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Indenylnickel Imidato Complexes: Synthesis, Characterization, and Reactivities

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The complex (1-Me-indenyl)Ni(PPh$_3$)(phthalimidate) has been prepared and fully characterized by IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and single-crystal X-ray diffraction. The analogous 4,5-dichlorophthalimidato, maleimidato, and succinimidato complexes have also been prepared and characterized spectroscopically. These complexes are thermally stable, in contrast to the analogous Ni−amido species, which could not be prepared. Reactivity studies have shown that the Ni−imidato bond is fairly unreactive in insertion and nucleophilic reactions, and VT ^{1}H NMR studies suggest that the rotation around the Ni−N bond in the maleimidato complex is hindered by ca. 11 kcal/mol. The solid-state structure of the phthalimidato derivative showed that the P, N, C1, and C3 atoms are arranged around the Ni atom in a distorted-square-planar coordination environment, while the C2 atom is within bonding distance above the main square plane. The phthalimidato ligand is η^1(N)-coordinated to Ni; the Ni−N bond is relatively short (1.895(4) Å), and the orientation of the imidato ligand is such that the planes bearing the atoms P, Ni, N and C9, N, C16 are rotated by ca. 76° with respect to each other. The hapticity of the indenyl ligand is characterized by an allyl-ene distortion ($\eta^5 \leftrightarrow \eta^3$) and a partial localization of bonding inside the indenyl ring ($\eta^3 \leftrightarrow \eta^1,\eta^2$). ^{1}H and ^{13}C{^{1}H} NMR spectra indicate that the nonsymmetrical coordination of the indenyl ligand, which can be attributed to the different trans influences of the phthalimidato and PPh$_3$ ligands, is maintained in the solution. The character of the Ni−imidato bond has been discussed in terms of electrostatic-covalent and π-bonding interactions.

Introduction

Recent reports by Caulton and others[1] have shown that the stabilities and reactivities of electronically unsaturated L$_n$MX complexes (X = halides, OR, SR, NR$_2$) may be influenced significantly by X→M π-donations. For example, the 16-electron complexes Cp*Ru(PR$_3$)X (X = halide, OR′, NHR′) are "operationally unsaturated" species which seem to derive further stabilization from X→M π-interactions.[2] In the case of d^8 square-planar complexes, however, such π-interactions are considered *destabilizing*[3] and the M−X bond should be stronger when the X→M π-interactions are minimized.

We became interested in the role played by X→M π-interactions during our studies on the structures and reactivities of the indenylnickel complexes [(1-R′-Ind)Ni(PPh$_3$)(X)]$^{n+}$ (Ind = indenyl; R′ = H and Me, X = Cl and Me, with $n = 0$;[4] X = PPh$_3$, PMe$_3$, and MeCN with $n = 1$[5]), including their catalytic activities in the dehydropolymerization of PhSiH$_3$.[6] Some of our initial results indicated that the equilibrium stabilities of (Ind)Ni(PPh$_3$)(halides) follows the order I > Br > Cl, while the Ni−F derivative could not be prepared.[7] Since the more efficient π-donors (i.e., F and Cl) appeared to form the more labile Ni−X bonds, we inferred that these compounds might involve destabilizing halide→Ni π-interactions. To investigate further the presence of π-interactions in the Ni−X bonds of this family of compounds, we set out to prepare the analogous Ni−NR$_2$ derivatives and study the stability/lability of the Ni−N bond as a function of the N substituents. In general, the NR$_2$ ligands are more suitable for probing the degree of X→M π-donation because the presence of substituents on these ligands serves as a means for both modulating and measuring the extent of π-interaction (e.g., by determining the degree of planarity around N and the ease of rotation around the M−N bond). The present paper reports the preparation of Ni−imidato derivatives and discusses the apparent lability of the analogous Ni−amido complexes.

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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'analyze élémentaire (Université de Montréal). Unless otherwise stated, the ^{1}H (400 MHz), ^{13}C{^{1}H} (100.56 and 75.44 MHz), and ^{31}P{^{1}H} (161.92 MHz) NMR spectra were recorded at ambient temperature; the IR spectra were recorded as KBr pellets. The Ni–Cl precursors IndNi(PPh$_3$)Cl (**1**) and (1-Me-Ind)Ni(PPh$_3$)Cl (**2**) were prepared as described elsewhere.[4a,b]

(1-Me-Ind)Ni(PPh$_3$)(phthalimidate) (**3**). **Method A.** A mixture of **2** (130 mg, 0.268 mmol), phthalimide (53 mg, 0.363 mmol), and NEt$_3$ (150 μL) in CH$_2$Cl$_2$ (20 mL) was stirred for 2 h at 45 °C. The resultant mixture was evaporated and the residue stirred in Et$_2$O and deoxygenated H$_2$O; separation of the organic layer followed by drying over MgSO$_4$ (under N$_2$), filtration, concentration, and layering with hexanes precipitated the product, which was filtered and dried (40 mg, 25%).

Method B. A stirred THF (20 mL) suspension of potassium phthalimide (433 mg, 2.34 mmol) was added dropwise to the stirred dark red solution of **2** (269 mg, 0.554 mmol) in THF (25 mL). The resultant dark red mixture was stirred for 2 h at 40 °C and filtered, and the filtrate was evaporated to dryness. The residual solid from the evaporation was stirred for 30 min in 25 mL of Et$_2$O and the solution filtered; the filtrate was layered with 50 mL of hexanes and cooled to −10 °C to yield dark red crystals. Concentration of the mother liquor to half the volume and cooling gave second and third crops for a total yield of 168 mg (51%). IR (KBr, cm^{-1}): 3060 (w), 1654 (s), 1631 (sh), 1605 (sh), 1475 (m), 1480 (m), 1372 (m), 1124 (m), 725 (m). ^{1}H NMR (C$_6$D$_6$): δ 7.62, 7.42, 6.99 (m, aromatic protons of PPh$_3$ and indenyl), 6.85 and 6.83 (d, $^3J_{H-H}$ = 3 Hz, H11–14), 6.76 (d, $^3J_{H-H}$ = 2.9, H2), 5.70 (d, $^3J_{H-H}$ = 6.6, H4), 3.88 (s, H3), 1.50 (d, $^3J_{H-H}$ = 3.9, CH$_3$). ^{1}H NMR (CD$_3$CN): δ 7.42 and 7.30 (m, aromatic protons of PPh$_3$), 7.20 (b, H11–14), 7.09 (t, $^3J_{H-H}$ = 7 Hz, H6), 6.97 (d, $^3J_{H-H}$ = 6.9, H7), 6.92 (d, $^3J_{H-H}$ = 2.6, H2), 6.83 (t, $^3J_{H-H}$ = 7.0, H5), 5.72 (d, $^3J_{H-H}$ = 6.9, H4), 4.18 (s, H3), 1.41 (d, $^4J_{P-H}$ = 4.8, CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): 35.5 (s). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 36.51 (s). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 34.9 (s). ^{13}C{^{1}H} NMR (75.345 MHz, CDCl$_3$): δ 180.0 (s, C9 and C16), 137.4 (s, C10 and C15), 133.6 (d, $^2J_{P-C}$ = 11.7 Hz, *o*-C of PPh$_3$), 130.9 (d, $^1J_{P-C}$ = 11.7, *i*-C of PPh$_3$), 130.3 (s, C12 and C13), 129.6 (d, $^4J_{P-C}$ = 2.3, *p*-C of PPh$_3$), 128.0 (d, $^3J_{P-C}$ = 10.3, *m*-C of PPh$_3$), 126.4 and 126.3 (s, C4 and C7), 126.2 (s, C3a or C7a), 119.6 (s, C11 and C14), 118.2 and 117.8 (s, C5 and C6), 104.6 (s, C2), 102.3 (d, $^2J_{P-C}$ = 12.4, C1), 62.6 (s, C3), 12.2 (s, C8); the second signal for C3a/C7a was not located. Anal. Calcd: C, 72.51; H, 4.73; N, 2.35. Found: C, 72.21; H, 4.80; N, 2.49.

(1-Me-Ind)Ni(PPh$_3$)(4,5-dichlorophthalimidate) (**4**). To the stirred solution of **2** (300 mg, 0.620 mmol) in Et$_2$O (30 mL) and THF (10 mL) was added a solution of deoxygenated H$_2$O (10 mL) containing KOH (383 mg, 6.82 mmol) and 4,5-dichlorophthalimide (720 mg, 3.33 mmol), and this mixture was stirred for 6 h at room temperature. Separation of the organic phase followed by drying over MgSO$_4$ (under N$_2$), filtration, concentration, and layering with hexanes precipitated the product, which was filtered and dried (206 mg, 50% crude). This was shown to be essentially pure **4** by ^{1}H NMR, but small amounts of PPh$_3$ and Ph$_3$P=O were also present and could not be eliminated completely even after three recrystallizations. IR (KBr, cm^{-1}): 3052 (w), 1729 (m), 1655 (s), 1601 (m), 1430 (m), 1338 (s), 1161 (m), 1094 (m), 748 (s). ^{1}H NMR (CDCl$_3$, 223 K): δ 7.52, 7.26 (m, PPh$_3$), 7.57 (b, H7), 7.17 (t, J = 8 Hz, H6), 7.14 (s, H$_a$), 7.01 (d, J = 8, H5), 6.90 (b, H2), 6.85 (t, J = 8, H5), 5.40 (d, J = 8, H4), 4.14 (b, H3), 1.45 (d, J = 5, Me). ^{1}H NMR (CD$_3$CN): δ 7.30 (m, PPh$_3$), 7.10 (t, J = 7.6 Hz, H6), 6.99 (d, J = 7.6, H7), 6.90 (d, J = 2.6, H2), 6.86 (t, J = 7.2, H5), 5.74 (d, J = 7.0, H4), 4.22 (br, H3), 1.40 (d, $^4J_{P-H}$ = 4.9, Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 35.0 (s). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 36.8. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 177.8 (s, C9 and C16), 136.6 and 134.9 (s, C10, C11, C14, and C15), 133.6 (d, $^2J_{P-C}$ = 11.1 Hz, *o*-C of PPh$_3$), 130.9 (d, $^1J_{P-C}$ = 43.7, *i*-C of PPh$_3$), 129.9 (d, $^4J_{P-C}$ = 2.1, *p*-C of PPh$_3$), 128.2 (d, $^3J_{P-C}$ = 9.7, *m*-C of PPh$_3$), 126.6 and 126,7 (s, C6 and C7), 121.9 (s, C11 and C14), 118.2 and 118.1 (s, C4 and C5), 104.6 (s, C2), 102.6 (d, $^2J_{P-C}$ = 11.8, C1), 63.0 (s, C3), 12.2 (s, C8); the signals for C3a and C7a were not located.

(1-Me-Ind)Ni(PPh$_3$)(maleimidate) (**5**). The procedure outlined above for **4** was used to give a first crop of **5** (182 mg, 54%), which was shown to be essentially pure by ^{1}H NMR, with small amounts of PPh$_3$ and Ph$_3$P=O also present. Repeated recrystallizations of a small portion gave an analytically pure sample. IR (KBr, cm^{-1}): 3056 (m), 1717 (sh), 1646 (s), 1598 (s), 1436 (m), 1347 (m), 1182 (m), 1120 (m), 695 (s). ^{1}H NMR (C$_6$D$_6$): δ 7.60, 6.99 (m, aromatic protons of PPh$_3$ and indenyl), 6.83 (d, $^3J_{H-H}$ = 3 Hz, H5 or H6), 6.71 (d, $^3J_{H-H}$ = 2.9, H2), 6.00 (s, H10 and H11), 5.68 (d, $^3J_{H-H}$ = 6.6, H4), 3.79 (s, H3), 1.48 (d, $^3J_{H-H}$ = 3.9, CH$_3$). ^{1}H NMR (CD$_3$CN): δ 7.36 (m, aromatic protons of PPh$_3$ and indenyl), 7.07 (t, $^3J_{H-H}$ = 7.4 Hz, H6), 6.80 (t, $^3J_{H-H}$ = 7.4, H5), 6.87 (d, $^3J_{H-H}$ = 2.6, H2), 6.96 (d, $^3J_{H-H}$ = 7.0, H7), 6.09 (s, H10 and H11), 5.67 (d, $^3J_{H-H}$ = 7.1, H4), 4.08 (br, H3), 1.39 (d, $^4J_{P-H}$ = 5.4, Me). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 35.5 (s). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 36.4 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 183.4 (C9 and C12), 136.8 (C10 and C11), 133.8 (d, $^2J_{P-C}$ = 11.1 Hz, *o*-C of PPh$_3$), 131.1 (d, $^1J_{P-C}$ = 43.7, *i*-C of PPh$_3$), 129.9 (d, $^4J_{P-C}$ = 2, *p*-C of PPh$_3$), 128.3 (d, $^3J_{P-C}$ = 9.7, *m*-C of PPh$_3$), 128.1 and 126.3 (C3a and C7a), 126.5, 126.4, 118.2, 117.9 (H4, H5, H6, H7), 104.4 (s, C2), 102.7 (d, $^2J_{P-C}$ = 11.8, C1), 62.5 (s, C3), 12.2 (C8). Anal. Calcd: C, 70.45; H, 4.81;, N, 2.57. Found: C, 70.01; H, 4.85;, N, 2.63.

(1-Me-Ind)Ni(PPh$_3$)(succinimidate) (**6**). To the stirred solution of **2** (350 mg, 0.720 mmol) in Et$_2$O (40 mL) and THF (5 mL) was added a solution of deoxygenated H$_2$O (20 mL) containing KOH (77 mg, 1.37 mmol) and succinimide (143 mg, 1,44 mmol), and this mixture was stirred for 2 h at room temperature. Separation of the organic phase followed by drying over MgSO$_4$ (under N$_2$), filtration, and evaporation to dryness gave the solid product, which was crystallized from hexane/CH$_2$Cl$_2$ to yield a red solid (120 mg, 30% crude). This was shown to be essentially pure **6** by ^{1}H NMR, but small amounts of PPh$_3$ and Ph$_3$P=O were also present and could not be eliminated completely after repeated recrystallizations. IR (KBr, cm^{-1}): 3047 (br, w), 1637 (s), 1601 (s), 1472 (m), 1437 (s), 1350 (s), 1277 (m), 1232 (s), 1095 (m), 758 (s). ^{1}H NMR (CDCl$_3$, 223 K): δ 7.46, 7.36 (m, PPh$_3$), 7.11 (t, J = 7 Hz, H6), 7.06 (b, H7), 6.83 (br, H2), 6.81 (br, H5), 5.63 (br, H4), 4.11 (b, H3), 1.93 (br, C(O)CH_2CH_2C(O)), 1.48 (d, J = 5, Me). ^{1}H NMR (CD$_3$CN): δ 7.43–7.40 (m, PPh$_3$), 7.05 (t, J = 7.1 Hz, H6), 6.99 (br, H7), 6.83 (br, H5), 6.79 (br, H5), 5.68 (br, H4), 4.15 (br, H3), 1.90–1.92 (br, C(O)CH_2CH_2C(O)), 1.45 (d, $^4J_{P-H}$ = 4.9, Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 35.38 (s). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 36.74. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 189.14 (s, C9 and C12), 133.83 (d, $^2J_{P-C}$ = 11.79 Hz, *o*-C of PPh$_3$), 131.4 (d, $^1J_{P-C}$ = 39.5, *i*-C of PPh$_3$), 129.92 (s, *p*-C of PPh$_3$), 128.2 (d, $^3J_{P-C}$ = 9.71, *m*-C of PPh$_3$), 128.36 and 126.70 (C3a and C7a), 126.53 and 126,41 (s, C6 and C7), 118.19 and 117.93 (s, H4 and H5), 104.82 (s, C2), 101.37 (d, $^2J_{P-C}$ = 11.8, C1), 62.73 (s, C3), 31.54 (s, CH_2CH_2), 12.11 (s, C8).

Reactivities of the Imidato Complexes. Sample solutions of the imidato complexes **3**–**6** were combined with 5–10 equiv of various substrates in NMR tubes (C$_6$D$_6$), and the reactions were monitored by ^{31}P NMR spectroscopy. No reaction took place with phenylacetylene, dimethyl acetylenedicarboxylate, 1-hexyne, styrene, 1-hexene, PhNCO, and NaF. With LiCl, LiBr, LiI, PhSH, HCl, PhCH$_2$Br, PhBr, and MeI the starting material was converted to the corresponding Ni–X derivative, as evident from the disappearance or diminution

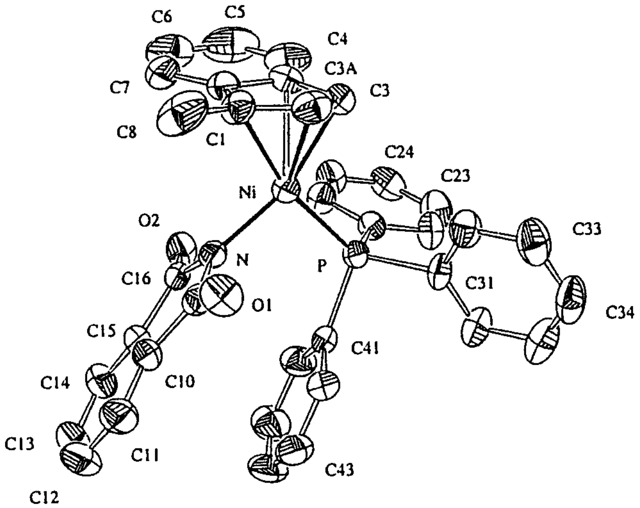

Figure 1. ORTEP plot of complex **3a** with atom-numbering scheme. Selected bond lengths (Å) and angles (deg): Ni−P = 2.181(2), Ni−N = 1.895(4), Ni−C1 = 2.118(5), Ni−C2 = 2.051(5), Ni−C3 = 2.025(5), Ni−C3a = 2.337(5), Ni−C7a = 2.341(5), C1−C2 = 1.388(6), C2−C3 = 1.396(6), C3−C3a = 1.444(6), C3a−C7a = 1.407(6), C7a−C1 = 1.459(6), C1−C8 = 1.488, N−C9 = 1.378(5), C9−O1 = 1.224(5), C9−C10 = 1.506(6), C10−C15 = 1.380(6), C15−C16 = 1.495(6), C16−O2 = 1.219(5), C16−N = 1.383(5); N−Ni−P = 96.75(12), N−Ni−C3 = 162.25(18), N−Ni−C2 = 128.3(2), N−Ni−C1 = 96.96, P−Ni−C1 = 165.51(15), P−Ni−C2 = 126.96(17), P−Ni−C3 = 100.58(16), C16−N−C9 = 108.7(4), N−C9−C10 = 108.5(4), N−C16−C15 = 109.4(4), N−C9−O1 = 125.8(5), N−C16−O2 = 124.5(5).

of the signal corresponding to the imidato complex and the emergence of the signal for Ni−X (δ, ppm (C_6D_6): 31.1 for X = Cl, 33.2 for X = Br, 37.4 for X = I, and 34.1 for X = SPh).

X-ray Diffraction Studies of 3. Dark red crystals of **3** were grown from Et_2O/hexane at −20 °C. Crystallographic data for $NiPO_2NC_{36}H_{28}$ (M = 596.27): monoclinic, $P2_1/c$, a = 11.853(7) Å, b = 10.938(7) Å, c = 22.840(9) Å, α = 90°, β = 97.27(4)°, γ = 90°, V = 2937(3) Å^3, ρ_{calcd} = 1.348 g/cm^3, Z = 4, μ(Cu Kα) = 1.726 mm^{-1}, λ(Cu Kα) = 1.540 56 Å, $2\theta_{max}$ = 140.0°, T = 293(2) K. A total of 20 613 reflections were measured using the $\omega/2\theta$ scan mode (5590 independent, 2120 observed); the structure was solved by direct methods using SHELXS96 and difference map synthesis using SHELXL96. Refinement on F^2 by full-matrix least squares gave R1 = 0.0508 and wR2 (all data) = 0.1119. The ORTEP diagram is shown in Figure 1 along with pertinent bond distances and angles. Complete crystallographic data are included in the Supporting Information.

Results and Discussion

Our initial attempts at the synthesis of the target amido complexes (1-R′-Ind)Ni(PPh_3)(NR_2) involved a number of different approaches which are known to lead to amido derivatives in other systems. For instance, Ni−amido compounds have been prepared by reacting the corresponding Ni−alkyl derivatives with azides (by elimination of N_2)[8] or with amines bearing relatively acidic hydrogens (by elimination of alkane).[9] We found, however, that the Ni−Me derivatives (1-R′-Ind)Ni(PPh_3)Me did not react with azides (PhN_3, Me_3SiN_3) or with R_2NH ($PhNH_2$, pK_a = ca. 30;[10] Ph_2NH, pK_a = ca. 25;[10] phthalimide, pK_a = ca. 8.3[11]). Metathetic reactions between Ni−halide and −amide salts are also known to lead to Ni−amide species,[12,13] but reduction of the starting halides to paramagnetic Ni(I) species is a possible side reaction.[14] The compound (Ind)Ni(PPh_3)Cl (**1**) reacted with LiNHAr (Ar = Ph, 1,3,5-$Me_3C_6H_2$), $LiNR_2$ (R = *i*-Pr, $SiMe_3$, Ph), and sodium imidazole in THF or Et_2O to give deep green-blue solutions whose ^1H NMR spectra showed the presence of varying quantities of the corresponding HNR_2 species, 1,1′-biindene (Ind-Ind), O=PPh_3, and $(Ind)_2Ni$[15] and broad signals characteristic of the known Ni(I) compound $(PPh_3)_3NiCl$.[16] The $^{31}P\{^1H\}$ NMR spectra of these solutions contained only weak signals attributable to free PPh_3 and Ph_3P=O (Scheme 1).

We had previously observed the formation of the byproducts Ind-Ind and $(PPh_3)_3NiCl$ in a side reaction during the preparation of **1**.[4a] Although the mechanism of this reaction is not established,[17] we have found that its occurrence can be minimized by using the 1-Me-Ind ligand. Accordingly, reacting (1-Me-Ind)Ni(PPh_3)Cl (**2**) with LiNHPh did prevent the formation of 1,1′-biindene and $(PPh_3)_3NiCl$, but instead of the expected amido species we obtained a compound which was identified, on the basis of its characteristic ^1H and $^{31}P\{^1H\}$ NMR spectra, to be the recently reported[5] cationic complex $[(1\text{-Me-Ind})Ni(PPh_3)_2]^+$ (Scheme 1).

We inferred from the above results that the Ni−N bond in the putative amido species is very labile and set out to determine whether strongly electron withdrawing N substituents would reduce the lability of the Ni−N bonds in these compounds. Thus, **2** was reacted with the alkali-metal salts of $^-N(COR)R'$, $^-N(COR)_2$, and $^-N(SO_2CF_3)_2$ with the following results. Whereas $^-NPh(COMe)$ did not react with **2**, the sulfonimidate anion $^-N(SO_2CF_3)_2$ replaced Cl^- to form $[(1\text{-Me-Ind})Ni(PPh_3)_2]^+[N(SO_2CF_3)_2]^-$ instead of the expected Ni−N species, presumably because of the highly noncoordinating nature of the N atom in this anion. On the other hand, we obtained the expected imidato derivatives **3** and **4** with the phthalimidate and 4,5-dichlorophthalimidate anions, respectively (Scheme 1). The maleimi-

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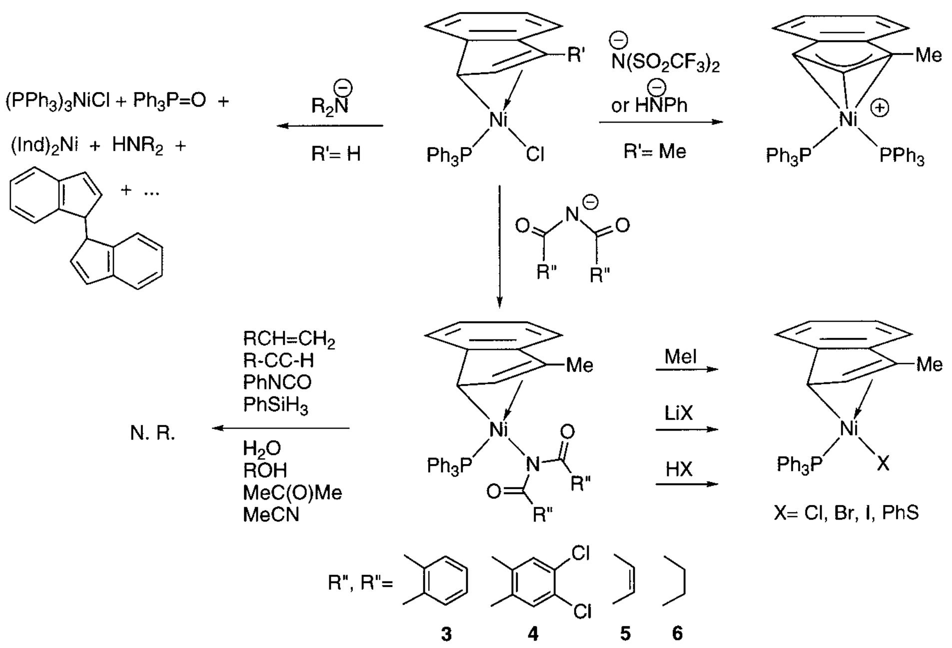
[17] We have proposed a Ni-promoted oxidative coupling of IndLi,[4a] but other mechanisms (e.g., electron transfer) cannot be ruled out. The formation of a number of analogous Cp−Cp compounds is also known, including Schrock's observation of Cp*−Cp* during the synthesis of Cd−NR_2 compounds: Cummins, C. C.; Schrock, R. R., Davis, W. M. *Organometallics* **1991**, *10*, 3781.

Scheme 1



dato and succinimidato derivatives **5** and **6** can also be prepared by this approach, but these reactions do not proceed to completion even in the presence of excess imidate. Indeed, **5** may be converted to the Ni–Cl precursor **2** by stirring it with excess LiCl in Et_2O (vide infra). In an effort to drive the equilibrium further toward the Ni–imidato species, we carried out the synthesis of **5** and **6** in a biphasic medium ($Et_2O/H_2O + KOH$) to remove Cl^- from the organic layer; this approach led to a higher conversion of **2,** but the reactions were somewhat sluggish and gave other byproducts (e.g., $Ph_3P{=}O$). It seems, therefore, that the ease of formation of $Ni{-}NR_2$ derivatives from **2** decreases in the order 4,5-dichlorophthalimidate $\approx$ phthalimidate $>$ maleimidate $\approx$ succinimidate $\gg$ N(COR)R′.

Characterization of (1-Me-Ind)Ni(PPh$_3$)(imidato). The ^1H and $^{31}P\{^1H\}$ NMR spectra of the imidato derivatives **3**–**6** are similar to those of the Ni–Cl precursor **2**. For instance, the H2 and H3 resonances for these complexes appear at ca. 6.7–6.9 and 3.8–4.1 ppm, respectively, as compared to 6.3 and 3.4 ppm in **2**; the $^{31}P\{^1H\}$ NMR spectra of these complexes contained a single resonance at ca. 35–36 ppm as compared to 31.1 ppm for **2**.[4]

The IR spectra of the imidato complexes showed ν(CO) bands at ca. 1654 (**3**), 1655 (**4**), 1646 (**5**), and 1637 (**6**) cm^{-1} corresponding to the imido carbonyl groups. It is noteworthy that these values are intermediate between the corresponding ν(CO) values in primarily ionic imide derivatives such as potassium phthalimidate (ca. 1600 cm^{-1}) and the more covalent derivatives such as phthalimide-CH_3 (ca. 1705 cm^{-1}) and phthalimide-Ph (ca. 1710–1720 cm^{-1}).[18] Colquhoun[19] has reported similar ν(CO) values for the d^8 imidato complexes $(PR_3)_2$-Pd(Ph)(imidato) (phthalimidato, 1640–1620 cm^{-1}; succinimidato, 1615–1605 cm^{-1}) and *trans*-$(PPh_3)_2M(CO)$-(imidato) (M = Rh, Ir; phthalimidato, 1640–1630 cm^{-1}; succinimidato, 1620–1610 cm^{-1}).

A single-crystal X-ray diffraction study was carried out on **3** in order to obtain more information on the Ni–N interactions and also to determine the influence of the Ni–N bond on the hapticity of the 1-Me-Ind ligand. Some of the structural features of **3** (Figure 1) are very similar to those found in the Ni–Cl analogues **1** and **2**.[4a,b] Thus, the atoms P, N, C1, C2, and C3 are within expected bonding distance from the nickel center, while the atoms C3a and C7a are considerably farther. The geometry around Ni may be described alternatively as distorted square planar (with C1=C2 occupying a single coordination site) or a highly distorted square pyramidal environment. An interesting difference between **3** and the Ni–Cl analogues **1** and **2** is the conformation adopted by PPh_3: in **1** and **2** one of the phenyl rings points toward the Ind ligand and two point in the opposite direction; in **3**, on the other hand, two phenyl rings point toward the Ind ligand while the third points toward the phthalimidato ligand (see Figure 1). This conformation presumably allows π-stacking interactions between a PPh_3 phenyl ring and the benzo ring of the phthalimidato group, which are ca. 3.9 Å apart.

The phthalimidato ligand is bonded in an η^1(N) fashion to the Ni center. To our knowledge, this is the first report of a structurally characterized Ni–imidato compound, but imidato complexes of other metals have been shown to adopt η^1(N)- and μ,η^2(N,O)-bonding modes.[20] The Ni–N bond length of 1.895(4) Å in **3** is shorter than the Ni–N distances found in *trans*-$(PMe_3)_2$-Ni(1,3,5-$Me_3C_6H_2$)(NPh(R)) (Ni–N = 1.974(5) Å for R = C(O)CHPh$_2$, 1.978(6) Å for R = C(O)NHBu^t, and 1.932(3) Å for R = H)[12] but comparable to that in Cp*Ni-(PEt$_3$)(NHAr) (Ar = tolyl; Ni–N = 1.903(5) Å).[21] The orientation of the phthalimidato ligand is such that the planes bearing the atoms P, Ni, N and C9, N, C16 are

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[18] The Sadtler Standard Spectra, Infrared Prism Standard Spectra, Sadtler Research Laboratories Inc., 1976: spectra # 10984 (N^-K^+), 1705 (N–Me), 658 (N–Ph), 47993P, 3495 (N–(*p*-NO_2-Ph)), 35177 (N–OC(O)Bu^t).

[19] Adams, H.; Bailey, N. A.; Briggs, T. N.; McCleverty, J. A.; Colquhoun, H. M.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1986**, 813.

rotated by 75.94(0.21)° with respect to each other. The planes formed by the atoms P, Ni, and N, on one hand, and C1, C2, C3, C3a, and C7a, on the other, are nearly perpendicular to each other (ca. 88°); this feature is also present in the structures of 1-Me-CpNi(PPh_3)I,[22] CpNi(PPh_3)Ph,[23] Cp*Ni(acac),[24] and Cp*Ni(PEt_3)X (X = Br, CH_2Ph, Me, OMe, N(H)Ar, SAr).[21]

The tendency of Ni(II) to form 16-electron complexes results in a substantial degree of allyl-ene distortion in the Ind ligand; this "slippage" is reflected in the different C−C bond lengths inside the five-membered-ring moiety (C1−C7a and C3−C3a > C1−C2 and C2−C3) and the Ni−C bond distances (Ni−C(3a,7a) > Ni−C(1−3)).[25] A second type of distortion in the coordination of the Ind ligand in complex **3** is evident from the *unsymmetric* nature of the Ni−C bonds, i.e., Ni−C1 > Ni−C3, which results in a partial localization of bonding in the allyl moiety of the Ind ligand (i.e., $\eta^3 \leftrightarrow \eta^1$(C3), η^2(C2═C1)).[26] Thus, C3 resembles an sp^3-hybridized carbon atom, while C1 is closer to an sp^2 hybridization, as reflected in the closeness of the $^{13}C\{^1H\}$ NMR chemical shifts of C1 (102.3 ppm) and C3 (62.6 ppm) in **3** to the corresponding sp^2 (ca. 139 ppm) and sp^3 (ca. 45 ppm) carbon atoms in free 1-methyl-substituted indenes.[27] These structural and spectroscopic features are also present in complexes **1** and **2** and support our proposal[4a,b] that (a) the Ind hapticity in complexes of the type IndNi(PPh_3)X is strongly affected by the relative trans influences of the ancillary ligands PPh_3 and X (Me ≈ PPh_3 > Cl ≈ phthalimidato) and (b) the solid-state hapticities of the Ind ligands in these compounds are maintained in solution.

Reactivities of (1-Me-Ind)Ni(PPh_3)(imidato). Late-transition-metal amido compounds have been implicated in a number of important catalytic reactions,[28] industrial processes,[29] and biological phenomena.[30] An important reactivity is the promotion of N−C bond formations via insertion and displacement reactions, as exemplified by recent reports by Boncella (insertion of isocyanates and alkynes into Ni−N bonds),[12a] Togni (Ir-catalyzed hydroamination of olefins),[28a] and Hartwig[13g] and Buchwald[28b,c] (cross coupling of aryl halides and amines via Pd−N intermediates). On the other hand, the reactivities of late-metal imidato complexes are less well-known. To our knowledge, the only report on Ni−imidato compounds is Yamamoto's study of the complexes (bipy)Ni(phthalimidate)(R) (R = Me, Et), which are thermally stable to above 200 °C but react with R′Br (R′ = $PhCH_2$ and Ph; 80−120 °C) to give *N*-R′-phthalimides in high yields.[9] Analogous Pd(II), Rh(I), and Ir(I) imidates do not promote this reaction.[19]

We studied the reactivities of complexes **3**−**6** in insertion and nucleophilic addition/exchange reactions in order to examine the lability of the Ni−N bonds; the results of these are summarized in Scheme 1. Complexes **3**−**6** are completely inert toward the insertion of olefins (e.g., styrene, 1-hexene, etc.), alkynes (e.g., $MeO_2CC{\equiv}CCO_2Me$, PhC≡CH, etc.), and PhNCO. They react with MeI to give the Ni−I derivative and *N*-Me-imidate (40% conversion in 1 h at room temperature in C_6D_6), but reactions with $PhCH_2Br$ and PhBr are more sluggish (<5% conversion to the Ni−Br derivative after 2 h at 45 °C). Reacting **3**−**6** with LiCl leads to the formation of the Ni−Cl species **2**; an analogous exchange also takes place with Br^- and I^- but not with F^-. As expected from pK_a considerations, protonation of the Ni−N bond in the imidato complexes **3**−**6** proceeds with relatively strong acids HX (e.g., PhSH and HCl) to give the corresponding Ni−X derivatives, but no reaction takes place with less acidic substrates such as alcohols, water, acetone, and acetonitrile. The Ni−N bond is also inert toward $PhSiH_3$. In contrast, the Ni−N bond in the analogous complexes Cp*Ni(PEt_3)(NHAr) reacts with ROH and R_3Si−H,[31] whereas the Pt−N bond in $L_2Pt(Me)NR_2$ reacts with acetone and acetonitrile.[13a]

Nature of Ni−N Interactions. The reactivities of late-transition-metal amido compounds are linked to the general lability of the M−N bond, a characteristic which has been attributed to (a) the presumed mismatch between the "soft" late metals and the "hard" amide ligands (when R = H, alkyl, aryl, etc.), and (b) the destabilizing π-donation from the amide ligands into the filled orbitals of the low-valent (electron-rich) late metals.[32] On the other hand, electrostatic-covalent (E-C) bonding models describe M−X bonds primarily in terms of ionic and covalent (σ) interactions, attributing less importance to π-effects.[33] Thus, M−N bonds may, in principle, involve both E-C and π-donation interactions, but the relative importance of these interactions is open to debate and may vary in each specific case. In this context, Bergman et al. have reported a detailed study on the thermodynamics of the reactions interconverting Cp*Ni(PEt_3)X + HX′ and Cp*Ni(PEt_3)X′ + HX (X, X′ = halides, NHR, OR, SR, etc.).[31] According to these authors, the Ni−X bond in these compounds has a substantial electrostatic component and the relative

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[20] (a) Shaver, A.; Hartgerink, J.; Lal, R. D.; Bird, P.; Ansari, N. *Organometallics* **1983**, *2*, 938 ($Pt^{II}-\eta^1(N)$-imidato). (b) Price, S. J. B.; DiMartino, M. J.; Hill, D. T.; Kuroda, R.; Mazid, M. A.; Sadler, P. J. *Inorg. Chem.* **1985**, *24*, 3425 (Ag^I−and $Au^I-\eta^1(N)$-imidato). (c) Reference 19 ($Ir^I-\eta^1(N)$-imidato and $Pd^{II}-\mu,\eta^2(N,O)$-imidato). (d) Treichel, P. M.; Nakagaki, P. C.; Haller, K. J. *J. Organomet. Chem.* **1987**, *327*, 327 ($Mn^I-\eta^1(N)$-imidato). (e) B.-Strzyzewska, M.; Tosik, A.; Wodka, D.; Zakrzewski, J. *Polyhedron* **1994**, *13*, 1689 ($Fe^{II}-\eta^1(N)$-imidato). (f) Sahajpal, A.; Robinson, S. D.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1993**, 393 ($Ru^{II}-\mu,\eta^2(N,O)$-imidato).

[21] Holland, P. L.; Smith, M. E.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 12815.

[22] Ballester, L.; Perez, S.; Gutierrez, A.; Perpinan, M. F.; Gutierrez-Puebla, E.; Monge, A.; Ruiz, C. *J. Organomet. Chem.* **1991**, *414*, 411.

[23] Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. (A)* **1970**, 161.

[24] Smith, M. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 11119.

[25] (a) This type of "slip-fold" distortion may be measured in terms of such parameters as the slip value, defined as $\Delta(M-C) = {}^1/_2(M-C3a + M-C7a) - {}^1/_2(M-C1 + M-C3)$, and the hinge and fold angles (HA and FA), representing the bending of the Ind ligand at C1/C3 and C3a/C7a, respectively.[25b,c] The values of these parameters for **3** are very close to those found for complexes **1** and **2**:[4a,b] ΔNi−C = 0.27 Å, HA = 11.1°, and FA = 12.3°. (b) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839. (c) Westcott, S. A.; Kakkar, A.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777.

[26] Note that [Ni−C1] − [Ni−C3] > 18σ.

[27] Edlund, U. *Org. Magnet. Reson.* **1978**, *11*, 516.

[28] (a) Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857. (b) Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6054. (c) Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2755 and references therein. (d) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738.

[29] Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1.

[30] Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239.

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stabilities of the various species are dependent on the stabilization of the partial negative charge on X. This reasoning, as opposed to π-bonding arguments, has been used to account for the observations of higher relative stabilities for Ni−OR over Ni−NR$_2$ species (oxygen being the more electronegative atom) and the direct relationship between the binding of the amide ligands and the electron-withdrawing nature of their N substituents.

Since we were unable to prepare thermally stable amido derivatives of our compounds, we could not measure equilibrium constants for the interconversion of these derivatives with various Ni−X analogues. We have, therefore, relied on a combination of structural, spectroscopic, and reactivity data to glean some information on the character of the Ni−imidato bonds in the present complexes. Thus, a VT ^{1}H NMR study carried out on complex **5** showed that the vinylic protons of the maleimidato ligand are inequivalent at lower temperatures (coalescence temperature 233 K, $\Delta\nu = 84$ Hz, $\Delta G^\ddagger = 11.1$ kcal/mol);[34] this implies a hindered rotation of the maleimidato ligand about the Ni−N axis which renders the halves of this otherwise symmetric ligand nonequivalent.

This hindrance might be caused by the steric interactions between the imidate O lone pairs and the Me group on the 1-Me-Ind ligand; similarly hindered rotations about the M−N bonds in the complexes Cp*Ni(PEt$_3$)(HN(p-C$_6$H$_4$Me)) ($\Delta G^\ddagger =$ ca. 11 kcal/mol)[31] and Cp*$_2$Hf(H)(NHMe) ($\Delta G^\ddagger =$ ca. 10 kcal/mol)[35] have been attributed to steric factors. On the other hand, electronic π-interactions may also be contributing to the observed hindered rotation. For instance, freely rotating imidato ligands would experience destabilizing pπ−dπ N→Ni interactions when they approach coplanarity with the main plane of coordination. A reflection of this phenomenon is also observed in the solid-state structure of **3,** in which the phthalimidate moiety was found to be rotated by ca. 76° with respect to the main plane of coordination, presumably to avoid these interactions. Similar spatial orientations have been adopted by imidato ligands in other square-planar, d^8 complexes.[19,20a] Another possibility is a Ni→N back-bonding interaction, which may be energetically feasible because the LUMO of the imidato complexes is primarily the low-lying imidato π* orbital. Such *stabilizing* π-back-bonding would serve to strengthen the Ni−N bond and render it relatively inert, consistent with our observations. A pertinent example which illustrates this possibility is presented by the d^6 complexes CpFe(CO)L(phthalimidato), in which the Fe→N back-bonding is evident from the increase in the ν(CO,imide) values on going from a more electron rich center (1640 cm^{-1} when L = PPh$_3$) to a poorer center (1660 cm^{-1} when L = CO).[36]

Conclusion. The Ni−imidato compounds **3**−**6** are much more stable than their Ni−amido counterparts presumably because of the more strongly electron withdrawing character of the N substituents in the imidato complexes. The delocalization of the N lone pair in the imidato ring and the rotation of the imidato ligand away from the main plane of coordination serve to reduce the overlap of the N lone pair with the HOMO of the complex, thereby minimizing destabilizing N→Ni pπ−dπ interactions. As a result, the Ni−N bonds are rather robust and inert in nucleophilic and insertion reactions.

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Supporting Information Available: Complete details on the X-ray analyses of **3**, including tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(34) The barrier was calculated using the Gutowsky−Holm approximation, which is based on the Eyring equation for a two-site exchange process involving a molecualr rotation: Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; Wiley: New York, 1985; pp 165−168.

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