Unexpected Solvent-Induced Cis/Trans Isomerization and Catalytic Application of a Bis-bidentate Nickel(II) Complex with N-Heterocyclic Carbene and Amido Functionalities

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A series of bis-bidentate nickel(II) complexes with bifunctional ligands of N-heterocyclic carbene and amido moieties were prepared from the ligand precursors, $[L^1H^1H^2]Cl$ and $[L^2H^1{}_2H^2]Cl$ (H^1 = N*H*C=O, H^2 = NC*H*N), in 48−82% yields. The complexes $NiL^1{}_2$ and $Ni(L^2H^1)_2$ are stable in the air and toward moisture. They are characterized by NMR (1D and 2D) and single-crystal X-ray diffraction studies. According to the NMR, crystallographic, and PXRD studies, one of the $NiL^1{}_2$ complexes undergoes an intriguing reversible solvent-induced cis/trans transformation process, producing the cis form with DMSO and trans with $CHCl_3$. The exchange process is highly specific and can be explained by the higher polarity of cis-$NiL^1{}_2$, which favors the polar DMSO solvent, whereas the less polar trans form due to cancellation of polarity from the trans disposition of ligands favors the less polar $CHCl_3$ solvent. A DFT calculation is in support of the experimental findings. Unlike the previous reported palladium analogues, $NiL^1{}_2$ and $Ni(L^2H^1)_2$, in the presence of PPh_3 as cocatalyst, are highly efficient in catalyzing the Suzuki cross-coupling reaction of aryl chlorides with phenylboronic acid. A 3 mol % of $NiL^1{}_2$ (Ni:PPh_3 = 1:2) was sufficient to mediate the formation of 4-methoxy-1,1′-biphenyl from 4-chloroanisole in 95% yield in 12 h.

Introduction

Even though palladium catalysts are widely used in C−C cross-coupling reactions because of their remarkable catalytic activities,[1] the use of catalysts based on nickel has advantages of cheaper cost, higher activities toward unreactive aryl chloride, and easier removal from the final products.[2] Some of the nickel catalysts, in fact, have been shown to be more effective than their corresponding palladium systems.[3] Since palladium complexes with N-heterocyclic carbene (NHC) ligands are proven to be very versatile in catalyzing various cross-coupling reactions,[4] there is growing interest in exploring nickel NHC complexes as catalytic precursors.[5−8] Lately, we have demonstrated that nickel complexes with bidentate ligands of phosphine and NHC functionalities are very effective in utilizing unreactive, electron-rich aryl chlorides as substrates for the Suzuki cross-coupling reactions.[8]

Herein, we report on chelate complexes of nickel(II) with NHC and amido functionalities (Scheme 1). The palladium(II) systems derived from $[L^1H^1H^2]Cl$ and $[L^2H^1{}_2H^2]Cl$ were reported by us recently.[9] Our results indicated that bis-bidentate palladium complexes with L^1 are not effective in mediating the Suzuki cross-coupling reactions due to stable chelate ring formation. However, in light of the large difference in activities between palladium and nickel systems with the bidentate ligand of NHC and phosphine functionalities,[8a,10] we are interested to see if nickel(II) complexes based on $[L^1H^1H^2]Cl$ and $[L^2H^1{}_2H^2]$-Cl can be more effective in mediating the catalytic reaction. Herein, we report that the bis-bidentate nickel(II) system in combination with PPh_3 as cocatalyst is indeed efficient. Rather unexpectedly, in the course of our investigation, we also discovered an intriguing solvent-induced cis/trans isomerization exchange in the bis-bidentate nickel(II) complex. The cis/trans isomerization in square-planar d^8 complexes containing monodentate ligands is a well-documented phenomenon.[11] Recent examples involving the isomerization reaction are the molecular devices reported by Yam et al.[12] The monodentate palladium-

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(1) (a) *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, 95, 2457.

(2) Tucker, C. E.; de Vries, J. G. *Top. Catal.* **2002**, *19*, 111.

(3) (a) Blakey, S. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2003**, *125*, 6046. (b) Liu, J.; Robins, M. J. *Org. Lett.* **2004**, *6*, 3421.

(4) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69. (c) Herrmann, W. A.; Öfele, K.; von Preysing, D.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229. (d) Christmann, U.; Vilar, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 366.

(5) (a) Ho, C.-Y.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 782. (b) Mahandru, G. M.; Liu, G.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 3698. (c) Ng, S.-S.; Jamison, T. F. *Tetrahedron* **2006**, *62*, 11350. (d) Sato, Y.; Sawaki, R.; Mori, M. *Organometallics* **2001**, *20*, 5510.

(6) (a) Schleicher, K. D.; Jamison, T. F. *Org. Lett.* **2007**, *9*, 875. (b) Schaub, T.; Radius, U. *Chem.−Eur. J.* **2005**, *11*, 5024.

(7) (a) Inamoto, K.; Kuroda, J.; Hiroya, K.; Noda, Y.; Watanabe, M.; Sakamoto, T. *Organometallics* **2006**, *25*, 3095. (b) Schaub, T.; Backes, M.; Radius, U. *J. Am. Chem. Soc.* **2006**, *128*, 15964. (c) Matsubara, K.; Ueno, K.; Shibata, Y. *Organometallics* **2006**, *25*, 3422. (d) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3387. (e) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596. (f) Inamoto, K.; Kuroda, J.; Danjo, T.; Sakamoto, T. *Synlett* **2005**, *10*, 1624.

(8) (a) Lee, C.-C.; Ke, W.-C.; Chan, K.-T.; Lai, C.-L.; Hu, C.-H.; Lee, H. M. *Chem.−Eur. J.* **2007**, *13*, 582. (b) Chiu, P. L.; Lai, C.-L.; Chang, C.-F.; Hu, C.-H.; Lee, H. M. *Organometallics* **2005**, *24*, 6169.

(9) Liao, C.-Y.; Chan, K.-T.; Zeng, J.-Y.; Hu, C.-H.; Tu, C.-Y.; Lee, H. M. *Organometallics* **2007**, *26*, 1692.

(10) Lee, H. M.; Chiu, P. L.; Zeng, J. Y. *Inorg. Chim. Acta* **2004**, *357*, 4313.

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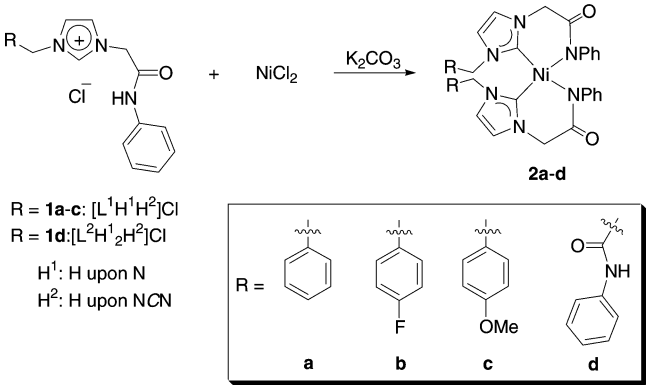
Scheme 1



(II) complexes involved can undergo a cis/trans exchange process upon allosteric interactions of metals and anions.[12] In contrast, the isomerization reaction observed in square-planar d^8 systems with two bidentate ligands is very rare in the literature.[13] The solvent-induced interconversion between the cis and trans forms of bis(bidentate) NiL^1_2 reported herein is highly specific toward solvent molecules. Our DFT calculations reveal that the change in configuration in response to specific solvents can be related to the high polarity difference between the two stereoisomers.

Results and Discussion

Preparation of Bidentate Complexes of Nickel(II). The ligand precursors $[L^1H^1H^2]Cl$ (**1a**−**c**) and $[L^2H^1{}_2H^2]Cl$ (**1d**) (H^1 = H on N, H^2 = H on NCN) were reported by us previously.[9] The initial strategy was to employ their silver complexes[14] as carbene transfer reagent for the preparation of nickel(II) complexes. The use of silver carbene complexes in transmetalation reactions is a well-established synthetic route.[15] Even though NMR spectroscopy indicated the successful formation of bidentate nickel complexes, other side products were detectable as well. The clean way to prepare the nickel complexes is by a procedure similar to that for its palladium analogue.[9] Thus, a direct reaction between imidazolium precursor **1**, $NiCl_2$, and K_2CO_3 in either DMF or pyridine gives **2a**−**d** in 48−82% yields (Scheme 1). The nickel complexes are stable in air and toward moisture. The complexes, except **2a**, have very limited solubility in halogenated solvent but dissolve readily in highly polar solvents such as DMF and DMSO.

According to subsequent structural determination, complex **2** is neutral bis-bidentate NiL^1_2 for L^1 and $Ni(L^2H^1)_2$ for L^2H^1. Their ^1H NMR spectra in DMSO-d_6 exhibit sharp signals in the diamagnetic region, reflecting their singlet spin multiplicity and square-coordination geometry. For **2a**−**c**, the lack of the original downfield signals due to H^1 and H^2 strongly indicates

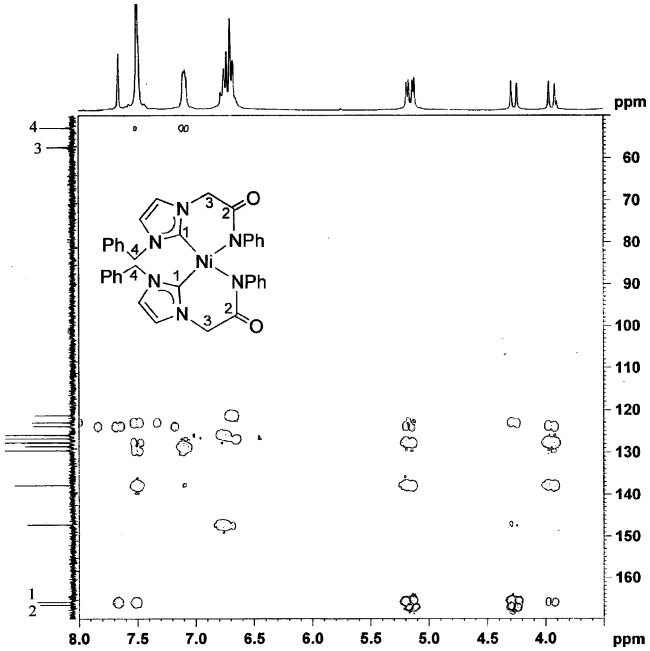


Figure 1. HMBC NMR spectrum of **2a** in DMSO-d_6.

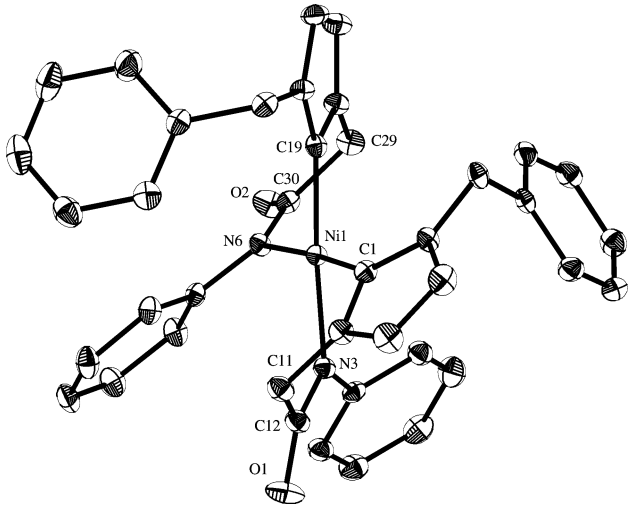


Figure 2. Thermal ellipsoid plot of **2a** at the 35% probability level. Selected bond distances (Å): Ni1−C1, 1.860(2); Ni1−C19, 1.853(3); Ni1−N3, 1.939(2); Ni1−N6, 1.938(2). Selected bond angles (deg): C1−Ni1−C19, 96.21(11); C1−Ni1−N3, 86.43(10); C19−Ni1−N6, 87.11(10); N3−Ni1−N6, 90.59(9); C1−Ni1−N6, 175.37(11); C19−Ni1−N3, 173.78(10).

the formation of bidentate nickel complexes. For **2d**, the singlet at 10.21 ppm and its integration value show that only one of the H^1 hydrogens in $[L^2H^1{}_2H^2]Cl$ was deprotonted, reflecting the formation of a bidentate complex as well. Attempts had been made to mediate full deprotonation of $[L^2H^1{}_2H^2]Cl$ for the formation of a pincer-type $[NiL^2(py)]$ complex. The palladium analogue, $[PdL^2(py)]$, was prepared by us previously.[9] However, such efforts always resulted in the isolation of only **2d**. In each complex, the upfield region shows four well-resolved doublets attributable to the diastereotopic protons of the two methylene groups. Since the two geminal coupling constants involved are so similar (14−15 Hz), we obtained their 2D HMBC spectra for unambiguous assignments of these proton signals (Figure 1 and Figures 1S−2S in the Supporting Information). For example in the spectrum of **2a**, correlation peaks were found from the doublets at 4.27 and 5.15 ppm to the carbonyl carbon at 166.6 ppm, indicating that these protons are attached to the C atom

(11) (a) Nelson J. H.; Redfield, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 6219. (b) Redfield, D. A.; Nelson, J. H.; Henry, R. A.; Moore D. W.; Jonassen, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 6298. (c) Kim, Y. J.; Park, J. I.; Lee, S. C.; Osakada, K.; Tanabe, M.; Choi, J. C.; Koizumi T.; Yamamoto, T. *Organometallics* **1999**, *18*, 1349. (d) Alibrandi, G.; Scolaro L. M.; Romeo, R. *Inorg. Chem.* **1991**, *30*, 4007. (e) Minniti, D. *Inorg. Chem.* **1994**, *33*, 2631.

(12) (a) Yam, V. W.-W.; Lu, X.-X.; Ko, C.-C. *Angew. Chem., Int. Ed.* **2003**, *42*, 3385. (b) Lu, X.-X.; Tang, H.-S.; Ko, C.-C.; Wong, J. K.-Y.; Zhu, N.; Yam, V. W.-W. *Chem. Commun.* **2005**, 1572.

(13) Boeré, R. T.; Montgomery, C. D.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1985**, *24*, 3680.

(14) Silver(I) complexes derived from **1** will be reported elsewhere.

(15) (a) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972. (b) Bildstein, B.; Malaun, M.; Kopacka, H.; Wurst, K.; Mitterböck, M.; Ongania, K.-H.; Opromolla, G.; Zanello, P. *Organometallics* **1999**, *18*, 4325.

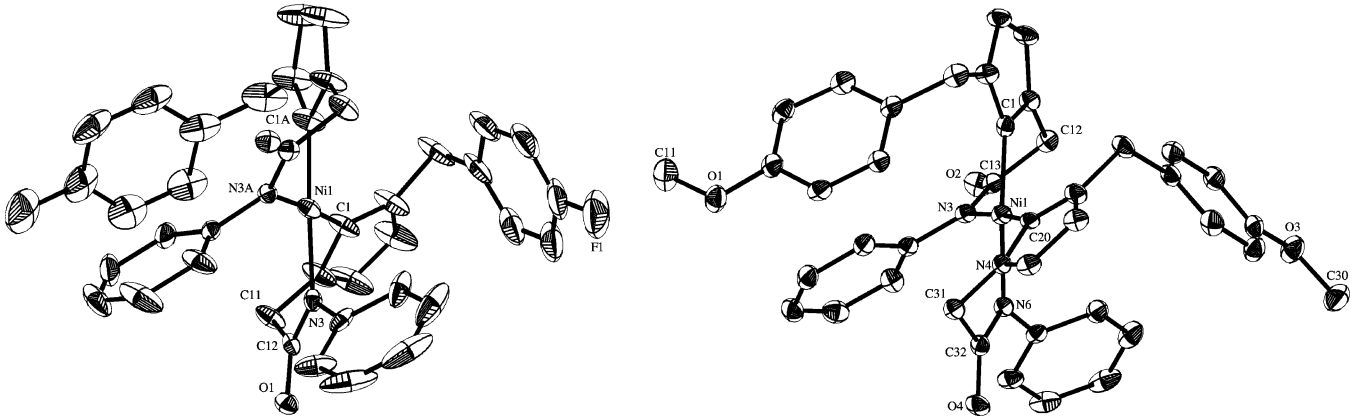


Figure 3. Left: Thermal ellipsoid plot of **2b** at the 35% probability level. Selected bond distances (Å): Ni1−C1, 1.858(3); Ni1−C1A, 1.858(3); Ni1−N3, 1.937(2); Ni1−N3A, 1.937(2). Selected bond angles (deg): C1−Ni1−C1A, 94.52(19); N3−Ni1−N3A, 91.10(13); C1−Ni1−N3, 87.28(11); C1A−Ni1−N3A, 87.28(11); C1−Ni1−N3A, 176.32(11); C1A−Ni1−N3, 176.32(11). Right: Thermal ellipsoid plot of **2c** at the 35% probability level. Selected bond distances (Å): Ni1−C1, 1.864(3); Ni1−C20, 1.866(3); Ni1−N3, 1.941(3); Ni1−N6, 1.934(3). Selected bond angles (deg): C1−Ni1−C20, 96.86(14); N3−Ni1−N6, 90.18(11); C1−Ni1−N3, 86.49(12); C20−Ni1−N6, 86.88-(12); C1−Ni1−N6, 173.59(11); C20−Ni1−N3, 174.54(12).

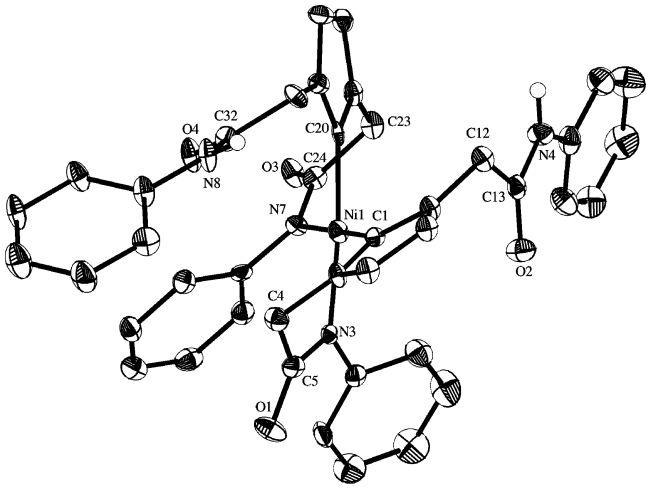


Figure 4. Left: Thermal ellipsoid plot of **2d** at the 35% probability level. Hydrogen atoms except NH are omitted for clarity. Selected bond distances (Å): Ni1−C1, 1.843(5); Ni1−C20, 1.846(5); Ni1−N3, 1.939(4); Ni1−N7, 1.950(4). Selected bond angles (deg): C1−Ni1−C20, 90.5(2); N3−Ni1−N7, 92.40(18); C1−Ni1−N3, 87.4(2); C20−Ni1−N7, 89.5(2); C1−Ni1−N7, 177.9(2); C20−Ni1−N3, 173.4(2).

adjacent to the C═O group. The HMBC spectrum also distinguishes the carbene and the carbonyl carbons, which resonate very closely. The presence of HMBC correlations from the protons of both methylene groups to the signal at 165.9 ppm reveals its carbene carbon identity. Another noticeable feature of their ^{1}H NMR spectrum is the presence of upfield phenyl signals in the range 6.5−6.9 ppm. These protons are likely in the vicinity of shielding zones of aromatic systems. The observation reflects steric crowding around the nickel centers and, hence, is consistent with a 2:1 L to Ni ratio for these complexes.

Subsequently, we discovered that **2a** exhibits a solvent-induced cis and trans isomerization (vide infra). On the basis of the X-ray crystallographic structure of **2a**·DMSO, we conclude that the NMR data of **2a** in DMSO-d_6 correspond to a similar structure with cis disposition of ligands. Complexes **2b**-**d** are also cis isomers in DMSO solution because of the similarity of their NMR data to those of **2a**.

Structural Characterizations of Nickel(II) Complexes. To establish the cis/trans configuration of the complexes, we determined their solid structures from crystals obtained from DMSO or DMF solutions of the compounds. Figures 2−4 show the molecular structures of **2a**−**d** with selected bond lengths and bond angles listed in the captions. Complexes **2a**, **2b**, and **2d** crystallized with guest solvent molecules of DMSO, H_2O, and DMF, respectively, in their asymmetric units. These solvent molecules do not interact with the nickel atoms. The complex **2c** shows no solvent incorporation. The structural determinations reveal the bis-bidentate $NiL^1{}_2$ and $Ni(L^2H^1)_2$ structures and cis disposition of the ligands. In each structure, the two C−Ni−N bonds deviate from linearity, reflecting the distorted square coordination geometry of the nickel center. For example, the C1−Ni1−N6 and C19−Ni1−N3 angles in *cis*-**2a** are 175.37-(11)° and 173.78(10)°, respectively. Generally, the Ni−C bonds (1.843(5)−1.866(3) Å) are shorter than the Ni−N bonds (1.938-(2)−1.950(4) Å). The Ni−carbene bonds are comparable to those of nickel(II) complexes with NHC moieties in cis disposition.[8,16]

The bidentate ligands in **2d** contains NH protons, which are involved in strong hydrogen-bonding interactions with C═O groups of guest solvent DMF (d(O···H) = 2.064 Å, ∠(O···H−N) = 154.3°) and the N(Ni)C═O moiety of a neighboring complex (d(O···H) = 1.945 Å, ∠(O···H−N) = 159.9°). The latter synthon links molecules of **2d** into 1D chains along the *b*-axis (Figure 3S). No such chain structure exists in **2a**−**c**.

From the same powder sample leading to the crystal structure of **2a**·DMSO, crystals were also formed by slow evaporation from its chloroform solution. Markedly, the full structural determination reveals a new structure of chloroform solvate in which the two ligands are in trans disposition. Figure 5 shows the molecular structure of *trans*-**2a** (**2a′**). Ni1 sits on a special position of inversion site symmetry with only half of the metal complex and a chloroform molecule present in an asymmetric unit. The symmetry operation generates the whole molecule, and as a result, in contrast to that in *cis*-**2a**, Ni1 in *trans*-**2a** is in ideal square coordination geometry. The chloroform solvent molecules do not interact with the nickel atom. Notably, the Ni−C bond of 1.908(5) Å is significantly longer than those of 1.860(2) and 1.853(3) Å in *cis*-**2a**, whereas the Ni−N bond is

(16) (a) Wang, X.; Liu, S.; Jin, G.-X. *Organometallics* **2004**, *23*, 6002. (b) Baker, M. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *J. Chem. Soc., Dalton Trans.* **2001**, 111. (c) Li, W.-F.; Sun, H.-M.; Wang, Z.-G.; Chen, M.-Z.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2005**, *690*, 6227.

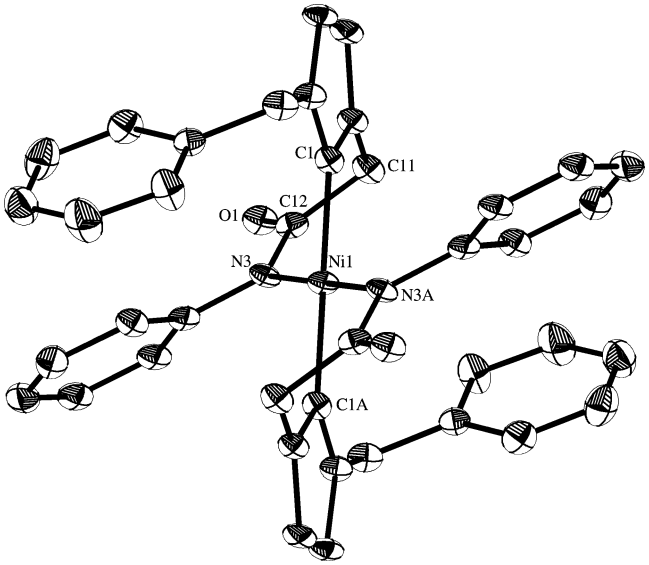


Figure 5. Thermal ellipsoid plot of **2a′** at the 35% probability level. Selected bond distances (Å): Ni1−C1, 1.908(5); Ni1−C1A, 1.908(5); Ni1−N3, 1.916(4); Ni1−N3A, 1.916(4). Selected bond angles (deg): C1−Ni1−C1A, 180.0; N3−Ni1−N3A, 180.0; C1−Ni1−N3, 87.70(19); C1−Ni1−N3A, 92.29(19); C1A−Ni1−N3, 92.30(19); C1A−Ni1−N3A, 87.70(19).

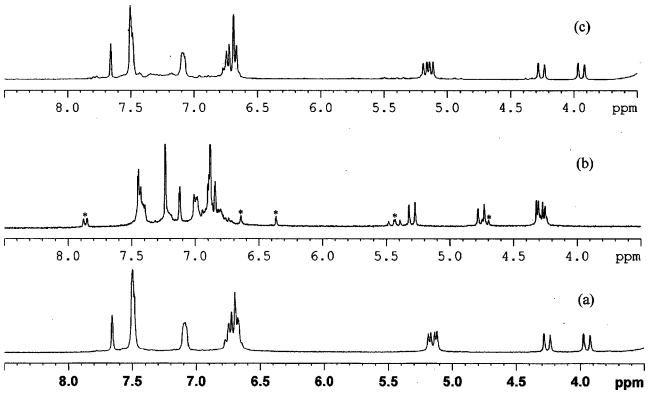


Figure 6. Solvent-dependent NMR spectra of **2a**: (a) in DMSO-d_6; (b) DMSO-d_6 removed, and then redissolved in $CDCl_3$; (c) the $CDCl_3$ in (b) removed, and then redissolved in DMSO-d_6. Asterisks (*) denote signals from unidentified species.

shorter (1.914(4) vs 1.939(2) and 1.938(2) Å). Again, these are consistent with the stronger trans influence of the carbene than that of the amido group. The Ni−C bond is in the normal range of nickel(II) complexes with NHC groups trans to each other.[8a,17]

Solvent-Induced Isomerism. Since the ^{1}H NMR spectrum of **2a** in DMSO-d_6 indicated a single cis product of very high purity, the crystallographic results of *trans*-**2a**·2$CHCl_3$ prompted us to acquire an ^{1}H NMR spectrum of **2a** in $CDCl_3$. Indeed, the spectrum of **2a** in $CDCl_3$ is sharply different from that in DMSO-d_6. The spectrum exhibits a major product albeit with signals of low intensities from other species (Figure 6). Similar to the spectrum in DMSO-d_6, four well-resolved doublets are observed for the two methylene groups. According to the HMBC spectrum, the protons at 4.30 and 5.30 ppm (J = 14.4 Hz) are on the C atom next to the C═O group, whereas the protons at 4.28 and 4.76 pm (J = 15.0 Hz) are on the benzylic methylene carbon. Intriguingly, removal of the $CDCl_3$ solvent and redissolution of the residue in DMSO-d_6 regenerated the original spectrum in the latter solvent. On the basis of the crystallographic structure of *trans*-**2a**·2$CHCl_3$, the ^{1}H NMR spectrum of sample **2a** in $CDCl_3$ is mostly consistent with a similar trans-NiL^1_2 structure.[18] Interestingly, the more polar DMSO exerts a predominate effect, as a 1:1 mixture of DMSO-d_6/$CDCl_3$ gave a clean spectrum of *cis*-**2a**. The exchange behavior was also observed with solvent combinations of DMF-d_7/$CDCl_3$ and DMSO-d_6/CD_2Cl_2. The limited solubility of complexes **2b**−**d** in halogenated solvent, however, precludes the observation of such phenomenon.

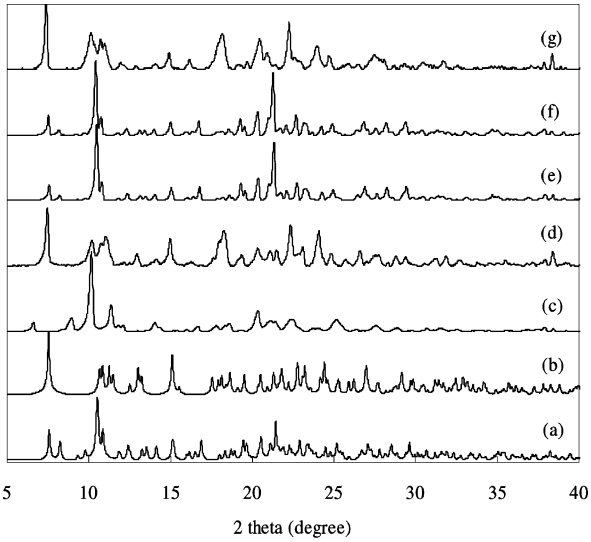
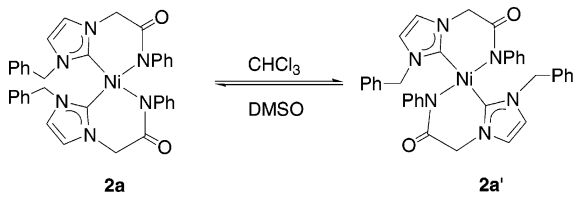


Figure 7. PXRD patterns: (a) simulation based on the single-crystal analysis of *cis*-**2a**; (b) simulation based on the single-crystal analysis of *trans*-**2a**; (c) as-synthesized **2a**; (d) as-synthesized **2a** after stirring in $CHCl_3$; (e) as-synthesized **2a** after stirring in DMSO; (f) as-synthesized **2a** after stirring in $CHCl_3$ and then DMSO; (g) as-synthesized **2a** after stirring in DMSO and then $CHCl_3$. Radiation: Cu Kα, λ = 1.54060 Å.

Scheme 2



The crystallographic and NMR results, therefore, suggest a solvent-induced cis and trans isomeric exchange (Scheme 2). In DMSO solvent, the cis isomer is solely formed, whereas it converts to the trans form upon introduction of $CHCl_3$ solvent. Although this exchange process was observed in solution and solvated crystal structures of *cis*-**2a**·C_2H_6SO and *trans*-**2a**·2$CHCl_3$ were obtained from the appropriate solvents, whether structural change occurred in the bulk solid isolated after solvent treatment (i.e., in the absence of solvent matrix) needs to be clarified. Thus, we carried out PXRD analysis (Figure 7). Traces a and b show the simulated PXRD patterns based on the crystallographic data of *cis*-**2a**·C_2H_6SO and *trans*-**2a**·2$CHCl_3$, respectively. The solvate-free structure of the as-synthesized **2a** gives a unique powder pattern (trace c). Since **2a** was prepared in pyridine, which is of similar polarity to DMSO, it is reasonable to suggest a cis configuration of ligands in the

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

(18) Crystals confirmed to be *trans*-**2a**·2$CDCl_3$were formed on standing in the NMR solution for a few hours.

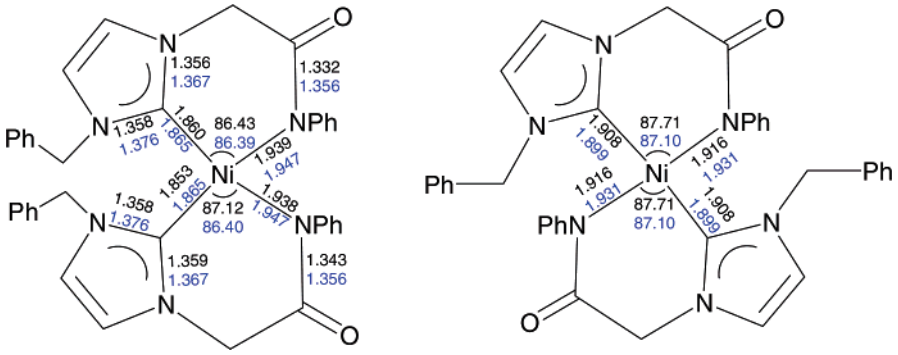
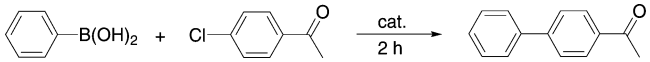


Figure 8. Selected geometrical parameters of the cis and trans forms of **2a** from X-ray crystallography (in black) and from DFT optimization (in blue). Bond distances and angles are in Å and deg, respectively.

solvate-free **2a**. Interestingly, after stirring the as-synthesized **2a** in chloroform for 0.5 h, the residue upon removal of the solvent shows a PXRD pattern of trace d, which matches well with that of *trans*-**2a**·2$CHCl_3$ in trace b (extra peaks were detected that may be contributed from the unidentified species (vide supra)). Similarly, after stirring the as-synthesized sample in DMSO, the remaining powder shows a PXRD trace matching very well with that of *cis*-**2a**·DMSO structure (trace e). The reversible interconversion between cis and trans isomers with appropriate solvents is clearly demonstrated from traces f and g. Therefore, the PXRD analyses provide supportive evidence for the cis and trans configuration change in the bulk solid **2a** in response to solvents.

Theoretical Studies. Solvent effects have been shown to be crucial in isomerization reactions.[19,20] For example, a work related to this exchange phenomenon was reported by Goddard et al.[20] They analyzed the cis/trans isomerization equilibrium of chloride ligands in ruthenium NHC complexes related to olefin metathesis by DFT calculation. The study shows that the cis form is 1.1 kcal/mol more stable than the trans form in dichlormethane, whereas the cis form becomes 2 kcal less stable than the trans form in benzene. Thus, their results suggest that the product ratios can be shifted from either mostly trans to mostly cis by simply changing solvents. For the palladium system with L^1 reported by us previously,[9] contrastingly, both cis-PdL^1_2 and trans-PdL^1_2 were formed generally and, in certain cases, either one of them can be isolated in pure form by virtue of their solubility difference. Computational study shows that trans-PdL^1_2 is more stable by ca. 5.8 kcal/mol; nevertheless, the trans/cis forms are not interconvertible by changing solvents and no isomerization process occurs at all accessible temperatures, as demonstrated by variable-temperature NMR study. To understand the relative stability of the cis and trans isomers of **2a**, DFT computations using the B3LYP/6-31G(d)//B3LYP/6-31G approach were carried out. Our DFT-optimized geometrical parameters for the two isomers are in excellent agreement with those obtained from X-ray crystallography (Figure 8). In the gas phase, we found that the trans isomer is 8.9 kcal/mol lower in energy than the cis isomer. It was noticed that the cis isomer is very polar, having a dipole moment of 14.6 D. In contrast, the trans isomer is nonpolar. The polar property of the cis isomer lowers its relative energy with respect to the trans isomer in the presence of solvent molecules. When we accounted for the solvation free energies with $CHCl_3$, the trans isomer is 0.6 kcal/mol lower in energy than the cis isomer. When we applied the much polar solvent DMSO, the cis isomer is 2.1 kcal/mol lower in energy than the trans isomer. Thus, the computational data using DFT are in accord with our experimental findings; that is, the trans isomer was isolated in $CHCl_3$, while the cis isomer was isolated in DMSO. As illustrated by variable-temperature NMR studies, however, no isomerization occurs in a solution of **2a** in either DMSO or $CHCl_3$ at all accessible temperatures.

Table 1. Suzuki Coupling with 4-Chloroacetophenone[a]



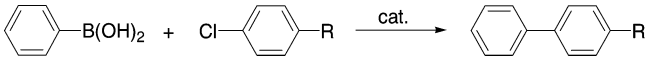
entry	cat.	mole of PPh_3	yield (%)
1	**2a**		10
2	**2b**		11
3	**2c**		12
4	**2d**		15
5	**2a**	2	100 (95)
6	**2b**	2	100 (94)
7	**2c**	2	100 (92)
8	**2d**	2	100 (92)

[a] Reaction conditions: 1 mmol of aryl chlorides, 1.3 mmol of $PhB(OH)_2$, 2.6 mmol of $K_3PO_4·H_2O$ as base, 1 mol % of catalyst, 3 mL of toluene, 80 °C, GC yield. Isolated yield in parentheses.

Catalytic Studies. The catalytic property of **2** in the Suzuki cross-coupling was tested using a range of standard aryl halides with different electronic properties. We employed similar catalytic conditions reported by us[8] and others[21] with the use of 1−3 mol % of **2** as precatalyst in the presence of 2−6 mol % of PPh_3 (1:2 Ni/PPh_3). The solvent employed is toluene, in which **2** is insoluble. It is anticipated that the cis/trans configuration of catalytic precursor **2** is invariant to the catalytic activity, as previously demonstrated by their palladium analogues.[9] Table 1 clearly shows that the addition of PPh_3 is essential for **2** to mediate the cross-coupling reaction with the reactive substrate 4-chloroacetophenone. The use of monophosphines as co-ligands has been shown to enhance activities of several catalytic systems,[8a,22] and there has been interest in complexes with both phosphine and NHC moieties.[8a,23] Without the cocatalyst, low yields of products were obtained (entries 1−4), whereas quantitative production of coupled products can be achieved in 2 h with the addition of PPh_3 (entries 5−8). The NiL_2/2PPh_3 system is also effective in utilizing less reactive aryl chlorides as substrates (Table 2). In general, excellent yields of 4-methyl-1,1′-biphenyl and 4-methoxy-1,1′-biphenyl can be

(19) Kail, B. W.; Basu, P. *Dalton Trans.* **2006**, 1419.
(20) Benitez, D.; Goddard, W. A., III. *J. Am. Chem. Soc*. **2005**, *127*, 12218.
(21) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. *J. Org. Chem.* **2004**, *69*, 3447.
(22) (a) Schnyder, A.; Indolese, A. F.; Studer, M.; Blaser, H.-U. *Angew. Chem., Int. Ed*. **2002**, *41*, 3668. (b) Bedford, R. B.; Cazin, J. C. S.; Hazelwook, S. L. *Chem. Commun.* **2002**, 2608. (c) Spencer, J.; Sharratt, D. P.; Dupont, J.; Monteiro, A. L.; Reis, V. I.; Stracke, M. P.; Rominger, F.; McDonald, I. M. *Organometallics* **2005**, *24*, 5665.

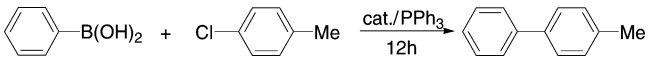
Table 2. Suzuki Coupling with Unactivated and Deactivated Aryl Chlorides[a]



entry	cat.	mole of cat.	R	time (h)	yield (%)
1	**2a**	2	Me	12	97
2		3	OMe	18	92
3	**2b**	2	Me	6	93
4		3	OMe	18	88
5	**2c**	2	Me	12	97
6		3	OMe	18	100
7	**2d**	2	Me	12	100 (>99)
8		3	OMe	12	95

[a] Reaction conditions: 1 mmol of aryl chlorides, 1.3 mmol of $PhB(OH)_2$, 2.6 mmol of $K_3PO_4 \cdot H_2O$ as base, 2−3 mol % of catalyst, cat:PPh_3 = 1:2, 3 mL of toluene, 80 °C, GC yield; isolated yield in parentheses.

Table 3. Suzuki Coupling Mediated by Different Complexes[a]



entry	cat.	yield (%)
1	NiL^1_2 (**2a**)	97
2[b]	cis-PdL^1_2 (R = **a**)	0
3	$Ni(dppe)Cl_2$	93
4	trans-$[NiL'_2]Cl_2$	95

[a] Reaction conditions: 1 mmol of aryl chloride, 1.3 mmol of $PhB(OH)_2$, 2.6 mmol of $K_3PO_4 \cdot H_2O$ as base, 2 mol % of catalyst, cat:PPh_3 = 1:2, 3 mL of toluene, 80 °C, GC yield. [b]Reaction conditions according to those reported in ref 9.

achieved in 6−18 h with 2−3 mol % of catalyst. The NiL_2/$2PPh_3$ system is equally effective toward aryl bromide albeit with a longer reaction time. For example, complex **2b** utilizes 4-bromoacetophenone to produce the cross-coupled product quantitatively in 6 h. Finally, it is necessary to gauge the effectiveness of **2** with relevant catalytic systems reported in the literature (Table 3). Entries 1, 3, and 4 show that **2a** in the presence of PPh_3 is equally effective with $NiCl_2(dppe)$[21] and trans-$[NiL'_2]Cl_2$[8a] (L′ is a bidentate ligand of NHC and phosphine functionalities). Notably, a comparison of entries 1 and 2 clearly demonstrates the much higher effectiveness of the present Ni system than the corresponding Pd system reported by us earlier.[9]

Conclusions

A series of air- and moisture-stable bis-bidentate nickel complexes with L^1 and L^2H^1 were prepared. On the basis of NMR, crystallographic, and PXRD studies, we confirm that bis-(bidentate) complex **2a** undergoes a rare solvent-induced cis/trans interconversion, yielding cis-NiL^1_2 with DMSO and trans-NiL^1_2 with $CHCl_3$. The trans and cis forms of PdL^1_2 do not exhibit this solvent-induced exchange process. The change in configuration in response to solvents can be explained by the higher polarity of the cis-NiL^1_2, which favors the polar DMSO solvent, whereas the trans form, due to cancellation of polarity from the trans disposition of ligands, favors the less polar $CHCl_3$ solvent. A DFT calculation is in agreement with the experimental findings. In $CHCl_3$, the trans form is 0.6 kcal/mol more stable than the cis form, whereas the cis form becomes more stable by 2.1 kcal/mol in DMSO. The highly specific nature of the isomerization exchange in response to external stimuli (DMSO vs $CHCl_3$) is, in fact, an important property of molecular switching devices.

Previously, we demonstrated that PdL^1_2 is an inefficient catalytic precursor in the Suzuki coupling reaction. The stable chelate ring due to the nondissociative property of NHC and anionic amido groups precludes the availability of coordination sites for substrate binding. From this work, the effectiveness of NiL^1_2 in the Suzuki coupling reactions and the phenomenon of facile exchange process indicate a markedly different reactivity pattern of NiL^1_2 from PdL^1_2.

Experimental Section

General Procedure. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified according to standard procedures.[24] Commercially available chemicals were purchased from Aldrich or Acros. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13 and 75.48 MHz, respectively, on a Bruker AV-300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual proton of $CDCl_3$ (^1H: 7.24 ppm; ^{13}C: 77.0 ppm) and DMSO-d_6 (^1H: 2.50 ppm; ^{13}C: 39.5 ppm). Elemental analyses and ES-MS mass spectra were performed on a Heraeus CHN-OS Rapid elemental analyzer and a Finnigan/Thermo Quest MAT 95XL, respectively, at the Instruments Center of National Chung Hsing University, Taiwan. Powder X-ray diffraction (PXRD) measurements were recorded on a Shimadzu Lab-X XRD-6000 diffractometer with Cu Kα, λ = 1.54060 Å. The syntheses of imidazolium salts **1a**−**e** were according to the literature procedure.[9]

Synthesis of 2a. A mixture of **1a** (0.106 g, 0.324 mmol), K_2CO_3 (0.134 g, 0.972 mmol), and $NiCl_2$ (0.0210 g, 0.162 mmol) in pyridine (10 mL) was heated at 80 °C for 16−20 h. After cooling, the solvent was completely removed under vacuum. The residue was redissolved in dichloromethane (15 mL), and the organic layer was washed twice with water and dried with anhydrous $MgSO_4$. The volume of the solvent was reduced to ca. 3 mL under vacuum. Addition of diethyl ether gave a yellow solid, which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 0.0849 g, 82%. Mp: 278−279 °C. Anal. Calc for $C_{36}H_{32}N_6O_2Ni$: C, 67.63; H, 5.04; N, 13.14. Found: C, 68.01; H, 5.04; N, 13.03. ^1H NMR (DMSO-d_6): δ 3.94 (d, J_{HH} = 15.3 Hz, 2H, CH_aH_bPh), 4.27 (d, J_{HH} = 14.7 Hz, 2H, $CH_aH_bC{=}O$), 5.15 (d, J_{HH} = 14.7 Hz, 2H, $CH_aH_bC{=}O$), 5.17 (d, J_{HH} = 15.3 Hz, 2H, CH_aH_bPh), 6.68−6.78 (m, 10H, Ph-*H*), 7.09−7.10 (m, 4H, Ph-*H*), 7.49−7.51 (m, 8H, Ph-*H*, imi-*H*), 7.66 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 52.9 (*C*H_2Ph), 57.5 (*C*H_2C═O), 121.2 (*C*H), 122.9 (imi-*C*H), 123.8 (imi-*C*H), 125.8 (*C*H), 126.6 (*C*H), 127.6 (*C*H), 128.5 (*C*H), 129.5 (*C*H), 137.7 (quaternary *C*), 147.1 (quaternary *C*), 165.9 (Ni−*C*), 166.6 (*C*═O).

Synthesis of 2b. The compound was synthesized following a procedure similar to that for **2a**. A mixture of **1b** (0.163 g, 0.470 mmol), K_2CO_3 (0.130 g, 0.941 mmol), and $NiCl_2$ (0.0305 g, 0.235 mmol) in DMF (10 mL) was used. A yellow solid was obtained. Yield: 0.111 g, 70%. Mp: 250 °C. Anal. Calc for $C_{36}H_{30}N_6O_2F_2Ni \cdot 0.5CH_2Cl_2$: C, 61.07; H, 4.35; N, 11.70. Found: C, 61.33; H, 4.60; N, 11.79. ^1H NMR (DMSO-d_6): δ 3.97 (d, J_{HH} = 15.3 Hz, 2H, CH_aH_bPh), 4.29 (d, J_{HH} = 14.5 Hz, 2H, $CH_aH_bC{=}O$), 5.12 (d, J_{HH} = 15.3 Hz, 2H, CH_aH_bPh), 5.23 (d, J_{HH} = 14.5 Hz, 2H,

(23) See, for example: (a) Albert, K.; Gisdakis, P.; Rösch, N. *Organometallics* **1998**, *17*, 1608. (b) Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, G. R. J. *Chem.−Eur. J.* **1996**, *2*, 1627. (c) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511. (d) Danopoulos, A. A.; Winston, S.; Gelbrich, T.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commun.* **2002**, 482. (e) Tsoureas, N.; Danopoulos, A. A.; Tulloch, A. A. D.; Light, M. E. *Organometallics* **2003**, *22*, 4750. (f) Wang, A.-E.; Zhong, J.; Xie, J.-H.; Li, K.; Zhou, Q.-L. *Adv. Synth. Catal.* **2004**, *346*, 595. (g) Lee, H. M.; Zeng, J. Y.; Hu, C.-H.; Lee, M.-T. *Inorg. Chem.* **2004**, *43*, 6822. (h) Gischig, S.; Togni, A. *Eur. J. Inorg. Chem.* **2005**, 4745. (i) Zhong, J.; Xie, J.-H.; Wang, A.-E.; Zhang, W.; Zhou, Q.-L. *Synlett* **2006**, *8*, 1193.

(24) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Elsevier Science: Burlington, 2003.

Table 4. Crystallographic Data of 2

	cis-**2a**·C_2H_6SO	*trans*-**2a**·$2CHCl_3$	*cis*-**2b**·H_2O	*cis*-**2c**	*cis*-**2d**·$2C_3H_7NO$
empirical formula	$C_{36}H_{32}N_6NiO_2 \cdot C_2H_6SO$	$C_{36}H_{32}N_6NiO_2 \cdot 2CHCl_3$	$C_{36}H_{30}F_2N_6NiO_2 \cdot H_2O$	$C_{38}H_{36}N_6NiO_4$	$C_{38}H_{34}N_8NiO_4 \cdot 2C_3H_7NO$
fw	717.51	878.12	711.40	699.44	871.63
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	*Pbca*	$P2_1/n$	C_2/c	$P\bar{1}$	$P2_1/n$
a, Å	16.2756(18)	9.904(6)	15.809(3)	10.9810(5)	17.657(4)
b, Å	18.041(2)	3.413(13)	15.718(2)	11.8396(6)	14.385(3)
c, Å	23.284(3)	9.309(6)	13.543(2)	12.7934(6)	17.884(4)
α, deg	90	90	90	85.275(3)	90
β, deg	90	116.437(9)	101.777(3)	86.123(3)	112.732(7)
γ, deg	90	90	90	89.313(3)	90
V, Å^3	6837.0(13)	1932.8(19)	3294.6(10)	1653.80(14)	112.732(7)
D_c, mg m^{-3}	1.394	1.509	1.434	1.405	90
T, K	150(2)	150(2)	150(2)	150(2)	150(2)
Z	8	2	4	2	4
no. of unique data	8860	4262	3976	7575	9147
no. of params refined	451	242	222	444	554
R_1[a] [$I > 2\sigma I$]	0.0488	0.0625	0.0545	0.0552	0.0718
wR_2[b] (all data)	0.1216	0.1691	0.1285	0.1390	0.1658

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

$CH_aH_bC{=}O$), 6.70−6.81 (m, 10H, Ph-*H*), 7.10−7.15 (m, 4H, Ar-*H*), 7.33 (t, J_{HH} = 7.5 Hz, 4H, Ar-*H*), 7.50 (s, 2H, imi-*H*), 7.64 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): *δ* 52.1 (CH_2Ar), 57.5 ($CH_2C{=}O$), 116.3 (J_{CF} = 21.7 Hz, Ar-*C*H), 121.4 (Ph-*C*H), 123.0 (imi-*C*H), 123.7 (imi-*C*H), 125.8 (Ph-*C*H), 126.6 (Ph-*C*H), 129.8 (J_{CF} = 8.3 Hz, Ar-*C*H), 134.0 (Ar-quaternary *C*), 147.1 (Ph-quaternary *C*), 162.3 (d, J_{CF} = 244.4 Hz, *C*−F), 165.8 (Ni−*C*), 166.6 (*C*=O).

Synthesis of 2c. The compound was synthesized following a procedure similar to that for **2a**. A mixture of **1c** (0.129 g, 0.360 mmol), K_2CO_3 (0.0995 g, 0.720 mmol), and $NiCl_2$ (0.0233 g, 0.180 mmol) in DMF (10 mL) was used. A yellow solid was obtained. Yield: 0.0632 g, 50%. Mp: 295−298 °C. Anal. Calc for $C_{38}H_{36}N_6O_4Ni \cdot 2H_2O$: C, 62.06; H, 5.48; N, 11.42. Found: C, 62.04; H, 5.06; N, 11.37. ^1H NMR (DMSO-d_6): *δ* 3.83 (s, 6H, OCH_3), 3.88 (d, J_{HH} = 14.7 Hz, 2H, CH_aH_bPh), 4.28 (d, J_{HH} = 14.7 Hz, 2H, $CH_aH_bC{=}O$), 5.06 (d, J_{HH} = 14.7 Hz, 2H, CH_aH_b-Ph), 5.24 (d, J_{HH} = 14.7 Hz, 2H, $CH_aH_bC{=}O$), 6.70−6.77 (m, 10H, Ph-*H*), 7.05 (s, 8H, Ar-*H*), 7.49 (s, 2H, imi-*H*), 7.64 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): *δ* 52.4 (CH_2Ar), 55.7 (CH_3), 57.6 ($CH_2C{=}O$), 114.8 (Ar-*C*H), 121.3 (Ph-*C*H), 122.8 (imi-*C*H), 123.5 (imi-*C*H), 125.8 (Ph-*C*H), 126.7 (Ph-*C*H), 129.1 (Ar-*C*H), 129.8 (Ar-quaternary *C*), 147.2 (Ph-quaternary *C*), 159.5 (*C*-O), 165.8 (Ni−*C*), 166.6 (*C*=O).

Synthesis of 2d. The compound was synthesized following a procedure similar to that for **2a**. A mixture of **1d** (0.156 g, 0.423 mmol), K_2CO_3 (0.233 g, 1.69 mmol), and $NiCl_2$ (0.0547 g, 0.422 mmol) in DMF (10 mL) was used. A yellow solid was obtained. Yield: 0.147 g, 48%. Mp: 280 °C (dec). Anal. Calc for $C_{38}H_{34}N_8O_4Ni \cdot C_3H_7NO \cdot CH_2Cl_2$: C, 57.10; H, 4.91; N, 14.27. Found: C, 57.80; H, 5.43; N, 14.04. ^1H NMR (DMSO-d_6): *δ* 4.11 (d, J_{HH} = 16.8 Hz, 2H, CH_aH_bCONH), 4.26 (d, J_{HH} = 14.4 Hz, 2H, CH_aH_b-CONNi), 4.80 (d, J_{HH} = 16.8 Hz, 2H, CH_aH_bCONH), 5.54 (d, J_{HH} = 14.4 Hz, 2H, CH_aH_bCONNi), 6.72 (t, J_{HH} = 14.1 Hz, 2H, *p*-Ph-*H*), 6.83 (t, J_{HH} = 15.0 Hz, 4H, Ph-*H*), 7.11−7.16 (m, 4H, imi-*H*, Ph-*H*), 7.22 (d, J_{HH} = 7.8 Hz, 4H, Ph-*H*), 7.37−7.44 (m, 6H, Ph-*H*, imi-*H*), 7.80 (d, J_{HH} = 8.1 Hz, 4H, Ph-*H*), 10.21 (s, 2H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): *δ* 52.3 (CH_2CONH), 57.3 (CH_2-CONNi), 119.7 (*C*H), 121.2 (*C*H), 122.5 (imi-*C*H), 124.0 (imi-*C*H or Ph-*C*H), 124.1 (imi-*C*H or Ph-*C*H), 125.9 (*C*H), 127.0 (*C*H), 129.3 (*C*H), 138.9 (quaternary *C*), 147.5 (quaternary *C*), 165.3 (NH*C*=O), 166.8 (Ni-*C*), 167.1 (N*C*=O).

X-ray Data Collection. Crystals of **2** (except *trans*-**2a**) suitable for X-ray diffraction studies were grown by vapor diffusion of diethyl ether into a DMF or DMSO solution of the corresponding compound. Crystals of *trans*-**2a** were grown by slow evaporation from its chloroform solution. Typically, the crystals were removed from the vial with a small amount of mother liquor and immediately coated with silicon grease on a glass slide. A suitable crystal was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II with graphite-monochromated Mo Kα radiation (*λ* = 0.71073 Å) at 150(2) K. Crystallographic data are listed in Table 4.

Solution and Structure Refinements. All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[25] All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. The structure of **2a** consists of a disordered DMSO solvent molecule in an asymmetric unit. There are two orientations of 75:25 site of occupancy. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 644057 (*cis*-**2a**·C_2H_6SO), 644058 (*trans*-**2a**·$2CHCl_3$), 644059 (*cis*-**2b**·H_2O), 644060 (*cis*-**2c**), and 644061 (*cis*-**2d**·$2C_3H_7NO$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Computational Details. The three-parameter hybrid of exact exchange and Becke's exchange energy functional,[26] plus Lee, Yang, and Parr's gradient-corrected correlation energy functional[27] (B3LYP), were used. The 6-31G basis set for the optimization of molecular geometries was used. The relative energies of the cis and trans isomers are computed using the 6-31G-(d) basis set. The solvation free energies were computed using the conductor-like polarizable continuum model (CPCM) of Barone and Cossi.[28] The molecular free energy of the solute embedded in a continuum medium was computed with this method, in which the solute is polarized by the solvent. The approach also allows for the evaluation of the solute−solvent dispersion−repulsion energy. It has been demonstrated that the CPCM model provides predictions for the free energy of hydration that are comparable with experimental results.[28] We incorporated the dielectric constant of DMSO (*ϵ* = 46.7) and $CHCl_3$ (*ϵ* = 4.9) in the CPCM computations. The Gaussian03 suite of programs were used in our study.[29]

(25) Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker AXS Inc.: Madison, WI, 1998.
(26) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(27) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(28) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

Suzuki Coupling Reactions. In a typical reaction, a mixture of aryl halides (1.0 mmol), phenylboronic acid (1.3 mmol), $K_3PO_4 \cdot H_2O$ (2.6 mmol), and nickel(II) precatalyst (1−3 mol %) in 3 mL of toluene was stirred at 80 °C for 2−24 h under nitrogen. The solution was allowed to cool to ambient temperature for GC analysis. GC yields were calculated using benzophenone (with 4-acetylbiphenyl and 4-phenyltoluene as products) or biphenyl (with 4-phenylanisole as product) as internal standards. In the standard workup, the solvent was removed completely under vacuum. A 1:1 mixture of diethyl ether/water (20 mL) was added. The organic layer was washed, separated, further washed with another 10 mL portion of diethyl ether, and dried with anhydrous $MgSO_4$. The solution was then filtered. The solvent and any volatiles were removed completely under high vacuum to give a crude product, which was either subjected to flash chromatography or analyzed by ^{1}H NMR spectroscopy.

(29) Frisch, M. J.; et. al. *Gaussian03*, Revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003 (the full author list is provided in the Supporting Information).

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Supporting Information Available: Full crystallographic data for all the structures are provided as a CIF file. Additional HMBC spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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