New Pincer-Type Diphosphinito (POCOP) Complexes of Nickel

Valerica Pandarus and Davit Zargarian*

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

Received April 25, 2007

This report describes the synthesis, characterization, and reactivities of a new series of pincer-type nickel complexes based on the diphosphinito (POCOP) ligands 1,3-(i-$Pr_2PO)_2C_6H_4$, **1**, and (i-$Pr_2POCH_2)_2$-CH_2, **2**. Reacting these ligands with $(THF)_{1.5}NiCl_2$, $(THF)_2NiBr_2$, or $(CH_3CN)_nNiX_2$ (X = Br, n = 2; I, n = 3) gives pincer-type complexes by metalation of the central carbon atom. The yields of these (POCOP)-NiX complexes vary with the type of ligand and Ni precursor used, as well as the reaction conditions. In general, the aromatic ligand **1** was metalated more readily to give excellent yields of the pincer complexes {2,6-(i-$Pr_2PO)_2C_6H_3$}NiX (X = Cl, **1a**, 85% yield; X = Br, **1b**, 95% yield; X = I, **1c**, 85% yield), especially when the reaction mixture was heated to 60 °C for 1 h in the presence of 1 equiv of 4-dimethylaminopyridine (DMAP). The analogous reactions of ligand **2** were more sluggish and required refluxing in toluene to give {(i-$Pr_2POCH_2)_2CH$}NiX (X = Cl, **2a**, 33% yield; X = Br, **2b**, 93% yield; X = I, **2c**, 70% yield). Displacement of Br from **1b** and **2b** by $Ag(O_3SCF_3)$, acetonitrile, or acrylonitrile gave, respectively, the neutral Ni−O_3SCF_3 derivatives **1d** and **2d** and the cationic adducts of CH_3CN (**1e** and **2e**) and CH_2=CHCN (**1f** and **2f**). Reacting **1b** with MeMgCl or EtMgCl gave the corresponding Ni−alkyl derivatives **1g** and **1h**, respectively, whereas alkylation of complexes **2a**−**c** was unsuccessful. The $POC_{sp3}OP$-based complexes **2a** and **2b** could be oxidized to paramagnetic, 17-electron species {(i-$Pr_2POCH_2)_2CH$}$Ni^{III}X_2$ (X = Cl, **2i**; Br, **2j**). Solid-state structures are reported for Ni−halide derivatives, the neutral complexes **2d**, **1g**, and **1h**, the cationic adduct **1e**, and the Ni(III) derivative **2i**. The cationic acrylonitrile derivative **1f** promotes the Michael addition of morpholine, cyclohexyl amine, or aniline to acrylonitrile, methacrylonitrile, or crotonitrile, whereas the paramagnetic Ni^{III} complex **2j** promotes the addition of CCl_4 to methyl acrylate, methyl methacrylate, styrene, 4-methylstyrene, acrolein, and acrylonitrile (Kharasch reaction).

Introduction

Transition metal complexes featuring PCP-type pincer ligands have displayed remarkable reactivities ranging from unusual stoichiometric transformations[1] to exceptionally efficient catalytic reactions.[2] Although it is not known with certainty how PCP-type pincer ligands bestow superior reactivities to metals to which they are ligated, it appears that their strongly chelating and electron-rich nature and the rigid geometries they impose on metals help maintain a robust architecture and stabilize unusual oxidation states.[3]

The most commonly investigated PCP-type pincer complexes are based on the diphosphine ligands 1,3-($R_2PCH_2)_2C_6H_4$ and $R_2PCH_2(CH_2)_3CH_2PR_2$ (Chart 1; X = Y= CH_2), which were originally reported by Shaw and co-workers over 30 years ago.[4,5] Similarly to other diphosphines, the ligating properties of pincer ligands can be modulated by systematic modifications of the group linking the PR_2 moieties and the nature of the substituents R. Thus, a large variety of such ligands and their complexes have been prepared, including diphosphines (X = Y = CH_2; R_1 and R_2 = alkyl or aryl),[3,5,6] diphosphinites (POCOP: X = Y = O; R_1 and R_2 = alkyl or aryl),[7] diphosphites (X = Y = O; R_1 and R_2 = O-alkyl or O-aryl),[2b,8] and phosphinophosphinites (X = CH_2, Y = O; R_1, R_2 = alkyl or aryl).[9]

A number of recent reports have shown that Ru, Rh, Ir, Pd, and Pt complexes bearing diphosphinite-type $POC_{sp2}OP$ ligands catalyze a number of interesting transformations more effectively than the corresponding complexes bearing the diphosphine-type $PC_{sp2}P$ ligands.[7] For instance, Jensen and co-workers have reported that {2,6-(i-$Pr_2PO)_2C_6H_3$}PdCl is a more efficient

(1) (a) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42. (b) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531. (c) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 6652. (d) Cohen, R.; van der Boom, M. E.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 7723. (e) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144. (f) Kanzelberger, M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13644. (g) Gusev, D. G.; Fontaine, F. G.; Lough, A. J.; Zargarian, D. *Angew. Chem., Int. Ed.* **2003**, *42* (2), 216.

(2) (a) Jensen, C. M. *Chem. Commun.* **1999**, 2443. (b) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379. (c) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550. (d) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39* (4), 743. (e) Amoroso, D.; Jabri, A.; Yap, G. P. A.; Gusev, D. G.; dos Santos, E. N.; Fogg, D. E. *Organometallics* **2004**, *23*, 4047.

(3) For recent reviews on the various aspects of the chemistry of PCP-type pincer ligands see: (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (b) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (c) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837.

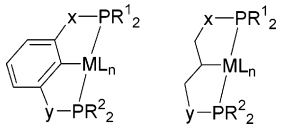
(4) For some of the original reports on $PC_{sp2}P$-type pincer complexes see: (a) Moulton, C. J.; Shaw, B. L. *Dalton Trans.* **1976**, 1020. (b) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *Dalton Trans.* **1979**, 1972.

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

(6) PCyP (C_{sp3}): (a) Sjövall, S.; Wendt, O. F.; Andersson, *C. Dalton Trans.* **2002**, 1396. (b) Kuznetsov, V. F.; Lough, A. J.; Gusev, D. G. *Inorg. Chim. Acta* **2006**, *359* (9), 2806.

10.1021/om700400x CCC: $37.00
Publication on Web 07/13/2007

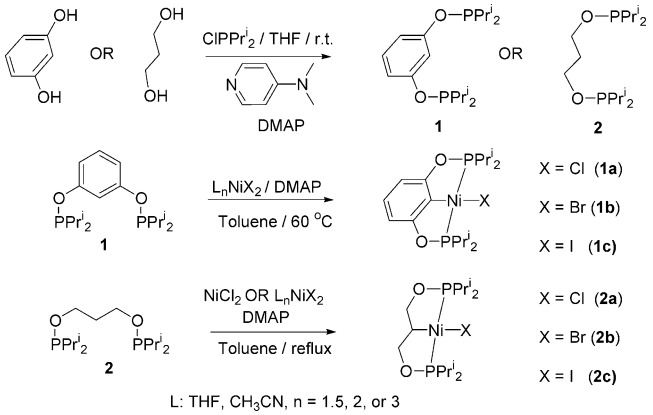
Chart 1



catalyst than its PCP counterpart for the Heck olefination of aryl chlorides.[7a,10] The complex {2,6-$(Ph_2PO)_2$-C_6H_3}Pd{OC(O)CF_3} has also shown better activities than its $PC_{sp2}P$ analogue in the Suzuki biaryl coupling reaction,[11] and the complex ($POC_{sp2}OP$)IrH_4 is more active than its $PC_{sp2}P$ counterpart for the dehydrogenation of linear alkanes to alkenes.[7b,12]

Our long-standing interest in the chemistry of organonickel complexes[13] and the emerging chemistry of PCP−Ni complexes[14] inspired us to investigate the synthesis and reactivities of this family of compounds. In earlier reports, we have described the chemistry of the $PC_{sp2}P$−Ni^{II} species {1,3-($Ph_2PCH_2CH_2$)$_2$-2-indenyl}$NiCl$[15] and the $PC_{sp3}P$−Ni^{II} complexes {(*t*-$Bu_2PCH_2CH_2$)$_2$CH}NiX (X = Cl, Br, I, Me, H) and [{(*t*-$Bu_2PCH_2CH_2$)$_2$CH}NiL]$^+$ (L = CH_3CN, CH_2=CHCN).[16] As an extension of the latter studies, we set out to explore the synthesis and reactivities of Ni complexes based on diphosphinito-type $POC_{sp2}OP$ and $POC_{sp3}OP$ ligands (Chart 1, X = Y = O) in order to probe the influence of the ligand electronics

Scheme 1



on the structures and reactivities of these closely related families of pincer complexes. A recent communication[17] has given a preliminary account of some of our results, including the syntheses of the compounds {2,6-(*i*-Pr_2PO)$_2$$C_6H_3$}$Ni^{II}Br$ (**1b**) and {(*i*-Pr_2POCH_2)$_2$CH}$Ni^{II}Br$ (**2b**) and the oxidation of the latter to the pentacoordinated 17-electron species {(*i*-Pr_2POCH_2)$_2$-CH}$Ni^{III}Br_2$ (**2j**). Recent reports have also appeared on the closely related POCOP complexes [{2,6-$(OPPh_2)_2C_6H_3$}$NiCl$[18] and the analogous PNCNP systems {2,6-(*t*-Bu_2PNH)$_2$$C_6H_3$}-$NiCl$.[19]

The present report describes the synthesis and full characterization of the complexes ($POC_{sp2}OP$)$Ni^{II}X$ (X = Cl, **1a**; I, **1c**; OSO_3CF_3, **1d**; Me, **1g**; Et, **1h**) and ($POC_{sp3}OP$)$Ni^{II}X$ (X = Cl, **2a**; I, **2c**; OSO_3CF_3, **2d**), the cationic adducts [($POC_{sp2}OP$)-$Ni^{II}L]^+$ (L = CH_3CN, **1e**; CH_2=CHCN, **1f**) and [($POC_{sp3}OP$)-$Ni^{II}L]^+$ (L = CH_3CN, **2e**; CH_2=CHCN, **2f**), and the Ni^{III} species [($POC_{sp3}OP$)$Ni^{III}Cl_2$] (**2i**). We will also describe the reactivities of **2j** in the Kharasch-type addition of CCl_4 to different olefins and the activities of the cationic species **1f** in promoting the Michael addition of morpholine, cyclohexyl amine, or aniline to acrylonitrile, methacrylonitrile, or crotonitrile.

Results and Discussion

Synthesis and Characterization of Ligands and Ni−Halide Derivatives. In comparison to the synthetic procedures required for the preparation of 1,3-bis(phosphino)xylenes[4] and 1,5-bis(phosphino)pentanes, the POCOP-type (phosphinito) pincer ligands can be obtained in good yields from inexpensive precursors via straightforward synthetic procedures. The ligands {1,3-(*i*-Pr_2PO)$_2$-C_6H_4}, **1**, and {(*i*-Pr_2POCH_2)$_2$$CH_2$}, **2**, were thus

(7) (a) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redón, R.; Cramer, R. E. and Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*, 958. (b) Göttker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804. (c) Morales-Morales, D.; Redón, R.; Yung, C.; Jensen, C. M. *Inorg. Chim. Acta* **2004**, *357*, 2953. (d) Wang, Z; Sugiarti, S.; Morales, C. M.; Jensen, C. M.; Morales-Morales, D. *Inorg. Chim. Acta* **2006**, *359*, 1923. (e) Salem, H.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2006**, *25*, 2292. (f) Bedford, R. B.; Betham, M.; Blake, M. E.; Coles, S. J.; Draper, S. M.; Hursthouse, M. B.; Scully, P. N. *Inorg. Chim. Acta* **2006**, *359*, 1870.

(8) Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabó, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767.

(9) (a) Wang, Z.; Eberhard, M. R.; Jensen, C. M.; Matsukawa, S.; Yamamoto, Y. *J. Organomet. Chem.* **2003**, *681*, 189. (b) Eberhard, M. R.; Matsukawa, S.; Yamamoto, Y.; Jensen C. M. *J. Organomet. Chem.* **2003**, *687*, 185. (c) Naghipour, A.; Sabounchei, S. J.; Morales-Morales, D.; Hernández-Ortega, S.; Jensen, C. M. *J. Organomet. Chem.* **2004**, *689*, 2494.

(10) Morales-Morales, D.; Redón, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619.

(11) Bedford, R. B.; Draper, S. M.; Scully P. N.; Welch, S. L. *New J. Chem.* **2000**, *24*, 745.

(12) (a) Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766. (b) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044.

(13) (a) Baho, N.; Zargarian, D. *Inorg. Chem.* **2007**, *46*, 299. (b) Gareau, D.; Sui-Seng, C.; Groux, L. F.; Brisse, F.; Zargarian, D. *Organometallics* **2005**, *24*, 4003. (c) Chen, Y.; Sui-Seng, C.; Zargarian, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 7721. (d) Boucher, S.; Zargarian, D. *Can. J. Chem.* **2005**, *84*, 233. (e) Chen, Y.; Sui-Seng, C.; Boucher, S.; Zargarian, D. *Organometallics* **2005**, *24*, 149. (f) Fontaine, F.-G.; Zargarian, D. *J. Am. Chem. Soc.* **2004**, *126*, 8786. (g) Groux, L. F.; Zargarian, D. *Organometallics* **2003**, *22*, 4759. (h) Fontaine, F.-G.; Nguyen, R.-V.; Zargarian, D. *Can. J. Chem.* **2003**, *81*, 1299. (i) Groux, L. F.; Zargarian, D. *Organometallics* **2003**, *22*, 3124. (j) Groux, L. F.; Zargarian, D.; Simon, L. C.; Soares, J. B. P. *J. Mol. Catal. A* **2003**, *19*, 51. (k) Rivera, E.; Wang, R.; Zhu, X. X.; Zargarian, D.; Giasson, R. *J. Mol. Catal. A* **2003**, *325*, 204−205. (l) Zargarian, D. *Coord. Chem. Rev.* **2002**, *157*, 233−234. (m) Wang, R.; Groux, L. F.; Zargarian, D. *J. Organomet. Chem.* **2002**, *660*, 98. (n) Fontaine, F.-G.; Zargarian, D. *Organometallics* **2002**, *21*, 401. (o) Dubois, M.-A.; Wang, R.; Zargarian, D.; Tian, J.; Vollmerhaus, R.; Li, Z.; Collins, S. *Organometallics* **2001**, *20*, 663. (p) Groux, L. F.; Zargarian, D. *Organometallics* **2001**, *20*, 3811. (q) Groux, L. F.; Zargarian, D. *Organometallics* **2001**, *20*, 3811. (r) Fontaine, F.-G.; Dubois, M.-A.; Zargarian, D. *Organometallics* **2001**, *20*, 5156. (s) Wang, R.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1999**, *18*, 5548. (t) Fontaine, F.-G.; Kadkhodazadeh, T.; Zargarian, D. *Chem. Commun.* **1998**, 1253. (u) Vollmerhaus, R.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1997**, *16*, 4762. (v) Huber, T. A.; Bayrakdarian, M.; Dion, S.; Dubuc, I.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1997**, *16*, 5811. (w) Bayrakdarian, M.; Davis, M. J.; Reber, C.; Zargarian, D. *Can. J. Chem.* **1996**, *74*, 2194. (x) Huber, T. A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1995**, *14*, 4997.

(14) (a) Kennedy, A. R.; Cross, R. J.; Muir, K. W. *Inorg. Chim. Acta* **1995**, *231*, 195. (b) Bachechi, F. *Struct. Chem.* **2003**, *14* (3), 263. (c) Kozhanov, K. A.; Bubnov, M. P.; Cherkasov, V. K.; Fukin, G. K.; Abakumov, G. A. *Chem. Commun.* **2003**, 2610. (d) Cámpora, J.; Palma, P.; del Río, D.; Canejo, M. M.; Álvarez, E. *Organometallics* **2004**, *23*, 5653. (e) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652. (f) van der Boom, M. E.; Liou, S-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Inorg. Chim. Acta* **2004**, *357*, 4015. (g) Castonguay, A.; Charbonneau, F.; Beauchamp, A. L.; Zargarian, D. *Acta Crystallogr.* **2005**, *E61*, m2240.

(15) Groux, L. F.; Bélanger-Gariépy, F.; Zargarian, D. *Can. J. Chem.* **2005**, *83*, 634.

(16) (a) Castonguay, A.; Sui-Seng, C.; Zargarian, D.; Beauchamp, A. L. *Organometallics* **2006**, *25*, 602. (b) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Acta Crystallogr*. **2007**, *E63*, m196. (c) Sui-Seng, C.; Castonguay, A.; Chen, Y.; Gareau, D.; Groux, L. F.; Zargarian, D. *Top. Catal.* **2006**, *37*, 81.

(17) Pandarus, V.; Zargarian, D. *Chem. Commun.* **2007**, 978.

(18) Gómez-Benítez, V.; Baldovino-Pantaleón, O.; Herrera-Álvarez, C.; Toscano, R. A.; Morales-Morales, D. *Tetrahedron Lett.* **2006**, *47*, 5059.

(19) Benito-Garagorri, D.; Bocokić, V.; Mereiter, K.; Kirchner, K. *Organometallics* **2006**, *25*, 3817.

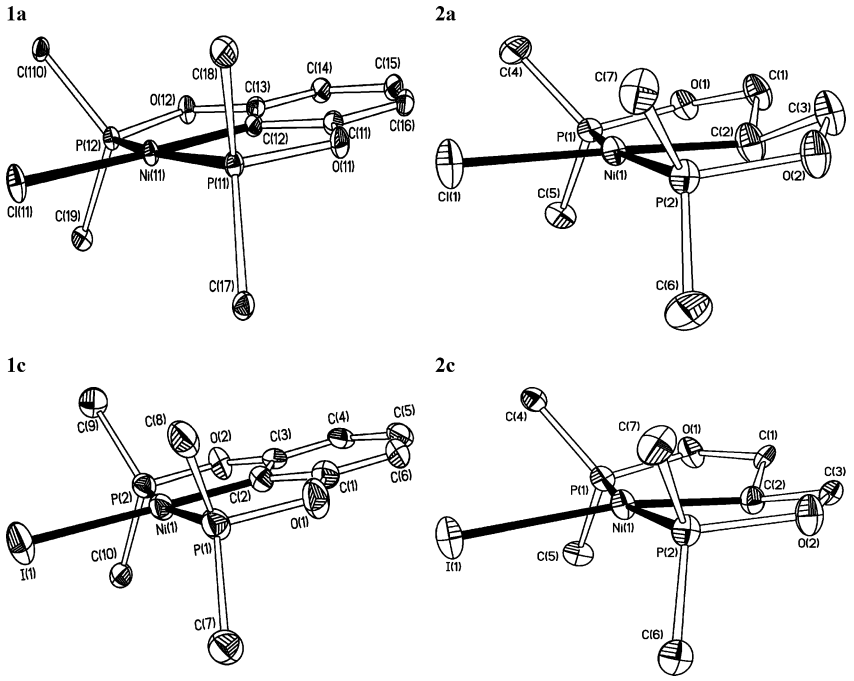


Figure 1. ORTEP diagrams for complexes **1a**, **1c**, **2a**, and **2c**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and methyl groups are omitted for clarity.

Table 1. Crystal Data, Collection, and Refinement Parameters for Complexes 1a, 1c, 2a, and 2c

	1a	**1c**	**2a**	**2c**
chemical formula	$C_{18}H_{31}ClNiP_2O_2$	$C_{18}H_{31}INiP_2O_2$	$C_{15}H_{33}ClNiP_2O_2$	$C_{15}H_{33}INiP_2O_2$
fw	435.53	526.98	401.51	492.96
T (K)	100(2)	150(2)	150(2)	150(2)
wavelength (Å)	1.542	1.542	1.542	1.542
cryst syst	triclinic	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)2(1)2(1)$	$P21/c$
a (Å)	12.9455(2)	8.3950(4)	8.72950(10)	8.8178(1)
b (Å)	12.9983(2)	10.4148(5)	13.9371(2)	12.8678(2)
c (Å)	13.4011(2)	13.1212(7)	17.0320(2)	18.3162(2)
α (deg)	78.455(1)	81.803(3)	90	90
β (deg)	76.121(1)	80.886(3)	90	93.163(1)
γ (deg)	87.062(1)	88.316(3)	90	90
Z	4	2	4	4
V (Å^3)	2144.86(6)	1121.13(10)	2072.18(5)	2075.09(5)
ρ_{calcd} (g cm^{-3})	1.349	1.561	1.287	1.578
M (cm^{-1})	39.81	134.63	40.03	144.95
θ range (deg)	3.46 to 72.89	3.45 to 68.41	4.10 to 72.90	4.20 to 72.89
R1[a] [$I > 2\sigma(I)$]	0.0352	0.0568	0.0417	0.410
wR2[b] [$I > 2\sigma(I)$]	0.0906	0.1303	0.0900	0.0913
R1 [all data]	0.0430	0.0908	0.0447	0.0539

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

prepared in 90−95% yields by reacting chlorodi(isopropyl)-phosphine with resorcinol[7a] or 1,3-propanediol, respectively, in the presence of 4-dimethylaminopyridine (DMAP, Scheme 1). Ligands **1** and **2** require handling under an inert atmosphere to avoid hydrolysis, which takes place slowly in ambient atmosphere.

NMR spectra of the previously reported ligand **1** matched the literature values.[7a] The ^{1}H NMR spectrum of the new ligand **2** displayed a doublet of triplets at ca. 3.8 ppm (POCH_2CH$_2$), a quintuplet at ca. 1.8 ppm (CH$_2$CH_2CH$_2$), a multiplet at ca. 2.6 ppm (PC*H*), and two doublets of doublets at ca. 1.0−1.1 ppm (P{CH(CH_3)$_2$}$_2$). The ^{31}P{^{1}H} NMR spectrum showed a singlet at ca. 152 ppm for the equivalent P nuclei, while the ^{13}C{^{1}H} spectrum showed doublets for the carbon nuclei {(*C*H$_3$)$_2$*C*H}$_2$-PO*C*H$_2$ and a characteristic triplet for the central carbon nucleus (CH$_2$*C*H$_2$CH$_2$).

Stirring a toluene mixture of ligand **1** and (THF)$_{1.5}$NiCl$_2$, (THF)$_2$NiBr$_2$, or (CH$_3$CN)$_3$NiI$_2$ for 1 h at room temperature gave complexes **1a**, **1b**, or **1c**, respectively, in 55−80% yields. The yields of these reactions can be increased to 85−95% by heating the mixture to ca. 60 °C for 1 h in the presence of 1 equiv of DMAP (Scheme 1). The analogous reactions with ligand **2** gave complexes **2a** (15% yield after 48 h reflux), **2b** (60−65% yield after 5 h reflux), and **2c** (70% yield after 5 h reflux). Complexes **2a** and **2b** were also obtained in 33% and 93% yields, respectively, by using the precursors NiCl$_2$ and (CH$_3$CN)$_2$NiBr$_2$. The generally greater yields for the metalation of ligand **1** is presumably due to its more rigid and planar skeleton that results in a favorable spatial disposition of the C−H bond in the vicinity of the Ni center.

The diamagnetic pincer complexes **1a**−**c** and **2a**−**c** were identified readily based on their NMR spectra. For instance, the ^{31}P{^{1}H} NMR spectra displayed one singlet resonance each at ca. δ 186 (**1a**), 188 (**1b**), 194 (**1c**), 183 (**2a**), 186 (**2b**), and 192 (**2c**); this is in accord with the trans disposition of the *i*-Pr$_2$P moieties that renders the two ^{31}P nuclei pairwise equivalent in

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 1a−c and 2a−c

	1a (X = Cl)	**1b** (X = Br)	**1c** (X = I)	**2a** (X = Cl)	**2b** (X = Br)	**2c** (X = I)[a]
Ni−C2	1.879(2)	1.885(3)	1.880(7)	1.957(3)	1.964(3)	1.986(7)
Ni−P1	2.1582 (6)	2.1534(8)	2.155(2)	2.1504(8)	2.1574 (8)	2.155(1)
Ni−P2	2.1603 (6)	2.1422(8)	2.145(2)	2.1544(8)	2.1527(8)	2.152(1)
Ni−X1	2.1944 (6)	2.3231(5)	2.492(1)	2.2125(8)	2.3458(5)	2.5307(7)
C2−Ni−X1	178.31 (6)	178.10(8)	178.9(2)	178.63(13)	176.29(14)	170.3(3)
P1−Ni−P2	164.01 (3)	164.92(4)	165.10(2)	166.13(3)	166.50(3)	166.33(5)

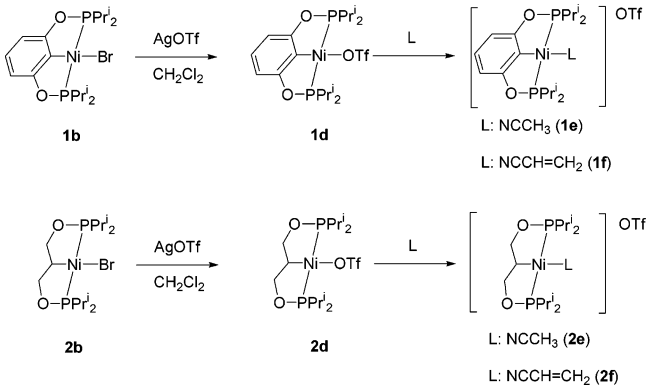
[a] Bond distances and angles for one of the two positions of the CH_2CHCH_2 moiety.

Table 3. Crystal Data, Collection, and Refinement Parameters for Complexes 1e, 1g, 1h, 2d, and 2i

	1e	**1g**	**1h**	**2d**	**2i**
chemical formula	$C_{21}H_{34}NNiSP_2O_5F_3$	$C_{19}H_{34}NiP_2O_2$	$C_{20}H_{36}NiP_2O_2$	$C_{16}H_{33}NiSP_2O_5F_3$	$C_{15}H_{33}Cl_2NiP_2O_2$
fw	590.19	415.11	429.14	515.13	436.96
T (K)	150 (2)	150(2)	150(2)	150(2)	150(2)
wavelength (Å)	1.542	1.542	1.542	1.542	1.542
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P21/c$	$P\bar{1}$	$P21/n$	$P\bar{1}$	$P21/c$
a (Å)	20.0267(4)	13.0447(3)	9.7318(2)	9.6621(3)	13.5766(3)
b (Å)	12.6735(2)	13.0888(4)	16.9949(4)	9.9213(2)	6.9842(2)
c (Å)	33.2826(6)	13.3978(4	14.0405(3)	28.2123(7)	22.2642(5)
α (deg)	90	78.418(1)	90	80.107(1)	90.00
β (deg)	102.516(1)	76.138(1)	103.733(1)	83.663(1)	104.721(1)
γ (deg)	90	87.343(1)	90	60.950(1)	90.00
Z	12	4	4	4	4
V (Å^3)	8246.7(3)	2175.7(1)	2255.79(9)	2327.9(1)	2041.83(9)
ρ_{calcd} (g cm^{-3})	1.426	1.267	1.264	1.47	1.421
M (cm^{-1})	32.87	27.32	26.51	37.74	52.85
θ range (deg)	2.26 to 68.97	3.45 to 69.00	4.16 to 68.84	1.59 to 68.75	3.37 to 68.95
R1[a] [$I > 2\sigma(I)$]	0.0364	0.0331	0.0281	0.0550	0.0305
wR2[b] [$I > 2\sigma(I)$]	0.0974	0.0951	0.0752	0.1402	0.0879
R1 [all data]	0.0521	0.0356	0.0347	0.0756	0.0319

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

Scheme 2



these compounds. The ^{1}H NMR spectra of **1a−c** showed two signals corresponding to the nonequivalent methyl groups in each *i*-Pr moiety, but only one signal for the four equivalent methyne protons; these features are consistent with the presence of a mirror plane encompassing the square plane and the planar aromatic system of the ligand backbone. In complexes **2a−c**, on the other hand, the nonplanar aliphatic linker system breaks the symmetry relating the groups above and below the coordination plane, thus giving rise to two signals for the nonequivalent methyne protons and four signals for the nonequivalent methyl groups. The $^{13}C\{^1H\}$ NMR spectra of **1a−c** and **2a−c** were also consistent with these symmetry considerations; moreover, these spectra showed the characteristic virtual triplets for *C*−P−O−*C* and for the metalated carbon nuclei.

These new ($POC_{sp2}OP$)− and ($POC_{sp3}OP$)−Ni(halide) complexes are stable to atmospheric oxygen and moisture, both in the solid state and in solution; they are also thermally stable in refluxing DMF solutions. Purification of these compounds was achieved by crystallization from hexane. Low-temperature recrystallizations yielded single crystals for all of these complexes, thereby allowing us to confirm their identities by X-ray diffraction studies. Figure 1 shows the ORTEP diagrams for **1a**, **1c**, **2a**, and **2c**; the solid-state structures of **1b** and **2b** have been reported previously.[17] Table 1 lists the crystal data and details of data collection, while Table 2 gives selected bond distances and angles. The asymmetric unit of complexes **1a** and **1b** each contains two molecules that are related by an approximate mirror plane and have very similar metrical parameters; a similar observation was made for the analogous Pd−POCOP complexes.[7a] A 2-fold disorder has also been observed in the structure of the Ni−I derivative **2c**, so that two different positions were found for the C atoms on the aliphatic skeleton of the $POC_{sp3}OP$ ligand.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 2d

molecule 1		molecule 2	
Ni(11)−C(12)	1.922(5)	Ni(21)−C(22)	1.949(4)
Ni(11)−P(11)	2.187(1)	Ni(21)−P(21)	2.173(1)
Ni(11)−P(12)	2.182(1)	Ni(21)−P(22)	2.185(1)
Ni(11)−O(13)	1.964(9)	Ni(21)−O(23)	1.935(10)
C(12)−Ni(11)−O(13)	177.3(4)	C(22)−Ni(21)−O(23)	173.7(4)
P(11)−Ni(11)−P(12)	164.93(5)	P(21)−Ni(21)−P(22)	165.59(5)

The overall geometry around the Ni center in all complexes **1a−c** and **2a−c** is square planar, as defined by the atoms C2, P1, P2 and the halide. A slight tetrahedral distortion arises primarily from the relatively small P−Ni−P angles (ca. 165°); similar distortions have been reported for the analogous Ni−PCP[14a] and Pd−POCOP[7a] complexes. As expected, the Ni−C_{sp2} bonds in **1** are shorter than the Ni−C_{sp3} bonds in **2**. On the other hand, the Ni−P and Ni−C bond distances are fairly uniform in each series of complexes and slightly shorter than the corresponding distances in the related complexes {(*t*-Bu_2-$PCH_2CH_2)_2CH$}NiBr[16] and {2,6-(*t*-$Bu_2PNH)_2C_6H_3$}NiCl;[19] this

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 1e

molecule 1		molecule 2		molecule 3	
Ni(11)−C(12)	1.881(2)	Ni(21)−C(22)	1.882(2)	Ni(31)−C(32)	1.883(2)
Ni(11)−P(11)	2.1683(7)	Ni(21)−P(21)	2.1552(8)	Ni(31)−P(31)	2.1785(7)
Ni(11)−P(12)	2.1704(7)	Ni(21)−P(22)	2.1638(7)	Ni(31)−P(32)	2.1702(7)
Ni(11)−N(11)	1.874(2)	Ni(21)−N(21)	1.877(2)	Ni(31)−N(31)	1.884(2)
N(11)−C(119)	1.140(3)	N(21)−C(219)	1.137(3)	N(31)−C(319)	1.138(3)
C(12)−Ni(11)−N(11)	175.8(1)	C(22)−Ni(21)−N(21)	177.25(10)	C(32)−Ni(31)−N(31)	172.61(9)
P(11)−Ni(11)−P(12)	164.38(3)	P(21)−Ni(21)−P(22)	164.39(3)	P(31)−Ni(31)−P(32)	163.69(3)

discrepancy may be attributed to the increased π-acidity of the OPR_2 moieties in **1** and **2**, which is expected to strengthen Ni−ligand interactions.

Synthesis and Characterization of the Triflate Derivatives (POCOP)Ni(OTf) (OTf = O_3SCF_3). Addition of AgOTf to solutions of **1b** or **2b** in CH_2Cl_2 resulted in halide displacement and formation of the triflate complexes {2,6-(*i*-$Pr_2PO)_2C_6H_3$}-Ni(OTf) (**1d**) and {(*i*-$Pr_2POCH_2)_2CH$}Ni(OTf) (**2d**), which were isolated as yellow solids (Scheme 2). In the solid state, these derivatives are air-stable for 24 h under relatively anhydrous conditions, but gradual decomposition was observed upon longer exposures. In solution, **1d** and **2d** decompose after being exposed to air for several minutes. The presence of the triflate group in **1d** and **2d** was established from the IR and ^{19}F NMR spectra and the results of X-ray diffraction studies, as described below.

The observation in the IR spectra of an asymmetric sulfonyl stretching mode at 1324 cm^{-1} for **1d** and at 1319 cm^{-1} for **2d**[20] and the presence of a singlet resonance at ca. −79 ppm in the ^{19}F NMR spectra of both complexes support the presence in these compounds of an η^1-coordinated triflate group.[20a] The NMR spectra show that the displacement of the bromide by the triflate resulted in minor changes only, such as a 2 ppm upfield shift in the $^{31}P\{^1H\}$ NMR resonances. The identity of **2d** was also confirmed by the results of single-crystal X-ray diffraction studies, which showed that the asymmetric unit contains two molecules related by an approximate mirror plane and having very similar metrical parameters (Table 4), including similarly disordered triflate groups in both molecules. As seen in the ORTEP diagram (Figure 2), the overall geometry around the Ni center in **2d** is a slightly distorted square-planar geometry with a P−Ni−P angle of 178° and C−Ni−O angle of 165°. The considerably longer Ni−P bond distances observed in **2d** (ca. 2.18 Å) versus **2b** (2.15 Å) seem to arise from the steric repulsion between the noncoordinating oxygens of the unidentate OTf ligand and the *i*-Pr substituents of the pincer ligand. The Ni−O distance of 1.964(9) Å is comparable to the corresponding distance in the Ni−OTf complexes (1-$PhCH_2$-indenyl)Ni(PPh_3)-(OTf) (1.972(9) Å)[13c] and *trans*-[$(PEt_3)_2$Ni(OTf)(2-C_5F_4N)] (1.957(2) Å),[20b] but longer than the Ni−O distances in the complexes ($PC_{sp2}P$)Ni(OR) (1.865(2) Å for R = H, and 1.855 Å for R = OMe);[14d] this is consistent with the lower nucleophilicity of OTf compared to OH or OMe.

Synthesis and Reactivities of Cationic Species. The facile displacement of the labile triflate ligand in **1d** and **2d** by acetonitrile or acrylonitrile gave the pale yellow cationic species [{2,6-(*i*-$Pr_2PO)_2C_6H_3$}Ni(RCN)][OTf] (R = Me, **1e**; CH_2=CH, **1f**) and [{(*i*-$Pr_2POCH_2)_2CH$}Ni(RCN)][OTf] (R = Me, **2e**; CH_2=CH, **2f**) in 65−75% yields (Scheme 2). Complete characterization by NMR and IR spectroscopy and by X-ray crystallography for **2e** confirmed the structural features attributed to these complexes, as described below.

The formation of the cationic complexes was signaled by the disappearance of the $^{31}P\{^1H\}$ NMR signals for the precursor triflate complexes and the emergence of new resonances at ca. 192−194 ppm; interestingly, the ^{19}F NMR singlet resonance for the new species was at the same frequency as in the neutral triflate compound (ca. −79 ppm). The ^1H and $^{13}C\{^1H\}$ NMR spectra of the cationic complexes displayed the expected signals characteristic of the aromatic or aliphatic POCOP ligands and some of the signals for CH_3CN or CH_2=CHCN. For instance, the C*H*$_3$CN and *C*H$_3$CN signals in **1e** were found at 2.20 and 3.40 ppm in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively,[21,22] while the C*H*$_2$=C*H*CN and *C*H$_2$=*C*HCN signals in **1f** were detected at ca. 4.55, 4.78, and 5.16 ppm in the ^1H NMR spectrum and at ca. 107 and 143 ppm in the $^{13}C\{^1H\}$ NMR spectrum.[16] On the other hand, the quaternary nitrile carbon was not detected, presumably because coupling to the P nuclei reduces the intensity of this signal. Similar observations have been reported for other N-bound acrylonitrile adducts (M = Pd,[23] Ir[24]).

The IR spectra of the cationic species also helped estimate the extent of σ-donation and π-back-bonding type of interactions in the Ni−N≡CR moiety on the basis of the frequencies of the ν(C≡N) bands. Thus, the enhanced energy of the ν(C≡N) absorption bands in **1e** (2292 cm^{-1}), **2e** (2284 cm^{-1}), **1f** (2257 cm^{-1}), and **2f** (2252 cm^{-1}) compared to the corresponding frequencies in free CH_3CN (2253 cm^{-1}) and free CH_2=CHCN (2229 cm^{-1}) indicated that the C≡N bond is reinforced upon coordination in all the cationic species. We conclude, therefore, that the Ni−nitrile interactions are dominated by N → Ni σ-donation, which is known to diminish the antibonding character of the N lone pair with respect to the C−N bond.[21,24,25] Moreover, the frequencies of the asymmetrical sulfonyl stretching mode $\nu(SO_3)$ decreased from 1324 cm^{-1} and 1319 cm^{-1} in the neutral Ni−OTf species **1d** and **2d**, respectively, to 1274 cm^{-1} (**1e**), 1279 cm^{-1} (**2e**), 1266 cm^{-1} (**1f**), and 1270 cm^{-1} (**2f**) in the cationic complexes. The decrease in the frequency of $\nu(SO_3)$ is characteristic of noncoordinating sulfonyl anions.[20a]

X-ray diffraction studies have revealed that the solid-state structure of **1e** consists of three independent molecules in the

(20) (a) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17. (b) Braun, T.; Parsons, S.; Perutz, R. N.; Voith, M. *Organometallics* **1999**, *18*, 1710. (c) Wang, R.; Groux, L. F.; Zargarian, D. *Organometallics* **2002**, *21*, 5531. (d) Poverenov, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2005**, *24* (24), 5937.

(21) For characterization of Ni−$NCCH_3$ complexes by NMR spectroscopy see refs 16, 20c, and: Uehara, K.; Hikichi, S.; Akita, M. *Dalton Trans.* **2002**, 3529.

(22) For characterization of other transition metal−$NCCH_3$ complexes by NMR spectroscopy see: (a) Liu, S. H.; Ng, S. M.; Wen, T. B.; Zhou, Z. Y.; Lin, Z.; Lau, C. P.; Jia, G. *Organometallics* **2002**, *21*, 4281. (b) Li, K.; Horton, P. N.; Hursthouse, M. B.; Hii, K. K. (Mimi) *J. Organomet. Chem.* **2003**, *665*, 250. (c) Lail, M.; Gunnoe, T. B.; Barakat, K. A.; Cundari, T. R. *Organometallics* **2005**, *24*, 1301.

(23) Stojcevic, G.; Prokopchuk, E. M.; Baird, M. C. *J. Organomet. Chem.* **2005**, *690*, 4349.

(24) Chin, C. S.; Chong, D.; Lee, S.; Park, Y. J. *Organometallics* **2000**, *19*, 4043.

(25) (a) Bryan, S. J.; Huggett, P. G.; Wade, K.; Daniels, J. A.; Jennings, J. R. *Coord. Chem. Rev.* **1982**, *44*, 149. (b) Groux, L. F.; Weiss, T.; Reddy, D. N.; Chase, P. A.; Piers, W. E.; Ziegler, T.; Parvez, M.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2005**, *127*, 1854.

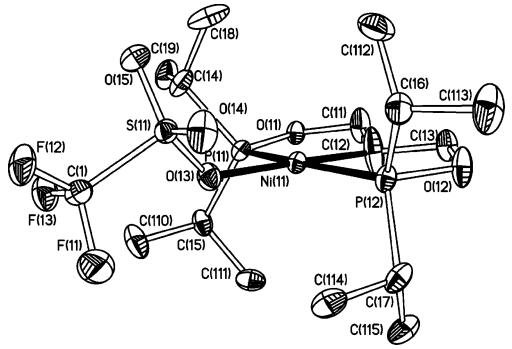


Figure 2. ORTEP diagram for complex **2d**. Thermal ellipsoids are shown at the 30% probability level. All hydrogen atoms and disordered OSO_2CF_3 groups are omitted for clarity.

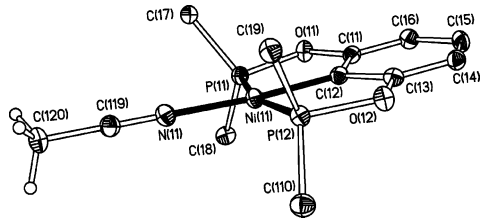


Figure 3. ORTEP diagram for complex **1e**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and methyl groups are omitted for clarity.

asymmetric unit, one of which is shown in Figure 3. The crystal data and refinement parameters are summarized in Table 3, and the structural metrics for all three molecules are listed in Table 5. The geometry around the Ni center in **1e** is best described as distorted square planar. That the overall structure observed in **1b** is largely maintained in **1e** is evident from the more or less unchanged Ni−P and Ni−C2 distances and the P−Ni−P and C−Ni−X (X = Br, N) angles. The fairly short N−C distance of ca. 1.14 Å is consistent with the strong C≡N bond implied from the IR data. The Ni−N bond distance of 1.874(2) Å is significantly shorter than the corresponding distances in the analogous PCP species $[\{(t\text{-}Bu_2PCH_2CH_2)_2CH\}Ni(NCCH_3)]^+$ [16] and other cationic Ni−$NCCH_3$ complexes reported in the literature.[26] This is presumably an indication that the Ni center in [POCOP−Ni]$^+$ is fairly electrophilic, which bodes well for using these cations in Lewis acid-promoted transformations (vide infra).

Synthesis and Characterization of the Alkyl Derivatives ($POC_{sp2}OP$)Ni(Me) and ($POC_{sp2}OP$)Ni(Et). Given the importance of transition metal−alkyl complexes in a variety of catalytic reactions, we undertook to prepare alkyl derivatives of our pincer complexes and study their structural and reactivity profiles. Reacting the Ni−Cl derivative **1a** with 1 equiv of MeMgCl or EtMgCl in E_2O gave the corresponding Ni−R derivatives, as confirmed by NMR spectroscopy, but the purification of the desired products was complicated by the gradual regeneration of the Ni−Cl precursor; this is presumably because the $MgCl_2$ generated in the reaction did not separate from the Ni−alkyl product. We also failed to isolate any Ni−alkyl derivatives generated from the reactions of the POC_{sp3}OP precursor **2b** with Grignard reagents, because these species appear to be thermally labile. In contrast, the analogous reaction of the Ni−Br precursor **1b** with the appropriate Grignard reagents gave the corresponding Ni−Me and Ni−Et derivatives **1g** and **1h**, respectively, which could be isolated in analytically pure form after a workup routine that included washing the final mixture with deoxygentated water to remove the undesired salts generated during the syntheses. The Ni−Me and Ni−Et derivatives **1g** and **1h** are thermally stable for days in ambient temperature solutions, but decomposition sets in at higher temperatures. The stability of **1h** toward β-H elimination (at room temperature) is particularly noteworthy. The compounds **1g** and **1h** were fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography, as described below.

The $^{31}P\{^1H\}$ NMR spectra of these complexes display a single resonance at 191.9 ppm (**1g**) and 189 ppm (**1h**), in agreement with the trans geometry of the phosphine moieties. In the ^1H and $^{13}C\{^1H\}$ NMR spectra, compound **1g** displays a characteristically high-field virtual triplet (^1H: −0.63 ppm, J = 8.7 Hz; ^{13}C: −21.38 ppm, J = 18.21 Hz). The ^1H NMR spectrum of compound **1h** displays a triplet (1.14 ppm; J_{HH} = 7.6 Hz) and a multiplet (0.61 ppm) for the Ni−Et moiety. The latter is also identified in the $^{13}C\{^1H\}$ NMR spectrum by a singlet (16.85 ppm, CH_2CH_3) and a high-field virtual triplet (−9.0 ppm, J = 17.8 Hz, CH_2CH_3). Single crystals suitable for X-ray crystallography were obtained by recrystallization of **1g** and **1h** in hexane at −20 °C. The ORTEP diagrams for these compounds are shown in Figure 4, and selected distances and angles are given in Table 6. The asymmetric unit of complex **1g** contains two "head-to-head" packed molecules of $\{2,6\text{-}(i\text{-}Pr_2PO)_2C_6H_3\}$-NiMe,[27] while only one molecule is observed in the asymmetric unit of **1h**. The overall coordination geometry in both complexes is distorted square-planar (P−Ni−P ≈ 164°, C−Ni−C ≈ 179°). The solid-state structure of complex **1h** constitutes a relatively rare example for a Ni−alkyl complex bearing β-hydrogens.[28] The Ni−Me and Ni−Et bond lengths are fairly equivalent (ca. 1.99 Å). These bonds are quite similar to other Ni−C distances that are trans from another Ni−C bond such as the Ni−Me bond distance in the 2-pyridyl derivative *trans*-$[NiMe(3\text{-}C_5NF_4)(PEt_3)_2]$,[29] but somewhat longer than Ni−C_{sp3} bonds that are trans to ligands with weaker trans influences, such as the Ni−Me bonds in *trans*-$[(PMe_3)_2Ni(OPh)Me]\cdot PhOH$ (ca. 1.95 Å)[30] and $\{N(o\text{-}C_6H_4PR_2)_2\}$Ni−Me (ca. 1.97 Å).[28]

17-Electron Ni(III) Species. Cyclic voltammetry studies of the halide derivatives **1a**−**c** and **2a**−**c** showed that they undergo a one-electron oxidation process that is quasi-reversible in the case of **1b** ($E_{1/2}$ = 1.17 V) and irreversible in the case of **2b** (peak maximum at 0.87 V). Interestingly, the voltammogram for the $POC_{sp3}OP$ system **2b** indicates that this species might be undergoing a second oxidation process ($Ni^{III} \rightarrow Ni^{IV}$, peak maximum at 1.37 V).[17] Tests showed that complexes **2a** and **2b** could be oxidized by mild oxidants such as $CuBr_2$, $CuCl_2$, CCl_4, and $FeCl_3$; the Ni^{III} pincer complexes $\{(i\text{-}Pr_2POCH_2)_2CH\}NiX_2$ (**2i**, X = Cl; **2j**, X = Br) were then prepared in 90−95% yields by reacting the corresponding Ni^{II} precursors with CuX_2. Curiously, the $POC_{sp2}OP$ analogues **1a** and **1b** did not

(26) For examples of structurally characterized Ni−$NCCH_3$ complexes see ref 16 and the following: (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. (d) Barbaro, P.; Togni, A. *Organometallics* **1995**, *14*, 3570. (e) Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 3068.

(27) A similar "head-to-head packing" has been observed for the Ni(I)−Me complex (terpyridine)Ni(Me) (Ni−C= 1.95(13) Å): Anderson, T. J.; Jones, G. D.; Vicic, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 8100.

(28) For other examples see this report and the references therein: Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399.

(29) Sladek, M. I.; Braun, T.; Neumann, B.; Stammler, H.-G. *New J. Chem.* **2003**, *27*, 313.

(30) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.

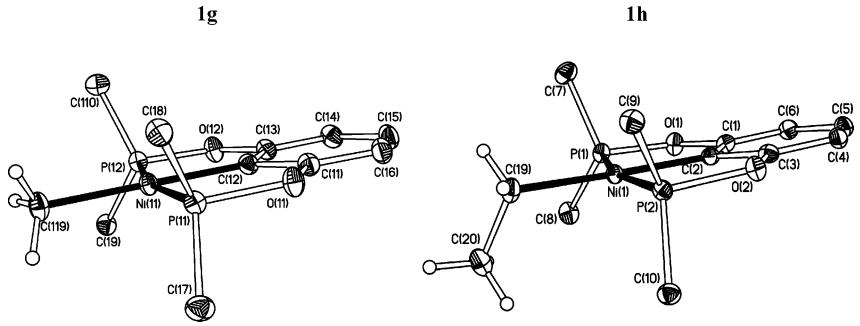


Figure 4. ORTEP diagram for complexes **1g** and **1h**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and methyl groups are omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complexes 1g and 1h

($POC_{sp2}OP$)NiMe (**1g**)				($POC_{sp2}OP$)NiEt (**1h**)	
molecule 1		molecule 2			
Ni(11)−C(12)	1.901(2)	Ni(21)−C(22)	1.903(2)	Ni(1)−C(2)	1.911(2)
Ni(11)−P(11)	2.1287(4)	Ni(21)−P(21)	2.1306(4)	Ni(1)−P(1)	2.1433(5)
Ni(11)−P(12)	2.1158(4)	Ni(21)−P(22)	2.1322(4)	Ni(1)−P(2)	2.1204(5)
Ni(11)−C(119)	1.994(2)	Ni(21)−C(219)	1.997(2)	Ni(1)−C(19)	1.995(2)
C(12)−Ni(11)−C(119)	179.07(6)	C(22)−Ni(21)−C(219)	177.67(7)	C(2)−Ni(1)−C(19)	176.57(7)
P(11)−Ni(11)−P(12)	164.28(2)	P(21)−Ni(21)−P(22)	163.31(2)	P(1)−Ni(1)−P(2)	163.98(2)

undergo oxidation in the presence of these reagents. Complexes **2i** and **2j** and the closely related NCN−Ni^{III} compounds reported earlier by van Koten's group[31] constitute rare examples of pincer-type compounds of Ni^{III}. The analogous PCP complexes [2,6-(Ph_2PCH_2)$_2$(C_6H_3)Ni(catecholate)] (catecholate = 3,5- or 3,6-di-*tert*-butyl-*o*-benzosemiquinono)[14c] are also paramagnetic, but the unpaired electron in these complexes is thought to be stabilized on the catecholate ligand, thus giving Ni^{II} species.

The ^{1}H NMR spectra of **2i** and **2j** displayed broad, featureless signals, while their ^{31}P NMR spectra showed no signals at all, implying that the paramagnetic character of these complexes is maintained in solution. However, monitoring by NMR showed that the signals for their precursors, **2a** and **2b**, reappear after about 30 h, implying that **2i** and **2j** have limited stability in solution. This is presumably due to the spontaneous, homolytic cleavage of the relatively weak Ni−halide bond (vide infra), but we have not studied this reaction in any detail. Consistent with the maintenance of the paramagnetic character of these Ni(III) species in solution, magnetic moments corresponding to one unpaired electron were obtained by the Evans method[32] on $CDCl_3$ solutions of **2j**. Comparison of the UV−visible spectra (Figure 5) of **2a** and **2b** to those of **2i** and **2j**, respectively, showed that the one-electron oxidation results in a 16 nm red-shift in the MLCT bands of these complexes, consistent with the observed color changes from yellow (**2a** and **2b**) to orange (**2i**) and red (**2j**). In addition, a new band emerged in both cases beyond 500 nm.[33]

Single crystals of **2i** and **2j** were grown by slow evaporation of a hexane−acetone solution and their solid-state structures determined by X-ray diffraction studies. The structure of **2j** has been communicated recently.[17] The ORTEP diagram for **2i** is shown in Figure 6, the crystal data and collection details are listed in Table 3, and the metric parameters for both structures are listed in Table 7. These 17-electron, isostructural species adopt a square-pyramidal geometry displaying a slight pyramidal distortion reflected in (a) the out-of-plane displacement of the Ni center from the equatorial plane defined by the atoms P1, C1, P2, and X (by ca. 0.1 Å) and (b) the angles C1−Ni−X1 (ca. 158°) and X1−Ni−X2 (ca. 104−106°).[34] The unusually large difference between the Ni−X1 and Ni−X2 distances (2.26 vs 2.32 Å in **2i**; 2.37 vs 2.44 Å in **2j**) arises presumably from the partial occupation of the p_z/d_{z^2} hybrid orbital that has antibonding character with respect to the Ni−X_{axial} bond. Similar observations have been made for the axial and equatorial Ni−X bonds in the above-mentioned PCP−Ni^{II}(catecholate) compounds (Ni−O1 = 1.92 Å vs Ni−O2 = 2.06 Å),[14c] whereas the two Ni−I bond distances in van Koten's NCN−$Ni^{III}(I)_2$ complex are fairly similar (2.61 and 2.63 Å).[35]

Table 7. Selected Bond Distances (Å) and Angles (deg) for Complexes 2i and 2j

	2i (X = Cl)	**2j** (X = Br)
Ni−C2	2.012(2)	2.011(5)
Ni−P1	2.2259(5)	2.235(1)
Ni−P2	2.2440(5)	2.251(1)
Ni−X1	2.2620(5)	2.3683(9)
Ni−X2	2.3236(5)	2.436(1)
C2−Ni−X1	157.52(6)	157.09(15)
C2−Ni−X2	97.96(5)	93.54(4)
X1−Ni−X2	104.41(2)	106.13(4)
P1−Ni−P2	161.53(2)	160.57(6)

Catalytic Activities of Ni−Pincer Complexes. Kharasch Additions. A variety of paramagnetic complexes are known to

(31) (a) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoet, R. *Organometallics* **1984**, *3*, 1003. (b) Grove, D. M.; van Koten, G.; Mul, W. P.; van der Zeijden, A. A. H.; Terheijden, J.; Zoutberg, M. C.; Stam, C. H. *Organometallics* **1986**, *5*, 322. (c) Grove, D. M.; van Koten, G.; Mul, P.; Zoet, R.; van der Linden, J. G. M.; Legters, J.; Schmitz, J. E. J.; Murrall, N. W.; Welch, A. J. *Inorg. Chem.* **1988**, *27*, 2466.

(32) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Ayers, T.; Turk, R.; Lane, C.; Goins, J.; Jameson, D.; Slattery, S. J. *Inorg. Chim. Acta* **2004**, *357*, 202.

(33) For a discussion of the UV−visible spectra of the analogous NCN−Ni compounds see: van de Kuil, L. A.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Chem. Mater.* **1994**, *6*, 1675.

(34) The degree of trigonal distortion in the solid structures of these complexes can also be expressed in terms of the angular structural parameter τ, which is defined by the equation $\tau = (\beta - \alpha)/60$, wherein β and α are the largest basal angles ($\beta > \alpha$) (Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *Dalton Trans.* **1984**, 1349). The values of the τ parameter for ($POC_{sp3}OP$)−$NiCl_2$ and −$NiBr_2$ were calculated to be 0.07 and 0.05, respectively, implying only a small degree of distortion toward a trigonal bipyramidal geometry. For comparison, the corresponding values of τ for a purely square-pyramidal and trigonal-bipyramidal structure would be 0 and 1, respectively.

(35) Grove, D. M.; van Koten, G.; Zoet, R. *J. Am. Chem. Soc.* **1983**, *105*, 1379.

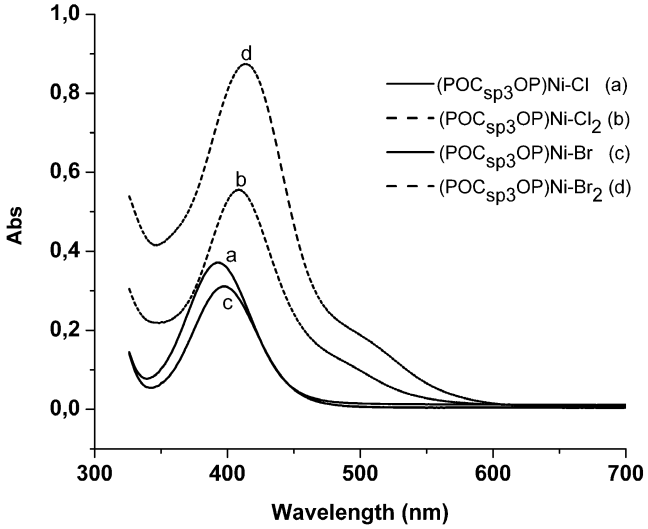


Figure 5. Solution UV−visible spectra of complexes **2a** (curve a), **2i** (curve b), **2b** (curve c), and **2j** (curve d), all samples having an approximate concentration of 0.57×10^{-4} M in acetone.

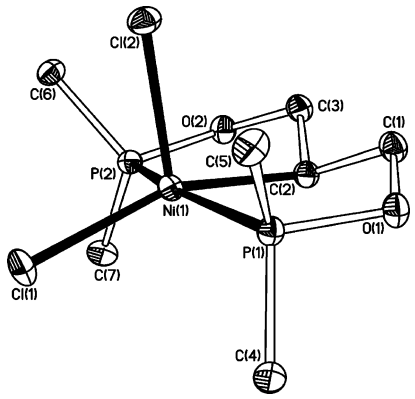
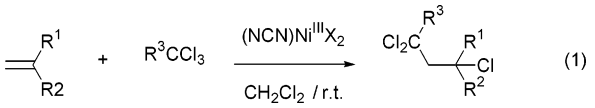


Figure 6. ORTEP diagram for complex $(POC_{sp3}OP)NiCl_2$, **2i**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and methyl groups are omitted for clarity.

promote the Kharasch addition of CCl_4 to various olefins. Of relevance to our studies, van Koten's group has shown that Ni^{III} complexes based on NCN-type pincer ligands are efficient promoters of the addition of polyhalogenated alkanes to olefins to give the anti-Markovnikov product (eq 1). Mechanistic studies



(1)

by this group have concluded that this reaction proceeds through a nonchain cycle wherein the carbon-based radical entities are held within the solvent cage of the Ni complex, which results in 1:1 additions exclusively as opposed to polymerization or telomerization reactions. We have examined the reactivities of our (POCOP)−Ni^{III} systems in the Kharasch addition of CCl_4 to styrene, 4-methylstyrene, methyl acrylate (MA), methyl methacrylate (MMA), acrylonitrile, and acrolein in order to allow a comparison to the reactivities of van Koten's NCN−Ni^{III} systems, as described below.

The addition of CCl_4 to MMA in CH_2Cl_2 was selected as a test reaction for evaluating the efficacy of our system in comparison to van Koten's,[36] which gives about 200 turnovers in 1 h at room temperature ([Ni]:[olefin] ≈ 1:300; 65% yield). Initial experiments showed that **2j** was completely ineffective

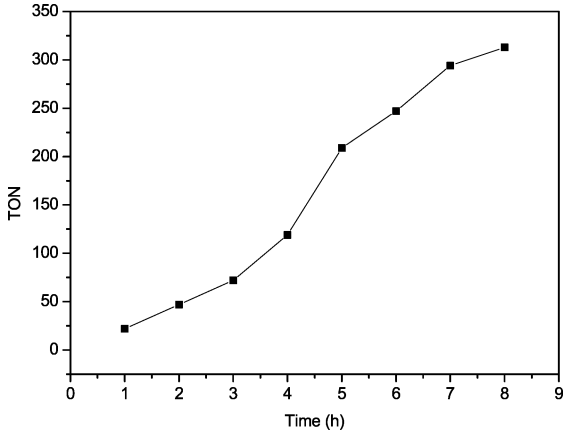


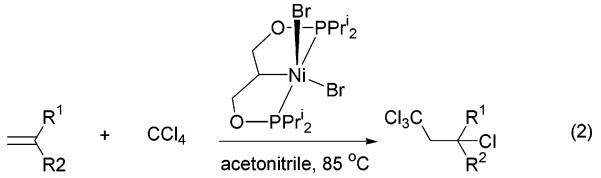
Figure 7. Reaction profile (turnover vs time) for the Kharasch addition of CCl_4 to methyl methacrylate promoted by compound **2j** in refluxing acetonitrile.

Table 8. Kharasch Addition of CCl_4 to Olefins Promoted by 2j[a]

run	substrate	[Ni]:[alkene]	time (h)	yield (%)
1	MMA	1:300	8	100
2	MMA	1:1000	24	100
3	MMA	1:1000	24	97[b]
4	styrene	1:300	8	100
5	styrene	1:1000	24	100
6	styrene	1:1000	24	96[b]
7	4-methylstyrene	1:1000	24	95[b]
8	acrolein	1:250	24	85[b]
9	methyl acrylate	1:250	24	80[b]
10	acrylonitrile	1:250	24	65[b]
11	α-methylstyrene	1:250	24	0

[a] Unless otherwise noted, yields were determined by GC/MS analysis based on a calibration curve prepared by using *p*-xylene as internal standard. [b] Isolated yields.

in promoting this reaction at room temperature, even after 24 h, but in refluxing CH_2Cl_2 the reaction proceeded with 90 and 300 turnovers over 8 and 24 h, respectively. In agreement with van Koten's findings, the reaction gives the 1:1 anti-Markovnikov addition product exclusively. The catalysis proceeded somewhat faster in refluxing acetonitrile (eq 2; R^1 = Me, R^2 = COOMe), giving 300 turnovers in 8 h (Figure 7) and up to 1000 turnovers in 24 h (runs 1−3, Table 8). The reaction works



(2)

equally well with styrene (runs 4−6) and 4-methylstyrene (run 7), somewhat less efficiently with acrolein (run 8), methyl acrylate (run 9), and acrylonitrile (run 10), and not at all with α-methylstyrene (run 11), 1-hexyne, and 3-hexyne.

We have confirmed van Koten's observations regarding the important reaction parameters. For instance, the addition can be initiated either by using preformed Ni^{III} or generating the latter in situ by premixing the Ni^{II} precursors with CCl_4. In either method, strictly anaerobic conditions should be maintained during the catalysis in order to avoid quenching the active species. GC/MS analyses of the reaction mixtures from the

(36) van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1997**, *16*, 4985.

unsuccessful runs (e.g., with α-methylstyrene) found ca. 10% CCl_3-CCl_3, implying that the in situ generated CCl_3 radicals eventually leave the solvent cage and recombine if the addition to the olefin is sluggish.

Michael Additions. Catalytic amination of olefins is an attractive route to industrially important amines,[37] and many reports have described olefin hydroamination processes catalyzed by complexes of lanthanides,[38] group 4 metals,[39] Rh,[40] Ir,[41] Ni,[42] Pd,[43] Pt,[44] and Cu.[45] Interestingly, a number of reports have also shown that homogeneous intermolecular hydroamination of styrene by electron-rich anilines can be promoted by acids such as HOTf[46] or even HCl,[47] while $PhNH_3B(C_6F_5)_4 \cdot Et_2O$ promotes both the hydroamination and hydroarylation of styrene and cyclic olefins such as norbornene and *cis*-cyclooctene.[48]

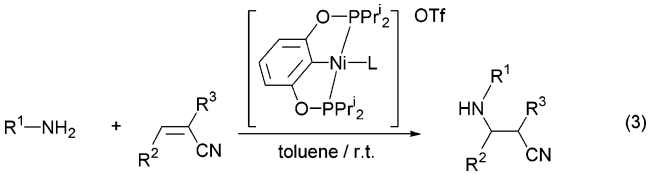
The Michael addition of amines to activated olefins is somewhat analogous to olefin hydroamination. Although in some cases these reactions proceed in the absence of a catalyst,[49] a large variety of Lewis acids ($AlCl_3$, $InCl_3$, $TiCl_4$, etc.)[50] have been employed to accelerate the addition rate or impart stereoselectivity. Metal-catalyzed Michael additions are thought to proceed by the nucleophilic attack of the amine on the olefin that is coordinated to a Lewis acidic metal center via either the C═C moiety or a coordinating substituent. A recent report has also invoked the possibility of nucleophilic attack by Cu−amido species on free olefins.[45] Hartwig's group has reported that the combination of Ru, Rh, Ir, and Pd salts with various ligands can catalyze the addition of aniline, piperidine, and *n*-$BuNH_2$ to acrylic acid derivatives.[51] Togni's group has reported that a dicationic Ni−tris(phosphine) complex catalyzes the anti-Markovnikov addition of aniline, piperidine, or morpholine to acrylic acid derivatives.[52]

Table 9. Michael Addition of Amines to Activated Olefins Promoted by 1f[a]

Amine	Olefin	Run	% **1f**	Time	Isolated Yield (%)	TON[b]
		1	0.05	5 min	---	2 000
		2	1.00	5 min	93	100
		3[c]	0.20	5 min	94	500
		4	1.00	5 min	93	100
		5[c]	0.20	3 h	---	425
		6[c]	0.10	15 h	---	900
		7	1.00	5 min	97	100
		8	0.10	15 min	---	630
				1 h	80	880
		9	1.00	3 h	83	89
		10	1.00	3 h	78	83
		11[d]	3.00	72 h	---	16
		12[d]	2.00	24 h	---	45
		13[d]	0.54	4 h	---	105
				24 h	---	155

[a] The catalytic reactions were carried out at room temperature (22−24 °C) for all runs except runs 12 and 13, which were conducted at 115 °C. [b] The catalytic turnover numbers were determined by GC/MS analysis of the reaction mixtures, as explained in the Experimental Section. [c] The concentration of the substrates was 1.00 M in these runs. [d] For these runs, a 1:3 ratio of aniline to acrylonitrile was used.

The facile access to the cationic $[POCOP-NiL]^+$ complexes discussed above prompted us to evaluate their effectiveness in promoting the addition of morpholine, cyclohexyl amine, and aniline to acrylonitrile, crotonitrile, and methacrylonitrile (eq 3). Comparing the results of the Ni-catalyzed and control



(3)

R^1: Ar, Cy; R^2: H, Me; R^3: H, Me

experiments (see Experimental Section) has shown that in all cases the addition reaction is accelerated dramatically in the presence of our cationic pincer complexes. For instance, in the presence of 0.05% mol of the acrylonitrile adduct **1f**, the addition of morpholine to acrylonitrile proceeded quantitatively within 5 min at 22 °C (run 1, Table 9); under similar reaction conditions (ca. 0.52 M toluene solutions of the substrates at room temperature), the uncatalyzed reactions gave no conversion after 1 h, 7% yield after 6 h, and 25% yield after 24 h. The **1f**-catalyzed addition of morpholine to crotonitrile appeared somewhat slower, giving about 500 catalytic turnovers in 5 min (run 3). The addition to methacrylonitrile seemed slower still (run 5 vs run 3), but up to 900 catalytic turnovers could be obtained over 15 h (run 6). (N.B.: The latter reaction could be run for longer periods because the uncatalyzed addition of

(37) (a) Brunet, J. J.; Neibecke, D. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Ed.; VCH: Weinheim, 2001; pp 91−141. (b) Müller, T.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.

(38) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568.

(39) (a) Ackermann, L.; Bergman, R. G. *Org. Lett.* **2002**, *4* (9), 1475. (b) Ackermann, L.; Kaspar, L. T.; Gschrei, C. J. *Org. Lett.* **2004**, *6* (15), 2515. (c) Bexrud, J. A.; Beard, J. D.; Leitch, D. C.; Schafer, L. L. *Org. Lett.* **2005**, *7* (10), 1959. (d) Thomson, R. K.; Bexrud, J. A.; Schafer, L. L. *Organometallics* **2006**, *25*, 4069. (e) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 354.

(40) (a) Brunet, J. J.; Commenges, G.; Neibecker, D.; Philippot, K. *J. Organomet. Chem.* **1994**, *469*, 221. (b) Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Müller, T. *Eur. J. Inorg. Chem.* **1999**, 1121.

(41) (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (b) Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857.

(42) Pawlas, J.; Nakao, Y.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 3669.

(43) (a) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 744. (b) Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 9546. (c) Löber, O.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4366. (d) Nettekoven, U.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1166.

(44) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 12640.

(45) Munro-Leighton, C.; Delp, S. A.; Blue, E. D.; Gunnoe, T. B. *Organometallics* **2007**, *26*, 1483, and references therein.

(46) Beller, M.; Thiel, O. R.; Trauthwein, H. *Synlett* **1999**, 243.

(47) Hart, H.; Kosak, J. R. *J. Org. Chem.* **1962**, *27*, 116.

(48) Anderson, L. L.; Arnold, J.; Bergman, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 14542.

(49) A recent report has shown, for example, that Michael addition of some amines to acrylic acid derivatives is particularly facile when the reaction is carried out in neat substrate (solvent-free). For instance, morpholine and cyclopentyl amine add to acrylonitrile with ca. 91−93% yield in 2−3 h. (Ranu, B. C.; Dey, S. S.; Hajra, A. *ARKIVOC* **2002** (vii), 76). Kinetic studies of the uncatalyzed addition of amines to acrylic acid derivatives have been reported (Simonyan, G. S.; Beileryan, N. M.; Pirumyan, E. G.; Roque, J.-P.; Boyer, B. *Kinet. Catal.* **2001**, *42*, 526, and references therein). It should be noted, however, that uncatalyzed additions to acrylonitrile are much more sluggish in diluted media, and especially in nonpolar solvents, whereas no additions have been observed with crotonitrile and methacrylonitrile over 24 h. See control experiments in the Experimental Section for more details.

(50) (a) Cabral, J.; Laszlo, P.; Mahé, L.; Montaufier, M.-T.; Randriamahefa, S. L. *Tetrahedron Lett.* **1989**, *30*, 3969. (b) Loh, T. P.; Wei, L.-L. *Synlett* **1998**, 975.

(51) Kawatsura, M.; Hartwig, J. F. *Organometallics* **2001**, *20*, 1960.

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

morpholine to methacrylonitrile does not occur under the reaction conditions and hence does not distort the results of the catalyzed addition.)

A simple competition experiment was performed to confirm the relative rates of the catalyzed additions involving acrylonitrile, crotonitrile, and methacrylonitrile. One equivalent of morpholine was added to a toluene solution containing 1 equiv each of acrylonitrile, crotonitrile, and methacrylonitrile (1% catalyst, 0.5 M concentration of substrates) and the mixture stirred at room temperature. GC/MS analyses showed a quantitative conversion for acrylonitrile ($t = 5$ min), but no trace of the products of the addition to crotonitrile or methacrylonitrile. The latter were detected in a 60:40 ratio 5 min after a second equiv of morpholine was added to the reaction mixture, implying that the addition to crotonitrile is about 50% more facile. The more sluggish conversion of methacrylonitrile is likely due to the greater steric bulk of this substrate, which hinders its coordination to the Ni center.

The analogous addition of (cyclohexyl)NH_2 to acrylonitrile was examined next. We found catalytic turnover numbers of 630 (15 min) and 800 (1 h) for the addition to acrylonitrile (runs 7 and 8); the uncatalyzed addition gave no conversion after 6 h, and only traces of product were detected after 24 h. It is noteworthy that the product of this addition, (cyclohexyl)NH-(CH_2CH_2CN), can further react with excess acrylonitrile to give the tertiary amine (cyclohexyl)N($CH_2CH_2CN)_2$; the second addition is more sluggish, however, requiring 24 h for a 40% conversion (1% catalyst, 0.5 M concentration of substrates). The additions of (cyclohexyl)NH_2 to crotonitrile and methacrylonitrile gave about 80 turnovers in 3 h (runs 9 and 10). Finally, the addition of weakly nucleophilic aniline to acrylonitrile was very sluggish at room temperature (run 11), but ca. 150 catalytic turnovers were obtained in refluxing toluene (runs 12 and 13).

Conclusion

The relatively facile access to a new series of pincer-type nickel complexes based on the diphosphinito (POCOP) ligands 1,3-(i-$Pr_2PO)_2C_6H_4$, **1**, and (i-$Pr_2POCH_2)_2CH_2$, **2**, has allowed us to explore the reactivities of these complexes. Of particular interest to us is the possibility to prepare Ni(III) derivatives by one-electron oxidation of the more electron-rich derivatives based on **2**. The complexes {(i-$Pr_2POCH_2)_2CH$}NiX_2 are rare examples of organonickel(III) complexes, which should reveal interesting reactivities. Like their NCN counterparts {2,6-(Me_2-$NCH_2)_2$-C_6H_3}NiX_2 reported earlier by van Koten's group,[31,35,36] our POCOP−Ni^{III} species promote the Kharasch addition reaction, albeit somewhat more sluggishly. Future studies will examine the influence of less bulky P-substituents on the rate of this reaction, the use of alkyl halides other than CCl_4, and the derivatization of the products of the addition reaction.

The easy access to the neutral OTf derivatives **1d** and **2d** and the cationic nitrile adducts **1e**, **2e**, **1f**, and **2f** bearing fairly labile Ni−O and Ni−N linkages, respectively, has provided an opportunity to examine the Lewis acidity of the in situ generated cations [POCOP−Ni]$^+$. Preliminary tests have shown, for instance, that **1f** is an efficient catalyst for the Michael addition of morpholine, $CyNH_2$, and aniline to acrylonitrile, crotonitrile, and methacrylonitrile. The reaction of the more nucleophilic amine morpholine proceeds at room temperature with the highest catalytic efficiencies reported thus far (TONs in the range of 10^3). Future studies will focus on examining these and other Michael additions catalyzed by enantiopure C_2-symmetric precursors. Finally, we will also investigate the myriad of reactions possible with the Ni^{II}− and Ni^{III}−alkyl derivatives of our POCOP complexes.

Experimental Section

General Procedures. Unless otherwise indicated, all manipulations were carried out under nitrogen using standard Schlenk procedures and a drybox. Solvents were dried over sodium (hexane), sodium/benzophenone (benzene, toluene, THF, diethyl ether), or CaH_2 (acetonitrile) and then distilled under a nitrogen atmosphere. Unless otherwise indicated, all reagents used in this study were purchased from Aldrich and used without further purification.

The NMR spectra were recorded at 400 (^{1}H, ^{1}H{^{31}P}) and 161.9 MHz (^{31}P{^{1}H}) using a Bruker AV400rg spectrometer, at 400 (^{1}H) and 100.56 MHz (^{13}C{^{1}H}) using a Bruker ARX400 spectrometer, and at 121.5 (^{31}P{^{1}H}) and 282 MHz (^{19}F{^{1}H}) using a Bruker AV300 spectrometer. Chemical shift values are reported in ppm (δ) and referenced internally to the residual solvent signals (^{1}H and ^{13}C: 7.26 and 77.16 ppm for $CDCl_3$; 7.16 and 128.06 ppm for C_6D_6) or externally (^{31}P, H_3PO_4 in D_2O, $\delta = 0$; ^{19}F, C_6F_6 ($\delta = -164.9$). Coupling constants are reported in Hz. UV/vis spectra were measured on a Varian Cary 500i. The IR spectra of samples prepared as KBr pellets were recorded on a Perkin-Elmer 1750 FTIR (4000−450 cm^{-1}) spectrometer. The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire, Département de Chimie, Université de Montréal. Accurate mass measurements were performed on a LC-MSD-Tof instrument from Agilent technologies in positive electrospray mode. Samples were directed toward the mass spectrometer at a flow rate of 0.5 mL/min with 100% methanol. Sodium adduct peaks $(M + Na)^+$ were used for empirical formula confirmation.

Preparation of the Ni Precursors. $(THF)_{1.5}NiCl_2$ was prepared following a procedure reported in the literature.[53] $(THF)_2NiBr_2$ was prepared using a slightly modified version of a procedure reported in the literature.[54] Using this modified procedure (see below) with acetonitrile instead of THF allowed us to prepare $(CH_3CN)_nNiX_2$ (X = Br, $n = 2$; I, $n = 3$).

[$(THF)_2NiBr_2$]. Bromine (1.96 mL, 6.126 g, 38.33 mmol, 1.5 equiv) was added dropwise to a slurry of nickel powder (1.500 g, 26 mmol, 1 equiv) in 50 mL of THF under an atmosphere of nitrogen. A hygroscopic, salmon-colored solid formed after 1 day of stirring at room temperature. Filtration (under nitrogen) gave the solid product, which was washed with Et_2O (2 × 40 mL) and dried under a stream of nitrogen for 10 min. Yield: 8.81 g (95%).

[$(CH_3CN)_2NiBr_2$]. The above procedure was used in 40 mL of acetonitrile. The mixture was concentrated under vacuum to 20 mL and cooled to 0 °C, and the hygroscopic green-yellow solid was collected by filtration, washed with acetonitrile (2 × 20 mL), and dried under a stream of nitrogen. Yield: 5.78 g (75%). The elemental analysis of this complex corroborated the coordination of two acetonitrile molecules to Ni. Anal. Calcd for $C_4H_6Br_2N_2Ni_1$ (300.605): C, 15.98; H, 2.01; N, 9.32. Found: C, 15.6; H, 1.8; N, 8.9.

[$(CH_3CN)_3NiI_2$]. To a mixture of nickel powder (1.500 g, 26 mmol) and iodine (10.292 g, 39 mmol, 1.5 equiv) that had been purged under nitrogen for 30 min was added 40 mL of acetonitrile. After stirring for 1 day at room temperature, the mixture was concentrated under vacuum to 10 mL and cooled to 0 °C to give a dark red solid, which was collected by filtration, washed with acetonitrile (2 × 10 mL), and dried under a stream of nitrogen. Yield: 8.07 g (72%). The elemental analysis of this complex

(53) Eckert, N. A.; Bones, E. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2003,** *42* (5), 1720.

(54) Casalnuovo, A. L; RajanBabu, T. V. Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869.

corroborated the coordination of three acetonitrile molecules to Ni. Anal. Calcd for $C_6H_9I_2N_3Ni_1$(435.658): C, 16.54; H, 2.08; N, 9.65. Found: C, 15.94; H, 2.14; N, 9.27.

Preparation of the Ligands. The pincer ligands {1,3-(*i*-$Pr_2PO)_2C_6H_4$}, **1**, and {(*i*-$Pr_2POCH_2)_2CH_2$}, **2**, were prepared according to a slightly modified version of a literature procedure,[7a] as follows.

(*i*-$Pr_2POCH_2)_2CH_2$, 2. A solution of 1,3-propandiol (0.5 mL, 527 mg, 6.93 mmol) and DMAP (1.778 g, 13.85 mmol) in 50 mL of THF was added slowly to a solution of ClP(*i*-Pr)$_2$ (2.221 g, 14.55 mmol) in 25 mL of THF, while stirring at 0 °C. The resulting mixture was allowed to reach room temperature (rt) and stirred for an additional 24 h. After removal of the solvent under vacuum, the solid residue was extracted with several portions of hexane (3 × 40 mL) and the combined extracts were evaporated to give the crude product as a colorless oil (2.03 g, 95%). NMR spectroscopy showed the product to be greater than 98% pure, and it was used without further purification. ^{1}H NMR (δ, C_6D_6): 1.00 (dd, J_{HP} = 15.5, J_{HH} = 7.3, 12H, C*H*$_3$), 1.12 (dd, J_{HP} = 10.1, J_{HH} = 7.0, 12H, C*H*$_3$), 1.61 (m, 4H,PC*H*(CH$_3$)$_2$), 1.82 (q, J_{HH} = 6.3, 2H, CH$_2$C*H*$_2$-CH$_2$), 3.80 (dt, J_{HP} = 8.3 and J_{HH} = 6.3, 4H, OC*H*$_2$). ^{13}C{^{1}H} NMR (δ, C_6D_6): 17.18 (d, J_{PC} = 8, 4C, PCH(*C*H$_3$)$_2$), 18.22 (d, J_{PC} = 21, 4C, PCH(*C*H$_3$)$_2$), 28.45 (d, J_{PC} = 17, 4C,P*C*H(CH$_3$)$_2$), 34.23 (t, J_{PC} = 6.9, 1C, CH$_2$*C*H$_2$CH$_2$), 69.28 (d, J_{PC} = 20.8, 2C, *C*H$_2$CH$_2$*C*H$_2$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 151.6 ppm (s). Mass measurements for $(C_{15}H_{34}O_2P_2 + Na)^+$: calcd MW, 331.19262; found, 331.19397.

General Procedure for the Synthesis of the Pincer Complexes 1a, 1b, and 1c. Method A. A solution of ligand **1** in toluene (20 mL) was slowly added to a stirred suspension of freshly prepared nickel precursor ([(THF)$_{1.5}$NiCl$_2$], [(THF)$_2$NiBr$_2$], or [(CH$_3$-CN)$_3$NiI$_2$]) in toluene (20 mL), and the reaction mixture was stirred at room temperature for 1 h. The resulting residue was filtered (in the air), and the filtrate was evaporated to dryness. The crude product was extracted with several portions of hexanes, and the combined extracts were concentrated to 10 mL. Slow evaporation of this solution gave the pincer complex as large crystals that were covered by oily residues. Rapidly washing the crystals with acetone and hexane, followed by drying under vacuum, gave analytically pure **1a**, **1b**, or **1c**.

Method B. Inside the drybox, a 100 mL Schlenk vessel was charged with a freshly prepared sample of the nickel precursor ([(THF)$_{1.5}$NiCl$_2$], [(THF)$_2$NiBr$_2$], or [(CH$_3$CN)$_3$NiI$_2$]), toluene (40 mL), ligand **1**, and 1 equiv of DMAP. The reaction vessel was taken out of the drybox, and the mixture was heated to ca. 60 °C under nitrogen for 1 h. Cooling the reaction mixture to room temperature and filtration (in the air) gave a yellow-orange filtrate that was evaporated to dryness. The crude product was extracted with several portions of hexane, and the combined extracts were evaporated to dryness. Analytically pure **1a**, **1b**, or **1c** was obtained as a dark yellow-orange, crystalline solid.

[{2,6-(*i*-$Pr_2PO)_2C_6H_3$}NiCl], 1a. Using 500 mg of ligand **1** (1.46 mmol, 1 equiv) and 417 mg of [(THF)$_{1.5}$NiCl$_2$] (1.75 mmol, 1.2 equiv), in addition to 1 equiv of DMAP for method B, gave the final product as large, dark yellow crystals (method A: 413 mg, 65%; method B: 541 mg, 85%). ^{1}H NMR (δ, $CDCl_3$): 1.34 (dt^v, J_{HH} = 7.0 and $^vJ_{HP}$ = 7.1, 12H, C*H*$_3$), 1.43 (dt^v, J_{HH} = 7.2 and $^vJ_{HP}$ = 7.4, 12H, C*H*$_3$), 2.42 (m, $J \approx$ 7.0, 4H, PC*H*(CH$_3$)$_2$), 6.39 (d, J_{HH} = 8.0, 2H, *m*-H), 6.94 (t, J_{HH} = 8.0, 1H, *p*-H). ^{1}H{^{31}P} NMR (δ, $CDCl_3$): 1.33 (d, J_{HH} = 7.0, 12H, C*H*$_3$), 1.43 (d, J_{HH} = 7.2, 12H, C*H*$_3$), 2.42 (m, $J \approx$ 7.0, 4H, PC*H*(CH$_3$)$_2$), 6.39 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.94 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 16.79 (s, 4C, *C*H$_3$), 17.57 (s, 4C, *C*H$_3$), 27.84 (vt, $^vJ_{PC}$ = 11.1, 4C, P*C*H(CH$_3$)$_2$), 105.21 (vt, $^vJ_{PC}$ = 5.9, 2C, C$_{meta}$), 125.2 (vt, $^vJ_{PC}$ = 21.5, 1C, C$_{ipso}$), 128.71 (s, 1C, C$_{para}$), 168.97 (vt, $^vJ_{PC}$ = 10.0, 2C, C$_{ortho}$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 185.50 (s). Anal. Calcd for $C_{18}H_{31}ClO_2P_2Ni$ (435.531): C, 49.64; H, 7.17. Found: C, 49.42; H, 7.53.

[{2,6-(*i*-$Pr_2PO)_2C_6H_3$}NiBr], 1b. Using 500 mg of ligand **1** (1.46 mmol, 1 equiv) and 636 mg of [(THF)$_2$NiBr$_2$] (1.75 mmol, 1.2 equiv), in addition to 1 equiv of DMAP for method B, gave the final product as large dark yellow-orange crystals (method A: 561 mg, 80%; method B: 666 mg, 95%). ^{1}H NMR (δ, $CDCl_3$): 1.33 (dt^v, J_{HH} = 7.0 and $^vJ_{HP}$ = 7.1, 12H, C*H*$_3$), 1.43 (dt^v, J_{HH} = 7.1 and $^vJ_{HP}$ = 7.6, 12H, C*H*$_3$), 2.46 (m, $J \approx$ 7.0, 4H, PC*H*(CH$_3$)$_2$), 6.42 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.96 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{1}H-{^{31}P} NMR (δ, $CDCl_3$): 1.33 (d, J_{HH} = 7.0, 12H, C*H*$_3$), 1.43 (d, J_{HH} = 7.1, 12H, C*H*$_3$), 2.46 (m, $J \approx$ 7.0, 4H, PC*H*(CH$_3$)$_2$), 6.42 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.96 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{13}C NMR (δ, $CDCl_3$): 16.86 (s, 4C, *C*H$_3$), 17.92 (s, 4C, *C*H$_3$), 28.14 (vt, $^vJ_{PC}$ = 11.4, 4C, P*C*H(CH$_3$)$_2$), 105.23 (vt, $^vJ_{PC}$ = 6.2, 2C, C$_{meta}$), 127.9 (vt, $^vJ_{PC}$ = 20.8, 1C, C$_{ipso}$), 128.85 (s, 1C, C$_{para}$), 168.84 (vt, $^vJ_{PC} \approx$ 10.0, 2C, C$_{ortho}$) ^{31}P NMR (δ, $CDCl_3$): 188.21 (s). Anal. Calcd for $C_{18}H_{31}BrO_2P_2Ni$(479.983): C, 45,04; H, 6.51. Found: C, 45.24; H, 6.23.

[{2,6-(*i*-$Pr_2PO)_2C_6H_3$}NiI], 1c. Using 500 mg of ligand **1** (1.46 mmol, 1 equiv) and 691 mg of [(CH$_3$CN)$_3$NiI$_2$] (1.59 mmol, 1.09 equiv), in addition to 1 equiv of DMAP for method B, gave the final product as large, dark yellow-orange crystals (method A: 423 mg, 55%; method B: 654 mg, 85%). ^{1}H NMR (δ, $CDCl_3$): 1.31 (dt^v, J_{HH} = 6.7 and $^vJ_{HP}$ = 7.1, 12H, C*H*$_3$), 1.42 (dt^v, J_{HH} = 6.9 and $^vJ_{HP}$ = 7.9, 12H, C*H*$_3$), 2.54 (m, $J \approx$ 7.0, 4H, PC*H*(CH$_3$)$_2$), 6.47 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.99 (t, $J_{HH} \approx$ 8.0, 1H, *o*-H). ^{1}H {^{31}P} NMR (δ, $CDCl_3$): 1.31 (d, J_{HH} = 6.7, 12H, C*H*$_3$), 1.42 (d, J_{HH} = 6.9, 12H, C*H*$_3$), 2.54 (m, $J \approx$ 7.0,4H, PC*H*(CH$_3$)$_2$), 6.47 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.99 (t, $J_{HH} \approx$ 8.0, 1H, *o*-H). ^{13}C NMR (δ, $CDCl_3$): 16.84 (s, 4C, *C*H$_3$), 18.39 (s, 4C, *C*H$_3$), 28.60 (vt, $^vJ_{PC}$ = 11.8, 4C, P*C*H(CH$_3$)$_2$), 104.99 (vt, $^vJ_{PC}$ = 6.2, 2C, C$_{meta}$), 128.89 (s, 1C, C$_{para}$), 132.49 (vt, $^vJ_{PC}$ = 19.4, 1C, C$_{ipso}$), 168.40 (vt, $^vJ_{PC}$ = 9.7, 2C, C$_{ortho}$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 194.39 (s). Anal. Calcd for $C_{18}H_{31}IO_2P_2Ni$ (526.983): C, 41.02; H, 5.93. Found: C, 40.84; H, 6.03.

{(*i*-$Pr_2POCH_2)_2CH$}NiCl, 2a. To a stirred mixture of ligand **2** (500 mg, 1.62 mmol, 1 equiv) and anhydrous $NiCl_2$ (420 mg, 3.24 mmol, 2 equiv) in toluene (40 mL) was added 1 equiv of DMAP. The mixture was heated to reflux under nitrogen for ca. 48 h and then cooled to room temperature. The resulting mixture was filtered (in the air) and the filtrate evaporated to dryness. The residues were extracted with several portions of hexane, and the combined extracts were concentrated to 10 mL. Slow evaporation of this solution gave the pincer complex as large crystals that were covered by oily residues. Rapidly washing the crystals with acetone and hexane, followed by drying under vacuum, gave analytically pure **2a**. Yield: 216 mg (33%). ^{1}H NMR (δ, C_6D_6): 1.18 (dt^v, J_{HH} = 7.0 and $^vJ_{HP}$ = 6.8,6H, C*H*$_3$), 1.25 (dt^v, J_{HH} = 7.0 and $^vJ_{HP}$ = 7.0,6H, C*H*$_3$), 1.40 (dt^v, J_{HH} = 7.2 and $^vJ_{HP}$ = 7.6, 6H, C*H*$_3$), 1.51 (dt^v, J_{HH} = 7.2 and $^vJ_{HP}$ = 7.5, 6H, C*H*$_3$), 2.02 (br m, 2H, PC*H*(CH$_3$)$_2$), 2.23 (m, $J \approx$ 7.0,2H, PC*H*(CH$_3$)$_2$), 2.87−2.78 (m,1H, CH$_2$C*H*CH$_2$), 3.24 (dd, J_{HH} = 11.7 and J_{HH} = 9.4, 2H, C*H*$_2$CHC*H*$_2$), 3.50−3.37 (m, 2H, C*H*$_2$CHC*H*$_2$). ^{1}H{^{31}P} NMR (δ, C_6D_6): 1.18 (d, J_{HH} = 7.0, 6H, C*H*$_3$), 1.25 (d, J_{HH} = 7.0, 6H, C*H*$_3$), 1.40 (d, J_{HH} = 7.2, 6H, C*H*$_3$), 1.51 (d, J_{HH} = 7.2, 6H, C*H*$_3$), 2.02 (m, $J \approx$ 7, 2H, PC*H*(CH$_3$)$_2$), 2.23 (m, $J \approx$ 7.1, 2H, PC*H*(CH$_3$)$_2$), 2.87−2.78 (m, 1H, CH$_2$C*H*CH$_2$), 3.24 (dd, J_{HH} = 11.7 and J_{HH} = 9.4, 2H, C*H*$_2$-CHC*H*$_2$), 3.43 (m, 2H, C*H*$_2$CHC*H*$_2$). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.30 (s, 2C, *C*H$_3$), 17.15 (s, 2C, *C*H$_3$), 17.78 (s, 2C, *C*H$_3$), 18.63 (s, 2C, *C*H$_3$), 27.96 (vt, $^vJ_{PC}$ = 12.5, 2C, P*C*H(CH$_3$)$_2$), 28.70 (vt, $^vJ_{PC}$ = 10.8, 2C, P*C*H(CH$_3$)$_2$), 51.21 (vt, $^vJ_{PC}$ = 11.8, 1C, *C*H−Ni), 76.37 (vt, $^vJ_{PC}$ = 7.6, 2C, *C*H$_2$CHCH$_2$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 183.46 (s). Anal. Calcd for $C_{15}H_{33}ClO_2P_2Ni$ (401.515): C, 44.87; H, 8.28. Found: C, 45.46; H, 8.63.

{(*i*-$Pr_2POCH_2)_2CH$}NiBr, 2b. To a stirred mixture of ligand **2** (500 mg, 1.62 mmol, 1 equiv) and freshly prepared [(CH$_3$-CN)$_2$NiBr$_2$] (1.28 g, 3.24 mmol, 2 equiv) in toluene (40 mL) was added 1 equiv of DMAP. The mixture was heated to reflux under

nitrogen for ca. 5 h and then cooled to room temperature. The resulting mixture was filtered (in the air) and the filtrate evaporated to dryness. The residues were then extracted with several portions of hexane, and the combined extracts were evaporated to give analytically pure **2b** as a deep yellow crystalline solid. Yield: 672 mg (93%). ^{1}H NMR (δ, C_6D_6): 1.16 (dt^v, J_{HH} = 6.9 and $^vJ_{HP}$ = 6.8, 6H, CH_3), 1.23 (dt^v, J_{HH} = 6.8 and $^vJ_{HP}$ = 7.0, 6H, CH_3), 1.40 (dt^v, J_{HH} = 7.0 and $^vJ_{HP}$ = 7.6, 6H, CH_3), 1.50 (dt^v, J_{HH} = 7.0 and $^vJ_{HP}$ = 7.7, 6H, CH_3), 2.06 (br, 2H, PCH(CH$_3$)$_2$), 2.31 (m, $J_{HH} \approx$ 7.1, 2H, PCH(CH$_3$)$_2$), 2.83−2.92 (m, 1H, CH$_2$CHCH$_2$), 3.24 (dd, J_{HH} = 11.6 and J_{HH} = 9.5, 2H, CH_2CHCH_2), 3.41−3.54 (m, 2H, CH_2CHCH_2). ^{1}H{^{31}P} NMR (δ, C_6D_6): 1.16 (d, J_{HH} = 6.9,6H, CH_3), 1.23 (d, J_{HH} = 6.8, 6H, CH_3), 1.40 (d, J_{HH} = 7.0, 6H, CH_3), 1.50 (d, J_{HH} = 7.0, 6H, CH_3), 2.06 (m, $J \approx$ 7,2H, PCH(CH$_3$)$_2$), 2.31 (m, $J_{HH} \approx$ 7.1, 2H, PCH(CH$_3$)$_2$), 2.83−2.92 (m, 1H, CH$_2$CHCH$_2$), 3.24 (dd, J_{HH} = 11.6 and J_{HH} = 9.5, 2H, CH_2CHCH_2), 3.46−3.50 (m, 2H, CH_2CHCH_2). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.29 (s, 2C, *C*H$_3$), 17.16 (s, 2C, *C*H$_3$), 18.20 (s, 2C, *C*H$_3$), 18.87 (s, 2C, *C*H$_3$), 28.26 (vt, $^vJ_{PC}$ = 13.2, 2C, P*C*H(CH$_3$)$_2$), 29.03 (vt, $^vJ_{PC}$ = 11.1, 2C, P*C*H(CH$_3$)$_2$), 54.78 (vt, $^vJ_{PC}$ = 11.1, *C*H−Ni), 75.97 (vt, $^vJ_{PC}$ = 7.3, 2C, *C*H$_2$CH*C*H$_2$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 186.33 (s). Anal. Calcd for $C_{15}H_{33}BrO_2P_2Ni$ (445.966): C, 40.40; H, 7.46. Found: C, 40.45; H, 7.42.

{(*i*-Pr$_2$POCH$_2$)$_2$CH}NiI, 2c. To a stirred mixture of ligand **2** (500 mg, 1.62 mmol, 1 equiv) and freshly prepared [(CH$_3$CN)$_3$NiI$_2$] (1.280 g, 2.94 mmol, 1.8 equiv) in toluene (40 mL) was added 1 equiv of DMAP. The mixture was heated to reflux under nitrogen for ca. 5 h and then cooled to room temperature. The resulting mixture was filtered (in the air) and the filtrate evaporated to dryness. The residues were then extracted with several portions of hexane, and the combined extracts were evaporated to give analytically pure **2c** as a deep orange crystalline solid. Yield: 550 mg (70%). ^{1}H NMR (δ, C_6D_6): 1.13 (dt^v, J_{HH} = 6.7 and $^vJ_{HP}$ = 6.8, 6H, CH_3), 1.19 (dt^v, J_{HH} = 6.6 and $^vJ_{HP}$ = 7.1, 6H, CH_3), 1.41 (dt^v, J_{HH} = 6.8 and $^vJ_{HP}$ = 7.7, 6H, CH_3), 1.46 (dt^v, J_{HH} = 6.7 and $^vJ_{HP}$ = 7.6, 6H, CH_3), 2.13 (br, 2H, PCH(CH$_3$)$_2$), 2.43 (m, $J \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.91−3.00 (m, 1H, CH$_2$CHCH$_2$), 3.26 (dd, J_{HH} = 11.7 and J_{HH} = 9.3, 2H, CH_2CHCH_2), 3.50−3.63 (m, 2H, CH_2CHCH_2). ^{1}H{^{31}P} NMR (δ, C_6D_6): 1.14 (d, J_{HH} = 6.7, 6H, CH_3), 1.19 (d, J_{HH} = 6.6, 6H, CH_3), 1.41 (d, J_{HH} = 7.0, 6H, CH_3), 1.46 (d, J_{HH} = 6.7, 6H, CH_3), 2.13 (m, $J \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.43 (m, $J \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.91−3.00 (m, 1H, CH$_2$CHCH$_2$), 3.26 (dd, J_{HH} = 11.7 and J_{HH} = 9.3, 2H, CH_2CHCH_2), 3.50−3.63 (m, 2H, CH_2CHCH_2). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.41 (s, 2C, *C*H$_3$), 17.17 (s, 2C, *C*H$_3$), 19.07 (s, 2C, *C*H$_3$), 19.23 (s, 2C, *C*H$_3$), 28.86 (vt, $^vJ_{PC}$ = 13.9, 2C, P*C*H(CH$_3$)$_2$), 29.81 (vt, $^vJ_{PC}$ = 11.8, 2C, P*C*H-(CH$_3$)$_2$), 60.64 (vt, $^vJ_{PC}$ = 10.1, 1C, *C*H−Ni), 75.4 (vt, $^vJ_{PC}$ = 6.9, 2C, *C*H$_2$CH*C*H$_2$). ^{31}P NMR (δ, CDCl$_3$): 191.98 (s). Anal. Calcd for $C_{15}H_{33}IP_2O_2Ni$ (492.967): C, 36.55; H, 6.75. Found: C, 36.62; H, 6.94.

{2,6-(*i*-Pr$_2$PO)$_2$C$_6$H$_3$}Ni(O$_3$SCF$_3$), 1d. A mixture of {2,6-(*i*-Pr$_2$-PO)$_2$C$_6$H$_3$}NiBr, **1b** (200 mg, 0.417 mmol), and 1 equiv of Ag-(O$_3$SCF$_3$) was stirred in CH$_2$Cl$_2$ (20 mL) at room temperature. After 2 h, 30 mL of hexane was added, and the mixture was filtered by cannula to remove AgBr. Evaporation of the filtrate to dryness gave analytically pure product as a pale yellow solid. Yield: 175 mg (76%). ^{1}H NMR (δ, C_6D_6): 1.07 (dt^v, J_{HH} = 7.0 and $^vJ_{HP}$ = 7.0, 12H, CH_3), 1.36 (dt^v, J_{HH} = 7.2 and $^vJ_{HP}$ = 7.4, 12H, CH_3), 2.30 (m, $J \approx$ 7.0, 4H, PCH(CH$_3$)$_2$), 6.40 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.76 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{1}H{^{31}P} NMR (δ, C_6D_6): 1.07 (d, J_{HH} = 7.0, 12H, CH_3), 1.36 (d, J_{HH} = 7.2, 12H, CH_3), 2.30 (m, $J \approx$ 7.0, 4H, PCH(CH$_3$)$_2$), 6.40 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.76 (t, $J_{HH} \approx$ 8.0, 2H, *p*-H). ^{13}C NMR (δ, C_6D_6): 16.64 (s, 4C, *C*H$_3$), 17.48 (s, 4C, *C*H$_3$), 28.44 (vt, $^vJ_{PC}$ = 10.7, 4C, P*C*H(CH$_3$)$_2$), 106.18 (vt, ^vJ_p = 5.9, 2C, C$_{meta}$), 115.8 (vt, $^vJ_{PC}$ = 21.1, 1C, C$_{ipso}$), 130.4 (s, 1C, C$_{para}$), 169.99 (vt, $^vJ_{PC}$ = 9.0, 2C, C$_{ortho}$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 186.03 (s). ^{19}F{^{1}H} NMR (δ, C_6D_6): −78.62 (s). IR (ν_{max}; KBr disk): 1015 (SO$_3$), 1180 (CF$_3$), 1237 (CF$_3$), 1324 (SO$_3$) cm^{-1}. Anal. Calcd for $C_{19}H_{31}O_5F_3P_2SNi$ (549.149): C, 41.56; H, 5.69; S, 5.84. Found: C, 41.90; H, 5.69; S, 5.83.

{(*i*-Pr$_2$POCH$_2$)$_2$CH}Ni(O$_3$SCF$_3$), 2d. A mixture of {(*i*-Pr$_2$-POCH$_2$)$_2$CH}NiBr, **2b** (200 mg, 0.448 mmol), and 1 equiv of Ag-(O$_3$SCF$_3$) was stirred in CH$_2$Cl$_2$ (20 mL) at room temperature. After 1 h, 30 mL of hexane was added and the mixture was filtered by cannula to remove AgBr. Evaporation of the filtrate to dryness gave analytically pure product as a pale yellow solid. Yield: 167 mg (72%). ^{1}H NMR (δ, C_6D_6): 1.09 (dt^v, J_{HH} = 6.8 and $^vJ_{HP}$ = 6.8, 6H, CH_3), 1.10 (dt^v, J_{HH} = 6.9 and $^vJ_{HP}$ = 7.0, 6H, CH_3) 1.37 (dt^v, J_{HH} = 7.1 and $^vJ_{HP}$ = 7.5, 6H, CH_3), 1.44 (dt^v, J_{HH} = 7.2 and $^vJ_{HP}$ = 7.5, 6H, CH_3), 2.12 (m, $J_{HH} \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.26 (m, $J \approx$ 7.1, 2H, PCH(CH$_3$)$_2$), 2.55−2.64 (m, 1H, CH$_2$CHCH$_2$), 2.80−2.92 (m, 2H, CH_2CHCH_2), 2.99 (dd, J_{HH} = 11.7 and J_{HH} = 9.9, 2H, CH_2CHCH_2). ^{1}H{^{31}P} NMR (δ, C_6D_6): 1.09 (d, J_{HH} = 6.8, 6H, CH_3), 1.10 (dt^v, J_{HH} = 6.9, 6H, CH_3), 1.37 (d, J_{HH} = 7.1, 6H, CH_3), 1.44 (d, J_{HH} = 7.2, 6H, CH_3), 2.12 (m, $J \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.26 (m, $J \approx$ 7.1, 2H, PCH(CH$_3$)$_2$), 2.55−2.64 (m, 1H, CH$_2$CHCH$_2$), 2.80−2.91 (m, 4H, CH_2CHCH_2), 3.00 (dd, J_{HH} = 11.7 and J_{HH} = 9.9, 2H, CH_2CHCH_2). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.39 (s, 2C, *C*H$_3$), 16.72 (s, 2C, *C*H$_3$), 17.78 (s, 2C, *C*H$_3$), 18.38 (s, 2C, *C*H$_3$), 28.10 (vt, $^vJ_{PC}$ = 12.8, 2C, P*C*H(CH$_3$)$_2$), 29.33 (vt, $^vJ_{PC}$ = 10.4, 2C, P*C*H(CH$_3$)$_2$), 45.74 (m, 1C, *C*H−Ni), 76.22 (vt, $^vJ_{PC}$ = 6.6, 2C, *C*H$_2$CH*C*H$_2$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 184.46 (s). ^{19}F{^{1}H} NMR (δ, C_6D_6): −78.77 ppm (s). IR (ν_{max}; KBr disk): 1024 (SO$_3$), 1171 (CF$_3$), 1233 (CF$_3$), 1319 (SO$_3$) cm^{-1}. Anal. Calcd for $C_{16}H_{33}O_5F_3P_2SNi$ (515.132): C, 37.31; H, 6.46; S, 6.22. Found: C, 37.71; H, 6.45; S, 5.56.

[{2,6-(*i*-Pr$_2$PO)$_2$C$_6$H$_3$}Ni(NCCH$_3$)](O$_3$SCF$_3$), 1e. A mixture of {2,6-(*i*-Pr$_2$PO)$_2$C$_6$H$_3$}NiBr, **1b** (200 mg, 0.417 mmol), and 1 equiv of Ag(O$_3$SCF$_3$) was stirred in CH$_2$Cl$_2$ (20 mL) at room temperature. After 2 h, 20 mL of hexane was added and the mixture was filtered by cannula to remove AgBr. To the filtrate was added ca. 2 mL of acetonitrile, and the mixture was stirred for ca. 10 min and then concentrated to ca. 1 mL. After adding 5 mL of Et$_2$O and cooling the mixture at 0 °C the final product was precipitated and isolated by filtration as an analytically pure pale yellow crystalline solid. Yield: 197 mg (80%). ^{1}H NMR (δ, C_6D_6): 1.12 (dt^v, J_{HH} = 6.8 and $^vJ_{HP}$ = 7.0, 12H, CH_3), 1.32 (dt^v, J_{HH} = 7.0 and $^vJ_{HP} \approx$ 7.6, 12H, CH_3), *2*.38 (br s, 3H, NCCH_3), 2.45 (m, $J_{HH} \approx$ 7.0, 4H, PCH(CH$_3$)$_2$), 6.43 (d, J_{HH} = 8.0, 2H, *m*-H), 6.78 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{1}H{^{31}P} NMR (δ, C_6D_6): 1.12 (d, J_{HH} = 6.8, 12H, CH_3), 1.32 (d, J_{HH} = 7.0, 12H, CH_3), *2*.38 (br s, 3H, NCCH_3), 2.45 (m, $J_{HH} \approx$ 7.0, 4H, PCH(CH$_3$)$_2$), 6.43 (d, J_{HH} = 8.0, 2H, *m*-H), 6.78 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{13}C NMR (δ, C_6D_6): 3.63 (s, NCCH$_3$), 16.67 (s, 4C, *C*H$_3$), 17.59 (s, 4C, *C*H$_3$), 28.51 (vt, $^vJ_{PC} \approx$ 11.4, 4C, P*C*H-(CH$_3$)$_2$), 106.26 (vt, $^vJ_{PC}$ = 5.9, 2C, C$_{meta}$), 121.62 (m, 1C, C$_{ipso}$), 131.17 (s, 1C, C$_{para}$), 169.79 (vt, $^vJ_{PC}$ = 9.0, 2C, C$_{ortho}$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 192.86 (s). ^{19}F{^{1}H} NMR (δ, C_6D_6): −78.98 (s). IR (ν_{max}; KBr disk): 1032 (SO$_3$), 1144 (CF$_3$), 1274 (SO$_3$), 2292 (N≡C) cm^{-1}. Anal. Calcd for $C_{21}H_{34}NO_5F_3P_2SNi$ (590.201): C, 42.74; H, 5.81; N, 2.37; S, 5.43. Found: C, 42.34; H, 5.83; N, 2.34; S, 5.25.

[{(*i*-Pr$_2$POCH$_2$)$_2$CH}Ni(NCCH$_3$)](O$_3$SCF$_3$), 2e. A mixture of {(*i*-Pr$_2$POCH$_2$)$_2$CH}NiBr, **2b** (200 mg, 0.448 mmol), and 1 equiv of Ag(O$_3$SCF$_3$) was stirred in CH$_2$Cl$_2$ (20 mL) at room temperature. After 1 h, 20 mL of hexane was added and the mixture was filtrated by cannula to remove AgBr, followed by addition of ca. 1 mL of acetonitrile. The mixture was stirred for ca. 10 min and concentrated to 1 mL. After adding 5 mL of Et$_2$O and cooling the mixture at 0 °C the final product was precipitated and isolated by filtration as an analytically pure pale yellow crystalline solid. Yield: 186 mg (75%). ^{1}H NMR (δ, C_6D_6): 1.10−1.17 (m, 12H, CH_3), 1.25 (dt^v, J_{HH} = 6.9 and $^vJ_{HP}$ = 7.7, 6H, CH_3), 1.35 (dt^v, J_{HH} = 7.0 and $^vJ_{HP}$ = 7.7, 6H, CH_3), 2.12 (m, $J \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.29 (m, $J \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.68−2.78 (m, 1H, CH$_2$CHCH$_2$), 3.06−3.20

(m, 4H, CH_2CHCH_2). ^{1}H{^{31}P} NMR (δ, 4C_6D_6): 1.14 (m, 12H, CH_3), 1.25 (d, J_{HH} = 6.9, 6H, CH_3), 1.35 (d, J_{HH} = 7.0, 6H, CH_3), 2.12 (m, 2H, PCH(CH$_3$)$_2$), 2.29 (m, $J \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.68−2.78 (m, 1H, CH$_2$CHCH$_2$), 3.06−3.20 (m, 4H, CH_2CHCH_2). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.39 (s, 2C, *C*H$_3$), 16.92 (s, 2C, *C*H$_3$), 17.69 (s, 2C, *C*H$_3$), 18.33 (s, 2C, *C*H$_3$), 28.26 (vt, $^vJ_{PC}$ = 13.5, 2C, P*C*H(CH$_3$)$_2$), 29.48 (vt, $^vJ_{PC}$ = 11.4, 2C, P*C*H(CH$_3$)$_2$), 55.14 (m, 1C, *C*H−Ni), 76.44 (vt, $^vJ_{PC}$ = 5.6, 2C, *C*H$_2$CH*C*H$_2$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 191.54 (s). ^{19}F{^{1}H} NMR (δ, C_6D_6): −78.00 (s). IR (ν_{max}; KBr disk): 1030 (SO_3), 1151 (CF_3), 1279 (SO_3), 2284 (N≡C) cm^{-1}. Anal. Calcd for $C_{18}H_{36}NO_5F_3P_2SNi$ (556.184): C, 38.87; H, 6.52; N, 2.52; S, 5.77. Found: C, 39.00; H, 6.59; N, 2.49; S, 5.35.

[{2,6-(*i*-Pr$_2$PO)$_2$C$_6$H$_3$}Ni(NCCH=CH$_2$)](O$_3$SCF$_3$), 1f. Repeating the above procedure for the preparation of **1e**, except for the use of 1 mL of acrylonitrile instead of acetonitrile, gave the final product as a pale yellow crystalline solid. Yield: 195 mg (78%). ^{1}H NMR (δ, C_6D_6): 1.06 (dt^v, J_{HH} = 6.8 and $^vJ_{HP}$ = 7.1, 12H, CH_3), 1.35 (dt^v, J_{HH} = 7.1 and $^vJ_{HP}$ = 7.7, 12H, CH_3), 2.30 (m, $J \approx$ 7.0, 4H, PCH(CH$_3$)$_2$), 4.55 (dd, J_{HH} = 17.8 and J_{HH} = 11.7, 1H, NCCH=CH$_2$), 4.78 (d, J_{HH} = 11.7, 1H, NCCH=CH_2), 5.16 (d, J_{HH} = 17.8, 1H, NCCH=CH_2), 6.40 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.76 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{1}H{^{31}P} NMR (δ, C_6D_6): 1.06 (d, J_{HH} = 6.8, 12H, CH_3), 1.35 (d, J_{HH} = 7.1, 12H, CH_3), *2*.30 (m, $J \approx$ 7.0, 4H, PCH(CH$_3$)$_2$), 4.55 (dd, J_{HH} = 17.8 and J_{HH} = 11.7, 1H, NCCH=CH$_2$), *4*.78 (d, J_{HH} = 11.7, 1H, NCCH=CH_2), 5.16 (d, J_{HH} = 17.8, 1H, NCCH=CH_2), 6.40 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.76 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.71 (s, 4C, *C*H$_3$), 17.58 (s, 4C, *C*H$_3$), 28.62 (vt, $^vJ_{PC}$ = 11.4, 4C, P*C*H(CH$_3$)$_2$), 106.34 (vt, $^vJ_{PC}$ = 5.9, 2C, C$_{meta}$), 107.10 (s, 1C, NCCH=*C*H$_2$), 121.99 (m, 1C, C$_{ipso}$), 131.4 (s, 1C, C$_{para}$), 143.01 (s, 1C, NC*C*H=CH$_2$), 169.72 (vt, $^vJ_{PC}$ = 8.7, 2C, C$_{ortho}$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 193.69 ppm (s). ^{19}F{^{1}H} NMR (δ, C_6D_6): −78.79 ppm (s). IR (ν_{max}; KBr disk): 1032 (SO_3), 1142 (CF_3), 1266 (SO_3), 2257 (N≡C) cm^{-1}. Anal. Calcd for $C_{22}H_{34}NO_5F_3P_2SNi$ (602.211): C, 43.88; H, 5.69; N, 2.33; S, 5.32. Found: C, 43.92; H, 5.67; N, 2.30; S, 5.20.

[{(*i*-Pr$_2$POCH$_2$)$_2$CH}Ni(NCCH=CH$_2$)](O$_3$SCF$_3$), 2f. Repeating the above procedure for the preparation of **2e**, except for the use of 1 mL of acrylonitrile instead of acetonitrile, gave the final product as a pale yellow crystalline solid. Yield: 186 mg (73%). ^{1}H NMR (δ, C_6D_6): 1.08 (dt^v, J_{HH} = 6.2 and $^vJ_{HP}$ = 6.7, 6H, CH_3), 1.10 (dt^v, J_{HH} = 6.2 and $^vJ_{HP}$ = 6.7, 6H, CH_3), 1.35 (dt^v, J_{HH} = 6.8 and $^vJ_{HH}$ = 7.7, 6H, CH_3), 1.43 (dt^v, J_{HH} = 7.0 and $^vJ_{HH}$ = 7.7, 6H, CH_3), 2.11 (m, 2H, PCH(CH$_3$)$_2$), 2.26 (m, $J_{HH} \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.56−2.65 (m, 1H, CH$_2$CHCH$_2$), 2.81−2.94 (m, 2H, CH_2CHCH_2), 3.00 (m, 2H, CH_2CHCH_2), 4.68 (br, 1H, NCCH=CH$_2$), 4.89 (d, J_{HH} = 10.5, 1H, NCCH=CH_2), 5.27 (d, J_{HH} = 16.4, 1H, NCCH=CH_2). ^{1}H{^{31}P} NMR (δ, C_6D_6): 1.08 (d, J_{HH} = 6.2, 6H, CH_3), 1.10 (d, J_{HH} = 6.2, 6H, CH_3), 1.35 (d, J_{HH} = 6.8, 6H, CH_3), 1.43 (d, J_{HH} = 7.0, 6H, CH_3), 2.11 (m, J_{HH} = 7.0, 2H, PCH(CH$_3$)$_2$), 2.26 (m, $J_{HH} \approx$ 7.0, 2H, PCH(CH$_3$)$_2$), 2.56−2.65 (m, 1H, CH$_2$CHCH$_2$), 2.81−2.94 (m, 2H, CH_2CHCH_2), 3.00 (m, 2H, CH_2CHCH_2), 4.68 (br, 1H, NCCH=CH$_2$), 4.89 (d, J_{HH} = 9.4, 1H, NCCH=CH_2), 5.27 (d, J_{HH} = 17.3, 1H, NCCH=CH_2). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 16.39 (s, 2C, *C*H$_3$), 16.952 (s, 2C, *C*H$_3$), 17.55 (s, 2C, *C*H$_3$), 18.21 (s, 2C, *C*H$_3$), 28.33 (vt, $^vJ_{PC}$ = 13.5, 2C, P*C*H(CH$_3$)$_2$), 29.53 (vt, $^vJ_{PC}$ = 11.4, 2C, P*C*H(CH$_3$)$_2$), 56.36 (m, 1C, *C*H−Ni), 76.38 (vt, $^vJ_{PC}$ = 6.9, 2C, *C*H$_2$CH*C*H$_2$), 106.67 (s, 1C, NCCH=*C*H$_2$), 142.97 (s, 1C, NC*C*H=CH$_2$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 192.16 (s). ^{19}F{^{1}H} NMR (δ, C_6D_6): −78.79 (s). IR (ν_{max}; KBr disk): 1032 (SO_3), 1150 (CF_3), 1270 (SO_3), 2252 (N≡C) cm^{-1}. Anal. Calcd for $C_{19}H_{36}$ $NO_5F_3P_2SNi$ (568.194): C, 40.16; H, 6.39; N, 2.47; S, 5.64 Found: C, 40.11; H, 6.45; N, 2.39; S, 5.79

[{2,6-(*i*-Pr$_2$PO)$_2$C$_6$H$_3$}NiMe], 1g. A stirred, room-temperature solution of **1b** (200 mg, 0.417 mol) in 20 mL of Et_2O was treated with 2 equiv of MeMgCl, added dropwise using a microsyringe. After 15 min, 30 mL of hexane was added and the mixture was filtered by cannula, washed with deoxygenated water (2 × 40 mL), and dried over $MgSO_4$. Removal of the volatiles gave the analytically pure product as a pale yellow solid. Yield: 149 mg (86%). ^{1}H NMR (δ, $CDCl_3$): −0.63 (vt, ^vJ = 8.7, 3H, Ni−CH_3), 1.22−1.29 (m, 24H, CH_3), 2.37 (m, $J \approx$ 7.0,4H, PCH(CH$_3$)$_2$), 6.47 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.91 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{13}C NMR (δ, $CDCl_3$): −21.38 (vt, $^vJ_{PC}$ = 18.21, Ni−*C*H$_3$), 17.15 (s, 4C, PCH(*C*H$_3$)$_2$), 17.85 (s, 4C, PCH(*C*H$_3$)$_2$), 27.98 (vt, $^vJ_{PC}$ = 11.0, 4C, P*C*H(CH$_3$)$_2$), 104.00 (vt, $^vJ_{PC}$ = 5.9, 2C, C$_{meta}$), 127.45 (s, 1C, C$_{para}$), 139.79 (vt, $^vJ_{PC}$ = 20.9, 1C, C$_{ipso}$), 167.62 (vt, $^vJ_{PC}$ = 19.2, 2C, C$_{ortho}$). ^{31}P{^{1}H} NMR (δ, C_6D_6): 191.87 (s). Anal. Calcd for $C_{19}H_{34}O_2P_2Ni$ (415.113): C, 54.97; H, 8.26. Found: C, 55.24; H, 8.54.

[{2,6-(*i*-Pr$_2$PO)$_2$C$_6$H$_3$}NiEt], 1h. A stirred, room-temperature solution of **1b** (200 mg, 0.417 mol) in 20 mL of Et_2O was treated with 2 equiv of EtMgCl, added dropwise using a microsyringe. After 30 min, the mixture was filtered by cannula, washed with deoxygenated water (2 × 40 mL), and dried over $MgSO_4$. Removal of the volatiles gave the analytically pure product as a pale yellow solid. Yield: 145 mg (81%). ^{1}H NMR (δ, $CDCl_3$): 0.58−0.64 (m, 2H, NiCH_2CH$_3$), 1.14 (t, J_{HH} = 7.6, 3H, NiCH$_2$CH_3), 1.23−1.29 (m, 24H, PCH(CH_3)$_2$), 2.40 (m, $J \approx$ 7.0, 4H, PCH(CH$_3$)$_2$), 6.44 (d, $J_{HH} \approx$ 8.0, 2H, *m*-H), 6.89 (t, $J_{HH} \approx$ 8.0, 1H, *p*-H). ^{13}C NMR (δ, $CDCl_3$): −9.00 (vt, $^vJ_{PC}$ = 17.78, 1C, Ni*C*H$_2$CH$_3$), 16.85 (s, 1C, NiCH$_2$*C*H$_3$), 17.16 (s, 4C, PCH(*C*H$_3$)$_2$) 17.88 (s, 4C, PCH(*C*H$_3$)$_2$), 28.23 (vt, $^vJ_{PC}$ = 10.6, 4C, P*C*H(CH$_3$)$_2$), 103.81 (s, 2C, C$_{meta}$), 127.50 (s, 1C, C$_{para}$), 139.68 (vt, $^vJ_{PC}$ = 19.9, 1C, C$_{ipso}$), 167.38 (vt, $^vJ_{PC}$ = 10.2, 2C, C$_{ortho}$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 189 (s). Anal. Calcd for $C_{20}H_{36}O_2P_2Ni$ (429.140): C, 55.98; H, 8.46. Found: C, 55.46; H, 8.58.

[{(*i*-Pr$_2$POCH$_2$)$_2$CH}NiCl$_2$], 2i. To a solution of **2a** (100 mg, 0.249 mmol, 1 equiv) in a hexane/acetone mixture (5:2 mL, both solvents nondistilled) stirring at room temperature and exposed to ambient air was added $CuCl_2$ (101 mg, 0.744 mmol, 3 equiv). The addition caused an immediate color change from yellow to orange. The mixture was stirred for 15 min and filtered (in the air), and the filtrate was evaporated to dryness to give analytically pure **2i** as an orange crystalline solid. Yield: 89 mg (90%). Anal. Calcd for $C_{15}H_{33}Cl_2O_2P_2Ni$ (436.968): C, 41.23; H, 7.61. Found: C, 40.92; H, 7.73.

General Procedures for the Catalytic Runs. Kharasch Additions. For the large-scale reactions, a 25 mL two-neck, round-bottom flask equipped with a condenser and a rubber septum was charged with the desired mass of complex **2j** to give a **2j**:CCl_4:olefin ratio of 1:1000:250 (for methyl acrylate, acrolein, acrylonitrile) or 1:4000:1000 (for styrene, 4-methyl styrene, methyl methacrylate). The reaction vessel was then purged with nitrogen for 15 min and charged with dry, air-free acetonitrile (14 mL), deoxygenated CCl_4 (12 mL), and olefin (3 mL). The reaction mixture was heated to reflux for 24 h under nitrogen. The final mixture was then evaporated to dryness (in the air) and purified by flash chromatography using as eluent hexane (for acrylonitrile, methyl methacrylate, styrene, and 4-methylstyrene) or a 50:50 mixture of hexane and acetone (for acrolein). The reaction products were characterized by GC/MS and ^{1}H NMR. Smaller-scale reactions were carried out using 25% of the above quantities for all components. The yields of the styrene and methyl methacrylate runs were determined by direct isolation of the products and by GC/MS using a calibration curve based on *p*-xylene as internal standard. For the other reactions, the yields were determined by direct isolation of the products, as indicated above.

Michael Additions. Most of the catalyzed runs were carried out as follows: a mixture of the amine (1.14 mmol), the olefin (1.14 mmol), and **1f** (1 mol % or less) in anhydrous toluene (2 mL) was stirred in the air and at ambient temperature for 5 min or more. For runs using smaller amounts of the catalyst, the mass of **1f** was

kept constant while the masses of the substrates were increased. For the high-temperature reactions using aniline, the same procedure was followed, but the runs were conducted in two-neck flasks equipped with a condenser and kept under nitrogen. The reaction progress was monitored by GC/MS, as follows. A small portion of the mixture was drawn and diluted in hexane to precipitate the less-soluble cationic complex, and the soluble portion was then analyzed by GC/MS. The final yields of the runs involving aniline were determined using a GC/MS calibration curve based on *p*-xylene as internal standard. The yields and turnover numbers (TON) determined for other runs were corroborated in some cases by direct isolation of the product, which was affected by flash chromatography (eluent used was a 1:1 hexane−ethyl acetate solution).

The uncatalyzed (control) experiments were conducted by stirring toluene solutions of the substrates (ca. 0.52 M) at the appropriate reaction temperature. The final reaction mixtures were analyzed as above. In all cases examined, little or no conversion was observed during the reaction times specified for the corresponding catalytic runs. For example, uncatalyzed addition of morpholine to acrylonitrile showed no conversion after 1 h, 7% yield after 6 h, and 25% yield after 24 h. Similarly, the uncatalyzed addition of cyclohexyl amine to acrylonitrile gave no conversion after 6 h, and only traces of product were detected after 24 h. The uncatalyzed additions of morpholine or cyclohexyl amine to crotonitrile and methacrylonitrile showed no conversion after 24 h. Finally, addition of aniline to acrylonitrile did not proceed after 24 h even in refluxing toluene.

X-ray Crystal Structures of Complexes 1a, 1c, 1e, 1g, 1h, 2a, 2c, 2d, and 2i. Single crystals of these compounds were grown from hexanes solutions at −20 °C (for **1a**, **1c**, **1g**, **1h**, **2a**, and **2c**) or benzene-d_6 solution at 4 °C (for **1d**) or slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane (for **1e**). The crystallographic data for all complexes were collected on a Bruker AXS diffractometer equipped with a SMART 2K CCD detector with graphite-monochromatic Cu Kα radiation (λ = 1.54178) using SMART.[55] Cell refinement and data reduction were done using SAINT.[56] All structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques using SHELXS-97[57] and difmap synthesis using SHELXL97;[58] the refinements were done on F^2 by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms (isotropic) were constrained to the parent atom using a riding model. The crystal data, collection details, and refinement parameters are presented in Tables 1 (**1a**, **1c**, **2a**, and **2c**) and 3 (**1e**, **1g**, **1h**, **2d**, and **2i**). Bond distances and angles are listed in Tables 2 (**1a**, **1b**, **1c**, **2a**, **2b**, and **2c**), 4 (**2d**), 5 (**1e**), 6 (**1g** and **1h**), and 7 (**2i** and **2j**).

The complete crystallographic data for structural analysis have been deposited at the Cambridge Crystallographic Data Centre; deposition numbers are CCDC No. 640874 (**1a**), 640878 (**1c**), 640876 (**2a**), 640875 (**2c**), 640877 (**1e**), 640880 (**2d**), 640881 (**1g**), 640882 (**1h**), and 640879 (**2i**). These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK (fax, +44-1223-336-033; e-mail, deposit@ccdc.cam.ac.uk; web, www:http://www.ccdc.cam.ac.uk).

Acknowledgment. The Natural Sciences and Engineering Research Council of Canada and Fonds Québéqois de la Recherche sur la Nature et les Technologies are gratefully acknowledged for their financial support. We are grateful to Dr. M. Simard and F. Bélanger-Gariépy for their assistance with the X-ray analyses, and to Profs. D. Rochefort and G. Hannan and their groups for their valuable help with the electrochemical and UV−vis measurements.

Supporting Information Available: The complete crystallographic data for structural analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700400X

(55) *SMART*, Release 5.059, Bruker Molecular Analysis Research Tool; Bruker AXS Inc.: Madison, WI, 1997.

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

(57) Sheldrick, G. M. *SHELXS97*, Program for the Solution of Crystal Structures; University of Gottingen: Germany, 1997.

(58) Sheldrick, G. M. *SHELXS97*, Program for the Refinement of Crystal Structures; University of Gottingen, Germany, 1997.