Syntheses and Reactivities of New $PC_{sp3}P$ Pincer Complexes of Nickel

Annie Castonguay, Christine Sui-Seng, Davit Zargarian,* and André L. Beauchamp*

Département de Chimie, Université de Montréal, Montréal (Québec), Canada H3C 3J7

Received October 1, 2005

Heating Ni(II) halides with 1 equiv of $Bu^t_2P(CH_2)_5PBu^t_2$ gives the $PC_{sp3}P$ pincer complexes [{$(Bu^t_2P(CH_2)_2)_2CH$}NiX] (X = Cl, **1a**; Br, **1b**; I, **1c**). These compounds react with MeMgCl or *n*-BuLi to give, respectively, the methyl species {$(Bu^t_2P(CH_2)_2)_2CH$}NiMe, **2**, or the hydride species {$(Bu^t_2P(CH_2)_2)_2CH$}NiH, **3**, while reaction with $NaBPh_4$ in a mixture of benzene/acetonitrile gives the cationic species [{$(Bu^t_2P(CH_2)_2)_2CH$}Ni ($N{\equiv}CCH_3$)][BPh_4], **4**. Complexes **1**−**3** are inert toward olefins, but react with $PhSiH_3$ to give $(PhSiH)_n$. The cationic complex **4** is also inert toward most olefins, but its reaction with excess acrylonitrile results in displacement of coordinated acetonitrile to give [{$(Bu^t_2P(CH_2)_2)_2CH$}Ni($N{\equiv}CCH{=}CH_2$)][BPh_4], **5**. Complexes **1**−**5** have been characterized by NMR spectroscopy and, in the case of **1**, **4**, and **5**, by X-ray crystallography.

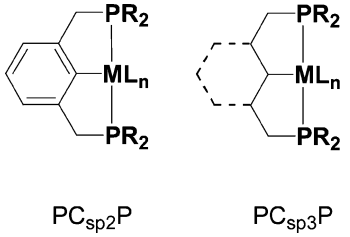
Introduction

The strongly chelating nature of PCP type pincer ligands and the rigid geometries they impose on transition metals bestow high thermal and oxidative stabilities to their complexes and facilitate novel reactivities.[1] Hence, PCP pincer complexes have been studied intensively during the past decade, and a number of interesting reactivities[2] and highly efficient catalytic reactions[3] involving these complexes have been reported. The catalytic applications of pincer complexes have been reviewed recently.[4]

The most commonly investigated pincer complexes feature $PC_{sp2}P$ type ligands consisting of mutually *trans* PR_2 moieties linked by a *m*-xylyl group (Chart 1), but the analogous complexes featuring $PC_{sp3}P$ ligands are receiving increasing attention and have shown interesting reactivities in their own rights.[5] Noteworthy examples include Pd−$PC_{sp3}P$ complexes that promote the hydroamination of acrylonitrile[6] and the Heck vinylation of aryl halides;[7] for the latter reaction, the $PC_{sp3}P$ complexes are believed to be more active than their $PC_{sp2}P$ counterparts.[7,8] Furthermore, a number of spectacular transformations have been observed with Ru−, Os−, and Ir−$PC_{sp3}P$ complexes.[9]

The interesting reactivities promoted by $PC_{sp3}P$ ligands and the virtually unexplored chemistry of their Ni derivatives[10] motivated us to prepare a series of Ni−$PC_{sp3}P$ complexes and study their reactivities.[11] Herein, we report convenient synthetic routes to a series of Ni−$PC_{sp3}P$ complexes based on the ligand 1,5-bis(di-*tert*-butylphosphino)pentane and describe a preliminary account of their reactivities.

Chart 1



Results and Discussion

Synthesis, Characterization, and Reactivities of $\kappa^P,\kappa^C,\kappa^P$-[{(*t*-$Bu_2PCH_2CH_2)_2CH$}NiX], 1. Heating mixtures of 1,5-bis(di-*tert*-butylphosphino)pentane and different nickel halides gave

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(2) (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699. (b) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42. (c) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531. (d) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 6652. (e) Cohen, R.; van der Boom, M. E.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 7723. (f) Ashkenazi, N.; Vigalok, A.; Parthiban, S.; Ben-David, Y.; Shimon, L. J. W.; Martin, J. M.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 8797. (g) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017. (h) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144. (i) Kanzelberger, M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13644.

(3) For instance, Ru−PCP compounds catalyze transfer hydrogenation of ketones at high turnover numbers: Amoroso, D.; Jabri, A.; Yap, G. P. A.; Gusev, D. G.; dos Santos, E. N.; Fogg, D. E. *Organometallics* **2004**, *23*, 4047, and references therein.

(4) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837.

(5) For some of the original reports on $PC_{sp3}P$ type pincer complexes see: (a) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972. (b) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59. (c) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373. (d) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 387. (e) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217. (f) Briggs, J. R.; Constable, A. G.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1225.

(6) (a) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 738. (b) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 744.

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10.1021/om050844x CCC: $33.50
Publication on Web 12/24/2005

Scheme 1

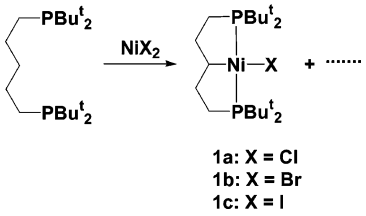
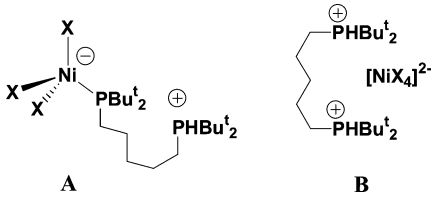


Chart 2



37−47% yields of orange solids that were identified readily as our target $PC_{sp3}P$ pincer complexes **1** (Scheme 1; X = Cl, **1a**; Br, **1b**; I, **1c**). These reactions also produced unexpected byproducts that proved difficult to identify, because they were paramagnetic and only sparingly soluble in common solvents. The colors of these byproducts, i.e., blue, green, and red for the Cl, Br, and I derivatives, respectively, would be consistent with tetrahedral species of the type $[L_nNiX_{4-n}]^{n-2}$.[12] Indeed, repeated recrystallizations of the byproduct obtained from the $NiCl_2$ reaction yielded blue microcrystals that were identified as the tetrahedral, zwitterionic complex [{(*t*-Bu_2PH)$(CH_2)_5$(*t*-Bu_2P)}$NiCl_3$], **A** (Chart 2).[13]

The formation of compound **A** likely arises from the reaction of **1a** with HCl, which is generated in-situ during the cyclometalation reaction; alternatively, protonation of the bis(phosphine) ligand might occur prior to its coordination to $NiCl_2$. Curiously, carrying out the cyclometalation reactions in the presence of NEt_3 did not circumvent the formation of the byproducts, implying that the phosphorus moieties are protonated in preference to the added base. Moreover, protonating isolated samples of **1a** with HCl (etherate) did not stop at the singly protonated product (complex **A**), proceeding instead to double protonation and formation of a blue solid that was identified as complex [{(*t*-Bu_2PH)$(CH_2)_2$}$_2CH_2$][$NiCl_4$], **B** (Chart 2).[13,14] These observations indicate that the byproducts formed during the syntheses of **1** are tetrahedral species analogous to **A** and **B**, but the available experimental evidence does not allow us to draw firm conclusions on their identities, structural details, or the pathways that lead to their formation.

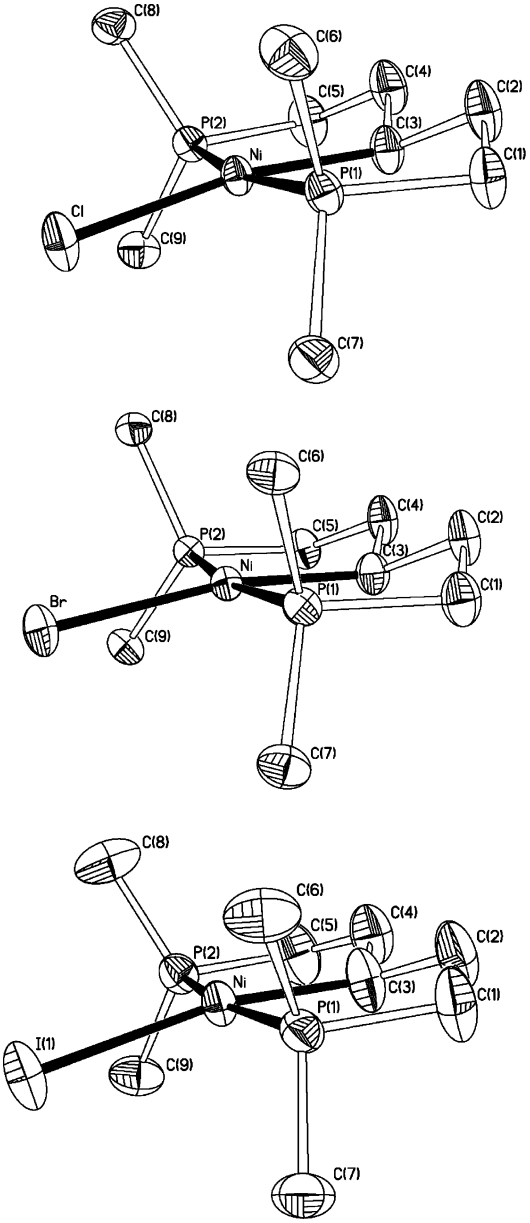


Figure 1. ORTEP diagrams for complexes **1a**, **1b**, and **1c**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and methyl groups are omitted for clarity. The iodide atom in **1c** is disordered over two positions (54:46), only one of which is shown in the ORTEP.

Complexes **1** are thermally stable and can be handled in air, both in the solid state and in solution, without noticeable decomposition even after weeks. Their $^{31}P\{^1H\}$ NMR spectra contain a sharp singlet resonance that confirms the equivalence of the phosphorus nuclei in accord with a *trans* geometry; the chemical shift of this signal (ca. 73−74 ppm) is very close to that of the analogous $PC_{sp2}P$ complex {2,6-$(CH_2PBu^t_2)_2C_6H_3$}-NiCl (ca. 74.7 ppm).[11a] The appearance in the ^1H NMR spectra of the characteristic pattern of virtual triplets for the *t*-Bu protons is also consistent with strong coupling of these nuclei to

(10) To our knowledge, the only example of a Ni−$PC_{sp3}P$ compound reported previously is [Ni{1-CH_2-2,6-$(CH_2PPr^i_2)_2$-3,5-$(CH_3)_2C_6H$}I]: van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Inorg. Chim. Acta* **2004**, *357*, 4015.

(11) For examples of Ni−$PC_{sp2}P$ complexes see ref 10 and the following reports: (a) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (b) Kennedy, A. R.; Cross, R. J.; Muir, K. W. *Inorg. Chim. Acta* **1995**, *231*, 195. (c) Huck, W. T. S.; Snellink-Ruël, B.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Organometallics* **1997**, *16*, 4287. (d) Bachechi, F. *Struct. Chem*. **2003**, *14*, 263. (e) Kozhanov, K. A.; Bubnov, M. P.; Cherkasov, V. K.; Fukin, G. K.; Abakumov, G. A. *Chem. Commun*. **2003**, 2610. (f) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652. (g) Cámpora, J.; Palma, P.; del Río, D.; Conejo, M. M.; Álvarez, E. *Organometallics* **2004**, *23*, 5653. (h) Groux, L. F.; Bélanger-Gariépy, F.; Zargarian, D. *Can. J. Chem.* **2005**, *83*, 634.

(12) For example, $[NiCl_3(PPh_3)][NEt_4]$ is blue (Smith, M. C.; Davies, S. C.; Hughes, D. L.; Evans, D. J. *Acta Crystallogr*. **2001**, *E57*, m509), $[NiBr_3(PPh_3)][AsPh_4]$ (Hanton, L. R.; Raithby, P. R. *Acta Crystallogr*. **1980**, *B36*, 2417) and $[NiBr_3(P^tBu_3)][HP^tBu_3]$ (Alyea, E. C.; Costin, A.; Ferguson, G.; Fey, G. T.; Goel, R. G.; Restivo, R. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1294) are green, and $[NiI_3(PPh_3)][AsPh_4]$ is red (Taylor, R. P.; Templeton, D. H.; Zalkin, A.; Horrocks, W. *Inorg. Chem*. **1968**, *7*, 2629).

(13) X-ray diffraction studies carried out on the blue crystals of **A** and **B** have confirmed the empirical formulae and the connectivities in these compounds, but the poor quality of the data obtained does not allow firm commentary on the structural details.

(14) The ^1H NMR spectrum of this species contained poorly defined, broad peaks, but its $^{31}P\{^1H\}$ NMR (CD_2Cl_2) spectrum showed only a singlet at 17.4 ppm, which is tentatively assigned to the phosphonium moiety.

Table 1. Crystal Data Collection and Refinement Parameters for Complexes 1a, 1b, 1c, 4, and 5

	1a	**1b**	**1c**	**4**	**5**
chemical formula	$C_{21}H_{45}ClNiP_2$	$C_{21}H_{45}BrNiP_2$	$C_{21}H_{45}INiP_2$	$C_{47}H_{68}NBNiP_2$	$C_{48}H_{68}NBNiP_2$
fw	453.67	498.13	545.12	778.48	790.49
T (K)	293 (2)	220 (2)	220 (2)	220 (2)	200 (2)
wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a (Å)	12.1335 (2)	12.1501 (5)	11.8960 (5)	15.3450 (3)	14.3311(8)
b (Å)	14.2189 (2)	14.3036 (5)	14.1665 (5)	14.4944 (3)	18.2163(11)
c (Å)	14.8382 (2)	14.8142 (6)	15.1062 (6)	19.9357 (5)	17.4551(10)
α (deg)	90	90	90	90	90
β (deg)	104.4970 (10)	104.337 (3)	90	90.368 (2)	100.655(3)
γ (deg)	90	90	90	90	90
Z	4	4	4	4	4
V (Å^3)	2478.45 (6)	2494.38 (17)	2545.77 (17)	4433.94 (17)	4478.3(4)
ρ_{calcd} (g cm^{-3})	1.216	1.326	1.422	1.166	1.172
M (cm^{-1})	33.37	42.07	118.06	15.34	15.27
θ range (deg)	3.76−72.92	3.75−72.97	4.28−72.92	2.88−72.92	3.14−68.66
R1[a] [$I > 2\sigma(I)$]	0.0611	0.0688	0.0686	0.0639	0.0402
wR2[b] [$I > 2\sigma(I)$]	0.1838	0.2088	0.1720	0.1457	0.0860
R1 [all data]	0.0661	0.0888	0.0743	0.1134	0.0744
wR2 [all data]	0.1882	0.2940	0.1767	0.1641	0.0959
GOF	1.052	1.228	1.033	0.912	0.872

[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 1a, 1b, 1c, 4, and 5

	1a (X = Cl)	**1b** (X = Br)	**1c** (X = I)	**4** (X = N)	**5** (X = N)
Ni−C(3)	1.979(3)	1.971(4)	1.985(7)	1.969(3)	1.982(2)
Ni−P(1)	2.2079(8)	2.2182(12)	2.2353(17)	2.2154(10)	2.2261(7)
Ni−P(2)	2.2130(8)	2.2123(12)	2.2295(13)	2.2142(10)	2.2272(7)
Ni−X	2.2490(8)	2.3866(7)	2.561(3)	1.908(3)	1.899(2)
			2.547(4)		
C(3)−Ni−X	169.59(11)	169.89(13)	168.4(3)	173.98(16)	173.81(9)
			178.1(5)		
P(1)−Ni−P(2)	169.70(3)	170.16(5)	169.69(7)	169.31(4)	167.84(3)
P(1)−Ni−X	94.92(3)	94.48(3)	96.49(10)	95.08(9)	96.34(6)
			94.93(13)		
P(2)−Ni−X	94.95(3)	95.00(4)	93.75(10)	95.56(8)	94.60(6)
			95.37(13)		
P(1)−Ni−C(3)	85.24(9)	85.90(13)	84.5(3)	84.75(12)	84.64(7)
P(2)−Ni−C(3)	85.59(9)	85.22(13)	85.2(3)	84.79(12)	85.05(7)

mutually *trans* phosphorus nuclei. The $^{13}C\{^1H\}$ NMR spectra also contained virtual triplets for *t*-Bu carbons in addition to low-field triplets (ca. 47−56 ppm; $^2J_{P-C} \approx 9$ Hz) attributed to the central carbon atom of the alkyl chain that is bonded to the nickel center.

X-ray diffraction studies helped establish the solid-state structures of **1a**, **1b**, and **1c**. The ORTEP views of these complexes are shown in Figure 1, the crystal data and collection details are listed in Table 1, and selected bond distances and angles are given in Table 2. The Ni center in all three structures adopts a distorted square-planar geometry defined by two phosphorus atoms, the central carbon atom of the $PC_{sp3}P$ ligand, and a halogen atom. All Ni−P bond lengths lie within the expected range for a *trans*-P−Ni−P arrangement, while the P(1)−Ni−P(2) angles of ca. 170° result from a slight tetrahedral distortion away from the ideal square-planar geometry expected for the d8 centres. The Ni−C(3) distances of ca. 1.98 Å are comparable to the mean of all Ni−C_{sp3} bond lengths reported to date (1.980 Å).[15]

We undertook to prepare alkyl derivatives of our pincer complexes in order to study their reactivities with olefins and hydrosilanes. Reaction of complex **1a** with 1 equiv of MeMgCl gave the corresponding Ni−Me species **2**, whereas the reaction of **1** with BuLi led to the formation of the Ni−H derivative **3** (Scheme 2). The ^1H NMR spectra of the latter reaction mixture contained signals attributed to 1-butene, while a considerable amount of free ligand was detected in both the ^1H and ^{31}P NMR spectra. These observations imply that an initially formed Ni−Bu intermediate undergoes β-H elimination to give **3**, and that this Ni−H species is itself prone to reductive elimination and phosphine dissociation.

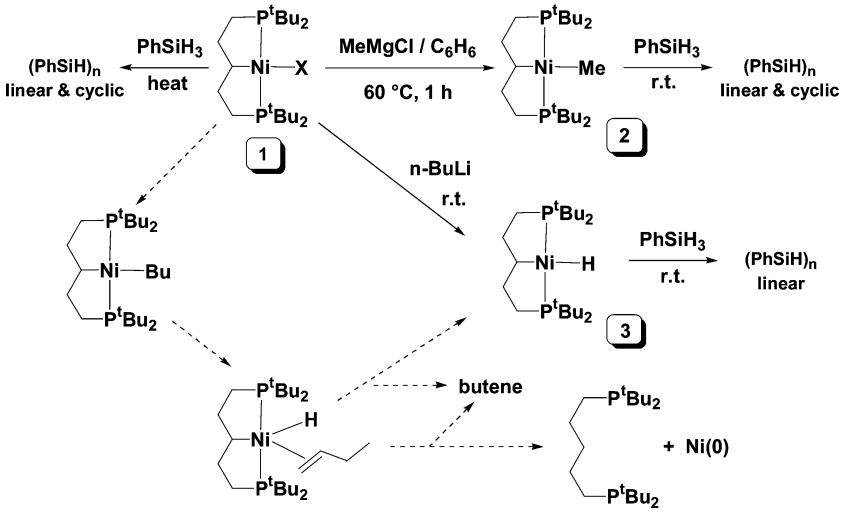
The Ni−Me compound **2** and the Ni−H derivative **3** could not be isolated in analytically pure form,[16] but their NMR spectra provided sufficient evidence for a convincing characterization. For instance, the Ni−CH_3 moiety in **2** gave rise to triplet resonances in the ^1H and the $^{13}C\{^1H\}$ NMR spectra (^1H: −0.27 ppm, $^3J_{P-H} = 8$ Hz; ^{13}C: −19.07 ppm, $^2J_{P-C} = 19$ Hz), whereas the $^{31}P\{^1H\}$ NMR spectrum showed a singlet resonance at 80 ppm. In the case of complex **3**, the appearance in the ^1H NMR spectrum of a triplet signal at ca. −10 ppm ($^2J_{P-H} = 53$ Hz) is characteristic of a hydride moiety. Moreover, the $^{31}P\{^1H\}$ NMR spectrum of **3** showed a singlet resonance at ca. 109 ppm, significantly downfield of the corresponding signals in the Ni−halide and Ni−Me derivatives, but fairly close to that of the analogous Pd−H complex reported by Trogler (ca. 106 ppm).[6a]

Our preliminary investigations of the reactivities of complexes **2** and **3** showed that these compounds are inert toward olefins, but they catalyze the oligomerization of $PhSiH_3$. Thus, reaction of excess $PhSiH_3$ (50−100 equiv) with these complexes (ca.

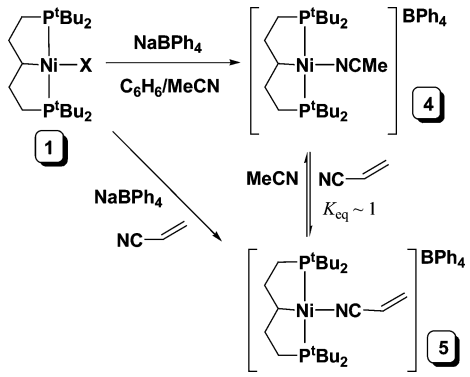
(15) Cambridge Crystallographic Data Center, ConQuest 1.7, 2004.

(16) The Ni−Me derivative reverts to its precursor Ni−Cl species, partially or completely, during workup, presumably because of the reverse metathesis reaction with in-situ-generated $MgCl_2$. Attempts to remove $MgCl_2$ from samples of **2** by washing with water or extraction in hexanes were not successful. The Ni−H derivative is thermally unstable.

Scheme 2



Scheme 3



0.05 M in C_6D_6) at room temperature for 24 h gave $(PhSiH)_n$ oligomers with ca. 50% conversion. The ^1H NMR spectra of these reaction mixtures indicated that the oligomers obtained from the reaction of the Ni−Me derivative **2** contained both cyclic and linear oligomers (Si−*H* signals at ca. 5.2−6.0 and ca. 4.4−4.8 ppm, respectively[17]), whereas those obtained from the reaction of the Ni−H derivative **3** showed only the signals characteristic of the linear oligomers. The halide derivatives reacted much more sluggishly with $PhSiH_3$; for instance, the reaction with the Ni−I analogue **1c** gave less than 5% conversion even after heating to ca. 100 °C for 24 h.

Synthesis, Characterization, and Reactivities of $\kappa^P,\kappa^C,\kappa^P$-[{(*t*-Bu$_2PCH_2CH_2$)$_2$CH}Ni(N≡CMe)][BPh$_4$], 4. Reacting complexes **1** with $NaBPh_4$ in a mixture of benzene and acetonitrile cleaved the Ni−X bond to form the pale yellow, cationic species **4** featuring a Ni−NCMe linkage (Scheme 3). The observation that halide abstraction does not take place in benzene or CH_2Cl_2 alone underscores the greater solubility of $NaBPh_4$ in MeCN and the latter's stabilizing role in such cationic species. Solid samples of complex **4** can be handled in air indefinitely, but oxidation can occur if solutions of **4** are left exposed to air over several weeks. Gradual decomposition was also noticed by $^{31}P\{^1H\}$ NMR spectroscopy when C_6D_6 solutions of **4** were heated above 40 °C.

The conversion of **1** to **4** was signaled by the disappearance of the $^{31}P\{^1H\}$ NMR signals for the precursors at ca. 74 ppm and the emergence of a new resonance at ca. 87 ppm. The formation of the C*H*$_3$CN→Ni moiety in **4** was also indicated by the presence in the ^1H NMR spectra of a new singlet at 0.70 ppm, indicating a significant upfield shift of this signal relative to free acetonitrile (ca. 2.1 ppm in $CDCl_3$). Comparison of the ^{13}C chemical shift for the nitrile carbon would have been very informative in this context, but this signal was not detected in the $^{13}C\{^1H\}$ NMR spectrum of complex **4**, presumably because of the coupling with the P nuclei that reduces the intensity of this signal. The IR spectrum of **4** shows a very weak band at 2270 cm^{-1}, which was assigned to $\nu_{C\equiv N}$.[18] Comparison to the corresponding band in free MeCN (2254 cm^{-1}) indicates that the N≡C bond order is reinforced upon coordination; we conclude, therefore, that the Ni−NCMe bond is dominated by ligand to metal σ-donation, which is known to diminish the antibonding character of the N lone pair with respect to the C−N bond.[19]

The spectral features of this complex are in agreement with its crystal structure (Figure 2, Table 1). The more or less unchanged Ni−P and Ni−C3 bond distances and P−Ni−P and P−Ni−C3 angles indicate that the slightly distorted square-planar geometry found for complexes **1** is largely maintained in **4** (Table 2). The end-bonded acetonitrile molecule has the expected attachment linearity (Ni−N−C(10) ≈ 177°; N−C(10)−C(11) ≈ 180°), whereas the Ni−N bond distance in **4** (1.908(3) Å) is significantly shorter than the mean value of Ni−NCMe bond lengths reported in the literature (2.068 Å).[20] The fairly short N−C distance (1.122(4) Å) points to a strong C≡N bond, as inferred from the IR data (vide supra).

The important reactivities of cationic species in catalytic settings prompted us to investigate the substitution lability of the acetonitrile moiety in **4** and its reactions with $PhSiH_3$ and a number of olefins, with the following results. No reaction was

(17) (a) Fontaine, F. G.; Zargarian, D. *Organometallics* **2002**, *21*, 401. (b) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (c) Dioumaev, V. K.; Rahimian, K.; Gauvin, F.; Harrod, J. F. *Organometallics* **1999**, *18*, 2249.

(18) It is noteworthy that the IR spectrum also displayed two equally weak bands (ca. 2182 and 2304 cm^{-1}) that have not been assigned, but might arise from overtones of the BPh_4 anion or from a complex bearing two acetonitrile moieties, one engaging in π-back-bonding and the other in σ-donation with the Ni center.

(19) For comparison, the corresponding IR band for the acetonitrile moiety in the complex [PPP−Ni(NCMe)]$^{2+}$ was found to be 2285 or 2319 cm^{-1}, consistent with greater σ-donation and less π-back-bonding in this dicationic species: Barbaro, P.; Togni, A. *Organometallics* **1995**, *14*, 3570.

(20) For examples of structurally characterized Ni−NCMe complexes see: (a) Jircitano, A. J.; Mertes, K. B. *Inorg. Chem.* **1983**, *22*, 1828. (b) Freeman, G. M.; Barefield, E. K.; Van Derveer, D. G. *Inorg. Chem.* **1984**, *23*, 3092. (c) Adhikary, B.; Liu, S.; Lucas, C. R. *Inorg. Chem.* **1993**, *32*, 5957.

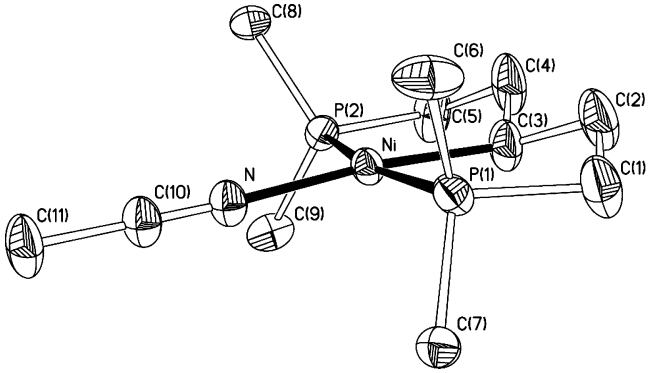


Figure 2. ORTEP diagram for complex **4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and methyl groups of the *t*-Bu substituents are omitted for clarity.

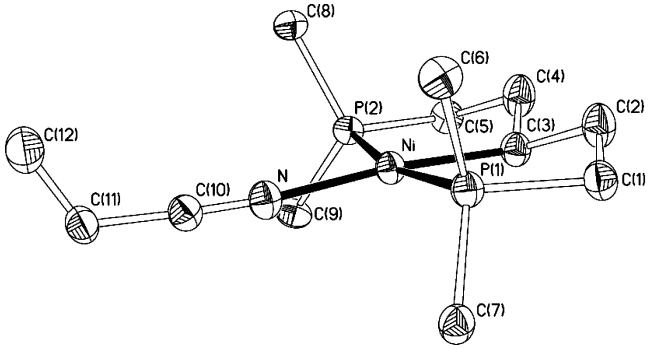


Figure 3. ORTEP diagram for complex **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogens and methyl groups of the *t*-Bu substituents are omitted for clarity.

noted when **4** was allowed to react for ca. 18 h in $CDCl_3$ ([**4**] $\approx$ 0.02 M) with 100 equiv of $PhSiH_3$, isoprene, styrene, norbornene, COD, 4-vinylaniline, and methyl methacrylate. The target Ni−olefin cations were also inaccessible from the reaction of **1** with $NaBPh_4$ in neat olefin.[21] On the other hand, reaction of **4** with an excess of acrylonitrile led to the reversible exchange of MeCN ($K_{eq} = 0.98 \pm 0.07$) to form complex **5** (Scheme 3). Complex **5** was also prepared directly via the reaction of **1** with $NaBPh_4$ in neat acrylonitrile and was isolated in ca. 61% yield.

The NMR features of **5** seem to indicate that the acrylonitrile molecule is linked to the Ni center by its nitrogen lone pair.[22] For example, very similar chemical shifts were observed for the ^{31}P signals in **5** (ca. 90 ppm) and **4** (ca. 88 ppm). In addition, the ^{1}H and ^{13}C signals for the vinyl moiety in **5** (ca. 4.8, 5.6, and 5.7 ppm for ^{1}H, and ca. 105 and 143 ppm for ^{13}C) are quite close to those of the corresponding signals in free acrylonitrile (ca. 5.6, 6.1, and 6.2 ppm for ^{1}H, and ca. 108 and 137 ppm for ^{13}C). As was the case for complex **4**, the ^{13}C signal for N*C* was not detected. These observations are consistent with an N-coordinated acrylonitrile moiety. On the other hand, the $\nu_{C\equiv N}$ band in the IR spectrum of **5** appears at ca. 2232 cm^{-1}, almost identical to that of free acrylonitrile (2231 cm^{-1} in CCl_4 solution). Since a shift to higher frequencies is normally expected for the $\nu_{C\equiv N}$ band in N-coordinated acrylonitrile complexes,[23] we invoke some Ni $\rightarrow$ acrylonitrile π-back-donation.[24]

Nevertheless, an X-ray diffraction study carried out on a single crystal of **5** allowed us to establish that the acrylonitrile ligand is N-bound in the solid state (Figure 3, Table 1). The distorted square-planar geometry around the nickel center resembles those of complexes **1** and **4** (Table 2). The Ni−N bond distance (ca. 1.90 Å) and the angles Ni−N−C (174°) and N−C−C (178°) in complex **5** are nearly equivalent to the corresponding values in complex **4**, while the C≡N (1.144(3) Å) and C═C (1.300(3) Å) bond distances are very similar to the corresponding bond lengths reported for a dicationic, N-bound methacrylonitrile−Ni complex (1.132(4) and 1.307-(5) Å, respectively).[25]

Conclusion

Formation of the new Ni−$PC_{sp3}P$ pincer complexes **1** proceeds by an uncommon Ni-promoted C−H bond activation process. Access to complexes **1**−**5** should facilitate a systematic exploration of their reactivities. Our preliminary results show that the Ni−methyl (**2**) and Ni−hydride (**3**) species are, as expected, more reactive toward $PhSiH_3$ than the precursor Ni−halide complexes (**1**). The acetonitrile adduct (**4**) is surprisingly inert toward a range of olefins, but it does undergo reversible substitution of the acetonitrile moiety by acrylonitrile. Recent reports of successful Ni-promoted hydrophosphination[25] and hydroamination[26] reactions with methacrylonitrile and other activated olefins indicate that similar reactivities might be promoted by our cationic $PC_{sp3}P$−Ni compounds **4** and **5**. Studies are underway to probe such reactivities.

Experimental Section

General Comments. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and/or in a nitrogen-filled glovebox, except where noted. Solvents were purified by distillation from appropriate drying agents before use. All reagents were used as received from commercial vendors. The diphosphine ligand $Bu^t_2P(CH_2)_5PBu^t_2$ was prepared according to a literature procedure[27] and distilled before use. The NMR spectra were recorded at ambient temperature on a Bruker ARX400 instrument. The ^{1}H and ^{13}C NMR spectra were referenced to solvent resonances, as follows: 7.26 and 77.16 ppm for $CHCl_3$ and $CDCl_3$, respectively, and 7.15 and 128.06 ppm for C_6D_5H and C_6D_6, respectively. The ^{31}P NMR spectra were referenced to an external 85% H_3PO_4 sample (0 ppm). The IR spectra were recorded on a Perkin-Elmer 1750 FTIR (4000−450 cm^{-1}) with samples prepared as KBr pellets. The ^{v}J term used refers to the apparent coupling constant of the virtual triplets. The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montreal).

[{$Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2$}NiCl] (1a). 1,5-Bis(di-*tert*-butylphosphino)pentane (250 mg, 0.69 mmol) was added to a suspension of anhydrous nickel(II) chloride (90 mg, 0.69 mmol) in toluene (15 mL), and the reaction mixture was refluxed for 12 h. Filtration of the final mixture in the air and evaporation of the

(21) To be sure, the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1a** with norbornene showed a small new peak (<5%), which might be the target olefin product, but isolation of this species was not pursued.

(22) For examples of N-bound M−acrylonitrile complexes, see: (a) Stojcevic, G.; Prokopchuk, E. M.; Baird, M. C. *J. Organometallic Chem.* **2005**, *690*, 4349 (M = Pd). (b) Chong, S. C.; Chong, D.; Lee, S.; Park, Y. J. *Organometallics* **2000**, *19*, 4043 (M = Ir).

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(24) It should be mentioned, however, that a dynamic exchange between the N-bound and π-bound forms should also be considered possible in solution. Consistent with this proposal, a recent report has shown that N-bound and π-bound Pd−acrylonitrile species can exist in equilibrium: Groux, L. F.; Weiss, T.; Reddy, D. N.; Chase, P. A.; Piers, W. E.; Ziegler, T.; Parvez, M.; Benet-Buchholz. *J. Am. Chem. Soc.* **2005**, *127*, 1854.

(25) Sadow, A. D.; Haller, I.; Fadini, L.; Togni, A. *J. Am Chem. Soc.* **2004**, *126*, 14704.

(26) Fadini, L.; Togni, A. *Chem. Commun.* **2003**, 30.

(27) For an optimized synthesis of this ligand see: Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 5091.

filtrate gave complex **1a** as an orange solid (148 mg, 47%). ^{1}H NMR (C_6D_6): 1.07−1.85 (m, 9H), 1.41 (vt, ^vJ = 5.7 Hz, PC(CH_3)$_3$, 18H), 1.46 (vt, ^vJ = 6.4 Hz, PC(CH_3)$_3$, 18H). ^{1}H NMR ($CDCl_3$): 1.10−2.10 (m), 1.48 (vt, ^vJ = 5.9 Hz, PC(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): 23.44 (vt, ^vJ = 9.0 Hz, *C*H$_2$, 2C), 29.46 (vt, ^vJ = 2.4 Hz, PC(*C*H$_3$)$_3$, 6C), 30.19 (vt, ^vJ = 2.8 Hz, PC(*C*H$_3$)$_3$, 6C), 34.63 (vt, ^vJ = 6.9 Hz, P*C*(CH$_3$)$_3$, 2C), 35.43 (vt, ^vJ = 5.2 Hz, P*C*(CH$_3$)$_3$, 2C), 39.43 (vt, ^vJ = 10.0 Hz, *C*H$_2$, 2C), 46.86 (t, *J* = 9.7 Hz, *C*H, 1C). ^{13}C{^{1}H} NMR ($CDCl_3$): 23.00 (vt, ^vJ = 9.3 Hz, *C*H$_2$, 2C), 29.27 (vt, ^vJ = 2.4 Hz, PC(*C*H$_3$)$_3$, 6C), 30.04 (vt, ^vJ = 2.4 Hz, PC(*C*H$_3$)$_3$, 6C), 34.50 (vt, ^vJ = 6.9 Hz, P*C*(CH$_3$)$_3$, 2C), 35.36 (vt, ^vJ = 5.5 Hz, P*C*(CH$_3$)$_3$, 2C), 38.95 (vt, ^vJ = 9.7 Hz, *C*H$_2$, 2C), 46.70 (t, *J* = 9.7 Hz, *C*H, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 73.8 (s). ^{31}P{^{1}H} NMR ($CDCl_3$): 74.0 (s). Anal. Calcd for $C_{21}H_{45}ClP_2Ni$: C, 55.60; H, 10.00. Found: C, 55.43; H, 10.43.

[{Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$}NiBr] (1b). The procedure described for the preparation of complex **1a** was used with nickel(II) bromide to give complex **1b** as an orange solid (152 mg, 44%). ^{1}H NMR (C_6D_6): 0.90−1.85 (m, 9H), 1.42 (vt, ^vJ = 6.4 Hz, PC(CH_3)$_3$, 18H), 1.47 (vt, ^vJ = 6.4 Hz, PC(CH_3)$_3$, 18H). ^{13}C{^{1}H} NMR (C_6D_6): 23.89 (vt, ^vJ = 8.6 Hz, *C*H2, 2C), 29.63 (s, PC(*C*H$_3$)$_3$, 6C), 30.54 (s, PC(*C*H$_3$)$_3$, 6C), 35.12 (vt, ^vJ = 5.9 Hz, P*C*(CH$_3$)$_3$, 2C), 35.74 (vt, ^vJ = 5.5 Hz, P*C*(CH$_3$)$_3$, 2C), 39.31 (vt, ^vJ = 9.3 Hz, *C*H$_2$, 2C), 50.21 (t, *J* = 8.6 Hz, *C*H, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 73.5 (s). Anal. Calcd for $C_{21}H_{45}BrP_2Ni$: C, 50.64; H, 9.11. Found: C, 50.67; H, 9.37.

[{Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$}NiI] (1c). The procedure described for the preparation of complex **1a** was used with nickel(II) iodide to give complex **1c** as an orange solid (141 mg, 37%). ^{1}H NMR (C_6D_6): 0.80−1.85 (m, 9H), 1.43 (vt, ^vJ = 5.1 Hz, PC(CH_3)$_3$, 18H), 1.49 (vt, ^vJ = 5.1 Hz, PC(CH_3)$_3$, 18H). ^{13}C{^{1}H} NMR (C_6D_6): 24.62 (vt, ^vJ = 8.3 Hz, *C*H$_2$, 2C), 29.91 (s, PC(*C*H$_3$)$_3$, 6C), 31.19 (s, PC(*C*H$_3$)$_3$, 6C), 35.83 (vt, ^vJ = 7.2 Hz, P*C*(CH$_3$)$_3$, 2C), 36.11 (vt, ^vJ = 5.5 Hz, P*C*(CH$_3$)$_3$, 2C), 39.10 (vt, ^vJ = 9.3 Hz, *C*H$_2$, 2C), 56.02 (t, *J* = 8.6 Hz, *C*H, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 74.7 (s). Anal. Calcd for $C_{21}H_{45}IP_2Ni$: C, 46.27; H, 8.32. Found: C, 46.73; H, 8.66.

[{Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$}NiMe] (2). MeMgCl (0.20 mL of a 3.0 M solution in THF, 0.60 mmol) was added to a solution of complex **1a** (272 mg, 0.60 mmol) in benzene (10 mL), and the mixture was refluxed for 1 h. The solvent was then evaporated to dryness to give a crude sample of complex **2** as a yellow solid. This sample contained some in-situ-formed $MgCl_2$, which could not be removed by washing with water or extraction into hexane. ^{1}H NMR (C_6D_6): −0.27 (t, *J* = 7.6 Hz, NiCH_3, 3H), 1.29 (vt, *J* = 6.4 Hz, PC(CH_3)$_3$, 18H), 1.30 (vt, *J* = 5.1 Hz, PC(CH_3)$_3$, 18H). ^{13}C{^{1}H} NMR (C_6D_6): −19.07 (t, *J* = 19.0 Hz, Ni*C*H$_3$, 1C), 27.69 (vt, ^vJ = 9.3 Hz, *C*H$_2$, 2C), 29.78 (vt, ^vJ = 2.8 Hz, PC(*C*H$_3$)$_3$, 6C), 30.43 (vt, ^vJ = 2.4 Hz, PC(*C*H$_3$)$_3$, 6C), 34.52 (vt, ^vJ = 6.2 Hz, P*C*(CH$_3$)$_3$, 2C), 35.84 (vt, ^vJ = 4.8 Hz, P*C*(CH$_3$)$_3$, 2C), 38.15 (vt, ^vJ = 10.0 Hz, *C*H$_2$, 2C), 57.67 (t, *J* = 9.7 Hz, *C*H, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 80.5 (s).

[{Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$}NiH] (3). *n*-BuLi (0.05 mL of a 2.5 M solution in hexanes, 0.125 mmol) was added to a concentrated solution of **1a** (57 mg, 0.125 mmol) in benzene-d_6 (0,5 mL). Monitoring by NMR spectroscopy showed that the signals for **1a** were replaced over 30 min by new signals assigned to the hydride species **3**, 1-butene, and free ligand. Evaporation of the volatiles gave a mixture of complex **3** and the free ligand. ^{1}H NMR (C_6D_6): −10.14 (t, *J* = 53.4 Hz, Ni*H*, 1H), 1.25 (vt, ^vJ = 7.6 Hz, PC(CH_3)$_3$, 18H), 1.26 (vt, ^vJ = 6.3 Hz, PC(CH_3)$_3$, 18H). ^{13}C{^{1}H} NMR (C_6D_6): 27.37 (vt, ^vJ = 7.9 Hz, *C*H$_2$, 2C), 29.68 (vt, ^vJ = 3.5 Hz, PC(*C*H$_3$)$_3$, 6C), 30.25 (vt, ^vJ = 3.1 Hz, PC(*C*H$_3$)$_3$, 6C), 33.02 (vt, ^vJ = 8.6 Hz, P*C*(CH$_3$)$_3$, 2C), 33.58 (vt, ^vJ = 12.4 Hz, P*C*(CH$_3$)$_3$, 2C), 38.80 (vt, ^vJ = 10.3 Hz, *C*H$_2$, 2C), 60.39 (t, *J* = 6.9 Hz, *C*H, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 108.8 (s).

[(Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$)Ni(N≡CCH$_3$)][BPh$_4$] (4). A solution of complex **1a** (345 mg, 0.813 mmol) in benzene (10 mL) was added to a solution of $NaBPh_4$ (293 mg, 0.813 mmol) in acetonitrile (15 mL), and the mixture was stirred at room temperature for 3 h. Evaporation of the final mixture and extraction of the solid residues with CH_2Cl_2 (15 mL) gave a yellow solution, which was filtered and evaporated to give compound **4** as a pale yellow solid (373 mg, 63%). ^{1}H NMR ($CDCl_3$): 0.70 (s, CH_3CN, 3H), 0.90−2.25 (m, 9H), 1.29 (vt, ^vJ = 7.6 Hz, PC(CH_3)$_3$, 18H), 1.34 (vt, ^vJ = 6.4 Hz, PC(CH_3)$_3$, 18H), 6.88 (t, *J* = 7.6 Hz, Ar, 4H), 7.05 (t, *J* = 7.6 Hz, Ar, 8H), 7.47 (br s, Ar, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): 22.32 (vt, ^vJ = 11.0 Hz, *C*H$_2$, 2C), 29.38 (m, PC(*C*H$_3$)$_3$, 6C), 29.61 (m, PC(*C*H$_3$)$_3$, 6C), 34.94 (vt, ^vJ = 7.2 Hz, P*C*(CH$_3$)$_3$, 2C), 36.21 (vt, ^vJ = 6.2 Hz, P*C*(CH$_3$)$_3$, 2C), 39.07 (m, *C*H$_2$, 2C), 54.03 (m, *C*H, 1C), 121.82 (s, Ar, 4C), 125.88 (s, Ar, 8C), 136.10 (s, Ar, 8C), 164.40 (q, *J* = 49.0 Hz, Ar, 4C). ^{31}P{^{1}H} NMR ($CDCl_3$): 88.4 (s). IR (KBr): 2270 cm^{-1} ($\mu_{C\equiv N}$). Anal. Calcd for $C_{47}H_{68}BNP_2Ni\cdot H_2O$: C, 70.87; H, 8.86; N, 1.76. Found: C, 70.73; H, 9.33; N, 1.54.

[(Bu$^t_2$P(CH$_2$)$_2$CH(CH$_2$)$_2$PBu$^t_2$)Ni(N≡CCH═CH$_2$)][BPh$_4$] (5). $NaBPh_4$ (77 mg, 0.225 mmol) was added to a solution of complex **1a** (102 mg, 0.225 mmol) in neat acrylonitrile (4 mL). The reaction mixture was stirred for 16 h at room temperature. Evaporation of the final mixture and extraction of the solid residues with CH_2Cl_2 (10 mL) gave a yellow solution, which was filtered and evaporated to give compound **5** as a pale yellow solid (109 mg, 61%). ^{1}H NMR ($CDCl_3$): 0.90−2.30 (m, 9H), 1.30 (vt, ^vJ = 6.7 Hz, PC(CH_3)$_3$, 18H), 1.34 (vt, ^vJ = 6.7 Hz, PC(CH_3)$_3$, 18H), 4.76 (dd, *J* = 17.2 Hz, 11.4 Hz, N≡CCH═CH$_2$, 1H), 5.57 (d, *J* = 11.4 Hz, N≡CCH═CH$_2$, 1H), 5.74 (d, *J* = 17.2 Hz, N≡CCH═CH$_2$, 1H), 6.87 (t, *J* = 6.7 Hz, Ar, 4H), 7.02 (t, *J* = 7.6 Hz, Ar, 8H), 7.42 (br s, Ar, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): 22.41 (vt, ^vJ = 11.0 Hz, *C*H$_2$, 2C), 29.38 (vt, ^vJ = 2.1 Hz, PC(*C*H$_3$)$_3$, 6C), 29.66 (vt, ^vJ = 2.1 Hz, PC(*C*H$_3$)$_3$, 6C), 35.25 (vt, ^vJ = 7.2 Hz, P*C*(CH$_3$)$_3$, 2C), 36.48 (vt, ^vJ = 6.6 Hz, P*C*(CH$_3$)$_3$, 2C), 39.21 (vt, ^vJ = 7.6 Hz, *C*H$_2$, 2C), 55.63 (m, *C*H, 1C), 105.06 (s, N≡CCH═CH$_2$, 1C), 121.73 (s, Ar, 4C), 125.66 (s, Ar, 8C), 136.35 (s, Ar, 8C), 142.57 (s, N≡CCH═CH$_2$, 1C), 164.39 (q, *J* = 48.9 Hz, Ar, 4C). ^{31}P{^{1}H} NMR ($CDCl_3$): 90.1 (s). IR (KBr): 2232 cm^{-1}, ν(C≡N). Anal. Calcd for $C_{48}H_{68}BNP_2Ni\cdot H_2O$: C, 71.30; H, 8.73; N, 1.73. Found: C, 71.53; H, 8.86; N, 1.64.

Determination of K_{eq} for the Reaction of 4 with Acrylonitrile. This experiment was performed by adding different amounts of acrylonitrile to an NMR sample containing a solution of **4** in $CDCl_3$ ([**4**] = 0.05−0.09 M) and recording successive ^{1}H and ^{13}P{^{1}H} NMR spectra until the signal intensities were unchanged from one spectrum to the next. The K_{eq} values were determined on the basis of data obtained from eight different experiments; the calculations were based on the relationship K_{eq} = [**5**][MeCN]/[**4**][acrylonitrile], using ratios of the NMR signal integrations for these species as an approximation for concentration ratios. Since the ^{1}H NMR signals for **4** and MeCN were difficult to measure with precision, the K_{eq} was determined by combining ^{1}H and ^{31}P NMR data, as follows: the [**5**]/[**4**] ratio was determined from the integration values of the ^{31}P{^{1}H} signals for **5** and **4**, whereas the [MeCN]/[acrylonitrile] ratio was determined from the integration values of the ^{1}H signals for **5** and acrylonitrile, since the equilibrium mixture must contain equimolar quantities of **5** and MeCN.

X-ray Crystal Structures of 1a, 1b, 1c, 4, and 5. Single crystals of these complexes were grown from the following: hexanes solutions at room temperature (**1a**, **1b**, **1c**); slow diffusion of hexanes into a saturated solution of the complex in benzene-d_6 (**4**); slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane (**5**). The crystallographic data (Table 1) were collected on a Bruker AXS diffractometer equipped with a SMART 2K CCD area detector with graphite-monochromatic Cu Kα radiation using SMART. Cell refinement and data reduction

were done using SAINT.[28] An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[29] The space group was confirmed by XPREP routine[30] in the program SHELXTL.[31] The absolute configuration of the centrosymmetric crystal was determined using the FALCK parameters. The structures were solved by direct methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-97.[32] 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. The autoindexing program for twinned crystals GEMINI[33] was used to resolve the molecular structure of complex **1b**. Some disorder was taken into account for two of the *t*-Bu groups of complex **1c**, as well as the iodine atom (two positions).

Complete details of the X-ray analyses for complexes **1a**, **1b**, **1c**, **4**, and **5** have been deposited at The Cambridge Crystallographic Data Centre (CCDC 283327−283729 (**1**), 283330 (**4**), 284336 (**5**)). 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.

Acknowledgment. The authors are grateful to NSERC of Canada for financial support of this work and to Prof. D. Gusev for his advice on the synthesis of the $PC_{sp3}P$ ligands.

OM050844X

(28) *SAINT*, Release 6.06, Integration Software for Single-Crystal Data; Bruker AXS Inc.: Madison, WI, 1999.

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(33) *GEMINI 1.02*, Release 5, 2000.