Anagostic Interactions and Catalytic Activities of Sterically Bulky Benzannulated N-Heterocyclic Carbene Complexes of Nickel(II)

ARTICLE *in* ORGANOMETALLICS · APRIL 2008

Impact Factor: 4.13 · DOI: 10.1021/om800004j

3 AUTHORS, INCLUDING:

Han Vinh Huynh
National University of Singapore
93 PUBLICATIONS **2,337** CITATIONS

Anagostic Interactions and Catalytic Activities of Sterically Bulky Benzannulated N-Heterocyclic Carbene Complexes of Nickel(II)

Han Vinh Huynh,* Ling Rong Wong, and Pearly Shuyi Ng

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

Received January 4, 2008

Nickel(II) bis(benzimidazolin-2-ylidene) complexes of the general formula $[NiBr_2(NHC)_2]$ (NHC = 1,3-dibenzylbenzimidazolin-2-ylidene, **7**; NHC = 1,3-diisopropylbenzimidazolin-2-ylidene, **8**; NHC = 1,3-dibenzhydrylbenzimidazolin-2-ylidene, **9**; NHC = 1,3-diisobutylbenzimidazolin-2-ylidene, **10**; NHC = 1-isopropyl-3-benzylbenzimidazolin-2-ylidene, **11**; NHC = 1-benzhydryl-3-benzylbenzimidazolin-2-ylidene, **12**) have been prepared and fully characterized by spectroscopic methods and single-crystal X-ray structure analyses. All complexes adopt a square-planar geometry with nickel as the crystallographic inversion center and a trans arrangement of the carbene ligands. For complexes **11** and **12**, bearing unsymmetrically substituted ligands, only the trans-anti configuration was found in the solid state. In addition, the structures of **8**, **9**, **11**, and **12** reveal a fixed orientation of the *N*-isopropyl and *N*-benzhydryl substituents with the C−H groups pointing to the nickel(II) center to maximize rare intramolecular C−H···Ni anagostic or preagostic interactions. The large downfield shift of these C−H protons in the ^{1}H NMR spectrum compared to their precursor salts indicates that these interactions are retained in solution. Preliminary catalytic studies show that complexes **7**−**12** are active in the Ullmann coupling of bromobenzene and 4-bromoanisole. In particular, complexes **8**, **9**, and **12**, with sterically more demanding ligands, exhibit the best catalytic activities. The coupling reaction was found to be successful when carried out in neat $[Bu_4N]Br$ as ionic liquid, but not in dry DMF or in DMF with $[Bu_4N]Br$ as an additive.

Introduction

Recently, N-heterocyclic carbenes (NHCs) have attracted increasing attention as potential substitutes for the commonly used phosphine ligands, opening up many new opportunities in homogeneous catalysis.[1] The most intensively studied catalytic processes to date have been C−C coupling reactions promoted by NHC complexes of palladium. Nickel NHC complexes have been comparatively less thoroughly studied, although the replacement of palladium with nickel in transition metal catalysts would represent significant cost savings. Only recently have NHC complexes of nickel garnered more attention. Some of these complexes were shown to be catalytically active for a wide range of reactions such as Suzuki−Miyaura[2] and Kumada−Corriu[3] couplings, olefin dimerization[4] and polymerization,[5] C−C bond activation of biphenylene,[6] transfer hydrogenation of imines,[7] amination,[8] and dehalogenation[9] of aryl halides. Notably, all these nickel complexes contain NHC ligands that are derived from either imidazole or imidazoline precursors. To the best of our knowledge, nickel(II) complexes with benzannulated NHCs[10] were unknown until our recent report on a simple and inexpensive method for the synthesis of nonbulky nickel(II) bis(benzimidazolin-2-ylidene) complexes by reacting $Ni(OAc)_2$ with benzimidazolium salts in molten $[Bu_4N]X$ (X = Br, I, BF_4) as ionic liquid.[11] Since the steric bulk of a ligand is believed to enhance reductive elimination as a crucial step in a typical C−C coupling catalytic cycle, we herein describe the extension of our methodology to the synthesis of nickel(II) complexes with sterically bulky benzimidazolin-2-ylidene ligands and their catalytic activities in the Ullmann coupling reaction of aryl bromides. In addition, we have observed rare C−H···Ni anagostic or preagostic interac-

* Corresponding author. E-mail: chmhhv@nus.edu.sg.

(1) (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (b) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175. (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (e) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69. (f) Cavell, K. J.; McGuinness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671. (g) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619. (h) Hahn, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1348.

(2) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596.

(3) (a) Böhm, V. P. W.; Weskamp, T.; Gstöttmayr, C. W. K.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1602. (b) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3387. (c) Matsubara, K.; Ueno, K.; Shibata, Y. *Organometallics* **2006**, *25*, 3422.

(4) McGuinness, D. S.; Mueller, W.; Wasserscheid, P.; Cavell, K. J.; Skelton, B. W.; White, A. H.; Englert, U. *Organometallics* **2002**, *21*, 175.

(5) (a) Wang, X.; Liu, S.; Jin, G.-X. *Organometallics* **2004**, *23*, 6002. (b) Li, W.; Sun, H.; Chen, M.; Wang, Z.; Hu, D.; Shen, Q.; Zhang, Y. *Organometallics* **2005**, *24*, 5925. (c) Ketz, B. E.; Ottenwaelder, X. G.; Waymouth, R. M. *Chem. Commun.* **2005**, 5693. (d) Cámpora, J.; de la Tabla, L. O.; Palma, P.; Álvarez, E.; Lahoz, F.; Mereiter, K. *Organometallics* **2006**, *25*, 3314.

(6) Schaub, T.; Backes, M.; Radius, U. *Organometallics* **2006**, *25*, 4196.

(7) Kuhl, S.; Schneider, R.; Fort, Y. *Organometallics* **2003**, *22*, 4184.

(8) Gradel, B.; Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* **2001**, *42*, 5689.

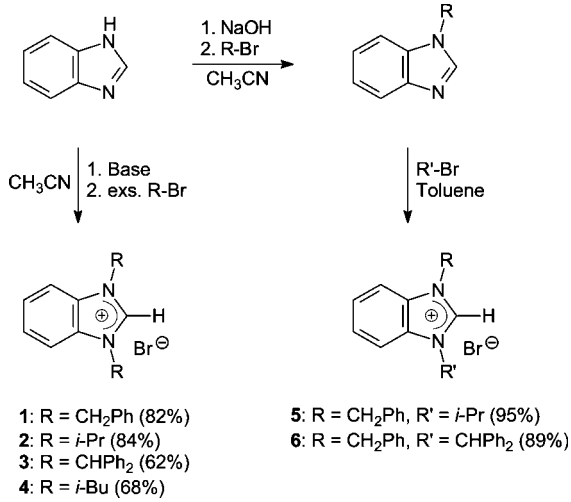
(9) Desmarets, C.; Kuhl, S.; Schneider, R.; Fort, Y. *Organometallics* **2002**, *21*, 1554.

(10) (a) Hahn, F. E.; Wittenbecher, L.; Boese, R. ; Bläser, D. *Chem.−Eur. J.* **1999**, *5*, 1931. (b) Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 541.

(11) Huynh, H. V.; Holtgrewe, C.; Pape, T.; Koh, L. L.; Hahn, E. *Organometallics* **2006**, *25*, 245.

10.1021/om800004j CCC: $40.75
Publication on Web 04/24/2008

Scheme 1. Synthesis of Benzimidazolium Salts 1−6



tions[12] exhibited by some of these complexes, the nature of which will be discussed as well.

Results and Discussion

Synthesis of Benzimidazolium Salts. A range of benzimidazolium bromide salts **1**−**6** as NHC precursors with different steric demands have been synthesized from commercially available benzimidazole by standard N-alkylation methods[13] (Scheme 1) in yields of 62–95%. The symmetrically substituted ligand precursors **1**−**4** were prepared by heating benzimidazole with excess alkyl bromide in the presence of a suitable base in CH_3CN. The asymmetrically substituted salts **5** and **6** require stepwise N-alkylation steps. As described earlier,[14] it is important to use a weaker base (e.g., K_2CO_3) and prolonged reaction time when alkyl bromides with secondary carbon atoms and a β-hydrogen are employed as alkylating agents (e.g., ^{i}PrBr and ^{i}BuBr). Stronger bases, such as NaOH or KOH, catalyze elimination reactions of the alkylating agents, leading to undesirable side products and a poor yield. The ^{1}H NMR spectra of all ligand precursors **1**−**6** show a characteristic downfield shift in the range δ = 9.89–12.04 ppm for the NCHN proton attributable to the positive charge of the molecule. In addition, their identities have also been confirmed by a base peak for the $[M - Br]^+$ fragments in their positive mode ESI mass spectra.

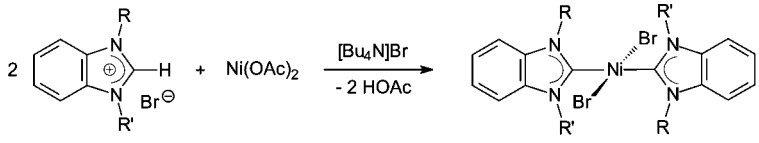
Synthesis and Characterization of Nickel(II) Complexes. Complexes **7**−**12** were prepared by heating a mixture of anhydrous $Ni(OAc)_2$ and the corresponding benzimidazolium bromide in $[Bu_4N]Br$ as ionic liquid (Scheme 2) under vacuum.[10] Complexes **7** and **11**, with comparatively less sterically demanding carbene ligands, afforded higher yields of 71% and 80%, respectively. It was observed that the yield of the complexes drops with increasing steric bulk of the ligand. This is most likely because the bulky substituents on the carbene ligand will hinder a fast coordination to the nickel center, giving rise to side reactions. In fact, during the synthesis of **7**, **8**, **10**, and **11** deep red mixtures were obtained at the end of the reaction, whereas **9** and **12** yielded initially dark blue mixtures probably containing tetrabromonickelate(II) species. The orange-red Ni(II) NHC complexes were only observed upon trituration of the cold reaction mixture with water and subsequent washing with EtOH. In order to minimize the formation of tetrabromonickelate(II) species, we have also investigated the synthesis of **9** in $[Bu_4N]BF_4$ as alternative ionic liquid with higher melting point (160 °C). However, no significant improvement of the yield was observed.

All complexes have generally low solubilities in common organic solvents. Complexes **7**, **8**, and **10**−**12** can be dissolved in chlorinated solvents, but complex **9** is only sparingly soluble in chloroform, DMF, and DMSO. As a result of their insufficient solubilities in common solvents, the ^{13}C NMR spectra for **8** and **9** could not be obtained. The absence of a downfield NCHN signal in all the ^{1}H NMR spectra for **7**−**12**, however, indicates a successful complex formation. In addition, the ^{1}H NMR spectra of complexes **11** and **12**, bearing unsymmetrically substituted carbene ligands, show a double set of signals for the aliphatic protons in a 1:1.5 and 1:3 intensity ratio, respectively, suggesting the presence of trans-anti and trans-syn rotamers in solution. However, attempts to separate the geometrical isomers were unsuccessful. More importantly, complexes **8**, **9**, **11**, and **12** show a remarkable downfield shift of $\Delta\delta$H = 1.79–2.43 ppm for the N-CH proton of the N-isopropyl and N-benzhydryl substituents of the carbene ligand upon coordination as compared to their ligand precursors, indicating some sort of C−H···Ni interactions (vide infra). Due to the aforementioned low solubility, well-resolved ^{13}C NMR spectra could only be obtained for complexes **10**−**12**. The carbenoid carbon in these complexes resonates at δ 183–187 ppm, which is in the usual range found for trans-configured nickel(II) benzimidazolin-2-ylidene complexes. Notably, these values are in between those typically found for nickel(II) imidazolin-2-ylidenes ($\delta_{carbene}$ ∼170 ppm)[4,10] and nickel(II) imidazolidin-2-ylidenes ($\delta_{carbene}$ ∼200 ppm).[10] The formation of the complexes as $[NiBr_2(NHC)_2]$ was further confirmed by ESI mass spectrometry, which showed fragment peaks for $[M - Br]^+$ from loss of a bromo ligand.

Intramolecular Anagostic or Preagostic C−H···M Interactions. As noted above, remarkable downfield shifts of $\Delta\delta$H = 1.79–2.43 ppm for the N-CH proton of the *N*-isopropyl and *N*-benzhydryl substituents of the carbene ligand are observed in complexes **8**, **9**, **11**, and **12** as compared to their ligand precursors. Such a phenomenon together with the geometric characteristics of these complexes (vide infra) are indicative of rare intramolecular anagostic or preagostic C−H···Ni interactions. Similar but less pronounced C−H···M interactions in d^8 square-planar monocarbene and bis(carbene) complexes of Pd(II)[12,15] and Pt(II)[16] of the 1,3-diisopropylbenzimidazolin-2-ylidene ligand have been reported recently. In general, there are three forms of C−H···M interactions including (i) agostic, (ii) anagostic or preagostic, and (iii) hydrogen bond.[17] The first (i) is usually referred to as a 3c-2e interaction, resulting in a pronounced highfield chemical shift of the corresponding H atom. Agostic interactions are often found in d^6 complexes with small M−H distances of ∼1.8–2.2 Å and C−H···M angles of ∼90–130°. Hydrogen bonds (iii) on the other hand are 3c-4e interactions with an almost linear geometry accompanied by a downfield ^{1}H NMR shift of the participating H atom. Rare anagostic or preagostic interactions (ii) occurring in square-planar d^8 systems are of broad general interest due to possible

(12) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6909.
(13) Hahn, F. E.; Holtgrewe, C.; Pape, T.; Martin, M.; Sola, E.; Oro, L. A. *Organometallics* **2005**, *24*, 2203.
(14) Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267.
(15) (a) Han, Y.; Huynh, H. V.; Koh, L. L. *J. Organomet. Chem.* **2007**, *692*, 3606. (b) Han, Y.; Huynh, H. V.; Tan, G. K. *Organometallics* **2007**, *26*, 6447.
(16) Han, Y.; Huynh, H. V.; Tan, G. K. *Organometallics* **2007**, *26*, 4612.
(17) (a) Brammer, L. *Dalton Trans.* **2003**, 3145. (b) Lewis, J. C.; Wu, J.; Bergman, R. G.; Ellman, J. A. *Organometallics* **2005**, *24*, 5737.

Scheme 2. Synthesis of Nickel(II) Bis(benzimidazolin-2-ylidene) Complexes 7−12



1 - 6

7: R = R' = CH_2Ph (71%, 12 h, 130 °C)
8: R = R' = *i*-Pr (78%, 12 h, 130 °C)
9: R = R' = $CHPh_2$ (34%, 36 h, 170 °C)
10: R = R´ = *i*-Bu (41%, 12 h, 130 °C)
11: R = CH_2Ph, R´ = *i*-Pr (80%, 12 h, 130 °C)
12: R = CH_2Ph, R´ = $CHPh_2$ (21%, 12 h, 130 °C)

Table 1. Comparison of Selected Structural and Spectroscopic Data for the Anagostic or Preagostic C−H Protons in Complexes 8, 9, 11, and 12 with Pd(II), Pt(II), and Au(III) Analogues

complex	δH^a ($\Delta\delta H$)^b [ppm]	d(C−H···M) [Å]	θ(C−H···M) [deg]
8	7.39 (2.18)	2.6412(1), 2.6670(1)	121.0(2), 121.3(2)
9	9.73 (1.97)	2.7501(1), 2.7552(2)	118.4(3), 118.2(3)
11	7.43 (2.43)	2.6205(12)	121.3(2), 117.8(2)
12	9.51 (1.88), 9.42 (1.79)^c	2.6923(1)	119.2(2), 117.0(2)
$[PdBr_2(^iPr_2\text{-bimy})_2]$[15a]	6.25 (1.04)	2.6856(1), 2.7143(1)	124.0(2), 124.1(2)
$[PtBr_2(^iPr_2\text{-bimy})_2]$[14]	6.52 (1.32)	2.7341(1), 2.7659(1)	123.7(3), 123.8(2)
$[AuI_2(^iPr_2\text{-bimy})_2]BF_4$[20]	5.06 (−0.15)	2.7508(2), 2.7643(2)	121.4(5), 121.9(4)

[a] Measured in $CDCl_3$. [b] $\Delta\delta H = \delta H$ (complex) − δH (corresponding azolium salt). [c] Two signals due to trans-anti and trans-syn rotamers.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 7–12

	7	**8**	**9**	**10**	**11**	**12**·DMF
Ni1−Br1	2.3025(3)	2.3111(1)	2.3091(5)	2.3003(4)	2.3175(11)	2.3092(3)
Ni1−C1	1.908(3)	1.898(2)	1.922(4)	1.913(3)	1.910(3)	1.902(3)
N1−C1	1.347(3)	1.352(3)	1.349(5)	1.353(4)	1.359(3)	1.350(3)
N1−C2	1.398(3)	1.398(3)	1.397(5)	1.384(4)	1.396(4)	1.378(4)
N1−C8	1.454(3)	1.473(3)	1.475(5)	1.429(18)	1.471(4)	1.468(4)
N2−C1	1.360(3)	1.351(3)	1.344(5)	1.359(4)	1.347(4)	1.357(4)
N2−C7	1.393(3)	1.393(3)	1.400(5)	1.384(4)	1.389(3)	1.407(4)
N2−C11		1.474(3)			1.469(3)	
N2−C12				1.460(4)		
N2−C15	1.469(3)					1.470(4)
N2−C21			1.485(5)			
Br1−Ni1−C1	88.89(8)	89.46(7)	93.41(12)	89.79(9)	89.71(8)	88.95(8)
C1−N1−C2	111.1(2)	110.6(2)	110.1(4)	111.2(2)	110.5(2)	111.1(3)
C1−N2−C7	111.0(0)	110.7(2)	110.9(4)	110.8(2)	111.1(2)	110.5(2)
N1−C1−N2	105.8(2)	106.6(2)	106.8(4)	105.5(2)	106.1(2)	106.1(2)
NiC_2X_2/carbene dihedral angle	80.18(8)	87.60(6)	86.56(12)	76.42(8)	84.96(6)	83.40(7)

implications for the mechanism of C−H activation. They are in between the former two with characteristic downfield shifts of the anagostic protons, H−M distances of ∼2.3–2.9 Å, and C−H···M angles usually in the range 130–170°. The origin of these interactions is still under debate and may involve donation of filled d_{z^2} or $d_{xz/yz}$ orbitals of the metal center into the C−H σ^* orbital.[18] A comparison of spectroscopic and structural data supporting these interactions for complexes **8**, **9**, **11**, and **12** with Pd(II), Pt(II), and Au(III) analogues is shown in Table 1. Notably, more flexible N-substituents with an N-CH_2 group in complexes **7** and **10**−**12** show only small downfield shifts (0.42–0.66 ppm) of these protons upon complexation. We are attributing this observation to a competition between the two protons for the electron donation from the metal center. In this series, complex **11** exhibits the strongest anagostic interactions with a largest downfield shift of $\Delta\delta H = 2.43$ ppm. A comparison of complex **8** with isoelectronic and isostructural analogues shows a decrease of anagostic interactions in the order Ni(II) > Pt(II) > Pd(II) ≫ Au(III) (Table 1). Interestingly, this observation may be related to the Shannon effective ionic radii[19] of these d^8 ions in square-planar geometry, which increase in the order 0.49 Å {Ni(II)} < 0.60 Å {Pt(II)} < 0.64 Å {Pd(II)} < 0.68 Å {Au(III)}. The strong donation of the carbene ligand to the smallest Ni(II) ion would result in the least Lewis acidic metal center, which translates into the observed strongest anagostic interaction. The most Lewis acidic Au(III) complex, on the other hand, does not show any C−H···M interactions in solution at all, as corroborated by a slight upfield shift of the corresponding C−H proton. A similar correlation of such ana-/preagostic interactions with the Lewis acidity of the metal center has been used to compare the σ-donor strengths of some ligands L in complexes of the type $[PdBr_2(^iPr_2\text{-bimy})L]^{n-}$ ($n = 0, 1$).[15b]

Molecular Structures. Single crystals of complexes **7**−**12** suitable for X-ray diffraction were obtained at ambient temperature either by slow evaporation of chloroform/ethanol (**7**, **8**), chloroform/DMF (**9**), and chloroform (**10**) solutions or by vapor diffusion of diethyl ether into saturated chloroform (**11**) or DMF (**12**) solutions. Selected bond parameters and crystallographic data are listed in Tables 2 and 4, respectively. As found by solution NMR data, the molecular structures of **7**−**12** depicted in Figure 1 confirm the mutual trans configurations of

(18) (a) Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 105. (b) Zhang, Y.; Lewis, J. C.; Bergman, R.; Ellman, J. A.; Oldfield, E. *Organometallics* **2006**, *25*, 3515.

(19) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(20) Jothibasu, R.; Huynh, H. V.; Koh, L. L. *J. Organomet. Chem.* **2008**, *693*, 374.

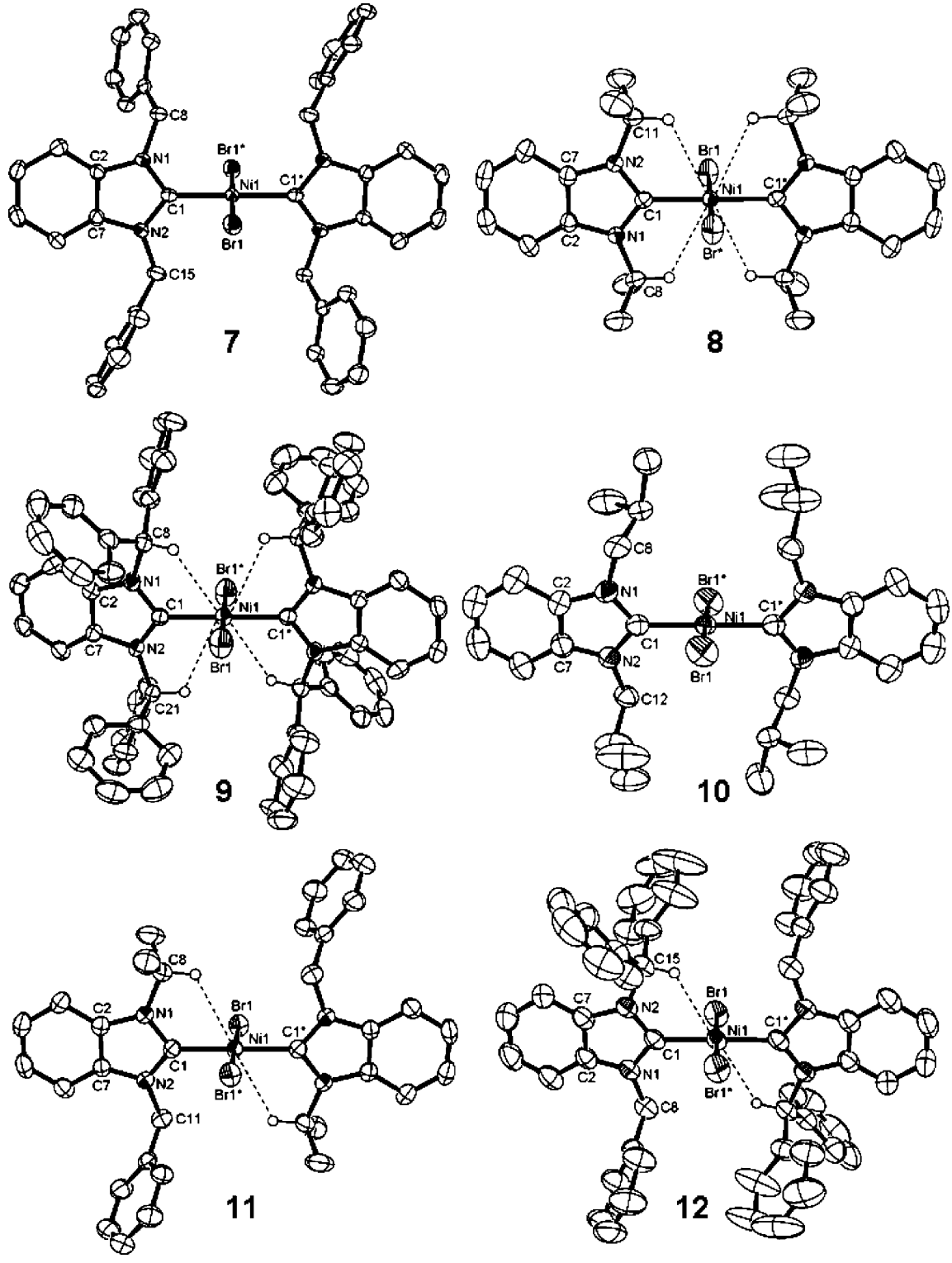
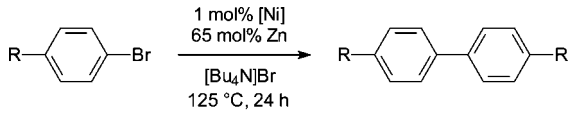


Figure 1. Molecular structures of complexes **7**−**12** showing 50% probability ellipsoids. Solvent molecules and hydrogen atoms except for C−H···Ni interactions have been omitted for clarity.

the essentially square-planar complexes with the nickel atoms as the inversion center. To the best of our knowledge, cis-configured dihalo-bis(carbene) complexes of nickel(II) have not been reported so far. For complexes **11** and **12**, bearing unsymmetrically substituted benzimidazolin-2-ylidenes, only the more favorable trans-anti arrangement was detected in the solid state. The Pd−C bond lengths are found in the narrow range 1.898–1.922 Å, and the Pd−Br bond lengths amount to 2.3003–2.3175 Å. These values are common for this type of complex and do not require any further comments. More importantly, a more detailed investigation of the structures **8**, **9**, **11**, and **12** reveals a fixed orientation for all isopropyl and benzhydryl substituents with their C−H groups pointing to the nickel center, resulting in C−H···Ni distances shorter than the sum of van der Waals radii of 2.83 Å for Ni and H (Table 1). This observation corroborates the aforementioned anagostic interactions found in solution. Interestingly, it was also observed that the number of these C−H···Ni interactions is directly

Table 3. Ullmann Coupling Reactions[a] of Aryl Bromides Catalyzed by Complexes 7–12



entry	catalyst	aryl halide	yield[b] [%]
1	**7**	bromobenzene	76
2	**8**	bromobenzene	92
3	**9**	bromobenzene	88
4	**10**	bromobenzene	79
5	**11**	bromobenzene	71
6	**12**	bromobenzene	95
7	**7**	4-bromoanisole	40
8	**8**	4-bromoanisole	65
9	**9**	4-bromoanisole	67
10	**10**	4-bromoanisole	56
11	**11**	4-bromoanisole	58
12	**12**	4-bromoanisole	62
13	$Ni(OAc)_2$/salt **5**	bromobenzene	82

[a] Reaction conditions generally not optimized. [b] Isolated yield.

related to the dihedral angle between the carbene ring plane and the NiC_2Br_2 coordination plane. For example, complexes **8** and **9**, with four C−H···Ni interactions, have the largest dihedral angles of 87.60° and 86.56°, whereas **11** and **12**, with two such interactions, still have angles of 84.96° and 83.40°, respectively. Complexes **7** and **10** exhibit the smallest dihedral angle of only 80.18° and 76.42° due to the absence of such interactions.

Catalysis. In a preliminary study, complexes **7**−**12** were screened for their catalytic activities in the reductive Ullmann coupling reaction, and the results obtained are summarized in Table 3. The homocoupling of bromobenzene and 4-bromoanisole with 1 mol % catalyst loading and 65 mol % Zn as reducing agent was chosen as standard test reactions. Disappointingly, it was found that the coupling reactions were successful neither in dry DMF nor in DMF with 1.5 mmol of $[Bu_4N]Br$ as an additive. The unsuccessful coupling observed here may be due to autoionization of the nickel(II) carbene complexes in DMF, which resulted in catalyst deactivation. Nickel(II) phosphine analogues are known to undergo such autoionization processes in polar solvent with weakly coordinating anions, leading to catalyst inactivity.[21] Ionic liquids (ILs) as alternatives to common organic solvents have been found to give rise to remarkable improvements in many transition metal-catalyzed reactions.[22] It was also reported previously that nickel(II) carbene catalysts give rise to highly active catalysts in olefin dimerization when stabilizing imidazolium-based ionic liquids were used as reaction media.[4] Since the Ni(II) complexes described here were synthesized and found to be stable in $[Bu_4N]Br$, we opted for its use as IL for further catalytic studies. The use of $[Bu_4N]Br$ as IL also avoids carbene scrambling, which is likely to occur with imidazolium-based ILs, and the simple ammonium salt can be easily removed after the reaction by triturating with deionized water. Indeed, catalytic coupling of aryl bromides occurs in molten $[Bu_4N]Br$ at 125 °C. It was found that complexes **8**, **9**, and **12**, with sterically more demanding substituents on the carbene ligands, exhibit the best catalytic activity for both bromobenzene (entries 2, 3, 6) and 4-bromoanisole (entries 8, 9, 12). This is in agreement with the general notion that sterically bulky ligands can facilitate the reductive elimination under formation of the desired biaryl products together with the regeneration of the catalytically active species. The yields for the coupling of bromobenzene is generally higher than that for 4-bromoanisole, which is expected. In addition to the well-defined precatalysts **7**−**12**, we have also studied the potential of in situ-generated catalyst by employing mixtures of 1 mol % of $Ni(OAc)_2$ and 4 mol % of the carbene precursor **5**, ceteris paribus. Notably, this simple mixture shows a better performance compared to the preformed catalyst precursor **11** and could effectively couple bromobenzene in 82% yield (entry 13). We attribute this to a slight excess of the carbene precursor, which helps to stabilize the catalytically active nickel species during the reaction. The preliminary results obtained here are encouraging thus far in comparison to other reported systems. For example, a similar coupling of 4-bromoanisole employing 10 mol % of $[NiBr_2(PPh_3)_2]$ and 150 mol % of Zn in the presence of 100 mol % of NEt_4I gave a yield of 66%.[23] The hydroquinone-mediated Pd-catalyzed Ullmann coupling of 4-bromoanisole utilizing 4 mol % of more costly $Pd(OAc)_2$ and $As(o\text{-tol})_3$, 50 mol% of hydroquinone, and 100 mol % of Cs_2CO_3 afforded an even lower yield of 54%.[24] In contrast, satisfactory yields could be obtained with only 1 mol % of the nickel(II) carbene complexes **7**−**12**. However, a coupling of aryl chlorides has been unsuccessful so far. Further studies are underway to optimize the reaction conditions and to extend the scope of Ni(II)-benzimidazolin-2-ylidene complexes in catalysis.

Conclusion

Six bis(benzimidazolin-2-ylidene) complexes of nickel(II), **7**−**12**, with increasing steric demands have been synthesized and fully characterized. Complexes **8**, **9**, **11**, and **12**, bearing *N*-isopropyl and *N*-benzhydryl substituents, exhibit rare intramolecular C−H···Ni anagostic or preagostic interactions. A comparison of these interactions with those found in Pd(II), Pt(II), and Au(III) analogues suggests a direct correlation to the Lewis acidity of the metal center. A preliminary study also reveals that all complexes show a moderate to good catalytic activity in the Ullmann homocoupling of simple aryl bromides. Complexes with bulkier ligands were found to be more active. Studies to extend the application of these complexes in catalysis as well as to gain a better understanding of their rare anagostic interactions are ongoing.

Experimental Section

General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. All solvents were used as received. All chemicals were used as received without any further treatment if not noted otherwise. Benzimidazolium salt **2** was prepared according to a literature procedure.[12] ^1H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 spectrometer, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^1H, ^{13}C). ESI mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

(21) Angulo, I. M.; Bouwman, E.; Lutz, M.; Mul, W. P.; Spek, A. L *Inorg. Chem.* **2001**, *40*, 2073.

(22) (a) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772. (b) Hermann, W. A.; Böhm, V. P. W. *J. Organomet. Chem.* **1999**, *572*, 141. (c) Böhm, V. P. W.; Hermann, W. A. *Chem.−Eur. J.* **2000**, *6*, 1017.

(23) Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80.

(24) Hennings, D. D.; Iwama, T.; Rawal, V. H. *Org. Lett.* **1999**, *1*, 1205.

1,3-Dibenzylbenzimidazolium Bromide (1). Benzimidazole (1.182 g, 10 mmol) was suspended in CH_3CN (20 mL), NaOH (1.60 mL, 10 mmol, 6.25 M) was added, and the reaction mixture was left to stir for 30 min before benzyl bromide (1.20 mL, 10 mmol) was added. The mixture was stirred overnight at 80 °C, and the solvent was removed. The residue was dissolved in THF, and insoluble NaBr was filtered off before the solvent was removed in vacuo. The resulting residue was dissolved in toluene (30 mL), and another portion of benzyl bromide (1.20 mL, 10 mmol) was added. The reaction mixture was stirred overnight at 80 °C. The white precipitate formed was filtered off and washed with toluene and diethyl ether. Yield: 3.110 g (8.20 mmol, 82%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.16 (s, 1 H, NCHN), 7.98 (dd, 2 H, Ar−H), 7.63 (dd, 2 H, Ar−H), 7.56–738 (m, 10 H, Ar−H), 5.82 (s, 4 H, CH_2). ^{13}C NMR (75.48 MHz, DMSO-d_6): δ 142.7 (NCN), 133.9, 131.1, 129.0, 128.7, 128.3, 126.8, 114.0 (Ar−C), 50.0 (CH_2). MS (ESI): *m*/*z* 299 [M − Br]$^+$.

1,3-Dibenzhydrylbenzimidazolium Bromide (3). Benzimidazole (1.181 g, 10 mmol) was suspended in CH_3CN (20 mL). NaOH (1.60 mL, 10 mmol, 6.25 M) was added to the suspension, and the reaction mixture was stirred for 30 min before a solution of benzhydryl bromide (2.471 g, 10 mmol) dissolved in CH_3CN (10 mL) was added. The reaction mixture was heated under reflux overnight, and another portion of benzhydryl bromide (2.471 g, 10 mmol) dissolved in CH_3CN (10 mL) was added. Stirring of the reaction mixture under reflux continued overnight. After cooling to ambient temperature, all volatiles were removed under vacuum, and deionized water was added to the residue. The product was extracted using CH_2Cl_2 (5 × 50 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was evaporated off under reduced pressure. The crude product was washed several times with ethyl acetate and dried under vacuum to yield a white solid. Yield: 2.389 g (6.20 mmol, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.89 (s, 1 H, NCHN), 7.76 (s, 2 H, CH), 7.48–7.10 (m, 24 H, Ar−H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 143.0 (NCN), 135.7, 132.3, 129.8, 129.7, 128.8, 127.4, 115.7 (Ar−C), 66.9 (CH). MS (ESI): *m*/*z* 451 [M − Br]$^+$.

1,3-Diisobutylbenzimidazolium Bromide (4). A mixture of benzimidazole (591 mg, 5 mmol) and K_2CO_3 (760 mg, 5.5 mmol) was suspended in CH_3CN (3 mL) and stirred at ambient temperature for 1 h. To the suspension was added isobutyl bromide (1.40 mL, 15 mmol). The reaction mixture was stirred under reflux conditions for 24 h followed by a second addition of isobutyl bromide (1.40 mL, 15 mmol). Stirring under reflux continued for an additional 72 h. After removing the volatiles in vacuo, CH_2Cl_2 (50 mL) was added to the residue and the resulting suspension was filtered over Celite. The remaining solid was washed with CH_2Cl_2 (5 × 20 mL), and the solvent of the filtrate was removed in vacuo to give a spongy solid, which upon washing with ethyl acetate afforded the product as a white powder. Yield: 1.058 g (3.4 mmol, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.60 (s, 1 H, NCHN), 7.58–7.75 (m, 4 H, Ar−H), 4.48 (d, 4 H, $^3J_{HH}$ = 7.6 Hz, CH_2), 2.44 (m, 2 H, $^3J_{HH}$ = 6.9 Hz, CH), 1.05 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 143.1 (NCN), 131.5, 127.4, 113.5 (Ar−C), 54.3 (CH_2), 29.0 (CH), 19.9 (CH_3). MS (ESI): *m*/*z* 231 [M − Br]$^+$.

1-Isopropyl-3-benzylbenzimidazolium Bromide (5). Benzimidazole (1.181 g, 10 mmol) was suspended in CH_3CN (20 mL). NaOH (1.60 mL, 10 mmol, 6.25 M) was added to the suspension, and the reaction mixture was stirred for 30 min before benzyl bromide (1.20 mL, 10 mmol) was added. The reaction mixture was heated under reflux overnight and the solvent removed under vacuum. The precipitated NaBr was dissolved in deionized water, and the monosubstituted product was extracted using CH_2Cl_2. The crude product obtained after removal of the solvent was then dissolved in CH_3CN (20 mL), and isopropyl bromide (1.87 mL, 20 mmol) was added. The reaction mixture was heated under reflux overnight. Isopropyl bromide (5.61 mL, 60 mmol) was added every 24 h in three portions, and the reaction was monitored by TLC. The solvent was removed under vacuum, and the resulting residue was washed with ethyl acetate and dried under vacuum to yield a white solid. Yield: 3.134 g (9.46 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.81 (s, 1 H, NCHN), 7.74–7.72 (m, 1 H, Ar−H), 7.64–7.54 (m, 6 H, Ar−H), 7.42–7.33 (m, 2 H, Ar−H), 6.00 (s, 2 H, CH_2), 5.00 (m, 1 H, $^3J_{HH}$ = 6.7 Hz, CH), 1.87 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 140.7 (NCN), 133.0, 131.3, 130.7, 129.1, 128.9, 128.4, 127.2, 127.1, 114.0, 113.7 (Ar−C), 51.7 (CH_2), 51.1 (CH), 22.3 (CH_3). MS (ESI): *m*/*z* 251 [M − Br]$^+$.

1-Benzhydryl-3-benzylbenzimidazolium Bromide (6). Benzimidazole (1.181 g, 10 mmol) was suspended in CH_3CN (20 mL). NaOH (1.60 mL, 10 mmol, 6.25 M) was added to the suspension, and the reaction mixture was stirred for 30 min before benzyl bromide (1.20 mL, 10 mmol) was added. The reaction mixture was heated under reflux overnight, and CH_3CN was removed under vacuum. The precipitated NaBr was dissolved in deionized water, and the monosubstituted product was extracted using CH_2Cl_2. The crude product obtained after removal of the solvent was then dissolved in CH_3CN (20 mL), and a solution of benzhydryl bromide (2.471 g, 10 mmol) dissolved in CH_3CN (10 mL) was added. The reaction mixture was heated under reflux overnight, and the solvent was removed under vacuum. The resulting residue was washed with ethyl acetate and dried under vacuum to yield a white solid. Yield: 4.064 g (8.92 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.79 (s, 1 H, NCHN), 7.63 (s, 1 H, CH), 7.60–7.15 (m, 19 H, Ar−H), 5.97 (s, 2 H, CH_2). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 142.1 (NCN), 135.3, 132.8, 131.6, 131.2, 129.4, 129.3, 129.2, 129.0, 128.5, 128.2, 127.3, 127.2, 115.0, 114.1 (Ar−C), 66.2 (CH), 51.5 (CH_2). MS (ESI): *m*/*z* 375 [M − Br]$^+$.

General Procedure for the Preparation of *trans*-Dibromobis(benzimidazolin-2-ylidene)nickel(II) Complexes (7–12). A sample of $Ni(OAc)_2$ (0.177 g, 1 mmol) and the appropriate benzimidazolium bromide (2 mmol) were mixed with $[Bu_4N]Br$ (2 g, excess) and thoroughly dried under vacuum at 80 °C. After slow heating to 130 °C (170 °C for **9**) the molten mixture was stirred at this temperature for 12 h (36 h for **9**) under vacuum. Upon cooling, the solid mixture was triturated with water (∼50 mL). The insoluble red product was filtered, washed with ethanol, and dried under vacuum.

Dibromobis(1,3-dibenzylbenzimidazolin-2-ylidene)nickel(II) (7). Yield: 0.578 g (0.71 mmol, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (b, 2 H, Ar−H), 7.28 (b, 4 H, Ar−H), 6.96 (b, 2 H, Ar−H), 6.46 (b, 2 H, CH_2). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 135.6, 135.1, 128.6, 127.8, 127.7, 122.3, 110.7 (Ar−C), 52.8 (CH_2). Anal. Calc for $C_{42}H_{36}Br_2N_4Ni$: C, 61.88; H, 4.45; N, 6.87. Found: C, 61.64; H, 4.50; N, 6.81. MS (ESI): *m*/*z* 735 [M − Br]$^+$.

Dibromobis(1,3-diisopropylbenzimidazolin-2-ylidene)nickel(II) (8). Yield: 0.486 g (0.78 mmol, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (dd, 4 H, Ar−H), 7.39 (m, 4 H, NC*H*(CH_3)$_2$), 7.14 (dd, 4 H, Ar−H), 1.95 (d, 24 H, CH_3). The ^{13}C NMR spectrum of **8** could not be obtained due to low solubility. Anal. Calc for $C_{26}H_{36}Br_2N_4Ni$: C, 50.12; H, 5.82; N, 8.99. Found: C, 50.04; H, 5.92; N, 9.03. MS (ESI): *m*/*z* 543 [M − Br]$^+$.

Dibromobis(1,3-dibenzhydrylbenzimidazolin-2-ylidene)nickel(II) (9). Yield: 0.381 g (0.34 mmol, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.73 (s, 4 H, CH), 7.45–7.10 (m, 44 H, Ar−H), 6.83–6.68 (m, 4 H, Ar−H). The ^{13}C NMR spectrum of **9** could not be obtained due to low solubility. Anal. Calc for $C_{66}H_{52}Br_2N_4Ni$: C, 70.80; H, 4.68; N, 5.00. Found: C, 71.00; H, 4.39; N, 5.17. MS (ESI): *m*/*z* 1039 [M − Br]$^+$.

Dibromobis(1,3-diisobutylbenzimidazolin-2-ylidene)nickel(II) (10). Yield: 278 mg (0.41 mmol, 41%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.14 (m, 8 H, Ar−H), 5.14 (d, 8 H, $^3J_{HH}$ = 7.7 Hz, CH_2), 3.28 (m, 4 H, CH), 1.26 (d, 24 H, $^3J_{HH}$ = 5.9 Hz, CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 183.4 (NCN), 135.8, 122.2, 110.9 (Ar−C),

Table 4. Selected X-ray Crystallographic Data for Nickel(II) Complexes 7–12

	7	**8**	**9**	**10**	**11**	**12**·DMF
formula	$C_{42}H_{36}Br_2N_4Ni$	$C_{26}H_{36}Br_2N_4Ni$	$C_{66}H_{52}Br_2N_4Ni$	$C_{30}H_{44}Br_2N_4Ni$	$C_{34}H_{36}Br_2N_4Ni$	$C_{60}H_{58}Br_2N_6O_2Ni$
M_r	815.28	623.12	1119.65	679.22	719.20	1113.65
color, habit	orange, rod	orange, block	orange, plate	red, block	orange, plate	orange, block
cryst size [mm]	0.56 × 0.14 × 0.12	0.20 × 0.16 × 0.10	0.16 × 0.10 × 0.04	0.36 × 0.20 × 0.18	0.34 × 0.24 × 0.04	0.40 × 0.32 × 0.20
temperature [K]	223(2)	223(2)	295(2)	223(2)	223(2)	223(2)
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	*Pbca*	$P2_1/c$	*Pbca*	$P2_1/c$	$P2_1/c$
a [Å]	5.8346(4)	17.0371(9)	10.8585(6)	11.2799(7)	10.993(7)	10.5341(5)
b [Å]	18.1330(11)	9.4576(5)	15.3435(9)	15.3817(4)	10.787(7)	17.8161(8)
c [Å]	16.3959(10)	17.5727(8)	15.6337(8)	18.4142(12)	13.442(9)	14.2407(7)
α [deg]	90	90	90	90	90	90
β [deg]	91.495(2)	90	90.693(2)	90	94.954(15)	94.9870(10)
γ [deg]	90	90	90	90	90	90
V [Å^3]	1734.08(19)	2831.5(2)	2604.5(2)	3194.9(4)	1588.0(18)	2662.5(2)
Z	2	4	2	4	2	2
D_c [g cm^{-3}]	1.561	1.462	1.428	1.412	1.504	1.389
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	2.901	3.527	1.954	3.133	3.156	1.914
θ range [deg]	1.67–27.50	2.32–27.49	1.86–25.00	2.21–27.50	2.30–27.50	1.83–27.50
no. of unique data	12006	18702	15232	21424	10874	18906
max., min. transmn	0.7222, 0.2934	0.7193, 0.5389	0.9259, 0.7451	0.8343, 0.3034	0.8841, 0.4133	0.7008, 0.5148
final *R* indices	$R_1 = 0.0408$	$R_1 = 0.0353$	$R_1 = 0.0600$	$R_1 = 0.0441$	$R_1 = 0.0395$	$R_1 = 0.0497$
[$I > 2\sigma(I)$]	$wR_2 = 0.1054$	$wR_2 = 0.0777$	$wR_2 = 0.1228$	$wR_2 = 0.1057$	$wR_2 = 0.0900$	$wR_2 = 0.1144$
R indices (all data)	$R_1 = 0.0511$, $wR_2 = 0.1108$	$R_1 = 0.0551$, $wR_2 = 0.0839$	$R_1 = 0.1073$, $wR_2 = 0.1394$	$R_1 = 0.0755$, $wR_2 = 0.1178$	$R_1 = 0.0583$, $wR_2 = 0.0968$	$R_1 = 0.0880$, $wR_2 = 0.1283$
goodness-of-fit on F^2	1.045	1.027	1.005	1.034	1.033	0.993
peak/hole [e Å^{-3}]	1.521/−0.282	0.602/−0.330	0.464/−0.342	0.585/−0.251	0.813/−0.323	0.915/−0.316

55.9 (CH_2), 29.0 (CH), 21.4 (CH_3). Anal. Calc for $C_{30}H_{44}Br_2N_4Ni$: C, 53.05; H, 6.53; N, 8.25. Found: C, 53.02; H, 6.30; N, 8.49. MS (ESI): *m*/*z* 599 [M − Br]$^+$.

Dibromobis(1-isopropyl-3-benzylbenzimidazolin-2-ylidene)-nickel(II) (11). Yield: 0.575 g (0.80 mmol, 80%, mixture of trans-anti and trans-syn isomers). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, 2 H, Ar−H), 7.55–6.90 (m, 16 H, Ar−H), 7.43 (m, 2 H, CH), 6.56 (s, CH_2), 6.42 (s, CH_2), 1.99 (d, $^3J_{HH} = 7.1$ Hz, CH_3), 1.77 (d, $^3J_{HH} = 7.1$ Hz, CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 184.3 (NCN), 136.5, 136.2, 133.4, 129.7, 129.2, 129.0, 128.3, 128.2, 112.2, 111.3 (Ar−C), 54.6 (CH_2), 53.0 (CH), 30.0 (CH_3). Anal. Calc for $C_{34}H_{36}Br_2N_4Ni$: C, 56.78; H, 5.05; N, 7.79. Found: C, 56.99; H, 4.85; N, 7.89. MS (ESI): *m*/*z* 639 [M − Br]$^+$.

Dibromobis(1-benzhydryl-3-benzylbenzimidazolin-2-ylidene)-nickel(II) (12). Yield: 0.203 g (0.21 mmol, 21%, mixture of trans-anti and trans-syn isomers). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.51 (s, CH), 9.42 (s, CH), 7.45–6.45 (m, 38 H, Ar−H), 6.57 (s, CH_2), 6.52 (s, CH_2). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 186.6 (NCN), 137.6, 137.3, 135.1, 134.9, 134.5, 134.4, 133.8, 128.5, 128.2, 127.7, 127.5, 127.1, 112.3, 110.3 (Ar−C), 66.6 (CH), 53.0 (CH_2). Anal. Calc for $C_{54}H_{44}Br_2N_4Ni$: C, 67.04; H, 4.58; N, 5.79. Found: C, 67.29; H, 4.21; N, 5.65. MS (ESI): *m*/*z* 887 [M − Br]$^+$.

General Procedure for the Ullmann Coupling Reaction. The nickel(II) carbene complex (0.02 mmol), zinc powder (0.085 g, 1.30 mmol), and [Bu_4N]Br (2 g, excess) were placed in a Schlenk tube together with a stirring bar. The mixture was dried at 80 °C under vacuum for 1 h and subsequently slowly heated to 125 °C under nitrogen until the ionic liquid melted. Then the mixture was stirred for 15 min. Liquid aryl halides (2 mmol) were then injected using a syringe. Solid aryl halides were dried together with the other reagents. The reaction mixture was stirred at 125 °C for 24 h, quenched with deionized water, and filtered. The biaryl product was then extracted with ether and dried over $MgSO_4$. After removal of the solvent the product was washed with hexane and dried under vacuum. The identity of the biaryl product was confirmed by ^{1}H NMR spectroscopy and TLC by comparison of the R_f values with authentic samples.

X-ray Diffraction Studies. Diffraction data for **7**−**12** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least-squares on F^2 using SHELXL-97[25] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. A summary of the most important crystallographic data is given in Table 4.

Acknowledgment. We thank the National University of Singapore for financial support (Grant No. R 143-000-268-112). Technical support from staff at the CMMAC of our department is appreciated.

Supporting Information Available: Crystallographic data for **7**−**12** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800004J

(25) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Germany, 1997.