Preparation and Characterization of Nickel Complexes with η-Indenyl Ligands Bearing a Pendant Aminoalkyl Chain

Laurent F. Groux, Francine Bélanger-Gariépy, Davit Zargarian,* and Rainer Vollmerhaus†

Département de chimie, Université de Montréal, Montréal, Québec, Canada H3C 3J7

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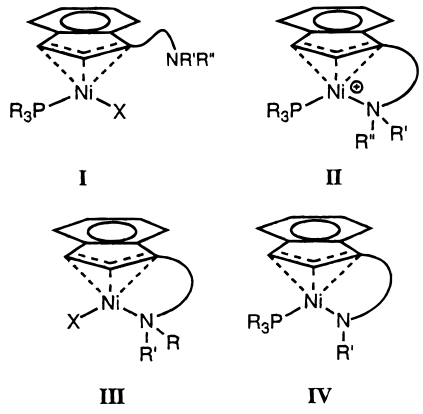
The aminoindenyl complexes {Ind$(CH_2)_{3,4}$N(*t*-Bu)H}Ni(PPh_3)Cl (**7**, **8**) and {Ind$(CH_2)_{2,3}$-NMe_2}Ni(PPh_3)Cl (**9**, **10**) have been prepared and characterized by spectroscopy and, in the case of **7** and **9**, by X-ray structural studies. Although there is no interaction between the Ni center and the amine moiety of these complexes in the solid state, solution spectra point to a temperature-dependent, intramolecular N→Ni coordination in complex **9** and a more facile, intermolecular interaction in **10**. Abstraction of Cl^- from these complexes led to the formation of the cations $[\{\eta^3{:}\eta^0$-Ind$(CH_2)_{3,4}$N(*t*-Bu)H}Ni$(PPh_3)_2]^+$ and $[\{\eta^3{:}\eta^1$-Ind$(CH_2)_{2,3}$-NMe_2}Ni$(PPh_3)]^+$ (**11**, **12**). The origin of the observed differences in the reactivities of these complexes is discussed in terms of the lengths of the tether and the nature of the N-substituents.

Introduction

There has been a growing interest over the recent years in the reactivities of complexes containing Cp-type ligands bearing amine- or amide-functionalized side chains, Cp∧NR_n (∧ = tethering side chains). A few of these compounds are excellent catalysts for the polymerization of olefins,[1] while others catalyze the dehydropolymerization of silanes[2] and show other intriguing properties.[3] A survey of the literature reveals that most of the reported studies on Cp∧NR_n systems have focused on the complexes of early transition metals (groups 3−6) and relatively few complexes of this type are known for later metals. This is especially true in the case of group 10 metals, for which only a few examples have been reported by Fischer (e.g., ($\eta^5{:}\eta^0$-Cp∧NMe_2)Ni(CO)-($SnMe_3$), ($\eta^5{:}\eta^0$-Cp∧NMe_2)Ni(PPh_3)($Si(SiMe_3)_3$), and ($\eta^5{:}\eta^1$-Cp∧NMe_2)NiI)[4] and Jutzi (e.g., ($\eta^5{:}\eta^0$-Cp∧NMe_2)-Ni(PMe_3)I, ($\eta^5{:}\eta^0$-Cp∧NMe_2)Pd(η^3-allyl), and ($\eta^5{:}\eta^0$-Cp∧NH_2)$PtMe_3$).[5]

Our interest in the structural properties and catalytic activities of the nickel indenyl complexes IndNi(PR_3)X[6] prompted us to explore the chemistry of analogous compounds bearing amino- and amidoalkyl side chains tethered to the Ind ligand. Thus, we set out to prepare the first examples of neutral and cationic Ind∧NR_2 complexes of nickel with both dangling (η^0) and coordinating (η^1) N-functionalities, as illustrated in Chart 1. The present paper reports the preparation of the complexes ($\eta^3{:}\eta^0$-Ind∧NRR′)Ni(PPh_3)X (∧ = $(CH_2)_{2-4}$; R,R′ = H, Me, *t*-Bu; X = Cl, Me, Bu) and $[(\eta^3{:}\eta^1$-Ind$(CH_2)_2NMe_2)Ni(PPh_3)]^+$.

Chart 1



Results and Discussion

Preparation of the Ligands. The syntheses of the aminoindenyl ligands **1**−**6** are outlined in Scheme 1.

† Present address: Technische Universiteit Eindhoven, Postbus 513, 5600 MB Eindhoven, The Netherlands.

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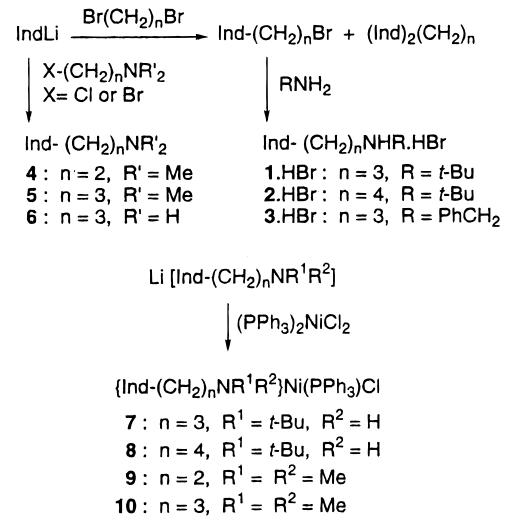
Scheme 1



The reaction of IndLi with an excess of 1,3-dibromopropane in Et_2O produced the desired (3-bromopropyl)-indene in addition to the undesired byproduct 1,3-diindenylpropane. The former was isolated in ca. 60% yield after vacuum distillation and subsequently reacted with *t*-$BuNH_2$ to give the HBr salt of $Ind(CH_2)_3N(t\text{-}Bu)H$ (**1**) as an air-stable, white powder in ca. 85% yield. Using 1,4-dibromopropane in this synthesis yields the desired aminoindenyl ligand with a butyl side chain (**2**), whereas 1,2-dibromopropane leads to a known[7] spirocyclic byproduct. Using $BzNH_2$ (Bz = $PhCH_2$) instead of *t*-$BuNH_2$ gave $Ind(CH_2)_3N(Bz)H$ (**3**). The NMe_2 and NH_2 ligands (**4**−**6**) were prepared by reacting IndLi with $X(CH_2)_n$-NR'_2 (n = 2, 3; X = Cl, Br; R′ = Me, H; Scheme 1).

Type I Complexes. The preparation of (η^3:η^0-aminoindenyl)nickel complexes was attempted by reacting $(PPh_3)_2NiCl_2$ with the singly deprotonated aminoindenes. Thus, reacting $[Ind(CH_2)_3N(t\text{-}Bu)H]^-$ with $(PPh_3)_2$-$NiCl_2$ in Et_2O gave a dark red solution from which the complex **7** could be isolated in 63% yield; similar protocols with the ligands **2**, **4**, and **5** allowed the formation of the Ni complexes **8**−**10**, respectively (Scheme 1). These compounds have been characterized by spectroscopy and, in the case of **7** and **9**, by X-ray diffraction studies (vide infra).

In contrast to the syntheses of **7**−**10**, the preparation of the analogous derivatives with the aminoindenyl ligands $Ind(CH_2)_3NHR$ (R = Bz (**3**), H (**6**)) did not result in the isolation of stable compounds. For instance, addition of an Et_2O solution of singly deprotonated **3** (i.e., $[Ind(CH_2)_3N(PhCH_2)H]^-$) to the dark green Et_2O suspension of $(PPh_3)_2NiCl_2$ resulted, at first, in the appearance of the red color characteristic of the compounds (Ind)Ni(PR_3)X; however, the reaction mixture turned brown and then beige over a few minutes and no tractable compound could be isolated in the end. Lowering the temperature of the reaction did not prevent the decomposition of this material. A similar observation was made in the reaction of ligand **6**. The ^1H NMR spectra of the reaction mixtures in both reactions showed broad, featureless signals characteristic of paramagnetic or polymeric species, while the $^{31}P\{^1H\}$ spectra contained only the signal attributed to uncoordinated PPh_3.

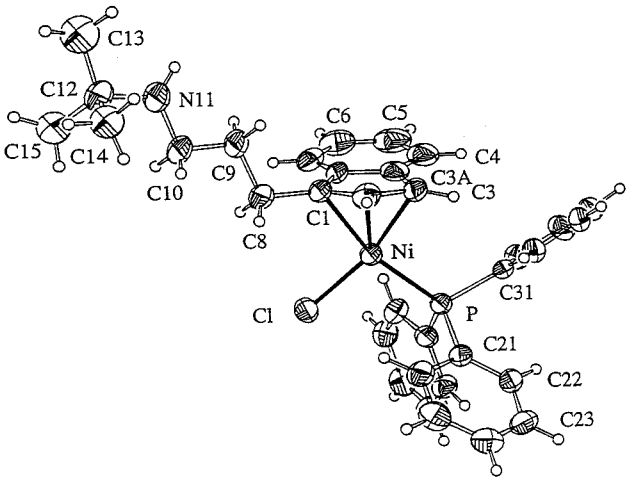


Figure 1. ORTEP plot of complex **7** with atom-numbering scheme. Selected bond lengths (Å) and angles (deg): Ni−P = 2.181(3), Ni−Cl = 2.187(2), Ni−C1 = 2.135(6), Ni−C2 = 2.057(6), Ni−C3 = 2.028(6), Ni−C3a = 2.296(7), Ni−C7a = 2.357(8), C1−C2 = 1.409(10), C2−C3 = 1.423(9), C3−C3a = 1.456(10), C3a−C7a = 1.422(9), C7a−C1 = 1.452-(9), C1−C8 = 1.497(9); Cl−Ni−P = 96.75(12), Cl−Ni−C3 = 162.4(2), Cl−Ni−C2 = 122.7(2), Cl−Ni−C1 = 95.8(2), P−Ni−C1 = 166.0(2), P−Ni−C2 = 130.6(2), P−Ni−C3 = 99.2(2), C1−Ni−C2 = 39.2(3), C1−Ni−C3 = 67.0(3), C2−Ni−C3 = 40.8(3).

It is conceivable that the complexes (η^3:η^0-$Ind(CH_2)_3$-NRH)Ni(PPh_3)Cl (R = Bz, H) form at first but decompose afterward as a result of the interaction of the amine moieties with the Ni center (either intra- or intermolecularly). To test the validity of this supposition, we reacted the otherwise stable complex (1-Me-Ind)Ni-(PPh_3)Cl with a number of amines and found that it decomposed readily upon contact with $BzNH_2$ and pyridine; BzN(Me)H also caused the decomposition of this complex, but at a slower rate, while *t*-$BuNH_2$ and Et_3N did not react at all. We conclude, therefore, that the stabilities of complexes (Ind∧NRR′)Ni(PPh_3)Cl depend on the nature of the substituents on the amine moiety: the NH(*t*-Bu) and NMe_2 groups give the relatively stable species **7**−**10**, whereas NHBz and NH_2 groups allow side reactions which eventually lead to the decomposition of the complexes.

Characterization and Dynamic Behavior of (Ind∧NRR′)Ni(PPh_3)Cl. The general features of the NMR spectra obtained for compounds **7** and **8** are similar to those of the analogous complexes (1-Me-Ind)-Ni(PPh_3)Cl. For instance, the ^1H NMR resonances for the H2 and H3 protons appear at ca. 6.5 and 3.5 ppm, respectively, while the $^{31}P\{^1H\}$ NMR spectra consist of a singlet resonance at ca. 33 ppm; these are very close to the corresponding resonances for (1-Me-Ind)Ni(PPh_3)-Cl,[6c] indicating that the geometry around the Ni atom and the hapticity of the Ind ligand in **7** and **8** are very similar to those found in (1-Me-Ind)Ni(PPh_3)Cl. The solid-state structure of **7** (Figure 1, vide infra) and variable-temperature ^1H and $^{13}C\{^1H\}$ NMR experiments showed that the N(*t*-Bu)H moiety in these complexes is not coordinated to Ni. Similarly, the X-ray structure of complex **9** (Figure 2; vide infra) showed that the NMe_2 moiety in this compound is not coordinated to the Ni

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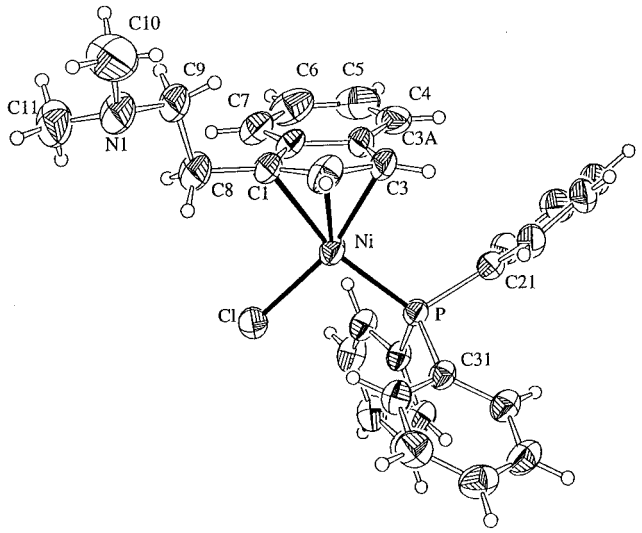
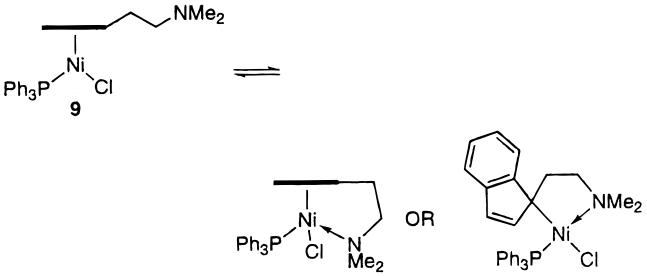


Figure 2. ORTEP plot of complex **9** with atom-numbering scheme. Selected bond lengths (Å) and angles (deg): Ni−P = 2.1838(15), Ni−Cl = 2.1763(14), Ni−C1 = 2.137(4), Ni−C2 = 2.060(4), Ni−C3 = 2.028(5), Ni−C3a = 2.283(5), Ni−C7a = 2.341(4), C1−C2 = 1.405(6), C2−C3 = 1.440(6), C3−C3a = 1.419(6), C3a−C7a = 1.424(6), C7a−C1 = 1.464(6), C1−C8 = 1.487(5); Cl−Ni−P = 98.01(6), Cl−Ni−C3 = 162.44(13), Cl−Ni−C2 = 122.61(15), Cl−Ni−C1 = 96.09-(13), P−Ni−C1 = 165.87(13), P−Ni−C2 = 130.41(14), P−Ni−C3 = 99.32(13), C1−Ni−C2 = 39.07(15), C1−Ni−C3 = 66.65(17), C2−Ni−C3 = 41.25(18).

Scheme 2



atom *in the solid state*; in this case, however, the solution spectra indicated the presence of relatively fast equilibria which convert **9** and **10** into species involving N→Ni interactions, as described below.

The first indication of a dynamic process involving complex **9** was the observation that some of the ^{1}H and $^{13}C\{^{1}H\}$ NMR signals were either broadened or missing from the ambient and higher temperature spectra (up to +50 °C) of this complex; at lower temperatures, the broad peaks sharpened and the missing peaks emerged. Significantly, the peaks corresponding to the nuclei on the side chain were the most affected during this process. In addition, the variable-temperature $^{31}P\{^{1}H\}$ NMR spectra showed that the singlet resonance for **9** moved from ca. 31 ppm at 22 °C to ca. 38 ppm at +50 °C; cooling the sample to room temperature resulted in the reappearance of the signals for **9**. These observations imply that in solution the η^3:η^0-aminoindenyl complex **9** is in equilibrium with a species in which the NMe_2 moiety reversibly coordinates to the Ni center (Scheme 2). Given that the spectral features of this new complex are very different from those of the cationic complex which would arise from the displacement of Cl by the amine moiety (vide infra), we believe that the species in question is a *neutral* compound in which the Cl ligand remains coordinated to Ni. It is not certain, however, whether the Ind moiety remains η^3-coordinated (giving an 18-electron species) or slips into an η^1-mode (giving a 16-electron species).

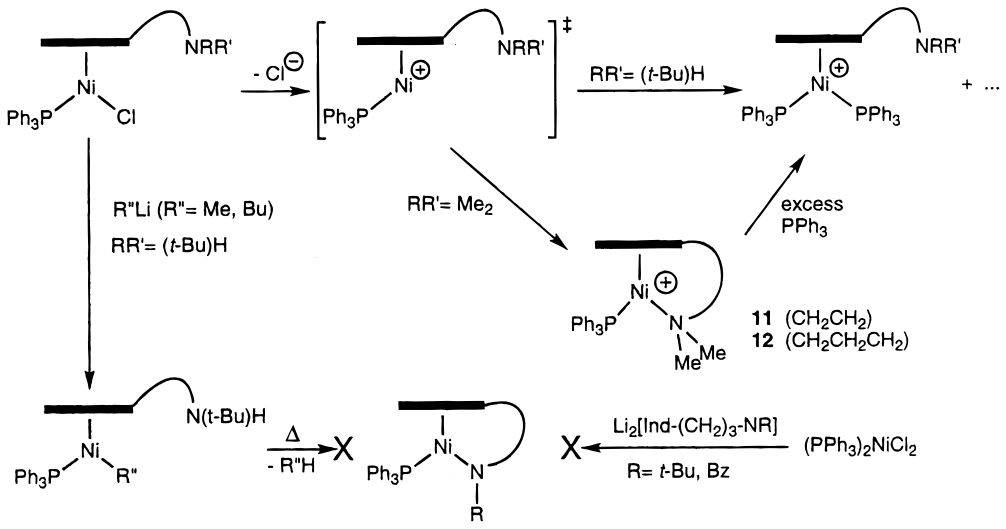
In contrast to the above-described dynamic behavior displayed by complex **9**, complex **10** was found to undergo a gradual and irreversible transformation in solution, one which ultimately prevented the purification and complete characterization of this compound. Thus, repeated recrystallizations of complex **10** precipitate solid samples which are increasingly insoluble and give poorly resolved NMR spectra. For example, whereas **9** and freshly prepared samples of **10** were soluble in Et_2O, C_6H_6, toluene, etc., the solids obtained after recrystallizing **10** were soluble only in DMSO. Moreover, whereas the ^{1}H and $^{13}\{^{1}H\}$ NMR spectra of pre-recrystallization samples of **10** contained well-resolved signals quite similar to those of complex **9**, the aged solutions and recrystallized samples of **10** showed broad, featureless peaks. We believe that this "decomposition" of complex **10** is caused by the interaction between the NMe_2 moiety and the Ni center and suggest that the longer side chain in this compound allows an *inter*molecular coordination which results in the formation of a sparingly soluble polymeric species.

Solid-State Structures of 7 and 9. As seen in Figures 1 and 2, the nickel centers in both **7** and **9** are within reasonable bonding distance from the P (ca. 2.18 Å), Cl (ca. 2.19 Å), C1 (ca. 2.14 Å), C2 (ca. 2.06 Å), and C3 (ca. 2.03 Å) atoms but considerably farther away from C3a (average 2.29 Å) and C7a (average 2.35 Å). The geometry around the Ni is irregular but may be described as distorted square planar with C1═C2 occupying a single coordination site. The planes formed by P, Ni, and Cl on one hand and C1, C2, and C3 on the other are nearly perpendicular to each other. In both structures, the aminoalkyl side chain is oriented away from the Ni center.

The main features of **7** and **9** are very similar to those present in the solid-state structure of (1-Me-Ind)Ni-(PPh_3)Cl.[6c] For instance, all three structures exhibit virtually identical (i.e., within $\pm 3\sigma$) Ni−P (2.181(3), 2.1838(15), and 2.1782(11) Å) and Ni−Cl (2.187(2), 2.1763(14), and 2.1865(10) Å) bond lengths. Moreover, in all three structures the distortion of the Ind hapticity away from an η^5 mode and toward a fairly nonsymmetric η^3 coordination is reflected in the unequal Ni−C and C−C bond lengths: Ni−C7a > Ni−C3a ≫ Ni−C1 > Ni−C2 > Ni−C3 and C1−C7a (1.452(9) Å) ≈ C3−C3a (1.456(10) Å) > C3−C2 (1.423(9) Å) > C2−C1 (1.409-(10) Å). These distortions are attributed to the tendency of the d^8 Ni center to form 16-electron complexes ($\eta^5 \rightarrow \eta^3$ slippage of Ind) and the unequal trans influences of the PPh_3 and Cl groups (unsymmetrical coordination of Ind).[6c]

Type II Complexes. We reacted the complexes **7**−**10** with $AgBF_4$, $NaBPh_4$, or $AlCl_3$ in order to abstract the Cl^- ligand from these complexes and facilitate the formation of the target η^3:η^1 cationic species. Abstraction of Cl^- from **7** resulted in the formation of a major species displaying an AB set of resonances in the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture (ca. 34 and 32 ppm, dd, $^{2}J_{P-P} = 26$ Hz); the spectrum also contained a singlet

Scheme 3



resonance at ca. 24 ppm corresponding to a minor product. The major product was readily identified as $[\{\eta^3{:}\eta^0\text{-Ind}(CH_2)_3NH(t\text{-Bu})\}Ni(PPh_3)_2]^+$ on the basis of comparison to the $^{31}P\{^1H\}$ NMR spectrum of the fully characterized[6d] compound $[(1\text{-Me-Ind})Ni(PPh_3)_2]^+$, which displays a similar AB signal. The inequivalence of the PPh_3 ligands in these compounds is consistent with the hindered rotation of the unsymmetrically substituted Ind ligands. When the Cl^- abstraction from **7** is carried out in the presence of an excess of PPh_3, only the bis(phosphine) cation is obtained, suggesting that the minor product observed in the original reaction might be the desired $[\{\eta^3{:}\eta^1\text{-Ind}(CH_2)_3NH(t\text{-Bu})\}Ni(PPh_3)]^+$. Abstraction of the Cl^- ligand from complex **8** *with or without added* PPh_3 gave only the bis-PPh_3 cation $[\{\eta^3{:}\eta^0\text{-Ind}(CH_2)_4NH(t\text{-Bu})\}Ni(PPh_3)_2]^+$. These results indicate that N→Ni coordination is fairly unfavorable in the $\eta^3{:}\eta^0$-aminoindenyl complexes bearing the N(*t*-Bu)H moiety. Consequently, the electronically and coordinatively unsaturated species $[\{\eta^3{:}\eta^0\text{-Ind}(CH_2)_nNH(t\text{-Bu})\}Ni(PPh_3)]^+$ resulting from the abstraction of Cl^- from **7** and **8** undergo a phosphine redistribution reaction to form the observed bis-PPh_3 cations (Scheme 3).

In contrast to the case for complexes **7** and **8**, Cl^- abstraction from **9** gave a new species which showed a singlet resonance at ca. 29 ppm in its $^{31}P\{^1H\}$ NMR spectrum instead of the AB pattern characteristic of the above-discussed bis-PPh_3 cations. Though we have not succeeded in our attempts to obtain suitable single crystals of this new compound for X-ray diffraction studies, the spectral and analytical data collected strongly support its formulation as $[\{\eta^3{:}\eta^1\text{-Ind}(CH_2)_2NMe_2\}Ni(PPh_3)]^+$ (**11**) (Scheme 3). Monitoring the reaction of complex **11** with a ca. 30-fold excess of PPh_3 by $^{31}P\{^1H\}$ NMR ($CDCl_3$) showed the gradual emergence of the characteristic signals for the bis(phosphine) cation (two doublets at 36.4 and 32.5 ppm, $^2J_{P-P} = 20$ Hz); the conversion was complete within 60 min. In the case of complex **10**, Cl^- abstraction also leads to a new complex which shows a singlet at 26 ppm in its $^{31}P\{^1H\}$ NMR spectrum (Scheme 3). We conclude, therefore, that the ease of formation of $\eta^3{:}\eta^1$ cationic complexes of the type **II** is strongly influenced by the coordinating ability of the amine moiety, with the NMe_2 moiety being more suitable for this purpose than N(*t*-Bu)H.

Type III and IV Complexes. All our attempts to prepare phosphine-free $\eta^3{:}\eta^1$ complexes of the type **III** have resulted in the decomposition of these materials. It appears that strong trans-influence ligands such as phosphines are needed to stabilize the coordination of the Ind moiety. We have also explored the deprotonation of the N(*t*-Bu)H moiety in complexes **7** and **8** as a route to neutral $\{\eta^3{:}\eta^1\text{-Ind}\wedge N(t\text{-Bu})\}Ni(PPh_3)$ complexes of the type **IV**. Reacting these complexes with $LiN(i\text{-Pr})_2$ led to side reactions which produced a complex mixture of intractable products. Attempts at deprotonation with BuLi at both low and high temperatures led instead to the formation of the Ni−Bu complex; analogous reactions with MeLi gave the Ni−Me analogue (Scheme 3). The identities of these compounds were established by comparing their ^1H and $^{31}P\{^1H\}$ NMR spectra to those of the analogous methyl complex $(1\text{-Me-Ind})(PPh_3)Ni\text{−}Me$.[6c] For example, the downfield shifts in the $^{31}P\{^1H\}$ NMR resonances of these compounds (ca. 33 ppm in the Ni−Cl compound vs 46−48 ppm in the Ni−Me and Ni−Bu analogues) are characteristic for Ni−C bond formation in these compounds. Additional evidence for this assignment includes the characteristically upfield ^1H NMR resonances for the Ni−CH_n protons (ca. −0.7 ppm for Ni−Me) and the downfield shift of the H3 signal (ca. 3.4 ppm for **7** and ca. 4.2 ppm for its Ni−Me derivative); the latter results from the change in the hapticity of the Ind ring brought about by the stronger trans influences of alkyl ligands compared to Cl.

The formation of these Ni−alkyl complexes raised the possibility that the target amidoindenyl complexes might be accessible via the intramolecular deprotonation of the dangling N−H bonds with the Ni−R moiety; this type of alkane elimination reaction has precedents in early-metal complexes[8] but did not take place with our Ni−Me and Ni−Bu compounds even upon extended heating (Scheme 3). We also attempted the preparation of type **IV** complexes via direct metathetic reactions between $(PPh_3)_2NiCl_2$ and the dianionic ligands $[\mathbf{1}]^{2-}$ and $[\mathbf{3}]^{2-}$. These reactions gave deep green-blue solutions whose ^1H NMR spectra consisted of broad, fea-

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tureless resonances while the $^{31}P\{^1H\}$ NMR spectra showed no signals; no tractable solids could be isolated from the reaction mixtures. These observations are reminiscent of the results from our previous studies on the preparation of the (nonchelating) amido compounds $IndNi(PPh_3)(NRR')$; these studies revealed that the Ni−NR_2 moiety in these compounds is very labile, precluding the isolation of thermally stable complexes except when the R substituents are strongly electron withdrawing.[6f]

Conclusion. New complexes of the type $\{\eta^3:\eta^0\text{-Ind}\wedge NRR'\}Ni(PPh_3)Cl$ (**7**−**10**) can be synthesized with NMe_2 and N(*t*-Bu)H moieties, but the NH_2 and N(Bz)H analogues decompose during synthesis. The N(*t*-Bu)H and NMe_2 moieties in these compounds are oriented away from the Ni atom in the solid state. The interaction of the N(*t*-Bu)H functionality with the Ni center in complexes **7** and **8** is also weak in the solution, whereas the coordination of the NMe_2 moiety to Ni in the solutions of complexes **9** and **10** can be detected. The N→Ni interaction appears to be intramolecular and reversible in the case of **9** but irreversible and intermolecular in the case of **10**. Therefore, the stability of these $\eta^3:\eta^0$-aminoindenyl compounds is modulated by the nature of the N-substituents as well as the length of the tethering chain. The cationic species $[\{\eta^3:\eta^0\text{-Ind}\wedge N(t\text{-Bu})H\}Ni(PPh_3)_2]^+$, $[\{\eta^3:\eta^1\text{-Ind}\wedge NMe_2\}Ni(PPh_3)]^+$, and $[\{\eta^3:\eta^0\text{-Ind}\wedge NMe_2\}Ni(PPh_3)_2]^+$ were prepared by abstracting the Cl^- ligand from the neutral precursors. Experiments aimed at evaluating the catalytic reactivities of the $\eta^3:\eta^0$- and $\eta^3:\eta^1$-aminoindenyl compounds are in progress.

Experimental Section

General Comments. All manipulations and experiments were performed under an inert atmosphere of nitrogen using standard Schlenk techniques and/or in an argon-filled glovebox. Dry, oxygen-free solvents were employed throughout. The elemental analyses were performed by Laboratoire d'analyse élémentaire (Université de Montréal). An AMXR400 spectrometer was used for recording the ambient-temperature ^1H (400 MHz), $^{13}C\{^1H\}$ (100.56 and 75.44 MHz), and $^{31}P\{^1H\}$ (161.92 MHz) NMR spectra; the variable-temperature NMR studies were carried out on a Varian VXR4000 spectrometer. The ligand $IndCH_2CH_2NMe_2$ (**4**) has been reported previously.[1e] The remaining (aminoalkyl)indenes were prepared either by the reaction of IndLi with the appropriate alkyl halides $X(CH_2)_nNR_2$ (n = 2, 3; X = Cl, Br; R = Me, H), which were purchased from Aldrich and used as received, or by reacting the appropriate amine with $Ind(CH_2)_nX$ (n = 3, 4; X = Br, I), as described below.

$IndH(CH_2)_3N(t\text{-Bu})H\cdot HBr$ (1·HBr). $IndH(CH_2)_3Br$ (7.04 g, 29.7 mmol) and *t*-$BuNH_2$ (ca. 15 mL) were stirred in CH_3CN (ca. 30 mL) at room temperature and then refluxed for 24 h, during which time a white precipitate appeared. The final reaction mixture was evaporated to dryness, and the resulting white solid was recrystallized from MeOH/Et_2O (2:1), yielding a white powder (8.10 g, 87%). The acid-free ligand was obtained by deprotonation with KOH or BuLi. ^1H NMR of the acid-free ligand (CD_3CN): δ 7.44 and 7.38 (d, $^3J_{H-H}$ = ca. 7.3, H4 & H7), 7.27 and 7.18 (t, $^3J_{H-H}$ = 7.2, H5 & H6), 6.24 (br s, H2), 3.31 (br s, H1), 2.60 (m, $CH_2CH_2CH_2$), 1.72 (quint, $^3J_{H-H}$ = 7.4, $CH_2CH_2CH_2$), 1.03 (s, $C(CH_3)_3$). ^1H NMR of the HBr salt ($CDCl_3$): 8.91 (br, NH_2), 7.38 and 7.31 (d, $^3J_{H-H}$ = ca. 7.7, H4 & H7), 7.28 and 7.17 (t, $^3J_{H-H}$ = ca. 6, H5 & H6), 6.30 (s, H2), 3.23 (s, H1), 3.00 (m, CH_2N), 2.6−2.4 (m, $IndCH_2CH_2$), 1.48 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR of the HBr salt ($CDCl_3$): δ 144.7 & 144.2 & 141.9 (C3a, C7a, C3), 128.5 & 126.0 & 124.6 & 123.6 (C4−7), 118.8 (C2), 57.7 (CMe_3), 41.7 (CH_2N), 37.6 (C1), 25.9 ($IndCH_2$), 24.8 ($CH_2CH_2CH_2$), 24.4 (Me). HRMS of acid-free ligand: 230.191 70 (calcd 230.190 87). Anal. Calcd for $C_{16}H_{23}N\cdot HBr$: C, 61.94; H, 7.80; N, 4.51. Found: C, 61.67; H, 7.81; N, 4.51.

$IndH(CH_2)_4N(t\text{-Bu})H\cdot HBr$ (2·HBr). The above procedure for the preparation of $IndH(CH_2)_3NH(t\text{-Bu})$ was repeated with $IndH(CH_2)_4Br$ to give a white powder (1.47 g, 28%). ^1H NMR of the HBr salt ($CDCl_3$): δ 8.88 (br, NH_2), 7.43 and 7.30 (d, $^3J_{H-H}$ = 7.3, H4 & H7), 7.24 and 7.17 (ps t, $^3J_{H-H}$ = 7.4, H5 & H6), 6.21 (s, H2), 3.32 (d, $^3J_{H-H}$ = 1.7, H1), 2.96 (br, CH_2N), 2.57 (t, $^3J_{H-H}$ = 7.3, $IndCH_2$), 2.25 (quint, $^3J_{H-H}$ = 8.1, NCH_2CH_2), 1.77 (quint, $^3J_{H-H}$ = 7.8, $IndCH_2CH_2$), 1.50 (s, *t*-Bu). $^{13}C\{^1H\}$ NMR of the HBr salt ($CDCl_3$): δ 145.0 & 144.3 & 143.2 (C3a, C7a, C3), 128.2 & 125.9 & 124.4 & 123.6 (C4−7), 118.7 (C2), 57.6 ($NCMe_3$), 41.9 (CH_2N), 37.6 (C1), 27.1 ($IndCH_2$), 26.4 & 25.9 ($CH_2CH_2CH_2N$), 25.5 (Me). Anal. Calcd for $C_{17}H_{25}N\cdot HBr$: C, 62.96; H, 8.08; N, 4.32. Found: C, 62.57; H, 8.13; N, 4.29.

$IndH(CH_2)_3N(CH_2Ph)H\cdot HCl$ (3·HCl). $IndH(CH_2)_3Cl$ (932 mg, 4.84 mmol) and NaI (725 mg, 4.84 mmol) were stirred in CH_3CN (20 mL) for 10 min at room temperature, followed by the addition of $PhCH_2NH_2$ (2.5 g, 24 mmol) and heating to reflux for 16 h. The reaction mixture containing a white precipitate was evaporated to dryness and extracted with Et_2O (ca. 50 mL) and a 10% solution of HCl (ca. 75 mL). The solid suspended between the two phases was isolated by filtration and recrystallized from MeOH/Et_2O (2:1) to yield 890 mg of a white solid. Two further recrystallizations were necessary to produce analytically pure product (766 mg, 52%). The acid-free product was obtained by deprotonation with NaOH or BuLi. ^1H NMR of acid-free ligand (C_6D_6): δ 7.3−7.0 (m), 5.92 (br t, H2), 3.55 (s, CH_2Ph), 3.02 (br d, $^3J_{H-H}$ = 2, H1), 2.45 (t, $^3J_{H-H}$ = 7.2, $CH_2CH_2CH_2$), 1.68 (quint, $^3J_{H-H}$ = 7.2, $CH_2CH_2CH_2$), 0.68 (br, NH). $^{13}C\{^1H\}$ NMR of HCl salt ($CDCl_3$): δ 143.8 & 142.3 (C3a, C7a), 128.6 & 128.1 (*o*- & *m*-C), 127.8, 127.5, 125.4, 123.9, 123.1, 118.3 (C2), 51.6 ($PhCH_2N$), 46.7 (NCH_2CH_2), 37.0 (C1), 25.5 ($IndCH_2$), 24.4 ($CH_2CH_2CH_2$). Anal. Calcd for $C_{19}H_{21}N\cdot HCl$: C, 76.11; H, 7.40; N, 4.67. Found: C, 76.03; H, 7.50; N, 4.69. The solid-state structure of the HBr salt of this ligand has been reported.[9]

$IndH(CH_2)_3NMe_2$ (5). A mixture of BuLi (6.9 mL of a 2.5 M solution) and IndH (1.74 g, 15 mmol) in Et_2O was stirred for 3 h and added dropwise to an Et_2O mixture (ca. 100 mL) of $Cl(CH_2)_3NMe_2\cdot HCl$ (1.90 g, 12 mmol) and BuLi (6.0 mL of a 2.5 M solution). The resultant mixture was stirred for 4 days at room temperature and extracted with a 10% HBr solution. The aqueous portion was neutralized (KOH) and extracted with hexane; the hexane portion was dried ($MgSO_4$) and evaporated to give 1.15 g of a pale yellow oil (47% yield). ^1H NMR (C_6D_6): δ 7.38 and 7.29 (d, $^3J_{H-H}$ = 9, H4 & H7), 7.21 and 7.11 (t, $^3J_{H-H}$ = 8, H5 & H6), 6.02 (s, H2), 3.07 (s, H1), 2.55 (t, $^3J_{H-H}$ = 8, CH_2N), 2.22 (t, $^3J_{H-H}$ = 8, $IndCH_2$), 2.14 (s, NMe_2), 2.10 (quint, $^3J_{H-H}$ = 8, CH_2CH_2N). ^1H NMR ($CDCl_3$): δ 7.48 and 7.37 (d, $^3J_{H-H}$ = 8, H4 & H7), 7.29 and 7.20 (t, $^3J_{H-H}$ = 8, H5 & H6), 6.22 (s, H2), 3.33 (s, H1), 2.58 (t, $^3J_{H-H}$ = 8, CH_2N), 2.40 (t, $^3J_{H-H}$ = 8, $IndCH_2$), 2.27 (s, NMe_2), 1.88 (quint, $^3J_{H-H}$ = 8, CH_2CH_2N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.3 & 144.4 & 144.0 (C3a, C7a, C3), 127.7 & 125.6 & 124.4 & 123.6 (C4−7), 118.8 (C2), 59.7 (CH_2N), 45.4 (NMe), 37.6 (C1), 25.9 & 25.4 ($IndCH_2CH_2$). Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.58; H, 9.63; N, 6.85.

$IndH(CH_2)_3NH_2\cdot HBr$ (6·HBr). Using the above procedure for the preparation of $IndH(CH_2)_3NMe_2$ (**5**) with $Br(CH_2)_3NH_2\cdot HBr$ gave a white solid which remained suspended between the organic and aqueous layers during the extraction step. Filtration gave the desired $IndH(CH_2)_3NH_2\cdot HBr$ (2.48 g, 88%). ^1H NMR of the acid-free ligand ($CDCl_3$): δ 7.45 and 7.36 (d, $^3J_{H-H}$ = 7.4, H4 & H7), 7.30 and 7.20 (t, $^3J_{H-H}$ = 7.3, H5 & H6), 6.22 (s, H2), 4.83 (s, NH_2), 3.33 (s, H1), 2.80 (t, $^3J_{H-H}$ =

7.0, CH_2N), 2.60 (t, $^3J_{H-H}$ = 7.0, Ind-CH_2), 1.85 (quint, $^3J_{H-H}$ = 7.3, IndCH$_2$CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.3 & 144.4 & 143.9 (C3a, C7a, C3), 127.8, 125.9, 124.4, 123.7 (C4−7), 118.8 (C2), 42.0 (*C*H$_2$NH$_2$), 37.6 (C1), 31.9 (Ind*C*H$_2$), 25.0 (CH$_2$*C*H$_2$CH$_2$). Anal. Calcd for $C_{12}H_{15}N$·HBr: C, 56.71; H, 6.34; N, 5.51. Found: C, 56.64; H, 6.40; N, 5.47.

(η^3:η^0-Ind(CH$_2$)$_3$N(*t*-Bu)H)Ni(PPh$_3$)Cl (7). The mixture of **1**·HBr (1.07 g, 3.45 mmol) and BuLi (2.76 mL of a 2.5 M solution in hexane, 6.90 mmol) in Et_2O (200 mL) was stirred for 16 h at room temperature and then transferred (dropwise over 2 h) to the stirred suspension of $(PPh_3)_2NiCl_2$ (2.93 g, 4.49 mmol) in Et_2O (50 mL). The final mixture was stirred for a further 30 min after the addition was complete and then filtered and evaporated. The solid residue was then dissolved in CH_2Cl_2 (ca. 15 mL), diluted with hexane (ca. 200 mL), and cooled to give the desired product as a dark red solid (1.27 g, 63%). ^{1}H NMR (C_6D_6): δ 7.64 and 6.97 (m, PPh$_3$), 7.24 (d, $^3J_{H-H}$ = 7.7, H7), 7.10 (t, $^3J_{H-H}$ = 7.4, H6), 6.84 (t, $^3J_{H-H}$ = 7.4, H5), 6.54 (s, H2), 6.18 (d, $^3J_{H-H}$ = 7.7, H4), 3.47 (s, H3), 2.70 and 2.35−2.13 (br m, IndCH_2CH_2CH_2) 1.10 (s, *t*-Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 134.2 (d, $^2J_{P-C}$ = 11.4, *o*-C), 134.0 (C3a/C7a), 132.0 (d, J_{P-C} = 43.9, *i*-C), 130.2 (*p*-C), 128.1 (d, $^3J_{P-C}$ = 10.1, *m*-C), 125.6 & 126.1 (C5 & C6), 118.2 & 116.7 (C4 & C7), 105.9 (C1), 102.1 (s, C2), 69.3 (s, C3), 53.3 (N*C*Me$_3$), 42.6 (*C*H$_2$N), 28.9 (Me), 28.5 (Ind*C*H$_2$), 23.2 (s, CH$_2$*C*H$_2$CH$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 33.6. The missing signal for C3a/C7a is presumably obscured by the other aromatic signals. Anal. Calcd for $C_{34}H_{37}$-ClNNiP·CH_2Cl_2: C, 62.77; H, 5.87; N, 2.09. Found: C, 62.84; H, 5.44; N, 1.62.

(η^3:η^0-Ind(CH$_2$)$_4$N(*t*-Bu)H)Ni(PPh$_3$)Cl (8). The above procedure for **7** was repeated using **2**·HBr to yield 419 mg of the crude product (46%). ^{1}H NMR (C_6D_6): δ 7.62 and 6.98 (m, PPh$_3$ and H6), 7.22 (d, $^3J_{H-H}$ = ca. 7, H7), 6.85 (t, $^3J_{H-H}$ = ca. 7, H5), 6.37 (s, H2), 6.12 (d, $^3J_{H-H}$ = 7.2, H4), 3.58 (s, H3), 2.54 (br, CH_2N), 2.43 & 2.19 (br, IndCH_2), 1.96 & 1.86 (br, IndCH$_2$CH_2), 1.62 (br, IndCH$_2$CH$_2$CH_2), 1.05 (s, *t*-Bu), 0.41 (br, N*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 134.7 (d, $^2J_{P-C}$ = 10.8, *o*-C), 133.0?? (C3a/C7a), 133.0 (d, J_{P-C} = 43.8, *i*-C), 130.2 (*p*-C), 128.1 (d, $^3J_{P-C}$ = 10.1, *m*-C), 126.6 & 126.1 (s, C5 & C6), 119.0 & 116.9 (s, C4 & C7), 106.8 (s, C1), 102.4 (s, C2), 69.5 (s, C3), 50.0 (N*C*Me$_3$), 42.6 (*C*H$_2$N), 29.3 (Me), 27.5 (Ind*C*H$_2$), 25.2 & 23.0 (s, IndCH$_2$*C*H$_2$*C*H$_2$). The signal for *m*-C of PPh$_3$ is obscured by the solvent peak at 128 ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 33.5 (s). Anal. Calcd for $C_{35}H_{39}$ClNNiP: C, 70.20; H, 6.56; N, 2.34. Found: C, 70.02; H, 6.78; N, 2.22.

(η^3:η^0-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)Cl (9). An Et_2O solution (200 mL) containing **4** (500 mg, 2.67 mmol) and BuLi (1.08 mL of a 2.5 M solution in hexane) was stirred for 30 min and then transferred (dropwise over 4 h) to a stirred slurry of $(PPh_3)_2NiCl_2$ (2.62 g, 4.0 mmol) in Et_2O (20 mL). Evaporation of the resulting red mixture gave a reddish solid which was extracted with hexane (3 × 50 mL), concentrated, and cooled. Filtration of the cold mixture gave a first crop of the desired product (ca. 800 mg of a reddish solid) which was found to contain some PPh_3 and Ph_3P═O. Addition of hexane to the filtrate and cooling gave ca. 300 mg of a red solid. Microcrystals suitable for X-ray analysis were obtained by repeated recrystallization of the combined solids in Et_2O/hexane and cyclohexane/hexane. ^{1}H NMR (C_6D_6): δ 7.63 and 6.99 (m, PPh$_3$), 7.22 (d, $^3J_{H-H}$ = 7.3, H7), 7.10 (t, $^3J_{H-H}$ = 7.4, H6), 6.84 (t, $^3J_{H-H}$ = 7.4, H5), 6.70 (s, H2), 6.11 (d, $^3J_{H-H}$ = 7.3, H4), 3.42 (s, H3), 2.89 and 2.74 (br, CH_2N), 2.40 and 2.16 (br, IndCH_2), 2.23 (br, NMe$_2$). ^{13}C{^{1}H} NMR (toluene-d_8, 208 K): δ 134.4 (d, $^2J_{P-C}$ = 11.5, *o*-C), 132.2 (d, J_{P-C} = 43.2, *i*-C), 130.3 (*p*-C), 126.4 & 126.1 (C5 & C6), 118.3 & 116.4 (C4 & C7), 105.3 (d, $^2J_{P-C}$ = ca. 10, C1), 103.7 (C2), 66.9 (C3), 56.8 (*C*H$_2$N), 45.6 (Ni−Me), 24.6 (Ind*C*H$_2$); the signals corresponding to *m*-C of PPh$_3$ and C3a and C7a of the Ind are obscured by the solvent resonances. ^{31}P{^{1}H} NMR (C_6D_6): δ 30.8 (s). Anal. Calcd for $C_{31}H_{31}$ClNNiP: C, 68.61; H, 5.76; N, 2.58. Found: C, 68.01; H, 5.72; N, 2.40.

(η^3:η^0-Ind(CH$_2$)$_3$NMe$_2$)Ni(PPh$_3$)Cl (10). An Et_2O solution (70 mL) containing **5** (802 mg, 3.98 mmol) and BuLi (1.60 mL of a 2.5 M solution in hexane) was stirred for 16 h and then transferred (dropwise over 3 h) to a stirred slurry of $(PPh_3)_2$-$NiCl_2$ (3.90 g, 6.0 mmol) in Et_2O (30 mL). Filtration of the resulting wine red mixture followed by evaporation gave the desired product as a red solid (1.90 g, ca. 85% crude yield) which also contained some PPh_3 and Ph_3P═O. Repeated recrystallizations with CH_2Cl_2/hexane failed to yield analytically pure samples because of the formation of what appears to be a polymeric material (see Results and Discussion). ^{1}H NMR of crude solid (DMSO-d_6): δ 7.7−7.2 (m, aromatic protons of PPh$_3$ and Ind), 7.06 (s), 6.92 (t, J = 6.0), 6.74 (d, J = 7.2), 4.13 (s), 2.33 and 2.19 (s, NMe$_2$), 1.9−1.4 (m, CH_2CH_2CH_2). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 30.9 (s).

Reaction of Li[IndCH$_2$CH$_2$NHCH$_2$Ph] with (PPh$_3$)$_2$-NiCl$_2$. Slow addition of an Et_2O solution (30 mL) of Li[**3**] (152 mg, 0.57 mmol) to the stirred slurry of $(PPh_3)_2NiCl_2$ (373 mg, 0.57 mmol) in Et_2O (30 mL) led to the formation of a reddish color characteristic of the complexes IndNi(PPh$_3$)Cl. The red color turned brown over a few minutes, and a brown powder precipitated. Both the filtrate and the solid were analyzed by NMR spectroscopy: the ^{31}P{^{1}H} spectra showed no peaks except for free PPh$_3$, and the ^{1}H spectra contained very broad, featureless peaks. Repeating the reaction at −50 °C did not yield a tractable product.

Reaction of Li[Ind(CH$_2$)$_3$NH$_2$] with (PPh$_3$)$_2$NiCl$_2$. Stirring an Et_2O (100 mL) mixture containing **6**·HBr (500 mg, 1.97 mmol) and BuLi (1.57 mL of a 2.5 M solution in hexane) for 1 h, followed by slow addition to the stirred slurry of $(PPh_3)_2$-$NiCl_2$ (1.93 g, 2.95 mmol) in Et_2O (30 mL) led to the formation of a dark red color. Filtration and evaporation of the solvent gave a dark solid (1.05 g) which was analyzed by NMR spectroscopy: the ^{31}P{^{1}H} NMR spectrum contained a signal attributable to free PPh$_3$, while the ^{1}H NMR spectrum contained only broad, featureless peaks.

Reaction of Li$_2$[IndCH$_2$CH$_2$NCH$_2$Ph] with (PPh$_3$)$_2$NiCl$_2$. The mixture of **3**·HCl (250 mg, 0.83 mmol) and 3 equiv of BuLi (1.0 mL of a 2.5 M solution in hexane) was stirred in Et_2O (30 mL) for 16 h and added dropwise to the suspension of $(PPh_3)_2$-$NiCl_2$ (818 mg, 1.25 mmol) in Et_2O (30 mL). The resulting red-brown mixture was filtered to remove the residual solids, evaporated, and analyzed by NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum showed only a peak corresponding to free PPh$_3$, while the ^{1}H NMR spectrum contained broad, featureless peaks.

[(η^3:η^1-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)]$^+$ (11). To a CH_2Cl_2 solution (ca. 30 mL) of complex **9** (110 mg, 0.20 mmol) at room temperature was added $NaBPh_4$ (478 mg, 1.40 mmo), and the mixture was stirred for 1 h. Filtration of the mixture followed by washing with CH_2Cl_2 allowed the removal of the excess $NaBPh_4$ (solid); evaporation of the filtrate gave a reddish solid (ca. 100 mg, 60%). ^{1}H NMR ($CDCl_3$): δ 7.7−7.1 (m, aromatic signals of PPh$_3$, [BPh$_4$]$^-$, and H5, H6, and H7 of Ind), 6.78 (s, H2), 5.54 (d, $^3J_{H-H}$ = 7.8, H4), 3.94 (s, H3), 2.62 (m, IndCH_2), 1.73 (m, CH_2NMe$_2$), 1.67 (s, N*Me*), 1.30 (s, N*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.5 (4-line multiplet, J_{B-C} = 50, *i*-C of BPh$_4$), 136.9 (*m*-C of BPh$_4$), 134.1 (d, $^2J_{P-C}$ = 11.9, *o*-C of PPh$_3$), 132.2 (*p*-C of PPh$_3$), 129.9 (d, $^2J_{P-C}$ = 9.9, *m*-C of PPh$_3$), 131.1 & 125.5 (C3a/C7a), 129.0 & 128.4 (C5/C6), 126.3 (*o*-C of BPh$_4$), 122.5 (*p*-C of BPh$_4$), 119.0 & 118.7 (C4/C7), 109.8 (d, $^3J_{P-C}$ = 11.8, C1), 108.2 (C2), 76.3 (*C*H$_2$N), 70.2 (C3), 51.5 (NMe), 24.3 (Ind*C*H$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 29.1 (s). Anal. Calcd for $C_{55}H_{51}$BNNiP: C, 79.93; H, 6.22; N, 1.69. Found: C, 79.64; H, 6.54; N, 1.56.

[(η^3:η^1-Ind(CH$_2$)$_3$NMe$_2$)Ni(PPh$_3$)]$^+$ (12). To a CH_2Cl_2 solution (ca. 30 mL) of complex **10** (112 mg, 0.20 mmol) at room temperature was added $NaBPh_4$ (342 mg, 1.00 mmol), and the mixture was stirred for 1 h. Filtration of the mixture followed by washings with CH_2Cl_2 allowed the removal of the excess

Table 1. X-ray Crystallographic Data for 7 and 9

	7	**9**
formula	$C_{34}H_{37}NiPNCl{\cdot}CH_2Cl_2$	$C_{31}H_{31}NiPNCl$
mol wt	669.73	542.72
cryst color	orange-red	dark red
cryst habit	thin plate	block
cryst dimens, mm	0.43 × 0.15 × 0.07	0.29 × 0.11 × 0.07
cell setting	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.910(3)	9.215(2)
b, Å	10.383(12)	10.228(4)
c, Å	19.556(9)	16.250(6)
α, deg	90.24(6)	76.60(3)
β, deg	92.10(3)	87.94(2)
γ, deg	115.72(4)	65.43(2)
V, Å^3	1680(2)	1351.8(8)
Z	2	2
D(calcd), g cm^{-3}	1.3324	1.3333
λ(Cu Kα), cm^{-1}	1.540 56	1.540 56
temp, K	293(2)	293(2)
diffractometer	Nonius CAD-4	Nonius CAD-4
$2\theta_{max}$, deg	140.0	140.0
data collecn method	*ω*/2*θ* scan	*ω*/2*θ* scan
no. of rflns used ($I > 2\sigma(I)$)	6366	5137
R, R_w	0.0820, 0.2346	0.0509, 0.1007

$NaBPh_4$ (solid); evaporation of the filtrate gave a reddish solid (ca. 110 mg, 65%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.9 (s).

X-ray Diffraction Studies of 7 and 9. Orange-red crystals of **7** were grown from CH_2Cl_2/hexane at −20 °C; complex **7** cocrystallizes with one molecule of CH_2Cl_2 in each unit cell. Dark red crystals of **9** were grown from Et_2O/hexane at room temperature. Crystallographic data for **7** and **9** are collected in Table 1. The structures were solved by direct methods using SHELXS96 and difmap synthesis using SHELXL96; refinements were done on F^2 by full-matrix least squares. The disorder observed in the positions of the solvent molecule and the *t*-Bu group in **7** is responsible for the relatively high *R* value of 8.2%. The occupancy factors for these groups were refined and in the last cycle fixed at 60% (for C12, C13, C14, and C15 of the *t*-Bu group and C50, Cl51, and Cl52 of CH_2Cl_2) and 40% (for C16, C17, C18, and C19 of the *t*-Bu group and C60, Cl61, and Cl62 of CH_2Cl_2) over the two observed positions. The atoms C12 and C16 are 0.088 Å apart; their thermal parameters were kept identical and the carbon atoms C13−C15 and C17−C19 as well as all the solvent atoms were refined isotropically. No hydrogen bonding was found between N−H and Cl atoms in **7**. The CH_2NMe_2 moiety in **9** is also disordered over two positions, but this does not have a significant impact over the overall quality of the data obtained for this structure. The ORTEP diagrams are shown in Figures 1 and 2, along with selected bond distances and angles. Complete crystallographic data for both structures are included in the Supporting Information.

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Supporting Information Available: Complete details on the X-ray analyses of **7** and **9**, including tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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