Novel Metal-Mediated (M = Pd, Pt) Coupling between Isonitriles and Benzophenone Hydrazone as a Route to Aminocarbene Complexes Exhibiting High Catalytic Activity (M = Pd) in the Suzuki−Miyaura Reaction

Konstantin V. Luzyanin,*[†] Alexander G. Tskhovrebov,[†,‡] M. Carolina Carias,[†]
M. Fátima C. Guedes da Silva,[†,§] Armando J. L. Pombeiro,*[†] and Vadim Yu. Kukushkin*[‡,⊥]

[†]*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Avenida Rovisco Pais, 1049-001 Lisbon, Portugal,* [‡]*St.Petersburg State University, 198504 Stary Petergof, Russian Federation,* [§]*Universidade Lusófona de Humanidades e Tecnologias, ULHT Lisbon, 1749-024 Lisbon, Portugal, and* [⊥]*Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoii Pr. 31, 199004 St.Petersburg, Russian Federation*

Received August 2, 2009

Metal-mediated reaction between equimolar amounts of *cis*-[MCl$_2$(C≡NR)$_2$] [M = Pd, R = cyclohexyl (Cy) **1**, *t*Bu **2**, 2,6-Me$_2$C$_6$H$_3$ (Xyl) **3**, 4-MeOC$_6$H$_4$ **4**; M = Pt, R = cyclohexyl (Cy) **5**, 2,6-Me$_2$C$_6$H$_3$ (Xyl) **7**, 4-MeOC$_6$H$_4$ **8**] and benzophenone hydrazone, H$_2$N−N=CPh$_2$, proceeds in CHCl$_3$ under reflux for 8 h. The subsequent workup provides the carbene species *cis*-[MCl$_2${<u>C</u>(N(H)N=CPh$_2$)=N(H)R}(C≡NR)] (M = Pd, **9**−**12**; M = Pt, **13**−**15**) in good (80−85%) isolated yields. Complexes **9**−**15** are air- and moisture-stable in the 20−80 °C temperature range and were characterized by elemental analyses (C, H, N), ESI$^+$-MS, IR, and 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC/^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC) NMR spectroscopies. In addition, the structures of two metallacarbenes, **11** and **14**, were elucidated by single-crystal X-ray diffraction. The catalytic properties of **9**−**15** in the Suzuki−Miyaura cross-coupling of the aryl bromides 4-R^{2}C$_6$H$_4$Br (R^2 = H, Me, OMe, and NO$_2$) with phenylboronic acid (in EtOH as a solvent, K$_2$CO$_3$ as a base, 80 °C), yielding biaryl species, were evaluated, and it was found that the palladium-aminocarbene species **9**−**12** exhibit a high catalytic activity (yields up to 97%, TONs up to 1.4 × 10^6).

Introduction

Attractive properties of the N-heterocyclic carbenes (NHCs), such as high chemical and thermal stability, low toxicity, and availability,[1,2] resulted in complexes with these species (in particular, with cyclic diaminocarbenes, Figure 1, A) having been able to challenge the dominance of the commonly used tertiary phosphine-based catalysts in a wide range of cross-coupling systems such as Suzuki−Miyaura, Heck, and Sonogashira reactions.[1−3] The frequently superior catalytic activity of the metallaNHCs over phosphine complexes is habitually explained by a stronger σ-donation

of NHCs relative to phosphines.[4,5] However, several recent studies[6] have demonstrated that the common NHCs show little variation of *donor ability* with changing N-substituents or the backbone saturation, implying that *steric factors* may be primarily responsible for the observed differences in catalyst activities.[6] Although a few recent reports introduced NHCs with tunable donor properties,[2,7] the N-heterocyclic carbenes cannot yet compete with the diversity of those available for phosphines.[8] Hence, the search for carbene species that combine a wider range of donor abilities with the advantages of NHCs represents an important goal.

Being structurally relevant to NHCs, acyclic diaminocarbenes (ADCs, Figure 1, B) possess similar electronic stabilization, but exhibit stronger net electron-donor properties than

---

*Corresponding authors. E-mail: kluzyanin@ist.utl.pt; pombeiro@ist.utl.pt; kukushkin@VK2100.spb.edu.

(1) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008,** *47,* 3122–3172.

(2) Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009,** *253,* 862–892.

(3) Nolan, S. P.; Navarro, O. C−C bond formation by cross-coupling. In *Comprehensive Organometallic Chemistry III,* 1st ed.; Canty, A., Ed.; Elsevier: Oxford, 2007; Vol. *11,* Chapter 11.01, pp 1−38, and references therein.

(4) (a) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999,** *18,* 2370–2375. (b) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003,** *22,* 1663–1667. (c) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005,** *127,* 2485–2495.

(5) (a) Pombeiro, A. J. L. *J. Organomet. Chem.* **2005,** *690,* 6021–6040. (b) Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2007,** 1473–1482.

(6) (a) Mercs, L.; Labat, G.; Neels, A.; Ehlers, A.; Albrecht, M. *Organometallics* **2006,** *25,* 5648–5656. (b) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Peterson, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003,** *22,* 4322–4326. (c) Dible, B. R.; Sigman, M. S. *Inorg. Chem.* **2006,** *45,* 8430–8441. (d) Diéz-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007,** *251,* 874–883.

(7) (a) Präsang, C.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2005,** *127,* 10182–10183. (b) Leuthäusser, S.; Schwarz, D.; Plenio, H. *Chem.—Eur. J.* **2007,** *13,* 7195–7203.

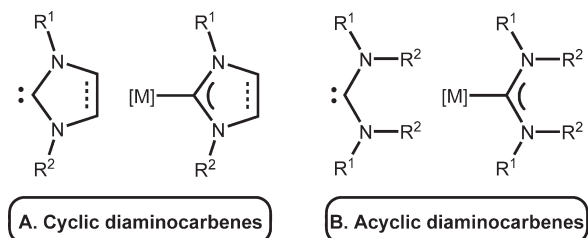(8) Tolman, C. A. *Chem. Rev.* **1977,** *77,* 313–348.

Figure 1. Cyclic (A) and acyclic (B) diaminocarbenes and corresponding metal complexes.

N-heterocyclic carbenes,[9,10] and it is believed[10] that their closer position to a metal center gives greater steric control. Indeed, a few recent reports have demonstrated that palladium(II) complexes with ADCs promote several cross-coupling reactions with activities comparable to those of Pd-NHCs,[11] thus making these species worthy targets for further exploration. All these data appeared only recently, and ADCs have not yet attracted the same degree of attention as NHCs.

Generation of the acyclic diaminocarbene complexes (Scheme 1) may be accomplished through (i) a direct complexation of free carbenes prepared *in situ* by the deprotonation of the corresponding precursors (N,N,N',N'-tetraalkylformamidinium[12] and N,N-dialkyliminium salts[12] bearing bulky substituents) to a metal center[10,11a] or (ii) a metal-mediated nucleophilic addition to isonitriles.[11b−e,13,14] The former experimental approach habitually requires a purification of either carbene precursors or target metallacarbenes,[10−12] while the *in situ* deprotonation of the corresponding precursors fre-

Scheme 1. Direct Complexation (C) and Metal-Mediated Nucleophilic Addition (D) Approaches to Acyclic Diaminocarbene Complexes
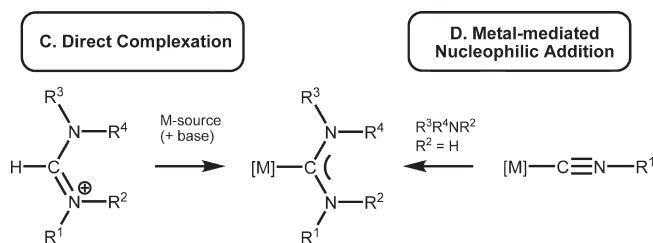
quently involves the excess of the latter, thus being economically and environmentally unfavorable.[11a]

In this context, an alternative approach based on a metal-mediated nucleophilic addition to isonitriles (Scheme 1, D) provides an attractive route to hindered and unhindered acyclic metallacarbenes.[13,14] Furthermore, a strict control of the ratio between the metal species and the carbene ligands (which are generated via a stoichiometric reaction) ensures the preparation of well-defined complexes, avoiding additional workup. To date, the vast majority of the reported examples for the metal-mediated nucleophilic addition to isonitriles includes the reactions of nucleophiles bearing sp^3-N- or O-donor centers, viz., amines/hydrazines and alcohols, affording *acyclic* diamino- and oxyaminocarbenes, $C(NR^2R^3)N(H)R^1$ and $C(OR^2)N(H)R^1$,[2,13,14] and NHCs via the intermolecular cyclization process.[13]

Recently, within our project on the reactivity of metal-activated nitrile[15,16] and isonitrile[13a,17,19] substrates, we reported the first examples of the integration of metal-bound isonitriles with sp^2-N nucleophiles, such as benzophenone imine[18c] (Scheme 2, E) and 3-iminoisoindolin-1-ones[18b] (Scheme 2, F), furnishing a novel type of aminocarbene complexes, viz., aminoimino-carbene species.

Inspired by these results, we sought other compounds bearing incorporated sp^2/sp^3-N nucleophilic centers and focused our attention, in general, on hydrazones, $R^3R^4N-N=CR^2_2$, and, in particular, on N-unsubstituted (R^3, R^4 = H) commercially available species, such as

(9) (a) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121–1123. (b) Tafipolsky, M.; Scherer, W.; Öfele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865–5880. (c) Alder, R. W.; Blake, M. E.; Chaker, L.; Paolini, F. P. V. *Chem. Commun.* **2004**, 2172–2173. (d) Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896–5911. (e) Otto, M.; Conejero, S.; Canac, Y.; Romanenko, V. D.; Rudzevitch, V.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 1016–1017. (f) Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, *23*, 976–983. (g) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717–8724.

(10) Rosen, E. L.; Sanderson, M. D.; Saravanakumar, S.; Bielawski, C. W. *Organometallics* **2007**, *26*, 5774–5777. (b) Frey, G. D.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2006**, *691*, 2465–2478. (c) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235–248. (d) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219–224.

(11) (a) Dhudshia, B.; Thadani, A. N. *Chem. Commun.* **2006**, 668–670. (b) Moncada, A. I.; Tanski, J. M.; Slaughter, L. M. *J. Organomet. Chem.* **2005**, *690*, 6247–6251. (c) Moncada, A. I.; Khan, M. A.; Slaughter, L. M. *Tetrahedron Lett.* **2005**, *46*, 1399–1403. (d) Wanniarachchi, Y. A.; Kogiso, Y.; Slaughter, L. M. *Organometallics* **2008**, *27*, 21–24. (e) Moncada, A. I.; Manne, S.; Tanski, J. M.; Slaughter, L. M. *Organometallics* **2006**, *25*, 491–505. (f) Kremzow, D.; Seidel, G.; Lehmann, C. W.; Fürstner, A. *Chem.—Eur. J.* **2005**, *11*, 1833–1853.

(12) Alder, R. W.; Blake, M. E.; Bufali, S.; Butts, C. P.; Orpen, A. G.; Schutz, J.; Williams, S. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1586–1593.

(13) (a) Michelin, R.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *Coord. Chem. Rev.* **2001**, *218*, 75–112. (b) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lügger, Th.; Fehlhammer, W. P. *Chem.—Eur. J.* **2003**, *9*, 704–712. (c) Hahn, F. E.; Plumed, C. G.; Münder, M.; Lügger, Th. *Chem.—Eur. J.* **2004**, *10*, 6285–6293. (d) Hahn, F. E.; Langenhahn, V.; Lügger, Th.; Pape, T.; Van, D. Le. *Angew. Chem., Int. Ed.* **2005**, *44*, 3759–3763. (e) Hahn, F. E.; Langenhahn, V.; Pape, T. *Chem. Commun.* **2005**, 5390–5392.

(14) (a) Cavell, K. J.; McGuiness, D. S. Palladium complexes with carbonyl, isocyanide, and carbene ligands. In *Comprehensive Organometallic Chemistry III*, 1st ed.; Canty, A., Ed.; Elsevier: Oxford, 2007; Vol. 8, Chapter 8.04, pp 197−268. (b) Rourke, J. P. Platinum complexes with carbonyl, isocyanide and carbene ligands. In *Comprehensive Organometallic Chemistry III*, 1st ed.; Canty, A., Ed.; Elsevier: Oxford, 2007; Vol. 8, Chapter 8.07, pp 405−444. (c) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175−209.

(15) (a) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771–1802. (b) Pombeiro, A. J. L. *New J. Chem.* **1994**, *18*, 163–174.

(16) (a) Wagner, G.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *J. Am. Chem. Soc.* **2000**, *122*, 3106–3111. (b) Kopylovich, M. N.; Pombeiro, A. J. L.; Fischer, A.; Kloo, L.; Kukushkin, V. Yu. *Inorg. Chem.* **2003**, *42*, 7239–7248. (c) Kopylovich, M. N.; Kukushkin, V. Yu.; Haukka, M.; Luzyanin, K. V.; Pombeiro, A. J. L. *J. Am. Chem. Soc.* **2004**, *126*, 15040–15041. (d) Luzyanin, K. V.; Kukushkin, V. Yu.; Ryabov, A. D.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2005**, *44*, 2944–2953. (e) Luzyanin, K. V.; Kukushkin, V. Yu.; Kuznetsov, M. L.; Ryabov, A. D.; Galanski, M.; Haukka, M.; Tretyakov, E. V.; Ovcharenko, V. I.; Kopylovich, M. N.; Pombeiro, A. J. L. *Inorg. Chem.* **2006**, *45*, 2296–2306. (f) Makarycheva-Mikhailova, A. V.; Golenetskaya, J. A.; Bokach, N. A.; Balova, I. A.; Haukka, M.; Kukushkin, V. Yu. *Inorg. Chem.* **2007**, *46*, 8323–8331. (g) Kopylovich, M. N.; Haukka, M.; Kirillov, A. M.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *Chem.—Eur. J.* **2007**, *13*, 786–791. (h) Lasri, J.; Charmier, M. A. J.; Haukka, M.; Pombeiro, A. J. L. *J. Org. Chem.* **2007**, *72*, 750–755. (i) Gushchin, P. V.; Luzyanin, K. V.; Kopylovich, M. N.; Haukka, M.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem.* **2008**, *47*, 3088–3094.

(17) (a) Pombeiro, A. J. L.; Guedes da Silva, M. F. C.; Michelin, R. A. *Coord. Chem. Rev.* **2001**, *218*, 43–74. (b) Pombeiro, A. J. L. *Inorg. Chem. Commun.* **2001**, *4*, 585–597.

(18) (a) Luzyanin, K. V.; Tskhovrebov, A. G.; Guedes da Silva, M. F. C.; Haukka, M.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Chem.—Eur. J.* **2009**, *15*, 5969–5978. (b) Luzyanin, K. V.; Pombeiro, A. J. L.; Haukka, M.; Kukushkin, V. Yu. *Organometallics* **2008**, *27*, 5379–5389. (c) Luzyanin, K. V.; Guedes da Silva, M. F. C.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **2009**, *362*, 833–888.

Scheme 2. Examples of Aminocarbene Complexes Derived from the Addition of sp^2-N Nucleophiles to Coordinated Isonitriles
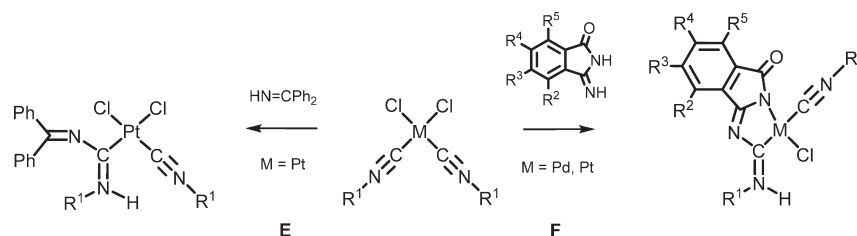
benzophenone hydrazone, $H_2N-N=CPh_2$ [IUPAC name:[20] (diphenylmethylene)hydrazine]. Extensive experimental and theoretical studies on the structural, chemical, and physical properties of hydrazones[21] revealed that the hybridization of the NH_2 center is somehow intermediate between sp^3-N and sp^2-N and depends strongly on the nature of the substituents, approaching sometimes the pure sp^2-N state.[21] Although the reaction between uncomplexed *nitriles* $RC\equiv N$ and hydrazones is well investigated,[21,22] the nucleophilic attack of $H_2N-N=CPh_2$ on both the free and complexed isoelectronic *isonitrile* species $RN\equiv C$ has never been reported.

Hence, in the framework of our studies on the activation of isonitriles upon coordination to metal centers toward nucleophiles[18b,c] and dipoles,[18a] we decided to study the integration between $H_2N-N=CPh_2$ and isonitriles and report herein on the novel metal-mediated coupling of the benzophenone hydrazone with palladium(II)- and platinum(II)-bound $RN\equiv C$ species. In addition, we found that the aminocarbene complexes generated in the reaction exhibit a high catalytic activity in the Suzuki−Miyaura cross-coupling, and the achieved results are uncovered in the sections that follow.

Results and Discussions

Metal-Mediated Nucleophilic Addition of Benzophenone Hydrazone to Isonitriles. For this study we employed, on one hand, the known palladium(II) and platinum(II)

isonitrile complexes *cis*-$[MCl_2(C\equiv NR)_2]$ [M = Pd, R = cyclohexyl (Cy) **1**, *t*Bu **2**, $2,6$-$Me_2C_6H_3$ (Xyl) **3**, 4-$MeOC_6H_4$ **4**; M = Pt, R = cyclohexyl (Cy) **5**, *t*Bu **6**, $2,6$-$Me_2C_6H_3$ (Xyl) **7**, 4-$MeOC_6H_4$ **8**].[23] The complexes of these two metal centers exhibit different kinetic lability and thermodynamic stability and different degrees of electrophilic activation of the isonitrile upon coordination,[13] and they also have different solubilities in various solvents. On the other hand, we used a commercially available representative of the hydrazone family, viz., benzophenone hydrazone, $H_2N-N=CPh_2$.

At the initial experiments, we observed no reaction between the equimolar amounts of *cis*-$[MCl_2(C\equiv NR)_2]$ (**1−5**, **7**, and **8**) and $H_2N-N=CPh_2$ in $CHCl_3$ at $20-25$ °C even after 2 days; only mixtures of the starting materials were recovered. However, in refluxing $CHCl_3$, the reaction between the equimolar amounts of *cis*-$[MCl_2(C\equiv NR)_2]$ (**1−5**, **7**, and **8**) and $H_2N-N=CPh_2$ proceeds for ca. 8 h (Scheme 3, Table 1), and the subsequent workup provides the carbene species *cis*-$[MCl_2\{C(N(H)N=CPh_2)=N(H)R\}(C\equiv NR)]$ (M = Pd, **9−12**; M = Pt, **13−15**) in good (80−85%) isolated yields. All complexes **9−15** are air- and moisture-stable in the $20-80$ °C temperature range. No coupling between *cis*-$[PtCl_2(C\equiv NtBu)_2]$ (**6**) and $H_2N-N=CPh_2$ in $CHCl_3$ was accomplished even under prolonged reflux. Thus, after heating the reactants for 1 day only a mixture of the starting materials and small amounts of yet unidentified decomposition species was isolated.

(19) (a) Kuznetsov, M. L.; Pombeiro, A. J. L. *Dalton Trans.* **2003**, 738–747. (b) Almeida, S. S. P. R.; Guedes da Silva, M. F. C.; Jerzykiewicz, L. B.; Sobota, P.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **2003**, *356*, 259–266. (c) Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *J. Organomet. Chem.* **2001**, *617−618*, 65–69. (d) Guedes da Silva, M. F. C.; Lemos, M. A. N. D. A.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **2000**, 373–380. (e) Almeida, S. S. P. R.; Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1999**, 467–472. (f) Costa, M. T. A. R. S.; Dilworth, J. R.; Duarte, M. T.; Fraústo da Silva, J. J. R.; Galvão, A. M.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1998**, 2405–2410. (g) Guedes da Silva, M. F. C.; Hitchcock, P. B.; Hughes, D. L.; Marjani, K.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1997**, 3725–3731. (h) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1996**, 2763–2772. (i) Wang, Y.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A.; Henderson, R. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1995**, 1183–1191. (j) Bertani, R.; Mozzon, M.; Michelin, R. A.; Benetollo, F.; Bombieri, G.; Castilho, T. J.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **1991**, *189*, 175–187.

(20) http://www.iupac.org/nomenclature/index.html.

(21) (a) Kitaev, Yu. P.; Buzykin, B. I.; Troepol'skaya, T. V. *Usp. Khim.* (*Russ. Chem. Rev.*) **1970**, *39*, 441–456. (b) Kitaev, Yu. P.; Buzykin, B. I. *Usp. Khim.* (*Russ. Chem. Rev.*) **1972**, *41*, 495–515. (c) Zverev, V. V.; Kitaev, Yu. P. *J. Struct. Chem.* **1974**, *15*, 128–132.

(22) (a) Conde, S.; Corral, C.; Madronero, R. *Synthesis* **1974**, 28. (b) Paulvannan, K.; Chen, T.; Hale, R. *Tetrahedron* **2000**, *56*, 8071–8076. (c) Broggini, G.; Garanti, L.; Molteni, G.; Zecchi, G. *Synthesis* **1996**, 1076–1078. (d) Garanti, L.; Sala, A.; Zecchi, G. *Synthesis* **1975**, 666–668. (e) Bruche, L.; Zecchi, G. *Tetrahedron* **1989**, *45*, 7427–7432. (f) Hassaneen, H. M.; Shawali, A. S.; Khalil, M. S.; Abdallah, T. A. *Heterocycles* **1993**, *36*, 1775–1781.

Scheme 3. Reaction between $H_2N-N=CPh_2$ and 1−5, 7, and 8 Furnishing Aminocarbene Complexes 9−15
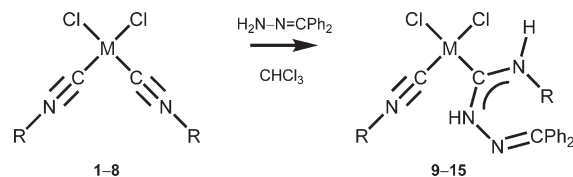
Table 1. Numbering of Carbene Complexes

	R in Pd(CNR) species	Product	R in Pt(CNR) species	Product
	Cy (**1**)	**9**	Cy (**5**)	**13**
	*t*Bu (**2**)	**10**	*t*Bu (**6**)	–
	Xyl (**3**)	**11**	Xyl (**7**)	**14**
	4-$MeOC_6H_4$ (**4**)	**12**	4-$MeOC_6H_4$ (**8**)	**15**

(23) (a) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1970**, *24*, 251–256. (b) Crociani, B.; Boschi, T.; Belluco, U. *Inorg. Chem.* **1970**, *9*, 2021–2025. (c) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 85–92. (d) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 93–99. (e) Bertani, R.; Mozzon, M.; Michelin, R. A. *Inorg. Chem.* **1988**, *27*, 2809–2815. (f) Bertani, R.; Mozzon, M.; Michelin, R. A.; Benetollo, F.; Bombieri, G.; Castilho, T. J.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **1991**, *189*, 175–187.

One should mention that the addition of $H_2N-N=CPh_2$ along the $C\equiv N$ triple bond of an isonitrile has a metal-mediated character. Indeed, in a blank experiment, no reaction was observed between the uncomplexed isonitrile ($C\equiv NCy$) and $H_2N-N=CPh_2$ upon reflux in $CHCl_3$ for 2 days.

Furthermore, we found that the coupling between $H_2N-N=CPh_2$ and **1**–**5**, **7**, and **8** proceeds in a rather efficient way at both palladium(II) and platinum(II) centers with the isonitriles RNC bearing alkyl or aryl R groups. Previously, we observed that the addition of the sp^2-N nucleophilic moiety of 3-iminoisoindolin-1-ones along the isonitrile $C\equiv N$ triple bond (Scheme 2, F) proceeds at a higher degree of selectivity in the case of the palladium(II) species as compared to the corresponding platinum(II) complexes.

We attempted to shorten the reaction time by increasing the temperature (via application of a solvent with a higher boiling point, such as 1,2-dichloroethane; bp = 84 °C) and by using an excess of the nucleophile $H_2N-N=CPh_2$. In refluxing 1,2-dichloroethane, the coupling between the equimolar amounts of **1** and $H_2N-N=CPh_2$ proceeds faster than in $CHCl_3$, and no starting *cis*-[$MCl_2(C\equiv NCy)_2$] was detected by TLC after 2 h. However, this procedure gives lower selectivity (4 spots on TLC apart from the spot of the target complex), furnishing **9** in ca. 55% isolated yield. In addition, monitoring of the reaction between *cis*-[$MCl_2(C\equiv NCy)_2$] and 2 equiv of $H_2N-N=CPh_2$ in $CHCl_3$ indicated no significant difference in the coupling rates; in the latter case, decomposition of the excess $H_2N-N=CPh_2$ results in the necessity for an additional purification of the target metallacarbenes.

Characterization of the Aminocarbene Complexes 9–15. Complexes **9**–**15** were characterized by elemental analyses (C, H, N), ESI$^+$-MS, IR, and 1D (^1H, $^{13}C\{^1H\}$) and 2D ($^1H,^1H$-COSY, $^1H,^{13}C$-HMQC/$^1H,^{13}C$-HSQC, $^1H,^{13}C$-HMBC) NMR spectroscopies. In addition, the structures of complexes **11** and **14** were elucidated by single-crystal X-ray diffraction analysis.

Compounds **9**–**15** gave satisfactory C, H, and N elemental analyses, which are consistent with the proposed formulations of the mixed complexes *cis*-[$MCl_2\{\underline{C}(N(H)N=CPh_2)=N(H)R\}(C\equiv NR)$]. The ESI$^+$-MS mass spectra of **9**–**15** display molecular ion peaks and/or a fragmentation corresponding to the loss of Cl's from the molecular ion, viz., [$M - n$Cl]$^+$, with the characteristic isotopic distribution.

The examination of the IR spectra of **9**–**15** revealed the presence of one strong $\nu(C\equiv N)$ stretching vibration in the range between 2226 and 2196 cm^{-1}, while the starting *cis*-[$MCl_2(C\equiv NR)_2$] (**1**–**5**, **7**, and **8**) complexes usually display two overlapped $\nu(C\equiv N)$ stretches in the interval 2270–2150 cm^{-1}.[23] This suggests the presence of only one isonitrile ligand in **9**–**15**. Moreover, the existence of two broad $\nu(M-Cl)$ frequencies in the near-IR range of 336–274 cm^{-1} is consistent with the *cis* isomer and indicates that the initial geometry of the planar complexes is retained in the course of the reaction. It is known that $\nu(M-Cl)$ frequencies in *trans*-[MCl_2L_2] (M = Pd^{II}, Pt^{II}) fall in the range 355–365 cm^{-1}, and they are almost insensitive to the nature of ligands L.[23,24] In the formed $C=N(H)R$ carbene moiety, $\nu(N-H)$ bands emerge in the range 3256–3210 cm^{-1}, while the corresponding very strong bands due to $\nu(C=N)$ appear

between 1579 and 1506 cm^{-1}. The medium/weak intensity bands in the range 2980–2836 cm^{-1} are characteristic of $\nu_s(C-H)$ and $\nu_{as}(C-H)$ vibrations, while medium intensity bands due to $\delta(C-H$ from Ar) appear at ca. 700 cm^{-1}.

The ^1H NMR spectra of carbene complexes **9**–**15** display a broad peak in the range δ 8.74–9.79, assigned to the $M-C_{carbene}=N(H)R$ proton. The spectra indicate restricted rotation about the $N-C$(carbene) bonds, which was also previously observed in related diaminocarbene species.[25] Thus, for example, the spectrum of **11** in $CDCl_3$ contains five singlets in the range δ 2.50–2.15 that correspond to the Me groups. In **9** or **13**, derived from *cis*-[$MCl_2(C\equiv NCy)_2$], the characteristic signals of the proton and the carbon (in ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively) of the tertiary HC from the cyclohexyl ring of the carbene species emerge at ca. 4.5 and 58 ppm, correspondingly, while in the unreacted $C\equiv NR$ ligand the relevant signals appear at a higher field (ca. 4.0 and 55 ppm, respectively).

Addition of $H_2N-N=CPh_2$ to the coordinated isonitrile is accompanied by a pronounced δ ^{13}C shift to lower field of the quaternary C atom of one isonitrile to the carbene carbon ($C\equiv N$ to $C=N$). Thus, in **9**–**15**, the $C_{carbene}=NH$ ^{13}C signals were found to resonate in the range 180–160 ppm; that is, they are approximately 65–45 ppm downfield shifted in comparison with the starting (isonitrile)M^{II} complexes (e.g., 115 ppm for $C\equiv N$ in *cis*-[$PdCl_2(C\equiv NC_6H_{11})_2$]). These δ values for the $C_{carbene}=NH$ ^{13}C signals are downfield relative to those (157–159 ppm) reported for the series of chelated N-heterocyclic carbenes, such as bis(imidazolylidene) palladium dichloride complexes,[1,26a] but are upfield of the 194–227 ppm range found for the palladium-bound monodentate acyclic diaminocarbenes.[9,10,26b,26c]

The ^1H and ^{13}C signal assignments were performed by interpretation of gradient-enhanced two-dimensional $^1H,^1H$-COSY, $^1H,^{13}C$-HMQC/$^1H,^{13}C$-HSQC, and $^1H,^{13}C$-HMBC NMR spectra. The short-range correlations ($^1H,^1H$-COSY and $^1H,^{13}C$-HMQC/$^1H,^{13}C$-HSQC) were used to assign the signals of the rotational isomers of **9**–**15**, while the long-range shift correlation experiments via $^2J_{H,C}$ and $^3J_{H,C}$ coupling ($^1H,^{13}C$-HMBC) allowed the discrimination of the $C_{carbene}$ signal of the newly formed carbene species from the $C=N$ carbon of the hydrazone moiety.

The crystallographic data and processing parameters for **11** and **14** are very similar and are listed in Table 1 of the Supporting Information; bond lengths and angles are summarized in Table 2 and the plot for one of the structures (**11**) can be found in Figure 2.

In both complexes **11** and **14**, the chlorides are mutually *cis* [Cl1–Pd1–Cl2 91.76(3)°, Cl1–Pt1–Cl2 89.57(6)°], and the slightly distorted square-planar environments around the metal centers are completed with one unreacted isonitrile ligand, $C\equiv NXyl$, and one newly formed carbene ligand, $\underline{C}(N(H)N=CPh_2)=N(H)Xyl$.

The $M^{II}-C_{carbene}$ distances [Pd1–C11 1.973(3) Å for **11**, Pt1–C11 1.971(5) Å for **14**] are comparable to those reported for the related palladium and platinum carbene complexes *cis*-[$PdCl_2\{\underline{C}(OMe)=N(H)Me\}_2$] (1.953–1.972 Å),[27a]

(24) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science Publishers Ltd.: London, 1973.

(25) Lai, S.-W.; Chan, M. C.-W.; Cheung, K.-K.; Che, Ch.-M. *Organometallics* **1999**, *18*, 3327–3336.

(26) (a) Ahrens, S.; Zeller, A.; Taige, M.; Strassner, T. *Organometallics* **2006**, *25*, 5409–5415. (b) Kremzow, D.; Seidel, G.; Lehmann, C. W.; Furstner, A. *Chem.—Eur. J.* **2005**, *11*, 1833–1853. (c) Frey, G. D.; Herrmann, W. A. *J. Organomet. Chem.* **2005**, *690*, 5876–5880.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 11 (M = Pd) and 14 (M = Pt)

	11	14
	Bond Lengths	
M−C1	1.924(3)	1.894(6)
M−C11	1.973(3)	1.971(5)
M−Cl1	2.3004(8)	2.3051(16)
M−Cl2	2.3592(8)	2.3566(14)
C1−N1	1.147(4)	1.154(8)
C11−N11	1.332(4)	1.320(7)
C11−N2	1.323(4)	1.334(7)
C12−N11	1.448(4)	1.446(7)
C20−N3	1.288(4)	1.292(8)
N2−N3	1.384(4)	1.392(7)
	Bond Angles	
C1−M−C11	90.77(12)	91.9(2)
C1−M−Cl1	174.08(10)	175.22(19)
C1−M−Cl2	90.57(9)	90.54(17)
C11−M−Cl1	87.02(8)	88.07(16)
C11−M−Cl2	178.23(10)	177.21(17)
Cl1−M−Cl2	91.76(3)	89.57(6)
N1−C1−M	175.1(3)	178.2(6)
N2−C11−M	123.0(2)	123.4(4)
N2−C11−N11	116.1(3)	115.0(5)
N2−N3−C20	114.7(3)	114.9(5)
N11−C11−M	120.7(2)	121.4(4)
N3−N2−C11	121.4(3)	121.5(5)
C1−N1−C2	171.9(3)	170.2(6)
C11−N11−C12	123.1(3)	123.8(5)
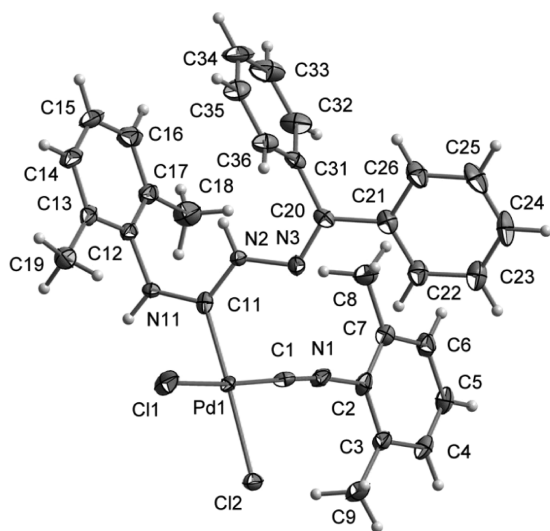
Figure 2. View of **11** with atomic numbering schemes. Thermal ellipsoids are drawn with 50% probability.

cis-[PdCl₂{$\underline{C}$(=NHCy)NHNH$\underline{C}$(=NHCy)}₂] (1.958−1.964 Å),[11e] [Pt{η²-(S,S')-S₂C=C($\underline{C}$(O)Me)}(CN*t*Bu){$\underline{C}$(NEt₂)-(NH*t*Bu)}] [2.053(2) Å],[27b] and *cis*-[PtCl₂($\underline{C}$NXyl){$\underline{C}$(NH₂)-N(H)Xyl}] [1.983(7) Å].[18c] In both complexes the carbene moiety is roughly planar (C11 deviates from the M−N11−N2 plane by *c*a. 0.0423(33) Å in **11** and 0.0392(61) Å in **14**) and the angles around the carbene C11 atoms range from 115.0(5)° to 123.4(4)°, therefore sustaining the sp^2 hybridization of this atom. Short and equal (within 3σ) N−C11 bond lengths (av 1.327 Å) imply substantial p_π−p_π interactions within the N2−C11−N11 fragments, as

detected in the related above-mentioned carbene complexes (av 1.29−1.33 Å).[11,18c,27] The diamino groups of the carbene moieties in **11** and **14** are orientated out of the [Cl₂M] plane to reduce steric repulsion and adopt the *Z,E* configuration.
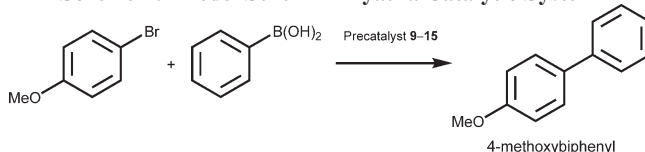
In the isonitrile moiety, the C≡N triple bonds [C1−N1 1.147(4) and 1.154(8) Å for **11** and **14**, respectively] have normal values for a triple CN bond (1.136−1.144 Å)[28] and are comparable with that observed in the related isonitrile palladium and platinum complexes *cis*-[PdCl₂(C≡NR)₂] [R = Cy (1.128−1.142 Å),[29a] *t*Bu (1.108−1.149 Å),[29b] Xyl (1.145−1.156 Å)[29c], [PtCl(CNXyl){$\underline{C}$(NH₂)N(H)Xyl}-(Ph₂C=NH)]Cl [1.151(9) Å],[18c] and [Pt{η²-(S,S')-S₂C=C{C(O)Me}₂}(CNXyl)₂] [1.152(3) Å].[27b]

The solid state structures of both compounds exhibit the presence of intramolecular π−π interactions between the C12−C17 and the C31−C36 phenyl rings. The distances of 4.172 Å (for **11**) and 4.185 Å (for **14**) between the centroids and the angles between the planes of the phenyl rings (18.70° and 17.10° for **11** and **14**, respectively) indicate medium-weak noncovalent interactions.[30] Additionally, in both complexes the N11−H11 protons are involved in intermolecular hydrogen bonding to the Cl2 atoms of a neighboring molecule [*D*−H, H···*A*, and *D*−H···*A* (Å, deg): N11−H11···Cl2 0.88, 2.42, 153.0].

All other bond lengths in **11** and **14** are of normal values, and they agree with those reported for related palladium(II)[11e,27a,29] and platinum(II)[18c,27b] carbene and isonitrile complexes.

Evaluation of the Catalytic Properties for the Prepared Aminocarbene Complexes in the Suzuki−Miyaura Cross-Coupling System. Since it is known that palladium(II) complexes with NHCs[3] display high catalytic activity in various cross-coupling systems, in particular in the Suzuki−Miyaura reaction, and in pursuit of the ongoing research in our laboratory[31] on such a coupling, we decided to evaluate the catalytic properties of the prepared aminocarbenes toward this reaction. It is worth mentioning that no examples of platinum-aminocarbene catalysts for the Suzuki−Miyaura cross-coupling have yet been reported.

As a model system, we have chosen the commonly used reaction of 4-methoxybromobenzene (4-bromoanisole) with phenylboronic acid, producing 4-methoxybiphenyl (Scheme 4).

Scheme 4. Model Suzuki−Miyaura Catalytic System

(27) (a) Domiano, P.; Musatti, A.; Nardelli, M.; Predieri, G. *J. Chem. Soc., Dalton Trans.* **1975**, 2165–2168. (b) Vicente, J.; Chicote, M. T.; Huertas, S. *Inorg. Chem.* **2003**, *42*, 4268–4274.

(28) (a) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(29) (a) Kitano, Y.; Hori, T. *Acta Crystallogr. B* **1981**, *37*, 1919–1921. (b) Perreaul, D.; Drouin, M.; Michel, A.; Harvey, P. D. *Inorg. Chem.* **1993**, *32*, 1903–1912. (c) Drouin, M.; Perreaul, D.; Harvey, P. D.; Michel, A. *Acta Crystallogr. C* **1991**, *47*, 752–754.

(30) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(31) (a) Lasri, J.; Kopylovich, M. N.; Guedes da Silva, M. F. C.; Charmier, M. A. J.; Pombeiro, A. J. L. *Chem.—Eur. J.* **2008**, *14*, 9312–9322. (b) Kopylovich, M. N.; Lasri, J.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Dalton Trans.* **2009**, 3074–3084. (c) Lasri, J.; Guedes da Silva, M. F. C.; Kopylovich, M. N.; Mukhopadhyay, S.; Charmier, M. A. J.; Pombeiro, A. J. L. *Dalton Trans.* **2009**, 2210–2216.

Taking into account the variety of reported experimental conditions and their influence on the catalytic activities of metal NHC or ADC complexes in Suzuki−Miyaura cross-coupling systems,[3,11a] we attempted the optimization of the reaction conditions (solvent, base, temperature; see the Supporting Information for a detailed description) in order to find a catalytic system operating under mild and "green" conditions.

Hence, we found that ethanol—one of the organic solvents with lowest environmental impact—can be used as an appropriate solvent for our catalytic runs. In refluxing EtOH, the conversion of 4-bromoanisole is essentially complete after ca. 2 h, furnishing the biphenyl product in ca. 97% yield, without visible catalyst decomposition. Moreover, K_2CO_3 was found to be the most appropriate base for the studied catalytic system (Table 2 of the Supporting Information).

The palladium complexes **9**−**12** are efficient catalysts for the cross-coupling, while the corresponding platinum species **13**−**15** expectedly do not exhibit any activity (Table 3 of the Supporting Information). Among the palladium aminocarbenes, complexes **9**, **11**, and **12** manifest the highest efficiencies, furnishing the coupling product in 94−97% yield, while compound **10**, derived from $[PdCl_2(C\equiv NtBu)_2]$, exhibits a moderate activity (64% yield).

We also checked the effect of the substituent of the aryl bromide and found that the organobromides $4\text{-}R^2C_6H_4Br$ bearing either electron-donor (R^2 = H, Me, OMe) or electron-withdrawing (NO_2) groups react with phenylboronic acid to give excellent yields of biphenyl species (Table 4 of the Supporting Information), thus showing a valuable versatility of our catalytic system.

Since it is important to achieve good product yields using a minimum amount of catalyst, we also examined the effect of catalyst loading in the model catalytic system (Table 3).

Table 3. Effect of Catalyst Loading (for 9) in the Suzuki−Miayura Cross-Coupling System[a]
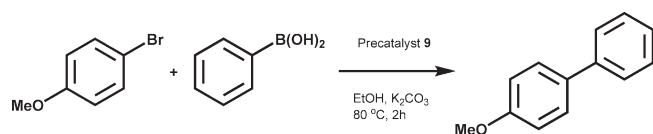
entry	**9**, mol	yield, %	TON
1		4	
2	1.0×10^{-8}	97	9.7×10^3
3	1.0×10^{-9}	97	9.7×10^4
4	1.0×10^{-10}	88	8.8×10^5
5	1.0×10^{-11}	14	1.4×10^6

[a] K_2CO_3 (1.5×10^{-4} mol, 1.5 equiv), 4-bromoanisole (1.0×10^{-4} mol, 1 equiv), phenylboronic acid (1.2×10^{-4} mol, 1.2 equiv); precatalyst **9** (1.0×10^{-8}−1.0×10^{-11} mol); EtOH (1 mL).

High yields (up to 88%), with a TON up to 8.8×10^5, were obtained even at catalyst loadings as low as 10^{-6} mol per mole of substrate. Moreover, we also evaluated the air/moisture stability of the catalytic system by performing some additional runs in nondried EtOH and in air (Table 4 of the Supporting Information) and observed no significant differences from those performed under air/moisture-free conditions. It is worth mentioning that to date the best reported examples for the cross-coupling between bromobenzenes and phenylboronic acid catalyzed by palladium(II) com-

plexes with acyclic diaminocarbenes include catalytic systems that (i) operate under harsh reaction conditions (120 °C),[11b,c] in environmentally unfavorable solvents (THF/toluene),[11a] or employing expensive and/or harmful bases (Cs_2CO_3 or $tBuOK$);[11a] (ii) require high catalyst loading (0.5−1 mol % of expensive catalysts),[11a−c] or (iii) require prolonged reaction times (16−24 h).[11a−c] Hence, the results obtained for our Pd complexes are among the best so far reported in the field, indicating that the metallacarbenes **9**−**12** are efficient precatalysts with promising synthetic potential.

Final Remarks. The results of this work may be considered from the following perspectives. First, in the course of this study, we have discovered a novel metal-mediated coupling between a hydrazone and the CN triple bond of an isonitrile. Thus, we have demonstrated that the reaction between benzophenone hydrazone, $H_2N\text{−}N\text{=}CPh_2$, and one isonitrile in *cis*-$[MCl_2(C\equiv NR)]$ (M = Pd^{II}, Pt^{II}) opens up a route to palladium and platinum complexes containing aminocarbene ligands (see Scheme 3) generated via attack of the NH_2 nucleophilic center of the hydrazone on the CN moiety of the coordinated $RN\equiv C$. We have also noted that the reaction between the metal-bound isonitrile and the hydrazone proceeds in a rather efficient way at both palladium(II) and platinum(II) centers and with the isonitriles bearing either alkyl or aryl R groups.

Second, to our knowledge, the vast majority of the reactions involving hydrazones includes oxidation of $R^3R^4N\text{−}N\text{=}CR^2_2$ forming substituted diazomethanes (further used, for example, as 1,3-dipoles in cycloaddition reactions with alkenes, as precursors to carbenes, and for homologation of cyclic ketones)[21,32] and azines;[21,33] preparation of vinyl iodides by the reaction of hydrazones with iodine in the presence of non-nucleophilic bases;[21,34] palladium-catalyzed N-arylation of $H_2N\text{−}N\text{=}CR^2_2$ furnishing *N*-arylhydrazones and pyrazoles;[21,35] Schiff condensation of hydrazones with carbonyl species forming imines;[21,36] and the Lewis-acid-catalyzed nucleophilic addition of hydrazones to nitriles with a consequent cyclization affording triazoles.[21,37] Hence, within our study we detected a novel type of reactivity for hydrazones, viz., nucleophilic attack of $H_2N\text{−}N\text{=}CPh_2$ on a

(32) (a) Moebius, D. C.; Kingsburya, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 878–879. (b) Javed, M. I.; Brewer, M. *Org. Lett.* **2007**, *9*, 1789–1792. (c) Furrow, M. E.; Myers, A. G. *J. Am. Chem. Soc.* **2004**, *126*, 12222–12223. (d) Holton, T. L.; Shechter, H. *J. Org. Chem.* **1995**, *60*, 4725–4729. (e) Ko, K.-Y.; Kim, J.-Y. *Bull. Korean Chem. Soc.* **1999**, *20*, 771–772. (f) Stojiljkovic, A.; Orbovic, N.; Sredojevic, S.; Mihailovic, M. L. *Tetrahedron* **1970**, *26*, 1101–1107. (g) Fischer, W.; Anselme, J. P. *J. Am. Chem. Soc.* **1967**, *89*, 5312–5313.

(33) (a) Singh, G. S.; Ibata, T. *Tetrahedron Lett.* **1994**, *35*, 2581–2584. (b) Korotchenko, V. N.; Shastin, A. V.; Nenaidenko, V. G.; Balenkova, E. S. *Russ. Chem. Bull.* **2003**, *52*, 492–497. (c) Ikeda, I.; Kogame, Y.; Okahara, M. *J. Org. Chem.* **1985**, *6*, 338–338.

(34) (a) Barton, D. H. R.; Bashiardes, G.; Fourrey, J.-L. *Tetrahedron* **1988**, *44*, 147–162. (b) Barton, D. H. R.; O'Brien, R. E.; Sternhell, S. *J. Chem. Soc.* **1962**, 470–476.

(35) (a) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *27*, 2090−2093, and references therein. (b) Haddad, N.; Baron, J. *Tetrahedron Lett.* **2002**, *43*, 2171–2173.

(36) (a) Murray, B. A. *Org. React. Mech.* **2003**, 1. *Chem. Abstr.*, **2003**, *138*, 368336. (b) Voloshin, Ya. Z.; Varzatskii, O. A.; Vorontsov, I. I.; Antipin, M. Yu.; Tkachenko, E. Yu. *Russ. Chem. Bull.* **2002**, *51*, 1015–1019. (c) Bagrov, F. V. *Russ. J. Org. Chem.* **2001**, *37*, 15–19. (d) Yilmaz, I.; Cukurovali, A. *Heteroat. Chem.* **2003**, *14*, 617–621. (e) Rana, A.; Dinda, R.; Ghosh, S.; Blake, A. *Polyhedron* **2003**, *22*, 3075–3082. (f) Mandlik, P. R.; Aswale, S. R.; Aswar, A. S. *J. Indian Chem. Soc.* **2002**, *79*, 689–692.

(37) Mathur, S. S.; Suschitsky, H. *J. Chem. Soc., Perkin Trans. 1* **1975**, *23*, 2474–2478.

C≡N triple bond of a metal-bound isonitrile furnishing a ligated aminocarbene.

Third, the obtained palladium(II) and platinum(II) aminocarbene complexes are air- and moisture-stable in the 20−80 °C temperature range, and we found that the Pd^{II} species (**9**−**12**) display a high activity (yields are up to 97%, TONs up to 1.4×10^6), under relatively mild conditions (air, EtOH, 80 °C), in the Suzuki−Miyaura cross-coupling of aryl bromides with phenylboronic acids.

Currently, we are seeking novel metal-mediated couplings between other sp^2/sp^3-N nucleophiles and isonitriles, with a particular emphasis on those mediated by Pd, Pt, and Ru metal centers. Moreover, we are also exploring the catalytic properties of the metallacarbenes derived from reactions of metal-activated isonitriles in order to develop mild and "green" catalytic systems and to establish catalyst structure−activity relationships in various cross-coupling systems.

Experimental Section

Materials and Instrumentation. Solvents, PdCl$_2$, K$_2$[PtCl$_4$], all isonitriles, and H$_2$N−N=CPh$_2$ were obtained from commercial sources and used as received, apart from chloroform, which was purified by conventional distillation over calcium chloride. The complexes *cis*-[PdCl$_2$(RNC)$_2$] (R = Cy **1**, *t*Bu **2**, Xyl **3**, 4-MeOC$_6$H$_4$ **4**)^{23} and *cis*-[PtCl$_2$(RNC)$_2$] (R = Cy **5**, *t*Bu **6**, Xyl **7**, 4-MeOC$_6$H$_4$ **8**)^{23} were prepared as previously reported. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ESI$^+$ mass spectra were obtained on a Varian 500-MS LC ion trap mass spectrometer in MeOH (ion spray voltage: +5 kV, capillary voltage: 30 V, RF loading: 100%). Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC, ^{1}H,^{13}C-HSQC, and ^{1}H,^{13}C-HMBC) NMR spectra were recorded on Bruker Avance II+ 400 MHz (UltraShield Magnet) and Bruker Avance II+ 500 MHz (Ultra-Shield Plus Magnet) spectrometers at ambient temperature.

X-ray Structure Determinations. The X-ray quality single crystals of **11** and **14** were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 150 K. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated Mo Kα (*λ* 0.71073) radiation. Data were collected using omega scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT^{38} on all the observed reflections. Absorption corrections were applied using SADABS.^{39} Structures were solved by direct methods by using the SHELXS-97 package^{40} and refined with SHELXL-97.^{41} Calculations were performed using the WinGX System, Version 1.80.03.^{30} All hydrogens were inserted in calculated positions. Least-squares refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. In **14**, the maximum and minimum peaks in the final difference electron density map are 2.61 and −2.34 e Å^{-3}, respectively, close to the Pt atom. Crystallographic and selected structural details are listed in Tables 2 and 3, respectively. CCDC 742155 and 742156 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.

Synthetic work. **Reactions of 1−8 and H$_2$N−N=CPh$_2$.** A solution of H$_2$N−N=CPh$_2$ (0.039 g, 0.20 mmol) in CHCl$_3$ (2 mL) was added to a solution (R = Cy, *t*Bu, 4-MeOC$_6$H$_4$) or a suspension (R = Xyl) of *cis*-[MCl$_2$(RNC)$_2$] (0.20 mmol) in CHCl$_3$ (5 mL), and the reaction mixture was refluxed for 8 h. During this period, the color of the mixture gradually turned from light orange to bright yellow. After 8 h, the reaction mixture was evaporated at 20−25 °C under a stream of dinitrogen to dryness, and the product was extracted with two 5 mL portions of CHCl$_3$. The bright yellow solution was filtered off to remove some insoluble material, and the filtrate was evaporated at room temperature to dryness under a stream of N$_2$ and washed with five 5 mL portions of Pr$^i_2$O, one 1 mL portion of cold (5 °C) Et$_2$O, and again with five 5 mL portions of Pr$^i_2$O, and then dried *in vacuo* at 20−25 °C. Yields of **9**−**15** were 80−85%, based on the metal.
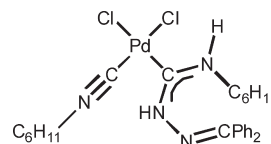
9. Anal. Calcd for C$_{27}$H$_{34}$N$_4$Cl$_2$Pd: C, 54.79; H, 5.79; N, 9.47. Found: C, 54.70; H, 6.18; N, 9.83. ESI$^+$-MS, *m/z*: 592 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 2934−2856 m *ν*(C−H); 2226 s *ν*(C≡N); 1636 s *ν*(N=CPh$_2$); 1557 s *ν*(N−C$_{carbene}$); 702 m *δ*(C−H from Ar). ^{1}H NMR (CDCl$_3$, *δ*): 8.91 (s, 1H, C$_{carbene}$−NH), 8.32 (s, 1H, C=NHN), 7.61−7.30 (m, 10H, aryls), 4.40 and 3.87 (two broad unresolved multiplets, 2H, CH), 2.16−1.24 (m, 20H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 176.9 and 156.3 (C$_{carbene}$−NH and C=N), 135.7−128.2 (aryls), 58.7 and 55.2 (CH), 33.5−22.3 (CH$_2$).
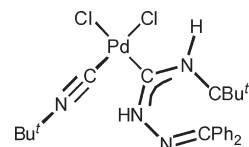
10. Anal. Calcd for C$_{23}$H$_{30}$N$_4$Cl$_2$Pd: C, 51.17; H, 5.60; N, 10.38. Found: C, 51.26; H, 5.56; N, 10.53. ESI$^+$-MS, *m/z*: 563 [M + Na]$^+$. IR (KBr, selected bands, cm^{-1}): 3365 mw, 3221 m *ν*(N−H); 2980 m, 2938 m *ν*(C−H); 2216 s *ν*(C≡N); 1579 s, 1560 s *ν*(N−C$_{carbene}$, N=CPh$_2$); 698 m *δ*(C−H from Ar). ^{1}H NMR (CDCl$_3$, *δ*): 8.83 (s, 1H, C$_{carbene}$−NH), 8.27 (s, 1H, C=NHN), 7.63−7.30 (m, 10H, aryls), 1.75, 1.52, and 1.50 (three singlets, 18H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, *δ*): 176.9 and 156.3 (C$_{carbene}$−NH and C=N), 135.7−128.2 (aryls), 113.0 (C≡N), 57.3 and 56.2 (*C*Me$_3$), 21.2 and 21.0 (Me).
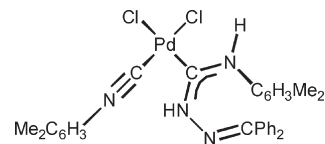
11. Anal. Calcd for C$_{31}$H$_{30}$N$_4$Cl$_2$Pd: C, 58.55; H, 4.76; N, 8.81. Found: C, 58.66; H, 4.75; N, 8.41. ESI$^+$-MS, *m/z*: 599 [M − Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3239 mw *ν*(N−H); 2967−2855 m *ν*(C−H); 2200 s *ν*(C≡N); 1638 mw, 1596 m, 1540 s *ν*(C$_{carbene}$−NH, N=CPh$_2$); 703 m *δ*(C−H from Ar). ^{1}H NMR (CDCl$_3$, *δ*): 9.79 (s, 1H, C$_{carbene}$−NH), 9.28 (s, 1H, C=NHN), 7.66−7.40 (m) and 7.26−6.99 (m, 16H, aryls), 2.50,

(38) *Bruker, APEX2 & SAINT*; Bruker AXS Inc.: Madison, WI, 2004.

(39) Sheldrick, G. M. *SADABS, Bruker Nonius scaling and absorption correction, v 2.10*; Bruker AXS, Inc.: Madison, WI, 2003.

(40) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

(41) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

2.48, 2.37, 2.16, and 2.15 (five singlets, 12H, Me). $^{13}C\{^1H\}$ NMR (CDCl$_3$, δ): 179.7 and 158.2 (C$_{carbene}$−NH and C=N), 135.5−127.9 (aryls), 19.4, 18.7, 18.1, and 15.3 (Me).
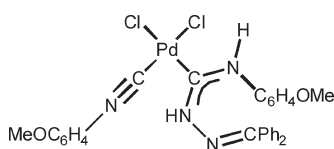
12. Anal. Calcd for C$_{29}$H$_{26}$N$_4$Cl$_2$O$_2$Pd: C, 54.43; H, 4.10; N, 8.76. Found: C, 54.52; H, 4.30; N, 8.64. ESI$^+$-MS, *m/z*: 638 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3238 mw ν(N−H); 3058−2836 m ν(C−H); 2204 s ν(C=N); 1601 s ν(N=CPh$_2$); 1540 s, 1508 s ν(N−C$_{carbene}$); 1256 s ν(C−OMe), 697 m δ(C−H from Ar). ^{1}H NMR (CDCl$_3$, δ): 9.64, 9.49, and 8.92 (three singlets, 2H, C$_{carbene}$−NH and C=NHN), 7.76−7.30 (m) and 7.03−6.75 (m, 18H, aryls), 3.84, 3.77, and 3.60 (three singlets, 6H, OMe). $^{13}C\{^1H\}$ NMR (CDCl$_3$, δ): 160.9, 158.9, and 158.2 (C$_{carbene}$−NH and C=N), 135.7−125.8, 114.8−114.1 (aryls), 55.7, 55.6, and 55.1 (OMe).
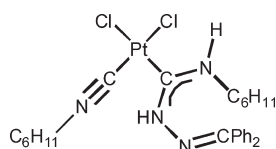
13. Anal. Calcd for C$_{27}$H$_{34}$N$_4$Cl$_2$Pt: C, 47.65; H, 5.04; N, 8.23. Found: C, 47.70; H, 5.18; N, 8.03. ESI$^+$-MS, *m/z*: 680 [M + H]$^+$. IR (KBr, selected bands, cm^{-1}): 3368, 3281 mw ν(N−H); 2932−2856 m ν(C−H); 2218 s ν(C=N); 1603 m ν(N=CPh$_2$); 1572 ν(N−C$_{carbene}$); 701 m δ(C−H from Ar). ^{1}H NMR (CDCl$_3$, δ): 8.75 (s, 1H, C$_{carbene}$−NH), 7.62−7.32 (m, 11H, C=NHN and aryls), 4.52 (m) and 4.06 (m, 2H, CH), 2.18−1.46 (m, 20H, CH$_2$). $^{13}C\{^1H\}$ NMR (CDCl$_3$, δ): 164.5 and 155.6 (C$_{carbene}$−NH and C=N), 136.0−128.3 (aryls), 58.1, 55.7, and 55.1 (CH), 33.6−22.4 (CH$_2$).
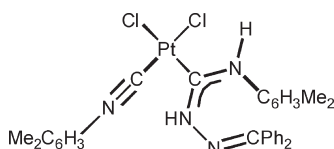
14. Anal. Calcd for C$_{31}$H$_{30}$N$_4$Cl$_2$Pt: C, 51.39; H, 4.17; N, 7.73. Found: C, 51.52; H, 4.09; N, 7.51. ESI$^+$-MS, *m/z*: 746 [M + Na]$^+$. IR (KBr, selected bands, cm^{-1}): 2967−2921 m ν(C−H); 2196 s ν(C=N); 1619 s ν(N=CPh$_2$); 1531 s ν(N−C$_{carbene}$); 700 m δ(C−H from Ar). ^{1}H NMR (CD$_2$Cl$_2$, δ): 9.72 (s, 1H, C$_{carbene}$−NH), 9.45 (s, 1H, C=NHN), 7.63−6.91 (m, 16H, aryls), 2.49, 2.41, 2.16, and 2.13 (four singlets, 12H, Me). $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$, δ): 166.0 and 157.2 (C$_{carbene}$−NH and C=N), 135.6−127.7 (aryls), 19.3, 18.6, and 18.5 (Me).
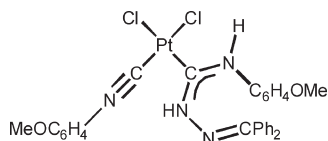
15. Anal. Calcd for C$_{29}$H$_{26}$N$_4$Cl$_2$O$_2$Pt: C, 47.81; H, 3.60; N, 7.69. Found: C, 47.64; H, 3.69; N, 7.37. ESI$^+$-MS, *m/z*: 727 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 2934−2837 m ν(C−H); 2200 s ν(C=N); 1601 s ν(N=CPh$_2$); 1506 s ν(N−C$_{carbene}$); 1254 s ν(C−OMe); 701 m δ(C−H from Ar). ^{1}H NMR (CDCl$_3$, δ): 9.76 (s, 1H, C$_{carbene}$−NH), 9.55 (s, 1H, C=NHN), 7.71−7.39 (m) and 6.94−6.79 (m, 18H, aryls), 3.79, 3.78, and 3.65 (three singlets, 6H, OMe). $^{13}C\{^1H\}$ NMR (CDCl$_3$, δ): 163.3, 160.4, and 157.3 (C$_{carbene}$−NH and C=N), 135.9−126.2 and 114.5 (C and CH from aryls), 55.6 and 55.5 (OMe).

General Procedure for the Catalytic Suzuki−Miyaura Cross-Coupling (specific conditions are provided in the legend to Table 4, and Tables 2−4 of the Supporting Information). Selected base (1.5 × 10^{-4} mol, 1.5 equiv), aryl bromide (1.0 × 10^{-4} mol, 1.0 equiv), and phenylboronic acid (1.2 × 10^{-4} mol, 1.2 equiv) were mixed in a round-bottom flask, followed by addition of a solution of the precatalyst (1 × 10^{-9} mol) in EtOH (1 mL). All the reactions (except those indicated in Table 4 of the Supporting Information) were performed under N$_2$, in a Schlenk tube, using high-vacuum/inert gas flow techniques; anhydrous EtOH was employed, and the Schlenk tube was connected to a reflux condenser provided with a takeoff with a connected dinitrogen balloon. For aerobic reactions (Table 4 of the Supporting Information), nondried EtOH was used, and the flask was connected to a reflux condenser open to air. The flask was placed in a preheated oil bath at 80 °C and stirred for 2 h. After cooling to 25 °C, the reaction mixture was evaporated to dryness under a stream of dinitrogen followed by addition of 1.0 equiv of 1,2-dimethoxyethane (NMR internal standard) and extraction of the reaction mixture with three 0.20 mL portions of CDCl$_3$. All fractions were joined and analyzed by ^{1}H NMR spectroscopy. The product peak assignments were based on authentic samples or on published data,[11] while quantifications were performed upon integration of the selected peak of the product relative to the peak of the standard. In some cases, the products were isolated by extraction of the residue after evaporation of the reaction mixture with CH$_2$Cl$_2$, followed by column chromatography on silica gel (10:1 hexane/ethyl acetate, v/v).

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.