation (*d*), the  $[\text{NHC} \leftarrow \pi \text{ Pd(pyridine)X}_2]$  donation (*b*) and the *d/b* ratio for the geometry optimized structures, **2'**, **3'** and **4'** are shown

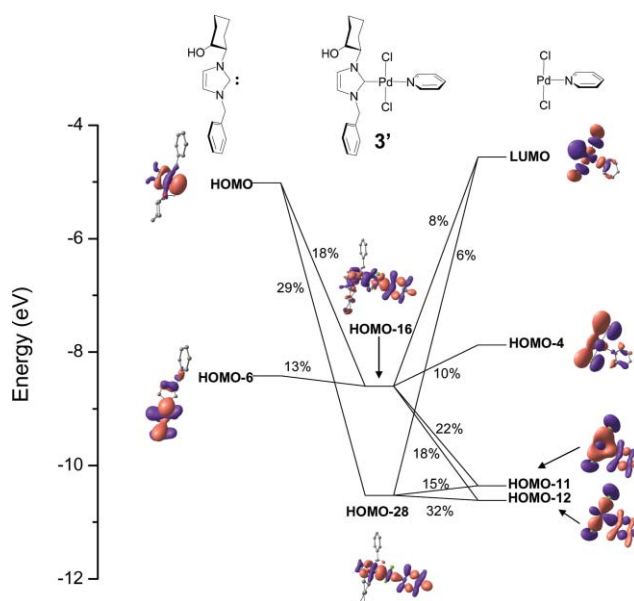
Complexes	$[\text{NHC} \rightarrow \sigma \text{ Pd(pyridine)X}_2]$	$[\text{NHC} \leftarrow \pi \text{ Pd(pyridine)X}_2]$	<i>d/b</i> ratio
<b>2'</b>	0.559	0.216	2.59
<b>3'</b>	0.570	0.204	2.79
<b>4'</b>	0.603	0.151	3.99

$\sigma$ -donating nature of the N-heterocyclic carbene ligands. In this regard, it is worth noting that theoretical studies earlier carried out by us<sup>18,23</sup> on Ag–NHC complexes and also by others<sup>35</sup> suggest that N-heterocyclic carbenes as ligands, in general, are strong  $\sigma$ -donors with minimal  $\pi$ -accepting abilities and, thus would be conducive to the stabilization of the Pd center after the pyridine dissociation.<sup>10,11</sup>

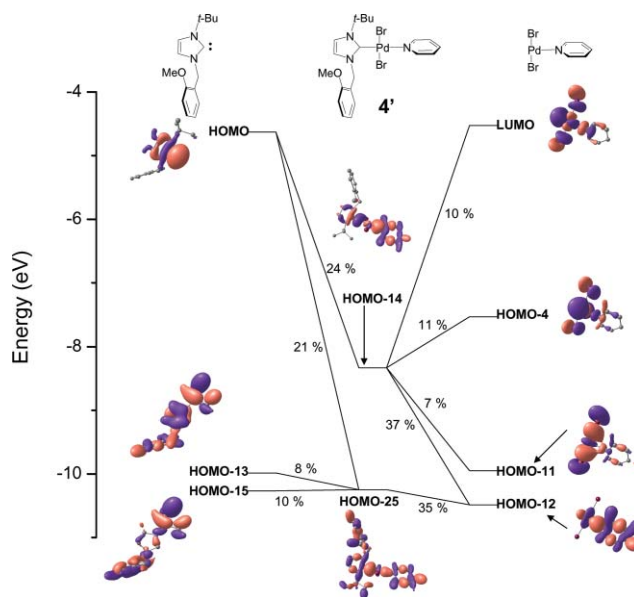
In order to gain insight about the NHC–palladium bonding, a detailed molecular orbital analysis was carried out using the AOMix-CDA software,<sup>36</sup> in which the orbital contributions to the frontier molecular orbitals of the geometry optimized (NHC)Pd(pyridine)X<sub>2</sub> type complexes, **2'** (X = Cl), **3'** (X = Cl) and **4'** (X = Br), from the individual NHC and the Pd(pyridine)X<sub>2</sub> fragments (X = Cl, Br) were considered. Interestingly, the molecular orbitals signifying the NHC–palladium interactions were found buried deep inside the surface *i.e.* in **2'** (HOMO-16 and HOMO-29, Fig. 6), **3'** (HOMO-16 and HOMO-28, Fig. 7) and **4'** (HOMO-14 and HOMO-25, Fig. 8) and were consistent with the inert character of the NHC–palladium bond that are often attributed to the “spectator” nature of the NHC ligand in general.<sup>1a</sup> Specifically, the contributions of the NHC and the Pd(pyridine)X<sub>2</sub> fragments to these molecular orbitals were, **2'** [HOMO-16 {20% NHC fragment, 71% from Pd(pyridine)Cl<sub>2</sub>}, HOMO-29 {29% NHC fragment, 52% from Pd(pyridine)Cl<sub>2</sub>}] (Fig. 6), **3'** [HOMO-16 {31% NHC fragment, 58% from Pd(pyridine)Cl<sub>2</sub>}, HOMO-28 {29% NHC fragment, 54% from Pd(pyridine)Cl<sub>2</sub>}] (Fig. 7) and **4'** [HOMO-14 {24% NHC fragment, 64% from Pd(pyridine)Br<sub>2</sub>}, HOMO-



**Fig. 6** Orbital interaction diagram showing the major contributions of the NHC–palladium bond in **2'**.



**Fig. 7** Orbital interaction diagram showing the major contributions of the NHC–palladium bond in **3'**.



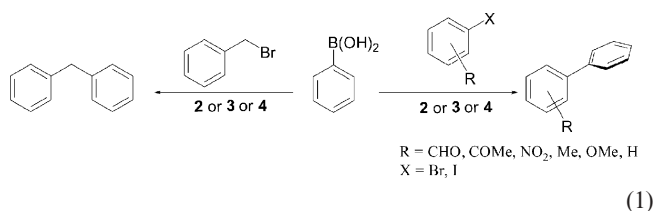
**Fig. 8** Orbital interaction diagram showing the major contributions of the NHC–palladium bond in **4'**.

**25** {39% NHC fragment, 35% from Pd(pyridine)Br<sub>2</sub>}] (Fig. 8). However, detailed orbital interactions are more intricate due to the contributions from various other fragment molecular orbitals (FMO) in the palladium complexes. It is interesting to note that

donation of the carbene lone pair partially occurs to the Pd–pyridine  $\sigma^*$  orbital as can be seen in Fig. 6, 7 and 8 thereby weakening the Pd–pyridine bond.

A comparison of the solid state crystal structures of **2**, **3** and **4** with that of the geometry optimized structures **2'**, **3'** and **4'** revealed good agreement between the X-ray and computed structures (See Tables S4, S5 and S6<sup>†</sup>).

The Pd complexes **2**, **3** and **4** efficiently catalyzed the Suzuki–Miyaura cross-coupling (eqn (1)) of a wide variety of aryl halide substrates with phenyl boronic acid at a low catalyst loading (0.35 mol%). It is interesting to note that high modulations of the yields (> 99–7%) of the cross-coupled products were seen, with higher yields observed for aryl halides containing activating substituents while lower conversions were observed for the ones with less electron withdrawing substituents (Table 3). For example, phenyl bromides having electron-withdrawing substituents like, –CHO, –COMe and –NO<sub>2</sub> moieties in the *o/p*-positions gave higher product yields for **2** (52–79%), **3** (64–85%) and **4** (59–> 99%) while those with electron-donating substituents like, –Me and –OMe moieties in the *o/p*-positions, gave comparatively much-lower product yields for **2** (37–48%), **3** (34–45%) and **4** (31–47%). The yields observed for iodobenzene is, however, lower than the activated bromo derivatives.



Quite interestingly, the commonly observed  $C_{sp^2}$ – $C_{sp^2}$  cross-coupling (Table 3, entries 1–8) between the two  $C_{sp^2}$  centers of aryl halide and phenyl boronic acid can even be extended to a relatively more challenging  $C_{sp^3}$ – $C_{sp^2}$  coupling (Table 3, entry 9) in which a  $C_{sp^3}$  carbon of benzyl bromide was coupled with the  $C_{sp^2}$  carbon of phenyl boronic acid, albeit in lower yields.

Though all the three **2**, **3** and **4** precatalysts displayed similar trends, quantitative conversions were observed in the case of **4** for the coupling of *o*- and *p*-bromobenzaldehydes. Hence, concentration dependence studies of the precatalyst **4** were carried out in order to gauge the maximum turnover efficiency of the catalyst (Table 4) and, indeed, high turnover numbers as high as 9700 at  $8.6 \times 10^{-3}$  mol% was observed for the *o*-bromobenzaldehyde (Table 4). Interestingly, the pyridine tilt as defined by the torsion angle between pyridine and the imidazolium ring<sup>32</sup> is the lowest for **4**, which coincidentally showed the highest conversion for *o*-bromobenzaldehyde. However, detailed theoretical studies are needed to elucidate the exact role of the catalyst structure in its mode of action.

Important is the comparison of the precatalysts **2**, **3** and **4** containing *N/O*-functionalized *N*-heterocyclic carbenes, with the other related PEPPSI precatalysts, *trans*-[1,3-bis-2,6-di-*i*-propylphenyl-imidazol-2-ylidene]PdCl<sub>2</sub>(3-chloropyridine),<sup>11</sup> *trans*-[1,3-bis-2,6-di-ethylphenyl-imidazol-2-ylidene]PdCl<sub>2</sub>(3-chloropyridine),<sup>11</sup> and *trans*-[1,3-bis-2,4,6-tri-methylphenyl-imidazol-2-ylidene]PdCl<sub>2</sub>(3-chloropyridine),<sup>11</sup> containing non-functionalized Arduengo type *N*-heterocyclic carbenes reported by Organ and coworkers.<sup>10,11</sup> Though the Organ's PEPPSI

**Table 3** Selected results of Suzuki–Miyaura cross-coupling reaction of aryl halides (ArX, X = Br, I) catalyzed by **2**, **3** and **4**.<sup>a</sup>

Entry	Reagent	Product	<b>2</b> <sup>b</sup>	<b>3</b> <sup>b</sup>	<b>4</b> <sup>b</sup>
1			79	85	99
2			72	82	99
3			66	67	73
4			52	64	59
5			48	43	47
6			43	45	38
7			37	34	31
8			36	32	30
9			7	11	22

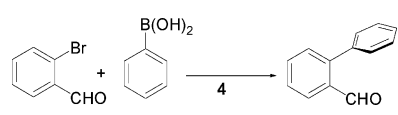
<sup>a</sup> Reaction conditions: 2.16 mmol of aryl halide (ArX, X = Br, I), 2.64 mmol of phenyl boronic acid, 3.24 mmol of K<sub>2</sub>CO<sub>3</sub>,  $7.5 \times 10^{-3}$  mmol of catalyst, 30 mL of CH<sub>3</sub>CN, 12 h at 85 °C. <sup>b</sup> The yields (%) were determined by GC using diethyleneglycol-di-n-butyl ether as an internal standard.

precatalysts<sup>11</sup> successfully carried out Suzuki–Miyaura cross-coupling of the more challenging aryl chlorides along with the frequently encountered aryl bromide substrates but at comparatively higher catalyst loadings (1–2 mol%) than the **2**, **3** and **4** precatalysts ( $3.5 \times 10^{-1}$ – $8.6 \times 10^{-3}$  mol%) showed activity toward the aryl bromide and iodide substrates.

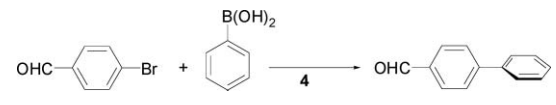
Also worthwhile is the comparison of the activity of a *trans*-(NHC)Pd(pyridine)X<sub>2</sub> (X = halide) type PEPPSI precatalyst with a similar *trans*-(NHC)<sub>2</sub>PdX<sub>2</sub> precatalyst supported over the same *N*-heterocyclic carbene (NHC) ligand. Interestingly, the activity of **4**, containing a *N/O*-functionalized *N*-heterocyclic carbene and a “throwaway” pyridine ligand, was found to be significantly lower than a *trans*-(NHC)<sub>2</sub>PdX<sub>2</sub> (X = halide) complex,<sup>12</sup> containing two of the same *N/O*-functionalized *N*-heterocyclic carbene ligand. For example, for the Suzuki–Miyaura cross-coupling of *o*-bromobenzaldehyde with phenyl boronic acid, the maximum TON (9700) (Table 4 entry 5) obtained for *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd(pyridine)Br<sub>2</sub>



**Table 4** Selected results of Suzuki coupling of *o/p*-bromobenzaldehyde with phenyl boronic acid catalyzed by **4**<sup>a</sup>



Entry	<b>4</b> (mol%)	Yield <sup>b</sup> (%)	TON
1	$3.5 \times 10^{-1}$	>99	288
2	$8.6 \times 10^{-2}$	>99	1160
3	$3.5 \times 10^{-2}$	>99	2900
4	$1.7 \times 10^{-2}$	>99	5500
5	$8.6 \times 10^{-3}$	83	9700



Entry	<b>4</b> (mmol)	Yield <sup>b</sup> (%)	TON
6	$3.5 \times 10^{-1}$	>99	288
7	$8.6 \times 10^{-2}$	>99	1160
8	$3.5 \times 10^{-2}$	58	1700

<sup>a</sup> Reaction conditions: 2.16 mmol of aryl halide, 2.64 mmol of phenyl boronic acid, 3.24 mmol of K<sub>2</sub>CO<sub>3</sub>, complex **4**, 30 mL of CH<sub>3</sub>CN, 12 h at 85 °C. <sup>b</sup> Determined by GC using diethyleneglycol-di-*n*-butyl ether as an internal standard.

(**4**) is significantly lower (TON = 49 700, after 12 h at 85 °C) than its bis-NHC analog, *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]<sub>2</sub>PdCl<sub>2</sub><sup>12</sup> also obtained under the same conditions (after 12 h at 85 °C). The greater activity of *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]<sub>2</sub>PdCl<sub>2</sub> may be due to the formation of a more electron-rich active species, *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]<sub>2</sub>Pd<sup>0</sup>, containing two electron-donating NHC ligands, as opposed to the active species, *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd<sup>0</sup> (solvent),<sup>10,11</sup> formed from the precatalyst **4** containing only one NHC ligand, and thereby greatly enhancing the oxidative addition of the aryl halide, often the rate-determining step in the catalytic cycle, in the case of the former.<sup>37</sup>

## Experimental

### General procedures

All manipulations were carried out using a combination of glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. The synthetic procedures of 1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazolium chloride<sup>21</sup> and 1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazolium bromide<sup>12</sup> were reported by us. Benzyl imidazole<sup>38</sup> and *N*-*t*-butyl-2-chloroacetamide<sup>39</sup> were synthesized according to literature procedures. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded in CDCl<sub>3</sub> on a Varian 400 MHz NMR spectrometer. <sup>1</sup>H NMR peaks are labeled as singlet (s), doublet (d) and multiplet (m). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were performed on a Micromass Q-ToF spectrometer. GC spectra were measured on a Shimadzu gas chromatograph GC-15A equipped with a

FID. X-Ray diffraction data for **1**, **2**, **3** and **4** were collected on an Oxford diffraction XCALIBUR-S instrument. The crystal data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on *F*<sup>2</sup> with SHELXTL (Version 6.10).

**Synthesis of 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride **1**.** A mixture of benzyl imidazole (1.06 g, 6.71 mmol) and *N*-*t*-butyl-2-chloroacetamide (1.00 g, 6.71 mmol) was dissolved in toluene (*ca.* 40 mL) and the reaction mixture was refluxed at 110 °C for 12 h when a sticky solid separated out. The solid was isolated by decanting off the solvent and washed with hot hexane (3 × *ca.* 10 mL) to obtain the product **1** as a light yellow solid (1.45 g, 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ 10.1 (s, 1H, NCHN), 8.66 (br, 1H, NH), 7.59 (br, 1H, NCHCHN), 7.41–7.39 (m, 5H, C<sub>6</sub>H<sub>4</sub>), 7.09 (br, 1H, NCHCHN), 5.45 (s, 2H, CH<sub>2</sub>), 5.31 (s, 2H, CH<sub>2</sub>), 1.37 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C): δ 163.5 (CO), 136.8 (NCHN), 132.6 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 129.1 (*o*-C<sub>6</sub>H<sub>5</sub>), 129.1 (*m*-C<sub>6</sub>H<sub>5</sub>), 128.6 (*p*-C<sub>6</sub>H<sub>5</sub>), 123.6 (NCHCHN), 120.9 (NCHCHN), 53.0 (CH<sub>2</sub>), 51.8 (CH<sub>2</sub>), 51.7 (C(CH<sub>3</sub>)<sub>3</sub>), 28.2 (C(CH<sub>3</sub>)<sub>3</sub>). IR data (KBr) cm<sup>-1</sup>: 3441 (m), 3212 (s), 3047 (m), 3011 (m), 2969 (m), 2928 (w), 2905 (w), 1685 (s), 1544 (s), 1497 (w), 1456 (m), 1396 (m), 1367 (m), 1283 (m), 1225 (m), 1162 (s), 1097 (w), 1032 (w), 1018 (w), 950 (w), 920 (w), 872 (w), 829 (w), 796 (w), 776 (w), 729 (m), 713 (s), 674 (w), 621 (m), 578 (m), 458 (w). Anal. Calcd. for C<sub>16</sub>H<sub>22</sub>ClN<sub>3</sub>O: C, 62.43; H, 7.20; N, 13.65. Found: C, 61.76; H, 8.02; N, 13.96%.

**Synthesis of *trans*-[1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]Pd(pyridine)Cl<sub>2</sub> **2**.** A mixture of 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride **1** (0.167 g, 0.543 mmol), PdCl<sub>2</sub> (0.105 g, 0.592 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.375 g, 2.71 mmol) were refluxed in pyridine (*ca.* 5 mL) for 16 h. The reaction mixture was filtered and the solvent was removed under vacuum. Then the residue was washed with aqueous CuSO<sub>4</sub> solution and the aqueous layer was extracted with dichloromethane (*ca.* 3 × 10 mL). Then the organic layer was collected and the solvent was removed under vacuum to obtain the product **2** as a yellow solid (0.116 g, 40%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ 8.93 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *o*-NC<sub>5</sub>H<sub>5</sub>), 7.74 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *p*-NC<sub>5</sub>H<sub>5</sub>), 7.40 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-NC<sub>5</sub>H<sub>5</sub>), 7.31 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 7.04 (br, 1H, NCHCHN), 6.71 (br, 1H, NCHCHN), 5.77 (s, 2H, CH<sub>2</sub>), 5.15 (s, 2H, CH<sub>2</sub>), 1.27 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C): δ 165.8 (CO), 153.3 (NCN–Pd), 151.1 (*o*-NC<sub>5</sub>H<sub>5</sub>), 138.5 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 138.2 (*p*-NC<sub>5</sub>H<sub>5</sub>), 128.9 (*o*-C<sub>6</sub>H<sub>5</sub>), 128.8 (*m*-C<sub>6</sub>H<sub>5</sub>), 128.6 (*p*-C<sub>6</sub>H<sub>5</sub>), 124.6 (*m*-NC<sub>5</sub>H<sub>5</sub>), 122.5 (NCHCHN), 122.1 (NCHCHN), 55.6 (CH<sub>2</sub>), 54.7 (CH<sub>2</sub>), 51.9 (C(CH<sub>3</sub>)<sub>3</sub>), 28.3 (C(CH<sub>3</sub>)<sub>3</sub>). IR data (KBr) cm<sup>-1</sup>: 3416 (s), 3306 (m), 3130 (m), 1682 (m), 1638 (m), 1618 (m), 1543 (w), 1450 (m), 1400 (s), 1262 (w), 1246 (w), 1165 (w), 1071 (w), 1017 (w), 804 (w), 761 (w), 722 (w), 691 (m), 617 (w), 481 (w). Anal. Calcd. for C<sub>21</sub>H<sub>27</sub>Cl<sub>2</sub>N<sub>4</sub>OPd·1/2(CH<sub>2</sub>Cl<sub>2</sub>): C, 45.20; H, 4.94; N, 9.81. Found: C, 45.59; H, 5.42; N, 8.99%.

**Synthesis of *trans*-[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]Pd(pyridine)Cl<sub>2</sub> **3**.** A mixture of 1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazolium chloride (0.440 g, 1.51 mmol), PdCl<sub>2</sub> (0.294 g, 1.66 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.04 g, 7.54 mmol) were refluxed in pyridine (*ca.* 5 mL) for 16 h. The reaction mixture

was filtered and the solvent was removed under vacuum. Then the residue was washed with aqueous CuSO<sub>4</sub> solution and the aqueous layer was extracted with dichloromethane (*ca.* 3 × 10 mL). Then the organic layer was collected and the solvent was removed under vacuum to obtain the product **3** as a yellow crystalline solid (0.364 g, 47%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ 9.03 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *o*-NC<sub>5</sub>H<sub>5</sub>), 7.79 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *p*-NC<sub>5</sub>H<sub>5</sub>), 7.47 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-NC<sub>5</sub>H<sub>5</sub>), 7.40–7.34 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 6.95 (br, 1H, NCHCHN), 6.76 (br, 1H, NCHCHN), 5.89 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 15 Hz, CH<sub>2</sub>), 5.82 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 15 Hz, CH<sub>2</sub>), 5.09–5.03 (m, 1H, C<sub>6</sub>H<sub>10</sub>), 3.30–3.27 (m, 1H, C<sub>6</sub>H<sub>10</sub>), 2.32–2.24 (m, 2H, C<sub>6</sub>H<sub>10</sub>), 1.92–1.85 (m, 3H, C<sub>6</sub>H<sub>10</sub>), 1.63–1.53 (m, 3H, C<sub>6</sub>H<sub>10</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C): δ 153.2 (NCN-Pd), 151.2 (*o*-NC<sub>5</sub>H<sub>5</sub>), 147.9 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 138.1 (*p*-NC<sub>5</sub>H<sub>5</sub>), 135.0 (*o*-C<sub>6</sub>H<sub>5</sub>), 129.0 (*m*-C<sub>6</sub>H<sub>5</sub>), 128.9 (*p*-C<sub>6</sub>H<sub>5</sub>), 124.5 (*m*-NC<sub>5</sub>H<sub>5</sub>), 122.0 (NCHCHN), 119.7 (NCHCHN), 72.7 (C<sub>6</sub>H<sub>10</sub>), 66.9 (C<sub>6</sub>H<sub>10</sub>), 54.9 (CH<sub>2</sub>), 34.9 (C<sub>6</sub>H<sub>10</sub>), 32.9 (C<sub>6</sub>H<sub>10</sub>), 25.0 (C<sub>6</sub>H<sub>10</sub>), 24.3 (C<sub>6</sub>H<sub>10</sub>). IR Data (KBr) cm<sup>-1</sup> 3118 (m), 2937 (w), 2849 (w), 1619 (m), 1605 (m), 1559 (w), 1448 (m), 1400 (s), 1278 (w), 1241 (w), 1215 (w), 1163 (w), 1069 (m), 1047 (w), 1032 (w), 955 (w), 868 (w), 761 (w), 732 (w), 691 (m), 615 (w), 472 (w). Anal. Calcd. for C<sub>21</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>3</sub>OPd: C, 49.19; H, 4.91; N, 8.19. Found: C, 48.83; H, 4.60; N, 8.04%.

**Synthesis of *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd(pyridine)Br<sub>2</sub> **4**.** A mixture of 1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazolium bromide (0.381 g, 1.17 mmol), PdCl<sub>2</sub> (0.229 g, 1.29 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.809 g, 5.85 mmol) were refluxed in pyridine (*ca.* 5 mL) for 16 h. The reaction mixture was filtered and the solvent was removed under vacuum. Then the residue was washed with aqueous CuSO<sub>4</sub> solution and the aqueous layer was extracted with ethyl acetate (*ca.* 3 × 10 mL). Then the organic layer was collected and the solvent was removed under vacuum to obtain the product **4** as a yellow crystalline solid (0.291 g, 42%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ 9.07 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *o*-NC<sub>5</sub>H<sub>5</sub>), 7.74 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *p*-NC<sub>5</sub>H<sub>5</sub>), 7.61 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-NC<sub>5</sub>H<sub>5</sub>), 7.34 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *o*-C<sub>6</sub>H<sub>4</sub>), 7.29 (br, 1H, NCHCHN), 7.02 (br, 1H, NCHCHN), 6.95 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-C<sub>6</sub>H<sub>4</sub>), 6.89 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *m*-C<sub>6</sub>H<sub>4</sub>), 6.78 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, *p*-C<sub>6</sub>H<sub>4</sub>), 6.09 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 15 Hz, CH<sub>2</sub>), 6.03 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 15 Hz, CH<sub>2</sub>), 3.89 (s, 3H, OCH<sub>3</sub>), 2.10 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C): δ 157.4 (NCN-Pd), 152.6 (*o*-NC<sub>5</sub>H<sub>5</sub>), 137.7 (*p*-NC<sub>5</sub>H<sub>5</sub>), 137.6 (OC<sub>6</sub>H<sub>4</sub>), 131.8 (*ipso*-C<sub>6</sub>H<sub>4</sub>), 129.8 (*o*-C<sub>6</sub>H<sub>4</sub>), 124.4 (*p*-C<sub>6</sub>H<sub>4</sub>), 124.3 (*m*-C<sub>6</sub>H<sub>4</sub>), 120.9 (NCHCHN), 120.8 (*m*-NC<sub>5</sub>H<sub>5</sub>), 120.3 (NCHCHN), 110.4 (*m*-C<sub>6</sub>H<sub>4</sub>), 58.6 (CH<sub>2</sub>), 55.3 (OCH<sub>3</sub>), 50.6 (C(CH<sub>3</sub>)<sub>3</sub>), 32.2 (C(CH<sub>3</sub>)<sub>3</sub>). IR data (KBr) cm<sup>-1</sup> 3416 (s), 3137 (m), 2974 (m), 1603 (s), 1496 (m), 1463 (m), 1445 (m), 1400 (s), 1372 (m), 1348 (w), 1283 (w), 1253 (s), 1154 (w), 1118 (m), 1064 (w), 1047 (m), 1027 (s), 913 (w), 819 (w), 754 (s), 730 (m), 700 (m), 687 (s), 623 (m). Anal. Calcd. for C<sub>20</sub>H<sub>26</sub>Br<sub>2</sub>N<sub>3</sub>OPd·1/2(NC<sub>5</sub>H<sub>5</sub>): C, 42.95; H, 4.41; N, 7.79. Found: C, 43.50; H, 4.43; N, 8.54%.

### Computational methods

The density functional theory calculations were performed on the **2**, **3** and **4** complexes using GAUSSIAN 03<sup>40</sup> suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP) have been employed in this study.<sup>41,42</sup> Stuttgart–Dresden

effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD) is used for palladium.<sup>43</sup> All other atoms are treated with 6-31G(d) basis set.<sup>44</sup> All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces.

Inspection of the metal–ligand donor–acceptor interactions was carried out using the charge decomposition analysis (CDA).<sup>45</sup> CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.<sup>46</sup> The orbital contributions in the geometry optimized NHC–Pd(pyridine)X<sub>2</sub> type complexes, **2'** (X = Cl), **3'** (X = Cl) and **4'** (X = Br), can be divided into three parts:

- (i) σ-donation from the [NHC → Pd(pyridine)X<sub>2</sub>] fragment
- (ii) π-back donation from [NHC ← Pd(pyridine)X<sub>2</sub>] fragment and
- (iii) repulsive polarization (*r*)

The CDA calculations are performed using the program AOMix,<sup>46</sup> using the B3LYP/SDD, 6-31G\* wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMix program.<sup>36,47</sup> The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, the charge decomposition analysis (CDA) was performed using the AOMix-CDA.<sup>48</sup>

### General procedure for the Suzuki coupling reaction

In a typical run, a round bottom flask was charged with a mixture of aryl halides (ArX, X = Br, I), phenylboronic acid and K<sub>2</sub>CO<sub>3</sub> and diethyleneglycol–di-*n*-butyl ether (internal standard) in a molar ratio of 1 : 1.2 : 1.5 : 1 and to this mixture was added precatalysts **2**, **3** or **4** at varying mol% amounts (Tables 3 and 4). Acetonitrile (30 mL) was added to the reaction mixture and refluxed for an appropriate period of time after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol–di-*n*-butyl ether as an internal standard.

### Conclusion

In summary, a series of air stable, user-friendly and conveniently synthesized Pd precatalysts **2**, **3** and **4** *trans*-(NHC)Pd(pyridine)X<sub>2</sub> (X = Cl, Br), stabilized over *N/O*-functionalized N-heterocyclic carbenes and containing “throwaway” pyridine ligand have been synthesized and structurally characterized. The weakly bound nature of the pyridine moiety was further supported by density functional theory studies as the estimated Pd–pyridine bond dissociation energy [*D*<sub>e</sub> (Pd–pyridine)] in the geometry optimized complexes **2'** (32.9 kcal mol<sup>-1</sup>), **3'** (32.7 kcal mol<sup>-1</sup>) and **4'** (30.8 kcal mol<sup>-1</sup>) were found to be significantly lower than the (NHC)–Pd bond dissociation energy [*D*<sub>e</sub> (Pd–C<sub>carbene</sub>)] in the same **2'** (81.9 kcal mol<sup>-1</sup>), **3'** (82.4 kcal mol<sup>-1</sup>) and **4'** (77.6 kcal mol<sup>-1</sup>) complexes. Furthermore, the NHCs were found to behave as strong σ-donor ligands with very little component of π-back-bonding from the metal center to NHC in the palladium complexes. The catalysis studies revealed that the **2**, **3** and **4** complexes are excellent precatalysts for Suzuki–Miyaura cross-coupling reactions at low catalyst loadings (0.35 mol%) and exhibit not only the commonly observed C<sub>sp2</sub>–C<sub>sp2</sub> coupling but also the more challenging C<sub>sp3</sub>–C<sub>sp2</sub> cross-coupling reactions.

## Acknowledgements

We thank the Department of Science and Technology for financial support of this research. We are grateful to the National Single Crystal X-ray Diffraction Facility at IIT Bombay, India, for the crystallographic results. P. G. thanks Professor R. B. Sunoj, IIT Bombay, for helpful discussions. L. R. thanks IIT Bombay, India, for a research fellowship. Computational facilities from the IIT Bombay computer center are gratefully acknowledged.

## References

- 1 C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247–2273; W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309.
- 2 A. Roglans, A. Pla-Quintana and M. Moreno-Mañas, *Chem. Rev.*, 2006, **106**, 4622–4643; J.-P. Corbet and G. Mignai, *Chem. Rev.*, 2006, **106**, 2651–2710; W. A. Herrmann, K. Öfele, D. v. Preysing and S. K. Schneider, *J. Organomet. Chem.*, 2003, **687**, 229–248; A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 4176–4211.
- 3 Y. Hatanaka and T. Hiyama, *J. Org. Chem.*, 1988, **53**, 918–920.
- 4 K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, 1972, **94**, 4374–4376.
- 5 E. Negishi, A. O. King and N. Okukado, *J. Org. Chem.*, 1977, **42**, 1821–1823; A. O. King, N. Okukado and E. Negishi, *J. Chem. Soc., Chem. Commun.*, 1977, 683–688.
- 6 N. Miayura, K. Yamada and A. Suzuki, *Tetrahedron Lett.*, 1979, **20**, 3437–3440.
- 7 D. Milstein and J. K. Stille, *J. Am. Chem. Soc.*, 1978, **100**, 3636–3638.
- 8 For example, incorporation of a sterically demanding *N*-heterocyclic carbene in place of one of the two PCy<sub>3</sub> ligands in the Grubbs 1st generation catalyst, [(PCy<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru=CHPh], yielded a more potent Grubbs 2nd generation catalyst [(H<sub>2</sub>IMes)(PCy<sub>3</sub>)(Cl)<sub>2</sub>Ru=CHPh] representing a mixed NHC–PCy<sub>3</sub> system. See: T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 2416–2419; T. Weskamp, W. C. Schattenmann, M. Spiegler and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 2490–2493.
- 9 J. A. Love, J. P. Morgan, T. M. Trnka and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2002, **41**, 4035–4037.
- 10 C. J. O'Brien, E. A. B. Kantachev, G. A. Chass, N. Hadei, A. C. Hopkinson, M. G. Organ, D. H. Setaidi, T.-H. Tang and D.-C. Fang, *Tetrahedron*, 2005, **61**, 9723–9735; M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, A. S. B. Kantachev, C. J. O'Brien and C. Valente, *Chem.–Eur. J.*, 2006, **12**, 4749–4755; M. G. Organ, M. Abdel-Hadi, S. Avola, N. H. Nasielski, C. J. O'Brien and C. Valente, *Chem.–Eur. J.*, 2007, **13**, 150–157.
- 11 C. J. O'Brien, E. A. B. Kantachev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson and M. G. Organ, *Chem.–Eur. J.*, 2006, **12**, 4743–4748.
- 12 L. Ray, M. M. Shaikh and P. Ghosh, *Organometallics*, 2007, **26**, 958–964.
- 13 A. Suzuki, *Chem. Commun.*, 2005, 4759–4763; S. Kotha, K. Lahiri and D. Kashinath, *Tetrahedron*, 2002, **58**, 9633–9695.
- 14 Y. Yuan, H. Men and C. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 14720–14721.
- 15 D. R. Williams and J. Li, *Tetrahedron Lett.*, 1994, **35**, 5113–5116.
- 16 K. C. Nicolaou, A. L. Nold, R. R. Milburn and C. S. Schindler, *Angew. Chem., Int. Ed.*, 2006, **45**, 6527–6532.
- 17 K. C. Nicolaou, J. M. Ramanjulu, S. Natarajan, S. Bräse, H. Li, C. N. C. Boddy and F. Rübsam, *Chem. Commun.*, 1997, 1899–1900.
- 18 M. K. Samantaray, V. Katiyar, D. Roy, K. Pang, H. Nanavati, R. Stephen, R. B. Sunoj and P. Ghosh, *Eur. J. Inorg. Chem.*, 2006, 2975–2984.
- 19 J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller and R. H. Crabtree, *Organometallics*, 2002, **21**, 700–706.
- 20 M. K. Samantaray, V. Katiyar, K. Pang, H. Nanavati and P. Ghosh, *J. Organomet. Chem.*, 2007, **692**, 1672–1682.
- 21 L. Ray, V. Katiyar, S. Barman, M. J. Raihan, H. Nanavati, M. M. Shaikh and P. Ghosh, *J. Organomet. Chem.*, 2007, DOI: 10.1016/j.jorganchem.2007.06.033.
- 22 L. Ray, V. Katiyar, M. J. Raihan, H. Nanavati, M. M. Shaikh and P. Ghosh, *Eur. J. Inorg. Chem.*, 2006, 3724–3730.
- 23 M. K. Samantaray, D. Roy, A. Patra, R. Stephen, M. Saikh, R. B. Sunoj and P. Ghosh, *J. Organomet. Chem.*, 2006, **691**, 3797–3805.
- 24 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.
- 25 J.-F. Huang, P.-Y. Chen, I.-W. Sun and S. P. Wang, *Inorg. Chim. Acta*, 2001, **320**, 7–11; A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.*, 1994, 3405–3413.
- 26 P. Kölle and R. Dronskowski, *Inorg. Chem.*, 2004, **43**, 2803–2809; A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan and Y.-M. Tan, *J. Chem. Soc., Dalton Trans.*, 1995, 3467–3472; D. Zhao, Z. Fei, R. Scopelliti and P. Dyson, *J. Inorg. Chem.*, 2004, **43**, 2197–2205.
- 27 S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller and R. H. Crabtree, *Organometallics*, 2001, **20**, 5485–5488; W. A. Herrmann, V. P. W. Böhm, C. W. K. Gstöttmayr, M. Grosche, C.-P. Reisinger and T. Weskamp, *J. Organomet. Chem.*, 2001, **617–618**, 616–628; W. A. Herrmann, J. Schwarz, M. G. Gardiner and M. Spiegler, *J. Organomet. Chem.*, 1999, **575**, 80–86; M. G. Gardiner, W. A. Herrmann, C.-P. Reisinger, J. Schwarz and M. Spiegler, *J. Organomet. Chem.*, 1999, **572**, 239–247.
- 28 A. Bertogg, F. Campanovo and A. Togni, *Eur. J. Inorg. Chem.*, 2005, 347–356.
- 29 A. A. Tulloch, D. S. Winston, A. A. Danopoulos, G. Eastham and M. B. Hursthouse, *Dalton Trans.*, 2003, 699–708; S. Gründemann, M. Albrecht, A. Kovacevic, J. W. Faller and R. H. Crabtree, *J. Chem. Soc., Dalton Trans.*, 2002, 2163–2167; A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White and B. W. Skelton, *J. Organomet. Chem.*, 2001, **617–618**, 546–560; A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz and M. B. Hursthouse, *Chem. Commun.*, 2000, 1247–1248; G. D. Frey, J. Schütz, E. Herdtweck and W. A. Herrmann, *Organometallics*, 2005, **24**, 4416–4426.
- 30 L. Pauling, *The Nature of The Chemical Bond*, 3rd edn, Cornell University Press, Ithaca, NY, 1960, pp. 224–228, 246–258.
- 31 For example, the Pd-bound pyridine resonances ( $\delta$  ppm) of **4** appeared at, 9.07 (d, 2H,  $^3J_{\text{HH}} = 8$  Hz), 7.75 (t, 1H,  $^3J_{\text{HH}} = 8$  Hz) and 7.61 (t, 2H,  $^3J_{\text{HH}} = 8$  Hz) while the free pyridine appeared at, 8.61 (d, 2H,  $^3J_{\text{HH}} = 8$  Hz), 7.66 (t, 2H,  $^3J_{\text{HH}} = 8$  Hz) and 7.28 (t, 1H,  $^3J_{\text{HH}} = 8$  Hz) in CDCl<sub>3</sub>.
- 32 For example, the torsion angles made by the pyridine with the imidazolium rings in these complexes are, C21–N4–C1–N2 (46°) for **2**, C21–N3–C1–N1 (43°) for **3** and C20–N3–C1–N1 (39°) for **4**.
- 33 J. R. Miecznikowski, S. Gründemann, M. Albrecht, C. Mégret, E. Clot, J. W. Faller, O. Eisenstein and R. H. Crabtree, *Dalton Trans.*, 2003, 831–838.
- 34 R. H. Crabtree, *J. Organomet. Chem.*, 2005, **690**, 5451–5457; S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller and R. H. Crabtree, *Organometallics*, 2001, **20**, 5485–5488.
- 35 E. Baba, T. R. Cundari and I. Firkin, *Inorg. Chim. Acta*, 2005, **358**, 2867–2875; M.-T. Lee and C.-H. Hu, *Organometallics*, 2004, **23**, 976–983; D. K. Wichmann and G. Frenking, *Organometallics*, 2004, **23**, 3640–3646.
- 36 S. I. Gorelsky, *AOMix: Program for Molecular Orbital Analysis*, York University, Toronto, Canada, 1997; <http://www.sg-chem.net/>.
- 37 C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247–2273.
- 38 H. M. Lee, C. Y. Lu, C. Y. Chen, W. L. Chen, H. C. Lin, P. L. Chiu and P. Y. Cheng, *Tetrahedron*, 2004, **60**, 5807–5825.
- 39 M. P. Dave, J. M. Patel, N. A. Langalia, S. R. Shah and K. A. Thaker, *J. Indian Chem. Soc.*, 1985, **LXII**, 386–387.
- 40 GAUSSIAN 03: *Gaussian 03, Revision C.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr., J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford, CT, 2004.



- 
- 41 A. D Becke, *Phys. Rev. A*, 1998, **38**, 3098–3100.  
42 C. Lee, W. Yang and R. G Parr, *Phys. Rev. B*, 1988, **38**, 785–789.  
43 K. Pang, S. M. Quan and G Parkin, *Chem. Commun.*, 2006, 5015–5016;  
G. Yang, C. Jin, J Hong, Z. Guo and L. Zhu, *Spectrochim. Acta, Part A*, 2004, **60**, 493–509; Y. Zhang, L. Zhang, H. Tao, X. Sun and L. Zhu, *Spectrochim. Acta, Part A*, 2003, **59**, 3187–3195.  
44 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.  
45 S. Dapprich and G. Frenking, *J. Phys. Chem.*, 1995, **99**, 9352–9362.  
46 S. F. Vyboishchikov and G. Frenking, *Chem.–Eur. J.*, 1998, **4**, 1439–1448; G. Frenking and U. Pidun, *J. Chem. Soc., Dalton Trans.*, 1997, 1653–1662.  
47 S. I. Gorelsky and A. B. P. Lever, *J. Organomet. Chem.*, 2001, **635**, 187–196.  
48 S. I. Gorelsky, S. Ghosh and E. I. Solomon, *J. Am. Chem. Soc.*, 2006, **128**, 278–290.

# Shorter Argentophilic Interaction than Auophilic Interaction in a Pair of Dimeric $\{(\text{NHC})\text{MCl}\}_2$ ( $\text{M} = \text{Ag}, \text{Au}$ ) Complexes Supported over a N/O-Functionalized N-Heterocyclic Carbene (NHC) Ligand

Lipika Ray,<sup>†</sup> Mobin M. Shaikh,<sup>‡</sup> and Prasenjit Ghosh<sup>\*†</sup>

Department of Chemistry and National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology Bombay, Powai, Mumbai 400 076

Received September 16, 2007

Synthesis, structure, bonding, and photoluminescence studies of a pair of neutral dimeric silver and gold complexes of a N/O-functionalized N-heterocyclic carbene ligand exhibiting closed-shell  $d^{10}\cdots d^{10}$  argentophilic and auophilic interactions, are reported. In particular, dimeric complexes of the type  $\{[1-(\text{benzyl})-3-(N\text{-}tert\text{-butylacetamido})\text{imidazol-2-ylidene}]\text{MCl}\}_2$  [ $\text{M} = \text{Ag}$  (**2**);  $\text{Au}$  (**3**)] displayed attractive metalophilic interaction in the form of a close ligand-unsupported metal $\cdots$ metal contact [3.1970(12) Å in **2**; 3.2042(2) Å in **3**] as observed from X-ray diffraction study and also was further verified by low temperature photoluminescence study at 77 K that showed the characteristic emission [527 nm for **2**; 529 nm for **3**] owing to the metal $\cdots$ metal interaction. The nature of the metalophilic interaction in these complexes was further probed using computational studies that estimated the metal $\cdots$ metal interaction energy to be 12.8 (**2**) and 8.6 kcal/mol (**3**). Notably, the argentophilic interaction was found to be stronger than the auophilic interaction in this series of neutral dimeric complexes. The complexes **2** and **3** were synthesized sequentially, with the silver **2** complex prepared by the reaction of the 1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazolium chloride with  $\text{Ag}_2\text{O}$  in 66% yield, while the gold **3** complex was obtained by the transmetalation reaction of the silver **2** complex with  $(\text{SMe}_2)\text{AuCl}$  in 86% yield.

## Introduction

While open-shell species interact to form covalent bonds and the closed-shell ones of opposing electric charges form ionic bonds, the attractive interaction between the closed-shell species of neutral or like (both cationic or anionic) charges,<sup>1</sup> which are expected to repel each other, thus runs counterintuitive to the conventional bonding principles and hence has been of interest lately.<sup>2–4</sup> Such weak attractive closed-shell interaction in transition metals was first wit-

nessed by Schmidbaur in the gold(I) complexes exhibiting close  $\text{Au}\cdots\text{Au}$  contacts.<sup>5</sup> Though originally seen in gold(I) and commonly referred to as auophilicity, similar closed-shell interactions are also shown by other transition metals, such as  $\text{Cu(I)}$ ,<sup>6</sup>  $\text{Ag(I)}$ ,<sup>7</sup>  $\text{Tl(I)}$ ,<sup>8</sup>  $\text{Pd(II)}$ ,<sup>9</sup> and  $\text{Pt(II)}$ ,<sup>10</sup> and, thus, are more aptly called metalophilic interactions.<sup>2,3</sup> These

\* To whom correspondence should be addressed. Fax: +91-22-2572-3480. E-mail: pghosh@chem.iitb.ac.in.

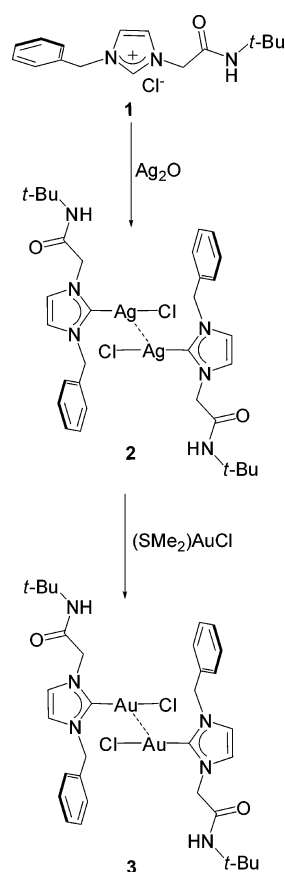
<sup>†</sup> Department of Chemistry.

<sup>‡</sup> National Single Crystal X-ray Diffraction Facility.

- (1) (a) Bauer, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1996**, *118*, 5324–5325. (b) Conzelmann, W.; Hiller, W.; Strähle, J.; Sheldrick, G. M. *Z. Anorg. Allg. Chem.* **1984**, *512*, 169–176. (c) Adams, H.-N.; Hiller, W.; Strähle, J. *Z. Anorg. Allg. Chem.* **1982**, *485*, 81–91.
- (2) (a) Schmidbaur, H.; Cronje, S.; Djordjevic, B.; Schuster, O. *Chem. Phys.* **2005**, *311*, 151–161. (b) Schmidbaur, H. *Nature* **2001**, *413*, 31–33. (c) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3–10. (d) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391–400.
- (3) (a) Pyykkö, P. *Inorg. Chim. Acta* **2005**, *358*, 4113–4130. (b) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412–4456. (c) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597–636.

- (4) (a) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395–403. (b) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180–3211. (c) Che, C.-M.; Lai, S.-W. *Coord. Chem. Rev.* **2005**, *249*, 1296–1309. (d) Harvey, P. D. *Coord. Chem. Rev.* **1996**, *153*, 175–198.
- (5) (a) Schmidbaur, H.; Graf, W.; Mueller, G. *Angew. Chem.* **1988**, *27*, 417–419. (b) Schmidbaur, H.; Scherbaum, F.; Huber, B.; Mueller, G. *Angew. Chem., Int. Ed.* **1988**, *27*, 419–421. (c) Scherbaum, F.; Huber, B.; Mueller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed.* **1988**, *27*, 1542–1544. (d) Scherbaum, F.; Grohmann, A.; Huber, B.; Krueger, C.; Schmidbaur, H. *Angew. Chem., Int. Ed.* **1988**, *27*, 1544–1546.
- (6) (a) Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R.; Diyabalanage, H. V. K.; Gamage, C. S. P.; Rasika, Dias, H. V. *Inorg. Chem.* **2005**, *44*, 8200–8210. (b) Sundararaman, A.; Zakharov, L. N.; Rheingold, A. L.; Jäkle, F. *Chem. Commun.* **2005**, 1708–1710. (c) Zhang, J.-P.; Wang, Y.-B.; Huang, X.-C.; Lin, Y.-Y.; Chen, X.-M. *Chem. Eur. J.* **2005**, *11*, 552–561. (d) Fu, W.-F.; Gan, X.; Che, C.-M.; Cao, Q.-Y.; Zhou, Z.-Y.; Zhu, N.-Y. *N. Chem. Eur. J.* **2004**, *10*, 2228–2236. (e) Hermann, H. L.; Boche, G.; Schwerdtfeger, P. *Chem. Eur. J.* **2001**, *7*, 5333–5342.

Scheme 1



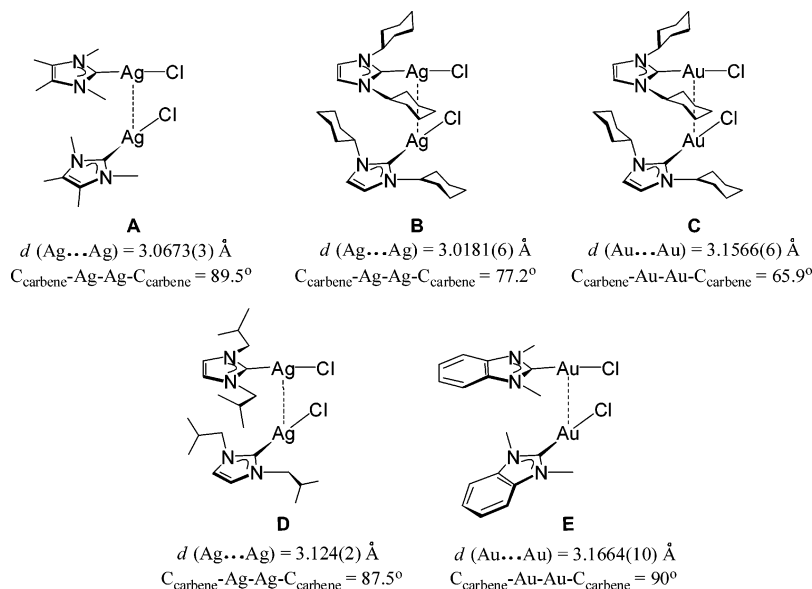
closed-shell interactions arise primarily due to the dispersive forces<sup>3</sup> and appear weakly attractive in lighter elements, e.g.,  $He_2$  ( $D_e = 2 \times 10^{-2}$  kcal/mol),<sup>11</sup> but are significantly

strengthened by relativistic effects in the heavier elements, such as in gold, for which the  $Au \cdots Au$  interaction energy is reported to vary from 6 to 12 kcal/mol and which displays a  $Au \cdots Au$  contact of 2.8–3.3 Å.<sup>2–4</sup> For example, in a series of the neutral dimeric  $[(PH_3)MCl]_2$  ( $M = Cu, Ag, Au$ ) complexes, the strength of metallophilic interaction increases by ~50% on going from the lighter to the heavier congener (Cu to Au) along the series due to greater dominance of relativistic effects.<sup>12</sup> The experimental evidence for these closed-shell interactions, particularly for the most commonly observed and also significantly stronger  $Au \cdots Au$  interactions, come from a variety of studies that involve X-ray single-crystal diffraction,<sup>13</sup> NMR,<sup>14</sup> and optical spectroscopic measurements.<sup>15</sup> It is noteworthy that the  $Au \cdots Au$  interactions are quite strong and are comparable to hydrogen bonding interactions.<sup>2–4</sup> In contrast to auriphilicity, which is more acute due to the predominating relativistic effects, cuprophilicity and argentophilicity have remained relatively obscured primarily due to fewer known examples of such interactions, and that in a sense has contributed to the hindrance in studying these interactions.<sup>2–4</sup>

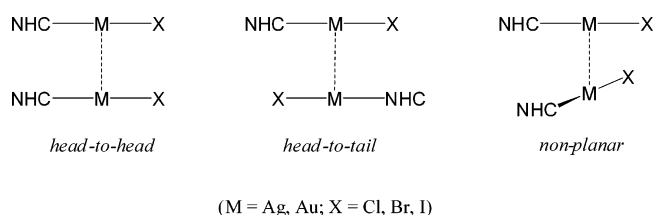
Significantly, the closed-shell metallophilic interactions are becoming extremely popular in a variety of exciting high-end materials related applications that include rewritable phosphorescent paper for use as color-switchable luminescent materials,<sup>16</sup> phosphorescent organogels for reversible RGB-color switching,<sup>17</sup> luminescence chemosensors,<sup>18</sup> optoelectronic “on–off” devices,<sup>19</sup> etc. In addition, the weak attractive nature of closed-shell metallophilic interaction is often gainfully exploited in building a wide array of extended supramolecular networks in designing engineering materials.<sup>20</sup> Thus, the closed-shell metallophilic interaction by virtue

- (7) (a) Chen, C. Y.; Zeng, J. Y.; Lee, H. M. *Inorg. Chim. Acta* **2007**, *360*, 21–30. (b) Liu, X.; Guo, G.-C.; Fu, M.-L.; Liu, X.-H.; Wang, M.-S.; Huang, J.-S. *Inorg. Chem.* **2006**, *45*, 3679–3685. (c) Dobrzanska, L.; Raubenheimer, H. G.; Barbour, L. J. *Chem. Commun.* **2005**, 5050–5052. (d) Mohamed, A. A.; Pérez, L. M.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **2005**, *358*, 1657–1662.
- (8) (a) Fernandez, E. J.; Laguna, A.; López-de-Luzuriaga, J. M. *Coord. Chem. Rev.* **2005**, *249*, 1423–1433. (b) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Montiel, M.; Olmos, M. E.; Pérez, J. *Inorg. Chim. Acta* **2005**, *358*, 4293–4300. (c) Gade, L. H. *Dalton Trans.* **2003**, 267–278. (d) Kristiansson, O. *Eur. J. Inorg. Chem.* **2002**, 2355–2361. (e) Gade, L. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 3573–3575. (f) Ghosh, P.; Rheingold, A. L.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 5464–5467.
- (9) (a) Xia, B.-H.; Che, C.-M.; Zhou, Z.-Y. *Chem. Eur. J.* **2003**, *9*, 3055–3064. (b) Tzeng, B.-C.; Chan, S.-C.; Chan, M. C. W.; Che, C.-M.; Cheung, K.-K.; Peng, S.-M. *Inorg. Chem.* **2001**, *40*, 6699–6704. (c) Garcia-Ruano, J. L.; López-Solera, I.; Masaguer, J. R.; Navarro-Ranninger, C.; Rodriguez, J. H.; Martinez-Carrera, S. *Organometallics* **1992**, *11*, 3013–3018. (d) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 1015–1021. (e) Clegg, W.; Garner, C. D.; Al-Samman, M. H. *Inorg. Chem.* **1982**, *21*, 1897–1901. (f) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144–1154. (g) Umakoshi, K.; Kinoshita, I.; Ooi, S. *Inorg. Chim. Acta* **1987**, *127*, L41–L42. (h) Bonamico, M.; Dessy, G.; Fares, V. J. *Chem. Soc., Dalton Trans.* **1977**, 2315–2319.
- (10) (a) Silva, N. de; Fry, C. G.; Dahl, L. F. *Dalton Trans.* **2006**, 1051–1059. (b) Wadas, T. J.; Wang, Q.-M.; Kim, Y.-j.; Flaschenreim, C.; Blanton, T. N.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 16841–16849.
- (11) (a) Wesendrup, R.; Schwerdtfeger, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 907–910. (b) Komasa, J.; Cencek, W.; Rychlewski, J. *Chem. Phys. Lett.* **1999**, *304*, 293–298. (c) Mourik, T. van; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *111*, 9248–9258. (d) Luo, F.; McBane, G. C.; Kim, G.; Giese, C. F.; Gentry, W. R. *J. Chem. Phys.* **1993**, *98*, 3564–3567.
- (12) Magnko, L.; Schweizer, M.; Rauhut, G.; Schütz, M.; Stoll, H.; Werner, H.-J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1006–1013.
- (13) (a) Yamamoto, Y.; Kosaka, Y.; Tsutsumi, Y.; Sunada, Y.; Tatsumi, K.; Fumie, T.; Shigetoshi, T. *Dalton Trans.* **2004**, 2969–2978. (b) Stefanescu, D. M.; Yuen, H. F.; Glueck, D. S.; Golen, J. A.; Zakharov, L. N.; Incarvito, C. D.; Rheingold, A. L. *Inorg. Chem.* **2003**, *42*, 8891–8901. (c) Vicente, J.; Singhal, A. R. *Organometallics* **2002**, *21*, 5887–5900. (d) Nunokawa, K.; Onaka, S.; Tatematsu, T.; Ito, M.; Sakai, J. *Inorg. Chim. Acta* **2001**, *322*, 56–64. (e) Tzeng, B.-C.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **1999**, *38*, 3978–3984.
- (14) (a) Feng, D.-F.; Tang, S. S.; Liu, C. W.; Lin, I. J. B. *Organometallics* **1997**, *16*, 901–909. (b) Tang, S. S.; Chang, C.-P.; Lin, I. J. B.; Liou, L.-S.; Wang, J.-C. *Inorg. Chem.* **1997**, *36*, 2294–2300. (c) Harwell, D. E.; Mortimer, M. D.; Knobler, C. B.; Anet, F. A. L.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1996**, *118*, 2679–2685. (d) Narayanaswamy, R.; Young, M. A.; Parkhurst, E.; Ouellette, M.; Kerr, M. E.; Ho, D. M.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. *Inorg. Chem.* **1993**, *32*, 2506–2517.
- (15) (a) Zheng, S.-L.; Nygren, C. L.; Messerschmidt, M.; Coppens, P. *Chem. Commun.* **2006**, 3711–3713. (b) Stott, T. L.; Wolf, M. O.; Patrick, B. O. *Inorg. Chem.* **2005**, *44*, 620–627. (c) White-Morris, R. L.; Olmstead, M. M.; Attar, S.; Balch, A. L. *Inorg. Chem.* **2005**, *44*, 5021–5029. (d) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L.; Elbjerrami, O.; Omary, M. A. *Inorg. Chem.* **2003**, *42*, 6741–6748.
- (16) (a) Kishimura, A.; Yamashita, T.; Yamaguchi, K.; Aida, T. *Nature* **2005**, *4*, 546–549. (b) Enomoto, M.; Kishimura, A.; Aida, T. *J. Am. Chem. Soc.* **2001**, *123*, 5608–5609.
- (17) Kishimura, A.; Yamashita, T.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 179–183.
- (18) Yam, V. W.-W.; Chan, C.-L.; Li, C.-K.; Wong, K. M.-C. *Coord. Chem. Rev.* **2001**, *216–217*, 173–194.
- (19) Mohamed, A. A.; Rawashdeh-Omary, M. A.; Omary, M. A.; Frackler, J. P., Jr. *Dalton Trans.* **2005**, 2597–2602.
- (20) Burini, A.; Mohamed, A. A.; Fackler, J. P., Jr. *Comm. Inorg. Chem.* **2003**, *24*, 253–280.





**Figure 1.** Representative examples of structurally characterized  $\{(\text{NHC})\text{MCl}\}_2$  ( $\text{M} = \text{Ag}, \text{Au}$ ) type dimeric complexes exhibiting metallophilic interactions.



**Figure 2.** Possible structural arrangements for  $\{(\text{NHC})\text{MX}\}_2$  ( $\text{M} = \text{Ag}, \text{Au}$ ) dimeric type complexes.

of its subtle but significant influence has aroused interest in recent years and has made an impact in frontline application oriented research.

Our interest lies in design and synthesis of transition metal complexes of nonfunctionalized and N/O-functionalized N-heterocyclic carbenes<sup>21</sup> for their potential use in chemical catalysis and biomedical applications.<sup>22</sup> In this regard we have recently reported a series of Pd-based N-heterocyclic carbene (NHC) complexes as efficient catalysts for C–C bond forming reactions<sup>23</sup> and also have employed a variety of Ag–NHC and Au–NHC complexes for producing biodegradable polylactide polymer through ring-opening polymerization (ROP) of L-lactide under solvent-free melt conditions.<sup>24,25</sup> During the course of developing the silver and gold chemistry of N-heterocyclic carbenes, we became

interested in looking for the existence of these weak closed-shell  $d^{10}\cdots d^{10}$  argentophilic<sup>26</sup> and aurophilic<sup>27</sup> interactions in these complexes.

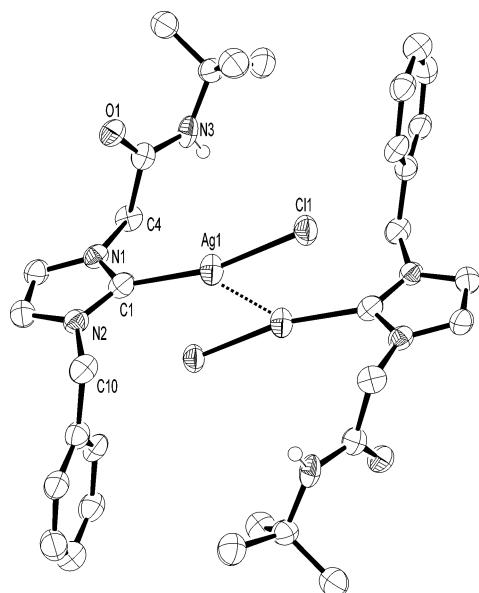
Here in this contribution we report the synthesis, structure, bonding, and photophysical studies of a pair of neutral dimeric silver and gold complexes namely,  $\{[1-(\text{benzyl})-3-(N\text{-tert-butylacetamido})\text{imidazol-2-ylidene}]\text{MCl}\}_2$  [ $\text{M} = \text{Ag}$  (**2**);  $\text{Au}$  (**3**)] (Scheme 1), which exhibit significant closed-shell metallophilic interactions in the form of a close  $\text{M}\cdots\text{M}$  contact observed in the X-ray diffraction studies and as emission peaks arising out of the  $\text{M}\cdots\text{M}$  interaction ( $\text{M} = \text{Ag}, \text{Au}$ ) in the photoluminescence studies. More importantly, contrary to the common notion of metallophilic interaction being maximum for gold among the coinage metals, this pair of dimeric silver **2** and gold **3** complexes display shorter argentophilic interaction than aurophilic interaction.

## Results and Discussion

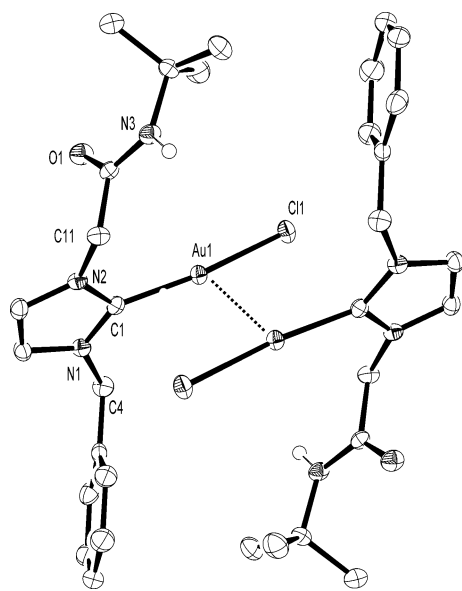
Of the extended and intriguing network of assemblies displayed by metallophilic interactions, the dimeric ones are by far the simplest of all and thus provide an ideal platform for studying such interactions. For example, pioneering studies by Pyykkö,<sup>28</sup> Magnko,<sup>12</sup> Werner,<sup>29</sup> and Kaltsoyannis<sup>30</sup> on simple dimeric  $\{(\text{PH}_3)\text{MX}\}_2$  ( $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ,  $\text{X} = \text{halide}, \text{pseudohalide}$ ) complexes spreading over the entire

- (21) Samantaray, M. K.; Roy, D.; Patra, A.; Stephen, R.; Saikh, M.; Sunoj, R. B.; Ghosh, P. *J. Organomet. Chem.* **2006**, 691, 3797–3805.
- (22) Ray, S.; Mohan, R.; Singh, J. K.; Samantaray, M. K.; Shaikh, M. M.; Panda, D.; Ghosh, P. *J. Am. Chem. Soc.* **2007**, 129, 15042–15053.
- (23) (a) Ray, L.; Shaikh, M. M.; Ghosh, P. *Dalton Trans.* **2007**, 4546–4555. (b) Ray, L.; Shaikh, M. M.; Ghosh, P. *Organometallics* **2007**, 26, 958–964.
- (24) (a) Ray, L.; Katiyar, V.; Barman, S.; Raihan, M. J.; Nanavati, H.; Shaikh, M. M.; Ghosh, P. *J. Organomet. Chem.* **2007**, 692, 4259–4269. (b) Ray, L.; Katiyar, V.; Raihan, M. J.; Nanavati, H.; Shaikh, M. M.; Ghosh, P. *Eur. J. Inorg. Chem.* **2006**, 3724–3730.
- (25) (a) Samantaray, M. K.; Katiyar, V.; Pang, K.; Nanavati, H.; Ghosh, P. *J. Organomet. Chem.* **2007**, 692, 1672–1682. (b) Samantaray, M. K.; Katiyar, V.; Roy, D.; Pang, K.; Nanavati, H.; Stephen, R.; Sunoj, R. B.; Ghosh, P. *Eur. J. Inorg. Chem.* **2006**, 2975–2984.

- (26) (a) Chi, Y.-N.; Huang, K.-L.; Cui, F.-Y.; Xu, Y.-Q.; Hu, C.-W. *Inorg. Chem.* **2006**, 45, 10605–10612. (b) Wang, Q.-M.; Mak, T. C. W. *Inorg. Chem.* **2003**, 42, 1637–1643. (c) Che, C.-M.; Tse, M.-C.; Chan, M. C. W.; Cheung, K.-K.; Phillips, D. L.; Leung, K.-H. *J. Am. Chem. Soc.* **2000**, 122, 2464–2468.
- (27) (a) Omary, M. A.; Mohamed, A. A.; Rawashdeh-Omary, M. A.; Frckler, J. P., Jr. *Coord. Chem. Rev.* **2005**, 249, 1372–1381. (b) Gimeno, M. C.; Laguna, A. *Chem. Rev.* **1997**, 97, 511–522.
- (28) (a) Pyykkö, P.; Runeberg, N.; Mendizabal, F. *Chem. Eur. J.* **1997**, 3, 1451–1457. (b) Pyykkö, P.; Mendizabal, F. *Chem. Eur. J.* **1997**, 3, 1458–1465.
- (29) Runeberg, N.; Schütz, M.; Werner, H.-J. *J. Chem. Phys.* **1999**, 110, 7210–7215.
- (30) O'Grady, E.; Kaltsoyannis, N. *Phys. Chem. Chem. Phys.* **2004**, 6, 680–687.



**Figure 3.** ORTEP of **2** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Ag–C(1) 2.116(8), Ag–Cl(1) 2.362(2), N(1)–C(1) 1.324(10), N(2)–C(1) 1.368(10), Ag(1)···Ag(1) 3.1970(12), C(1)–Ag–Cl(1) 167.3(2), N(2)–C(1)–N(1) 104.9(7).



**Figure 4.** ORTEP of **3** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Au–C(1) 1.983(3), Au–Cl(1) 2.3009(7), N(1)–C(1) 1.346(3), N(2)–C(1) 1.355(3), Au(1)···Au(1) 3.2042(2), C(1)–Au–Cl(1) 172.38(8), N(2)–C(1)–N(1) 104.9(2).

past decade provided the much-needed theoretical foundation for the metallophilic interaction. In this regard it is worth mentioning that, of the plethora of extended structures of silver and gold complexes of N-heterocyclic carbenes (NHC) that display such metallophilic interactions,<sup>31</sup> the structurally characterized examples of simple dimeric ones of the type

(31) For representative examples see: (a) Chiu, P. L.; Chen, C. Y.; Zeng, J. Y.; Lu, C. Y.; Lee, H. M. *J. Organomet. Chem.* **2005**, *690*, 1682–1687. (b) Liu, Q.-X.; Xu, F.-B.; Li, Q.-S.; Zeng, X.-S.; Leng, X.-B.; Chou, Y. L.; Zhang, Z. Z. *Organometallics* **2003**, *22*, 309–314. (c) Chen, W.; Liu, F. J. *Organomet. Chem.* **2003**, *673*, 5–12. (d) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204–5208.

**Table 1.** X-ray Crystallographic Data for **2** and **3**

compound	2	3
lattice	monoclinic	monoclinic
formula	C <sub>16</sub> H <sub>21</sub> AgClN <sub>3</sub> O	C <sub>16</sub> H <sub>21</sub> AuClN <sub>3</sub> O
formula weight	414.68	503.77
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	14.3695(10)	14.3314(2)
<i>b</i> /Å	6.0275(3)	6.16040(10)
<i>c</i> /Å	20.8243(13)	20.1740(3)
$\alpha$ /deg	90.00	90.00
$\beta$ /deg	103.407(7)	102.760(2)
$\gamma$ /deg	90.00	90.00
<i>V</i> /Å <sup>3</sup>	1754.48(19)	1737.12(5)
<i>Z</i>	4	4
temperature (K)	150(2)	150(2)
radiation ( $\lambda$ , Å)	0.710 73	0.710 73
$\rho$ (calcd), g cm <sup>−3</sup>	1.570	1.926
$\mu$ (Mo K $\alpha$ ), mm <sup>−1</sup>	1.306	8.627
$\theta$ , deg	3.53–25.00	3.18–24.99
no. of data	2939	3053
no. of parameters	202	206
<i>R</i> <sub>1</sub>	0.0785	0.0145
<i>wR</i> <sub>2</sub>	0.2210	0.0326
GO <sub>F</sub>	1.055	1.072

$\{(NHC)MX\}_2$  (*M* = Ag, Au; *X* = halide) exhibiting such interactions are conspicuously fewer. Indeed, we are aware of only a handful of  $\{(NHC)MCl\}_2$  (*M* = Ag, Au) type complexes of silver and gold, namely,  $\{(1,3,4,5\text{-tetramethylimidazol-2-ylidene})AgCl\}_2$  (**A**),<sup>32</sup>  $\{[1,3\text{-bis(cyclohexyl)imidazol-2-ylidene}]AgCl\}_2$  (**B**),<sup>32</sup>  $\{[1,3\text{-bis(cyclohexyl)imidazol-2-ylidene}]AuCl\}_2$  (**C**),<sup>33,34</sup>  $\{[1,3\text{-bis(iso-butyl)imidazol-2-ylidene}]AgCl\}_2$  (**D**),<sup>32</sup> and  $\{[1,3\text{-dimethylbenzimidazol-2-ylidene}]AuCl\}_2$  (**E**),<sup>35</sup> all of which are supported over nonfunctionalized N-heterocyclic carbene ligands (Figure 1). As our program revolves around designing new N/O-functionalized carbenes and their complexes, we became interested in looking for the existence of such metallophilic interactions in our N/O-functionalized carbene metal complexes, particularly in the silver and gold compounds.

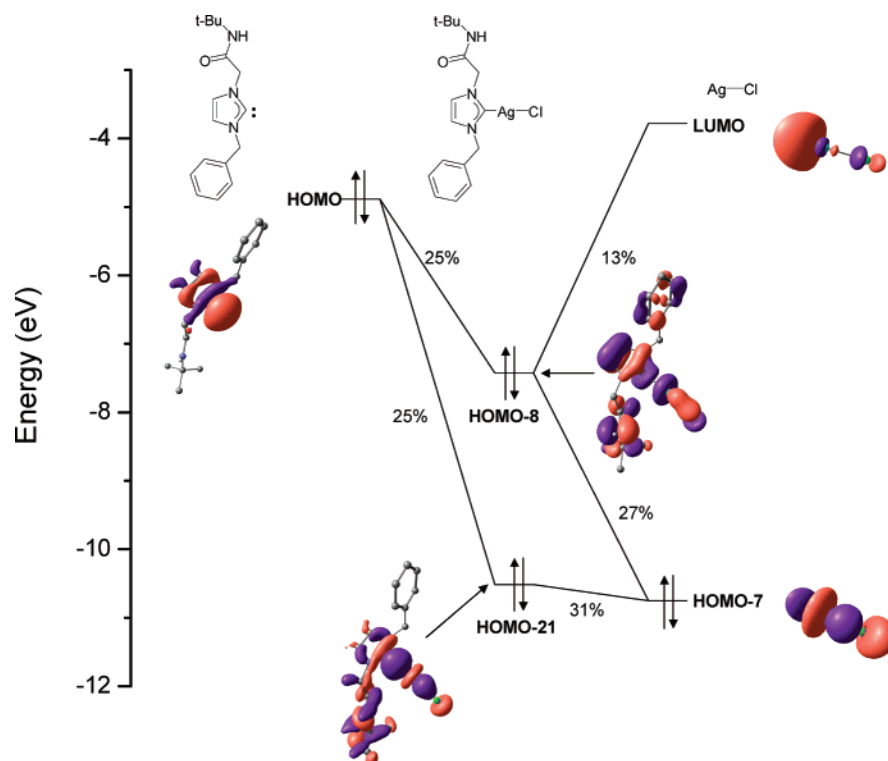
A pair of silver and gold complexes supported over an amido-functionalized N-heterocyclic carbene ligand was synthesized with the objective of investigating the influence of metallophilic interactions in these complexes. Specifically, the reaction of the imidazolium chloride salt, 1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazolium chloride<sup>23</sup> **1**, with Ag<sub>2</sub>O gave the silver complex  $\{[1\text{-}(benzyl)\text{-}3\text{-}(N\text{-}tert\text{-butylacetamido)imidazol-2-ylidene}]AgCl\}_2$  **2**, in 66% yield (Scheme 1). The formation of the silver complex **2** proceeded with the deprotonation of the (NCHN) proton of imidazolium chloride salt **1** by Ag<sub>2</sub>O and was verified by <sup>1</sup>H NMR spectroscopy that showed the absence of the characteristic acidic imidazolium (NCHN) resonance in the downfield

(32) Frémont, P. De; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301–6309.

(33) Baker, M. V.; Barnard, P. J.; Berners-Price, S. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2005**, *690*, 5625–5635.

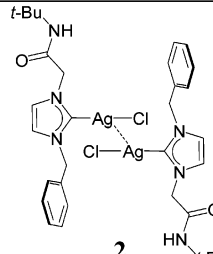
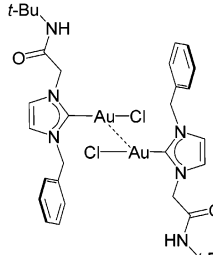
(34) Another similar dimeric structure of the same compound showing longer Au···Au separation of 3.787 Å has also been reported. See: Frémont, P. De; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411–2418.

(35) Wang, H. M. J.; Chen, C. Y. L.; Lin, I. J. B. *Organometallics* **1999**, *18*, 1216–1223.



**Figure 5.** Simplified orbital interaction diagram showing the major contributions of the NHC–silver bond in **2**.

**Table 2.** Wiberg Indices (Bond Order), M···M Interaction Energies, and M···M Distances for **2** and **3**

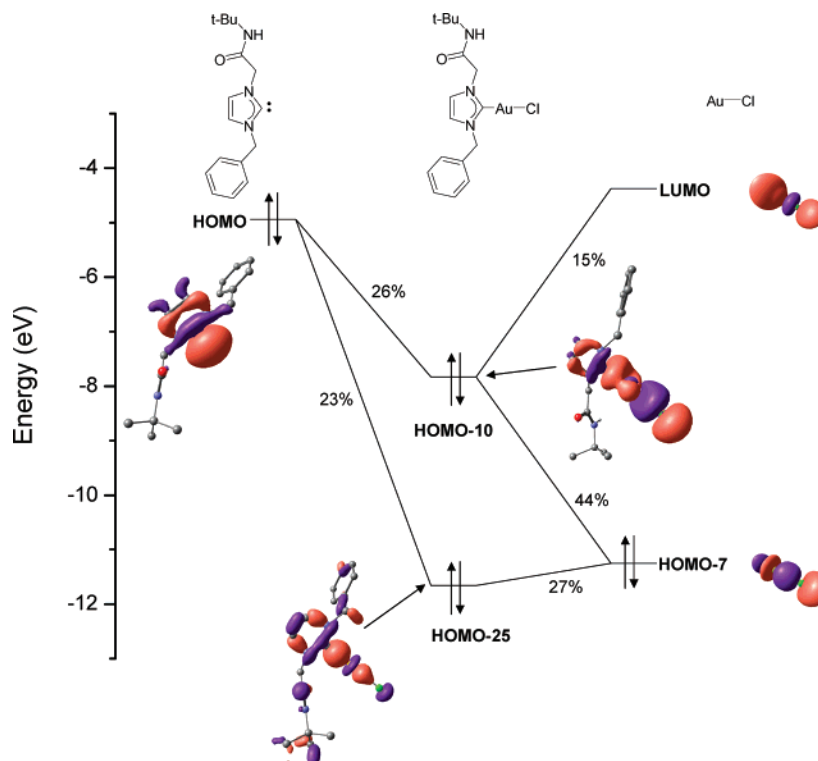
Complexes	M···M distance (Å)	Wiberg Indices (Bond Order) M···M interaction	M···M interaction energy (kcal/mol)
 <p><b>2</b></p>	3.1970(12)	0.216	12.8
 <p><b>3</b></p>	3.2042(2)	0.259	8.6

region of the spectrum, while the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum showed the appearance of the resulting metal bound carbene (NCN) peak at a much downfield shifted region at 181.7 ppm. The amido  $-\text{CONH}-$  moiety appeared at  $1681\text{ cm}^{-1}$  in the infrared spectrum.

The gold complex **3** was subsequently synthesized from the silver complex **2** by treatment with  $(\text{SMe}_2)\text{AuCl}$  in 86%

yield employing a frequently followed transmetalation route for preparing the transition metal complexes of N-heterocyclic carbene ligands (Scheme 1). In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, the gold–carbene (NCN) resonance appeared at 184.4 ppm, slightly shifted from that observed in the case of the silver complex **2** (181.7 ppm). Overall, the close resemblances of the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectral features





**Figure 6.** Simplified orbital interaction diagram showing the major contributions of the NHC–gold bond in **3**.

of the gold **3** with the silver **2** complex point toward their structural homology.

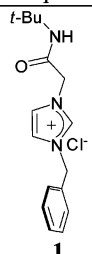
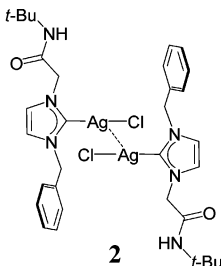
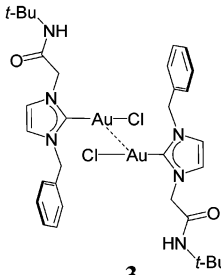
The molecular structures of the silver **2** and the gold **3** complexes as determined by X-ray-diffraction studies (Figures 3 and 4) show that they are indeed isostructural. The most remarkable aspect of these complexes is their dimeric nature,  $\{[1-(\text{benzyl})-3-(N\text{-tert-butylacetamido})\text{imidazol-2-ylidene}]MCl\}_2$  [ $M = \text{Ag}$  (**2**);  $\text{Au}$  (**3**)], that exhibits close  $M\cdots M$  contact [ $M = \text{Ag}$  (**2**) 3.1970(12) Å;  $\text{Au}$  (**3**) 3.2042(2) Å], thereby indicating the presence of significant closed-shell  $d^{10}\cdots d^{10}$  argentophilic and aurophilic interactions. Though numerous N-heterocyclic carbene complexes of silver and gold are known, examples of structurally characterized discrete dimeric  $\{(NHC)MX\}_2$  ( $M = \text{Ag}, \text{Au}$ ;  $X = \text{halide}$ ) type complexes exhibiting similar metallophilic interactions are surprisingly fewer. Specifically, in the silver **2** and gold **3** complexes, the two monomeric units,  $[1-(\text{benzyl})-3-(N\text{-tert-butylacetamido})\text{imidazol-2-ylidene}]MCl$  [ $M = \text{Ag}$  (**2**);  $\text{Au}$  (**3**)], approach in *head-to-tail* fashion through the central metal atom displaying close  $M\cdots M$  contact [ $M = \text{Ag}$  (**2**) 3.1970(12) Å;  $\text{Au}$  (**3**) 3.2042(2) Å], which is shorter than twice the van der Waals radii of the corresponding Ag (3.44 Å) and Au (3.32 Å) atoms<sup>36</sup> in the respective complexes. In this regard it is worth mentioning that in the dimeric  $\{(\text{ligand})MX\}_2$  ( $M = \text{Ag}, \text{Au}$ ,  $X = \text{halide}$ ) type complexes three possible arrangements, *head-to-tail*, *head-to-head*, and *nonplanar* orientations are often seen (Figure 2). It is worth noting that, of the handful of numbers of structurally characterized dimeric  $\{(NHC)MCl\}_2$  ( $M = \text{Ag}, \text{Au}$ ) type

complexes that exist,<sup>32,33,35</sup> all of them exhibit nonplanar orientations (Figures 1 and 2), and in that respect the silver **2** and the gold **3** complexes to our knowledge are the only examples of *head-to-tail* orientation. For example, the  $M\cdots M$  contact and the  $C_{\text{carbene}}-M-M-C_{\text{carbene}}$  dihedral angle displayed in various structurally characterized dimeric  $\{-(NHC)MCl\}_2$  ( $M = \text{Ag}, \text{Au}$ ) type complexes are  $\{[1,3,4,5\text{-tetramethylimidazol-2-ylidene}]AgCl\}_2$  (**A**) [3.0673(3) Å, 89.5°],<sup>32</sup>  $\{[1,3\text{-bis(cyclohexyl)imidazol-2-ylidene}]AgCl\}_2$  (**B**) [3.0181(6) Å, 77.2°],<sup>32</sup>  $\{[1,3\text{-bis(cyclohexyl)imidazol-2-ylidene}]AuCl\}_2$  (**C**) [3.1566(6) Å, 65.9°],<sup>33</sup>  $\{[1,3\text{-bis(isobutyl)imidazol-2-ylidene}]AgCl\}_2$  (**D**) [3.124(2) Å, 87.5°],<sup>32</sup> and  $\{[1,3\text{-dimethylbenzimidazol-2-ylidene}]AuCl\}_2$  (**E**) [3.1664(10) Å, ~90°]<sup>35</sup> (Figure 1). Interestingly enough, these complexes supported over nonfunctionalized N-heterocyclic carbene ligands, as in the compounds **A**, **B**, **C**, **D**, and **E** (Figure 1), displayed nonplanar arrangements, while the silver **2** and gold **3** complexes, supported over a N/O-functionalized N-heterocyclic carbene ligand, exhibited *head-to-tail* orientations (Figure 2).

Important is the comparison of the metal $\cdots$ metal contact in the silver **2** [3.1970(12) Å] and gold **3** [3.2042(2) Å] complexes with the other structurally characterized pairs of dimeric  $\{(NHC)MCl\}_2$  ( $M = \text{Ag}, \text{Au}$ ) type complexes. Quite interestingly, the only available pair,  $\{[1,3\text{-bis(cyclohexyl)imidazol-2-ylidene}]MCl\}_2$  ( $M = \text{Ag}$ ,<sup>32</sup>  $\text{Au}$ <sup>33,34</sup>), of the handful of examples of dimeric NHC complexes that exist,<sup>32–35</sup> showed similar a trend displaying shorter  $\text{Ag}\cdots\text{Ag}$  contact [3.0181(6) Å]<sup>32</sup> than the  $\text{Au}\cdots\text{Au}$  contact [3.1566(6) Å],<sup>33,34</sup> thereby implying stronger argentophilic than aurophilic

(36) Bondi, A. J. *Phys. Chem.* **1964**, 68, 441–451.

**Table 3.** Absorption and Emission Data for the **1**, **2**, and **3** Complexes

Compounds	$\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon_{\text{max}}$ $\text{mm}^3\text{mol}^{-1}\text{cm}^{-1}$ )	$\lambda_{\text{em}}/\text{nm}^a$
 <b>1</b>	242 (41600)	470, 575
 <b>2</b>	244 (54000)	483, 527, 580
 <b>3</b>	263 (52700)	427, 529, 575

<sup>a</sup> Excited at 244 nm and the spectrum recorded in glassy solution of EtOH:MeOH (4:1, v/v) mixture at 77 K.

interaction in this pair of complexes, analogous to what is observed in the pair of silver **2** and gold **3** complexes. However, more examples of structurally characterized pairs of dimeric silver and gold NHC complexes are needed before any generalization of the relative strengths of metalphilic interaction present in these complexes can be made.

The geometry around the metal centers in both these **2** and **3** complexes is off-linear [ $\angle\text{Cl}1-\text{Ag}1-\text{Cl}1 = 167.3(2)^\circ$  (**2**);  $\angle\text{Cl}1-\text{Au}1-\text{Cl}1 = 172.38(8)^\circ$  (**3**)] and is consistent with the linear geometries often observed for two-coordinated  $d^{10}$  metals.<sup>37</sup> Quite interestingly, a direct consequence of the strength of a  $\text{M}\cdots\text{M}$  ( $\text{M} = \text{Ag}, \text{Au}$ ) interaction occurring through the central metal atom ( $\text{Ag}1$  in **2** and  $\text{Au}1$  in **3**) in these dimeric complexes (Figures 3 and 4) is evidenced by the slightly bent  $\angle\text{Cl}1-\text{Ag}1-\text{Cl}1$  angle [ $167.3(2)^\circ$ ] at silver in **2** compared to the more linear  $\angle\text{Cl}1-\text{Au}1-\text{Cl}1$  angle [ $172.38(8)^\circ$ ] at gold in **3**, thereby suggesting stronger argentophilic interaction than the aurophilic interaction in this pair of complexes (**2** and **3**). Consistent with larger covalent radii of  $\text{Ag(I)}$  compared to  $\text{Au(I)}$ ,<sup>38</sup> the  $\text{Ag}-\text{C}_{\text{carbene}}$  distance in **2** [ $2.116(8)$  Å] is longer than the corresponding

$\text{Au}-\text{C}_{\text{carbene}}$  distance in **3** [ $1.983(3)$  Å] and compares well with that observed in other N-heterocyclic carbene complexes of silver and gold.<sup>39,40</sup> The two N-substituents, the benzyl and *tert*-butylacetamido, of the NHC ligand on one monomer unit  $(\text{NHC})\text{MCl}$  ( $\text{M} = \text{Ag}, \text{Au}$ ) are deposited trans to that of the other in the dimeric  $\{(\text{NHC})\text{MCl}\}_2$  [ $\text{M} = \text{Ag}$  (**2**),  $\text{Au}$  (**3**)] complexes due to obvious steric reasons.

In order to gain a better understanding of the metalphilic interactions present in the silver **2** and gold **3** complexes and also to obtain a deeper insight into the nature of NHC–metal interactions in these complexes, detailed density functional theory (DFT) studies were carried out. In particular, the  $\text{M}\cdots\text{M}$  interaction energies and the  $\text{M}\cdots\text{M}$  bond order (Wiberg indices) were computed using the B3LYP/SDD, 6-31G(d) level of theory with the objective of estimating the strength of the closed-shell metalphilic interaction present in these complexes (Table 2). The computed bond order (Wiberg indices) for the  $\text{M}\cdots\text{M}$  interaction in these silver **2** (0.22) and the gold **3** (0.26)

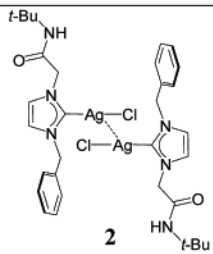
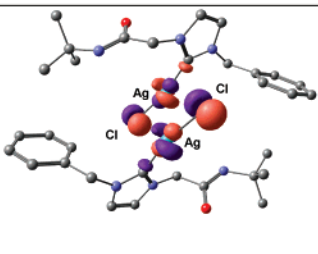
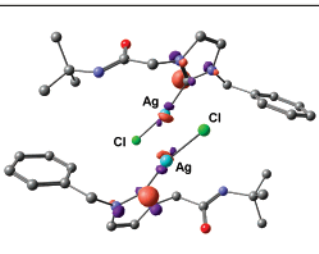
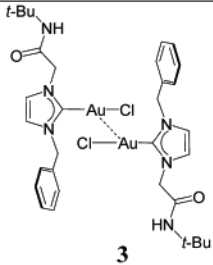
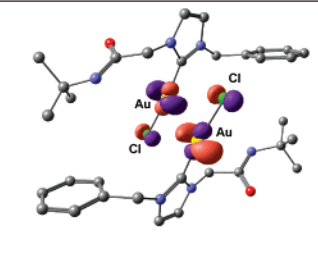
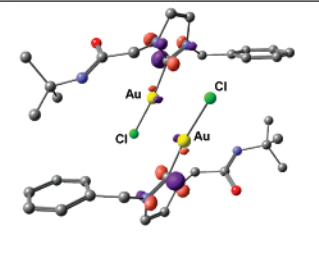
(37) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons, Inc.: New York, 1999; pp 1084–1107.

(38) Tripathi, U. M.; Bauer, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1997**, 2865–2868.

(39) (a) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978–4008. (b) Lin, I. J. B.; Vasam, C. S. *Can. J. Chem.* **2005**, *83*, 812–825. (c) Díaz-Requejo, M. M.; Pérez, P. J. *J. Organomet. Chem.* **2005**, *690*, 5441–5450. (d) Arnold, P. L. *Heteroat. Chem.* **2002**, *13*, 534–539. (e) Lee, K. M.; Wang, H. M. J.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2852–2856. (f) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972–975.

(40) Lin, I. J. B.; Vasam, C. S. *Can. J. Chem.* **2005**, *83*, 812–825.

**Table 4.** Singlet Excitation Energies Having Maximum Oscillatory Strengths for **2** and **3**<sup>a</sup>

Complexes	HOMO	LUMO	HOMO-LUMO Excitation wavelength (nm)	Oscillatory strength (f)	Type of Transition
 <b>2</b>	 Orbital # 182	 Orbital # 183	258	0.1737	4 % MLCT ( $\pi \rightarrow \pi^*$ )
 <b>3</b>	 Orbital # 182	 Orbital # 183	258	0.1737	37 % MLCT ( $\pi \rightarrow \pi^*$ )

<sup>a</sup> Computed using B3LYP/SDD, 6-31G(d) level of theory.

complexes were approximately on the order of about one-fourth of a single covalent bond. Consistent with the observation of a slightly shorter Ag $\cdots$ Ag contact in **2** [3.1970(12) Å] compared to the corresponding Au $\cdots$ Au contact in **3** [3.2042(2) Å], the M $\cdots$ M interaction energy in the silver **2** complex (12.8 kcal/mol) is estimated to be higher than that in the gold **3** complex (8.6 kcal/mol). Despite being bigger than gold in size,<sup>36,38</sup> the shorter Ag $\cdots$ Ag distance in **2** is indicative of a stronger argentophilic interaction, which becomes all the more interesting given the fact that metallophilic interaction is often perceived to be maximum for gold (aurophilicity) among the coinage metals (Cu, Ag, and Au) due to its greater relativistic effect. However, in this regard, it is worth mentioning that for a series of dimeric  $\{(PH_3)MCl\}_2$  (M = Cu, Ag, Au) complexes, O'Grady and Kaltsoyannis<sup>30</sup> have recently shown using several different computational methods that the argentophilic interaction is indeed the strongest among the three coinage metals and the metallophilic interaction need not increase upon going down group 11 (Cu, Ag, Au), as has been the popular belief.<sup>3</sup> The significance of stronger metallophilic interaction in **2** assumes importance when viewed in the backdrop of the fact that genuine examples of argentophilicity are much fewer than those of aurophilicity. Furthermore, the argentophilic interaction in the ligand-unsupported complex **2** becomes very interesting given the fact that majority of the silver complexes that are known to show such metallophilic interactions are primarily ligand assisted while the examples of ligand-unsupported ones are much rarer.

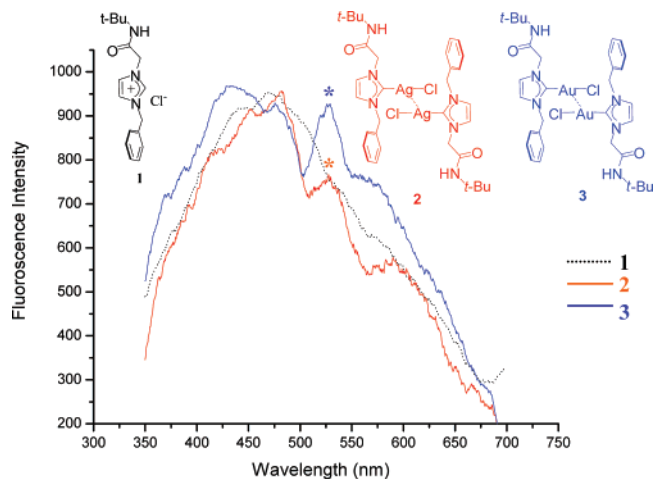
The nature of the NHC–M (M = Ag, Au) interaction in the silver **2** and gold **3** complexes was assessed by post-

wave function natural bond orbital (NBO)<sup>41</sup> analysis. Specifically, both the natural charge (Tables S5 and S6) and Mulliken charge (Tables S7 and S8) analyses show that, upon electron donation from the free carbene (NHC) fragment to the metal center in the respective MCl (M = Ag, Au) fragment in **2** and **3**, the positive charge at the metal is significantly reduced. Along the same line, the carbene carbon of the (NHC) fragment in **2** and **3** exhibits an opposite trend with significantly increased positive charge relative to the carbene carbon of the free (NHC) fragment. A similar relationship is also encountered in the case of the monomeric unit (NHC)MCl (M = Ag, Au) of the dimeric silver **2** and gold **3** complexes (Tables S5–S8). The electron donation from the carbene (NHC) fragment to the metal center in the respective MCl (M = Ag, Au) fragment in the **2** and **3** complexes occurs at the unfilled 5s (silver) and 6s (gold) orbitals. Specifically, the occupancy of the respective 5s (silver) and 6s (gold) orbitals in the **2** [5s<sup>0.64</sup>, 4d<sup>9.82</sup>, 5p<sup>0.01</sup>, 7p<sup>0.01</sup>] and **3** [6s<sup>0.96</sup>, 5d<sup>9.65</sup>, 7p<sup>0.01</sup>] complexes are substantially increased in comparison to that in the MCl [M = Ag (5s<sup>0.36</sup>, 4d<sup>9.95</sup>, 5p<sup>0.03</sup>), Au (6s<sup>0.65</sup>, 5d<sup>9.86</sup>, 6p<sup>0.02</sup>)] fragment upon coordination to the latter free carbene (NHC) ligand fragment.

The NHC–metal interaction in the silver **2** and gold **3** complexes was further probed using charge decomposition analysis (CDA), which estimated the [NHC  $\xrightarrow{\sigma}$  MCl] (M = Ag in **2**, Au in **3**) donation, designated by *d*, and the [NHC  $\xleftarrow{\pi}$  MCl] back donation, designated by *b*, occurring in these

(41) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899–926.





**Figure 7.** Overlay plot of the emission spectra of the ligand precursor **1**, the silver complex **2**, and the gold complex **3** measured in a glassy solution of EtOH:MeOH (4:1, v/v) mixture at low temperature (77 K) (excitation at 244 nm). The peak due to  $M\cdots M$  ( $M = \text{Ag}$  and  $\text{Au}$ ) interaction is marked by asterisks (\*) in the plot.

complexes. Hence the  $d/b$  ratio, which provides an insight into the extent of forward ( $\sigma$ ) and back ( $\pi$ ) donations occurring in the NHC–metal bond, suggests a higher  $[\text{NHC} \xrightarrow{\pi} \text{MCl}]$  back donation in the gold **3** complex relative to that in the silver **2** complex, implying a stronger NHC–Au bond in the former. Indeed, the NHC–metal bond dissociation energies  $D_e(\text{NHC}–\text{M})$  ( $M = \text{Ag}, \text{Au}$ ) in the silver **2** and gold **3** complexes as computed using the B3LYP/SDD, 6-31G(d) level of theory for the monomer unit (NHC)MCl ( $M = \text{Ag}, \text{Au}$ ) of **2** and **3** show that the NHC–Au bond energy (82.7 kcal/mol) is higher than the NHC–Ag bond energy (62.2 kcal/mol). It is worth noting that the greater back ( $\pi$ ) donation usually observed in Au–NHC complexes relative to its Ag counterparts is often ascribed to the dominant relativistic effects of gold that result from the contraction of  $s$  and  $p$  orbitals while the  $d$  and  $f$  orbitals remain diffuse.<sup>2a,3b,4a</sup>

Correlation diagrams depicting the contributions of the free carbene (NHC) and the MCl ( $M = \text{Ag}, \text{Au}$ ) fragments toward the molecular orbitals (MOs) of the monomer unit (NHC)–MCl ( $M = \text{Ag}, \text{Au}$ ) of the silver **2** and the gold **3** complexes provide further understanding of the NHC–metal bonding present in these complexes. The correlation diagram, constructed using AOMix software,<sup>42</sup> revealed that the NHC–metal interaction in the silver **2** and the gold **3** complexes is primarily a three-centered–four-electron interaction with a part of the electron donation from the NHC fragment occurring at the  $\sigma^* \text{M}–\text{Cl}$  ( $M = \text{Ag}, \text{Au}$ ) antibonding orbital (Figures 5 and 6) of the MCl ( $M = \text{Ag}, \text{Au}$ ) fragment. In this regard it is worth mentioning that Frenking and co-workers had earlier proposed a similar three-centered–four-electron interaction for the (NHC)MCl ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ) complexes.<sup>43</sup>

The electronic spectrum of these compounds showed single absorbance peaks for the silver **2** (244 nm) and the gold **3** (263 nm) complexes, like its N-heterocyclic carbene ligand precursor **1** (242 nm) (Table 3). The vertical transitions of the singlet excitation energies obtained using time-dependent DFT calculations at the B3LYP/SDD, 6-31G(d) level of theory suggest that the absorbance bands in the silver and the gold complexes arise due to  $\pi \rightarrow \pi^*$  metal–ligand charge transfer (MLCT) processes (Tables 4 and S12–S14 in the Supporting Information). Specifically, the experimentally observed 244 nm band in **2** (computed wavelength 258 nm) and the 263 nm band in **3** (computed wavelength 258 nm) have been assigned to the HOMO  $\rightarrow$  LUMO  $\pi \rightarrow \pi^*$  MLCT transitions (Tables 3 and 4) based on comparison of the observed and the computed transitions of comparable intensities and was arrived at by examining the respective absorptivity and oscillator strength values.

The presence of metallophilic interactions in the silver **2** and the gold **3** complexes received further substantiation from the photoluminescence studies carried out in a glassy solution at 77 K that showed emission peaks [527 nm (**2**); 529 nm (**3**)] arising out of the  $M\cdots M$  interaction. Specifically, the excitation wavelengths (244 nm) of these complexes were obtained from the respective electronic spectrum. The emission spectrum showed three peaks for the silver **2** (483 nm, 527 nm, 580 nm) and the gold **3** (427 nm, 529 nm, 575 nm) complexes (Figure 7). The two high and low energy emissions of the silver **2** (483 nm, 580 nm) and the gold **3** (427 nm, 575 nm) complexes have been assigned to ligand-based transitions based on the emissions of the ligand precursor **1** (Table 3 and Figure 7). In this regard, it is worth mentioning that similar emissions have been reported for several dimeric Ag–NHC and Au–NHC complexes.<sup>35,44,45</sup> It is noteworthy that attempts to seek a direct correlation between the luminescence energy and the crystallographic  $M\cdots M$  distance ( $M = \text{Ag}, \text{Au}$ ) in silver and gold complexes, at present, is difficult to obtain given the fact that these interactions are not fully understood and also because there exists a variety of examples showing such correlation or inverse correlation or even no correlations between the luminescence energy and the crystallographic  $M\cdots M$  distance. In contrast, for metals such as Pt(II), which has long been extensively studied, a clear correlation has been established between the luminescence energy and the Pt(II)–Pt(II) distance.<sup>46,47</sup>

## Conclusion

In summary, a pair of neutral dimeric silver and gold complexes, namely,  $\{[1-(\text{benzyl})-3-(N\text{-}tert\text{-butylacetamido})\text{-imidazol-2-ylidene}]\text{MCl}\}_2$  [ $M = \text{Ag}$  (**2**);  $\text{Au}$  (**3**)], displaying

- (42) Gorelsky, S. I. *AOMix: Program for Molecular Orbital Analysis*; York University: Toronto, Canada, 1997; <http://www.sg-chem.net/>.  
 (43) (a) Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**, *23*, 3640–3646. (b) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428–1438.

- (44) Wang, H. M. J.; Vasam, C. S.; Tsai, T. Y. R.; Chen, S.-H.; Chang, A. H. H.; Lin, I. J. B. *Organometallics* **2005**, *24*, 486–493.  
 (45) Catalano, V. J.; Moore, A. L. *Inorg. Chem.* **2005**, *44*, 6558–6566.  
 (46) (a) Ma, B.; Li, J.; Djurovich, P. I.; Yousufuddin, M.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 28–29. (b) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C.-M.; Li, C.; Hui, Z. *J. Am. Chem. Soc.* **2004**, *126*, 7639–7651.  
 (47) (a) Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, *62*, 87–153. (b) Yersin, H.; Gliemann, G. *Ann. N. Y. Acad. Sci.* **1978**, *313*, 539–559.

strong metallophilic interactions have been synthesized. The shorter  $M\cdots M$  contact in the silver **2** complex [3.1970(12) Å] relative to that in the gold **3** complex [3.2042(2) Å], despite the size, as indicated by the covalent as well as van der Waals radii of Ag being bigger than those of Au, indicate a stronger metallophilic interaction in the former. The metal-metal interaction energy in these complexes is estimated to be 12.8 (**2**) and 8.6 kcal/mol (**3**). Both structural and computational studies indicate that in this series of neutral dimeric silver and gold complexes the argentophilic interaction is stronger than the aurophilic interaction. The emission bands at 527 (**2**) and 529 nm (**3**) have been tentatively assigned to originate from the metal-metal interaction based on photoluminescence studies. The nature of the NHC-metal interaction has been examined by DFT studies that revealed that the NHCs are effective  $\sigma$ -donating ligands with relatively weaker  $\pi$ -accepting properties and that the electron donation from the carbene NHC fragment occurs primarily at the  $\sigma^*$   $M-Cl$  ( $M = Ag, Au$ ) antibonding orbital of the  $MCl$  ( $M = Ag, Au$ ) fragment in these complexes.

## Experimental Section

**General Procedures.** All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures.  $Ag_2O$  was purchased from SD-fine Chemicals (India) and used without any further purification.  $(SMe_2)AuCl^{48}$  and 1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazolium chloride<sup>23a</sup> **1** were synthesized according to reported literature procedures.  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra were recorded in  $CDCl_3$  on a Varian 400 MHz NMR spectrometer.  $^1H$  NMR peaks are labeled as singlet (s), doublet (d), and multiplet (m). Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Absorption and fluorescence spectra were recorded on a JASCO V570 spectrophotometer and Perkin-Elmer LS55 spectrofluorimeter, respectively. X-ray diffraction data for **2** and **3** were collected on Oxford diffraction XCALIBUR-S instrument. The crystal data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on  $F_2$  with SHELXTL (version 6.10).

**Synthesis of  $\{[1-(Benzyl)-3-(N-tert-butylacetamido)imidazol-2-ylidene]AgCl\}_2$  (**2**).** A mixture of 1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazolium chloride (**1**) (1.89 g, 6.15 mmol) and  $Ag_2O$  (0.713 g, 3.07 mmol) in dichloromethane (ca. 30 mL) was stirred at room temperature for 6 h. The reaction mixture was filtered and the solvent was removed under vacuum to give the product **2** as a white solid (1.67 g, 66%). Single crystals for X-ray diffraction studies were grown from acetonitrile employing slow-evaporation technique.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 25 °C):  $\delta$  8.55 (s, 1H, NH), 7.38 (br, 1H, NCHCHN), 7.23–7.22 (m, 3H, *o*- and *p*- $C_6H_5$ ), 7.03–7.02 (br, 2H, *m*- $C_6H_5$ ), 6.81 (br, 1H, NCHCHN), 5.14 (s, 2H,  $CH_2$ ), 5.11 (s, 2H,  $CH_2$ ), 1.37 (s, 9H,  $C(CH_3)_3$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz, 25 °C):  $\delta$  181.7 (NCN-Ag), 165.9 (CO), 135.4 (*ipso*- $C_6H_5$ ), 128.6 (*m*- $C_6H_5$ ), 128.0 (*p*- $C_6H_5$ ), 127.0 (*o*- $C_6H_5$ ), 123.2 (NCHCHN), 120.3 (NCHCHN), 55.0 ( $CH_2$ ), 54.2 ( $C(CH_3)_3$ ), 51.2 ( $CH_2$ ), 28.3 ( $C(CH_3)_3$ ). IR data  $cm^{-1}$  KBr pellet: 1681 (s) ( $\nu_{CO}$ ). Anal. Calcd for  $C_{16}H_{21}AgClN_3O \cdot 0.5CH_2Cl_2$ : C, 43.35; H, 4.85; N, 9.19. Found: C, 42.77; H, 4.99; N, 9.97.

**Synthesis of  $\{[1-(Benzyl)-3-(N-tert-butylacetamido)imidazol-2-ylidene]AuCl\}_2$  (**3**).** A mixture of  $\{[1-(benzyl)-3-(N-tert-butylacetamido)imidazol-2-ylidene]AgCl\}_2$  (**2**) (0.196 g, 0.475 mmol) and  $(SMe_2)AuCl$  (0.139 g, 0.475 mmol) in dichloromethane (ca. 30 mL) was stirred at room temperature for 6 h, when the formation of an off-white  $AgCl$  precipitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to give the product **3** as a white solid (0.205 g, 86%). Single crystals for X-ray diffraction studies were grown from acetonitrile employing slow-evaporation technique.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 25 °C):  $\delta$  8.96 (s, 1H, NH), 7.33 (br, 1H, NCHCHN), 7.26–7.24 (m, 3H, *o*- and *p*- $C_6H_5$ ), 7.09 (br, 2H, *m*- $C_6H_5$ ), 6.86 (br, 1H, NCHCHN), 5.30 (s, 2H,  $CH_2$ ), 5.16 (s, 2H,  $CH_2$ ), 1.39 (s, 9H,  $C(CH_3)_3$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz, 25 °C):  $\delta$  184.4 (NCN-Au), 165.5 (CO), 134.9 (*ipso*- $C_6H_5$ ), 128.7 (*m*- $C_6H_5$ ), 128.2 (*p*- $C_6H_5$ ), 127.0 (*o*- $C_6H_5$ ), 123.9 (NCHCHN), 120.3 (NCHCHN), 54.3 ( $CH_2$ ), 53.6 ( $C(CH_3)_3$ ), 51.3 ( $CH_2$ ), 28.4 ( $C(CH_3)_3$ ). IR data  $cm^{-1}$  KBr pellet: 1679 (s) ( $\nu_{CO}$ ). Anal. Calcd for  $C_{16}H_{21}AuClN_3O$ : C, 38.15; H, 4.20; N, 8.34. Found: C, 37.89; H, 4.35; N, 8.11.

**Computational Methods.** Density functional theory calculations were performed on the silver **2** and gold **3** complexes using the Gaussian 03<sup>49</sup> suite of quantum chemical programs. The Becke three-parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP) has been employed in this study.<sup>50,51</sup> The Stuttgart–Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD), is used for silver<sup>52</sup> and gold.<sup>53</sup> All other atoms are treated with the 6-31G(d) basis set.<sup>54</sup>

Inspection of the metal–ligand donor–acceptor interactions was carried out using charge decomposition analysis (CDA).<sup>55</sup> CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.<sup>56</sup> The orbital contributions in the  $(NHC)MCl$  ( $M = Ag, Au$ ) type complexes (**2** and **3**) complexes can be divided into three parts: (i)  $\sigma$ -donation from the  $[NHC \xrightarrow{\sigma} MCl]$  fragment, (ii)  $\pi$ -back-donation from the  $[NHC \xleftarrow{\pi} MCl]$  fragment, and (iii) a repulsive interaction arising between the occupied MOs of these two fragments.

The CDA calculations were performed using the program AOMix,<sup>42</sup> using the B3LYP/SDD, 6-31G(d) wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMix program.<sup>42,57</sup> The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, and the charge decomposition analysis (CDA) were

(48) Brandys, M.-C.; Jennings, M. C.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **2000**, 4601–4606.

(49) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(50) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.

(51) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(52) (a) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866–872. (b) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141. (c) Alkauskas, A.; Baratoft, A.; Bruder, C. *J. Phys. Chem. A* **2004**, *108*, 6863–6868.

(53) (a) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2001**, *123*, 12899–12900. (b) Faza, O. N.; López, C. S.; Álvarez, R.; de Lera, A. R. *J. Am. Chem. Soc.* **2006**, *128*, 2434–2437.

(54) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

(55) Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352–9362.

(56) Frenking, G.; Pidun, U. *J. Chem. Soc., Dalton Trans.* **1997**, 1653–1662.

(57) Gorelsky, S. I.; Lever, A. B. P. *J. Organomet. Chem.* **2001**, *635*, 187–196.

performed using AOMix-CDA.<sup>58</sup> Natural bond orbital (NBO) analysis was performed using the NBO 3.1 program implemented in the Gaussian 03 package.<sup>41</sup>

**Acknowledgment.** We thank the Department of Science and Technology for financial support of this research. We are grateful to the National Single Crystal X-ray Diffraction Facility at IIT Bombay, India, for the crystallographic results.

(58) Gorelsky, S. I.; Ghosh, S.; Solomon, E. I. *J. Am. Chem. Soc.* **2006**, *128*, 278–290.

Computational facilities from the IIT Bombay computer center are gratefully acknowledged. L.R. thanks IIT Bombay, India, for a research fellowship.

**Supporting Information Available:** CIF files giving crystallographic data for **2** and **3** and B3LYP coordinates of single-point geometries of **2** and **3** and of their respective monomer units. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC701830M



# Highly Convenient Amine-Free Sonogashira Coupling in Air in a Polar Mixed Aqueous Medium by *trans*- and *cis*-[(NHC)<sub>2</sub>PdX<sub>2</sub>] (X = Cl, Br) Complexes of *N/O*-Functionalized N-Heterocyclic Carbenes

Lipika Ray,<sup>[a]</sup> Samir Barman,<sup>[a]</sup> Mobin M. Shaikh,<sup>[b]</sup> and Prasenjit Ghosh\*<sup>[a]</sup>

**Abstract:** Two new *trans*- and *cis*-[(NHC)<sub>2</sub>PdX<sub>2</sub>] (X = Cl, Br) complexes of *N/O*-functionalized N-heterocyclic carbenes employed in a highly convenient amine-free Sonogashira cross-coupling reaction in air in a polar mixed aqueous medium are reported. Specifically, the *trans*-[1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]<sub>2</sub>PdBr<sub>2</sub>] (**3**) and *cis*-[1-benzyl-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]<sub>2</sub>PdCl<sub>2</sub>] (**4**) complexes effectively catalyzed the Sonogashira cross-coupling reaction of aryl iodides with substituted acetylenes in air in a mixed solvent (DMF/H<sub>2</sub>O, 3:1 v/v) under amine-free conditions. Interestingly, these *trans*- and *cis*-[(NHC)<sub>2</sub>PdX<sub>2</sub>]

(X = Cl, Br) complexes, with two N-heterocyclic carbene ligands, exhibited superior activity compared with the now popular PEPPSI (pyridine enhanced precatalyst preparation, stabilization and initiation)-themed analogues, *trans*-[(NHC)Pd(pyridine)X<sub>2</sub>] (X = Cl, Br), **3a** and **4a**, with one N-heterocyclic carbene ligand and a “throw away” pyridine ligand in a *trans* disposition to each other. The higher activities of **3** and **4** compared with PEPPSI analogues **3a** and **4a** are at-

tributed to more-electron-rich metal centers, as revealed by DFT studies, in the former complexes and is in concurrence with a more electron-rich metal center being effective in facilitating the oxidative addition of aryl halide, often a rate-determining step in palladium-mediated cross-coupling reactions. Complexes **3** and **4** were prepared from the corresponding silver analogues by transmetalation with [(cod)PdCl<sub>2</sub>], whereas the corresponding PEPPSI analogues **3a** and **4a** were obtained directly from the imidazolium halide salts by reaction with PdCl<sub>2</sub> in pyridine in the presence of K<sub>2</sub>CO<sub>3</sub> as base.

**Keywords:** carbenes • cross-coupling • heterocycles • palladium • Sonogashira reaction

## Introduction

The Sonogashira cross-coupling reaction provides an all important answer to the direct alkylation of aryl and alkenyl halides<sup>[1]</sup> and, not surprisingly, it has been effectively utilized over the years to construct conjugated enyne and arylalkyne frameworks in, for example, natural products,<sup>[2,3]</sup> pharma-

ceuticals,<sup>[4]</sup> biologically active molecules,<sup>[5]</sup> and molecular electronics.<sup>[6]</sup> The very popular Sonogashira cross-coupling reaction is catalyzed by palladium in a basic medium in the presence of copper as a co-catalyst. A copper-acetylide species is generated in situ, which transfers the acetylide moiety on to the palladium center for the desired sp<sup>2</sup>-sp coupling by a reductive elimination pathway.<sup>[7]</sup> Note, despite its critical role in catalysis, upon exposure to air or any oxidizing agents the copper-acetylide species also yields an unwanted homocoupled side-product by the so-called Glaser coupling reaction,<sup>[8]</sup> thereby seriously undermining the cross-coupling reaction. The extremely high reactivity and the explosive nature of the copper-acetylide species makes the Sonogashira reaction sensitive to air and moisture.<sup>[7,8]</sup> Consequently, a formidable challenge in this area lies in broadening the scope of the reaction by designing suitable catalysts that enable the reaction to be carried out under mild conditions without the need for any additional stringent measures, such as the exclusion of air and moisture. In this regard it is worth mentioning that a report of the Sonogashira cross-

[a] L. Ray, S. Barman, Prof. Dr. P. Ghosh  
Department of Chemistry, Indian Institute of Technology Bombay  
Powai, Mumbai 400 076 (India)  
Fax: (+91) 22-2572-3480  
E-mail: pghosh@chem.iitb.ac.in

[b] M. M. Shaikh  
National Single-Crystal X-ray Diffraction Facility  
Indian Institute of Technology Bombay  
Powai, Mumbai 400 076 (India)

Supporting information for this article is available on the WWW under <http://www.chemeurj.org> or from the author. It contains the CIF file with crystallographic data for **3** and **4** and the B3LYP coordinates of the optimized geometries of **3**, **3a**, **4**, and **4a**.

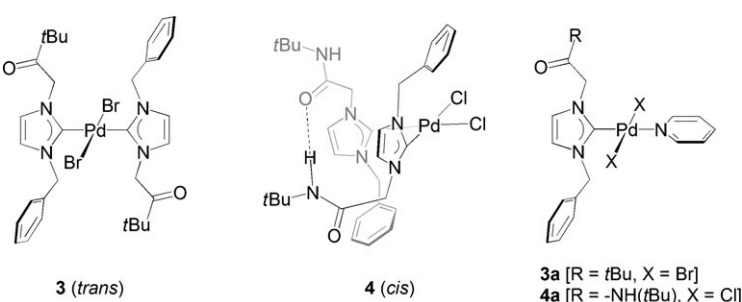
coupling reaction in air and in water has appeared only recently.<sup>[9]</sup> The other approach towards circumventing the difficulties associated with this reaction had been to develop a copper-free Sonogashira<sup>[10]</sup> cross-coupling reaction that focuses on enhancing the reactivity of the catalytic system so as to make the presence of copper unnecessary. However, this strategy was of limited success because these copper-free methods often involve the use of excess amines (even as solvents), which is not deemed to be environmentally friendly, and so the ultimate goal lies in developing a copper- and amine-free Sonogashira coupling reaction.<sup>[11]</sup>

Our objective was to advance the chemistry of nonfunctionalized and *N/O*-functionalized *N*-heterocyclic carbenes<sup>[12,13]</sup> for their use in biomedical applications<sup>[14]</sup> and in chemical catalysis.<sup>[15,16]</sup> Of special interest to us are palladium-mediated cross-coupling reactions, and in this regard we recently reported a highly efficient palladium precatalyst<sup>[17]</sup> that exhibits ultrahigh turnover numbers and also a series of convenient-to-handle air-stable PEPPSI (pyridine-enhanced precatalyst preparation, stabilization and initiation)-themed precatalysts<sup>[18]</sup> for the Suzuki–Miyaura cross-coupling reaction. During the design of these catalysts for cross-coupling reactions, we became particularly interested in knowing which of the two types of complexes, that is, the  $[(\text{NHC})_2\text{PdX}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes with two NHC ligands or the newly popular PEPPSI-themed *trans*- $[(\text{NHC})\text{Pd}(\text{pyridine})\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes<sup>[19]</sup> with one NHC ligand, would make a better catalyst? We rationalized that the NHCs, which are extremely good  $\sigma$ -donating ligands,<sup>[12,13,16b,18,20]</sup> would make the metal center in  $[(\text{NHC})_2\text{PdX}_2]$  more electron-rich, thereby assisting the aryl halide oxidative addition step compared with the corresponding PEPPSI analogues. Our other objective was to design highly efficient and robust catalysts that would be air-, moisture-, and functional-group-tolerant, which would facilitate cross-coupling reactions under ambient aerobic conditions.

Herein we report two new *trans*- and *cis*- $[(\text{NHC})_2\text{PdX}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes of *N/O*-functionalized *N*-heterocyclic carbenes, namely, *trans*- $[\{1\text{-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene}\}_2\text{PdBr}_2]$  (**3**) and *cis*- $[\{1\text{-benzyl-3-(*N*-tert-butylacetamido)imidazol-2-ylidene}\}_2\text{PdCl}_2]$  (**4**), for highly convenient Sonogashira coupling of aryl iodides with substituted acetylenes in air in a mixed solvent (DMF/ $\text{H}_2\text{O}$ , 3:1 v/v) under amine-free conditions. More interestingly, complexes **3** and **4** were found to exhibit superior activity compared with the corresponding PEPPSI counterparts **3a** and **4a**, which implies that a more electron-rich metal center yields a better catalyst.

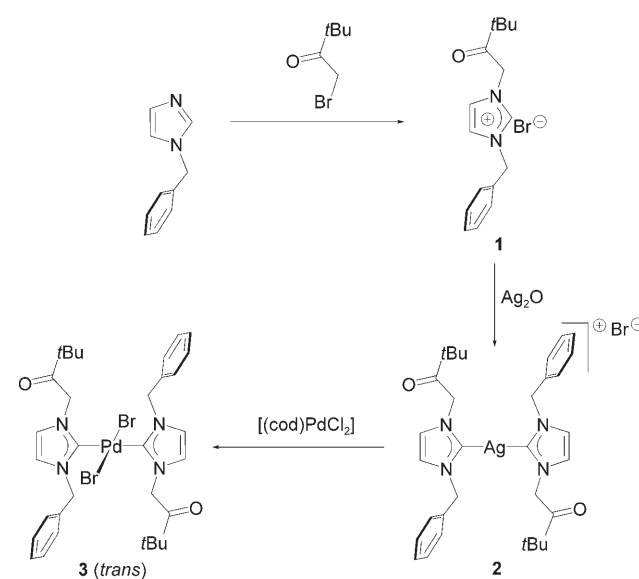
## Results and Discussion

Despite being phenomenally successful in the catalysis of many important transformations,<sup>[21–23]</sup> the application of *N*-heterocyclic carbenes in Sonogashira cross-coupling reactions has remained surprisingly unexplored.<sup>[24,25]</sup> With our

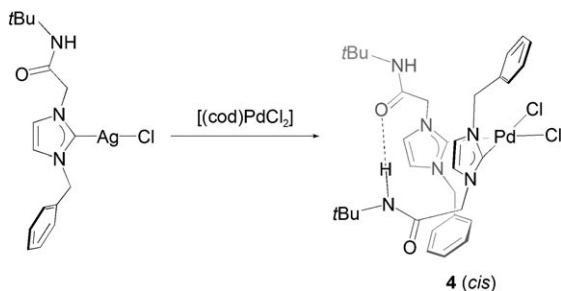


aim being to explore the utility of *N*-heterocyclic carbenes in palladium-mediated cross-coupling reactions, we became interested in designing *N*-heterocyclic carbene based precatalysts for Sonogashira coupling reactions. In particular, we were looking to develop highly efficient and robust catalysts that were tolerant to air, moisture, and various functional groups so as to allow Sonogashira cross-coupling reactions in mild aerobic conditions. With regards to the design of NHC-based catalysts for the cross-coupling reaction, we also wanted to know whether the more electron-rich  $[(\text{NHC})_2\text{PdX}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ )-type complexes with two NHC ligands would make better catalysts than the newly popular PEPPSI-themed *trans*- $[(\text{NHC})\text{Pd}(\text{pyridine})\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ )-type complexes containing one NHC ligand, and hence, to address this issue we set out to synthesize both these types of complexes to perform a comparative study.

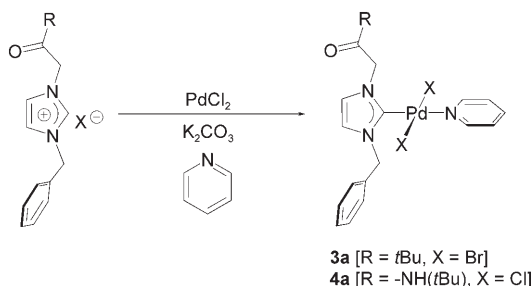
The two new *trans*- and *cis*- $[(\text{NHC})_2\text{PdX}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes **3** (Scheme 1) and **4** (Scheme 2) were synthesized from the corresponding silver complexes by a transmetalation reaction with  $[(\text{cod})\text{PdCl}_2]$  in yields of 80–87%, whereas the corresponding PEPPSI analogues **3a** and **4a**<sup>[18]</sup> were synthesized directly from the corresponding imidazolium



Scheme 1.



Scheme 2.



Scheme 3.

halide salts (Scheme 3) by reaction with  $\text{PdCl}_2$  in pyridine in the presence of  $\text{K}_2\text{CO}_3$  as base.

Remarkably, two different molecular geometries were obtained for **3** and **4** even though they were synthesized under very similar conditions. Specifically, the molecular structures of these complexes revealed that, whereas **3** (Figure 1) exhibited the expected *trans* geometry around the metal center, a unique hydrogen-bonded *cis* arrangement was observed in the case of **4** (Figure 2). In particular, a hydrogen-bonding interaction was seen between the amido N–H proton of the functionalized side-arm of one NHC ligand and the amido oxygen atom of the functionalized side-arm of the other displaying a close N–H···O contact of 3.061 Å, which is shorter than the sum of the van der Waals radii of nitrogen and oxygen (3.27 Å).<sup>[26]</sup> Such a *cis* arrangement is a rare consequence of a hydrogen-bonding interaction between the amido-functionalized side-arms of the NHC ligands in **4**, in the absence of which the *trans* geometry would be sterically preferred. The hydrogen-bonding interaction in *cis* complex **4** seriously highlights the rare and interesting structural possibility that emerges as a result of *N/O*-functionalization of the *N*-substituted side-arms of the N-heterocyclic carbene ligand. To the best of our knowledge, complex **4** represents the only structurally characterized example of a *cis*-[(NHC)<sub>2</sub>PdX<sub>2</sub>] (X = halide)-type complex in which the two NHC ligands are not conjoined by any covalent linker.

Barring the hydrogen-bonding interaction, the other structural aspects of complexes **3** and **4** are similar, including the square-planar metal centers. The metal–carbene ( $\text{Pd}-\text{C}_{\text{carb}}$ ) distance in **3** (2.018(9) Å) is slightly longer than in **4** (1.975(2) and 1.998(2) Å), but compares well with the sum of the individual covalent radii of palladium and carbon

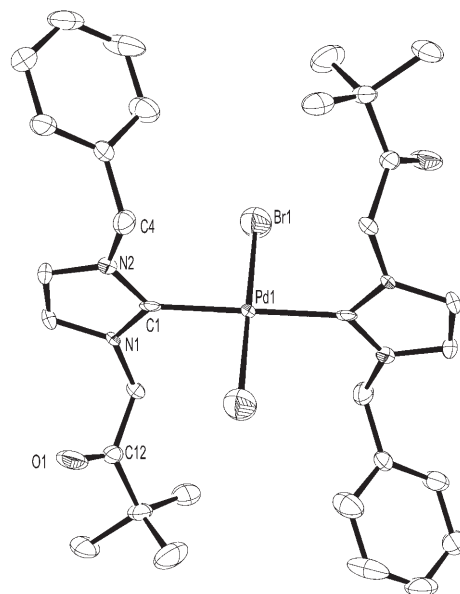


Figure 1. ORTEP drawing of **3** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1–C1 1.365(12), N2–C1 1.359(12), Pd1–C1 2.018(9), Pd1–Br1 2.3750(13); C1–Pd1–Br1 90.8(2), C1–Pd1–C1 180.0(7).

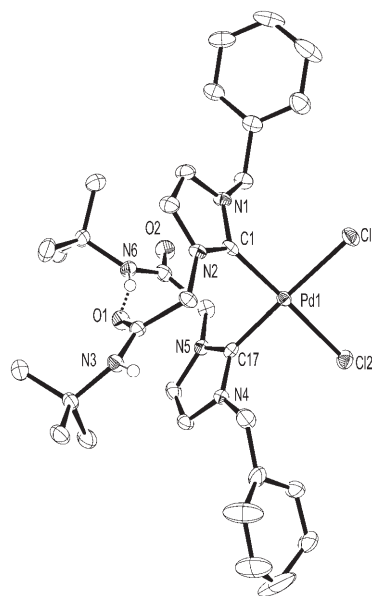


Figure 2. ORTEP drawing of **4** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1–C1 1.355(2), N2–C1 1.357(2), N5–C17 1.349(2), N4–C17 1.346(2), Pd1–C17 1.975(2), Pd1–C1 1.998(2), Pd1–Cl1 2.3615(5), Pd1–Cl2 2.3541(5); C17–Pd1–C1 92.50(8), C1–Pd1–Cl1 90.00(6). The phenyl group is disordered and for clarity one set of disordered atoms is not shown.

(2.055 Å)<sup>[27]</sup> and also falls well within the range (2.10–1.93 Å) observed in other structurally characterized examples.<sup>[28]</sup> The two imidazolyl rings in **3** are coplanar, similar to that observed in another related *trans*-(NHC) complex, [(1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene)<sub>2</sub>PdCl<sub>2</sub>].<sup>[17]</sup> Significantly, complex **3** also represents the only example of

a structurally characterized palladium bromide derivative of the type  $[(\text{NHC})_2\text{PdX}_2]$  ( $\text{X} = \text{halide}$ ).

To obtain a better understanding of the nature of the NHC–Pd interaction in the *trans* and *cis* complexes **3** and **4**, detailed density functional theory (DFT) studies were carried out by computing the geometry-optimized structures of **3** and **4** at the B3LYP/SDD level of theory with the 6-31G(d) basis set using the atomic coordinates determined by X-ray analysis. Subsequently a single-point calculation was performed at the same level of theory for a detailed prediction of the electronic properties of these complexes. Further insights into the carbene–metal bond came from a post-wavefunction analysis using the natural bond orbital (NBO) method,<sup>[29]</sup> which was performed on these complexes as well as on the corresponding ligands and metal-ion fragments. Specifically, both natural and Mulliken charge analyses revealed that upon binding of the two NHC ligands to the  $\text{PdX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) fragment, the metal center in **3** and **4** becomes more electron-rich compared with the free ion and the  $\text{PdX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) fragment (see Tables S4–S7, S12, and S13 of the Supporting Information). Consequently, the electron density at the carbene carbon atom in **3** and **4** is lower relative to that of the free NHC ligand upon coordination to the  $\text{PdX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) fragment. Comparison of the electronic configurations of the metal centers in **3** and **4** with that of the  $\text{PdX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) fragment reveals that electron donation from the free NHC ligand to the unfilled 5s orbital of palladium occurs in these complexes (see Tables S14 and S15 of the Supporting Information).

Further insights into the nature of the NHC–metal interaction were obtained from correlation diagrams depicting the fragment molecular orbital contribution of the free NHC ligand and the  $\text{PdX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) fragments to the frontier molecular orbitals (MOs) of complexes **3** and **4**. Of particular interest are the molecular orbitals that represent the NHC–Pd  $\sigma$  interactions, which were found to be low-lying in **3** (HOMO-37) and **4** (HOMO-35 and HOMO-36). Specifically, the NHC–Pd  $\sigma$ -bonding orbital, HOMO-37 (53% NHC, 29%  $\text{PdBr}_2$ ), in *trans* complex **3** showed an interaction of the carbene lone-pair (HOMO-1 of the free-NHC fragments) with a metal-based vacant LUMO (75% palladium with 33% s and 40% d character) of the  $\text{PdBr}_2$  fragment (Figure 3 and

Figure S1 of the Supporting Information). The corresponding NHC–Pd  $\sigma$  interactions in *cis* complex **4** consist of two adjacent interactions, HOMO-35 (47% NHC, 38%  $\text{PdCl}_2$ ) and HOMO-36 (37% NHC, 38%  $\text{PdCl}_2$ ). In HOMO-35, the carbene lone-pairs (HOMO (11%) and HOMO-1 (31%)) of the two free NHC fragments were seen to interact with another metal-based vacant LUMO+1 orbital (92% palladium with 69% s and 18% p character) of the  $\text{PdCl}_2$  fragment (Figures 4 and 5 and Figure S2 of the Supporting Information). Likewise, the other NHC–Pd  $\sigma$ -bonding orbital, HOMO-36 (37% NHC, 38%  $\text{PdCl}_2$ ), showed an interaction of the carbene lone-pairs (HOMO (11%) and HOMO-1 (31%)) of the two free NHC fragments with the vacant LUMO (51% Pd, 49% Cl with 39% d character) of the  $\text{PdCl}_2$  fragment.

A charge decomposition analysis (CDA) of **3** and **4** highlighted the relative extent of the  $[\text{NHC} \rightarrow \text{PdX}_2]$  forward donation ( $\text{X} = \text{Br}, \text{Cl}$ ), designated *d*, and the  $[\text{NHC} \leftarrow \text{PdX}_2]$  backward donation ( $\text{X} = \text{Br}, \text{Cl}$ ), designated *b*, that occurs in these complexes. The *d/b* ratio, a measure of the forward  $\sigma$  donation relative to the backward  $\pi$  donation, for **3** (2.90) and **4** (2.98) suggests the predominance of the  $\sigma$ -bonding interaction in concurrence with the greater  $\sigma$ -donating abilities of the NHC ligands, and the values compare well with those reported for other Pd–NHC complexes, namely, *trans*-[1-benzyl-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]Pd(pyri-

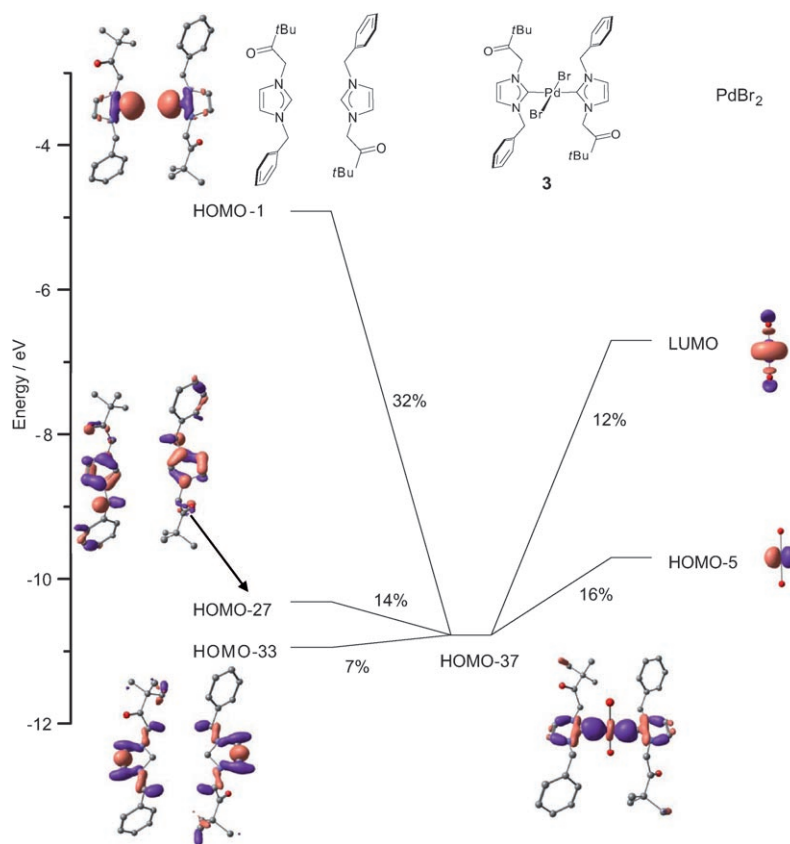


Figure 3. Simplified orbital interaction diagram showing the major contributions of the NHC–palladium bond in **3**.



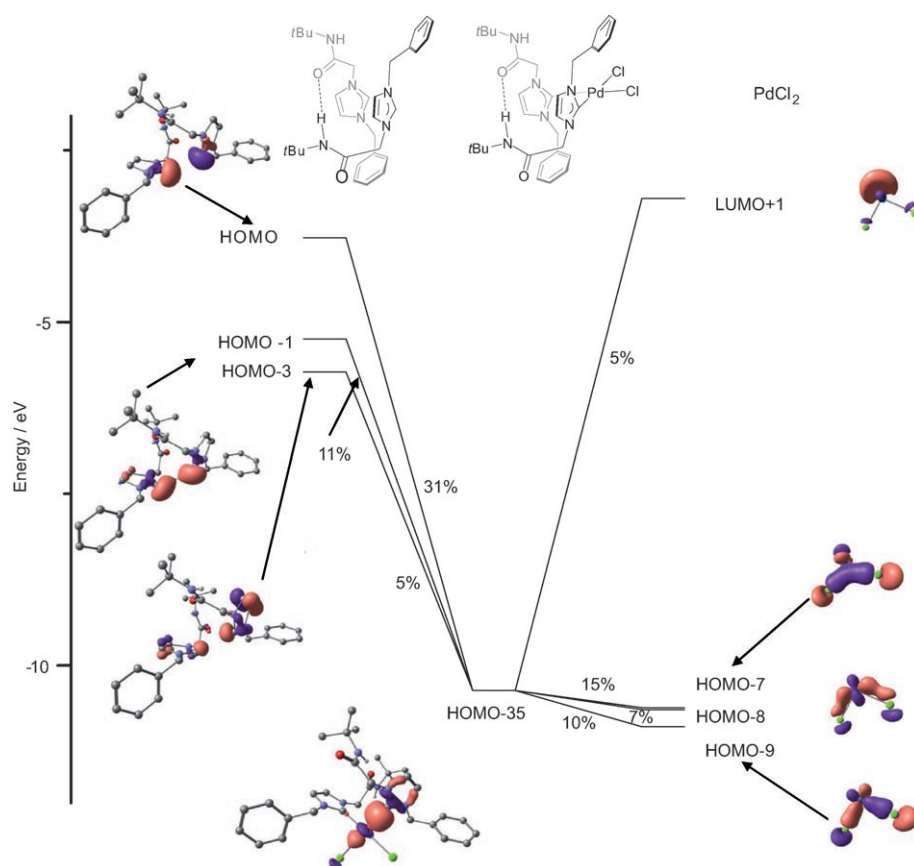


Figure 4. Simplified orbital interaction diagram showing the major contributions of the NHC–Pd  $\sigma$ -bonding orbital HOMO-35 in **4**.

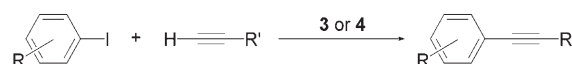
dine)Cl<sub>2</sub>] (2.59),<sup>[18]</sup> *trans*-[1-(2-hydroxycyclohexyl)-3-benzylimidazol-2-ylidene]Pd(pyridine)Cl<sub>2</sub> (2.79),<sup>[18]</sup> and *trans*-[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]Pd(pyridine)Br<sub>2</sub> (3.99)<sup>[18]</sup> (see Table S17 of the Supporting Information).

Lastly, the strength of the NHC–Pd interactions in **3** and **4** were computed at the B3LYP/SDD level of theory with the 6-31G(d) basis set and NHC–Pd bond energies ( $D_e$ ) of 74.8 kcal mol<sup>−1</sup> in **3** and 75.1 kcal mol<sup>−1</sup> in **4** are suggestive of a strong interaction comparable to those reported for *trans*-[1-benzyl-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]Pd-(pyridine)Cl<sub>2</sub>] (81.9 kcal mol<sup>−1</sup>),<sup>[18]</sup> *trans*-[1-(2-hydroxycyclohexyl)-3-benzylimidazol-2-ylidene]Pd(pyridine)Cl<sub>2</sub>] (82.4 kcal mol<sup>−1</sup>),<sup>[18]</sup> and *trans*-[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]Pd(pyridine)Br<sub>2</sub>] (77.6 kcal mol<sup>−1</sup>).<sup>[18]</sup> The stronger NHC–Pd interactions in **3** and **4** imply tighter binding of the ancillary NHC ligand to the metal center, which imparts greater stability to these complexes.

Significantly, both complexes **3** and **4** enabled highly convenient amine-free Sonogashira coupling reactions to take place in ambient aerobic conditions in a polar mixed aqueous medium (Scheme 4 and Tables 1 and 2). Specifically, when substituted terminal acetylenes were treated with aryl iodides in the presence of precatalysts **3** or **4** along with the co-catalyst CuBr, and Cs<sub>2</sub>CO<sub>3</sub> as the base in a mixed DMF/H<sub>2</sub>O (3:1 v/v) medium in air, Sonogashira cross-coupled products were obtained in high yields. A rapid rate of con-

version to products within two hours was observed for most of the substrates, which reflects the high performances of **3** and **4**.

Also remarkable is the robust nature of precatalysts **3** and **4** because the coupling reactions were successfully carried out in air in a polar DMF/H<sub>2</sub>O (3:1 v/v) mixed medium. Thus, the present catalysis by **3** and **4** under aerobic mixed aqueous conditions marks a significant improvement against the backdrop of the fact that Sonogashira reactions are traditionally air- and moisture-sensitive owing to the formation of a highly reactive copper–acetylide intermediate in the catalytic cycle.<sup>[7,8]</sup> Another very important feature of **3** and **4** is their high selectivity with regards to the formation of the desired cross-coupled product along with the negligible formation of the homocoupled product (up to 15% for **3** and 21% for **4**).



Scheme 4.

Note that the homocoupled products arise from an unwanted side-reaction of the reactive copper–acetylide intermediate by the so-called Glaser coupling reaction upon exposure to trace amounts of air or any oxidizing agent (Tables 1 and 2).<sup>[8]</sup> Lastly, these coupling reactions were carried out in amine-free conditions with Cs<sub>2</sub>CO<sub>3</sub> as the base instead of the more frequently used amines, which is of considerable importance given the fact that amines are not considered environmentally benign and substantial efforts, at present, are being directed towards the development of amine-free Sonogashira cross-coupling reactions.

Note that the Sonogashira cross-coupling reaction can be extended to heterocyclic terminal alkynes, which has much potential, particularly from a synthetic perspective, because many heterocyclic compounds are known to exhibit important biological properties.<sup>[30]</sup> Another notable aspect of the two precatalysts **3** and **4** is their selectivity towards the iodo derivative. This is evident from the reactions of the *p*-bromiodobenzene substrate; Sonogashira coupling was seen to occur at the iodo end and not at the bromo end, which remained intact.

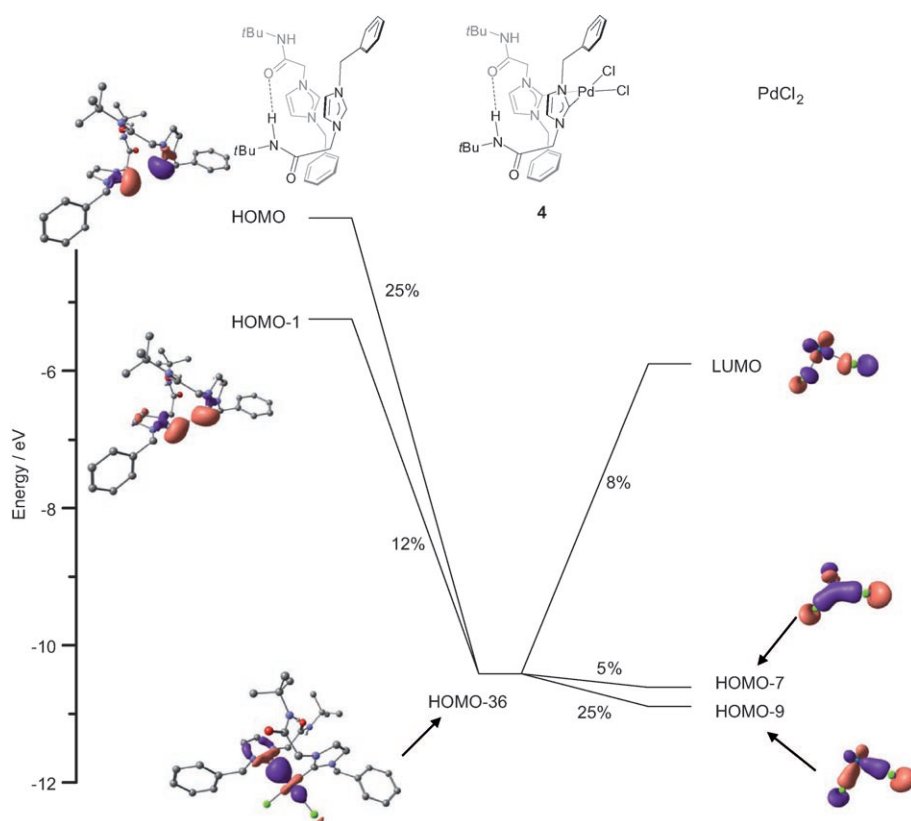


Figure 5. Simplified orbital interaction diagram showing the major contributions of the NHC–Pd  $\sigma$ -bonding orbital HOMO-36 in **4**.

Despite the existence of numerous phosphine-based catalysts for the Sonogashira reaction,<sup>[10]</sup> few N-heterocyclic carbene-based catalysts are known.<sup>[24,25]</sup> Also, in the light of the extraordinary successes enjoyed by NHCs in various catalytic reactions in general, and in palladium-mediated cross-coupling reactions in particular, the dearth of NHC-based catalysts for Sonogashira reactions prompted us to undertake the current study. Against this backdrop, complexes **3** and **4** assume importance because they represent the handful of

examples of well-defined N-heterocyclic carbene-based palladium precatalysts known for homogeneous Sonogashira cross-coupling reactions.

With regards to our initial objective of finding out whether mono- or di-NHC-substituted palladium complexes would exhibit greater activity, a detailed comparative study of the *trans*- and *cis*-[(NHC)<sub>2</sub>PdX<sub>2</sub>] (X = Cl, Br)-type complexes **3** and **4** were performed with the corresponding PEPPSI analogues **3a** and **4a**. Interestingly, complexes **3** and **4**, which have two NHC ligands, were found to exhibit superior activity compared with **3a** and **4a** (Tables 1–4). The better performances of **3** and **4** can be correlated to more-electron-rich metal centers in these complexes. For example, a comparison of both the natural and Mulliken charges reveal that the palladium centers in **3** and **4**, which contain two strongly  $\sigma$ -donating NHC ligands, are more electron-rich than those of the PEPPSI analogues **3a** and **4a** stabilized by a single NHC ligand (see Tables S4–S13 of the Supporting Information). In this regard, the more electron-rich metal centers would greatly promote the oxidative addition of the aryl halide, which represents a key step in the palladium-mediated cross-coupling reaction.

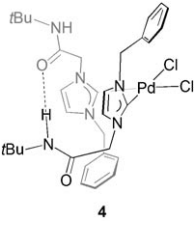

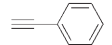

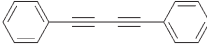
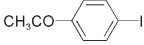
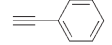
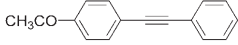
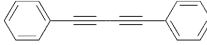
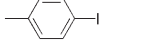
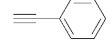

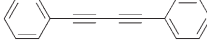

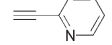
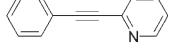
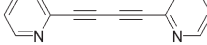
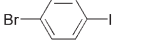
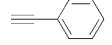
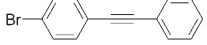
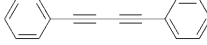
A comparison of the N-heterocyclic carbene-based palladium precatalysts **3** and **4** with the related phosphine-based precatalysts is important.<sup>[10]</sup> The NHC precatalysts **3** and **4**

Table 1. Selected results of the Sonogashira cross-coupling reaction of aryl halides (ArX, X = I) catalyzed by **3**.<sup>[a]</sup>

Catalyst	Reagent	Reagent	Desired cross-coupled product	Yield <sup>[b]</sup> [%]	Time [h]	Unwanted homocoupled product	Yield <sup>[b]</sup> [%]
				98	2		2
				80	2		3
				75	2		4
				97	2		0
				85	2		15
				68	2		0

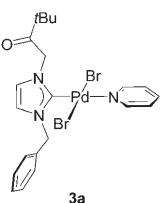

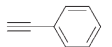

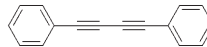
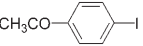
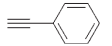
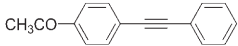
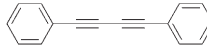
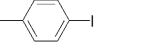
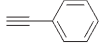
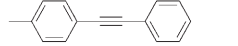
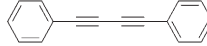

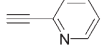

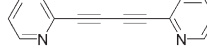
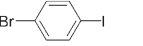
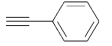
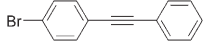
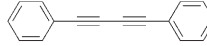
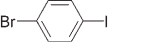
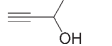
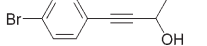
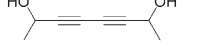
[a] Reaction conditions: aryl halide (ArX, X = I; 0.49 mmol), phenylacetylene (0.98 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2 mmol), catalyst (3 mol %), CuBr (10 mol %), DMF/H<sub>2</sub>O (3:1; 10 mL), at 100 °C. [b] The yields were determined by GC using diethyleneglycol-di-*n*-butyl ether as the internal standard.

Table 2. Selected results of the Sonogashira cross-coupling reaction of aryl halides (ArX, X=I) catalyzed by **4**.<sup>[a]</sup>

Catalyst	Reagent	Reagent	Desired cross-coupled product	Yield <sup>[b]</sup> [%]	Time [h]	Unwanted homocoupled product	Yield <sup>[b]</sup> [%]
 4				84	12		0
				88	2		9
				94	2		6
				81	2		0
				90	2		21

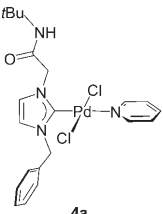

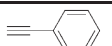
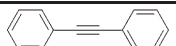
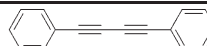
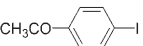
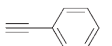
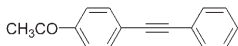
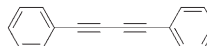
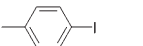
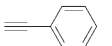

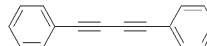

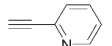

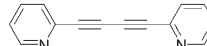
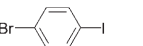
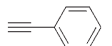
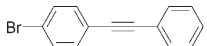
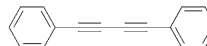
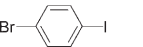
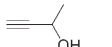
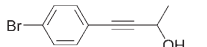

[a] Reaction conditions: aryl halide (0.49 mmol) (ArX, X=I), phenylacetylene (0.98 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2 mmol), catalyst (3 mol %), CuBr (10 mol %), DMF/H<sub>2</sub>O (3:1; 10 mL), at 100°C. [b] The yields were determined by GC using diethyleneglycol-di-*n*-butyl ether as the internal standard.

Table 3. Selected results of the Sonogashira cross-coupling reaction of aryl halides (ArI) catalyzed by **3a**.<sup>[a]</sup>

Catalyst	Reagent	Reagent	Desired cross-coupled product	Yield <sup>[b]</sup> [%]	Time [h]	Unwanted homocoupled product	Yield <sup>[b]</sup> [%]
 3a				4	2		5
				76	2		5
				42	2		0
				no reaction	2		0
				28	2		14
				no reaction	2		0

[a] Reaction conditions: aryl halide (0.49 mmol) (ArX, X=I), phenylacetylene (0.98 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2 mmol), CuBr (10 mol %), catalyst (3 mol %), DMF/H<sub>2</sub>O (3:1; 10 mL) at 100°C. [b] The yields were determined by GC using diethyleneglycol-di-*n*-butyl ether as the internal standard.

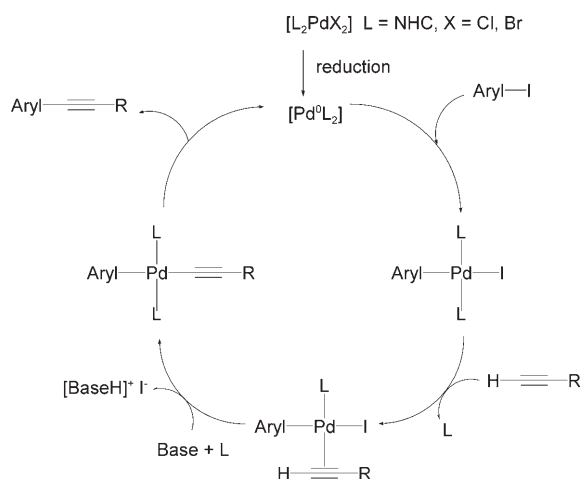
Table 4. Selected results of the Sonogashira cross-coupling reaction of aryl halides (ArX, X=I) catalyzed by **4a**.<sup>[a]</sup>

Catalyst	Reagent	Reagent	Desired cross-coupled product	Yield <sup>[b]</sup> [%]	Time [h]	Unwanted homocoupled product	Yield <sup>[b]</sup> [%]
 4a				27	2		13
				66	2		6
				11	2		12
				no reaction	2		0
				24	2		0
				no reaction	2		0

[a] Reaction conditions: aryl halide (ArX, X=I; 0.49 mmol), phenylacetylene (0.98 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2 mmol), CuBr (10 mol %), catalyst (3 mol %), DMF/H<sub>2</sub>O (3:1; 10 mL) at 100°C. [b] The yields were determined by GC using diethyleneglycol-di-*n*-butyl ether as the internal standard.

were found to be comparable to many of the phosphine-based precatalysts. Note that the latter are usually air- and moisture-sensitive and hence require anaerobic conditions, higher catalyst loading,<sup>[11]</sup> and also a longer reaction time (up to 48 h)<sup>[10]</sup> at higher temperatures (up to 140°C).<sup>[9]</sup>

A tentative mechanism for the Sonogashira cross-coupling reaction is proposed in Scheme 5. Note that the mechanism excludes the formation of a copper-acetylide intermediate in view of the fact that very little or almost negligible amounts of Glaser-type homocoupled products were observed despite the coupling reactions being performed in air



Scheme 5.

in a mixed aqueous solvent. The copper-acetylide species is extremely sensitive to air and moisture, and its formation under these reaction conditions seems highly unlikely. Thus, the role of the CuBr co-catalyst is restricted to the reduction of the Pd<sup>II</sup> center in **3** and **4** to the corresponding catalytically active Pd<sup>0</sup> species, which undergoes oxidative addition of the aryl iodide followed by the coordination and deprotonation of the terminal acetylene in the presence of a base, which leads to the desired cross-coupled product by a final reductive elimination step. In this regard, note that our attempt to independently synthesize and isolate the [(NHC)<sub>2</sub>Pd<sup>0</sup>] species for a direct entry to the catalytic cycle was not successful.

## Conclusions

In summary, two new precatalysts, namely, *trans*-[1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]<sub>2</sub>PdBr<sub>2</sub> (**3**) and *cis*-[1-benzyl-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]<sub>2</sub>PdCl<sub>2</sub> (**4**), have been designed and used in a highly convenient Sonogashira cross-coupling reaction of aryl iodides with substituted acetylenes in air in a mixed solvent (DMF/H<sub>2</sub>O, 3:1 v/v) under amine-free conditions. More importantly, these complexes, which have two strong σ-donating NHC ligands, were found to exhibit superior activity compared with their corresponding PEPSI counterparts, **3a** and **4a**, which support a single NHC ligand. Thus, a more electron-rich metal center acts as a better catalyst for the cross-coupling reaction.

## Experimental Section

**General procedures:** All manipulations were carried out by using standard Schlenk techniques. Solvents were purified and degassed by standard procedures. Ag<sub>2</sub>O was purchased from SD-Fine Chemicals (India) and used without any further purification. [(cod)PdCl<sub>2</sub>],<sup>[31]</sup> benzylimidazole,<sup>[32]</sup> 1-benzyl-3-(*N*-*tert*-butylacetamido)imidazolium chloride,<sup>[18]</sup> [1-benzyl-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]AgCl,<sup>[13]</sup> and *trans*-

[1-benzyl-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]Pd(pyridine)Cl<sub>2</sub> (**4a**)<sup>[18]</sup> were prepared according to reported literature procedures. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded in CDCl<sub>3</sub> on a Varian 400 MHz NMR spectrometer. <sup>1</sup>H NMR signals are labeled as singlet (s), doublet (d), and multiplet (m). Infrared spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with samples as KBr pellets. Mass spectrometry measurements were performed on a Micromass Q-ToF spectrometer. GC was carried out on a Shimadzu GC-15A gas chromatograph equipped with a FID detector. X-ray diffraction data for **3** and **4** were collected on an Oxford Diffraction Excalibur-S diffractometer. The crystal data collection and refinement parameters are summarized in Table 5. The structures were solved by using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F<sub>2</sub> with SHELXTL (Version 6.10).<sup>[33]</sup>

Table 5. X-ray crystallographic data for **3** and **4**.

Compound	<b>3</b>	<b>4</b>
lattice	monoclinic	monoclinic
formula	C <sub>16</sub> H <sub>20</sub> BrN <sub>2</sub> O·0.5 Pd	C <sub>23</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>2</sub> Pd
formula weight	389.45	720.02
space group	P <sub>21</sub> /a	C <sub>2</sub> /c
<i>a</i> [Å]	7.4702(2)	24.2317(5)
<i>b</i> [Å]	27.2734(7)	15.2987(4)
<i>c</i> [Å]	7.9624(2)	17.7705(4)
<i>α</i> [°]	90.00	90.00
<i>β</i> [°]	94.639(3)	91.655(2)
<i>γ</i> [°]	90.00	90.00
<i>V</i> [Å <sup>3</sup> ]	1616.93(7)	6585.0(3)
<i>Z</i>	4	8
temperature [K]	120(2)	120(2)
radiation (λ [Å])	0.71073	0.71073
<i>ρ</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.600	1.453
<i>μ</i> (Mo <sub>Kα</sub> ) [mm <sup>-1</sup> ]	3.079	0.765
<i>θ</i> [°]	2.97–25.00	3.05–25.00
no. of data	2848	5775
no. of parameters	190	421
<i>R</i> <sub>1</sub>	0.0830	0.0226
<i>wR</i> <sub>2</sub>	0.2354	0.0559
GOF	1.060	0.922

CCDC-643953 (**3**) and 637065 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Synthesis of 1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazolium bromide (1):** A mixture of benzylimidazole (0.889 g, 5.50 mmol) and α-bromopinalcolone (1.00 g, 5.50 mmol) was dissolved in toluene (ca. 50 mL) and the reaction mixture was heated at reflux at 110 °C for 12 h until a white solid separated out. The solid was isolated by decanting off the solvent and washed with hot hexane (3 × ca. 10 mL) to give **1** as a white solid (1.12 g, 61 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C, TMS): δ = 10.07 (s, 1H; NCHN), 7.56 (brs 1H; NCHCHN), 7.42–7.38 (m, 5H; C<sub>6</sub>H<sub>5</sub>), 7.24 (brs 1H; NCHCHN), 5.93 (s, 2H; CH<sub>2</sub>), 5.47 (s, 2H; CH<sub>2</sub>), 1.28 ppm (s, 9H; C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C): δ = 206.2 (CO), 136.9 (NCN), 132.5 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 128.9 (*m*-C<sub>6</sub>H<sub>5</sub>), 128.2 (*p*-C<sub>6</sub>H<sub>5</sub>), 124.1 (*o*-C<sub>6</sub>H<sub>5</sub>), 120.6 (NCHCHN), 54.2 (CH<sub>2</sub>), 52.7 (CH<sub>2</sub>), 42.9 (C(CH<sub>3</sub>)<sub>3</sub>), 25.8 ppm (C(CH<sub>3</sub>)<sub>3</sub>); IR (KBr): *ν* = 1717 cm<sup>-1</sup> (*ν*<sub>CO</sub>); HRMS (ES): *m/z* calcd: 257.1654 [NHC-ligand]<sup>+</sup>; found: 257.1643.

**Synthesis of [1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]-Ag]Br (2):** A mixture of 1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazolium bromide (**1**) (0.500 g, 1.49 mmol) and Ag<sub>2</sub>O (0.171 g, 0.740 mmol) in dichloromethane (ca. 60 mL) was stirred at room temperature for 6 h. The reaction mixture was filtered and the solvent was removed under vacuum to give **2** as a brown solid (0.412 g, 80 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C, TMS): δ = 7.34–7.31 (m, 5H; C<sub>6</sub>H<sub>5</sub>), 6.92 (brs, 1H;



NCHCHN), 6.89 (brs, 1H; NCHCHN), 5.39 (s, 2H; CH<sub>2</sub>), 5.29 (s, 2H; CH<sub>2</sub>), 1.30 ppm (s, 9H; C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25°C): δ = 208.6 (CO), 183.9 (NCN-Ag), 135.7 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 128.6 (*m*-C<sub>6</sub>H<sub>5</sub>), 127.9 (*p*-C<sub>6</sub>H<sub>5</sub>), 127.5 (*o*-C<sub>6</sub>H<sub>5</sub>), 122.8 (NCHCHN), 120.4 (NCHCHN), 55.1 (CH<sub>2</sub>), 50.5 (CH<sub>2</sub>), 43.1 (C(CH<sub>3</sub>)<sub>3</sub>), 26.0 ppm (C(CH<sub>3</sub>)<sub>3</sub>); IR (KBr):  $\tilde{\nu}$  = 1719 cm<sup>-1</sup> (ν<sub>CO</sub>); HRMS (ES): *m/z* calcd: 619.2202 [(NHC)<sub>2</sub>Ag]<sup>+</sup>; found: 619.2212; elemental analysis calcd (%) for C<sub>32</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub>AgBr: C 54.87, H 5.76, N 8.00; found: C 55.23, H 6.53, N 8.16.

**Synthesis of [(1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene)<sub>2</sub>-PdBr<sub>2</sub>] (3):** A mixture of [(1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene)<sub>2</sub>Ag]Br (2) (0.151 g, 0.236 mmol) and [(cod)PdCl<sub>2</sub>] (0.030 g, 0.107 mmol) was heated at reflux in acetonitrile (ca. 30 mL) at 85°C for 6 h until the formation of an off-white AgBr precipitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to give **3** as a yellow solid (0.067 g, 81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25°C, TMS): δ = 7.37–7.31 (m, 5H; C<sub>6</sub>H<sub>5</sub>), 6.92 (brs, 1H; NCHCHN), 6.86 (brs, 1H; NCHCHN), 5.38 (s, 2H; CH<sub>2</sub>), 5.21 (s, 2H; CH<sub>2</sub>), 1.32 ppm (s, 9H; C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25°C): δ = 207.1 (CO), 172.2 (NCN-Pd), 134.8 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 129.0 (*m*-C<sub>6</sub>H<sub>5</sub>), 128.7 (*p*-C<sub>6</sub>H<sub>5</sub>), 127.9 (*o*-C<sub>6</sub>H<sub>5</sub>), 122.8 (NCHCHN), 120.3 (NCHCHN), 55.0 (CH<sub>2</sub>), 54.9 (CH<sub>2</sub>), 43.6 (C(CH<sub>3</sub>)<sub>3</sub>), 26.2 ppm (C(CH<sub>3</sub>)<sub>3</sub>); IR (KBr):  $\tilde{\nu}$  = 1721 cm<sup>-1</sup> (ν<sub>CO</sub>); elemental analysis calcd (%) for C<sub>32</sub>H<sub>40</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Pd-2(CH<sub>3</sub>CN): C 50.22, H 5.38, N 9.76; found: C 49.98, H 5.82, N 10.15.

**Synthesis of trans-[(1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene)Pd(pyridine)Br<sub>2</sub>] (3a):** A mixture of 1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazolium bromide (0.306 g, 0.908 mmol), PdCl<sub>2</sub> (0.193 g, 1.09 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.627 g, 4.54 mmol) were heated at reflux in pyridine (ca. 5 mL) for 16 h. The reaction mixture was filtered and the solvent was removed under vacuum. Then the residue was washed with aqueous CuSO<sub>4</sub> solution and the aqueous layer was extracted with dichloromethane (3 × ca. 10 mL). Then the organic layer was collected and the solvent was removed under vacuum to give **3a** as a light-yellow crystalline solid (0.182 g, 67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25°C, TMS): δ = 8.96 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H; *o*-NC<sub>5</sub>H<sub>5</sub>), 7.77 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1H; *p*-NC<sub>5</sub>H<sub>5</sub>), 7.50 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H; *m*-NC<sub>5</sub>H<sub>5</sub>), 7.39–7.35 (m, 5H; C<sub>6</sub>H<sub>5</sub>), 6.99 (brs, 1H; NCHCHN), 6.77 (brs, 1H; NCHCHN), 5.84 (s, 2H; CH<sub>2</sub>), 5.71 (s, 2H; CH<sub>2</sub>), 1.40 ppm (s, 9H; C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25°C): δ = 206.8 (CO), 153.3 (NCN-Pd), 151.9 (*o*-NC<sub>5</sub>H<sub>5</sub>), 151.1 (*m*-NC<sub>5</sub>H<sub>5</sub>), 138.0 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 137.9 (*p*-NC<sub>5</sub>H<sub>5</sub>), 129.0 (*o*-C<sub>6</sub>H<sub>5</sub>), 128.9 (*m*-C<sub>6</sub>H<sub>5</sub>), 128.4 (*p*-C<sub>6</sub>H<sub>5</sub>), 121.2 (NCHCHN), 121.1 (NCHCHN), 54.7 (CH<sub>2</sub>), 54.4 (CH<sub>2</sub>), 43.7 (C(CH<sub>3</sub>)<sub>3</sub>), 26.5 ppm (C(CH<sub>3</sub>)<sub>3</sub>); IR (KBr):  $\tilde{\nu}$  = 1718 cm<sup>-1</sup> (s, ν<sub>CO</sub>); elemental analysis calcd (%) for C<sub>21</sub>H<sub>25</sub>Br<sub>2</sub>N<sub>3</sub>OPd·1/3(NC<sub>5</sub>H<sub>5</sub>): C 43.35, H 4.28, N 7.43; found: C 43.85, H 4.15, N 8.02.

**Synthesis of [(1-benzyl-3-(*N*-tert-butylacetamido)imidazol-2-ylidene)<sub>2</sub>-PdCl<sub>2</sub>] (4):** A mixture of [(1-benzyl-3-(*N*-tert-butylacetamido)imidazol-2-ylidene)AgCl] (0.261 g, 0.631 mmol) and [(cod)PdCl<sub>2</sub>] (0.090 g, 0.315 mmol) was heated at reflux in acetonitrile (ca. 30 mL) at 85°C for 6 h when the formation of an off-white AgCl precipitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to obtain **4** as a yellow solid (0.197 g, 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25°C, TMS): δ = 7.43–7.29 (m, 10H; 2C<sub>6</sub>H<sub>5</sub>), 7.04 (brs, 1H; NCHCHN), 6.99 (brs, 1H; NCHCHN), 6.79 (brs, 1H; NCHCHN), 6.76 (brs, 1H; NCHCHN), 5.77 (s, 2H; CH<sub>2</sub>), 5.61 (s, 2H; CH<sub>2</sub>), 5.17 (s, 2H; CH<sub>2</sub>), 4.99 (s, 2H; CH<sub>2</sub>), 1.35 (s, 9H; C(CH<sub>3</sub>)<sub>3</sub>), 1.25 ppm (s, 9H; C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 25°C): δ = 164.9 (CO), 160.2 (NCN-Pd), 134.3 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 128.9 (*m*-C<sub>6</sub>H<sub>5</sub>), 128.5 (*p*-C<sub>6</sub>H<sub>5</sub>), 128.4 (*o*-C<sub>6</sub>H<sub>5</sub>), 122.0 (NCHCHN), 121.8 (NCHCHN), 55.1 (CH<sub>2</sub>), 54.4 (C(CH<sub>3</sub>)<sub>3</sub>), 51.9 (CH<sub>2</sub>), 28.5 ppm (C(CH<sub>3</sub>)<sub>3</sub>); IR (KBr):  $\tilde{\nu}$  = 1626 cm<sup>-1</sup> (ν<sub>CO</sub>); elemental analysis calcd (%) for C<sub>32</sub>H<sub>42</sub>N<sub>6</sub>O<sub>6</sub>PdCl<sub>2</sub>: C 53.38, H 5.88, N 11.67; found: C 53.75, H 5.96, N 11.15.

**Computational methods:** Density functional theory calculations were performed on the two palladium complexes **3** and **4** using the Gaussian 03<sup>[34]</sup> suite of quantum chemical programs. The Becke three-parameter exchange functional in conjunction with the Lee–Yang–Parr correlation functional (B3LYP) was employed in this study.<sup>[35,36]</sup> The Stuttgart–Dresden effective core potential (ECP), which represents 19 core electrons,

along with valence basis sets (SDD) were used for palladium.<sup>[37,38]</sup> All other atoms were treated with the 6-31G(d) basis set.<sup>[39]</sup> The metal–ligand donor–acceptor interactions were inspected by using charge decomposition analysis (CDA).<sup>[40]</sup> CDA is a valuable tool for analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on electron donation.<sup>[41]</sup> The orbital contributions in the [(NHC)<sub>2</sub>PdX<sub>2</sub>] (X = Br, Cl)-type complexes **3** and **4** can be divided into three parts: 1) σ donation from the [NHC<sup>σ</sup>-PdX<sub>2</sub>] fragment, 2) π back donation from the [NHC<sup>π</sup>-PdX<sub>2</sub>] fragment, and 3) a repulsive interaction between the occupied MOs of these two fragments.

The CDA calculations were performed by using the AOMix program<sup>[42]</sup> with the B3LYP/SDD, 6-31G(d) wavefunction. Molecular orbital (MO) compositions and the overlap populations were calculated by using the AOMix program.<sup>[43]</sup> Analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, and the charge decomposition analysis (CDA) were performed by using AOMix-CDA.<sup>[44]</sup> Natural bond orbital (NBO) analysis was performed by using the NBO 3.1 program implemented in the Gaussian 03 package.<sup>[34]</sup>

**General procedure for the Sonogashira coupling reaction:** In a typical run, performed in air, a 25 mL vial was charged with a mixture of aryl iodide, arylalkyne, Cs<sub>2</sub>CO<sub>3</sub>, and diethyleneglycol-di-*n*-butyl ether (internal standard) in a molar ratio of 1:2:4:1. Complexes **3**, **3a**, **4**, or **4a** (3 mol %) and CuBr (10 mol %) were added to the mixture (Tables 1–4). Finally, a mixed solvent (DMF/H<sub>2</sub>O, 3:1 v/v, 10 mL) was added to the reaction mixture and heated at 100°C for an appropriate period of time, after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol-di-*n*-butyl ether as the internal standard.

## Acknowledgements

We thank the CSIR, New Delhi, for the financial support of this research. We are grateful to the National Single-Crystal X-ray Diffraction Facility and Sophisticated Analytical Instrument Facility at IIT Bombay, India, for the crystallographic and other characterization data. Use of the computational facilities of the IIT Bombay Computer Center is gratefully acknowledged. L.R. thanks IIT Bombay, India, for a research fellowship.

- a) K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 16, 4467–4470; b) L. Cassar, *J. Organomet. Chem.* **1975**, 93, 253–257; c) H. A. Dieck, F. R. Heck, *J. Organomet. Chem.* **1975**, 93, 259–263.
- a) I. Paterson, R. D. M. Davies, R. Marquez, *Angew. Chem.* **2001**, 113, 623–627; *Angew. Chem. Int. Ed.* **2001**, 40, 603–607; b) M. W. Miller, C. R. Johnson, *J. Org. Chem.* **1997**, 62, 1582–1583.
- K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, 117, 4516–4563; *Angew. Chem. Int. Ed.* **2005**, 44, 4442–4489.
- a) P. Lang, G. Magnin, G. Mathis, A. Burger, J.-F. Biellmann, *J. Org. Chem.* **2000**, 65, 7825–7832; b) J. W. Grissom, G. U. Gunawardena, D. Klingberg, D. Huang, *Tetrahedron* **1996**, 52, 6453–6518.
- a) N. D. P. Cosford, L. Tehrani, J. Roppe, E. Schwelger, N. D. Smith, J. Anderson, L. Bristow, J. Brodtkin, X. Jiang, I. McDonald, S. Rao, M. Washburn, M. A. Verney, *J. Med. Chem.* **2003**, 46, 204–206; b) M. de Kort, V. Correa, A. R. P. M. Valentijn, G. A. van der Marel, B. V. L. Potter, C. W. Taylor, J. H. van Boom, *J. Med. Chem.* **2000**, 43, 3295–3303; c) K. C. Nicolaou, A. L. Smith, *Acc. Chem. Res.* **1992**, 25, 497–503.
- a) O. Mongin, L. Porres, L. Moreaux, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2002**, 4, 719–722; b) L. Brunsveld, E. W. Meijer, R. B. Prince, J. S. Moore, *J. Am. Chem. Soc.* **2001**, 123, 7978–7984; c) R. B. Prince, L. Brunsveld, E. W. Meijer, J. S. Moore, *Angew. Chem.* **2000**, 112, 234–236; *Angew. Chem. Int. Ed.* **2000**, 39, 228–230; d) R. B. Prince, J. G. Saven, P. G. Wolynes, J. S. Moore, *J. Am. Chem. Soc.* **1999**, 121, 3114–3121; e) J. Zhang, D. J. Pesak, J. L. Ludwick, J. S. Moore, *J. Am. Chem. Soc.* **1994**, 116, 4227–4239.

- [7] a) R. Chinchilla, C. Nájera, *Chem. Rev.* **2007**, *107*, 874–922; b) H. Doucet, J.-C. Hierso, *Angew. Chem.* **2007**, *119*, 850–888; *Angew. Chem. Int. Ed.* **2007**, *46*, 834–871; c) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979–2017; d) K. Sonogashira, *J. Organomet. Chem.* **2002**, *653*, 46–49; e) S. Thorand, N. Krause, *J. Org. Chem.* **1998**, *63*, 8551–8553.
- [8] P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem.* **2000**, *112*, 2740–2767; *Angew. Chem. Int. Ed.* **2000**, *39*, 2632–2657.
- [9] C. Wolf, R. Lerebours, *Org. Biomol. Chem.* **2004**, *2*, 2161–2164.
- [10] a) A. Soheili, J. Albaneze-Walker, J. A. Murry, P. G. Dormer, D. L. Hughes, *Org. Lett.* **2003**, *5*, 4191–4194; b) Y. Ma, C. Song, W. Jiang, Q. Wu, Y. Wang, X. Liu, M. B. Andrus, *Org. Lett.* **2003**, *5*, 3317–3319; c) T. Fukuyama, M. Shinmen, S. Nishitani, M. Sato, I. Ryu, *Org. Lett.* **2002**, *4*, 1691–1694; d) X. Fu, S. Zhang, J. Yin, D. P. Schumacher, *Tetrahedron Lett.* **2002**, *43*, 6673–6676; e) V. P. W. Böhm, W. A. Herrmann, *Eur. J. Org. Chem.* **2000**, 3679–3681.
- [11] a) J. Cheng, Y. Sun, F. Wang, M. Guo, J.-H. Xu, Y. Pan, Z. Zhang, *J. Org. Chem.* **2004**, *69*, 5428–5432; b) C. Nájera, J. Gil-Moltó, S. Karlström, L. R. Falvello, *Org. Lett.* **2003**, *5*, 1451–1454; c) D. A. Alonso, C. Nájera, M. C. Pacheco, *Tetrahedron Lett.* **2002**, *43*, 9365–9368.
- [12] a) M. K. Samantaray, K. Pang, M. M. Shaikh, P. Ghosh, *Inorg. Chem.* **2008**, *47*, 4153–4165; b) M. K. Samantaray, D. Roy, A. Patra, R. Stephen, M. Saikh, R. B. Sunoj, P. Ghosh, *J. Organomet. Chem.* **2006**, *691*, 3797–3805.
- [13] L. Ray, M. M. Shaikh, P. Ghosh, *Inorg. Chem.* **2008**, *47*, 230–240.
- [14] S. Ray, R. Mohan, J. K. Singh, M. K. Samantaray, M. M. Shaikh, D. Panda, P. Ghosh, *J. Am. Chem. Soc.* **2007**, *129*, 15042–15053.
- [15] a) L. Ray, V. Katiyar, S. Barman, M. J. Raihan, H. Nanavati, M. M. Shaikh, P. Ghosh, *J. Organomet. Chem.* **2007**, *692*, 4259–4269; b) L. Ray, V. Katiyar, M. J. Raihan, H. Nanavati, M. M. Shaikh, P. Ghosh, *Eur. J. Inorg. Chem.* **2006**, 3724–3730.
- [16] a) M. K. Samantaray, V. Katiyar, K. Pang, H. Nanavati, P. Ghosh, *J. Organomet. Chem.* **2007**, *692*, 1672–1682; b) M. K. Samantaray, V. Katiyar, D. Roy, K. Pang, H. Nanavati, R. Stephen, R. B. Sunoj, P. Ghosh, *Eur. J. Inorg. Chem.* **2006**, 2975–2984.
- [17] L. Ray, M. M. Shaikh, P. Ghosh, *Organometallics* **2007**, *26*, 958–964.
- [18] L. Ray, M. M. Shaikh, P. Ghosh, *Dalton Trans.* **2007**, 4546–4555.
- [19] a) M. G. Organ, M. Abdel-Hadi, S. Avola, N. Hadei, J. Nasielski, C. J. O'Brien, C. Valente, *Chem. Eur. J.* **2007**, *13*, 150–157; b) C. J. O'Brien, E. A. B. Kantachev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, *Chem. Eur. J.* **2006**, *12*, 4743–4748; c) M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantachev, C. J. O'Brien, C. Valente, *Chem. Eur. J.* **2006**, *12*, 4749–4755; d) C. J. O'Brien, E. A. B. Kantachev, G. A. Chass, N. Hadei, A. C. Hopkinson, M. G. Organ, D. H. Setaidi, T.-H. Tang, D.-C. Fang, *Tetrahedron* **2005**, *61*, 9723–9735.
- [20] a) D. Nemcsok, K. Wichmann, G. Frenking, *Organometallics* **2004**, *23*, 3640–3646; b) C. Boehme, G. Frenking, *Organometallics* **1998**, *17*, 5801–5809.
- [21] a) R. E. Douthwaite, *Coord. Chem. Rev.* **2007**, *251*, 702–717; b) L. H. Gade, S. Bellemin-Laponnaz, *Coord. Chem. Rev.* **2007**, *251*, 718–725; c) E. Colacino, J. Martinez, F. Lamaty, *Coord. Chem. Rev.* **2007**, *251*, 726–764; d) V. Dragutan, I. Dragutan, L. Delaude, A. Demonceau, *Coord. Chem. Rev.* **2007**, *251*, 765–794; e) W. J. Sommer, M. Weck, *Coord. Chem. Rev.* **2007**, *251*, 860–873; f) J. A. Mata, M. Poyatos, E. Peris, *Coord. Chem. Rev.* **2007**, *251*, 841–859; g) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239–2246.
- [22] a) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem.* **2007**, *119*, 2824–2870; *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813; b) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 3046–3058; *Angew. Chem. Int. Ed.* **2007**, *46*, 2988–3000.
- [23] a) S. T. Liddle, I. S. Edworthy, P. L. Arnold, *Chem. Soc. Rev.* **2007**, *36*, 1732–1744; b) O. Kühn, *Chem. Soc. Rev.* **2007**, *36*, 592–607.
- [24] R. R. Tykwinski, *Angew. Chem.* **2003**, *115*, 1604–1606; *Angew. Chem. Int. Ed.* **2003**, *42*, 1566–1568.
- [25] a) M. Weck, C. W. Jones, *Inorg. Chem.* **2007**, *46*, 1865–1875; b) W. J. Sommer, M. Weck, *Adv. Synth. Catal.* **2006**, *348*, 2101–2113.
- [26] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
- [27] L. Pauling, *The Nature of The Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, **1960**, pp. 224–228; L. Pauling, *The Nature of The Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, **1960**, pp. 246–258.
- [28] a) K. S. Coleman, S. Turberville, S. I. Pascu, M. L. H. Green, *J. Organomet. Chem.* **2005**, *690*, 653–658; b) F. Hannig, G. Kehr, R. Fröhlich, G. Erker, *J. Organomet. Chem.* **2005**, *690*, 5959–5972; c) R. E. Douthwaite, J. Houghton, B. M. Kariuki, *Chem. Commun.* **2004**, 698–699; d) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, J. Houghton, B. M. Kariuki, S. Simonovic, *Dalton Trans.* **2004**, 3528–3535; e) A. K. de K. Lewis, S. Caddick, F. G. N. Cloke, N. C. Billingham, P. B. Hitchcock, J. Leonard, *J. Am. Chem. Soc.* **2003**, *125*, 10066–10073; f) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, *Organometallics* **2003**, *22*, 4384–4386; g) Q.-X. Liu, H.-B. Song, F.-Bo. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng, Z.-Z. Zhang, *Polyhedron* **2003**, *22*, 1515–1521.
- [29] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.
- [30] D. M. D'Souza, T. J. J. Müller, *Chem. Soc. Rev.* **2007**, *36*, 1095–1108.
- [31] M. Müller, R. Penk, E. Rohlfing, J. Krickemeyer, *Inorg. Synth.* **1990**, *28*, 348–349.
- [32] H. M. Lee, C. Y. Lu, C. Y. Chen, W. L. Chen, H. C. Lin, P. L. Chiu, P. Y. Cheng, *Tetrahedron* **2004**, *60*, 5807–5825.
- [33] G. M. Sheldrick, SHELXL, version 6.10, Bruker AXS, Madison, WI, **2000**.
- [34] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- [35] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [36] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [37] a) A. Alkauskas, A. Baratoft, C. Bruder, *J. Phys. Chem. A* **2004**, *108*, 6863–6868; b) D. Andrae, U. Haussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141; c) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* **1987**, *86*, 866–872.
- [38] a) O. N. Faza, C. S. López, R. Alvarez, A. R. de Lera, *J. Am. Chem. Soc.* **2006**, *128*, 2434–2437; b) X. Wang, L. Andrews, *J. Am. Chem. Soc.* **2001**, *123*, 12899–12900.
- [39] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261.
- [40] S. Dapprich, G. Frenking, *J. Phys. Chem.* **1995**, *99*, 9352–9362.
- [41] a) S. F. Vyboishchikov, G. Frenking, *Chem. Eur. J.* **1998**, *4*, 1428–1438; b) G. Frenking, U. Pidun, *J. Chem. Soc., Dalton Trans.* **1997**, 1653–1662.
- [42] S. I. Gorelsky, AOMix: Program for Molecular Orbital Analysis, York University, Toronto (Canada), **1997**; <http://www.sg-chem.net/>.
- [43] S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* **2001**, *635*, 187–196.
- [44] S. I. Gorelsky, S. Ghosh, E. I. Solomon, *J. Am. Chem. Soc.* **2006**, *128*, 278–290.

Received: February 18, 2008  
Published online: June 18, 2008