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Monomeric and Dimeric Nickel Complexes Derived from a Pincer Ligand Featuring a Secondary Amine Donor Moiety

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Reaction of $NiBr_2(CH_3CN)_x$ with the unsymmetrical pincer ligand *m*-(*i*-Pr_2PO)(CH_2NHBn)C_6H_4 (Bn = CH_2Ph) gives the complex (*R*,*S*)-$\kappa^P,\kappa^C,\kappa^N$-{2-(*i*-$Pr_2PO$),6-($CH_2NHBn$)-$C_6H_3$}$Ni^{II}Br$, **1**, featuring an asymmetric secondary amine donor moiety. Deprotonation of the latter with methyl lithium gave a dark brown compound that could not be characterized directly, but fully characterized derivatives prepared from this compound indicate that it is the LiBr adduct of the 14-electron amido species [$\kappa^P,\kappa^C,\kappa^N$-{2-(*i*-$Pr_2PO$),6-($CH_2NBn$)-$C_6H_3$}Ni], **2**. Thus, **2**·**LiBr** reacts with water to regenerate **1**, while reaction with excess benzyl or allyl bromide gave the POCN-type pincer complexes **3** and **4**, respectively, featuring tertiary amine donor moieties. On the other hand, heating **2**·**LiBr** at 60 °C led to loss of LiBr and dimerization to generate the orange crystalline compound [$\mu^N;\kappa^P,\kappa^C,\kappa^N$-{2-(*i*-$Pr_2PO$),6-($CH_2NBn$)-$C_6H_3$}Ni]$_2$, **5**. Solid state structural studies show that **1**, **3**, and **4** are monomeric, square planar complexes involving one Ni−N interaction, whereas complex **5** is a C_2-symmetric dimer involving four Ni−N interactions and a Ni_2N_2 core featuring a short Ni−Ni distance (2.51 Å). Preliminary reactivity tests have shown that **5** is stable toward weak nucleophiles such as acetonitrile but reacts with strong nucleophiles such as CO or 2,6-$Me_2(C_6H_3)NC$. Reactions with protic reagents showed that phthalimide appears to break the dimer to generate a monomeric species, whereas alcohols appear to leave the dimer intact, giving rise instead to adducts through N···H···O interactions. These ROH adducts of **5** were found to be active precatalysts for the alchoholysis of acrylonitrile with up to 2000 catalytic turnover numbers.

Introduction

The chemistry of pincer complexes has experienced much progress over the past three decades as it has been shown that various metal-pincer ligand combinations can generate compounds that act as versatile catalysts, molecular sensors and switches, and diverse functional materials.[1] Pincer ligands can impart enhanced reactivity or thermal stability to the metals they bind, thus facilitating difficult reactions or allowing the isolation of rare reaction intermediates featuring unusual oxidation states or bonding patterns;[2] this capacity to modulate reactivities of metals is helping to advance our fundamental understanding of organometallic chemistry. During the early years following their introduction,[3] the most commonly studied pincer ligands were LXL-type ligands

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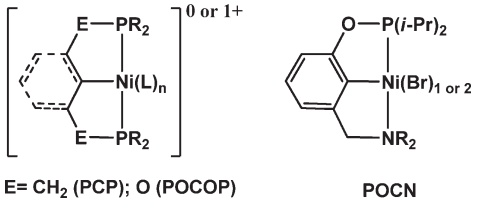
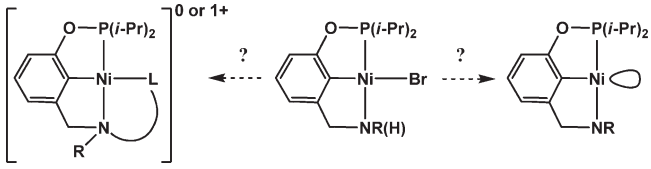
Chart 1



(monoanionic, terdentate) featuring tertiary phosphine or amine donor moieties linked to each other through an aliphatic or aromatic skeleton encompassing a carbon- or nitrogen-bound anionic anchor,[4] but a variety of ligand types has been introduced recently (L = carbenes, alkenes, RSR, κ^O-R_3P═O, RSeR, etc.; X = alkyl, aryl, SiR_3, BR_2, etc.).[5]

Our group has investigated the chemistry of nickel complexes based on symmetrical and unsymmetrical pincer ligands featuring tertiary phosphine, phosphinite, and amine donor moieties (Chart 1) and reported on their reactivities in catalytic transformations such as Kumada-Coriu coupling, hydroamination of acrylonitrile derivatives, Kharasch additions to olefins, as well as oligomerization of $PhSiH_3$ and its addition to styrene.[6] As an extension of these studies, we set out to prepare POCN-type complexes of nickel featuring secondary amine donor moieties that might offer two attractive advantages over their tertiary amine homologues.[6i] First, alkylation of the N−H moiety in these complexes should, in principle, provide an alternative pathway for the preparation of difficult-to-access tertiary amine derivatives, including species featuring tetradentate ligands encapsulating the Ni center (Scheme 1).[7] Second, dehydrohalogenation of (POCN)NiX complexes featuring a secondary amine donor

Scheme 1



moiety (X = halide) might generate 14-electron Ni-amido species that would be expected to display unique reactivities. The latter possibility was particularly intriguing since, to the best of our knowledge, all previously reported pincer-type compounds of Ni have more than 14 valence electrons (15,[8] 16,[9] or 17[10]).

Whereas 14-electron species are expected to be highly reactive because of the presence of two empty valence orbitals on the metal,[11] many of these compounds are only nominally unsaturated because their operational unsaturation is usually "quenched" by extraneous interactions that can be either intermolecular (e.g., solvent/anion association or dimerization) or intramolecular (e.g., π-donation or agostic interactions).[11a] We were, therefore, mindful of the possibility that our plan to generate a highly reactive 14-electron species (Scheme 1) might be thwarted by the propensity of the amido ligand to form a dimer. Initial tests showed that dimerization

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does indeed take place, but the resulting dimer is fairly reactive nonetheless. The present contribution describes the synthesis and reactivities of the dimeric species $[\mu^N;\kappa^P,\kappa^C,\kappa^N$-{2-(*i*-$Pr_2PO$),6-($CH_2NBn$)-$C_6H_3$}$Ni]_2$, **5**, which was obtained from deprotonation of the monomeric (*R*,*S*)-$\kappa^P,\kappa^C,\kappa^N$-{2-(*i*-$Pr_2PO$),6-($CH_2NHBn$)-$C_6H_3$}$Ni^{II}Br$, **1**; also reported are the synthesis and characterization of complexes **3** and **4**, the *N*-allyl and *N*-benzyl derivatives of **1**, respectively.

Results and Discussion

Syntheses. The POCN-type ligand **b** was prepared following a procedure used for the preparation of analogous ligands featuring 3° amines.[6i] Thus, reaction of 3-hydroxybenzaldehyde with benzyl amine followed by reduction of the in situ formed Schiff base with $NaBH_4$ in methanol gave 3-((*N*-benzylamino)methyl)phenol, **a** (Scheme 2). Reaction of the latter with *i*-Pr_2PCl in the presence of NEt_3 led to exclusive phosphination at the O−H (vs N−H) moiety, thus facilitating isolation of the new pincer-type ligand **b** as an analytically pure colorless oil in 96% yield. It is worth noting that the phosphinite moiety in **b** is quite sensitive to hydrolysis but relatively stable toward oxidation. Finally, heating a toluene suspension of **b** and $NiBr_2(CH_3CN)_x$ at 60 °C in the presence of NEt_3 led to cyclometalation of **b** and formation of the new pincer complex **1**. The presence of an added base in such 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.[6i]

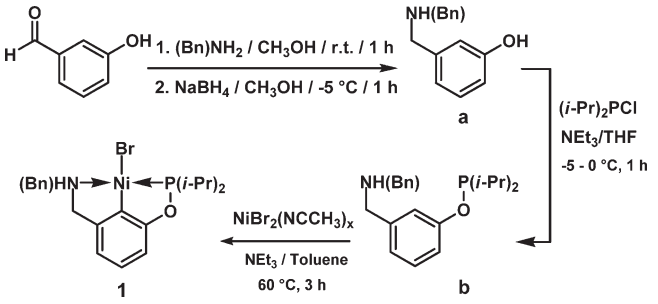
Reaction of **1** with MeLi in toluene at −78 °C gave an air-sensitive, oily material which could not be characterized directly, but its conversion to unambiguously characterized derivatives **3** and **4** has allowed us to identify this substance as the LiBr adduct of the 14-electron species generated from deprotonation of the NH moiety in **1** (Scheme 3).[12] For instance, the in situ generated **2·LiBr** reacted readily with water or benzyl bromide to give analytically pure samples of the starting material **1** or its Bn_2N analogue **4**, respectively. The reaction of **2·LiBr** with allyl bromide was more sluggish and produced significant amounts of intractable materials in addition to the anticipated *N*-allylated derivative **3** (Scheme 3); the latter was purified by chromatography on silica gel and isolated in about 60% yield. That **2·LiBr** can be hydrolyzed to regenerate **1** and allylated or alkylated to give **3** and **4** lends strong support for the proposed identity of **2**; the formation of **3** and **4** also indicates that this procedure is a viable synthetic route for modifying a metal-bound pincer ligand.

Solutions of **2·LiBr** lose LiBr slowly (over a week at r.t. or 32 h at 60 °C) to give the dimeric species **5** (Scheme 3). Attempts to trap the postulated 14 electron intermediate, **2**, as isolable monomeric adducts by doing the deprotonation reaction in the presence of N- or P-based ligands led to intractable mixtures of products, whereas running the deprotonation in coordinating solvents (THF, MeCN) gave **5**.

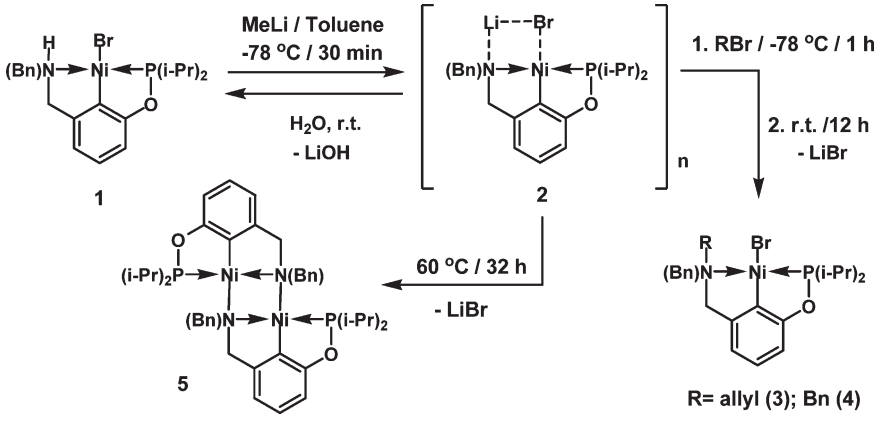
Characterization. The identities of the pre-ligand **a**, the ligand **b**, and the complexes **1** and **3**−**5** were discerned from NMR and elemental analyses, and corroborated by single crystal structure determination in the case of the complexes. As will be discussed below, the complex spectral features of the new pincer complexes were interpreted on the basis of data from ^{1}H-COSY, ^{1}H-NOESY, and HETCOR experiments as well as by comparisons to the characteristic NMR resonances of the ligand (vide infra).

The $^{31}P\{^1H\}$ NMR spectra were straightforward, displaying a single resonance for the ligand **b** (147 ppm) and the complexes **1** (202 ppm), **3** and **4** (201 ppm), and **5** (192 ppm). Analysis of the ^{1}H and ^{1}H-COSY NMR spectra confirmed the presence of an NH proton in **1**, indicating that complexation to the Ni center left the NH moiety of **b** intact. It is worth noting that complexation/cyclometalation of the POCN ligand **b** also leads to asymmetrization of the nitrogen center in **1**, which renders the NCH_2 protons diastereotopic and gives rise to complex spin coupling patterns. This is evident when the signal for

Scheme 2



Scheme 3



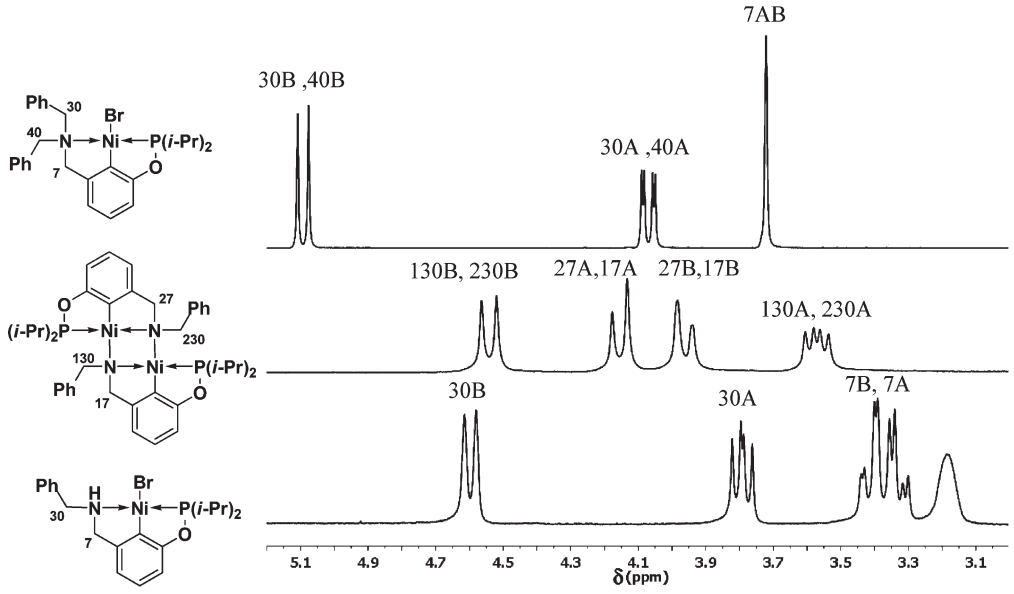


Figure 1. Methylene region in the ^{1}H NMR spectra (C_6D_6) of complexes **1** (bottom), **5** (middle), and **4** (top).

the NCH_2 protons in the ligand (a singlet resonance at ca. 3.3 ppm) is compared to the multiplets displayed in the spectrum of **1** (Figure 1). Thus, the signals for N*H* and the non-equivalent protons 7A and 7B[13] form an ABX pattern of which the AB portion is centered at about 3.4 ppm and displays coupling constants of 16 ($J_{H7A-H7B}$), 6 (J_{H7A-NH}), and 4 Hz (J_{H7B-NH}), whereas the corresponding signals for the benzylic protons 30A and 30B resonate at significantly different chemical shifts ($\Delta\delta\sim$ 1 ppm) but with a similar coupling constant ($J_{H30A-H30B}$ = 14 Hz); interestingly, H30A couples fairly strongly with the N*H* proton ($J_{H30A-NH}$ = 10 Hz) while H30B does not.

The ^{1}H and ^{13}C NMR spectra of complex **4** are simpler than those of **1**, because the Bn_2N moiety gives rise to a plane of symmetry in **4** and renders the symmetry-related nuclei above and below the plane of symmetry equivalent. Hence, we observe one signal for the symmetry-related methyne carbons and protons, two signals for the four methyl groups, one signal for the two benzylic protons labeled 7 (Figure 1), and one signal for the benzylic carbons (C30 and C40). Equivalence of the benzylic carbons coupled with the observation of two different signals for their protons (Figure 1) implies that the latter are pairwise equivalent (30A/40A, 30B/40B) and should appear as a pair of AB doublets, which is the case (ca. 4.1 and 5.1 ppm; $J\sim$ 13 Hz). Interestingly, the more upfield signal is further split into a doublet because of a through-space coupling with the P nucleus (J_{H-P} = 3 Hz). The ^{1}H NMR spectrum of complex **3** is similar to that of complex **1** since both of these complexes contain a chiral N center, but there are important differences: absence of NH in **3** eliminates a potential source of coupling such that ArCH_2N protons appear as two characteristic AB doublets, whereas coupling due to the P nucleus leads to different multiplicities for the methylene protons of the allyl moiety (ddd, J_{P-H} = 4 Hz) and the benzyl moiety (dd, J_{P-H} = 2 Hz). Finally, the ^{1}H and ^{13}C NMR spectra of complex **5** show the equivalence of all symmetry-related protons and carbon nuclei, indicating that the two halves of this dimer are related by a mirror plane and/or a C_2 axis of rotation. As above, the coupling patterns of the methylene protons indicate the pairwise equivalence of the chemically inequivalent protons (Figure 1: 130A/230A vs 130B/230B; 17A/27A vs 17B/27B); one of the benzylic protons is also coupled to the P nucleus with a rather large coupling constant (J_{P-H} = 10 Hz).

Single crystals for complex **1**, **3**, **4**, and **5** were obtained and subjected to crystallography to determine solid state structural parameters. Crystal and data collection details for all complexes are presented in Table 1, selected structural parameters are listed in Table 2 (**1**, **3**, and **4**) and Table 3 (**5**), and ORTEP diagrams are shown in Figures 2 (**3** and **4**) and 3 (**5**). Complexes **1** and **3** crystallize in the non-chiral space groups $Pna2_1$ and $P\bar{1}$, respectively. It is noteworthy that complex **3** crystallizes with one molecule per asymmetric unit so that the nitrogen atom adopts either S or R configuration to generate a racemic mixture, whereas **1** crystallizes with two molecules per asymmetric unit and both molecules adopt the same configuration (S,S or R,R) at the nitrogen atom. Ironically, the achiral complex **4** crystallizes in the chiral space group $P2_1$ because of crystal packing. The N*H* in complex **1** was located in the difference Fourier map, whereas all other hydrogen atoms were placed in calculated positions and refined by using a riding model. Although the amino

(12) It is worth emphasizing that (i) NMR spectra of the oily material obtained from reaction of **1** with MeLi allow us to confidently exclude formation of a Ni-Me derivative, and (ii) the structure proposed for **2**·**LiBr** in Scheme 2 is a simplified and tentative one. Alternative postulates might involve cluster-type structures such as those found in the following reports: (a) Aubrecht, K B.; Lucht, B. L.; Collum, D. B. *Organometallics* **1999**, *18*, 2981. (b) Strohmann, C.; Lehmen, K.; Ludwig, A.; Schildbach, D. *Organometallics* **2001**, *20*, 4138. (c) Sott, R.; Hakansson, M.; Hilmersson, G. *Organometallics* **2006**, *25*, 6047. (d) Paté, F.; Oulyadi, H.; Harrison-Marchand, A.; Maddaluno, J. *Organometallics* **2008**, *27*, 3564.

(13) Another cause for the non-equivalence of protons 7A and 7B is the absence of a plane of symmetry in complex **1**, which also results in the non-equivalence of the two *i*-Pr substituents of the phosphinite moiety sitting above and below the plane of coordination. Thus, we find four different signals for the proton and carbon nuclei of the Me groups and two different signals for the methyne carbons, whereas the signals for the two methyne C*H* appear as a poorly resolved multiplet at ca. 2.11−2.33 ppm.

Table 1. Crystal Data Collection and Refinement Parameters for Complexes **1**, **3**–**5**

	1	**3**	**4**	**5**
chemical formula	$C_{20}H_{27}NOPNiBr$	$C_{23}H_{31}NNiOPBr$	$C_{27}H_{33}NNiOPBr$	$C_{40}H_{52}N_2Ni_2O_2P_2$
Fw	467.01	507.08	557.13	772.20
T (K)	150(2)	150(2)	150(2)	150(2)
wavelength (Å)	1.54178	0.71073	1.54178	1.54178
space group	$Pna2_1$	$P\bar{1}$	$P2_1$	$P2_1/n$
a (Å)	10.7398(2)	8.6056(11)	7.3167(2)	13.0358(2)
b (Å)	10.8633(2)	11.1459(14)	11.0759(2)	21.2671(4)
c (Å)	34.2587(5)	13.3396(16)	16.2119(3)	13.9931(2)
α (deg)	90	79.686(2)	90	90
β (deg)	90	73.752(2)	101.144(1)	100.920(1)
γ (deg)	90	71.897(2)	90	90
Z	4 ($Z' = 2$)	2	2	4
V (Å^3)	3996.95(12)	1161.6(3)	1289.02(5)	3809.11(11)
ρ_{calcd} (g cm^{-3})	1.552	1.450	1.435	1.347
μ (cm^{-1})	41.32	26.37	36.25	22.96
θ range (deg)	2.58–68.16	2.38–27.45	2.78–58.00	3.83–67.81
R1[a] [$I > 2\sigma(I)$]	0.0330	0.0259	0.0202	0.0344
wR2[b] [$I > 2\sigma(I)$]	0.0875	0.0674	0.0520	0.0969
R1 [all data]	0.0337	0.0333	0.0204	0.0444
wR2 [all data]	0.0879	0.0694	0.0521	0.1017
GOF	1.157	1.037	1.028	1.028

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**, **3**, and **4**

	1	**3**	**4**
Ni(1)–C(1)	1.8540(50)	1.8492(17)	1.8560(2)
Ni(1)–P(1)	2.1055(13)	2.1103(6)	2.0997(6)
Ni(1)–N(1)	1.9830(40)	2.0329(15)	2.0426(18)
Ni(1)–Br(1)	2.3440(9)	2.3435(3)	2.3594(4)
C(1)–Ni(1)–Br(1)	171.85(14)	173.53(6)	175.41(8)
P(1)–Ni(1)–N(1)	166.22(15)	166.25(5)	163.86(5)
P(1)–Ni(1)–Br(1)	96.00(4)	95.00(2)	93.95(2)
N(1)–Ni(1)–Br(1)	97.55(15)	98.03(4)	99.51(5)
P(1)–Ni(1)–C(1)	82.14(16)	82.12(6)	82.27(7)
N(1)–Ni(1)–C(1)	84.10(20)	84.47(7)	83.83(9)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **5**

	5
Ni(1)–C(11)	1.8638(18)
Ni(1)–N(1)	1.9970(16)
Ni(1)–N(2)	1.9704(15)
Ni(1)–Ni(2)	2.5119(4)
Ni(1)–P(1)	2.1218(6)
C(11)–Ni(1)–N(2)	168.96(8)
C(11)–Ni(1)–P(1)	81.34(7)
C(11)–Ni(1)–N(1)	85.09(8)
N(1)–Ni(1)–N(2)	85.81(6)
N(1)–Ni(2)–N(2)	86.06(6)
N(2)- Ni(1)–P(1)	107.72(5)
N(1)–Ni(1)- P(1)	166.43(5)

moiety in complex **3** was disordered over two positions, the structure refined quite well (R1 = 2.6%).

The main structural parameters of the three monomeric complexes **1**, **3**, and **4** are quite comparable and similar to those of previously reported POCN-type complexes of nickel featuring tertiary amines.[6i] Thus, these complexes adopt moderately distorted square planar geometries wherein the nitrogen atom is slightly displaced from the coordination plane (Figure 2); similar observations have been reported for other nitrogen-containing pincer complexes.[4c,d,14] The Ni–C distances in these complexes fall within a narrow range and are very similar to the Ni–C distances in the previously reported analogues (1.849–1.856 Å vs 1.853–1.859 Å). Similar trends are observed for the Ni–Br (2.343–2.359 vs 2.332–2.362 Å) and Ni–P distances (2.106–2.110 vs 2.109–2.112 Å), but the Ni–N bond is somewhat shorter (by about 10 esd values) in **1** (1.9830(40) and 2.0160(40) Å) as compared to **4** (2.0426(18) Å), **3** (2.0329(15) Å), and the previously reported analogous complexes featuring tertiary amines (2.021–2.043 Å).[6i] Not unexpectedly, the olefinic moiety tethered to the new pincer ligand in **3** does not interact with the nickel center.

Single crystal structure analysis of **5** revealed a dimeric species that adopts an overall butterfly like shape (ORTEP diagram in Figure 3, views a and b). The structure consists of two T-shaped halves (as defined by the coordination planes involving the Ni, C, P, and N atoms) that are rotated with respect to each other by about 70° and connected to each other by two additional Ni–N linkages. The latter create a central Ni_2N_2 core that adopts a cyclobutane-like conformation featuring a Ni–Ni distance of about 2.51 Å, which is within one esd of the sum of the two Ni(II) covalent radii (1.24(4) Å),[15] four acute angles (Ni–N–Ni∼ 79°; N–Ni–N∼ 86°), and two Ni/N/Ni planes puckered at the Ni–Ni axis by about 124°; the puckering places the two *N*-benzyl groups *syn* to each other. In comparison to the monomeric species **3** and **4**, each half of complex **5** displays slightly longer Ni–C (ca. 1.864 vs 1.856 and 1.849 Å) and Ni–P bonds (ca. 2.122 vs 2.100 and 2.110 Å), but a shorter Ni–N bond (ca. 1.997 vs 2.043 and 2.033 Å). Interestingly, the shorter Ni–N distance in the Ni_2N_2 core (Ni–N∼ 1.970 Å) involves the Ni and N atoms belonging to different halves of the complex (ΔNi–N∼ 16 e.s.d.).

It is instructive to compare the main structural features of complex **5** to those of $[\mu^N,\kappa^P,\kappa^N,\kappa^P\text{-(PNP)Ni}^I]_2$ ($PNP^- = N[2\text{-P}(i\text{-Pr})_2\text{-4-methylphenyl}]_2$),[8b] to our knowledge the

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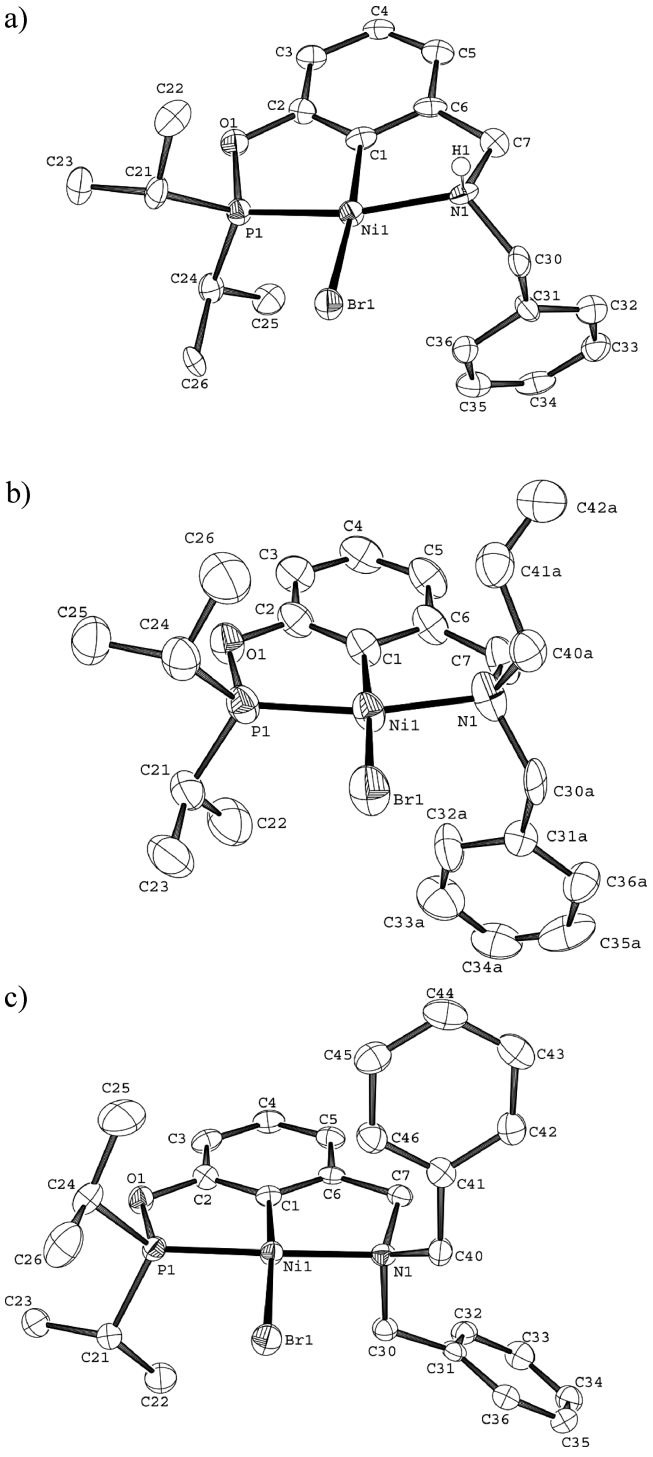


Figure 2. ORTEP diagrams for complex **1** (a), **3** (b), and **4** (c). Thermal ellipsoids are set at the 30% probability level for **1** and **4**, but 50% for **3**. Calculated hydrogen atoms are omitted for clarity.

only other structurally characterized pincer-nickel dimer.[16] The two phosphine moieties of each μ-PNP ligand in this dimer extend across the Ni^{I} centers to allow each phosphine to coordinate to a different Ni atom. The Ni_2N_2 core generated in this structure has a planar, diamond-like configuration containing two Ni−N−Ni angles $< 70°$ and two N−Ni−N angles of $\sim 111°$, in contrast to complex **5** that possesses a cyclobutane-like, puckered Ni_2N_2 core defined by four acute angles. Curiously, the two 17-electron Ni^{I} centers in $[\mu$-PNPNi$]_2$ interact only weakly in spite of the rather short intermetallic distance of about 2.33 Å; as a result, there is no $Ni^{I}-Ni^{I}$ bond and the dimer appears to be a diradical in the solid state. On the other hand, a number of observations seem to indicate that a dimer−monomer equilibrium might be operative in solutions of this complex, whereas **5** appears to retain its dimeric structure even in solution.

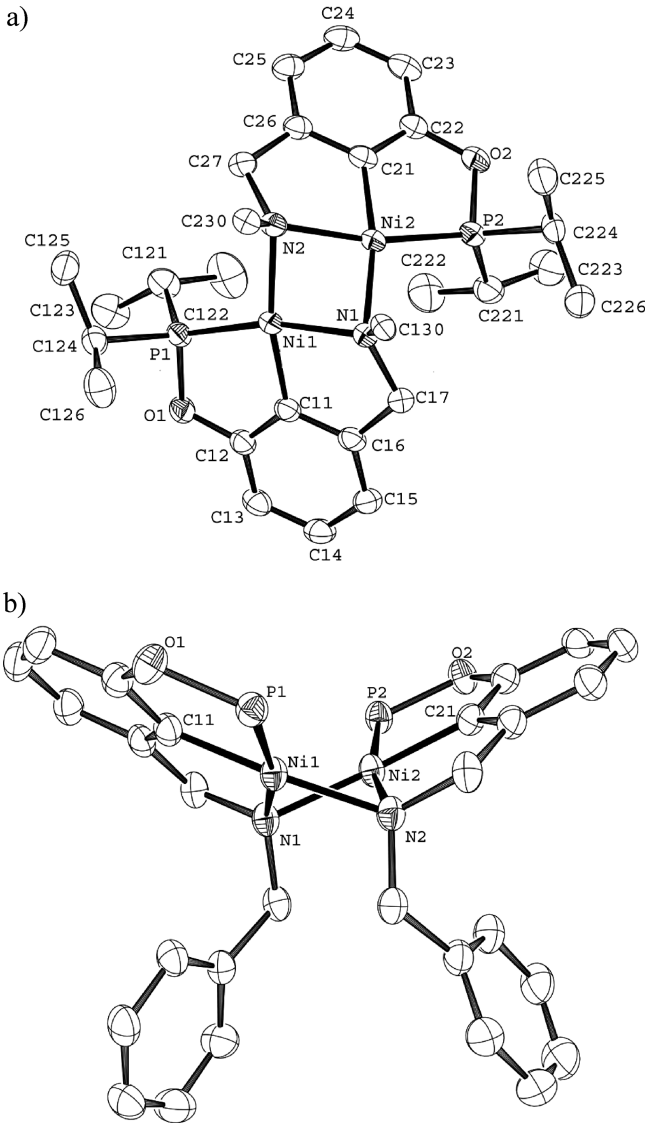
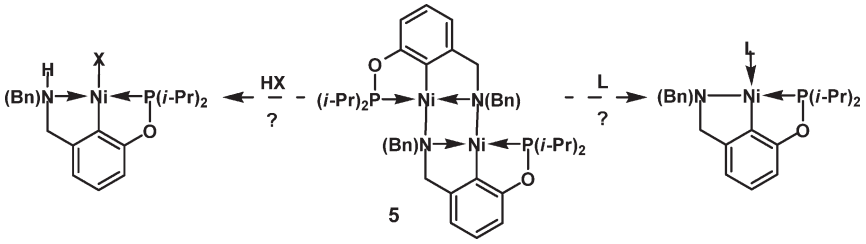


Figure 3. ORTEP diagram for complex **5** (view a, b). Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms (phenyl groups view (a), isopropyl groups view (b)) are omitted for clarity.

Reactivity Survey for 5. A series of NMR test reactions were undertaken to assess the reactivities of the dimeric complex **5**. Of primary interest is the reactivity with Lewis bases and reagents featuring X-H bonds of varying degrees of acidity, the main question being whether or not the dimer is prone to breaking up into monomeric species (Scheme 4).

(16) A recent report from Holm's group describes a dimeric Ni^{II} pincer complex $[\mu^{S},\kappa^{S},\kappa^{N},\kappa^{S}$-(SNS)Ni$]_2$ featuring a dianionic XLX-type SNS ligand, but no structural studies have been conducted on this species because of its limited solubility: Huang, D.; Deng, L.; Sun, J.; Holm, R. *Inorg. Chem.* **2009**, *48*, 6159.

Scheme 4



Monitoring ^{1}H NMR spectra of a 1:1 mixture of **5** and *m*-Cresol at room temperature showed that the O*H* signal shifted downfield from 3.9 ppm to 4.1 ppm, broadening and partially obscuring one of the doublets due to the methylene protons 130/230 (Figure 1 in the Supporting Information). Other spectral changes were also observed after the mixture was allowed to equilibrate at 50 °C for about 10 min: the cresol methyl group moved from 2.13 ppm to 2.34 ppm and a greater number of multiplets appeared in the methylene region, indicating a loss of symmetry (Figure 2 in the Supporting Information). The ^{31}P{^{1}H} NMR spectrum of the mixture showed the disappearance of the signal due to **5** (191.61 ppm) and emergence of two new peaks at 190.23 ppm and 191.23 ppm.

Adding 7 equiv of *m*-cresol to the above sample and allowing about 10 min for the mixture to equilibrate at 50 °C led to further spectral changes: the pattern for the methylene signals became simpler and more similar to the original signals for **5**, except for protons 130/230 that appeared as two overlapping doublets of doublets (Figure 3 in the Supporting Information); the ^{31}P{^{1}H} NMR spectrum showed only one signal very close to the original chemical shift for **5** (191.43 vs 191.61 ppm). Similar observations were noted in the reactions of **5** with 2,2,2-trifluoroethanol (TFE) or *N*-hydroxyphtalimide (NHP). For example, the ^{31}P{^{1}H} NMR spectra of the sample containing 8 equiv of these reagents showed that the original signal of **5** shifted slightly (from 191.61 to 192.46 ppm for TFE and 191.50 for NHP), while the ^{19}F{^{1}H} NMR spectrum of the mixture containing TFE showed two triplets, one at 78.24 ppm (free TFE) and the other at 77.69 ppm (TFE associated with **5**). To sum up, presence of excess *m*-cresol, TFE, and NHP appears to bring about observable but very subtle changes to the NMR spectra of **5**, implying that the original structure of **5** is mostly maintained in the presence of alcohols (dimer not broken up). We propose that reacting **5** with alcohols gives rise to N····H····O type interactions that only minimally perturb the solution structure of the dimer, while serving to enhance the nucleophilicities of ROH (vide infra).

In contrast to the reactions of ROH described above, distinct color changes were observed when **5** was reacted with 5 equiv of phthalimide (orange→pale yellow) or phenylacetylene (orange→ dark brown) and new ^{31}P{^{1}H} signals emerged in a chemical shift region associated with monomeric species (198.4 and 202.9 ppm, respectively).[17] Moreover, GC/MS analysis of the reaction mixture containing phenylacetylene showed the formation of cyclic trimers, 1,3,5- and 1,3,4-triphenylbenzene. Visible color changes were also noted during the reactions with excess phenylsilane (dark-brown) and *m*-toluidine (deep red). GC/MS analysis of the phenylsilane mixture showed the formation of diphenylsilane, but no new ^{31}P{^{1}H} signal was observed for this reaction, whereas the reaction with *m*-toluidine or aniline gave rise to new ^{31}P{^{1}H} signals at 188.8 or 190.5 ppm, respectively. Finally, reactions with CO or 2,6-dimethyl(phenyl)isonitrile did not cause any color change, but produced two new ^{31}P{^{1}H} signals at 186.0 and 179.3 ppm for the reaction with CO, and at 181.0 and 178.2 ppm for the reaction with 2,6-dimethyl-(phenyl)isonitrile. ^{1}H NMR spectra of the latter reaction mixtures indicate two non-equivalent pincer moieties that are fairly similar to the spectral pattern of complex **5**. These observations are consistent with the coordination of CO or 2,6-dimethyl(phenyl)isonitrile with only one of the Ni atoms in **5** to give inequivalent phosphinite moieties.

Catalytic Hydroalkoxylation of Acrylonitrile. Catalytic hydroalkoxylation of olefins or allenes represents an atom-efficient transformation that generates products with multiple commercial uses.[18] Interestingly, hydroalkoxylation of some olefins can be promoted by different acids[19] or bases,[20] and even nucleophilic phosphines,[21] but a great variety of hydroalkoxylations are also catalyzed by salts of Al[22] and complexes of Cu,[23] Ag,[24]

(17) For comparison, the closely related monomeric complexes $\kappa^{P},\kappa^{C},\kappa^{N}$-{2-(*i*-Pr$_2$PO),6-(NR$_2CH_2$)-C$_6H_3$}NiBr display ^{31}P{^{1}H} NMR chemical shifts at δ 201.5 (NR$_2$ = morpholino), 199.2 (NR$_2$ = NMe$_2$), and 197.9 (NR$_2$ = NEt$_2$). See ref 6i.

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Table 4. Alcoholysis of Acrylonitrile Catalyzed by Complex **5**[a]

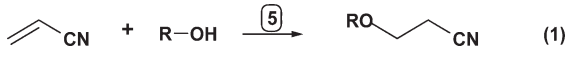
run	ROH	**5**: ACN: ROH	time (h)	yield (%)	TON
1	*m*-cresol	1: 200: 200	1	44	88
2		1: 200: 400	0.5	92	184
3		1: 200: 400	1.0	93	186
4		1: 200: 400	9.0[b]	71	142
5		1: 2000: 4000	6.0	59	1180
6		1: 2000: 4000	36	99	~2000
7	MeOH	1: 200: 200	1.0	8	16
8		1: 200: 400	1.0	16	32
9		1: 200: 2000	0.5	74	148
10		1: 200: 2000	1.0	100	200
11	EtOH	1: 200: 200	20	11	22
12		1: 200: 2000	0.5	49	98
13		1: 200: 2000	1.0	87	174
14	CF_3CH_2OH	1: 200: 2000	0.5	90	180
15		1: 200: 2000	5.5[b]	100	200
16	*n*-PrOH	1: 200: 2000	0.5	23	46
17		1: 200: 2000	1.0	43	86
18		1: 200: 2000	8	64	128
19	*i*-PrOH	1: 200: 2000	0.5	trace	
20		1: 200: 2000	24	23	46
21	BnOH	1: 200: 2000	0.5	61	122
22		1: 200: 2000	1.0	100	200
23	H_2O	1: 200: 2000	24	Trace[c]	

[a] The catalytic reactions were monitored by ^{1}H NMR, and the final mixtures analyzed by GC/MS; reaction yields were determined on the basis of calibration curves prepared using authentic samples of the anticipated products, as well as by ^{1}H NMR spectroscopy. [b] Catalysis conducted at ambient temperature. [c] The hydrolysis reaction was conducted in THF or acetone/benzene; the product found is $O(CH_2CH_2CN)_2$.

Au,[23a,25] Ru,[26] Rh,[27] Pd,[28] and Pt.[29] Metal-catalyzed hydroalkoxylation reactions involving activated olefins (Michael receptors) have been investigated more frequently, owing to the possibility of outer-sphere attack by nucleophiles on metal-bound olefins.

In this context, Yi et al. have shown that a Ru(II)-acetamido complex[26] promotes hydroalkoxylation of cyanoolefins via a novel bifunctional mechanism that involves (i) the heterolytic activation of the alcohol O−H bond by the acetamido moiety (Lewis basicity) to generate an alkoxide ion, and (ii) addition of this in situ generated alkoxide to the C=C moiety of the cyanoolefin that has become activated as a result of κ^N-nitrile binding to an empty coordination site of Ru(II) (Lewis acidity). The observation, in our studies, that alcohol O−H bonds can be activated through O···H···N interactions with the Ni centers in **5** raised the possibility that the latter might serve as a pre-catalyst for hydroalkoxylation of activated olefins according to the above-noted bifunctional mechanism. This possibility was borne out by a few initial tests: alcoholysis of acrylonitrile proceeded in the presence of catalytic amounts of **5** to give the anti-Markovnikov product (linear ether, eq 1). It is noteworthy that no such reactivity was detected with the monomeric bromo complexes **1**, **3**, and **4**. Optimization experiments have shown that catalytic efficiency of **5** requires an excess of alcohol and elevated temperatures, as described below.

^{1}H NMR and GC/MS analyses of a 1:1 mixture of acrylonitrile (ACN) and *m*-cresol in benzene (ca. 1.4 M with respect to ACN) that had been stirring in the presence of 0.5% of **5** at room temperature indicated little conversion after 5.5 h (ca. 11%), but repeating the reaction at 50 °C for 1 h led to 44% yield of the anti-Markovnikov addition product $ArOCH_2CH_2CN$ (Ar = 3-Me-Ph; Run 1, Table 4). Doubling the ACN:*m*-cresol ratio provided a 92% yield in 0.5 h (Run 2), while increasing the reaction time did not appear to have a significant beneficial effect on the yield (Run 3). It is worth noting that good yields can be obtained at ambient temperature if an excess of alcohol and longer reaction times are employed (Run 4), and significantly larger catalytic turnovers can be obtained with smaller catalyst loadings (Runs 5 and 6).



(1)

When 1 equiv of MeOH was used instead of *m*-cresol, the catalysis proceeded to about 8% yield over 1 h (Run 7), but much higher yields were obtained with higher ACN/MeOH ratios, up to quantitative yields over 1 h with a 10-fold excess of MeOH (Runs 8−10). Similar results were also obtained for the catalysis with EtOH (Runs 11−13), whereas 1,1,1-trifluoroethanol proved to be more reactive, giving 90% yield over 30 min at 50 °C (Run 14) and a quantitative yield over 5.5 h at ambient temperature (Run 15). These observations indicate that alcohol acidity has a favorable influence for the hydroalkoxylation reaction,[30] whereas comparing the catalytic results with MeOH, EtOH, *n*-PrOH, and *i*-PrOH (Runs 10, 13, 17, and 20) implies that the steric bulk of the alcohol is detrimental to its reactivity. Finally, BnOH proved very active (Runs 21 and 22), whereas water proved nearly unreactive, giving traces only of the ether arising from a double addition, $O(CH_2CH_2CN)_2$.

To our dismay, crotonitrile and methacrylonitrile reacted only very sluggishly (ca. 5%), whereas activated olefins bearing substituents other than nitrile were completely inert for the hydroalkoxylation reaction catalyzed by **5**. Benzene and toluene proved to be the most suitable solvents for the alcoholysis reaction, since the catalyst precursor is freely soluble and stable in these solvents. In contrast, little or no conversion was noted for the addition of *m*-cresol to acrylonitrile conducted in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$; solutions of **5** in these solvents undergo a color change from orange to green over minutes, signaling a decomposition. With

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acetonitrile as co-solvent with benzene,[31] the *m*-cresol reaction was found to be much less efficient, giving 23% yield after 1 h and about 60% over 24 h; in contrast, the catalysis proceeded unhindered in ethyl acetate. The observation of inhibition in acetonitrile but not in ethyl acetate, combined with the lack of reactivity observed for activated olefins bearing functionalities other than nitrile, implies that κ^N-nitrile binding of acrylonitrile might play an important role in the alcoholysis reaction, as stipulated by Yi et al.[26]

Conclusion

This work has presented a convenient protocol for synthesis of a POCN-type pincer complex of nickel bearing a secondary amine moiety, and shown that the N−H moiety in this complex opens interesting and little explored paths both for modification of the pincer ligand via *N*-alkylation and for synthesis of a dimeric pincer species such as complex **5**. N−Ni interactions in **5** stabilize the Ni centers sufficiently to allow isolation, but the dimeric species is reactive enough to activate alcohols for the hydroalkoxylation of acrylonitrile with up to 2000 catalytic turnovers. For comparison, the alcoholysis of acrylonitrile proceeds with up to 1000 TON (with aliphatic alcohols only) in the presence of the Ru(II)-acetamide system reported by Yi et al.,[26] whereas (NHC-carbene)CuX systems reported by Gunnoe et al.[23b] promote this reaction with about 20 TON with aliphatic alcohols and about 13 TON with phenol. Precursors based on Pd(II) reported by Abu-Omar et al. are inactive toward acrylonitrile, but they promote the addition of aliphatic alcohols to methyl vinyl ketone with up to 100 TON.[28b] Thus, the dimeric species **5** is highly active for the alcoholysis of acrylonitrile even with weakly nucleophilic alcohols; moreover, this complex is, to our knowledge, the first Ni complex to promote this reaction.

We note with interest that although **5** reacts with aniline and *p*-toluidine, it appears to be ineffective in promoting hydroamination of acrylonitrile with these amines; this suggests that reaction of amino alcohols with acrylonitrile might proceed selectively with the addition of the O−H bond, a possibility which will be probed in future studies. We will also investigate the feasibility of isolating monomeric 14-electron Ni-amido species from POCN-type complexes analogous to **1** bearing a sterically bulky *N*-substituent.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk and glovebox techniques under nitrogen atmosphere. All solvents used for experiments were dried to water contents of less than 10 ppm (determined using a Mettler Toledo C20 coulometric Karl Fischer titrator) by passage through activated aluminum oxide columns (MBraun SPS) and freeze−thaw degassed. C_6D_6 was dried over 4 Å molecular sieves and then freeze−thaw degassed. The following were purchased from Aldrich and, unless otherwise noted, used without further purification: Ni (metal), chlorodiisopropylphosphine, 3-hydroxybenzaldehyde, triethylamine, and all the alcohols and olefins used in the catalytic studies. A Bruker AV 400 spectrometer was used for recording ^{1}H, ^{13}C{^{1}H} (101 MHz), and ^{31}P{^{1}H} (162 MHz) and Bruker AV 300 was used to record ^{19}F NMR spectra. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of TMS and referenced against the residual C_6D_6 signals (7.15 ppm for ^{1}H and 128.02 ppm for ^{13}C); ^{31}P chemical shifts are reported in ppm and referenced against the signal for 85% H_3PO_4 (external standard, 0 ppm). Coupling constants are reported in hertz (Hz). The correlation and assignment of ^{1}H and ^{13}C NMR resonances were aided by ^{1}H COSY, HMQC, HMBC, DEPT, NOESY, and ^{1}H{^{31}P} experiments when necessary. GC/MS measurements were made on an Agilent 6890N spectrometer.

Ligand Synthesis. 3-((*N*-Benzylamino)methyl)phenol (a). To a solution of 3-hydroxybenzaldehyde (0.500 g, 4.10 mmol) in 10 mL of methanol at r.t. was added a solution of benzylamine (0.439 g, 4.10 mmol) in 10 mL of methanol. The resulting mixture was stirred for 1 h to obtain a white suspension (the Schiff base). The suspension was then cooled to −5 °C and $NaBH_4$ (0.30 g, 7.89 mmol) added portionwise over 1 h. The resulting mixture was concentrated under reduced pressure, treated with 10% HCl until pH = 1, and extracted with a 1:1 mixture of EtOAc: Et_2O (3 × 10 mL) to remove the components soluble in the organic phase. The remaining mass was then treated with concentrated aqueous ammonia solution until pH = 12 to free up the amine pre-ligand, which was extracted with a 1:1 mixture of EtOAc and Et_2O (5 × 10 mL). The organic extracts were then combined and evaporated to give a caramel-like compound which was crystallized by adding a 1:4 mixture of Et_2O/hexane and scratching the flask walls just under the solvent level. Filtration of the resulting suspension through a glass frit and drying under vacuum for 1 more hour gave an off-white powder. (0.780 g, 89%).

^{1}H NMR (δ, C_6D_6): 3.47 (s, 2H, CH_2Ph), 3.55 (s, 2H, CH_2N), 5.40 (br s, 2H, O*H*, N*H*), 6.65 (d, ^3J = 8, 1H, {Ar}H^4), 6.78 (dd, J = 8, 2, 1H, {Ar}H^6), 6.84 (s, 1H, {Ar}H^2), 7.06−6.99 (m, 2H, {Ar}H^5, {Bn}H^{para}), 7.11 (t, ^3J = 7, 2H, 2 × {Bn}H^{meta})), 7.16 (m, 2H, 2 × {Bn}H^{ortho}). ^{13}C{^{1}H} NMR (δ, C_6D_6): 52.71 (s, 1C, CH$_2$), 52.85 (s, 1C, CH$_2$), 115.39 (s, 1C, {Ar}C^6), 116.13 (s, 1C, {Ar}C^2), 120.22 (s, 1C, {Ar}C^4), 127.47 (s, 1C, {Ar}C^5), 128.71 (s, 2C, 2 × {Bn}C^{ortho}), 128.86 (s, 2C, 2 × {Bn}C^{meta}), 129.92 (s,1C, {Bn}C^{para}), 139.21 (s, 1C, {Ar}C^3), 140.69 (s, 1*C*, {Bn}C^{ipso}), 157.90 (s, 1C, {Ar}C^1).

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57; Found: C, 78.84; H, 7.24; N, 6.59.

3-((*N*-Benzylamino)methyl)phosphinitobenzene (b). To a solution of **a** (0.500 g, 2.34 mmol) and triethylamine (0.360 mL, 2.85 mmol) in THF (35 mL) stirring at 0−5 °C was added a solution of chlorodiisopropyl phosphine (0.385 mL, 2.34 mmol 96%) in THF (15 mL). The resulting mixture was allowed to warm to room temperature, stirred for an additional hour, and evaporated under reduced pressure to give an oily residue, which was extracted with Et_2O (3 × 25 mL). Evaporation of the combined extracts furnished the product as a colorless oil (0.740 g, 96%).

^{1}H NMR (δ, C_6D_6): 1.00 (dd, $^3J_{HP}$ = 16, $^3J_{HH}$ = 7, 6H, 2 × CHCH_3), 1.17 (dd, $^3J_{HP}$ = 11, $^3J_{HH}$ = 7, 6H, 2 × CHCH_3), 1.87 − 1.73 (m, 2H, 2 × PC*H*), 3.55 (s, 4H, 2 × CH_2) 6.94 (d, $^3J_{HH}$ = 8, 1H, {Ar}H^6), 7.07 − 7.13 (m, 2H, {Ar}H^5 and {Ar}H^4), 7.14 − 7.23 (m, 3H, 2 × {Bn}H^{meta} and {Bn}H^{para}, overlapping with C_6D_5H), 7.27 (d, $^3J_{HH}$ = 7, 2H, {Bn}H^{ortho}), 7.43 (s, 1H, {Ar}H^2). ^{13}C{^{1}H} NMR (δ, C_6D_6): 17.19 (d, $^2J_{CP}$ = 9, 2C, 2 × CHCH$_3$), 17.90 (d, $^2J_{CP}$ = 21, 2C, 2 × CHCH$_3$), 28.64 (d, $^1J_{CP}$ = 18, 2C, 2 × P*C*H), 53.21 (s, 1C, CH$_2$), 53.35 (s, 1C, CH$_2$), 117.26 (d, $^3J_{CP}$ = 11, 1C, {Ar}C^6), 118.60 (d, $^3J_{CP}$ = 10, 1C, {Ar}C^2), 121.70 (s, 1C, {Ar}C^4), 127.01 (s, 1C, {Ar}C^5), 128.42 (s, 2C, {Bn}C^{ortho}), 128.49 (s, 2C, {Bn}C^{meta}), 129.52 (s, 1C, {Bn}C^{para}), 141.11 (s, 1C, {Ar}C^3), 142.94 (s, 1C, {Bn}C^{ipso}), 160.08 (d, $^2J_{CP}$ = 9, 1C, {Ar}C^1). ^{31}P{^{1}H} NMR (δ, C_6D_6): 147.2 (s,P).

Anal. Calcd for $C_{20}H_{28}OPN$: C, 72.92; H, 8.57; N, 4.25; Found: C, 72.20; H, 8.57; N, 4.60.

Synthesis of Complexes 1−5. κ^P,κ^C,κ^N-{2,6-(*i*-Pr$_2$PO)-(C$_6$H$_3$)(CH$_2$NBnH)}NiBr (1). A solution of **b** (0.500 g, 1.52 mmol)

(31) Complex **3** is insoluble in pure acetonitrile.

in 20 mL of benzene was slowly added to the stirring suspension of $NiBr_2(CH_3CN)_x$ (0.503 g, 1.66 mmol) and triethylamine (0.230 mL, 1.66 mmol) in toluene (5 mL) at r. t. The resulting dark brown mixture was then heated for 3 h at 60 °C, washed with water (3 × 5 mL), and evaporated to dryness to give the crude product as an oily yellow powder (0.656 g, 93%). Chromatography through a short pad of silica gel (eluents: hexane followed by 50:50 CH_2Cl_2/Hexane) gave an analytically pure sample (0.553 g, 78%).

^{1}H NMR (δ, C_6D_6): 1.19 (dd, J_{HP} = 14, J_{HH} = 7, 3H, CHCH_3) 1.25 (dd, J_{HP} = 15, J_{HH} = 7, 3H, CHCH_3), 1.50 (dd, $J_{HP/HH}$ = 7, 3H, CHCH_3), 1.54 (dd, $J_{HP/HH}$ = 6, 3H, CHCH_3), 2.33−2.11 (m, 2H, 2 × PCH), 3.22 (br. s, 1H, NH), 3.33 (dd, $^2J_{HH}$ = 16, $^3J_{HH}$ = 6, 1H, ArCH_2N), 3.42 (dd, $^2J_{HH}$ = 16, $^3J_{HH}$ = 4, 1H, ArCH_2N), 3.83 (dd, $^2J_{HH}$ = 14, $^3J_{HH}$ = 10, 1H, {Bn}CH_2), 4.63 (d, $^2J_{HH}$ = 14, 1H, {Bn}CH_2), 6.32 (d, $^3J_{HH}$ = 7, 1H, {Ar}H^5), 6.62 (d, $^3J_{HH}$ = 8, 1H, {Ar}H^3), 6.86 (t, $^3J_{HH}$ = 8, 1H, {Ar}H^4), 7.04 (m, 3H, 2 × {Bn}H^{meta}, {Bn}H^{para}), 7.11 (d, $^3J_{HH}$ = 5, 2H, 2 × {Bn}H^{ortho}). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.61 (d, $^2J_{CP}$ = 2, 1C, CH$_3$), 17.14 (s, 1C, CH$_3$), 18.17 (d, $^2J_{CP}$ = 4, 2C, 2 × CH$_3$), 28.36 (d, $^1J_{CP}$ = 10, 2C, CH), 28.60 (d, $^1J_{CP}$ = 9, 1C, CH), 54.27 (s, 1C, CH$_2$), 57.62 (s, 1C, CH$_2$), 108.27 (d, $^3J_{CP}$ = 13, 1C, {Ar}C^3), 115.59 (s, 1C, {Ar}C^5), 127.10 (s, 1C, {Ar}C^4), 128.55 (s, 1C, {Bn}C^{para}), 128.83 (s, 2C, 2 × {Bn}C^{ortho}), 129.25 (s, 2C, 2 × {Bn}C^{meta}), 137.22 (s, 1C, {Bn}C^{ipso}), 143.46 (d, $^2J_{CP}$ = 32, 1C, {Ar}C^1Ni), 152.75 (s, 1C, {Ar}C^6), 166.16 (d, $^2J_{CP}$ = 10, 1C, {Ar}C^2). ^{31}P{^{1}H} NMR (δ, C_6D_6): 201.72 (s,1P).

Anal. Calcd for $C_{20}H_{27}OPNNiBr$: C, 51.44; H, 5.73; N, 3.00; Found: C, 51.28; H, 5.83; N, 2.90.

$\kappa^P,\kappa^C,\kappa^N$-{2-(*i*-Pr$_2$PO)(6-(CH$_2$N(Bn)(allyl)(C$_6H_3$))}NiBr (3). To a stirred solution of **1** (0.100 g, 0.216 mmol) in a dry and degassed 1:1 mixture of hexane: THF or dry and degassed toluene (5 mL) at −78 °C was added a MeLi solution in diethoxymethane (0.108 mL, 3 M, 0.323 mmol), and the resulting red mixture stirred for 30 min. Allyl bromide (0.042 mL, 0.485 mmol) was then added, and the mixture stirred for one more hour at −78 °C, and then overnight at r.t. Complex **3** was isolated by flash chromatography (SiO_2, benzene) as a yellow powder (0.071 g, 64%).

^{1}H NMR (δ, C_6D_6): 1.17 (2 × dd, $^3J_{HP}$ = 15, $^3J_{HH}$ = 7, 6H, 2 × CHCH_3), 1.48 (dd, $^3J_{HP}$ = 11, $^3J_{HH}$ = 7, 3H, CHCH_3), 1.53 (dd, $^3J_{HP}$ = 11, $^3J_{HH}$ = 7, 3H, CHCH_3), 2.24 (m, 2H, 2 × PCH), 2.87 (ddd, J_{HH} = 12, 9, J_{HP} = 4, 1H, CH_2CH), 3.65 (d, $^2J_{HH}$ = 16, 1H, ArCH_2), 3.81 (d, $^2J_{HH}$ = 16, 1H, ArCH_2), 4.03 (dd, $^2J_{HH}$ = 13, J_{HP} = 2, 1H, CH_2{Bn}), 4.33 (dd, $^2J_{HH}$ = 13, $^3J_{HH}$ = 5, 1H, CH_2CH), 4.84 (d, $^2J_{HH}$ = 13, 1H, CH_2{Bn}), 4.96 (d, $^3J_{HH}$ = 17, 1H, trans-CH_2=), 5.04 (d, $^3J_{HH}$ = 10, 1H, cis-CH_2=), 6.37 (d, $^3J_{HH}$ = 8, 1H, {Ar}H^5), 6.58 (d, $^3J_{HH}$ = 8, 1H, {Ar}H^3), 6.84 (t, $^3J_{HH}$ = 8, 1H, {Ar}H^4), 6.83−6,92 (m, 1H, CH$_2$CH), 7.13−7.02 (m, 3H, 2 × {Bn}H^{ortho}, {Bn}H^{para}), 7.58 (d, $^3J_{HH}$ = 6, 2H, {Bn}H^{meta}). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.88 (d, $^2J_{CP}$ = 22, 2C, 2 × CHCH$_3$), 18.19 (d, $^2J_{CP}$ = 4 Hz, 1C, CHCH$_3$), 18.24 (d, $^2J_{CP}$ = 4 Hz, 1C, CHCH$_3$), 28.37 (d, $^1J_{CP}$ = 25 Hz, 1C, PCH), 28.68 (d, $^1J_{CP}$ = 25 Hz, 1C, PCH), 61.07 (s, 1C, ArCH$_2$N), 61.20 (s, 1C, BnCH$_2$), 61.80 (s, 1C, Allyl$C$H$_2$), 108.16 (d, $^2J_{CP}$ = 13 Hz, 1C, {Ar}C^3), 115.41 (s, 1C, {Ar}C^5), 120.48 (s, 1C, CH$_2$=CH), 127.09 (s, 1C, {Ar}C^4), 128.25 (s, 1C, {Bn}C^{para} found by DEPT), 128.43 (s, 2C, 2 × {Bn}C^{meta}), 131.99 (s, 2C, 2 × {Bn}C^{ortho}), 133.98 (s, 1C, CH$_2$=CH), 134.03 (s, 1C, {Bn}C^{ipso}), 142.53 (d, $^2J_{CP}$ = 33 Hz, 1C, {Ar}C^1Ni), 152.21 (s, 1C, {Ar}C^6), 165.73 (d, $^2J_{CP}$ = 11 Hz, 1C, {Ar}C^2). ^{31}P{^{1}H} NMR (δ, C_6D_6): 200.64 (s, 1P).

Anal. Calcd for $C_{23}H_{31}OPNNiBr$: C, 54.48, H, 6.16; N, 2.76; Found: C, 54.70; H, 6.23; N, 2.73.

$\kappa^P,\kappa^C,\kappa^N$-{2,6-(*i*-Pr$_2$PO)(C$_6H_3$)(CH$_2NBn_2$)}NiBr (4). The procedure described above for the preparation of **3** was used to prepare this complex, which was isolated as a yellow powder (0.068 g, 57%).

^{1}H NMR (δ, C_6D_6): 1.17 (dd, $^3J_{HP}$ = 14, $^3J_{HH}$ = 7, 6H, 2 × CHCH_3), 1.54 (dd, $^3J_{HP}$ = 18, $^3J_{HH}$ = 7, 6H, 2 × CHCH_3), 2.21−2.34 (m, 2H, PCH), 3.73 (s, 2H, ArCH_2), 4.08 (dd, $^2J_{HH}$ = 13, $^2J_{HP}$ = 3, 2H, {Bn}CH_2), 5.09 (d, $^2J_{HH}$ = 13, 2H, {Bn}CH_2), 6.34 (d, $^3J_{HH}$ = 7, 1H, {Ar}H^5), 6.58 (d, $^3J_{HH}$ = 8, 1H, {Ar}H^3), 6.83 (t, $^3J_{HH}$ = 8, 1H, {Ar}H^4), 7.13−7.07 (m, 6H, 4 × {Bn}H^{metha}, 2 × {Bn}H^{para}), 7.75−7.67 (m, 4H, 4 × {Bn}H^{ortho}). ^{13}C{^{1}H} NMR (δ, C_6D_6): 16.81 (s, 2C, 2 × CHCH$_3$), 18.18 (d, $^2J_{CP}$ = 4, 2C, 2 × CHCH$_3$), 28.42 (d, $^1J_{CP}$ = 25, 2C, 2 × PCH), 58.91 (s, 1C, ArCH$_2$), 59.49 (s, 2C, 2 × BnCH$_2$), 108.26 (d, $^3J_{CP}$ = 13, 1C, {Ar}C^3), 115.94 (d, $^2J_{CP}$ = 2, 1C, {Ar}C^5), 127.15 (s, 1C, {Ar}C^4), 128.42 (s, 4C, 4 × {Bn}C^{metha}), 128.45 (s, 2C, 2 × {Bn}C^{para}), 132.04 (s, 4C, 4 × {Bn}C^{ortho}), 134.32 (s, 2C, {Bn}C^{ipso}), 142.60 (d, $^2J_{CP}$ = 34, 1C, {Ar}C^1Ni), 151.56 (s, 1C, {Ar}C^6), 165.80 (d, $^2J_{CP}$ = 10, 1C, {Ar}C^2) ^{31}P{^{1}H} NMR (δ, C_6D_6): 200.87 (s, 1P).

Anal. Calcd for $C_{27}H_{33}OPNNiBr$: C, 58.21, H, 5.97; N, 2.51; Found: C, 58.24; H, 6.03; N, 2.49.

[$\kappa^P,\kappa^C,\kappa^N$-{2,6-(*i*-Pr$_2$PO)(C$_6H_3$)(CH$_2$NBn)}Ni]$_2$ (5). To a stirred solution of **1** (0.500 g, 1.07 mmol) in dry and degassed toluene (10 mL) at −78 °C was added MeLi as a solution (0.393 mL of a 3 M solution in diethoxymethane, 1.18 mmol) or a solid (26 mg, 1.18 mmol), and the resulting red mixture was stirred for 30 min, allowed to warm to r.t., and stirred for additional 32 h at 60 °C (or stirred for 1 week at room temperature). Conversion of **1** to **5** was monitored by ^{31}P{^{1}H} NMR spectroscopy. At the end of reaction, the mixture was washed with water (10 mL × 3) and evaporated under reduced pressure to give an orange powder (0.367 g, 89%).

^{1}H NMR (δ, C_6D_6): 1.12−0.91 (m, 12H, 4 × CHCH_3), 1.23 (dd, $^3J_{HP}$ = 17, $^3J_{HH}$ = 7, 6H, 2 × CHCH_3), 1.71 (dd, $^3J_{HP}$ = 16, $^3J_{HH}$ = 7, 6H, 2 × CHCH_3), 2.13−1.86 (m, 4H, 4 × PCH), 3.58 (dd, $^2J_{HH}$ = 17, J_{HP} = 10 2H, BnCH_2), 3.97 (d, $^2J_{HH}$ = 18, 2H, ArCH_2), 4.16 (d, $^2J_{HH}$ = 18, 2H, ArCH_2), 4.55 (d, $^2J_{HH}$ = 17, 2H, BnCH_2), 6.49 (d, $^3J_{HH}$ = 7, 2H, 2 × {Ar}H^5), 6.67 (d, $^3J_{HH}$ = 8, 2H, 2 × {Ar}H^3), 6.92 (t, $^3J_{HH}$ = 8, 2H, 2 × {Ar}H^4), 7.06 (t, $^3J_{HH}$ = 7, 2H, 2 × {Bn}H^{para}), 7.17 (m, 4H, 4 × {Bn}H^{meta}, overlapping with C_6D_5H) 7.77 (d, $^3J_{HH}$ = 7, 4H, 4 × {Bn}H^{ortho}). ^{13}C{^{1}H} NMR (δ, C_6D_6): 15.08 (d, $^2J_{CP}$ = 6, 2C, 2 × CHCH$_3$), 16.60 (d, $^2J_{CP}$ = 9, 2C, 2 × CHCH$_3$), 18.57 (s, 2C, 2 × CHCH$_3$), 19.04 (s, 2C, 2 × CHCH$_3$), 28.97 (d, $^1J_{CP}$ = 24, 2C, 2 × PCH), 29.15 (d, $^1J_{CP}$ = 17, 2C, 2 × PCH,), 59.28 (s, 2C, 2 × BnCH$_2$), 72.42 (s, 2C, 2 × ArCH$_2$), 106.75 (d, $^3J_{CP}$ = 13, 2C, 2 × {Ar}C^3), 114.20 (s, 2C, 2 × {Ar}C^5), 126.09 (s, 2C, 2 × {Ar}C^6), 126.28 (s, 2C, 2 × {Bn}C^{para}), 126.94 (s, 4C, 4 × {Bn}C^{ortho}), 128.14 (s, 4C, 4 × {Bn}C^{meta}, found by DEPT), 142.51 (s, 2C, 2 × {Bn}C^{ipso}), 145.80 (d, $^2J_{CP}$ = 30, 2C, 2 × {Ar}C^1Ni), 158.31 (s, 2C, 2 × {Ar}C^6), 165.78 (d, $^2J_{CP}$ = 11, 2C, 2 × {Ar}C^2). ^{31}P{^{1}H} NMR (δ, C_6D_6): 191.6 (s, 2P).

Anal. Calcd for $C_{40}H_{52}O_2P_2N_2Ni_2$: C, 62.22, H, 6.97; N, 3.63; Found: C, 62.37; H, 6.94; N, 3.48.

General Procedure for the Reactivity Survey. An NMR tube was charged with a C_6D_6 solution of **5** (10.0 mg, 0.013 mmol, in 0.6 mL) and the desired amount of the reagent to be studied as follows: *m*-toluidine: 4.5 μL, 0.065 mmol; *m*-cresol: 10 μL of a 0.0013 M solution in C_6D_6 in the first step, followed by 9.5 μL of neat *m*-cresol, 0.091 mmol; 2,6-dimethyl(phenyl)isonitrile: 8.5 mg, 0.065 mmol; phthalimide: 9.5 mg, 0.065 mmol; CO: excess; TFE 7.5 μL, 0.104 mmol; *N*-hydroxyphthalimide: 10.6 mg, 0.065 mmol. The NMR tube was capped with a rubber septum and placed in an oil bath at 50 °C for a predetermined period of time. The progress of the reactions was monitored by NMR spectroscopy.

Typical Procedure Used for Catalytic Hydroalkoxylation of Acrylonitrile. The catalytic runs were conducted in air. The reaction vessel was charged with acrylonitrile (e.g., 0.100 g, 1.887 mmol), the alcohol (e.g., 0.810 g, 18.87 mmol of EtOH), and dodecane as the internal standard (0.046 g, 0.269 mmol). The catalyst precursor **5** was then added (1.00 mL of a 0.0094 M

solution in C_6H_6). The mixture was stirred at 50 °C for a predetermined length of time and then analyzed by GC/MS to identify the products and determine the yield using a previously prepared calibration curve. The products 3-methoxypropionitrile[32] and 3-benzyloxypropionitrile[33] are known compounds; characterization of the remaining products is given below.

3-Ethoxypropionitrile. ^{1}H NMR (δ, C_6D_6): 0.92 (t, J = 7, 3H, CH_3), 1.60 (t, J = 6, 2H, CNCH_2), 2.79 (t, J = 6, 2H, CH_2O), 2.97 (q, J = 7, 2H, OCH_2). ^{13}C{^{1}H} NMR (δ, C_6D_6): 15.02 (s, 1C, *C*H$_3$), 18.39 (s, 1C, CN*C*H$_2$), 65.00 (s, 1C, *C*H$_2$O), 66.36 (s,1C, O*C*H$_2$) 117.73 (s, 1C, *C*N).

3-(*m*-Tolyloxy)propionitrile. ^{1}H NMR (δ, C_6D_6): 1.67 (t, J = 6, 2H, CNCH$_2$CH_2), 2.08 (s, 3H, CH_3), 3.18 (t, J = 6, 2H, CH_2O), 6.44 (dd, J = 8, 2, 1H, {Ar}H^6), 6.51 (s, 1H, {Ar}H^2), 6.67 (d, J = 7, 1H, {Ar}H^4), 7.01 (t, J = 8, 1H, {Ar}H^5). ^{13}C{^{1}H} NMR (δ, C_6D_6): 18.00 (s, 1C, *C*H$_3$), 21.38 (s, 1C, CN*C*H$_2$), 62.39 (s, 1C, *C*H$_2$O), 111.73 (s, 1C, {Ar}*C*), 115.84 (s, 1C, {Ar}*C*), 117.40 (s, 1C, *C*N), 122.62 (s, 1C, {Ar}*C*), 129.53 (s, 1C, {Ar}*C*), 139.67 (s, 1C, {Ar}*C*^{3}), 158.26 (s, 1C, {Ar}*C*^{1})

3-(2,2,2-Trifluoroethoxy)propionitrile. ^{1}H NMR (δ, C_6D_6) 1.58 (t, $^3J_{HH}$ = 6, 2H, CH_2CN), 2.79 (t,$^3J_{HH}$ = 6, 2H, OCH_2), 3.10 (q, $^3J_{HF}$ = 9, 2H, CF_3CH_2). ^{13}C{^{1}H} NMR (δ, C_6D_6):18.48 (s, 1C, *C*H$_2$CN), 67.14 (s, 1C, O*C*H$_2$), 68.40 (q, J_{CF} = 34, 1C, CF_3*C*H$_2$), 117.51 (s, 1C, *C*N), 124.57 (q, J_{CF} = 279, 1C, *C*F$_3$). ^{13}F NMR (300 MHz, δ, C_6D_6) 76.0 (t, J_{HF} = 9, 3F). ^{19}F NMR (δ, C_6D_6): −75.94 (t, $^3J_{HF}$ = 9).

3-Propoxypropionitrile. ^{1}H NMR (δ, C_6D_6): 0.77 (t, J = 7, 3H, CH_3), 1.40−1.30 (m, 2H, CH_2CH$_3$), 1.63 (t, J = 6, 2H, CNCH$_2$CH_2), 2.83 (t, J = 6, 2H, CH_2CN), 2.93 (t, J = 6, 2H, OCH_2). ^{13}C{^{1}H} NMR (δ, C_6D_6): 10.62 (s, 1C, *C*H$_3$), 18.37 (s, 1C, *C*H$_2$O), 23.02 (s, 1C, *C*H$_2$CH$_3$), 65.24 (s, 1C, *C*H$_2$CN), 72.68 (s,1C, O*C*H$_2$), 117.71 (s,1C, *C*N).

Crystal Structure Determinations. Single crystals of **1** and **3**−**5** were grown by slow diffusion of hexanes into a saturated benzene solution of each complex. The crystallographic data for complexes **1**, **4**, and **5** were collected on a Bruker Microstar generator (micro source) equipped with a Helios optics, a Kappa Nonius goniometer, and a Platinum135 detector, whereas crystallographic data for complex **3** were collected on a Bruker APEX II generator (X-ray sealed tube), a Kappa Nonius goniometer, and a Platinum135 detector.

Cell refinement and data reduction were done using SAINT.[34] An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[35] The space group was confirmed by XPREP routine[36] in the program SHELXTL.[37] The structures were solved by direct-methods and refined by full-matrix least-squares and difference Fourier techniques with SHELX-97.[38] 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, except for those of the NH moiety of complexes **1**, which were positioned from residual peaks in the difference Fourier map.

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Supporting Information Available: ^{1}H NMR spectra for the reactions of **5** with *m*-cresol. This material is available free of charge via the Internet at http://pubs.acs.org. Complete details of the X-ray analyses for complexes **1**, **3**, **4**, and **5** have been deposited at The Cambridge Crystallographic Data Centre (CCDC) and can be retrieved with the following reference numbers: 699466 (**1**), 772484 (**3**), 772485 (**4**), 699467 (**5**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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