

New POCN-Type Pincer Complexes of Nickel(II) and Nickel(III)

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Received August 27, 2009

Unsymmetrical POC(H)N-type pincer ligands react with NiBr₂(NCMe)_x to give the complexes (POCN)Ni^{II}Br (POCN = $\kappa^{P}, \kappa^{C}, \kappa^{N}$ -{2-(*i*-Pr₂PO),6-(NR₂CH₂)-C₆H₃}; NR₂ = 3-morpholino (**3a**), NMe_2 (3b), and NEt_2 (3c)). The presence of an added base such as NEt_3 in these metalation reactions maximizes the yields of the target pincer complexes by suppressing the formation of side-products arising from protonation of the ligand by the *in situ*-generated HBr. The cyclic voltammograms of 3 exhibit a quasi-reversible, one-electron oxidation at ca. +1.0 V, in addition to an irreversible oxidation at higher potentials likely due to ligand oxidation. Reaction of the 16-electron, yellow complexes 3 with Br₂, N-bromosuccinimide, or CBr₄ gives black crystalline compounds identified as the 17-electron complexes (POCN) $Ni^{III}Br_2(5)$. Complexes 3 and 5 adopt square-planar and distorted square-pyramidal geometries, respectively. The Ni-Br bond lengths in 5 are significantly longer for the Br atom occupying the axial position (2.43-2.46 vs 2.37 Å), consistent with the repulsive interactions expected between the bromide lone pair and the singly occupied d_{z^2}/d_{pz} hybrid MO. In agreement with this picture, the g-values obtained from the EPR spectrum of **5a** are $g_{xx} \approx g_{yy} \approx 2.2$, $g_{zz} \approx 2.00$, and strong Br hyperfine coupling is observed on the g_{zz} component. Our preliminary studies indicate that the thermal stabilities of 5, both in the solid state (as probed by differential scanning calorimetry) and in solution (as probed by UV-vis spectroscopy), vary in the order $5a \approx 5b$ > 5c; this order of stability is consistent with the relative steric demands of the N-moiety. Complexes 5a (or 3a) and 5b (or 3b) promote the Kharasch addition of CX_4 (X = Cl, Br) to styrene at 80 °C, giving PhC(X)CH₂CX₃, the product of an anti-Markovnikov addition, in up to 50 catalytic turnovers.

Introduction

Since their initial introduction by Shaw's group over 30 years ago,¹ pincer-type complexes have been shown to promote many interesting and useful reactivities.² The initial phase in the development of the chemistry of pincer complexes was dominated by complexes featuring monoanionic, terdentate ligands based on bis(phosphine) (PCP)¹ and bis(amine) (NCN)³ donor moieties. More recent years have witnessed the introduction of complexes based on a large variety of new ligands, including

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bis(phosphino)amides (PNP),⁴ bis(phosphinites) (POCOP),⁵ bis(phosphinidines) (PNCNP),⁶ bis(amino)amides (NNN),⁷ and bis(carbenes) (CCC),⁸ as well as nonsymmetrical pincer ligands such as PCN^{9,10} and CNS.¹¹ The relatively facile access to such a diverse array of new ligands has accelerated the exploration of the reactivities of their metal complexes, which has led in turn to discovery of novel reactivities.¹²

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Our long-standing interest in the chemistry of organonickel complexes¹³ combined with van Koten's landmark reports on NCN-Ni complexes^{3b-d} and the emerging chemistry of PCP-Ni complexes¹⁴ inspired us to investigate the synthesis and reactivities of Ni compounds with various pincer-type ligands. In earlier reports, we have described the chemistry of the PC_{sp2}P-Ni^{II} species {1,3-(Ph₂PCH₂-CH₂)₂-2-indenyl}NiCl¹⁵ and the PC_{sp3}P-Ni^{II} complexes {(*t*-Bu₂PCH₂CH₂)₂CH}-NiX (X = Cl, Br, I, Me, H) and [{(*t*-Bu₂PCH₂CH₂)₂CH}NiL]⁺ (L = CH₃CN, CH₂=CHCN).¹⁶ Recently, we have described new POC_{sp2}OP and POC_{sp3}OP complexes of Ni^{II} and Ni^{III} as well as their catalytic activities

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in hydroamination (Michael addition) and Kharasch addition.^{17,18} Our studies to date indicate that the nature of the pincer ligand has a major influence on the metalation step as well as the stabilities and reactivities of the ensuing pincer complexes. For instance, metalation of the ligand's central C–H bond is more facile with POCOP versus PCP and with ligands based on aromatic versus aliphatic linkers. Furthermore, stable and isolable trivalent species are accessible with POCsp³OP-¹⁸ and PC_{sp3}P-type^{16a,b} ligands, whereas ligands based on aromatic linkers (POC_{sp2}OP- or PC_{sp2}P-type ligands) have not yielded high-valent nickel complexes.¹⁸

The latter observation, that PCP and POCOP ligands based on an aromatic linker do not yield Ni^{III} species, is in direct contrast to the relatively facile preparation of trivalent species based on aromatic NCN ligands, as reported by van Koten's group.^{3b-d} The discrepancy between the chemistry of PCP/POCOP versus NCN ligands featuring an aromatic skeleton prompted us to investigate the preparation of highvalent nickel complexes based on unsymmetrical PCN-type ligands. Since bis(phosphinite) ligands have been found to undergo metalation more readily than their bis(phopsphine) counterparts, our initial studies have been focused on the phosphinite-amine ligands R₂PO-C₆H₄-CH₂NR₂ (POCN). The present report describes the preparation of POCN-type pincer ligands and their di- and trivalent complexes of nickel.

Results and Discussion

Synthesis of Complexes. The synthetic route leading to the new complexes $3\mathbf{a}-\mathbf{c}$ is illustrated in Scheme 1. The aminophenol precursors for the POCN ligands 2 were prepared by condensation of 3-hydroxybenzaldehyde with the corresponding secondary amines, followed by reduction of the *in situ*-formed imine with NaBH₄ in methanol.¹⁹ Formation of the amino phenols 1 is quite exothermic, requiring stepwise addition of NaBH₄ and cooling of the reaction mixture to avoid forming side-products such as 3-(hydroxymethyl)phenol that complicate separation of pure 1. The preligands 1 were isolated in good yields as white solids (1a and 1b) or a pale yellow oil (1c); the identities of these

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compounds were established by elemental analysis and NMR spectroscopy. The phosphination of 1 with chlorodiisopropylphosphine and triethylamine gave the corresponding POC(H)N-type pincer ligands 2, which were isolated in high yields as colorless oils and characterized by NMR spectroscopy and elemental analysis. All ligands proved to be quite sensitive to residual moisture, but relatively inert to oxygen. Heating **2** with NiBr₂(MeCN)_x²⁰ in the presence of triethylamine (benzene, 60 °C, 3-4 h) led to the metalation of the ligands and gave the new complexes $3 \text{ in } \sim 86\%$ yields as yellow solids. Use of different precursors such as NiBr₂- $(THF)_x$ or NiBr₂, or different bases such as N,N-dimethylaminopyridine (DMAP), led to significantly lower yields of the complexes (~35%). Pd and Pt complexes based on similar POCN ligands have been reported previously,²¹ but complexes 3 are, to our knowledge, the first examples of POCN-type complexes of nickel.

It is noteworthy that the use of a base was found to be necessary in order to maximize the reaction yield of complexes 3a-c. When the reaction of 2a was performed without any added base, we obtained the desired pincer complex 3a in poor yields (< 50%) along with variable amounts of a sparingly soluble, NMR-silent turquoise-green solid 4. Interestingly, the latter side-product generates the desired pincer complex 3a when treated with 2 equiv of Et₃N. Unfortunately, we have not succeeded in growing suitable single crystals of this compound due to its poor solubility in common aprotic and noncoordinating solvents and its decomposition in coordinating solvents. Nevertheless, the above observations and the results of a combustion analysis carried out on this solid allow us to propose the structure shown in Scheme 2 (4). It should be noted that anionic, tetrahedral species analogous to 4 have been detected previously during the preparation of PCsp3P-type pincer complexes of Ni (Scheme 2).^{16a} Such side-products likely arise from the reaction of the HBr, liberated at the cyclometalation stage of the synthesis, with the amino moiety of the ligand, prior to or after the latter's coordination to the metal center.

The redox properties of complexes **3** were investigated by cyclic voltammetry measurements in CH_2Cl_2 . The voltammograms (Figure 1) showed quasi-reversible redox waves at ca.



Figure 1. Cyclic voltammograms of 1 mM solutions of complexes $3\mathbf{a}-\mathbf{c}$ in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate at 25 °C at a scan rate of 100 mV/s on a glassy carbon working electrode.

1.0 V; this redox process is assigned to oxidation of the Ni center (Ni^{II} \rightarrow Ni^{III}).²² Comparison of the oxidation potentials of these POCN complexes to that of the previously reported complex (POC_{sp2}OP)NiBr^{17,18} suggests that high-valent compounds should be easier to prepare and isolate with these POCN-based complexes. This is borne out by the successful chemical oxidation of **3** and the isolation of Ni^{III} species (*vide infra*). We conclude, therefore, that POCN ligands are more effective than their POCOP homologues in stabilizing high-valent nickel species, which can be understood in terms of both the greater nucleophilicity and "hardness" of amine moieties relative to OPR₂ moieties.

Chemical oxidation of **3** to their Ni^{III} counterparts was achieved by reaction with bromine in dry Et₂O, which gave

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⁽²²⁾ It should be noted that these redox processes appear to be more complex for **5a** and **5b**, as judged by the less symmetrical shapes of these waves; changing the cutoff potential or varying the scan rates (100-300 mV/s) did not produce more symmetrical redox couples. Moreover, complexes **3** undergo other (irreversible) oxidative processes at higher potentials; comparison to the CV of the free ligands indicates that these processes are ligand-based. See the Supporting Information for the full CV plots of **3**, the preligand **1a**, and ligand **2a**.

the corresponding (POCN)Ni^{III}Br₂ complexes (5a-c) as black solids in greater than 90% yields (Scheme 1). The relative thermal instability of 5c (vide infra) required that its synthesis be performed at -78 °C (in dry solvents) over 10 min, followed by addition of cold hexane to precipitate the product. N-Bromosuccinimide (NBS) and CBr4 were also competent oxidants for generation of Ni^{III} species, but these reagents furnished lower yields of the products (50-70%). The NBS reaction led to formation of succinimide that has solubility properties similar to those of 5, which complicated the isolation of pure products. Complexes 5 are soluble in Et₂O, THF, CH₂Cl₂, and CH₃CN. Et₂O or CH₂Cl₂ solutions of complexes 5a and 5b were found to be fairly stable at room temperature, whereas solutions of complex 5c were significantly less stable and had to be handled rapidly and at significantly lower temperatures (vide infra).

Characterization of 3a-c. The diamagnetic Ni^{II} complexes 3 were fully characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction studies. The ${}^{31}P{}^{1}H{}$ NMR spectra of 3 were straightforward, each consisting of a single resonance at about 200 ppm; this signal is significantly downfield of the corresponding signal for the free ligands (147 ppm) but close to the chemical shift region where we find the ³¹P signal for the analogous (POCOP)NiBr compounds (186 ppm).¹⁸ The ¹H and ¹³C $\{^{1}H\}$ NMR spectra were much more complex, but ¹H-COSY and HMQC correlation experiments allowed us to assign all ¹H and ¹³C signals. Together, these spectra indicate that complexes 3 possess a plane of symmetry in solution, as reflected in the equivalence of the two $CHMe_2$ and the NCH₂Ar protons in 3a-c, the two NCH₂ and OCH₂ carbons in 3a, and the two signals for $N(CH_2CH_3)$ (3c) and $N(CH_3)$ (3b). The plane of symmetry, which coincides with the plane of coordination, also renders the following nuclei (sitting above and below the plane) pairwise equivalent: $CH(CH_3)_2$ in 3a-c; morpholine protons in 3a; and NCH₂CH₃ signals in 3c.

Single-crystal X-ray diffraction studies of 3 showed that these complexes adopt moderately distorted square-planar geometries in the solid state (Figure 2), the greatest structural distortions appearing in the angles $P-Ni-N(162-167^{\circ})$ and P-Ni-C (82°); these distortions away from ideal geometry arise presumably from the terdentate nature of the pincer ligand. The Ni center and the aromatic ring are only slightly out of the coordination plane, which is consistent with the existence in solution of a plane of symmetry. The Ni-P distances in these POCN-type complexes are shorter than the corresponding distances in the analogous (POCOP)Ni-X compounds (ca. 2.11 vs 2.15-2.16 Å),¹⁸ implying a greater trans influence for the OPR2 moieties versus the amine ligands. Moreover, in comparison to their POCOP-type counterparts, the POCN-type complexes 3 display somewhat shorter Ni-C distances (ca. 1.85-1.86 vs 1.88 Å) and longer Ni-Br (ca. 2.33-2.36 vs 2.32 Å) distances.

Characterization of 5a–c. The identities of the Ni^{III} complexes **5a–c** were established by elemental analyses and singlecrystal X-ray diffraction studies. As can be seen from their ORTEP diagrams (Figure 3), these 17-electron compounds adopt square-pyramidal structures displaying a slight pyramidal distortion reflected in the out-of-plane displacement of the Ni center from the basal plane defined by the atoms P1, C1, N1, and Br1 (by ca. 0.31 (**5a**), 0.34 (**5b**), and 0.30 (**5c**) Å). This distortion results in trans angles of 158–162° and cis angles of $80–98^\circ$, in addition to significantly longer (>10 esd) Ni–X bonds relative to the corresponding distances in the Ni^{II} species



Figure 2. ORTEP diagram for complexes **3a** (a), **3b** (b), and **3c** (c). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

3: for Ni–C, ca. 1.89–1.90 vs 1.85–1.86 Å; for Ni–P, ca. 2.19–2.21 vs 2.11 Å; and for Ni–N, 2.05–2.07 vs 2.02–2.04 Å. The Ni–Br bond for the Br atom occupying the axial position is also much longer than that involving the basal Br atom (2.43–2.46 vs 2.37 Å); this is consistent with the repulsive interactions anticipated between the bromide lone pair and the half-filled d_{z^2}/d_{pz} hybrid MO. Unequal axial and basal Ni–X bonds have been observed in POCOPNi^{III}X₂¹⁸ and the closely related (but divalent) complex PCP-Ni^{II}(catecholate) (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)²³ and identical for

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Table 1. Crystal Data Collection and Refinement Parameters for Complexes 3a-c

	3a	3b	3c
chemical formula	C ₁₇ H ₂₇ NO ₂ PNiBr	C ₁₅ H ₂₅ NOPNiBr	C ₁₇ H ₂₉ NOPNiBr
Ffw	446.99	409.00	433.00
$T(\mathbf{K})$	150(2)	150(2)	150(2)
wavelength (Å)	1.54178	1.54178	1.54178
space group	$P2_1/n$	$P\overline{1}$	$Pna2_1$
a (Å)	9.9289(2)	9.3512(2)	20.5409(5)
b (Å)	8.2128(2)	9.4406(2))	8.1439(2)
c (Å)	23.0832(4)	10.7745(2)	11.5377(3)
α (deg)	90	67.668(1)	90
β (deg)	98.695(1)	79.819(2)	90
γ (deg)	90	75.681(1)	90
Z	4	2	4
$V(Å^3)$	1860.66(7)	847.19(2)	1930.06(8)
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.596	1.587	1.490
μ (cm ⁻¹)	48.94	52.60	46.56
θ range (deg)	3.87-67.94	4.46 - 67.81	4.30 -68.13
$R1^a [I > 2\sigma(I)]$	0.0293	0.0296	0.0218
$wR2^{b}[I > 2\sigma(I)]$	0.0763	0.0781	0.0576
R1 [all data]	0.0293	0.0301	0.0219
wR2 [all data]	0.0763	0.0784	0.0576
GOF	1.143	1.060	1.102
a R1 = $\Sigma(H)$	$F_{\rm o} = F_{\rm o} /\sum F_{\rm o} .$	b wR2 = { $\sum [w(B)]$	$E_0^2 - E_0^2)^2]/\sum [w - \frac{1}{2} $

 $(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 3a-c

	3a	3b	3c
Ni-C(1)	1.853(2)	1.859(2)	1.8557(19)
Ni-P(1)	2.1107(6)	2.1119(7)	2.1088(7)
Ni-N(1)	2.0428(18)	2.0206(19)	2.025(2)
Ni-Br	2.3319(4)	2.3407(5)	2.3615(4)
C(1)-Ni-Br	176.26(7)	177.16(8)	172.47(7)
P(1) - Ni - N(1)	162.20(6)	163.81(6)	166.63(5)
P(1)-Ni-Br	95.08(2)	95.56(2)	95.53(2)
N(1)-Ni-Br	99.65(5)	98.34(6)	97.82(5)
P(1)-Ni-C(1)	81.72(7)	81.99(9)	81.51(8)
N(1) - Ni - C(1)	83.85(9)	83.89(9)	85.15(9)

NCN-Ni^{III}(Cl)₂ (2.30 Å).²⁴ Finally, close inspection of the ORTEP diagrams for **5** reveals significant steric repulsions between the axial Br and the N-alkyl substituents; this repulsion appears to be greatest in complex **5c**, which displays the longest Ni–Br2 bond and the least thermal stability (*vide infra*).

The bonding and electronic structure of **5a** were investigated further by EPR analysis. The EPR spectrum of this compound (Figure 4) is typical of Ni^{III} pincer compounds with halogen ligands^{3d,23,25} and shows a nearly axial *g*-tensor with strong hyperfine coupling to the halogen nucleus on the g_{zz} component. The splitting due to the spin 3/2 Br nucleus is shown schematically above the spectrum. The *z*-component of the *g*-tensor is close to the free electron *g*-value (2.0023), while the *x*- and *y*-components are in the vicinity of g = 2.2. The deviation of the *g*-tensor from axial symmetry is hard to estimate accurately from the spectrum, because the Br hyperfine coupling on the g_{zz} component is of similar magnitude to the *g*-anisotropy and a so-called "anomalous line"



Figure 3. ORTEP diagram for complexes **5a** (a), **5b** (b), and **5c** (c). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

similar to that found in many Cu^{II} spectra²⁶ is expected. Hence, it is not clear whether the low-field peak is due to the g_{xx} component or the anomalous line. In any case, this combination of g-factors ($g_{xx} \approx g_{yy} > g_{zz} = 2.0023$) is expected for a low-spin d⁷ metal ion with tetragonally elongated octahedral symmetry such that the unpaired electron resides in the d_{z^2} orbital.^{3d,27} The strong Br hyperfine splitting seen only on the g_{zz} component indicates that the d_{z^2} orbital is involved in bonding to Br and is consistent with a bonding scheme in which the MOs involved in the axial Br bond are derived from d_{z^2} and p_z orbitals of the Ni^{III} and hold three electrons. Closer inspection of the spectrum reveals a large number of small, partially resolved hyperfine splittings due to coupling to the phosphorus (spin 1/2), nitrogen (spin 1), and/or in-plane Br (spin 3/2). In principle, these

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Table 3. Crystal Data Collection and Refinement Parameters for Complexes 5a-c

	5a	5b	5c
chemical formula	C ₁₇ H ₂₇ NO ₂ PNi	Br ₂ C ₁₅ H ₂₅ NOPNi	Br ₂ C ₁₇ H ₂₉ NOPNiBr ₂
fw	526.90	484.86	512.91
$T(\mathbf{K})$	150(2)	150(2)	150(2)
wavelength (Å)	1.54178	1.54178	1.54178
space group	$Pna2_1$	$P2_1/n$	$P2_1/n$
a (Å)	21.1300(16)	9.3685(2)	8.1481(2)
b (Å)	9.8048(8)	11.2260(3)	19.8813(4)
c (Å)	9.3608(9)	18.1186(4)	12.9752(3)
α (deg)	90	90	90
β (deg)	90	100.817(1)	104.770(1)
γ (deg)	90	90	90
Z	4	4	4
$V(Å^3)$	1939.30(30)	1871.69(8)	2032.46(8)
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.805	1.721	1.676
$\mu ({\rm cm}^{-1})$	71.30	72.84	67.43
θ range (deg)	4.18-68.38	4.66-67.69	4.17-67.84
$\mathrm{R1}^{a}\left[I > 2\sigma(I)\right]$	0.0362	0.0229	0.0220
$wR2^{b}[I > 2\sigma(I)]$	0.0869	0.0581	0.0580
R1 [all data]	0.0358	0.0259	0.0221
wR2 [all data]	0.0873	0.0593	0.0581
GOF	1.044	1.062	1.133

 ${}^{a}\mathbf{R1} = \sum(||F_{o}| - |F_{c}|) / \sum |F_{o}|. {}^{b}\mathbf{wR2} = \{\sum[w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum[w-(F_{o}^{2})^{2}]^{1/2}.$

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complexes 5a-c

	5a	5b	5c
Ni-C(1)	1.883 (4)	1.897(2)	1.8907(19)
Ni-P(1)	2.2013 (11)	2.1905(6)	2.2078(5)
Ni-N(1)	2.072(3)	2.0508(18)	2.0690(16)
Ni-Br(1)	2.3673(7)	2.3710(4)	2.3688(4)
Ni-Br(2)	2.4339(9)	2.4350(4)	2.4638(3)
C(1) - Ni - Br(1)	161.21(13)	159.60(6)	162.27(6)
C(1)-Ni-Br(2)	91.30(13)	95.24(6)	90.98(5)
P-Ni-N	159.92(10)	158.08(6)	159.42(5)
P-Ni-Br(1)	94.23(3)	92.43(2)	92.266(17)
N-Ni-Br(2)	95.78(11)	98.29(5)	98.09(4)
P-Ni-C(1)	80.09(12)	79.92(7)	80.31(6)
N-Ni-C(1)	83.94(15)	83.52(8)	84.47(7)

couplings could provide a clearer picture of the spin density distribution and, by extension, the bonding in the molecular plane; without additional information, however, the large number of unknown parameters precludes a meaningful simulation of the spectrum.

We have also subjected the Ni^{III} complexes 5 to cyclic voltammetry measurements and compared the results to those obtained with the divalent species 3. The voltammograms (see Supporting Information) show a reduction wave $(Ni^{III} \rightarrow Ni^{II})$ and an irreversible oxidation peak, which we assign to a ligand-based oxidation process.

Thermal Stabilities of 3 and 5. The thermal stability of Ni^{II} complexes was examined by thermogravimetric analysis (TGA). The results showed no decomposition of Ni^{II} complexes **3** even above their melting points; the compounds simply evaporated without leaving any significant amount of residue (see TGA thermograms in the Supporting Information). The thermal stabilities of the Ni^{III} complexes in the solid state were established by studying their thermal profiles using differential scanning calorimetry (DSC). As can be seen in Figure 5, complexes **5a** and **5b** appear to be stable to well above 130 °C, showing exothermic decomposition only above 150 and 140 °C, respectively. The onset of



Figure 4. X-band (9 GHz) EPR spectrum of **5a** in toluene at 120 K. Microwave frequency 9.405102 GHz, microwave power 2 mW, modulation amplitude 1.0 G.



Figure 5. DSC curve of complexes **5a**-**c**: nitrogen flow of 20 mL/min, heating rate of 10 °C/min, ca. 8 mg samples weighed in an alumina crucible.

decomposition (exothermic) for these complexes appears to coincide with an endothermic process at ca. 165-173 °C (**5a**) and 160-165 °C (**5b**), which we attribute to the melting of **3a** (observed at 175-177 °C) and **3b** (observed at 166-168 °C). A second endothermic process is observed for **5b** above 190 °C, which we attribute to the evaporation of the decomposition product **3b**. In constrast, **5c** appears to be stable only up to 60 °C, beginning to decompose significantly at ca. 80 °C; for this sample, too, there was an endothermic process at 105-110 °C, which we attribute to the melting of the decomposition product **3c** (observed at 110-111 °C).

An examination of the thermal stabilities of complexes **5** in solution was conducted by variable-temperature UV-vis spectroscopy (Figure 6), and the results point to the same order of thermal stability as in the solid state, namely, **5a** \sim **5b** > **5c**. Thus, **5a** and **5b** display a $t_{1/2}$ of about 4 and 3 h, respectively, at 70 °C, whereas **5c** begins to decompose upon dissolution at room temperature and displays a $t_{1/2}$ of about



Figure 6. UV-vis spectra of 0.001 M toluene solutions of 5a (70 °C), 5b (70 °C), and 5c (30 °C) as a function of time.

20 min at 30 °C. It is noteworthy that the solution decomposition is faster in more concentrated solutions, implying a bimolecular pathway.

Kharasch Additions. A wide variety of paramagnetic metal complexes are known to promote the Kharasch addition of CCl₄ to various olefins.²⁸ Of relevance to our studies, van Koten's group has shown that Ni complexes based on NCN-type pincer ligands are efficient promoters of the addition of polyhalogenated alkanes to olefins, giving the anti-Markovnikov product (eq 1). Mechanistic studies 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^{III} complex (NCN)-NiX₂, thereby favoring 1:1 additions over radical chain type polymerization or telomerization reactions.

$$\mathbf{R} \xrightarrow{\mathsf{Cl}} \mathsf{CCl}_4 \xrightarrow{\mathsf{Catalyst}} \mathbf{R} \xrightarrow{\mathsf{Cl}} \mathsf{CCl}_3 \tag{1}$$

We have reported recently that the $(POC_{sp3}OP)$ -Ni^{II}X/(POC_{sp3}OP)Ni^{III}X₂ systems promote the Kharasch addition of CCl₄ to a number of olefins, but the catalytic efficacy of these systems are inferior to the reactivities displayed by van Koten's (NCN)Ni^{II}X system. For example, the latter catalyzes the addition of CCl₄ to styrene and methyl methacrylate with catalytic turnover numbers (TON) of up to 1700 and an initial turnover frequency (TOF) of 400 h⁻¹ at room temperature, compared to a TON of 1000 over 24 h displayed by our POC_{sp3}OP systems in refluxing acetonitrile.¹⁸ Access to isolable samples of the (POCN)Ni^{III}X₂ complexes via the relatively facile oxidation of (POCN)Ni^{II}Br complexes **3** with CCl₄ prompted us to screen the reactivities of these complexes for the Kharasch addition reaction. The results of a preliminary study on the addition of CCl₄ to styrene are described below.

The catalytic runs were conducted over 18 h in acetonitrile at 80 °C with a Ni:styrene:CCl₄ ratio of 1:50:250. We obtained 95% yields of the anti-Markovnikov addition product when using **3a/5a** or **3b/5b** as precursors (TON = 45, TOF \approx 2.5/h), but no conversion was noted when using **3c/5c** as precursor. Analysis of the reaction mixture by NMR spectroscopy and GC-MS showed nearly total conversion to the expected product and no side-products arising from telomerization or oligomerization of styrene. In contrast to what was observed in van Koten's NCN system and our POC_{sp3}OP system, we found that virtually identical catalytic results are obtained whether the catalysis is carried out in air or in an inert atmosphere.

The progress of the catalytic reactions can be monitored by the colors of the catalytic mixtures: depending on whether divalent or trivalent Ni precursors were used, the initial colors of the catalytic mixtures are yellow (when using 3a or 3b) or dark brown (5a or 5b), but all mixtures become vellow-green as the catalysis progresses. No color change is observed and no conversion takes place over days when reaction mixtures are kept at room temperature. NMR monitoring of the catalytic reactions in which 3a or 3b was the Ni precursor revealed that the ³¹P signals of these species disappeared ca. 10 min after the start of the reaction, whereas reaction mixtures in which 3c or 5c was used as the Ni precursor displayed the ³¹P signal expected for 3c throughout the reaction. These observations indicate that promotion of the Kharasch addition requires relatively stable and longlived Ni^{III} intermediates, which is consistent with the generally accepted mechanism for this type of reaction.²⁹

Conclusions

The current study has shown that POCN-type pincer ligands serve as very attractive templates for preparing organonickel complexes: they undergo relatively facile nickelation and form thermally robust (POCN)Ni^{II}(Br)

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derivatives that can, in turn, furnish the high-valent species (POCN)Ni^{III}(Br)₂. Two of the latter, **5a** and **5b**, are thermally stable yet fairly reactive in the promotion of the Kharasch addition of CCl₄ to styrene

It is instructive to review the factors affecting the catalytic efficacy for the Kharasch additions catalyzed by pincernickel complexes. van Koten has established that the catalytic activities of (NCN)NiX complexes for the Kharasch addition correlate reasonably well with the redox potential for the one-electron oxidation of these complexes, the more easily oxidizable systems being more effective catalysts. This correlation appears to hold across the series NCN, POCOP, and POCN as the ease of oxidation $(Ni^{II} \rightarrow Ni^{III})$ and catalytic efficacy in the Kharasch addition follow the order NCN > $POC_{sp3}OP$ > POCN, whereas ($POC_{sp2}OP$)NiBr does not form isolable high-valent species and does not promote the Kharasch addition. Another important factor is the steric bulk of the donor moieties in these systems, the highest catalytic activities in the NCN systems being observed with the NMe₂ analogue. A similar phenomenon is in effect in the POCN systems, with the more bulky NEt₂ analogue 5c displaying the lowest thermal stability and being inactive in the Kharasch addition. By extension, we speculate that the greater steric bulk of the *i*-Pr₂P moiety in our POC_{sp3}OP and POCN systems might be an important factor contributing to their lower levels of catalytic activities and the lower stabilities of the high-valent species $LNi^{III}X_2$ in comparison to van Koten's NCN systems. These considerations might serve as guiding principles for the design of a new generation of catalysts for the Kharasch addition based on systems with less bulky donor moieties or larger and more flexible metallacycle rings.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk and glovebox techniques under a nitrogen atmosphere. Solvents were degassed and dried using standard procedures. The following were purchased from Aldrich and used without further purification: Ni (metal), chlorodiisopropylphosphine, 3-hydroxybenzaldehyde, triethylamine, and C_6D_6 . A Bruker AV 400 spectrometer was used for recording ¹H, ¹³C{¹H} (101 MHz), and ³¹P{¹H} (162 MHz) NMR spectra. ¹H and ¹³C chemical shifts are reported in ppm downfield of TMS and referenced against the residual C_6D_6 signals (7.15 ppm for ¹H and 128.02 ppm for ¹³C); ³¹P chemical shifts are reported in ppm and referenced against the signal for 85% H₃PO₄ (external standard, 0 ppm). Coupling constants are reported in Hz. The correlation and assignment of ¹H and ¹³C NMR resonances were aided by 2D COSY, HMQC, HMBC, DEPT, and ¹H{³¹P} experiments when necessary. GC/MS measurements were made on an Agilent 6890N spectrometer. UV/vis spectra were recorded on a Varian Bio 300 equipped with a temperature-controlling system using standard sampling cells (1 cm optical path length). The EPR spectra of 5a were collected on a Bruker Elexsys E580 spectrometer operating in CW mode. A solution of 5a in toluene (\sim 1 mM) was prepared, filtered, and placed in a 4 mm o.d. EPR tube. The solution was then degassed by repeated freeze-pump-thaw cycles, and the tube was sealed under vacuum. The sample was frozen to 120 K in the spectrometer resonator. DSC curves were obtained using a PerkinElmer Jade Thermoanalyser system with a nitrogen flow of 20 mL/ min, a heating rate of 10 °C/min, and samples weighing about 8 mg; an alumina crucible was used in the DSC measurements, and samples were prepared by using standard techniques. The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal). Melting points for

complexes **3a**, **3b**, and **3c** were determined using a Mel-TEMP 1010 melting point apparatus equipped with a digital thermometer. Thermal gravimetric analysis (TGA) was performed using a 2950 TGA HR V5.4A system with nitrogen as purge gas and a heating rate of 20 °C/min; a platinum crucible was used in the TGA measurements, and samples were prepared by using standard techniques.

Synthesis of Preligands. [3-((Morpholino)methyl)phenol], 1a. To a solution of 3-hydroxybenzaldehyde (0.500 g, 4.10 mmol) in 10 mL of methanol at rt was added a solution of morpholine (0.714 g, 8.20 mmol) in 6 mL of methanol. The resulting mixture was stirred for 1 h to obtain a yellow solution. The latter was then cooled to -5 °C, and NaBH₄ (0.200 g, 5.26 mmol) was added portionwise during 1 h. The preligand was purified in one of two ways. Purification Method A: The reaction mixture was concentrated under reduced pressure and then treated with 10% HCl until pH = 1, washed with a 1:1 mixture of EtOAc and Et_2O (3 × 10 mL), and finally treated with a concentrated aqueous ammonia solution until pH = 10. This mixture was then extracted with a 1:1 mixture of EtOAc and Et₂O (5 \times 10 mL), and the extracts were combined and dried over MgSO₄, filtered through a glass frit, and evaporated to give a colorless oil, which crystallized over time to give a white powder (0.664 g, 84%). Purification Method B: The reaction mixture was evaporated, and the residue was resolubilized in 20 mL of benzene, filtered through a short column of silica gel, and evaporated under dynamic vacuum to give a white powder. (0.736 g, 93%). ¹H NMR (δ , CDCl₃): 2.49 (m, 4H, 2 × NCH₂), 3.46 (s, 2H, ArCH₂N), 3.72 (t, ${}^{3}J = 5$, 4H, 2 × CH₂O), 6.70 (dd, ${}^{3}J = 8$, J = 3, 1H, {Ar}H⁶), 6.75 (s, 1H, {Ar}H²), 6.84 (d, ${}^{3}J = 8$, 1H, {Ar}H⁴), 7.15 (t, ${}^{3}J = 8$, 1H, {Ar}H⁵), 7.84 (br s, 1H, OH). ${}^{13}C{}^{1}H{}$ NMR (δ , CDCl₃); 53.48 (s, 2C, 2 × NCH₂), 63.22 (s). 1C, Ar CH_2N), 66.68 (s, 2C, 2 × O CH_2), 114.64 (s, 1 \tilde{C} , {Ar} C^6), 116.38 (s, 1C, $\{Ar\}C^2$), 121.48 (s, 1C, $\{Ar\}C^4$), 129.45 (s, 1C, $\{Ar\}C^{5}$, 138.70 (s, 1C, $\{Ar\}C^{3}$), 156.03 (s, 1C, $\{Ar\}C^{1}$). Anal. Calcd for C₁₁H₁₅NO₂: C, 68.44; H, 7.96; N, 7.18. Found: C, 68.37; H, 7.82; N, 7.25.

[3-((*N*,*N*-Dimethylamino)methyl)phenol], 1b. The procedure described above for the preparation of preligand 1a (purification method B) was used with dimethylamonium chloride (1.174 g, 12.3 mmol) and triethylamine (1.71 mL, 12.3 mmol) to prepare 3-((*N*,*N*-dimethylamino)methyl)phenol (1b), which was isolated as a white powder (0.390 g, 63%). ¹H NMR (δ , C₆D₆): 2.26 (s, 6H, 2 × CH₃), 3.41 (s, 2H, ArCH₂N), 6.74–6.67 (m, 2H, {Ar}H^{2.6}), 6.76 (d, ³J = 8, 1H, {Ar}H⁴), 7.13 (t, ³J = 8, 1H, {Ar}H⁵), 8.42 (br s, 1H, OH). ¹³C{¹H} NMR (δ , C₆D₆): 44.72 (s, 2C, 2 × CH₃), 63.78 (s, 1C, ArCH₂N), 115.44 (s, 1C,{Ar}C⁶), 117.19 (s, 1C, {Ar}C²), 121.24 (s, 1C, {Ar}C⁴), 129.36 (s, 1C, {Ar}C⁵), 138.15 (s, 1C,{Ar}C³), 157.09 (s, 1C, {Ar}C¹). Anal. Calcd for C₉H₁₃NO: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.55; H, 8.75; N, 9.13.

[3-((*N*,*N*-Diethylamino)methyl)phenol], 1c. The procedure described above for the preparation of preligand 1a (purification method A) was used with diethyl amine to prepare 3-((*N*,*N*-diethylamino)methyl)phenol, 1c, which was isolated as an off-white oil (0.594 g, 81%). ¹H NMR (δ , C₆D₆): 1.01 (t, ³*J* = 7, 6H, 2 × CH₃), 2.50 (q, ³*J* = 7, 4H, 2 × NCH₂), 3.49 (s, 2H, ArCH₂N), 6.83 (dd, ³*J* = 8, *J* = 2, 1H, {Ar}*H*⁶), 6.96 (d, ³*J* = 8, 1H, {Ar}*H*⁴), 7.03 (br s, 1H, OH), 7.06 (s, 1H, {Ar}*H*²), 7.17 (t, ³*J* = 8, 1H, {Ar}*H*⁵). ¹³C{¹H} NMR (δ , C₆D₆): 11.29 (s, 2C, 2 × CH₃), 46.61 (s, 2C, 2 × NCH₂), 57.69 (s, 1C, ArCH₂N), 115.03 (s, 1C, {Ar}C⁶), 116.93 (s, 1C, {Ar}C²), 121.15 (s, 1C, {Ar}C⁴), 129.59 (s, 1C, {Ar}C⁵), 140.79 (s, 1C, {Ar}C³), 157.36 (s, 1C, {Ar}C¹). Anal. Calcd for C₁₁H₁₇NO: C, 73.70; H, 9.56; N,7.81. Found: C, 73.3; H, 9.62; N, 7.38.

Synthesis of POCN Ligands. [3-((Morpholino)methyl)phosphinitobenzene], 2a. A solution of chlorodiisopropyl phosphine (0.427 mL, 2.59 mmol, 96%) in THF (15 mL) was added to a solution of 1a (0.500 g, 2.59 mmol) and triethylamine (0.400 mL, 2.85 mmol) in THF (35 mL), stirring at 0-5 °C. The resulting mixture was allowed to warm to room temperature and stirred for an additional 1 h. Evaporation of the solvent and extraction of the residue with Et₂O (3 × 25 mL) followed by filtration of the combined extracts and evaporation gave the desired product as a colorless oil (0.768 g, 96%). ¹H NMR (δ , C₆D₆): 0.72 (dd, ³J_{HP} = 9, J_{HH} = 7, 3H, CH₃), 0.73 (dd, ³J_{HP} = 8, J_{HH} = 7, 3H, CHCH₃), 0.93–0.85 (m, 6H, 2 × CHCH₃), 1.57–1.47 (m, 2H, CH), 1.90–1.92 (m, 4H, 2 × NCH₂), 2.95 (s, 2H, NCH₂), 3.28–3.30 (m, 4H, 2 × OCH₂), 6.67 (d, ³J_{HH} = 7, 1H,{Ar}H⁶), 6.85 (t, ³J_{HH} = 8, 1H,{Ar}H⁵), 6.89 (s, 1H, {Ar}H²), 6.95 (d, ³J_{HH} = 8, 1H, {Ar}H⁴). ¹³C{¹H} NMR (δ , C₆D₆): 17.17 (d, ²J_{CP} = 8, 2C, 2 × CHCH₃) 17.89 (d, ²J_{CP} = 20, 2C, 2 × CHCH₃), 28.64 (d, ¹J_{CP} = 19, 2C, 2 × OCH₂), 117.56 (d, ³J_{CP} = 11, 1C, {Ar}C⁶), 119.41 (d, ³J_{CP} = 10, 1C, {Ar}C²), 122.56 (s, 1C, {Ar}C⁴), 129.48 (s, 1C, {Ar}C⁵), 140.58 (s, 1C, {Ar}C³), 160.11 (d, ²J_{CP} = 9,1C, {Ar}C¹). ³¹P{¹H} NMR (δ , C₆D₆): 147.5 (s). Anal. Calcd for C₁₇H₂₈NO₂P: C, 66.00; H, 9.12; N, 4.53. Found: C, 66.18; H, 9.36; N, 4.32.

[3-((*N*,*N*-Dimethylamino)methyl)phosphinitobenzene], 2b. The procedure described above for the preparation of 2a was used to prepare 3-((*N*,*N*-diethylamino)methyl)phosphinitobenzene, 2b, which was isolated as a colorless oil (0.799 g, 91%). ¹H NMR (δ , C₆D₆): 0.68 (dd, J_{HP} = 15, J_{HH} = 7, 6H, 2 × CHCH₃), 0.84 (dd, J_{HP} = 10, J_{HH} = 7, 6H, 2 × CHCH₃), 1.46 (m, 2H, 2 × CH), 1.76 (s, 6H, 2 × NCH₃), 2.94 (s, 2H, ArCH₂), 6.68 (d, J_{HH} = 7, 1H, {Ar}H⁶), 6.81 (t, J_{HH} = 8, 1H, {Ar}H³), 6.85 (s, 1H, {Ar}H²), 6.89 (d, J_{HH} = 8, 1H, {Ar}H⁴). ¹³C{¹H} NMR (δ , C₆D₆): 17.17 (d, ²J_{CP} = 9, 2C, 2 × CH₃), 17.87 (d, ²J_{CP} = 21, 2C, 2 × CH₃), 28.64 (d, ¹J_{CP} = 19, 2C, 2 × CH), 45.34 (s, 2C, 2 × CH₃N), 64.29 (s, 1C, ArCH₂N), 117.48 (d, ³J_{CP} = 11, 1C, {Ar}C⁶), 119.29 (d, ³J_{CP} = 10, 1C, {Ar}C²), 122.43 (s, 1C, {Ar}C⁴), 129.44 (s, 1C, {Ar}C⁵), 160.08 (d, ²J_{CP} = 9, 1C, {Ar}C⁶). ³¹P{¹H} NMR (δ , C₆D₆): 147.4 (s). Anal. Calcd for C₁₅H₂₆NOP: C, 67.39; H, 9.80; N, 5.24. Found: C, 66.97; H, 9.96; N, 4.91.

[3-((*N*,*N*-Diethylamino)methyl)phosphinitobenzene], 2c. The procedure described above for the preparation of 2a was used to prepare 3-((*N*,*N*-diethylamino)methyl)phosphinitobenzene, 2c, which was isolated as a colorless oil (0.730 g, 89%). ¹H NMR (δ , C₆D₆): 0.56 (t, ³*J*_{HH} = 7, 6H, 2 × CH₂C*H*₃), 0.63 (dd, ³*J*_{HP} = 16, *J*_{HH} = 7, 6H, 2 × CHC*H*₃), 0.79 (dd, ³*J*_{HP} = 11, *J*_{HH} = 7, 6H, 2 × CHC*H*₃), 0.79 (dd, ³*J*_{HP} = 11, *J*_{HH} = 7, 6H, 2 × CHC*H*₃), 0.79 (dd, ³*J*_{HP} = 11, *J*_{HH} = 7, 6H, 2 × CHC*H*₃), 0.79 (dd, ³*J*_{HP} = 11, *J*_{HH} = 7, 6H, 2 × CHC*H*₃), 0.79 (dd, ³*J*_{HP} = 11, *J*_{HH} = 7, 6H, 2 × CHC*H*₃), 1.51–1.26 (m, 2H, 2 × CH), 2.03 (q, ³*J*_{HH} = 7, 4H, 2 × C*H*₂), 3.06 (s, 2H, ArC*H*₂N), 6.67 (d, ³*J*_{HH} = 8, 1H, {Ar}*H*⁶), 7.03–6.92 (m, 3H, {Ar}*H*^{4,2.5}). ¹³C{¹H} NMR (δ , C₆D₆): 12.00 (s, 2C, 2 × CH₂CH₃), 14.76 (d, ²*J*_{CP} = 3, 2C, 2 × CHCH₃), 15.85 (d, ²*J*_{CP} = 2, 2C, 2 × CHCH₃), 24.82 (d, ¹*J*_{CP} = 64, 2C, 2 × CH), 46.96 (s, 2C, 2 × CH₂CH₃), 58.15 (s, 1C, ArCH₂N), 114.73 (s, 1C, {Ar}*C*⁶), 116.67 (s, 1C, {Ar}*C*²), 119.93 (s, 1C, {Ar}*C*⁴), 129.44 (s, 1C, {Ar}*C*⁵), 158.86 (s, 1C, {Ar}*C*¹). ³¹P{¹H} NMR (δ , C₆D₆): 147.1 (s). Anal. Calcd for C_{17H₃₀NOP: C, 69.12; H, 10.24; N, 4.74. Found: C, 69.32; H, 10.37; N, 4.48.}

Synthesis of Complexes 3–5. $\kappa^{P}, \kappa^{C}, \kappa^{N}$ -{2,6-(*i*-Pr₂PO)-(C₆H₃)(CH₂[*c*-N(CH₂)₄O])}NiBr, 3a. Slow addition of a solution of 2a (0.500 g, 1.62 mmol) and NEt₃ (0.23 mL, 1.62 mmol) in 20 mL of benzene to the suspension of NiBr₂(CH₃CN)_{*x*} (0.485 g, 1.618 mmol) in benzene (10 mL) resulted in a dark brown mixture, which was heated for 3 h at 60 °C. Filtration of the final mixture through a pad of silica gel followed by evaporation of the volatiles gave the desired product as a yellow powder (0.659 g, 91%). ¹H NMR (δ , C₆D₆): 1.16 (dd, ³*J*_{HP} = 15, ³*J*_{HH} = 7, 6H, CH₃) 1.47 (dd, ³*J*_{HP} = 18, ³*J*_{HH} = 7, 6H, CH₃) 1.47 (dd, ³*J*_{HH} = 13, 2H, NCH₂CH₂), 3.14 (dd, ³*J*_{HH} = 12 and 3, 2H, NCH₂CH₂), 3.20 (td, ³*J*_{HH} = 12 and 2, 2H, OCH₂), 3.62 (s, 2H, ArCH₂N), 4.18 (m, 2H, OCH₂), 6.44 (d, ³*J*_{HH} = 8, 1H, {Ar}*H*⁴). ¹³C{¹H} NMR (δ , C₆D₆): 16.90 (s, 2C, 2 × CH₃) 18.34 (d, ²*J*_{CP} = 4, 2C, 2 × × CH₃), 28.61 (s, 2C, 2 × CH₃), 108.42 (s, 1C, 2K) (d, ³*J*_{CP} = 12, 1C, {Ar}C³, 108.42 (s, 1C, 2K)

{Ar}C⁵), 115.92 (s, 1C, {Ar}C⁴), 142.15 (d, ${}^{2}J_{CP} = 35$, 1C, {Ar}C¹-Ni), 150.75 (s, 1C, {Ar}C⁶), 165.96 (d, ${}^{2}J_{CP} = 9$, 1C, {Ar}C²). ${}^{31}P{}^{1}H{}$ NMR (δ , C₆D₆): 201.48 (s). Anal. Calcd for C₁₇H₂₇P₁O₂NiBr: C, 45.68; H, 6.09; N, 3.13. Found: C, 45.69; H, 6.04; N, 3.04.

H, 6.04; N, 3.04. $\kappa^{P}, \kappa^{C}, \kappa^{N}$ -{2,6-(*i*-Pr₂PO)(C₆H₃)(CH₂NMe₂)}NiBr, 3b. The procedure described above for the preparation of 3a was used to prepare this complex, which was isolated as a yellow powder (0.583 g, 77%). ¹H NMR (δ , C₆D₆): 1.17 (dd, ³J_{HP} = 15, ³J_{HH} = 7, 6H, 2 × CH₃), 1.47 (dd, ³J_{HP} = 18, ³J_{HH} = 7, 6H, 2 × CH₃), 2.19 (m, 2H), 2.44 (d, ³J_{HH} = 2, 6H, 2 × NCH₃), 3.25 (s, 2H, NCH₂), 6.40 (d, ³J_{HH} = 7, 1H, {Ar}H⁵), 6.62 (d, J_{HH} = 8, 1H, {Ar}H³), 6.93-6.87 (m, 1H, {Ar}H⁴). ¹³C{¹H} NMR (δ , C₆D₆): 16.87 (s, 2C, 2 × CH₃), 18.26 (d, ²J_{CP} = 4, 2C, 2 × CH₃), 28.49 (d, ¹J_{CP} = 24, 2C, 2 × CH), 49.11 (s, 2C, 2 × NCH₃), 71.84 (s, 1C, CH₂), 108.38 (d, ³J_{CP} = 13, 1C, {Ar}C³), 115.67 (s, 1C, {Ar}C⁵), 127.04 (s, 1C, {Ar}C⁴), 143.11 (d, ²J_{CP} = 33, 1C, {Ar}C¹-Ni), 151.09 (s, 1C, {Ar}C⁶), 166.16 (d, ²J_{CP} = 11, 1C, {Ar}C²). ³¹P{¹H} NMR (δ , C₆D₆): 199.16 (s, P). Anal. Calcd for C₁₅H₂₇P₁O₂NiBr: C, 44.50; H, 6.22; N, 3.46. Found: C, 44.56; H, 6.41; N, 3.53.

H, 6.41; N, 3.53. $\kappa^{P}, \kappa^{C}, \kappa^{N}$ -{2,6-(*i*-Pr₂PO)(C₆H₃)(CH₂NEt₂)}NiBr, 3c. The procedure described above for the preparation of 3a was used to prepare this complex, which was isolated as a yellow powder (0.616 g, 84%). ¹H NMR (δ , C₆D₆): 1.12 (dd, ³J_{HP} = 14, ³J_{HH} = 7, 6H, 2 × CHCH₃) 1.51–1.37 (m, 12H, 2 × CH₂CH₃ and 2 × CHCH₃), 2.08–1.96 (m, 2H, 2 × CH), 2.17 (m, 2H, CH₂CH3), 3.41–3.28 (m, 2H, CH₂CH₃), 3.43 (s, 2H, ArCH₂N), 6.35 (d, ³J_{HH} = 8, 1H, {Ar}H⁴). ¹³C{¹H} NMR (δ , C₆D₆): 13.34 (s, 2C, 2 × CH₂CH₃) 16.85 (d, ³J_{CP} = 2, 2C, 2 × CH₃), 18.19 (d, ²J_{CP} = 4, 2C, 2 × CH₂CH₃), 64.7 (d, ³J_{CP} = 2, 1C, ArCH₂N), 107.96 (d, ³J_{CP} = 13, 1C, {Ar}C³), 114.3 (d, ⁴J_{CP} = 2, C, {Ar}C⁵), 126.8 (s, 1C, {Ar}C⁴), 142.1 (d, ²J_{CP} = 11, 1C, {Ar}C¹-Ni), 154.1 (s, 1C, {Ar}C⁶), 165.8 (d, ²J_{CP} = 11, 1C, {Ar}C²). ³¹P{¹H} NMR (δ , C₆D₆): 197.92 (s). Anal. Calcd for C₁₇H₂₉OPNNiBr: C, 47.16; H, 6,75; N, 3.23. Found: C, 47.71; H, 6.68; N, 3.26.

 κ^{P} -[1,3-{(*i*-Pr₂PO)(C₆H₄)(CH₂[*c*-NH(CH₂)₄O])}]NiBr₃, 4. A solution of **2a** (0.500 g, 1.618 mmol) in benzene (15 mL) was added to NiBr₂(CH₃CN)_x (0.486 g, 1.62 mmol). The resulting brown mixture was stirred at 60 °C for 3 h, which resulted in the precipitation of a blue-green solid. Filtration through a glass frit (under inert atmosphere) and washing the solid on a filter with benzene followed by drying under vacuum gave a turquoise-green solid (0.423 g, 43%). The filtrate was passed through a pad of silica gel followed by removal of solvent to give **3a** as a yellow powder (0.333 g, 46%). Anal. Calcd for C₁₇H₂₉O₂P₁NiBr₃: C, 33.54; H, 4.80; N, 2.30. Found: C, 33.58; H, 4.81; N, 2.39.

 $\kappa^{P}, \kappa^{C}, \kappa^{N}$ -{2,6-(*i*-Pr₂PO)(C₆H₃)(CH₂[*c*-N(CH₂)₄O])}NiBr₂, 5a. A solution of Br₂ (6.5 μ L, 0.123 mmol) in E₂O (5 mL) was cooled to -15 °C and then added to a solution of **3a** (0.100 g, 0.224 mmol) in 10 mL of a 5:1 mixture of Et₂O and CH₂Cl₂. The resulting mixture was stirred for 20 min and then concentrated under reduced pressure to ~3-5 mL. The final mixture was layered with cold hexane (5 mL) and placed in a -15 °C freezer to obtain black crystals, which were collected by filtration (112 mg, 95%). Anal. Calcd for C₁₇H₂₇O₂PNNiBr₂: C, 38.75; H, 5.17; N, 2.66. Found: C, 38.47; H, 5.05; N, 2.57.

 $\kappa^{P}, \kappa^{C}, \kappa^{N-\{2,6-(i-Pr_2PO)(C_6H_3)(CH_2NMe_2)\}}$ NiBr₂, 5b. The procedure described above for the preparation of 5a was used to prepare this complex, which was isolated as black crystals (114 mg, 96%). Anal. Calcd for C₁₅H₂₅OPNNiBr₂: C, 37.16; H, 5.20; N, 2.89. Found: C, 37.13; H, 5.23; N, 2.97

 $\kappa^{P}, \kappa^{C}, \kappa^{N}$ -{2,6-(*i*-Pr₂PO)(C₆H₃)(CH₂NMe₂)}NiBr₂, 5b. A modified version of the procedure described above for the preparation of 5a (reaction temperature -78 °C) was used to prepare this complex, which was isolated as black crystals (93 mg, 80%). Anal. Calcd for C₁₇H₂₉OPNNiBr₂: C, 39.81; H, 5.70; N, 2.73. Found: C, 39.34; H, 5.86; N, 2.73.

Cyclic Voltammetry. Cyclic voltammetry measurements were performed using a BAS Epsilon potentiostat. The electrochemical properties of these compounds were measured at room temperature in dichloromethane using a standard three-electrode system consisting of a glassy carbon working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode. Bu₄NPF₆ was used as electrolyte (0.1 mol/L), and the solutions were bubbled with nitrogen before each experiment. Reversible redox waves of the ferrocenyl moieties were observed under these conditions ($E_{1/2}$ {FeCp₂⁺/FeCp₂} = +0.47 V).

Crystal Structure Determinations. Single crystals of **3a**-**c** were grown by slow diffusion of hexanes into saturated benzene solutions of the complexes. Single crystals of **5a**-**c** were grown from dichloromethane-hexane mixtures at -20 °C. The crystallographic data for complexes **3a**-**c** and **5a**-**c** were collected on a Bruker Microstar generator (micro source) equipped with a Helios optics, a Kappa Nonius goniometer, and a Platinum135 detector. Cell refinement and data reduction were done using SAINT.³⁰ An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.³¹ The space group was confirmed by XPREP routine³² in the program SHELXTL.³³ The structures were solved by direct methods and refined by fullmatrix least-squares and difference Fourier techniques with SHELX-97.³⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter.

Acknowledgment. The authors gratefully acknowledge financial support received from Université de Montréal (fellowships to D.M.S.) and NSERC of Canada (Research Tools and Instruments grants to D.Z. and Discovery grants to D.Z. and A.v.d.E.). Profs. D. Rochefort and M. S. Workentin are thanked for their valuable help with electrochemical studies.

Supporting Information Available: TGA for 3a-c and cyclic voltammograms for complexes 3, ligand 2a, and preligand 1a. This material is available free of charge via the Internet at http:// pubs.acs.org. Complete details of the X-ray analyses for complexes 3a-c and 5a-c have been deposited at The Cambridge Crystallographic Data Centre (CCDC 713853 (3a), 713856 (3b), 713854 (3c), 713856 (5a), 713855 (5b), 713857 (5c)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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