Structural and NMR Studies of Indenyl Hapticity and Rotational Barriers in the Complexes (η-1-R-Indenyl)Ni(PPh₃)(X) (R = H, Me; X = Cl, Me)

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The relative trans influences of Cl and Me in the complexes (1-Me-indenyl)Ni(PPh₃)Cl and (1-Me-indenyl)Ni(PPh₃)Me lead to different solid state hapticities for the 1-Me-indenyl ligands. Comparing the solution NMR data for these complexes and the energy barriers to the rotation of the indenyl ligands in their unsubstituted analogues demonstrates that solid state hapticities are preserved in solution.

In comparison to their Cp analogues, many transition metal Ind complexes (Ind = indenyl and its substituted derivatives) possess enhanced reactivities in various stoichiometric reactions, notably ligand substitution.[1,2] This feature has been recognized as potentially advantageous in catalytic systems where ligand substitution rates play a determining role in the overall catalytic cycle, and a few reactions are reported to be more efficiently catalyzed by Ind complexes relative to their Cp counterparts.[1r,3,4] The difference in the reactivities of these closely related compounds, the so-called "indenyl effect", is commonly attributed to the better stabilization of transition states and/or reaction intermediates by the relatively facile "ring slippage" of the Ind ligands (*i.e.*, their more flexible hapticity). It has also been suggested that, in some cases, the indenyl effect is due to less stable ground states in Ind complexes relative to their Cp analogues.[5]

To date, most of the structural and reactivity studies of late metal Ind complexes have focused on group 8 and group 9 metals, while group 10 metal Ind complexes have received little attention.[6] We have begun investigating the preparation and reactivities of these compounds and have found that the solid state hapticity of the Ind ligand in the complex (Ind)Ni(PPh₃)Cl (**1**) is significantly distorted toward an unsymmetrical and partially localized mode, *i.e.*, (η³ ↔ η¹,η²)-Ind.[6g] Moreover, the solution NMR studies of this complex indicated a considerable energy barrier to the rotation of the Ind ligand around the Ind−Ni axis. We proposed that both of these effects were caused by the relatively large difference in the trans influences of the ancillary ligands PPh₃ and Cl. This assertion was indirectly supported by the observation that replacing the Cl ligand in **1** by the higher trans influence ligand Me resulted in a more symmetrically coordinated Ind ligand, as inferred from ¹H NMR spectroscopy (*vide infra*). Unfortunately, however, the poor quality of the crystals obtained for the methyl derivative (Ind)Ni(PPh₃)Me (**2**) precluded a solid state structure determination and prevented a direct comparison of the indenyl hapticities in **1** and **2**. Therefore, we set out to prepare new derivatives of **1** and **2** and determine their solid state structures in order to unequivocally establish the influence of the ancillary

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(2) A recent report has suggested that substitution rates in 19-electron complexes are in fact *slower* for Ind than for Cp, the so-called "inverse indenyl effect": Pevear, K. A.; Banaszak Holl, M. M.; Carpenter, G. B.; Rieger, A. L.; Rieger, P. H.; Sweigart, D. A. *Organometallics* **1995,** *14,* 512.
(3) (a) Caddy, P.; Green, M.; Smart, L. E.; Smart, L. E. *J. Chem. Soc., Chem. Commun.* **1978,** 839. (b) Borrini, A.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Serra, G. *J. Mol. Catal.* **1985,** *30,* 181. (c) Bonneman, H. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 248. (d) Bonneman, H.; Brijoux, W. In *Aspects of Homogeneous Catalysis, Vol. 5;* Ugo, R., Ed.; D. Reidel: Dordrecht, 1984; p 75. (e) Marder, T. B.; Roe, D. C.; Milstein, D. *Organometallics* **1988,** *7,* 1451. (f) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990,** *112,* 7984. (g) Ceccon, A.; Gambaro, A.; Santi, S.; Venzo, A. *J. Mol. Catal.* **1991,** *69,* L1. (h) Lee, B. Y.; Chung, Y. K.; Jeong, N.; Lee, Y.; Hwang, S. H. *J. Am. Chem. Soc.* **1994,** *116,* 8793. (i) Mantovani, L.; Ceccon, A.; Gambaro, A.; Santi, S.; Ganis, P.; Venzo, A. *Organometallics* **1997,** *16,* 2682.
(4) The reports cited in ref 3 do not include examples of reactions catalyzed by Ind complexes of early metals (*e.g.,* olefin and silane polymerizations) because the ring slippage aptitude of the Ind ligand is not believed to be a factor in these, normally unsaturated, complexes.

(5) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991,** *10,* 2870.
(6) The following are, to our knowledge, the only other group 10 metal Ind complexes reported to date: (a) Fritz, H. B.; Köhler, F. H.; Schwarzhans, K. E. *J. Organomet. Chem.* **1969,** *19,* 449 (synthesis of Ni(Ind)₂). (b) Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990,** *394,* 777 (solid state structure of Ni(Ind)₂). (c) Nakasuji, K.; Yamaguchi, M.; Murata, I.; Tatsumi, K.; Nakamura, A. *Organometallics* **1984,** *3,* 1257 (synthesis of Pd₂Cl₂(Ind)₂). (d) O'Hare, D. *Organometallics* **1987,** *6,* 1766 (synthesis of [Pt(Ind)(COD)]⁺). (e) Lehmkuhl, H.; Näser, J.; Mehler, G.; Keil, T.; Danowski, F.; Benn, R.; Mynott, R.; Schroth, G.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1991,** *124,* 441 (synthesis of Ni(Ind)-(η³-allyl)). (f) Tanase, T.; Nomura, T.; Fukushima, T.; Yamamoto, Y.; Kobayashi, K. *Inorg. Chem.* **1993,** *32,* 4578 (synthesis and solid state structure of Pd₂(μ-Ind)2(CNR)2). (g) Huber, T. A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1995,** *14,* 4997 (synthesis and solid state structure of (Ind)Ni(PPh₃)Cl). (h) Vollmerhaus, R.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1997,** *16,* 4762. (synthesis and solid state structure of [(1-Me-Ind)Ni(PPh₃)(PMe₃)]⁺[AlCl₄]⁻).

Table 1. X-ray Crystallographic Data for 3 and 4

	3	4
formula, mol wt	C$_{28}$H$_{24}$ClNiP, 485.60	C$_{29}$H$_{27}$NiP, 465.19
crystal color and habit	orange-red, parallelepiped	dark red, parallelepiped
cryst dimens, mm	0.39 × 0.14 × 0.05	0.22 × 0.17 × 0.07
cell setting and space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
a, Å	9.086(3)	8.891(2)
b, Å	10.455(3)	28.089(9)
c, Å	13.466(4)	10.379(2)
α, deg	84.65(3)	90
β, deg	88.09(3)	113.92
γ, deg	64.40(3)	90
V, Å^3	1148.6(6)	2369.4(10)
Z	2	4
D (calc), g cm^{-1}	1.404	1.304
λ (Cu Kα), cm^{-1}	1.545 06	1.540 56
temp, K	220(2)	293(2)
diffractometer	Nonius CAD-4	Nonius CAD-4
$2\theta_{max}$, deg	140	140
data coll method	$\omega/2\theta$	$\omega/2\theta$
no. of reflns used ($I > 2\sigma$ (I))	4341	4492
R, R_w	0.0458, 0.1245	0.0383, 0.0819
max residual, e Å^{-3}	1.066	0.213

Table 2. Selected Bond Distances (Å) and Structural Parameters^a for 1,^{b} 3, and 4

|	1	3	4
Ni–P	2.1835(7)	2.1782(11)	2.1213(13)
Ni–Cl/C9	2.1822(7)	2.1865(10)	1.991(3)
Ni–C1	2.094(2)	2.137(2)	2.089(4)
Ni–C2	2.061(2)	2.072(2)	2.072(4)
Ni–C3	2.042(2)	2.026(3)	2.082(4)
Ni–C3a	2.318(2)	2.308(2)	2.275(4)
Ni–C7a	2.344(2)	2.351(2)	2.273(4)
C1–C2	1.399(4)	1.403(4)	1.407(5)
C2–C3	1.417(4)	1.421(4)	1.404(5)
C3–C3a	1.449(3)	1.451(4)	1.430(5)
C3a–C7a	1.422(3)	1.417(4)	1.424(5)
C7a–C1	1.459(3)	1.457(4)	1.438(5)
HA (deg)	10.9	11.0	8.1
FA (deg)	11.7	11.8	7.5
ΔM–C (Å)	0.26	0.25	0.19

^{a} See text for definitions. ^{b} Taken from ref 6g.

ligands *vis à vis* the coordination of the Ind ligand to the Ni center in these complexes.

The present paper reports the solid state structures of the 1-methylindenyl analogues of **1** and **2**, namely (1-Me-Ind)Ni(PPh₃)Cl (**3**) and (1-Me-Ind)Ni(PPh₃)Me (**4**), as well as the energy barrier for the rotation of the Ind ligand in **2**. Comparison of the structural data for **1**, **3**, and **4** on the one hand, and the rotational energy barriers for **1** and **2** on the other, demonstrates that (a) the hapticity of the Ind ligand is very sensitive to the electronic nature of the ancillary ligands and (b) the rate of rotation of the Ind ligand varies considerably with its hapticity.

Results and Discussion

Reacting 1-Me-IndLi with (PPh₃)₂NiCl₂ yields a mixture of products from which the dark-red complex **3** can be isolated as the major species in *ca.* 60% yield; the subsequent reaction of **3** with MeLi gave **4** in 65% yield. Suitable crystals of **3** and **4** were grown from cold hexane/Et₂O solutions and were subjected to X-ray diffraction studies. X-ray crystallographic data (Table 1), selected bond distances (Table 2), and ORTEP views (Figures 1 and 2) for these compounds are presented.
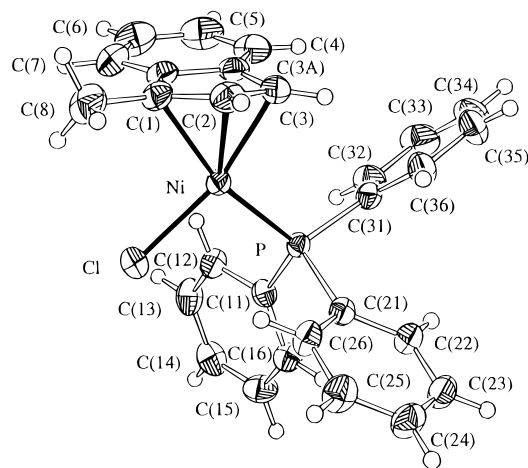
Figure 1. ORTEP plot of **3** with atom numbering scheme.
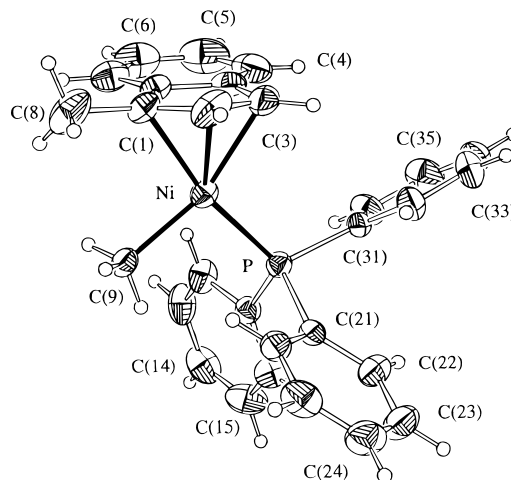
**Figure 2.** ORTEP plot of **4** with atom numbering scheme.

The nickel center in both complexes is pentacoordinate: the atoms P, Cl/C9, C1, C2, and C3 are within expected bonding distance from Ni, while C3a and C7a are considerably farther away. The geometry around the Ni center is quite irregular but may be described as either distorted square planar, with the C1=C2 occupying a single coordination site, or highly distorted square pyramidal, with P, Cl/C9, C1, and C3 in the basal plane and C2 above it. The planes formed by the atoms P, Ni, and Cl/C9 on the one hand, and C1, C2, C3, C3a, and C7a on the other, are nearly perpendicular to each other (*ca.* 88°).[7]

Inspection of the C–C and Ni–C bond distances for **3** revealed that there are two types of hapticity distortions in this complex. The first type is an allyl-ene distortion reflected in the substantially longer Ni–C bonds to the ring junction carbon atoms, *i.e.*, Ni–C(3a,-7a) > Ni–C(1–3), as well as the C–C bond lengths inside the five-membered ring moiety, *i.e.*, C1–C7a, C3–C3a > C1–C2, C2–C3 (Table 2). Varying degrees of such distortions (or "slippage") also occur in most η-Ind complexes;[8] in the present case, they can be attributed

(7) This feature is also present in the following structures: (a) 1-Me-CpNi(PPh₃)I (Ballester, L.; Perez, S.; Gutierrez, A.; Perpinan, M. F.; Gutierrez-Puebla, E.; Monge, A.; Ruiz, C. *J. Organomet. Chem.* **1991**, *414*, 411); (b) CpNi(PPh₃)Ph (Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. (A)* **1970**, 161); (c) Cp*Ni(acac) (Smith, M. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 11119); and (d) Cp*Ni(PEt₃)X for X = Br, CH₂Ph, Me, OMe, SAr (Holland, P. L.; Smith, M. E.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.*, in press).
(8) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

Chart 1

1 (R= H)
3 (R= Me)

2 (R= H)
4 (R= Me)
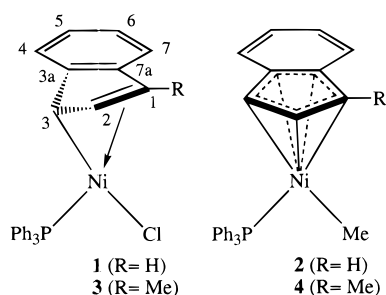
to the tendency of Ni(II) to avoid forming 18-electron complexes. The second and more unusual type of distortion found in **3** is evident from the *unsymmetric* nature of the Ni−C bonds, *i.e.*, Ni−C1 > Ni−C2 > Ni−C3 and Ni−C7a > Ni−C3a (Table 2). Thus, the Ind hapticity in this complex is very similar to that found in the solid state structure of **1**[6g] and seems to arise from a combination of tilting of the Ind ring and its "sideways slippage". The net result of these distortions is a partial localization of bonding in the allyl moiety of the Ind ligand (*i.e.*, η^1,η^2 distortion), which is reflected in a nominally shorter C1−C2 bond relative to C2−C3 (Table 2) and in the ^{1}H and ^{13}C{^{1}H} NMR chemical shifts of this complex (*vide infra*).

In contrast to **3**, there is no sideways slippage in the solid state structure of **4**, as the Ind ligand is virtually symmetrically coordinated to Ni, *i.e.*, Ni−C1 = Ni−C3 and Ni−C3a = Ni−C7a (Table 2). These types of symmetrical Ind hapticities are commonly found in complexes (Ind)RhL$_2$ (L = PR$_3$, CO, C$_2$H$_4$), which have identical ligands L on either side of the mirror plane bisecting the Ind ligand and incorporating the metal and the C2 atoms.[1p,9] We attribute the differences in the hapticity of the Ind ligands in **3** and **4** to the relative trans influences of the ancillary ligands PPh$_3$ and X in these complexes. The role of ancillary ligand trans influence differences in controlling the conformation of η-Ind complexes has been discussed previously,[10] but their effect on the hapticity of the Ind ligand has not been addressed. The present results demonstrate that, in complexes of the type IndMLX, wherein the ancillary ligands L and X are positioned pseudotrans in relation to the Ind carbon atoms C1 and C3, the M−Ind interaction is strongly influenced by the electronic natures of the ligands L and X in the following manner. When L and X possess comparable trans influences, as in **4**, the Ind hapticity is symmetrical; when the trans influences of L and X are sufficiently different, however, significant perturbations are observed in the normally symmetrical coordination of the Ind ligand, as observed in **1** and **3** (Chart 1).

The Ni−Ind interactions in **3** and **4** can also be compared in more quantitative terms by calculating the parameters such as the hinge and fold angles (HA and FA) and the slip value (ΔM−C), which are used fre-

quently for quantifying the degree of slip−fold distortions in η-Ind complexes.[11] In **3**, HA = 10.9°, FA = 11.8°, and ΔM−C = 0.25 Å (Table 2), almost exactly the same as the values found for **1**.[6g] In **4**, however, HA = 8.1°, FA = 7.5°, and ΔM−C = 0.19 Å (Table 2), indicating significantly *less* slip−fold distortion in **4** compared to that in **3**. In addition, the Ni−P distance is significantly *shorter* in **4** (2.1213(13) Å) than in **1** (2.1835(7)) and **3** (2.1782(11)). Stronger Ni−Ind and Ni−P interactions in **4** may serve to compensate for a reduction in the overall electron density at the Ni center in going from **3** to **4**.[12] However, a reduction in the electron richness of the Ni center resulting from replacing the Cl by the Me ligand, a better σ-donor, seems counterintuitive unless Cl → Ni π-donation is an important component of the overall Ni−Cl interaction in **1** and **3**. In this case, $\sigma + \pi$ donation from Cl would place more electron density on Ni than would σ-donation from Me. Cl → Ni π-donation would also contribute to the observed weakening of the Ni−C1 interaction in **1** and **3** (*i.e.*, the distortion toward η^1,η^2-Ind), since these types of interactions are believed to cause strong cis-labilizing effects.[13] It should be noted, however, that Cl → M π-donation is more prevalent in unsaturated, d^6 complexes and would be highly repulsive and destabilizing in these d^8 complexes. Alternatively, stronger Ni−P and Ni−Ind interactions may be attributed to the tendency of "soft" ligands such as PPh$_3$ and Ind to bind more strongly with a soft metal center such as the Ni in the methyl complex **4** than with the hard Ni center in the chloro complexes **1** and **3**.[14] Our results cannot determine which of these phenomena, if any, is responsible for the above structural observations.

Solution Hapticities of the Ind Ligands in 1−4. Since the nature of M−Ind interactions in the solution can influence substantially the reactivity of Ind complexes, it is important that Ind hapticities in solution be known. Baker and Tulip[8] and Marder's group[6b] have suggested that, to a large extent, solid state hapticities are maintained in solution, while Ceccon et al.[3g,i,15] have proposed that the solution hapticity of Ind complexes involves a fast equilibrium between η^3- and η^5-bound species, regardless of the solid state hapticity. We have relied on the solution NMR spectra (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) of our complexes to conclude that their solid state structures are maintained in the solution, as described below.

Solution hapticities of Ind ligands are believed to correlate with the ease of their rotations: the less distorted the Ind ligand, the more facile its rotation.[12b,16]

(9) (a) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; McGlinchey, M. J.; Rodger, C. A.; Churchill, M. R.; Ziller, J. W.; Kang, S.-K.; Albright, T. A. *Organometallics* **1986**, *5*, 1656. (b) Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012.

(10) (a) Faller, J. W.; Chen, C.-C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361. (b) Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *88*, 101. (c) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929. d) Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *Can. J. Chem.* **1995**, *73*, 981. (e) Husebo, T. L.; Jensen, C. M. *Organometallics* **1995**, *14*, 1087.

(11) HA and FA represent the bending of the Ind ligand at C1/C3 and C3a/C7a, respectively, and ΔM−C = [$^1/_2$(M−C3a + M−C7a) − $^1/_2$(M−C1 + M-C3)] (ref 6b).

(12) (a) Marder *et al.* (ref 9b) have shown that, in most cases, the Ind hapticity increases (*i.e.*, ring slippage decreases) as the overall electron density at the metal center decreases, but they have also noted some exceptions to this phenomenon (ref 12b). (b) Kakkar, A. K.; Taylor, N. J.; Calabrese, J. C.; Nugent, W. A.; Roe, D. C.; Connaway, E. A.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 990.

(13) (a) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25. (b) Poulton, J. T.; Folting, K.; Sreib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

(14) The influence of charge polarization in Ni−X bonds on bond lengths and ligand labilities has been discussed recently by Bergman and co-workers in the context of a generalized electrostatic-covalent bonding model (ref 7d).

(15) (a) Ceccon, A.; Elsevier, C. J.; Ernsting, J. M.; Gambaro, A.; Santi, S.; Venzo, A. *Inorg. Chim. Acta* **1993**, *204*, 15. (b) Bonifaci, C.; Carta, G.; Ceccon, A.; Gambaro, A.; Santi, S.; Ganis, P.; Venzo, A. *Organometallics* **1996**, *15*, 1630.

Complexes **1** and **2** possess C_1 symmetry in their ground state structures but can attain C_s symmetry as a result of the rapid rotation of the Ind ligand in solution; therefore, they exhibit temperature-dependent ^1H and $^{13}C\{^1H\}$ NMR spectra which can yield the energy barriers to indenyl rotations in these complexes. For instance, the H1 and H3 signals for **1** and **2** appear at *ca.* 5.4–5.9 and *ca.* 3.3–4.1 ppm, respectively, at below the coalescence temperature and merge into a singlet at *ca.* 4.5–4.7 ppm above the coalescence temperature. We conclude, therefore, that **1** and **2** undergo the same dynamic behavior, with the main difference being the coalescence temperature, which is significantly higher for **1** than for **2**.[17] The calculated energy barriers for the rotation of the Ind rings in **1** and **2** are *ca.* 16.0 and 10.1 kcal/mol, respectively; such a large difference between rotational energy barriers indicates that the Ind ligand is significantly more distorted in **1** than in **2**.[18]

In contrast to **1** and **2**, the ground state C_1 symmetry of **3** and **4** is not affected by Ind rotations because the unsymmetrically substituted 1-Me-Ind ligand is prochiral, which renders **3** and **4** dissymmetric (chiral at the Ni center) and their ^1H NMR spectra independent of temperature. In spite of this basic difference, pairwise comparisons of the ^1H NMR spectra of these complexes (*i.e.*, **1**/**3** and **2**/**4**) are very informative in terms of the solution hapticity of their Ind ligands. For example, the H3 resonance in **3** *at ambient temperature* (3.37 ppm) is very close to the corresponding resonance for **1** *at 188 K* (*ca.* 3.3 ppm); likewise, in **4**, the H3 resonance *at ambient temperature* (4.17 ppm) is very close to the corresponding resonance for **2** *at 188 K* (*ca.* 4.1 ppm). Hence, the solution hapticities of the Ind ligands in **1**–**4**, as reflected in their ^1H NMR spectra, are pairwise very similar.[19]

The above conclusion can also be reached from the $^{13}C\{^1H\}$ NMR data, which can be used for estimating solution hapticities of Ind ligands according to the formula $\Delta\delta_{av}C = \delta_{av}(C3a,C7a \text{ of } \eta\text{-Ind}) - \delta_{av}(C3a,C7a \text{ of } Na^+Ind^-)$.[8] The solution hapticity of the Ind ligand is thought to be closer to η^5 when $\Delta\delta_{av}C \ll 0$, closer to η^3 when $\Delta\delta_{av}C \gg 0$, and intermediate when $\Delta\delta_{av}C \approx 0$. The $\Delta\delta_{av}C$ values for our complexes are *ca.* −2 ppm for **1** and **3** and *ca.* −10 ppm for **2** and **4**, showing that, in solution, as in the solid state, there is less slip–fold distortion in the Ni–Me derivatives than in the Ni–Cl

derivatives. These results also support the suggestions of Baker and Tulip[8] and Marder and co-workers[6b] that there is a strong correlation between the $\Delta\delta_{av}C$ value for a complex and the degree of slip–fold distortion observed in its solid state structure.

Finally, the maintenance of the solid state structures of these complexes in solution is also supported by the solution $^{31}P\{^1H\}$ NMR spectra of **1**–**4**, which show a downfield shift in the $^{31}P\{^1H\}$ resonances on going from free PPh$_3$ (*ca.* −5 ppm in C_6D_6) to the Ni–Cl compounds **1** and **3** (28.2 and 31.1 ppm, respectively) and the Ni–Me derivatives **2** and **4** (47.1 and 47.7 ppm, respectively). This trend reflects the increasing P → Ni σ-donation in **4** and **2** compared to that in **3** and **1**, which is consistent with the shorter Ni–P bond length observed in the solid state structure of **4** relative to that in **3**.

In summary, the solid state structures of **1** and **3** show a "sideways slippage" of Ni which has resulted in $\eta^5\leftrightarrow\eta^3$ distortions and a partial localization of bonding inside the 1-Me-Ind ligand (η^1,η^2). In contrast, the $\eta^5\leftrightarrow\eta^3$ distortions found in the solid state structure of **4** are symmetric, this difference arising from the different trans influences of the ligands Cl and Me, *i.e.*, Me ≈ PPh$_3$ > Cl. In the case of the unsubstituted **1** and **2**, replacing Cl in **1** by Me effectively accelerates the rate of rotation of the Ind ligand, presumably because of the more symmetric coordination of the Ind ligand in **2**. In the absence of a solid state structure for **2**, we have relied on the similarities between the solid state structures and the NMR spectra of **1** and **3** on the one hand, and the similarities in the NMR spectra of **2** and **4** on the other, to argue that the solid state structure of **2** must be very similar to that of **4**, and that in all complexes the solid state Ind hapticity is maintained in the solution. The direct correlation observed here between structural and solution NMR data allow us to use the ^1H NMR resonances for the symmetry-related pairs of protons (H1/H3, H4/H7, and H5/6) as a convenient indicator of Ind hapticity. This is a very useful tool not only for extracting solid state structural information from solution spectra, but also for estimating rotational energy barriers in the case of dissymmetric complexes (*e.g.*, **3** and **4**), for which VT NMR spectroscopy cannot be used to yield such data.

Experimental Section

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. A Bruker AMX400 spectrometer was employed for recording ^1H (400 MHz), $^{13}C\{^1H\}$ (100.56 MHz), and $^{31}P\{^1H\}$ (161.92 MHz) NMR spectra. BuLi (2.5 M solution in hexanes), MeLi (1.4 M in Et$_2$O), indene (technical grade, distilled prior to use), PPh$_3$, and MeI were purchased from Aldrich and used as received. The preparation of **1** and **2** has been reported elsewhere.[6g]

(1-Me-Ind)Ni(PPh$_3$)Cl (3). An Et$_2$O solution (100 mL) of 1-Me-IndLi (371 mg, 2.73 mmol) was added dropwise to a stirring suspension of (PPh$_3$)$_2$NiCl$_2$ (3.331 g, 5.09 mmol) in Et$_2$O (60 mL) at ambient temperature. The resultant dark red mixture was stirred for approximately 15–30 min after the addition, filtered, and evaporated to dryness. The residue was washed with hexane (3 × *ca.* 20 mL) to remove PPh$_3$ and other byproducts and recrystallized from CH$_2$Cl$_2$/hexane at −20 °C to give the product as a dark red solid (720 mg, 61%). Recrystallization of a small portion of this solid from a cold

(16) Barr, R. D.; Green, M.; Marder, T. B.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1261.

(17) We have shown (ref 6g) that this dynamic process is not due to phosphine exchange.

(18) The present results also provide further support for the notion that solid state hapticities of Ind ligands correlate with their rotational energy barriers. For example, the complexes **1** and Cp$_2$Zr(μ-PPh$_2$)$_2$Rh-(Ind) (ref 8) have similar energy barriers of 16.0 and 14.0 kcal/mol, respectively, and exhibit similar solid state Ind hapticities evident from ΔM–C values of 0.26 and 0.23 Å, respectively. Moreover, complexes **2** and (1-Me-Ind)Rh(PMe$_3$)$_2$ (ref 9b) have similar energy barriers of 10.1 and 11.2 kcal/mol, respectively, and although the solid state hapticities of these compounds are not known, their close analogues **4** and (Ind)-Rh(PMe$_3$)$_2$ (ref 9b) have very similar ΔM–C values of 0.19 and 0.20 Å, respectively.

(19) Comparing ^1H NMR chemical shifts for the protons in coordinated Ind ligands and free indenes provides further support for the assertion that solid state hapticities of the Ind ligands are largely preserved in the solution. In **3**, for example, the ^1H resonances for H2 and H3 appear at *ca.* 6.3 and 3.4 ppm, respectively, compared to *ca.* 6.2 and 3.2 for the corresponding resonances in 3-alkylindenes *which have localized bonding in the five-membered ring*. The similarity of these shifts suggests that the partially localized, unsymmetric hapticity of the Ind ligand observed in the solid state of **3** is largely preserved in the solution.

Et$_2$O/hexane solution yielded crystals suitable for X-ray diffraction studies and elemental analysis. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.63 (m, PPh$_3$), 7.08 (t, J_{H-H} = 7.38 Hz, H6), 6.97 (m, PPh$_3$ and H7), 6.83 (t, J_{H-H} = 7.32 Hz, H5), 6.27 (br s, H2), 6.06 (d, J_{H-H} = 7.8 Hz, H4), 3.37 (br s, H3), 1.54 (d, J_{P-H} = 5.49 Hz, Me). ^{13}C {^{1}H} NMR (acetone-d_6, 100.56 MHz): δ 134.6 (d, J_{P-C} = 11.5 Hz, o-C), 132.6 (d, J_{P-C} = 44.1 Hz, i-C), 131.2 (p-C), 130.4 (C7a), 128.8 (d, J_{P-C} = $ca.$ 10 Hz, m-C), 127.1 (C3a), 127.0 (C6), 126.8 (C5), 118.7 (C7), 117.6 (C4), 107.5 (C2), 103.4 (d, J_{P-C} = 14.8 Hz, C1), 67.2 (C3), 12.7 (Me). ^{31}P {^{1}H} NMR (C$_6$D$_6$, 162 MHz): δ 31.1 (s). Anal. Calcd for C$_{28}$H$_{24}$NiPCl: C, 69.25; H, 4.98. Found: C, 68.56; H, 5.45.

(1-Me-Ind)Ni(PPh$_3$)Me (4). MeLi (1.4 M solution in Et$_2$O, 1.40 mL, 1.96 mmol) was added dropwise to an Et$_2$O (65 mL) solution of **3** (942 mg, 1.94 mmol) at 0 °C, and the mixture was stirred for 1 h, filtered, and evaporated to dryness. The residue was crystallized from a cold Et$_2$O/hexane solution to give the product as a green-brown solid (573 mg, 63%). Recrystallization of a portion of this solid from Et$_2$O/hexane yielded crystals suitable for X-ray diffraction studies and elemental analysis. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.31 (m, PPh$_3$), 7.22 (br, H5 or H6), 7.20 (br, H7 and H5 or H6), 6.99 (m, PPh$_3$), 6.47 (d, J_{H-H} = 7.8 Hz, H4), 6.22 (d, J_{H-H} = 2.92 Hz, H2), 4.17 (t, J_{H-H} = 2.34 Hz, H3), 1.89 (d, J_{P-H} = 3.92 Hz,

Ind-Me), −0.72 (d, J_{P-H} = 5.48 Hz, Ni−Me). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.56 MHz): δ 134.3 (d, J_{P-C} = 42.8 Hz, i-C), 133.8 (d, J_{P-C} = 11.9 Hz, o-C), 129.4 (p-C), 127.8 (d, J_{P-C} = $ca.$ 9 Hz, m-C), 122.1 (C6), 122.0 (C5), 120.8 (C7a), 120.0 (C3a), 116.7 (C7), 115.9 (C4), 101.7 (C2), 89.0 (d, J_{P-C} = 12.5 Hz, C1), 74.5 (C3), 11.1 (Ind-Me), −16.8 (d, J_{P-C} = 22.9 Hz, Ni−Me). ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 47.7 (s). Anal. Calcd for C$_{29}$H$_{27}$NiP: C, 75.20; H, 5.87. Found: C, 74.49; H, 5.80.

Supporting Information Available: Complete details on the X-ray analyses of **3** and **4** and VT ^{1}H NMR data used in calculating the energy barrier for the rotation of the Ind in **2** (44 pages). Ordering information and Internet access instructions are given on any current masthead page.

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