Regioselective Hydroamination of Acrylonitrile Catalyzed by Cationic Pincer Complexes of Nickel(II)

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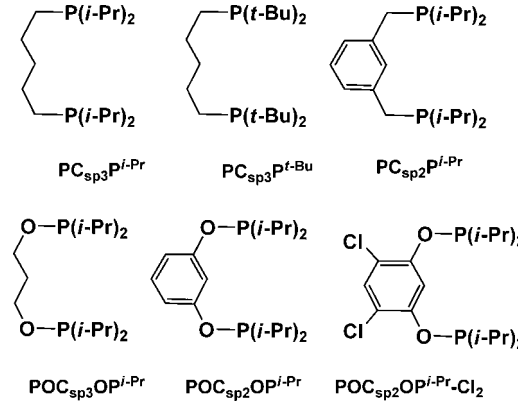
The cationic pincer-type complexes [{(i-$Pr_2PCH_2CH_2)_2CH$}Ni($NCCH_3$)][BPh_4] (**1**), [{2,6-(i-$Pr_2PCH_2)_2$-C_6H_3}Ni($NCCH_3$)][BPh_4] (**2**), [{2,6-(i-$Pr_2PO)_2$-C_6H_3}Ni($NCCH_3$)][BPh_4] (**3**), and [{2,6-(i-$Pr_2PO)_2$-3,5-Cl_2-C_6H}Ni($NCCH_3$)][BPh_4] (**6**) have been prepared and fully characterized by NMR spectroscopy and X-ray crystallography. Cyclic voltammetry measurements of the Ni−Br precursors of **2**, **3**, and **6** indicated that substituting the CH_2 moiety in the ligand skeleton by O, or some of the aromatic protons by Cl, renders the metal center less susceptible to oxidation. Evaluating the catalytic activities of **1**−**3**, **6**, and the *t*-Bu analogue of **1** for addition of aniline to acrylonitrile showed **3** to be the most competent catalyst precursor. Isolation of [{(t-$Bu_2PCH_2CH_2)_2CH$}Ni($NCCH_2CH_2NHPh$)][BPh_4] (**7**) from the reaction of [{(t-$Bu_2PCH_2CH_2)_2CH$}Ni($NCCH{=}CH_2$)][BPh_4] with aniline suggests that these cationic precursors act as Lewis acids that bind the nitrile moiety of acrylonitrile, thereby activating the olefinic moiety toward nucleophilic attack by aniline.

Introduction

A number of PCP-type pincer complexes, introduced by Shaw and co-workers in the 1970s,[1] have demonstrated good catalytic activities for a variety of organic reactions of interest.[2] In the past two decades, many groups have worked on modifying the pincer ligands to improve particular reactions or applications. Thus, Milstein, Andersson, Shibasaki, Sabounchei, and Jensen have shown that the efficiency of PCP-type Pd complexes for the Heck coupling can be increased by changing the nature of the cyclometalated carbon from sp^2 to sp^3 hybridization, incorporating oxygens in the ligand backbone, varying the phosphorus substituents from *t*-Bu to *i*-Pr, or increasing the size of the metallocycles from five- to six-membered.[3] Different donor moieties also play an important role in reactivities of pincer complexes. For instance, Milstein has found that systems based on PCN-type unsymmetrical ligands show reactivities different from those of their better-known PCP analogues in C−C vs C−H bond activation reactions,[4] and van Koten has demonstrated that the SO_2-sensing activities of Pt complexes based on NCN-type ligands can be completely altered by varying the amino substituents from Me to Et.[2a]

Chart 1



In the course of our recent studies on the PCP-type pincer complexes of nickel,[5] we have found that systems based on the ligand $PC_{sp3}P^{i\text{-}Pr}$ (Chart 1) are better catalysts for the Kumada−Corriu coupling in comparison to the closely analogous ligands $PC_{sp3}P^{t\text{-}Bu}$ and $PC_{sp2}P^{i\text{-}Pr}$.[5h] Electrochemical experiments have also shown that complexes based on $PC_{sp3}P^{i\text{-}Pr}$ and $POC_{sp3}OP^{i\text{-}Pr}$ ligands are easier to oxidize ($Ni^{II} \rightarrow Ni^{III}$) than their counterparts based on $PC_{sp2}P^{i\text{-}Pr}$ and

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(1) For some of the original reports on PCP-type pincer complexes see: (a) Moulton, C. J.; Shaw, B. L. *Dalton Trans.* **1976**, 1020. (b) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *Dalton Trans.* **1979**, 1972. (c) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *Dalton Trans.* **1980**, 59. (d) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373. (e) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Shaw, B. L. *Dalton Trans.* **1982**, 387. (f) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *Dalton Trans.* **1982**, 1217. (g) Briggs, J. R.; Constable, A. G.; McDonald, W. S.; Shaw, B. L. *Dalton Trans.* **1982**, 1225.

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(4) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870.

(5) (a) Groux, L. F.; Bélanger-Gariépy, F.; Zargarian, D. *Can. J. Chem.* **2005**, *83*, 634. (b) Sui-Seng, C.; Castonguay, A.; Chen, Y.; Gareau, D.; Groux, L. F.; Zargarian, D. *Top. Catal.* **2006**, *37*, 81. (c) Castonguay, A.; Sui-Seng, C.; Zargarian, D.; Beauchamp, A. L. *Organometallics* **2006**, *25*, 602. (d) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Acta Crystallogr.* **2007**, *E63*, m196. (e) Pandarus, V.; Zargarian, D. *Chem. Commun.* **2007**, 978. (f) Pandarus, V.; Zargarian, D. *Organometallics* **2007**, *26*, 4321. (g) Pandarus, V.; Castonguay, A.; Zargarian, D. *Dalton Trans.* **2008**, 4756. (h) Castonguay, A.; Zargarian, D.; Beauchamp, A. L. *Organometallics* **2008**, *27*, 5723.

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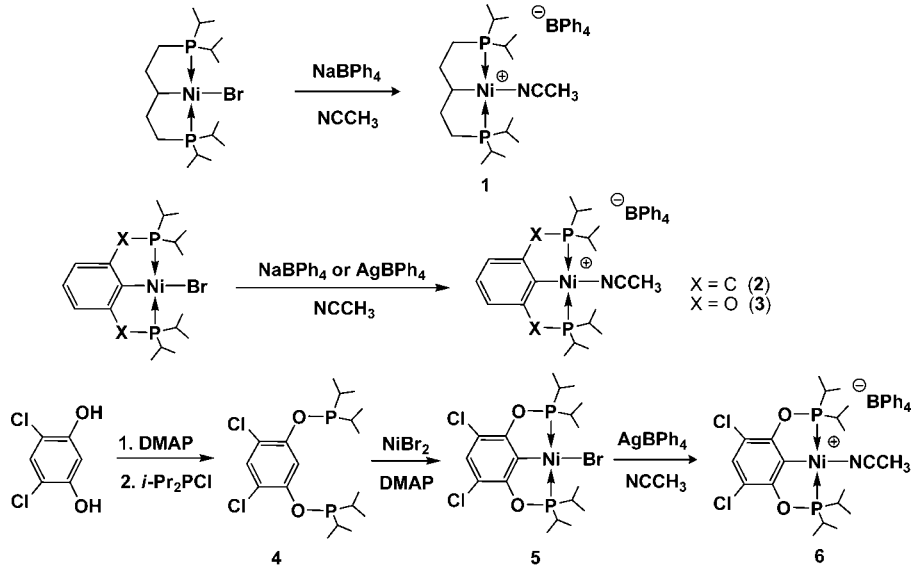
Scheme 1



$POC_{sp2}OP^{i\text{-}Pr}$ (Chart 1).[5e,h] Finally, we have shown that the cationic complexes $[(PC_{sp3}P^{t\text{-}Bu})Ni(NCCH{=}CH_2)]^+$ and $[(POC_{sp2}OP^{i\text{-}Pr})Ni(NCCH{=}CH_2)]^+$ catalyze the regioselective addition of aniline to acrylonitrile,[5b,f] but the influence of the various ligands on this reaction has not been studied.

As a continuation of the above studies, we have prepared a series of cationic adducts of acetonitrile and evaluated their catalytic activities for the addition of aniline to acrylonitrile. Previous studies[5c] have demonstrated that acrylonitrile and acetonitrile adducts are in equilibrium ($K_{eq} \approx 1$), which implies that the latter should be precatalysts for the target reaction. In addition to the ligands $PC_{sp3}P^{i\text{-}Pr}$, $PC_{sp3}P^{t\text{-}Bu}$, $PC_{sp2}P^{i\text{-}Pr}$, and $POC_{sp2}OP^{i\text{-}Pr}$, we selected a new ligand, $POC_{sp2}OP^{i\text{-}Pr}$-$Cl_2$ (Chart 1), in order to study the difference in reactivity brought about by the incorporation of electronegative Cl elements in the aromatic ring.

Results and Discussion

Synthesis and Characterization. The cationic species bearing the $PC_{sp3}P^{i\text{-}Pr}$ and $PC_{sp2}P^{i\text{-}Pr}$ ligands were prepared by reacting the previously reported precursors $(PC_{sp3}P^{i\text{-}Pr})NiBr$[5h] and $(PC_{sp2}P^{i\text{-}Pr})NiBr$[6] with $NaBPh_4$ in CH_3CN; the target complexes **1** and **2** were obtained as pale yellow powders in 85% and 79% yields, respectively (Scheme 1). Curiously, the analogous reaction of $(POC_{sp2}OP^{i\text{-}Pr})NiBr$[5e] with $NaBPh_4$ gave very low yields of $[(POC_{sp2}OP^{i\text{-}Pr})Ni(NCCH_3)][BPh_4]$, **3**, even with extended reaction times, but the use of $AgBPh_4$ allowed the preparation of the desired complex in 65% yield. The new ligand $POC_{sp2}OP^{i\text{-}Pr}$-$Cl_2$, **4**, bearing electronegative oxygen and chlorine atoms, was synthesized as shown in Scheme 1 with the intention of preparing a more electrophilic cationic complex. Reacting **4** with $NiBr_2$ and DMAP (4-(dimethylamino)pyridine) in refluxing toluene afforded complex **5** as an orange-brown solid (73% yield) that reacted with $AgBPh_4$ in acetonitrile to give the target cationic species **6** (73% yield, Scheme 1).[7]

All new complexes have been characterized by NMR spectroscopy using samples prepared in $CDCl_3$ (**1**−**3**), C_6D_6 (**5**), or CD_3CN (**6**).[8] Observation of one singlet in the $^{31}P\{^1H\}$ NMR spectra and virtual triplets in the ^1H and $^{13}C\{^1H\}$ NMR spectra of these complexes confirmed the equivalence of the two phosphorus nuclei and suggested their mutually *trans* disposition. The greater electrophilicity of the Ni centers in the cationic complexes is reflected in the more downfield ^{31}P chemical shifts of **1**−**3** and **6** compared to those of the corresponding neutral Ni−Br precursors: δ 76.5 for **1** vs 67.4 for $(PC_{sp3}P^{i\text{-}Pr})NiBr$ (C_6D_6); 70.6 for **2** vs 61.8 for $(PC_{sp2}P^{i\text{-}Pr})NiBr$ ($CDCl_3$); 191.6 for **3** vs 188.2 for $(POC_{sp2}OP^{i\text{-}Pr})NiBr$ ($CDCl_3$); 197.2 for **6** vs 192.2 for **5** (C_6D_6). The presence of a coordinated acetonitrile in **1**−**3** was indicated by a singlet resonance in their ^1H and $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$): 0.7−0.8 ppm (CH_3CN) and ∼1 ppm (CH_3CN).[9] On the other hand, the quaternary carbon of the coordinated acetonitrile molecule (CH_3CN) was only observed in the $^{13}C\{^1H\}$ NMR spectra recorded on a high-field spectrometer (176 MHz, CD_2Cl_2, δ): 130.7 (**1**), 133.0 (**2**), 128.8 (**3**), and 127.7 (**6**). These high-field spectra also allowed us to detect the triplet resonance for the cyclometalated carbon in **2** (∼153 ppm, $^2J_{PC}$ = 14 Hz), **3** (∼123 ppm, $^2J_{PC}$ = 20 Hz), and **6** (∼124 ppm, $^2J_{PC}$ = 20 Hz), while the corresponding signal for **1** (∼55 ppm, $^2J_{PC}$ = 6 Hz) was also detectable at lower fields. The assignment of the cyclometalated carbon resonance in **3** has been confirmed by a ^{31}P INEPT experiment performed in CD_3CN. Finally, bands in the 2274−2282 cm^{-1} range of the IR spectra for these complexes were assigned to $\nu(C{\equiv}N)$, consistent with a similar assignment for the previously reported $[(PC_{sp3}P^{t\text{-}Bu})Ni(NCCH_3)][BPh_4]$ (2270 cm^{-1});[5c] comparison of these values to $\nu(C{\equiv}N)$ for free acetonitrile (2254 cm^{-1}) implies little or no π-back-donation in these cationic complexes.

Solid state structural studies carried out on single crystals of all complexes allowed us to confirm the structural assignments

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(7) The high sensitivity of **4** to hydrolysis requires it to be used right after its preparation, whereas complex **6** is fairly stable to hydrolysis.

(8) Curiously, dissolving some batches of **6** in chloroform or methylene chloride converted this complex into either **3** or $(POC_{sp2}OP^{i\text{-}Pr}$-$Cl_2)NiCl$, as confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Residual hydrochloric acid, known to be present in chloroform, is known to transform our cationic pincer complexes into their Ni−Cl analogues, and we have confirmed that reaction of **6** with $HCl \cdot Et_2O$ gives the corresponding Ni−Cl derivative. However, the conversion of **6** into **3**, and the fact that this transformation is not reproducible, cannot be explained at this point.

(9) The $^{13}C\{^1H\}$ NMR spectrum of **6** in CD_2Cl_2 also displayed a singlet corresponding to CH_3CN (2.77 ppm).

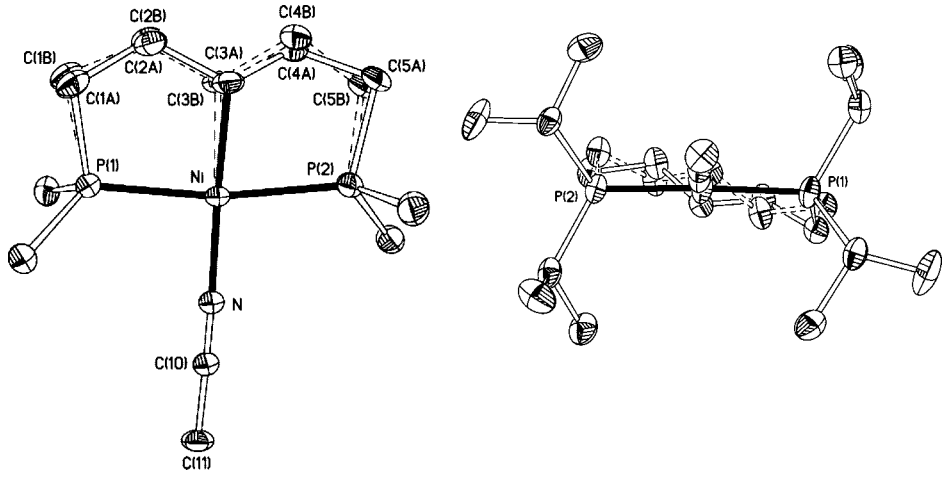


Figure 1. ORTEP diagrams for complex **1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens (and isopropyl methyl carbons of the left view) are omitted for clarity. The alkyl chain of the ligand was found to occupy two positions, in a 7:3 ratio (A:B).

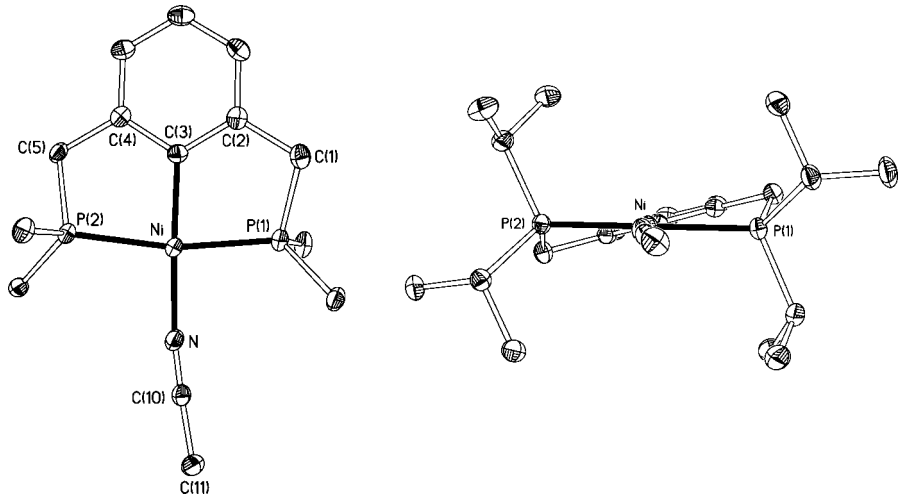


Figure 2. ORTEP views for complex **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens (and isopropyl methyl carbons of the left view) are omitted for clarity.

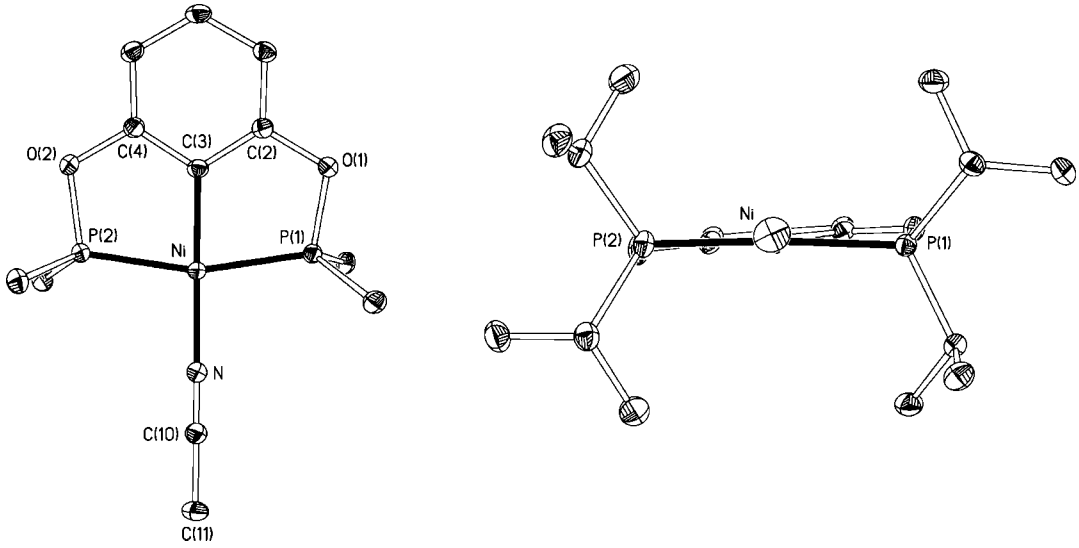


Figure 3. ORTEP views for complex **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens (and isopropyl methyl carbons of the left view) are omitted for clarity.

based on the above-discussed spectral data. ORTEP views of complexes **1**−**3** and **5** are shown in Figures 1−4, the crystal data and collection details are listed in Table 1, and selected bond distances and angles are given in Table 2; in the case of complex **6**, X-ray analysis allowed us to establish the connectivities, but low quality of the results obtained precludes

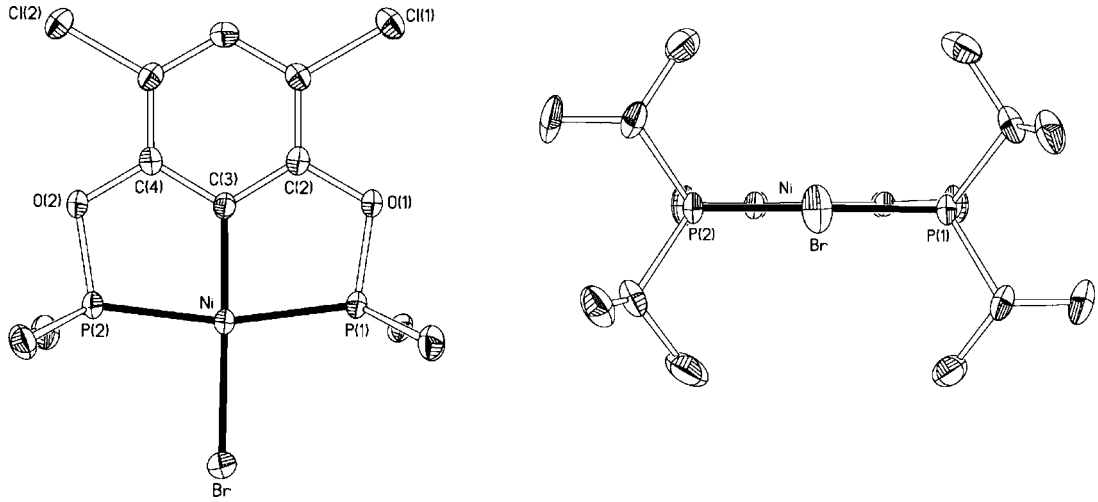


Figure 4. ORTEP diagrams for complex **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens (and isopropyl methyl carbons of the left view) are omitted for clarity.

Table 1. Crystal Data Collection and Refinement Parameters for Complexes 1−3, 5, and 7

	1	**2**	**3**	**5**	**7**
chemical formula	$C_{43}H_{60}NiP_2NB$	$C_{46}H_{58}NiP_2NB$	$C_{44}H_{54}NiP_2O_2NB.CH_3CN$	$C_{18}H_{29}BrNiCl_2P_2O_2$	$C_{54}H_{75}NiP_2N_2B$
fw	722.38	756.39	801.40	548.87	883.62
T (K)	150(2)	100(2)	153(2)	200(2)	150(2)
wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
space group	*Pbca*	*Pbca*	$P2_1/c$	$P2_1/n$	*Pbca*
a (Å)	17.8194 (6)	18.9665(9)	11.8122(4)	11.0281(5)	18.7220(3)
b (Å)	19.0036 (6)	17.7718(8)	17.2040(6)	17.9155(7)	18.4056(3)
c (Å)	23.9586 (7)	24.7209(11)	21.9175(8)	13.0131(5)	28.4880(5)
α (deg)	90	90	90	90	90
β (deg)	90	90	103.087(2)	111.017(2)	90
γ (deg)	90	90	90	90	90
Z	8	8	4	4	8
V (Å^3)	8113.2 (4)	8332.6(7)	4338.3(3)	2400.01(17)	9816.7(3)
ρ_{calcd} (g cm^{-3})	1.183	1.206	1.227	1.519	1.196
μ (cm^{-1})	16.41	16.23	16.31	65.08	14.52
θ range (deg)	3.69−78.99	3.58−69.05	3.30−72.06	4.40−72.41	3.10−69.04
R1[a] [$I > 2\sigma(I)$]	0.0524	0.0461	0.0376	0.0478	0.0499
wR2[b] [$I > 2\sigma(I)$]	0.1429	0.1128	0.0921	0.1224	0.1306
R1 [all data]	0.0704	0.0805	0.0442	0.0509	0.0761
wR2 [all data]	0.1566	0.1290	0.0949	0.1250	0.1473
GOF	1.137	0.935	0.971	1.129	1.036

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 1−3, 5, and 7

	$Ni(PC_{sp3}P^{i\text{-}Pr})^+$ (**1**)	$Ni(PC_{sp3}P^{t\text{-}Bu})^+$	$Ni(PC_{sp2}P^{i\text{-}Pr})^+$ (**2**)	$Ni(POC_{sp2}OP^{i\text{-}Pr})^+$ (**3**)	$Ni(POC_{sp2}OP^{i\text{-}Pr}\text{-}Cl_2)Br$ (**5**)	$Ni(PC_{sp3}P^{t\text{-}Bu})^+$ (**7**)
Ni−C(3)	1.9751(10) 1.9787(10)	1.969(3)	1.916(3)	1.8839(14)	1.879(2)	1.978(3)
Ni−P(1)	2.1495(9)	2.2154(10)	2.1724(8)	2.1692(5)	2.1571(6)	2.2208(8)
Ni−P(2)	2.1882(9)	2.2142(10)	2.1889(8)	2.1753(5)	2.1482(6)	2.2162(8)
Ni−N or −Br	1.807(2)	1.908(3)	1.887(3)	1.8862(13)	2.3114(5)	1.900(2)
N−C(10)	1.090(3)	1.122(4)	1.132(4)	1.140(2)		1.139(4)
C(10)−C(11)	1.383(4)	1.471(5)	1.452(4)	1.455(2)		1.461(4)
C(3)−Ni−N or −Br	174.93(15) 164.4(3)	173.98(16)	177.51(11)	177.78(7)	178.48(6)	175.40(12)
P(1)−Ni−P(2)	169.72(4)	169.31(4)	168.55(4)	162.719(1)	165.64(3)	170.54(3)
P(1)−Ni−N or −Br	91.49(8)	95.08(9)	93.75(8)	98.35(4)	98.30(2)	94.59(7)
P(2)−Ni−N or −Br	98.69(8)	95.56(8)	97.69(7)	98.66(4)	96.03(2)	94.86(7)
P(1)−Ni−C(3)	91.13(10) 84.3(2)	84.75(12)	83.78(9)	81.16(5)	82.80(6)	85.10(9)
P(2)−Ni−C(3)	78.61(10) 86.3(2)	84.79(12)	84.77(9)	81.95(5)	82.89(6)	85.44(9)

reporting the molecular structure of this compound here.[10] All complexes adopt a distorted square-planar geometry around the nickel center. The Ni−P bond distances vary between 2.15 and 2.19 Å, which is a typical range for this type of pincer complexes bearing *i*-Pr substituents on the phosphorus atoms. The Ni−C(3) bond lengths observed for complexes **2**, **3**, and **5** are also in the range, 1.88−1.92 Å, usually observed for $Ni-C_{sp2}$

(10) The X-ray data for **6** were recorded on a multiply twinned crystal; numerous attempts at growing better quality crystals of this compound failed.

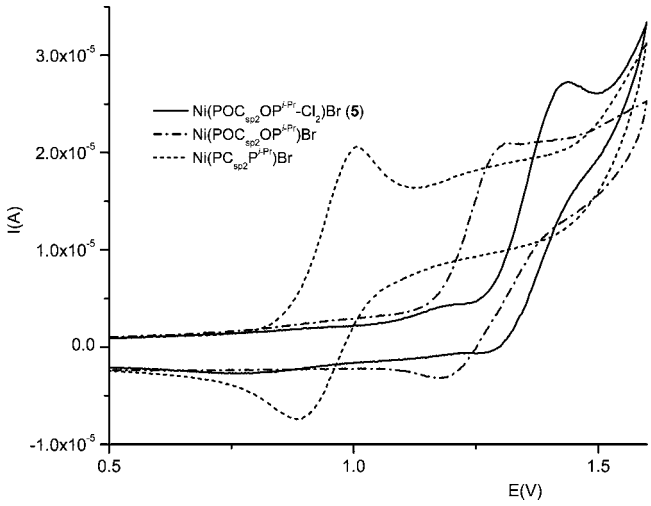


Figure 5. Cyclic voltammograms of **5**, ($POC_{sp2}OP^{i\text{-}Pr}$)NiBr, and ($PC_{sp2}P^{i\text{-}Pr}$)NiBr in CH_2Cl_2 (1 mM solutions) measured at 298 K with 0.1 M of tetrabutylammonium hexafluorophosphate as electrolyte (scan rate 100 mV s^{-1}, *E*(V) vs Ag/AgCl).

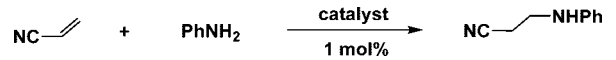
bonds.[11] The Ni−$N_{acetonitrile}$ bond distances in complexes **2** and **3** are very similar to the corresponding bond lengths seen in previously studied monocationic Ni−$NCCH_3$ complexes.[11,12] Finally, comparing the molecular structure of the neutral complex **5** to that of the previously reported ($POC_{sp2}OP^{i\text{-}Pr}$)NiBr analogue[5e] shows that introducing chloride atoms on the aromatic core of the ligand causes little or no change in ligand−metal bond distances and angles.

Electrochemical Measurements. The cyclic voltammogram of **5** was measured and compared to those of the analogous Ni−Br complexes based on the $PC_{sp2}P^{i\text{-}Pr}$ and $POC_{sp2}OP^{i\text{-}Pr}$ ligands (Figure 5). This comparison has confirmed the anticipated order of electron-richness for these complexes: ($PC_{sp2}P^{i\text{-}Pr}$)NiBr[5h,6] > ($POC_{sp2}OP^{i\text{-}Pr}$)NiBr[5e] > ($POC_{sp2}OP^{i\text{-}Pr}$-$Cl_2$)NiBr. Inspection of these voltammograms also shows that substituting hydrogens in the aromatic core of the ligand by chlorine atoms has a smaller impact on the electronic density around the metal than the substitution of carbons by oxygens in the ligand backbone; the higher electronegativity of oxygen atoms and their proximity to the metal center are the likely explanations for these observations.

Hydroamination of Acrylonitrile. Direct addition of N−H bonds to olefins is an atom-efficient approach toward the preparation of substituted amines since no byproducts are formed.[13] Although many transition metal complexes are known to catalyze amination of olefins, very few are commercially viable in terms of being based on inexpensive metals, operating at sufficiently low catalyst loadings and temperatures, and promoting the addition of weakly nucleophilic amines.[13t]

We have reported[5b,f] that [($PC_{sp3}P^{t\text{-}Bu}$)NiL]$^+$ and [($POC_{sp2}OP^{i\text{-}Pr}$)NiL]$^+$ (L = acrylonitrile) promote the addition of aniline to the activated olefin acrylonitrile.[13v,w] The present report extends these studies to the cationic acetonitrile complexes discussed above in order to allow a direct comparison of the catalytic activities as a function of ligand structure. The catalytic reactions were performed at 60 °C in THF or toluene for 6 or 18 h, using a 1 mol % loading of catalyst precursors and an aniline:olefin ratio of 1:1, 1:2, or 2:1. The main product of the catalysis is 3-anilinopropionitrile, which does not form in catalyst-free, control reactions. Small amounts of a second product were also detected in some of the runs performed in THF; the molecular ion of this product suggests that it arises from the addition of the N−H bond of the main product, 3-anilinopropionitrile, to acrylonitrile $PhN(CH_2CH_2CN)_2$ (*m*/*z* 199).

Table 3. Results of Catalytic Hydroamination of Acrylonitrile[a]



run	catalyst	solvent	time (h)	amine:olefin	yield (%)[b]
1	$PC_{sp3}P^{i\text{-}Pr}$ (**1**)	THF	18	1:1	18
2		THF	18	2:1	51
3		THF	18	1:2	12
4		toluene	6	2:1	44
5		toluene	18	2:1	74
6	$PC_{sp3}P^{t\text{-}Bu}$	THF	18	1:1	6
7		THF	18	2:1	14
8		THF	18	1:2	10
9		toluene	6	2:1	25
10		toluene	18	2:1	25
11	$PC_{sp2}P^{i\text{-}Pr}$ (**2**)	THF	18	1:1	37
12		THF	18	2:1	63
13		THF	18 h	1:2	45
14		toluene	6	2:1	70
15		toluene	18	2:1	70
16	$POC_{sp2}OP^{i\text{-}Pr}$ (**3**)	THF	18	1:1	63
17		THF	18	2:1	>95
18		THF	18	1:2	86
19		toluene	6	2:1	68
20		toluene	18	2:1	73
21	$POC_{sp2}OP^{i\text{-}Pr}$-$Cl_2$ (**6**)	THF	18	1:1	12
22		THF	18	2:1	6
23		THF	18	1:2	10
24		toluene	6	2:1	57
25		toluene	18	2:1	74

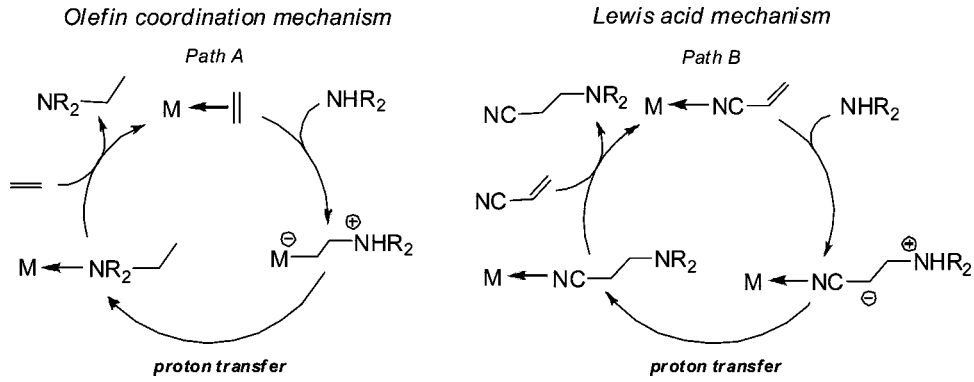
[a] Reaction conditions: 0.007 mmol of Ni complex, 100−200 equiv of the substrates, 1 mL of solvent, 60 °C. [b] Yields were determined by GC/MS and are the average of 3 experiments.

(11) Cambridge Structural Database search (Version 5.28 with updates up to November 2006: Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380).

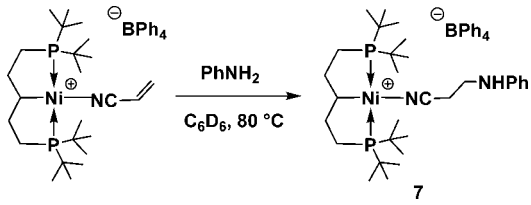
(12) We cannot include the comparison of the Ni−C bond distance observed in complex **1** with that of the analogous complex [($PC_{sp3}P^{t\text{-}Bu}$)-$Ni(NCCH_3)$][BPh_4] since the highly disordered alkyl chain in **1** required us to fix some of the distances during the refinement.

(13) For a few leading references on metal-catalyzed hydroamination reactions see: (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (b) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 744. (c) Brunet, J. J.; Commenges, G.; Neibecker, D.; Philippot, K. *J. Organomet. Chem.* **1994**, *469*, 221. (d) Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857. (e) Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Müller, T. *Eur. J. Inorg. Chem.* **1999**, 1121. (f) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568. (g) Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 9546. (h) Brunet, J. J.; Neibecke, D. In *Catalytic Heterofunctionalization*, Togni, A., Grützmacher, H., Eds.; VCH: Weinheim, 2001; pp 91−141. (i) Löber, O.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4366. (j) Ackermann, L.; Bergman, R. G. *Org. Lett.* **2002**, *4* (9), 1475. (k) Pawlas, J.; Nakao, Y.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 3669. (l) Nettekoven, U.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1166. (m) Ackermann, L.; Kaspar, L. T.; Gschrei, C. J. *Org. Lett.* **2004**, *6* (15), 2515. (n) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 12640. (o) Bexrud, J. A.; Beard, J. D.; Leitch, D. C.; Schafer, L. L. *Org. Lett.* **2005**, *7* (10), 1959. (p) Thomson, R. K.; Bexrud, J. A.; Schafer, L. L. *Organometallics* **2006**, *25*, 4069. (q) Munro-Leighton, C.; Delp, S. A.; Blue, E. D.; Gunnoe, T. B. *Organometallics* **2007**, *26*, 1483, and references therein. (r) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 354. (s) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (t) Nobis, M.; Drieâen-Hölscher, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3983. For a relevant article on addition of O−H bonds to activated olefins, see: (u) Miller, K. J.; Kitagawa, T. T.; Abu-Omar, M. M. *Organometallics* **2001**, *20*, 4403–4412. For some precedents on metal-catalyzed additions of anilines to acrylonitrile, see: (v) Munro-Leighton, C.; Delp, S. A.; Blue, E. D.; Gunnoe, T. B. *Organometallics* **2007**, *26*, 1483. (w) Seul, J. M.; Park, S. *Dalton Trans.* **2002**, 1153.

Scheme 2



Scheme 3



As can be noticed from the results listed in Table 3 (runs 1, 6, 11, 16, and 21), complex **3** is by far the most efficient to catalyze the addition of aniline to acrylonitrile. For reactions run in THF, varying the amine to olefin ratio from 1:1 to 2:1 gave better yields in all reactions except those catalyzed by complex **6** (runs 2, 7, 12, and 17 vs run 22), whereas a 1:2 ratio was significantly more beneficial only for reactions catalyzed by complex **3** (run 18); therefore, the 2:1 ratio was used for all reactions run in toluene. Overall, the catalysis proceeds better in toluene relative to THF in all cases except reactions of complex **3** (runs 5, 10, 15, and 25 vs run 20). Longer reaction times (18 vs 6 h) gave better yields only for reactions catalyzed by complexes **1** and **6** (runs 5 vs 4, and 25 vs 24). Interestingly, reactions run for 18 h and catalyzed by **1**, **2**, **3**, and **6** gave very similar yields (70−74%), while the reaction catalyzed by the *t*-Bu analogue of **1** gave quite low yields (runs 9 and 10, 25%); this can be explained by the greater steric hindrance of the bulky *t*-Bu groups.

Mechanistic Insights. The most frequently cited mechanistic proposal for olefin hydroaminations catalyzed by late transition metal complexes involves nucleophilic attack of the amine to the coordinated olefin, followed by proton transfer to generate the hydroaminated product (path A, Scheme 2). In the hydroamination of acrylonitrile, the nitrile moiety might compete with the olefin moiety for coordination to the electrophilic metal center, thus making possible the so-called Lewis-acid mechanism (path B, Scheme 2) involving the indirect activation of the C═C bond for a nucleophilic attack.

In order to obtain mechanistic information for the hydroamination reactions promoted by our cationic complexes, we monitored a typical catalytic experiment by $^{31}P\{^{1}H\}$ NMR spectroscopy using 2 mol % of [($PC_{sp3}P^{t\text{-}Bu}$)Ni(NCCH═CH_2)][BPh_4] and a 2:1 ratio of aniline to acrylonitrile in C_6D_6 at 80 °C. Throughout the course of this catalytic reaction, we observed the resonance due to the starting complex (89.4 ppm) in addition to a new singlet very close by (88.2 ppm) and a third singlet more downfield (95.6 ppm). In an attempt to isolate and identify these two unknown species, we reacted [($PC_{sp3}P^{t\text{-}Bu}$)Ni(NCCH═CH_2)][BPh_4] with an excess of aniline in C_6D_6 at 80 °C for 16 h. Monitoring this reaction by $^{31}P\{^{1}H\}$ NMR spectroscopy showed the disappearance of the starting compound and the emergence of a new species displaying a singlet at ∼88 ppm. This reaction mixture gave some crystals, which were isolated and analyzed by NMR spectroscopy and X-ray diffraction. The $^{31}P\{^{1}H\}$ NMR spectrum confirmed that the crystals represented one of the species observed during the catalytic run (∼88 ppm), whereas crystallography allowed us to identify this complex as **7** (Scheme 3), the 3-anilinopropionitrile adduct of the precursor. Unfortunately, we did not obtain any other evidence that might help identify the second unknown species observed during the catalysis.

The ORTEP diagram of complex **7** is shown in Figure 6, the crystal data and collection details are listed in Table 1, and selected bond distances and angles are given in Table 2. In this molecular structure, the metal−ligand bonds are quite similar to the previously reported acrylonitrile adduct bearing the same ligand.[5c] The N−C(10) bond is also about the same length in both complexes (1.139(4) Å in **7** vs 1.144(3) Å for the acrylonitrile adduct), indicating a similar degree of σ-donation/π-back-donation. The C(11)−C(12) bond distance is indeed longer in **7** and is characteristic of a single C−C bond (1.536(4) Å in **7** vs 1.300(3) Å).

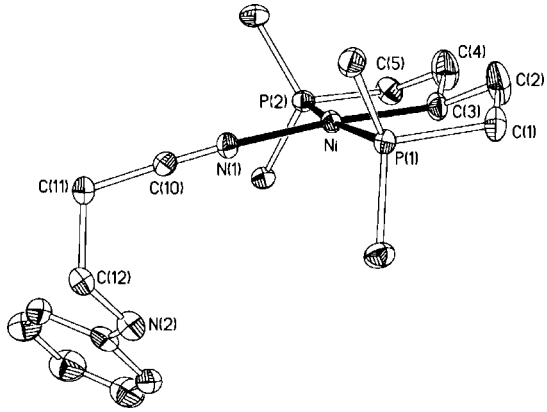


Figure 6. ORTEP diagrams for complex **7**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and *t*-Bu methyl groups are omitted for clarity.

Conclusion

Structural and reactivity studies have been performed on different cationic pincer complexes of nickel. The comparison of the oxidation potentials and solid state structures for ($POC_{sp2}OP^{i\text{-}Pr}$)NiBr and its dichloro analogue **5**, ($POC_{sp2}OP^{i\text{-}Pr}Cl_2$)NiBr, the neutral precursors of **3** and **6**, respectively, has shown that the introduction of chlorides on the aromatic moiety reduces the Ni center's electron-richness, whereas solid state

parameters such as Ni−C and Ni−P bonds are fairly insensitive to this substitution. Similarly, reactivity studies have shown that structural differences have little impact on the catalytic competence of the cationic complexes in promoting the hydroamination of acrylonitrile with aniline, the only major exception being the inhibiting effect introduced by the *t*-Bu substituents. Indeed, it appears that the catalysis is most sensitive to the choice of solvent, toluene giving the best results for all complexes except **3**. The amine:olefin ratio is also an important factor, 2:1 being the best ratio in most cases. The available data suggest that the hydroamination reaction probably proceeds via a mechanism in which the Ni center is acting simply as a Lewis acid for activating the olefin toward nucleophilic attack. Future studies will be directed to screening the catalytic activities of complex **3** for the addition of other nucleophiles.

Experimental Section

General Comments. Except where noted, all manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and/or in a nitrogen-filled glovebox. Solvents were purified by distillation from appropriate drying agents before use. All reagents were used as received from commercial vendors. Literature procedures were used to prepare the nickel precursors ($PC_{sp3}P^{i\text{-}Pr}$)NiBr,[5h] ($PC_{sp2}P^{i\text{-}Pr}$)NiBr,[5h] and ($POC_{sp2}OP^{i\text{-}Pr}$)NiBr;[5e] $AgBPh_4$ was prepared via the reaction of $AgNO_3$ and $NaBPh_4$ in H_2O, and 3-anilinopropionitrile[14] was isolated from a large-scale nickel-catalyzed reaction of aniline and acrylonitrile. The NMR spectra were recorded at ambient temperature on Bruker AV400 (^1H, $^{31}P\{^1H\}$) and Bruker ARX400 ($^{13}C\{^1H\}$) instruments. The ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to solvent resonances, and spectral assignments were confirmed by DEPT135, COSY, and HMQC experiments; ^vJ refers to the apparent coupling constant of the virtual triplets. The $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 (0 ppm). All chemical shifts and coupling constants are expressed in ppm and Hz, respectively. The IR spectra were recorded on a Perkin-Elmer 1750 FTIR (4000−450 cm^{-1}) with samples prepared as KBr pellets. The elemental analyses were performed by the Laboratoire d'Analyze Élémentaire (Université de Montréal).

[{(*i*-Pr$_2$PCH$_2$CH$_2$)$_2$CH}Ni(NCCH$_3$)][BPh$_4$] (1). CH_3CN (10 mL) was added to a Schlenk tube containing ($PC_{sp3}P^{i\text{-}Pr}$)NiBr (400 mg, 0.90 mmol) and $NaBPh_4$ (341 mg, 1.00 mmol), and the mixture was stirred at room temperature for 1 h. Evaporation of the solvent and extraction of the solid residue with CH_2Cl_2 (10 mL) gave a yellow suspension, which was filtered on a glass frit and evaporated to dryness to give compound **1** as a pale yellow solid (554 mg, 85%). ^1H NMR ($CDCl_3$): 0.71 (s, NCC*H*$_3$, 3H), 0.85−1.90 (m, CH(C*H*$_3$)$_2$, C*H*$_2$C*H*$_2$, NiC*H*, 33H), 2.03 (m, C*H*(CH$_3$)$_2$, 2H), 2.13 (m, C*H*(CH$_3$)$_2$, 2H), 6.91 (t, $^3J_{HH}$ = 7, B*Ph*$_4$, 4H), 7.08 (t, $^3J_{HH}$ = 7, B*Ph*$_4$, 8H), 7.50 (br s, B*Ph*$_4$, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 1.2 (s, NC*C*H$_3$, 1C), 17.7 (s, CH(*C*H$_3$)$_2$, 2C), 18.7 (s, CH(*C*H$_3$)$_2$, 2C), 19.3 (vt, $^vJ_{PC}$ = 3, CH(*C*H$_3$)$_2$, 2C), 19.4 (vt, $^vJ_{PC}$ = 2, CH(*C*H$_3$)$_2$, 2C), 20.4 (vt, $^vJ_{PC}$ = 12, *C*H$_2$P, 2C), 23.3 (vt, $^vJ_{PC}$ = 10, *C*H(CH$_3$)$_2$, 2C), 25.1 (vt, $^vJ_{PC}$ = 10 Hz, *C*H(CH$_3$)$_2$, 2C), 38.2 (vt, $^vJ_{PC}$ = 8, *C*H$_2$CH$_2$P, 2C), 54.9 (t, $^2J_{PC}$ = 6, Ni*C*, 1C), 121.8 (s, B*Ph*$_4$, 4C), 125.8 (s, B*Ph*$_4$, 8C), 136.1 (s, B*Ph*$_4$, 8C), 164.1 (q, $^1J_{BC}$ = 49, B*Ph*$_4$, 4C). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 176 MHz): 130.7 (s, N*C*CH$_3$, 1C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 76.5. IR (KBr): 2274 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{43}H_{60}Ni_1P_2N_1B_1$: C,71.49; H, 8.37; N,1.94. Found: C, 71.49; H, 8.41; N, 1.96.

[{(*i*-Pr$_2$PCH$_2$)$_2$C$_6$H$_3$}Ni(NCCH$_3$)][BPh$_4$] (2). CH_3CN (5 mL) was added to a Schlenk tube containing ($PC_{sp2}P^{i\text{-}Pr}$)NiBr (0.500 g, 1.05 mmol) and $NaBPh_4$ (0.431 g, 1.26 mmol), and the mixture was stirred at room temperature for 2 h. Evaporation of the solvent and extraction of the solid residues with CH_2Cl_2 (10 mL) gave a yellow suspension, which was filtered on a glass frit and evaporated to give compound **2** as a pale yellow solid (0.665 g, 79%). ^1H NMR ($CDCl_3$): 0.78 (s, NCC*H*$_3$, 3H), 1.14 (dvt, $^vJ_{PH} \approx J_{HH}$ = 7.0−7.2, CH(C*H*$_3$)$_2$, 12H), 1.30 (dvt, $^vJ_{PH} \approx J_{HH}$ = 7.5−8.5, CH(C*H*$_3$)$_2$, 12H), 2.14 (m, C*H*(CH$_3$)$_2$, 4H), 3.14 (s, C*H*$_2$P, 4H), 6.88 (t, $^3J_{HH}$ = 6.8, B*Ph*$_4$, 4H), 6.80−7.10 (m, Ar*H*, 3H), 7.05 (t, $^3J_{HH}$ = 7.4, B*Ph*$_4$, 8H), 7.49 (br s, B*Ph*$_4$, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 1.0 (s, NC*C*H$_3$, 1C), 18.3 (s, CH(*C*H$_3$)$_2$, 4C), 19.0 (s, CH(*C*H$_3$)$_2$, 4C), 23.9 (vt, $^vJ_{PC}$ = 11, *C*H(CH$_3$)$_2$, 4C), 30.8 (vt, $^vJ_{PC}$ = 15, *C*H$_2$P, 2C), 121.8 (s, B*Ph*$_4$, 4C), 123.5 (vt, $^vJ_{PC}$ = 9, *Ar*H, 2C), 125.8 (s, B*Ph*$_4$, 8C), 127.8 (s, *Ar*H, 1C), 136.2 (s, B*Ph*$_4$, 8C), 152 (vt, $^vJ_{PC}$ = 12, *Ar*CH$_2$P, 2C), 164.4 (q, $^1J_{BC}$ = 49, B*Ph*$_4$, 4C). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 176 MHz): 133.0 (s, N*C*CH$_3$, 1C), 153.0 (t, $^2J_{PC}$ = 14, Ni*C*, 1C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 70.6. IR (KBr): 2282 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{46}H_{58}Ni_1P_2N_1B_1$: C,73.04; H,7.73; N,1.85. Found: C, 72.67; H, 7.68; N, 1.91.

[{(*i*-Pr$_2$PO)$_2$C$_6$H$_3$}Ni(NCCH$_3$)][BPh$_4$] (3). CH_3CN (5 mL) was added to a Schlenk tube containing Ni($POC_{sp2}OP^{i\text{-}Pr}$)Br (0.500 g, 1.04 mmol) and $AgBPh_4$ (0.489 g, 1.15 mmol), and the mixture was allowed to react for 4 h. The resultant suspension was filtered in air through a layer of Celite on a glass frit; evaporation of the solvent gave complex **3** as a yellow solid (0.515 g, 65%). ^1H NMR ($CDCl_3$): 0.65 (s, NCC*H*$_3$, 3H), 1.30 (br m, CH(C*H*$_3$)$_2$, 24H, *coincidentally overlapped signals*), 2.34 (m, C*H*(CH$_3$)$_2$, 4H), 6.51 (m, Ar*H*, 2H), 6.91 (br s, B*Ph*$_4$, 4H), 7.07 (br s, B*Ph*$_4$, 8H), 7.52 (br s, B*Ph*$_4$ + Ar*H*, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 1.0 (s, NC*C*H$_3$, 1C), 17.0 (s, CH(*C*H$_3$)$_2$, 4C), 17.6 (s, CH(*C*H$_3$)$_2$, 4C), 28.6 (vt, $^vJ_{PC}$ = 12, *C*H(CH$_3$)$_2$, 4C), 106.6 (vt, $^vJ_{PC}$ = 7, *Ar*H, 2C), 121.8 (s, B*Ph*$_4$, 4C), 125.8 (m, B*Ph*$_4$, 8C), 131.8 (s, *Ar*H, 1C), 136.2 (s, B*Ph*$_4$, 8C), 164.4 ($^1J_{BC}$ = 49, B*Ph*$_4$, 4C), 168.8 (vt, $^vJ_{PC}$ = 9, *Ar*O, 2C). $^{13}C\{^1H\}$ NMR (CD_3CN): 17.0 (s, CH(*C*H$_3$)$_2$, 4C), 17.8 (s, CH(*C*H$_3$)$_2$, 4C), 29.3 (vt, $^vJ_{PC}$ = 10, *C*H(CH$_3$)$_2$, 4C), 107.1 (vt, $^vJ_{PC}$ = 5, *Ar*H, 2C), 122.8 (s, B*Ph*$_4$, 4C), 123.4 (very weak m, Ni*C*, 1C), 126.6 (m, B*Ph*$_4$, 8C), 132.6 (s, *Ar*H, 1C), 136.7 (s, B*Ph*$_4$, 8C), 164.8 (q, $^1J_{BC}$ = 39, B*Ph*$_4$, 4C), 170.1 (vt, $^vJ_{PC}$ = 7, *Ar*O, 2C). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 176 MHz): 122.5 (t, J_{PC} = 20, Ni*C*, 1C), 128.8 (s, N*C*CH$_3$, 1C). $^{31}P\{^1H\}$ NMR ($CDCl_3$ or CD_3CN): 191.6. IR (KBr): 2277 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{44}H_{54}Ni_1P_2O_2N_1B_1$: C, 69.50; H, 7.16; N, 1.84. Found: C, 69.27; H, 7.46; N, 1.82.

(*i*-Pr$_2$PO)$_2$C$_6$H$_2$Cl$_2$ (4). To a solution of 2,4-dichloro-1,3-resorcinol (0.562 g, 3.14 mmol) and DMAP (0.768 g, 6.28 mmol) in THF (40 mL) that had been stirred for 0.5 h and cooled to 0 °C was added dropwise *i*-Pr_2PCl (1.00 mL, 6.28 mmol), and the final reaction mixture allowed to react for 1 h at room temperature. Evaporation of THF to dryness, followed by addition of hexanes, stirring, filtration of the resultant suspension, and evaporation of hexanes gave ligand **4** as a highly water-sensitive oil (0.650 g, 50%); this material was used immediately after its preparation and without further purification. ^1H NMR (C_6D_6): 0.93 (dd, J_{PH} = 16, J_{HH} = 7, CH(C*H*$_3$)$_2$, 12H), 1.13 (dd, J_{PH} = 11, J_{HH} = 7, CH(C*H*$_3$)$_2$, 12H), 1.74 (m, C*H*(CH$_3$)$_2$, 4H), 7.24 (s, Ar*H*, 1H), 7.80 (t, J_{PH} = 4, Ar*H*, 1H). $^1H\{^{31}P\}$ NMR (C_6D_6): 0.93 (ps t, *J* = 7−8, CH(C*H*$_3$)$_2$, 12H), 1.13 (ps t, *J* = 6, CH(C*H*$_3$)$_2$, 12H), 1.75 (m, C*H*(CH$_3$)$_2$, 4H), 7.23 (s, Ar*H*, 1H), 7.79 (s, Ar*H*, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): 17.1 (d, J_{PC} = 8, CH(*C*H$_3$)$_2$, 4C), 17.7 (d, J_{PC} = 20, CH(*C*H$_3$)$_2$, 4C), 28.6 (d, J_{PC} = 19, *C*H(CH$_3$)$_2$ 4C), 109.7 (t, J_{PC} = 22, *Ar*H, 1C), 117.0 (s, *Ar*Cl, 2C), 130.5 (s, *Ar*H, 1C), 154.6 (d, J_{PC} = 10, *Ar*O, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): 156.0.

{(*i*-Pr$_2$PO)$_2$C$_6$HCl$_2$}NiBr (5). Ligand **4** (0.460 g, 1.12 mmol) was added to a suspension of anhydrous $NiBr_2$ (0.278 g, 1.27 mmol) and DMAP (0.137 g, 1.12 mmol) in toluene (15 mL), and the reaction mixture was refluxed for 5 h. The solvent was then evaporated to dryness, hexanes (20 mL) added, and the resultant mixture filtered in the air on a glass frit. The filtrate was washed with water and concentrated until a minimum of hexanes was left.

(14) For 3-anilinopropionitrile NMR data, see: Li, K.; Horton, P. N.; Hursthouse, M. B.; Hii, K. K. *J. Organomet. Chem.* **2003**, *665*, 250.

Orange-brown crystals of **5** formed by keeping the solution at −14 °C (0.450 g, 73%). ^{1}H NMR (C_6D_6): 1.08 (dvt, $^vJ_{PH} \approx J_{HH} = 7-8$, CH(C$H_3$)$_2$, 12H), 1.27 (dvt, $^vJ_{PH} \approx J_{HH} = 7-9$, CH(C$H_3$)$_2$, 12H), 2.14 (m, C$H$(CH$_3$)$_2$, 4H), 7.07 (s, Ar$H$, 1H). ^{1}H{^{31}P} NMR (C_6D_6): 1.1 (d, $J_{HH} = 7$, CH(CH_3)$_2$, 12H), 1.3 (d, $J = 7$, CH(CH_3)$_2$, 12H), 2.14 (m, CH(CH$_3$)$_2$, 4H), 7.07 (s, ArH, 1H). ^{13}C{^{1}H} NMR (C_6D_6): 16.6 (s, CH(*C*H$_3$)$_2$, 4C), 17.7 (vt, $^vJ_{PC} = 2$, CH(*C*H$_3$)$_2$, 4C), 28.4 (vt, $^vJ_{PC} = 11$, *C*H(CH$_3$)$_2$, 4C), 110.8 (vt, $^vJ_{PC} = 7$, ArCl, 2C), 128.9 (s, *Ar*H, 1C), 131.4 (t, $J_{PC} = 20$, Ni*C*, 1C), 162.3 (vt, $^vJ_{PC} = 11$, *Ar*O, 2C). ^{31}P{^{1}H} NMR (C_6D_6): 192.2. Anal. Calcd for $C_{18}H_{29}BrNiCl_2P_2O_2$: C, 39.39; H, 5.33. Found: C, 39.41; H, 5.20.

[{(*i*-Pr$_2$PO)$_2$C$_6$HCl$_2$}Ni(NCCH$_3$)][BPh$_4$] (6). CH$_3$CN (10 mL) was added to a Schlenk tube containing ($POC_{sp2}Cl_2OP^{i\text{-}Pr}$)NiBr (0.450 g, 0.82 mmol) and $AgBPh_4$ (0.419 g, 0.98 mmol), and the mixture was allowed to react for 15 min at room temperature. The resultant solution was filtered in air through a layer of Celite on a glass frit, and the solvent evaporated to dryness to give complex **6** as a pale yellow solid (0.496 g, 73%). ^{1}H NMR (CD_3CN): 1.00−1.20 (m, CH(CH_3)$_2$, 24H), 2.39 (m, CH(CH$_3$)$_2$, 4H), 6.62 (t, $^3J_{HH} = 7$, BPh_4, 4H), 6.78 (t, $^3J_{HH} = 7$, BPh_4, 8H), 6.90−7.10 (s, BPh_4 + ArH, 9H). ^{13}C{^{1}H} NMR (CD_3CN): 17.0 (s, CH(*C*H$_3$)$_2$, 4C), 17.7 (s, CH(*C*H$_3$)$_2$, 4C), 29.5 (vt, $^vJ_{PC} = 11$, *C*H(CH$_3$)$_2$, 4C), 111.7 (vt, $^vJ_{PC} = 7$, ArCl, 2C), 122.7 (s, B*Ph*$_4$, 4C), 126.6 (m, B*Ph*$_4$, 8C), 131.4 (s, *Ar*H, 1C), 136.7 (s, B*Ph*$_4$, 8C), 163.1 (vt, $^vJ_{PC} = 10$, *Ar*O, 2C), 164.8 (q, $^1J_{BC} = 49$, B*Ph*$_4$, 4C). ^{13}C{^{1}H} NMR (CD_2Cl_2, 176 MHz): 123.7 (t, $^2J_{PC} = 20$, Ni*C*, 1C), 127.7 (s, N*C*CH$_3$, 1C). ^{31}P{^{1}H} NMR (CD_3CN): 197.2. IR (KBr): 2282 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{44}H_{52}NiCl_2P_2O_2N_1B_1.H_2O$: C, 62.37; H, 6.42; N, 1.65. Found: C, 62.59; H, 6.36; N, 1.72.

[{(*t*-Bu$_2$PCH$_2$CH$_2$)$_2$CH}Ni(NCCH$_2$CH$_2$NHPh)][BPh$_4$] (7). Method A. Aniline (20 μL, 0.22 mmol) was added to a Schlenk tube containing a solution of [($PC_{sp3}P^{t\text{-}Bu}$)Ni(NCCH=CH$_2$)][BPh_4] (0.010 g, 0.01 mmol) in C_6D_6 (1 mL). The reaction mixture was heated at 80 °C for 16 h. ^{31}P{^{1}H} NMR spectroscopy showed the disappearance of the starting compound and the emergence of a new species, which was identified as complex **7**. Method B. 3-Anilinopropionitrile (0.147 g, 1.00 mmol) was added to a Schlenk tube containing ($PC_{sp3}P^{t\text{-}Bu}$)NiBr (0.500 g, 1.00 mmol), $AgBPh_4$ (0.514 g, 1.20 mmol), and CH_2Cl_2 (20 mL). The mixture was allowed to react for 10 min at room temperature. The resultant suspension was then filtered in air through a layer of Celite on a glass frit, and the solvent evaporated to dryness to give complex **7** as a pale yellow solid, which was fully characterized by NMR spectroscopy. ^{1}H NMR ($CDCl_3$): 0.80−2.20 (m, PCH_2CH_2CH, 9H), 1.27 (vt, $^vJ_{PH} = 6$, C(CH_3)$_3$, 18H), 1.32 (vt, $^vJ_{PH} = 6$, C(CH_3)$_3$, 18H), 2.57 (m, CH_2, 2H), 2.98 (t, $^3J_{HH} = 7$, CH_2, 2H), 6.33 (d, $^3J_{HH} = 7$, ArH, 2H), 6.74 (t, $^3J_{HH} = 7$, ArH, 1H), 6.91 (t, $^3J_{HH} = 7$, BPh_4, 4H), 7.05 (t, $^3J_{HH} = 7$, BPh_4, 8H), 7.13 (t, $^3J_{HH} = 7$, ArH, 2H), 7.48 (br s, BPh_4, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): 18.7 (s, *C*H$_2$, 1C), 22.3 (vt, $^vJ_{PC} = 11$, *C*H$_2$P, 2C), 29.3 (s, C(*C*H$_3$)$_3$, 6C), 29.6 (s, C(*C*H$_3$)$_3$, 6C), 34.9 (vt, $^vJ_{PC} = 7$, *C*(CH$_3$)$_3$, 2C), 36.2 (vt, $^vJ_{PC} = 6$, *C*(CH$_3$)$_3$, 2C), 38.5 (s, *C*H$_2$, 1C), 39.0 (vt, $^vJ_{PC} = 8$, *C*H$_2$CH$_2$P, 2C), 54.1 (t, $^2J_{PC} = 6$, Ni*C*, 1C), 113.2 (s, *Ar*H, 2C), 118.6 (s, *Ar*H, 1C), 121.9 (s, B*Ph*$_4$, 4C), 125.8 (s, B*Ph*$_4$, 8C), 129.3 (s, *Ar*H, 2C), 133.7 (weak s, N*C*, 1C), 136.2 (s, B*Ph*$_4$, 8C), 146.4 (s, *Ar*N, 1C), 164.1 (q, $^1J_{BC} = 49$, B*Ph*$_4$, 4C). ^{31}P{^{1}H} NMR (C_6D_6 or $CDCl_3$): 88.2. Anal. Calcd for $C_{54}H_{75}NiP_2N_2B_1 \cdot H_2O$: C, 71.93; H, 8.61; N, 3.11. Found: C, 71.65; H, 8.46; N, 3.20.

Typical Procedure for Hydroamination Reactions. Aniline (63 μL, 0.69 mmol), acrylonitrile (46 μL, 0.70 mmol), and the catalyst stock solution (1.0 mL of a 6.9 mM THF solution) were added into a sealable vessel, which was put in an oil bath at 60 °C for 6 or 18 h. The reaction vessel was then allowed to cool to room temperature, and *p*-xylene was added (to serve as an internal standard). Hexanes (5 mL) was then added to the tube. A small fraction of the resulting suspension/solution was filtered through a Celite pad, and the filtrate was analyzed by GC/MS. The yields were determined from a calibration curve based on the product (anilinopropionitrile/*p*-xylene).

Cyclic Voltammetry Experiments. Cyclic voltammetry measurements were performed using a BAS Epsilon potentiostat. A typical three-electrode system was used, consisting of a glassy carbon working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode ($E_{1/2}(FeCp_2^+/FeCp_2) = +0.60$ V under these conditions). The experiments were carried out in CH_2Cl_2 at room temperature with tetrabutylammonium hexafluorophosphate as electrolyte (0.1 M), and the solutions were bubbled with nitrogen before each experiment.

Crystal Structure Determinations. Single crystals of the complexes were grown by slow diffusion of diethyl ether into a saturated solution of the complex in $CDCl_3$ (**1**) or into a saturated solution of THF (**2** and **3**) and by slow evaporation (at room temperature) of a hexanes solution (**5**) or a C_6D_6 solution (**7**). The crystallographic data (Table 1) for all complexes were collected on a Nonius FR591 generator (rotating anode) equipped with a Montel 200, a D8 goniometer, and a Bruker Smart 6000 area detector.

Cell refinement and data reduction were done using SAINT.[15] An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[16] The space group was confirmed by XPREP routine[17] in the program SHELXTL.[18] The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques with SHELX-97.[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter.

Complete details of the X-ray analyses for complexes **1**−**3**, **5**, and **7** have been deposited at The Cambridge Crystallographic Data Centre (CCDC 691621 (**1**), 691622 (**2**), 691623 (**3**), 691624 (**5**), 691625 (**7**)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Supporting Information Available: Complete details of the X-ray analyses for complexes **1**−**3**, **5**, and **7** are available free of charge via the Internet at http://pubs.acs.org.

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