Preparation and Characterization of Cationic Nickel Indenyl Complexes [(1-methylindenyl)NiLL′]$^+$

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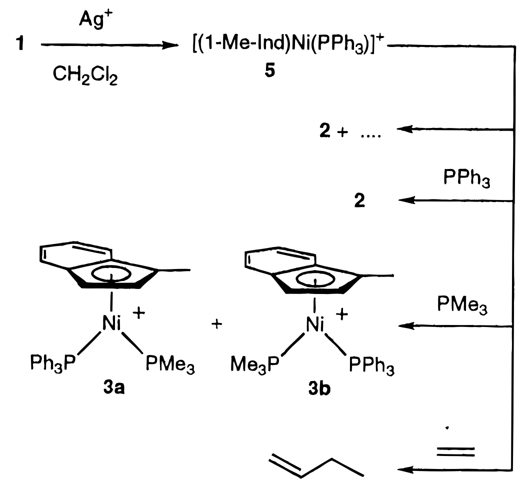
Summary: The cationic complexes [(1-Me-Ind)Ni(PPh$_3$)(L)]$^+$ (1-Me-Ind = 1-methylindenyl; L = PPh$_3$, PMe$_3$, or MeCN) have been prepared and characterized spectroscopically and by means of single-crystal X-ray structural analysis in the case of [(1-Me-Ind)Ni(PPh$_3$)(PMe$_3$)]AlCl$_4$. The in-situ-generated cations dimerize ethylene.

Recent reports have shown that metal-centered cationic species catalyze a number of important reactions[1] and can promote a variety of others, such as C−H bond activation,[2] ligand substitution and insertion,[3] and β-alkyl elimination.[4] Thus, the presence of a positive charge on certain transition metal complexes seems to confer to these species interesting patterns of reactivity. In conjunction with our ongoing investigations into the chemistry of neutral nickel indenyl complexes,[5] we were interested in studying the influence of a positive charge on the structural features and reactivities of these compounds. Although cationic Cp complexes of nickel have been reported,[6] little is known about their structural features and reactivities with olefins. Therefore, we set out to prepare cationic nickel indenyl complexes and report here the preparation, characterization, and some reactivities of the cationic species [(1-Me-Ind)NiLL′]$^+$.

When equimolar quantities of (1-Me-Ind)Ni(PPh$_3$)Cl, **1**,[5] AgBF$_4$, and PPh$_3$ are stirred in CH$_2$Cl$_2$, the bis(phosphine) cationic species [(1-Me-Ind)Ni(PPh$_3$)$_2$]$^+$, **2**, is obtained in 90% yield (eq 1). This methodology can also be used to prepare cationic complexes bearing different phosphine ligands, such as [(1-Me-Ind)Ni(PPh$_3$)(PMe$_3$)]$^+$, **3**.[7] These compounds have been characterized by NMR spectroscopy.[8,9] For example, the ^{31}P{^{1}H} NMR spectrum of complex **2**[8] shows two mutually coupled doublets reflecting the inequivalence of the PPh$_3$ groups due to the absence of a plane of symmetry in the complex. The ^{31}P{^{1}H} NMR spectrum of **3**[9] shows an AX + A′X′ spin system, with two doublets in the PPh$_3$ chemical shift region and two in the PMe$_3$ region. We have attributed these signals to the two rotamers **3a** and **3b** (Scheme 1), which arise from the hindered rotation of the indenyl ligand around the Ni−(1-Me-Ind) axis. The presence of the 1-Me substituent on the indenyl renders these rotamers inequivalent, and so their individual signals can be observed by NMR below the coalescence temperature (*ca.* 273 K).[10]

$$\mathbf{1} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{Ag}^+/\text{PR}_3} \underset{\text{R= Ph, }\mathbf{2}\text{; Me, }\mathbf{3}}{[(\text{1-Me-Ind})\text{Ni}(\text{PPh}_3)(\text{PR}_3)]^+} \qquad (1)$$

Scheme 1



The isolation of suitable single crystals of **3** allowed us to study its solid state structure in order to determine whether the indenyl hapticity increases on going from a neutral species to a cation; such an increase in the

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[1] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Collins, S.; Ward, D. G. *Ibid.* **1992**, *114*, 5460 and references therein.

[2] (a) Yi, C. S.; Wodka, D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 2. (b) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.

[3] Mecking, S.; Keim, W. *Organometallics* **1996**, *15*, 2650.

[4] Horton, A. D. *Organometallics* **1996**, *15*, 2675.

[5] (a) Huber, T. A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1995**, *14*, 4997. (b) Bayrakdarian, M.; Davis, M. J.; Reber, C.; Zargarian, D. *Can. J. Chem.* **1996**, *74*, 2194. (c) Huber, T. A.; Bayrakdarian, M.; Dion, S.; Dubuc, I.; Bélanger-Gariépy, F.; Zargarian, D. Manuscript in preparation.

[6] (a) Kuhn, N.; Heuser, N.; Winter, M. *J. Organomet. Chem.* **1984**, *267*, 221. (b) Kuhn, N.; Winter, M. *Ibid.* **1982**, *239*, C31. (c) Majima, T.; Kurosawa, H. *Ibid.* **1977**, *134*, C45. (d) Salzer, A.; Court, T. L.; Werner, H. *Ibid.* **1972**, *54*, 325. (e) Yamamoto, Y.; Yamazaki, H.; Hagihara, N. *Ibid.* **1969**, *18*, 189. (f) Kuhn, N.; Werner, H. *Synth. React. Inorg. Met-Org. Chem.* **1978**, *8*, 249. (g) Treichel, P. M.; Shubkin, R. L. *Inorg. Chim. Acta* **1968**, *2*, 485.

[7] AlCl$_3$ can also be used instead of AgBF$_4$, but in some cases the Cl$^-$ abstraction appears to be reversible and reforms **1**, presumably due to the slow formation of the AlCl$_3$·PR$_3$ adduct.

[8] **2**: ^{1}H NMR (δ, CDCl$_3$) *ca.* 7.9−6.96 (complex multiplets, PPh$_3$, H5 and H6), 6.91 (d, $^3J_{\text{H−H}}$ = *ca.* 2.8, H2), 6.22 (m, H4 or H7), 6.06 (m, H7 or H4), 5.01 (m, H3), 1.00 (dd, $^3J_{\text{P−H}}$ = *ca.* 5.6, 3.3 Hz, CH_3); ^{31}P{^{1}H} NMR (δ, CDCl$_3$) 35.8 (d, $^2J_{\text{P−P}}$ = 25 Hz), 32.5 (d, $^2J_{\text{P−P}}$ = 25 Hz). Although this compound appeared pure on the basis of its spectra, satisfactory analyses were not obtained.

[9] **3a**: H NMR (δ, CDCl$_3$, 273 K) 7.9−7.1 (m, PPh$_3$), 7.52 (m, H7), 7.38 (m, H6), 7.25 (t, $^3J_{\text{H−H}}$ = 8.0 Hz, H5), 6.58 (d, $^3J_{\text{H−H}}$ = 7.9 Hz, H4), 6.39 (d, $^3J_{\text{H−H}}$ = 3.1 Hz, H2), 4.43 (ddd, $^3J_{\text{PPh}_3\text{−H}}$ = 3.7 Hz, $^3J_{\text{PMe}_3\text{−H}}$ = 3.7 Hz, $^3J_{\text{H−H}}$ = 3.4 Hz, H3), 2.04 (dd, $^4J_{\text{PPh}_3\text{−H}}$ = 6.1 Hz, $^4J_{\text{PMe}_3\text{−H}}$ = 2.8 Hz, CH_3−Ind), 0.87 (d, $^2J_{\text{P−H}}$ = 9.4); ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 273 K) 40.9 (d, $^2J_{\text{P−P}}$ = 41.5, PPh$_3$), −15.3 (d, $^2J_{\text{P−P}}$ = 41.5 Hz, PMe$_3$). [**3b**]$^+$: ^{1}H NMR (δ, CDCl$_3$, 273 K) 7.9−7.1 (m, PPh$_3$), 7.39 (m, H4), 7.26 (m, H5), 7.23 (t, $^3J_{\text{H−H}}$ = 8.0 Hz, H6), 6.38 (d, $^3J_{\text{H−H}}$ = 7.9 Hz, H7), 6.35 (d, $^3J_{\text{H−H}}$ = 2.7 Hz, H2), 5.60 (ddd, $^3J_{\text{PMe}_3\text{−H}}$ = 6.4 Hz, $^3J_{\text{PPh}_3\text{−H}}$ = 2.8 Hz, $^3J_{\text{H−H}}$ = 2.7 Hz), 0.98 (d, $^2J_{\text{P−H}}$ = 9.7 Hz, P(CH_3)$_3$), 0.75 (dd, $^4J_{\text{PMe}_3\text{−H}}$ = 6.0 Hz, $^4J_{\text{PPh}_3\text{−H}}$ = 1.9 Hz, CH_3−Ind); ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 273 K) 41.2 (d, $^2J_{\text{P−P}}$ = 42 Hz, PPh$_3$), −10.1 (d, $^2J_{\text{P−P}}$= 42 Hz, PMe$_3$). Anal. Calcd for C$_{31}$H$_{33}$P$_2$NiAlCl$_4$: C, 53.57; H, 4.79. Found: C, 53.81; H, 4.75.

[10] We are studying the dynamic processes arising from the hindered rotation of the indenyl ligands in these and related complexes and will report our results in greater detail in due course.

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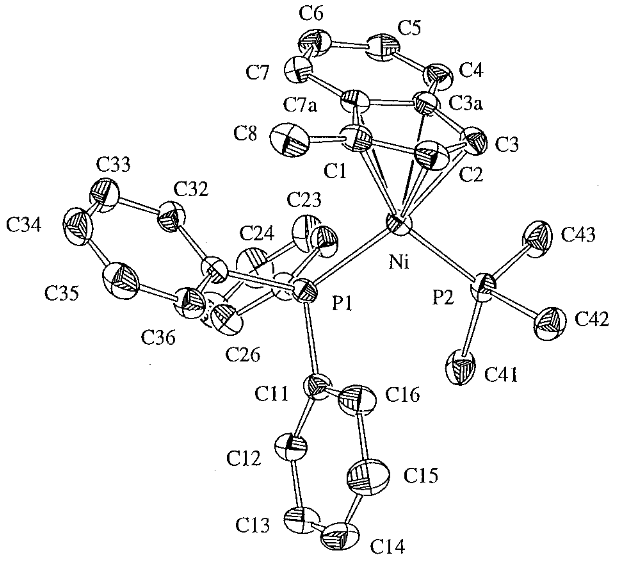

Figure 1. ORTEP view of complex **3b** and selected bond lengths (Å): Ni−P(1) = 2.1794(10), Ni−P(2) = 2.1909(11), Ni−C(1) = 2.160(2), Ni−C(2) = 2.096(2), Ni−C(3) = 2.033(2), Ni−C(3A) = 2.249(2), Ni−C(7A) = 2.305(2), C(1)−C(2) = 1.400(3), C(2)−C(3) = 1.416(3), C(3)−C(3A) = 1.459(3), C(3A)−C(7A) = 1.419(3), C(1)−C(7A) = 1.465(3).

hapticity would serve to transfer more electron density to the electrophilic Ni center, thereby stabilizing it. Figure 1 shows the ORTEP view of [(1-Me-Ind)Ni(PPh$_3$)(PMe$_3$)][AlCl$_4$][11] along with some pertinent bond distances. Indenyl hapticities can be determined conveniently by calculating the slip value, ΔM−C,[12] which is found to be 0.18 Å for **3**; comparing this to the ΔM−C of 0.26 Å for **1**[5c] confirms the significant increase in the indenyl hapticity upon cation formation.

It is interesting to note that the rotamer that crystallizes from the solution is that with the Me group on top of the PPh$_3$ ligand, **3b**, which might appear to be the more sterically crowded one of the two rotamers observed in solution until one notes that the coordination of 1-Me-Ind to Ni is quite nonsymmetrical (*i.e.*, Ni−C1 > Ni−C2 > Ni−C3). Such nonsymmetrical Ni−Ind interactions, which seem to result in a "tilting" of the indenyl ligand, have also been observed in **1**[5c] and the related complex (Ind)Ni(PPh$_3$)Cl.[5a] In the latter compounds, this "sideways slippage" has been shown to be caused by the unequal trans influences of the pseudo-trans ligands PPh$_3$ and Cl. By analogy, we propose that the large trans influence of PMe$_3$ is responsible for the nonsymmetrical coordination of the 1-Me-Ind ligand in complex **3**.

The reaction of **1** with AgBF$_4$ in MeCN without the added PPh$_3$ gave, after removal of the solvent, a yellow-brown solid which was identified as [(1-Me-Ind)Ni(PPh$_3$)(MeCN)]$^+$, **4**, on the basis of its NMR and IR spectra (eq 2).[13] The presence of a coordinated MeCN is supported by the increase in the value of ν(CN) resulting from a transfer of electron density from MeCN to the electrophilic Ni$^+$ center. A similar observation has been made for cationic Pt complexes bearing coordinated isocyanide ligands.[14] Although the coordinated MeCN in **4** can be displaced readily by stronger ligands such as phosphines (eq 2), weaker ligands such as olefins do not compete effectively with MeCN for coordination to Ni. Complex **4** is relatively unstable in solution and decomposes over several minutes at room temperature to produce an insoluble white solid and other unidentified products.

$$\mathbf{1} \xrightarrow[\text{MeCN}]{\text{Ag}^+} \underset{\mathbf{4}}{[(\text{1-Me-Ind})\text{Ni}(\text{PPh}_3)(\text{NCMe})]^+} \xrightarrow{\text{PR}_3} \mathbf{2}\text{ or }\mathbf{3} \qquad (2)$$

Evidently, the MeCN adduct **4** is not a suitable precursor to cationic complexes bearing weaker ligands (*e.g.*, olefins, alkynes, *etc.*) which may exhibit interesting reactivities. In an attempt to prepare the MeCN-free, "naked" cation [(1-Me-Ind)Ni(PPh$_3$)]$^+$, **5**, we reacted **1** with AgBF$_4$ in CH$_2$Cl$_2$ in the absence of any added donor ligand; interestingly, the only species detected in this reaction was **2** (*ca.* 30% yield). Thus, abstraction of Cl$^-$ from **1** initially forms the nonstabilized, coordinatively unsaturated, cationic intermediate **5**, which is highly electrophilic and, in the absence of an added donor such as MeCN, coordinates any residual PPh$_3$ from the reaction medium forming **2**.[15] In order to suppress the formation of **2**, we carried out the abstraction of Cl$^-$ in the presence of an excess of 1-hexene, which led, once again, to the formation of **2**. However, when **1** was reacted with AgBF$_4$ under a 5 atm pressure of ethylene in a semibatch type reactor, rapid uptake of ethylene began after a brief induction period and lasted during the entire experiment (20−30 min); the temperature of the reactor also rose significantly during the reaction. The apparent turnover (TO) frequency of this system is estimated to be *ca.* 100−500 TO/s, corresponding to an ethylene consumption rate of *ca.* 11 000 kg·(mol Ni)$^{-1}$·h^{-1}. GC/MS analyses of the final reaction mixtures showed only 1-butene, indicating that β-H elimination from the putative Ni−Bu intermediate is too rapid to allow chain propagation.

In conclusion, cationic species of the type [(1-Me-Ind)Ni(PPh$_3$)L]$^+$ display interesting structural and spectroscopic features pertaining to the hapticity of the indenyl ligand. The nonstabilized cationic species **5**, which could be generated *in-situ* but not isolated, dimerizes ethylene at a very high rate, reminiscent of the reac-

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[11] Orange-red crystals of [**3b**]$^+$[AlCl$_4$]$^-$ were grown from a CH$_2$Cl$_2$/hexane solution at −35 °C. Crystallographic data for NiP$_2$Cl$_4$AlC$_{31}$H$_{33}$ (M = 695.04): Triclinic, $P\bar{1}$, unit cell dimensions of a = 9.780(4) Å, b = 10.762(5) Å, c = 16.061(6) Å, α = 95.55(4)°, β = 91.90(3)°, γ = 97.40(3)°, V = 1666.7(12) Å^3, Z = 2, μ(Cu Kα) = 3.18 mm^{-1}, λ = 1.540 56 Å, $2\theta_{\max}$ = 140.0°, T = 223 K, 12 434 reflections measured using the $\theta/2\theta$ scan mode (6323 independent, 5791 observed), refinement by block-diagonal least-squares gave R_F = 0.0326 and R_w = 0.0351. The ORTEP diagram is shown in Figure 1 along with pertinent bond distances.

[12] (a) ΔM−C = $^1/_2$ (Ni−C7a + Ni−C3a) − $^1/_2$ (Ni−C1 + Ni−C3); ΔM−C values close to zero indicate little distortion from η^5 hapticity, whereas values above *ca.* 0.5 Å indicate nearly η^3 hapticity (ref 12b). (b) Westcott, S. A.; Kakkar, A.; Stringer, G.; Taylor, N. J.; Marder, T. B *J. Organomet. Chem.* **1990**, *394*, 777.

[13] **4**: ^{1}H NMR (δ, CDCl$_3$) 7.7−7.1 (PPh$_3$, H6 and H7), 7.06 (t, H5, $J_{\text{H−H}} \approx 6$ Hz), 6.47 (bs, H2), 6.00 (d, H4, $J_{\text{H−H}} \approx 5$ Hz), 4.16 (s, H3), 1.98 (b, CH_3CN), 1.73 (s, CH_3-Ind); ^{31}P{^{1}H} NMR (δ, CDCl$_3$) 34.94 (s); IR (cm^{-1}, Nujol) 2335, 2310 (compared to 2300 and 2260 for neat MeCN).

[14] Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1973**, *12*, 362.

[15] This can proceed in at least two different ways: (a) if the phosphine coordination step is much faster than the removal of Cl$^-$, any initial amount of cation formed would abstract PPh$_3$ from the unreacted starting material **1** to form **2** and other materials; (b) alternatively, all of the starting material may be converted to **5** in a rapid step, followed by a slower redistribution step producing **2** and [(Ind′)Ni]$^+$, which would decompose readily. Experiments are currently underway to determine which, if any, of these two mechanisms are at work in this reaction.

[16] Bogdanovic, B.; Spliethoff, B.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 622.

tivities displayed by Wilke's system of (π-allyl)Ni(PCy$_3$)Br/EtAlCl$_2$.[16] We believe that the hapticity of the Ind ligand plays an important role in the reactivity of these cationic species. The dynamic behavior of these complexes in solution and their reactivities with other substrates are under investigation.

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Supporting Information Available: Experimental data on the preparation and spectroscopic characterization of the species **2**, **3**, and **4**, tables of crystal data, collection, and refinement parameters, positional parameters, bond distances and angles, and anisotropic displacement parameters, and NMR spectra (29 pages). Ordering information is given on any current masthead page.

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