Organometallics **2005,** *24,* 149−155 149

Influence of $SiMe_3$ Substituents on Structures and Hydrosilylation Activities of $((SiMe_3)_{1\ \mathrm{or}\ 2}$-Indenyl)Ni($PPh_3$)Cl

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Received July 22, 2004

This report examines the effect of substituents R on structures and reactivities of the complexes (R-Ind)Ni(PPh_3)Cl (R-Ind = 1-Me-indenyl, **1**; 1-$SiMe_3$-indenyl, **2**; 1,3-$(SiMe_3)_2$-indenyl, **3**). NMR studies indicate that a relatively facile dissociation of PPh_3 takes place in solutions of complex **3** ($\Delta G^{\ddagger} \approx 10$ kcal/mol in C_6D_6) but not those of complexes **1** and **2**, implying that the presence of Ind substituents at the 1- and 3-positions can influence the kinetic lability of PPh_3. X-ray analyses have also shown that the PPh_3 ligand and the $SiMe_3$ group adjacent to it in complex **3** experience some steric repulsion, which is manifested in angular deformations (out-of-plane bending of the $SiMe_3$ group by about 0.56−0.65 Å and 5−10° variations in the P−Ni−Cl and P−Ni−C3 angles) and a somewhat longer Ni−P bond (ca. 2.19 Å). Reactivity studies have shown that complexes **1**−**3** are effective precatalysts for the addition of $PhSiH_3$ to styrene in the presence of the cationic initiator $NaBPh_4$; α-addition of the silyl moiety takes place regioselectively to give PhCH(Me)($SiPhH_2$). The catalytic activities depend on the styrene:$PhSiH_3$ ratio but not the Ind substituents; thus, catalytic turnover numbers increase from ca. 75 with a 1:1 ratio to ca. 95 with a 1:1.5 ratio for all three precursors. The hydrosilylation can also proceed in the absence of initiator, but in this case the activities are strongly dependent on Ind substituents, increasing in the order 1-Me-Ind ≪ 1-$SiMe_3$-Ind < 1,3-$(SiMe_3)_2$-Ind.

Introduction

Recent reports have shown that a number of interesting reactions can be catalyzed by species generated from the in-situ activation of the complexes IndNi(L)X (Ind = indenyl and its substituted derivatives; L = neutral ligands such as phosphines or heterocarbenes; X = anionic ligands such as halides, alkyls, triflate, etc.).[1] For instance, combining the Ni-Cl precursors with methylaluminoxanes (MAO) generates species that promote the polymerization of ethylene,[2] alkynes,[3] and $PhSiH_3$;[4] on the other hand, using cationic initiators such as $AgBF_4$, $NaBPh_4$, or $AlCl_3$ instead of MAO generates[5] the electronically unsaturated and highly electrophilic cations $[IndNi(PR_3)]^+$, which promote the oligomerization of some olefins[6] as well as the hydrosilylation of olefins and ketones.[7] Cationic species can also be generated in the absence of initiators by using the precursors (*i*-Pr-Ind)Ni(PPh_3)(OSO_2CF_3)[8] or $[(\eta^5,\eta^1\text{-Ind}^\wedge NR_2)Ni(PR_3)]^+$ (∧ = various side chains tethering the amine moiety to the Ind ligand)[9] or by heating the complexes $[IndNi(PR_3)_2]^+$ bearing bulky phosphine ligands.[10]

The available mechanistic information indicates that among the reactions promoted by IndNi(PR_3)X, only the hydrosilylation of olefins involves phosphine dissociation. Consistent with this assertion, the addition of $PhSiH_3$ to styrene gives a higher yield with the precatalyst (1-Me-Ind)Ni(PPh_3)Cl, **1**, relative to its PMe_3 analogue (69% vs 36%),[7] whereas the opposite is true for the polymerization reactions.[2a] It seemed reasonable, therefore, to suppose that the presence of sterically bulky substituents on the Ind ligand should favor the hydrosilylation reaction by inducing the dissociation of PPh_3. However, initial tests did not show any advantage in using bulkier Ind substituents; for instance, the complex (1-(*i*-Pr)-Ind)Ni(PPh_3)Cl catalyzed the hydrosilylation reaction no more effectively than its 1-Me-Ind

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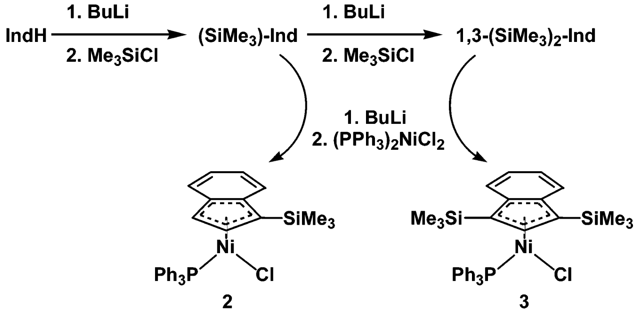
Scheme 1



analogue (61% vs 69%). On the other hand, since the complexes (1-R-Ind)Ni(PPh_3)X always adopt a configuration that places the PPh_3 ligand away from the Ind substituent to avoid steric congestion,[1] we reasoned that a more reliable way to evaluate the influence of ligand sterics on the dissociation of PPh_3 would require studying both 1-R-Ind and the 1,3-R_2-Ind analogues of these complexes. Therefore, we are examining the kinetic lability of the PPh_3 ligand in the complexes (1-R-Ind)Ni(PPh_3)Cl and (1,3-R_2-Ind)Ni(PPh_3)Cl and evaluating their reactivities. The results of our studies on the first series of these complexes (R = $SiMe_3$) are presented herein.

Results and Discussion

Synthesis and Characterization of (1-$SiMe_3$-Ind)Ni(PPh_3)Cl, 2, and (1,3-($SiMe_3$)$_2$-Ind)Ni(PPh_3)Cl, 3. The ligands $SiMe_3$-IndH and 1,3-($SiMe_3$)$_2$-IndH can be prepared by reacting Cl-$SiMe_3$ with LiInd or Li-[1-($SiMe_3$)-Ind],[11] respectively, whereas the target complexes **2** and **3** were prepared by reacting (PPh_3)$_2$NiCl_2 with Li[1-($SiMe_3$)-Ind] and Li[1,3-($SiMe_3$)$_2$-Ind], respectively (Scheme 1).[12] The full characterization of these complexes by NMR spectroscopy and X-ray analysis is described below.

The ^{1}H NMR spectrum of **2** displayed well-resolved signals for all Ind protons; the multiplicities and relative chemical shifts of these signals follow a pattern that is commonly observed for the previously studied 1-R-Ind analogues. For instance, the signals for H4 (d, 6.39 ppm) and H5 (t, 6.93 ppm) were strongly shielded in comparison to those for H6 (t, 7.20 ppm) and H7 (d, 7.59 ppm), and the signal for H3 was also very upfield (m, 3.54 ppm). The shielding of the signals for H3, H4, and H5 is caused by their proximity to the phenyl rings of the PPh_3 ligand.[1,13]

On the other hand, the ^{1}H NMR spectrum of **3** was quite different in that it showed only an unresolved multiplet for H4–H7 signals at ca. 7.0–7.2 ppm; moreover, only one signal, a sharp singlet at 0.19 ppm, was observed for the two, ostensibly inequivalent, $SiMe_3$ groups present in this complex. The unexpected equivalence of the symmetry-related signals in **3** hints at the existence, in solution, of a mirror plane that renders the two halves of the Ind ligand equivalent; in other words, the C_1 symmetry dictated by the solid state structure of this complex (vide infra) is converted to a C_s symmetry in the solution. On the other hand, the absence of any shielding effects for H4/H5 implies little or no interaction between these protons and the phenyl groups of PPh_3. These phenomena can occur as a result of two possible processes: a rapid rotation of the Ind ligand, which would create the requisite mirror plane, or a rapid dissociation/reassociation of PPh_3, which would render the two halves of the Ind ligand equivalent and minimize the above-discussed shielding effect. Consistent with the latter possibility, the ambient-temperature ^{31}P{^{1}H} NMR spectrum of **3** exhibits a very broad signal for the PPh_3 ligand coordinated to Ni (ca. 28 ppm in C_6D_6, width at half-height ~60–70 Hz)[14] and a less intense signal for free PPh_3 (ca. −5 ppm in C_6D_6). The nature of this dynamic process was further probed by variable-temperature (VT) NMR studies, as described below.

The VT NMR spectra of complex **3** showed that the broad ^{31}P{^{1}H} signal sharpened gradually upon lowering the temperature of the NMR probe, reaching a width at half-height of ~10 Hz at −70 °C; on the other hand, the ^{1}H singlet due to the $SiMe_3$ groups broadened upon lowering the temperature until it split into two broad singlets (0.64 and −0.19 ppm) at −70 °C (Figure 1). The coalescence temperature (ca. 223 K) and the $\Delta\delta$ for the individual ^{1}H NMR resonances due to $SiMe_3$ groups (ca. 330 Hz) have been used to estimate a $\Delta G^\ddagger$ value of ca. 10 kcal/mol.[15] This energy barrier is smaller than the $\Delta G^\ddagger$ values found for the rotation of the Ind ligands in the related complexes IndNiPPh$_3$Cl (16.0 kcal/mol), (2-Me-Ind)Ni(PPh_3)Cl (15.6 kcal/mol), and (1,3-Me_2-Ind)Ni(PPh_3)Cl (15.5 kcal/mol). We conclude, therefore, that the NMR features of complex **3** are more consistent with a dissociation/reassociation of PPh_3 as opposed to an Ind rotation. The kinetic lability of PPh_3 in **3** must be induced by the steric repulsion between the PPh_3 ligand and the $SiMe_3$ group adjacent to it; the effects of steric repulsion on the solid state structures of these complexes have been examined by X-ray crystallography, as described below.

Solid State Structures of 2 and 3. Two crystallographically independent molecules were found in the unit cells of both compounds. Complex **2** contains disordered Ph and Cl groups, as follows: there are two Ph groups disordered over two positions in molecule 1; in molecule 2, two Ph groups are disordered over two positions, the third Ph group is disordered over three positions, and the Cl is disordered over two positions. Despite these disorders, the structure was refined to a good degree of precision (R = 4.54%). Complex **3** was free of disorder and refined to a very good degree of precision (R = 3.63%). The ORTEP drawings for **2** and **3** (molecule no. 1 in both cases) are shown in Figures 2 and 3, respectively, the crystal data and refinement

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(12) The preparation of complex **2** has been described previously (ref 6a).

(13) (a) Huber, T. A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1995**, *14*, 4997. (b) Huber, T. A.; Bayrakdarian, M.; Dion, S.; Dubuc, I.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1997**, *16*, 5811.

(14) In comparison, the width at half-height for **1** and (1,3-Me_2-Ind)-Ni(PPh_3)Cl (ref 6a) are 2 and 6 Hz, respectively.

(15) The Holmes–Gutowski equation, $\Delta G^\ddagger = RT_c\{22.96 + \ln(T_c/\Delta\delta)\}$, wherein R is the gas constant (1.987 cal/K·mol), T_c (K) is the coalescence temperature, and $\Delta\delta$ (Hz) is the difference in the frequencies of the coalescing signals, can be used for this purpose: Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; Wiley: New York, 1985; Chapter 7, pp 165–168, eq 7.11.

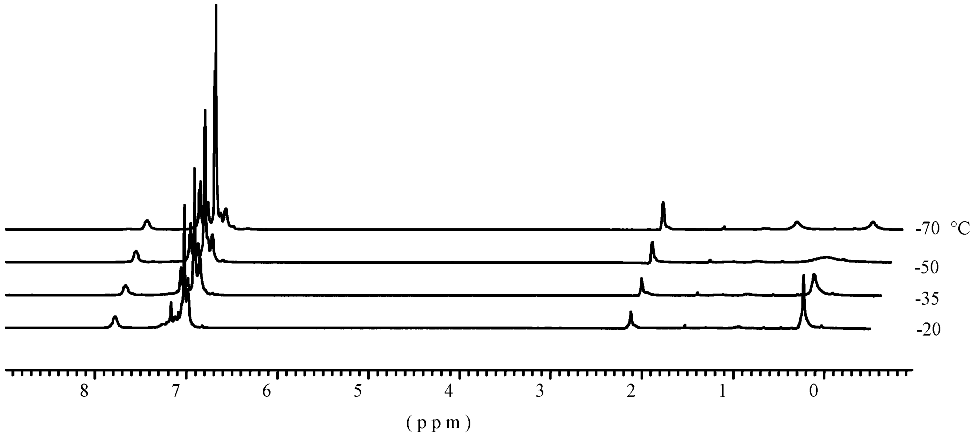


Figure 1. Variable-temperature ^{1}H NMR spectra for **3** (toluene-d_8, 400 MHz).

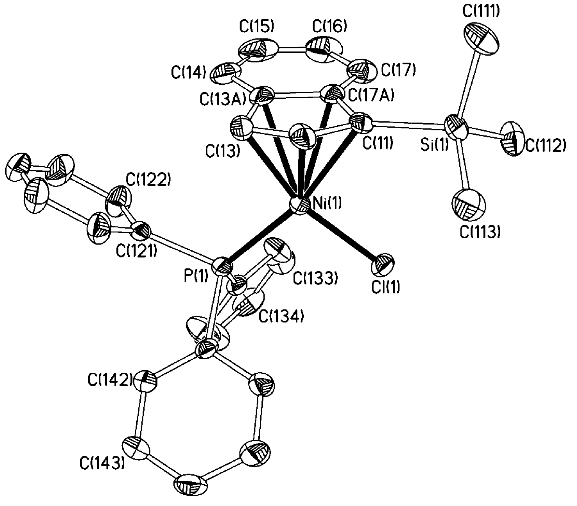


Figure 2. ORTEP diagram for complex **2** (molecule no. 1). Thermal ellipsoids are shown at 30% probability, and hydrogen atoms are omitted for clarity.

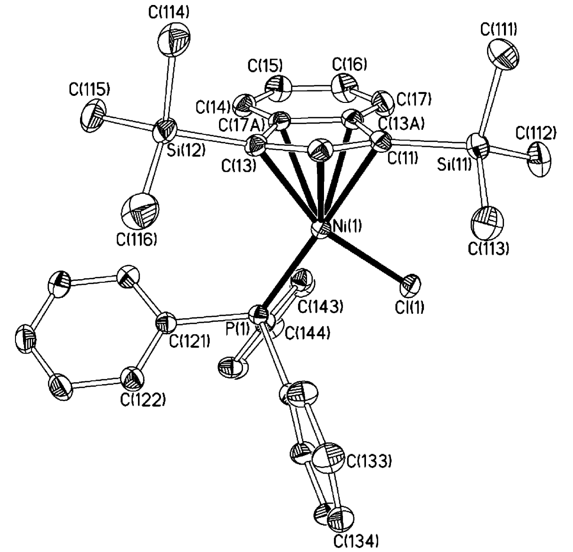


Figure 3. ORTEP diagram for complex **3** (molecule no. 1). Thermal ellipsoids are shown at 30% probability, and hydrogen atoms are omitted for clarity.

Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for 2 and 3

	2	**3**
formula	$C_{30}H_{30}ClNiPSi$	$C_{33}H_{38}ClNiPSi_2$
mol wt	543.76	615.94
cryst color, habit	red, plate	orange, plate
cryst dimens (mm)	0.26 × 0.24 × 0.10	0.50 × 0.50 × 0.07
symmetry	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.90640(10)	18.1219(2)
b (Å)	16.09400(10)	23.2566(2)
c (Å)	18.94740(10)	15.8556(2)
α (deg)	114.60(1)	90
β (deg)	90.32(1)	103.0050(10)
γ (deg)	92.57(1)	90
volume (Å^3)	2742.99(4)	6511.00(12)
Z	4	8
D(calcd) (g cm^{-1})	1.317	1.257
diffractometer	Bruker AXS SMART 2K	Bruker AXS SMART 2K
temp (K)	223(2)	220(2)
wavelength, λ (Å)	1.54178	1.54178
absorp coeff, μ (mm^{-1})	2.999	2.926
scan type	ω scan	ω scan
F(000)	1136	2592
$\theta_{\min} - \theta_{\max}$ (deg)	2.57−72.98	2.50−72.99
h,k,l range	$-11 \le h \le 12$ $-19 \le k \le 19$ $-23 \le l \le 23$	$-22 \le h \le 22$ $-28 \le k \le 28$ $-19 \le l \le 18$
indep reflns used ($I > 2\sigma(I)$)	10 438	12 907
absorp corr correction	multiscan SADABS	multiscan SADABS
transmn (min., max.)	0.5550, 0.8050	0.41, 0.86
R [$F^2 > 2\sigma(F^2)$], $wR(F^2)$	0.0454, 0.1246	0.0363, 0.1020
goodness of fit on F^2	1.060	1.028
largest diff peak and hole (e/Å^3)	0.918, −0.681	0.428, −0.326

parameters are given in Table 1, and a selection of structural parameters is listed in Table 2.

In both compounds, the coordination geometry around the Ni atom can be described as distorted square planar, with the largest distortion arising from the small C1−Ni−C3 angles (ca. 66−68°). As commonly observed in this family of complexes,[1] the Ind−Ni interaction in **2** and **3** is primarily through the allylic carbons, while the Ni−C bond distances for the benzo carbons are significantly longer. This "slippage" away from an ideal η^5 hapticity is attributed to the tendency of Ni(II) to form 16-electron complexes.

Another common type of slippage in this family of complexes is the so-called "sideways slippage", which is reflected in the unsymmetrical Ni−C bonds involving the allylic carbons (Ni−C1 > Ni−C3); this distortion is caused by the unequal trans influences of the PR$_3$ and X ligands (X = halides, phthalimidato, thiolato, triflato, etc.). Both molecules of complex **2** exhibit this type of

Table 2. Selected Bond Distances (Å) and Angels (deg) for Complexes 2 and 3

	2 (molec. 1, X = 1)	**2** (molec. 2, X = 2)	**3** (molec. 1, X = 1)	**3** (molec. 2, X = 2)
Ni(X)−P(X)	2.1886(7)	2.1819(8)	2.1841(5)	2.1984(5)
Ni(X)−Cl(X)	2.1828(7)	2.188(av.)	2.1959(5)	2.1865(5)
Ni(X)−C(X1)	2.128(2)	2.135(2)	2.0946(16)	2.1543(17)
Ni(X)−C(X2)	2.070(2)	2.060(3)	2.0577(17)	2.0422(17)
Ni(X)−C(X3)	2.052(3)	2.038(3)	2.1208(16)	2.0831(16)
Ni(X)−C(X3a)	2.323(3)	2.339(3)	2.3369(16)	2.3764(17)
Ni(X)−C(X7a)	2.335(2)	2.374(3)	2.3194(17)	2.4219(18)
C(X1)−C(X2)	1.423(3)	1.415(4)	1.417(2)	1.409(2)
C(X2)−C(X3)	1.402(4)	1.410(5)	1.432(2)	1.426(2)
C(X3)−C(X3a)	1.451(5)	1.449(5)	1.478(2)	1.470(2)
C(X3a)−C(X7a)	1.434(3)	1.430(4)	1.430(2)	1.434(2)
C(X7a)−C(X1)	1.471(3)	1.466(5)	1.473(2)	1.471(2)
C(X1)−Si(X1)	1.877(2)	1.871(3)	1.8838(17)	1.8795(18)
C(X3)−Si(X2)			1.8760(18)	1.8715(17)
P(X)−Ni(X)−Cl(X)	96.61(3)	95.26(6)	87.985(18)	91.172(18)
P(X)−Ni(X)−C(X1)	166.65(7)	165.40(8)	177.56(5)	169.44(5)
P(X)−Ni(X)−C(X3)	100.38(8)	99.14(9)	110.15(5)	106.63(5)
C(X1)−Ni(X)−Cl(X)	96.23(7)	99.32(9)	94.07(5)	95.68(5)
C(X3)−Ni(X)−Cl(X)	162.96(8)	163.87(11)	161.71(5)	162.08(5)
C(X3)−Ni(X)−C(X1)	66.9(1)	66.49(11)	67.85(7)	67.02(7)
ΔM−C[a] (Å)	0.24	0.26	0.22	0.28
HA[b] (deg)	11.10	11.19	9.57	10.24
FA[c] (deg)	10.19	10.30	7.90	9.41

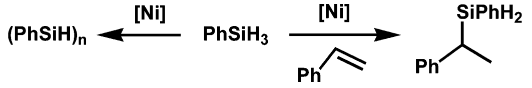
[a] $\Delta(M-C) = 0.5\{(M-C3a + M-C7a)\} - 0.5\{(M-C1 + M-C3)\}$. [b] HA is the angle formed between the planes defined by C1/C2/C3 and C1/C3/C3a/C7a. [c] FA is the angle formed between the planes defined by C1/C2/C3 and C3a/C4/C5/C6/C7/C7a.

"sideways slippage": Ni1−C11 = 2.128(2) Å > Ni1−C13 = 2.052(3) Å; Ni2−C21 = 2.135(2) Å > Ni1−C23 = 2.038(3) Å. In the case of complex **3**, however, one of the two independent molecules shows the opposite trend: Ni1−C11 = 2.0946(16) Å < Ni1−C13 = 2.1208(16) Å. This unusually longer Ni−C13 distance is presumably caused by the steric repulsion between PPh_3 and its neighboring $SiMe_3$ group; we suspect that the reason why a similar elongation is not observed for the corresponding bond in molecule 2 (Ni2−C23) is related to the greater out-of-plane bending of Si22 in this molecule, which tends to minimize steric repulsions between the adjacent $SiMe_3$ and PPh_3 groups (vide infra).

The effect of the aforementioned steric repulsion is most evident in the out-of-plane bending of the $SiMe_3$ group adjacent to PPh_3 in **3**. Thus, Si12 and Si22 atoms are bent out of the plane of Ind[16] (away from PPh_3) by 0.56 and 0.65 Å, respectively; in comparison, the out-of-plane bending of the $SiMe_3$ group adjacent to Cl is much smaller (0.10 and 0.23 Å in **3** and 0.15 and 0.16 Å in **2**). The steric repulsion between PPh_3 and the adjacent $SiMe_3$ group is also manifested in the relative sizes of the P−Ni−C3 and P−Ni−Cl angles: the former is larger in **3** (ca. 110° and 107°) relative to **2** (ca. 100° and 99°), while the latter is smaller in **3** (ca. 88° and 91°) relative to **2** (ca. 97° and 95°). The Ni−C5 ring distances in **2** (average ca. 1.82 Å) and **3** (average ca. 1.84 Å) are also somewhat longer than the corresponding distance of ca. 1.81 Å in $IndNi(PPh_3)Cl$[13a] and (1-Me-Ind)$Ni(PPh_3)Cl$.[13b] On the other hand, the effect of steric factors on the Ni−P bond distances is less clear-cut. Thus, the Ni−P bond distances in both molecules of **2** (2.182−2.189 Å) and in molecule 1 of **3** (Ni1−P1= 2.1841(5)) are quite similar to the corresponding distances in the complexes R-$IndNi(PPh_3)Cl$ (ca. 2.180−2.186 Å for R = H,[13a] Me,[13b] $(CH_2)_3N$(*t*-Bu)H,[9a] CH_2NMe_2[9b]), but the Ni−P distance in molecule 2 of **3** is somewhat longer (Ni2−P2 = 2.1984(5) Å).

Altogether, the above findings show that the proximity of the $SiMe_3$ and PPh_3 groups in **3** affects the solid state structure primarily through angular deformations, whereas in solution it increases the kinetic lability of PPh_3. The influence of Ind substituents on the catalytic activities of **2** and **3** is described in the following section.

Catalytic Reactivities of 2 and 3. We have reported previously that combining (1-Me-Ind)$Ni(PPh_3)Cl$ (**1**) and $NaBPh_4$ produces an active catalyst for the addition of $PhSiH_3$ to a number of olefins and ketones. With styrene, for instance, this system gives PhCH(Me)-($SiPhH_2$) in up to 80 catalytic turnovers (eq 1).[7] We have

(2) 

(1)

examined the activities of complexes **2** and **3** for catalyzing this reaction as a means for evaluating the influence of Ind substituents on reactivities. Initial tests were conducted under the same conditions that were used in our previous studies, i.e., a Ni:$NaBPh_4$:$PhSiH_3$:styrene ratio of 1:10:100:100 and a reaction time of 16−24 h at room temperature. The results of these tests showed that complexes **2** and **3** give the same product as **1**, with virtually none of the other regioisomer being detected by NMR. The final yields (69−77%) were similar for all three precatalysts when the reaction was run over 5−21 h (Table 3; compare runs 1a−c, 2a−c, and 3a−c), which implies that all three complexes have comparable reactivities for the addition of $PhSiH_3$ to styrene.

Next, we examined the catalytic activities of the precatalysts in the presence of excess $PhSiH_3$, for the following reason. An important side-reaction that occurs to different degrees during these Ni-catalyzed hydrosilylation reactions is the dehydrogenative coupling of

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[16] The central C atom (C2) was not included in the definition of this plane, because it is often out-of-plane and puckered.

Table 3. Addition of $PhSiH_3$ to Styrene Catalyzed by (R_n-Ind)Ni(PPh_3)Cl

run	Ni:$NaBPh_4$:$PhSiH_3$:styrene	R-Ind	time (h)	yield (%)
1a	1:10:100:100	1-Me-Ind	2	66
1b			5	69
1c			16	73
2a	1:10:100:100	1-$SiMe_3$-Ind	2	49
2b			5	75
2c			18	77
3a	1:10:100:100	1,3-$(SiMe_3)_2$-Ind	2	71
3b			5	74
3c			21	76
4	1:10:150:100	1-Me-Ind	5	>95
5	1:10:150:100	1-$SiMe_3$-Ind	5	>95
6	1:10:150:100	1,3-$(SiMe_3)_2$-Ind	5	92
7	1:0:100:100	1-Me-Ind	5	8
8	1:0:100:100	1-$SiMe_3$-Ind	5	23
9	1:0:100:100	1,3-$(SiMe_3)_2$-Ind	5	69
10	1:0:150:100	1-Me-Ind	5	7
11	1:0:150:100	1-$SiMe_3$-Ind	5	56
12	1:0:150:100	1,3-$(SiMe_3)_2$-Ind	5	82

$PhSiH_3$ (eq 2).[17] Since this side-reaction depletes the amount of silane available for the hydrosilylation reaction, we reasoned that using an excess of $PhSiH_3$ should help improve the yields of the hydrosilylation reaction. As an approximate measure of the extent to which this side reaction is promoted by each of the complexes under study, we reacted $PhSiH_3$ alone with the Ni precursors and $NaBPh_4$. Monitoring the evolution of gas[18] from these reactions showed that the rate of $PhSiH_3$ oligomerization follows the order **3** > **2** > **1**; therefore, we expected that using excess silane should have a greater influence on the hydrosilylation activities of **3** and **2**. Interestingly, however, tests showed that the presence of excess silane improved the hydrosilylation activities of all three complexes more or less equally (runs 4–6). It is not clear why the presence of excess silane improves the reaction of **1** to the same extent as those of **2** and **3**, since the above-mentioned side-reaction does not take place to a significant extent with **1**. Nevertheless, the comparable catalytic activities of complexes **1**–**3** show that the increased steric congestion on the Ind ligand does not have a favorable effect on the catalytic hydrosilylation reaction under these conditions.

The absence of a strong correlation between the steric congestion on Ind and the outcome of the hydrosilylation catalysis in the presence of $NaBPh_4$ prompted us to consider whether Ind substituents might have a greater influence on the reactivities in the absence of initiator. In principle, the highly electrophilic, coordinatively unsaturated Ni center in the cationic intermediates $[(R\text{-}Ind)Ni(PPh_3)]^+$ generated from **1**–**3** would be unlikely to undergo PPh_3 dissociation; moreover, these species should be much more reactive toward $PhSiH_3$ than the neutral precursors.[19] Thus, the presence of bulky Ind substituents might exert little influence over the reactivity of the cationic intermediates with $PhSiH_3$. On the other hand, phosphine dissociation should occur to a greater extent from the neutral precursor, so that the precursor that most readily forms the coordinatively unsaturated intermediate (R-Ind)Ni(Cl) in the absence of cationic initiators should promote the catalysis more effectively.

To test the above hypothesis, we carried out the hydrosilylation reaction in the absence of $NaBPh_4$ and found that the catalysis does indeed proceed with the unactivated neutral precursors. Thus, complex **3** was found to give the same product in almost the same yield whether or not $NaBPh_4$ was present in the reaction; on the other hand, complexes **1** and **2** gave much lower yields in the absence of the initiator (compare runs 1b, 2b, and 3b to runs 7–9). Using excess $PhSiH_3$ improved the yields of the hydrosilylation reactions catalyzed by **2** and **3** in the absence of initiator, but the catalysis by **1** was not affected (runs 10–12). These results show that complexes **2** and **3** are effective, single-component precatalysts for the addition of $PhSiH_3$ to styrene; the order of catalytic activities observed in the uninitiated reactions (**3** > **2** ≫ **1**) appears to reflect the greater PPh_3 dissociation occurring with **3**, which is presumably a function of the steric congestion on Ind.[20]

Proposed Mechanisms. The above findings have a number of mechanistic implications. First, the fact that both the uninitiated and initiated reactions give the same final product implies a common intermediate in these two catalytic systems. We propose that the catalytically active intermediate common to both catalytic systems is the species IndNi(H)L wherein L is either PPh_3 or one of the substrates (Scheme 2). This species can form via two different paths, depending on whether the cationic initiator is used: (a) in the presence of $NaBPh_4$, the in-situ generated cationic intermediate can abstract a hydride from $PhSiH_3$ to give the Ni-H species, in addition to a silylium ion;[21] (b) in the absence of initiator, the phosphine-dissociated species IndNi(Cl) can undergo a concerted σ-bond metathesis reaction with $PhSiH_3$ to form the putative Ni-H intermediate.[22]

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(17) Previous studies have shown that combining (1-Me-Ind)Ni(PPh_3)Cl with cationic initiators such as $AlCl_3$ generates species that homologate $PhSiH_3$ to $(PhSiH)_n$ (M_w < 1000): ref 4.

(18) The identity of the gas evolved from the reaction of $PhSiH_3$ with our complexes has been confirmed to be H_2 (using both GC and Raman spectroscopy) on several occasions during our studies on the oligomerization and hydrosilylation reactions. In the latter reactions, the evolution of gas subsides partially when the olefin is added. It is important to note that we have never detected the presence of SiH_4, the only other gas that is likely to evolve in the reactions of $PhSiH_3$; this is consistent with our findings that silane redistribution reactions do not occur to any appreciable extent in our systems.

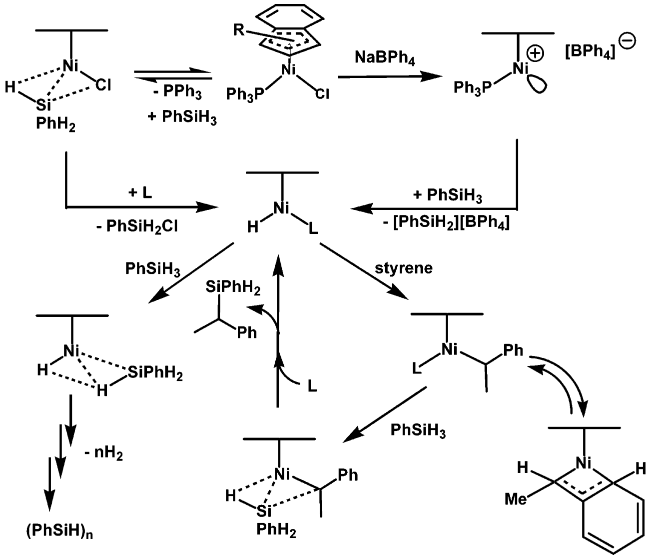
(19) It should be noted that the cationic intermediates can also react with styrene, but this reaction is much more sluggish than that with $PhSiH_3$; thus, heating mixtures of styrene and the in-situ-generated cations over several hours gives poly(styrene), but the presence of $PhSiH_3$ in the reaction mixture suppresses the polymerization in favor of the hydrosilylation.

(20) Throughout this discussion, we have assumed that the steric effects of the $SiMe_3$ groups are much more important than their inductive effects. In principle, this assumption is tentative because we have not made systematic measurements on the inductive effects of Ind substituents in these complexes. However, previous studies of the reduction potentials of these complexes have indicated that the electronics of the Ni center is primarily affected by the ligands X and PR_3 (e.g., Me ≫ Cl; PMe_3 > PCy_3 > PPh_3), while Ind substituents seem to have little influence over reduction potentials.

(21) In our original report on the Ni-catalyzed hydrosilylation of olefins (ref 7) we have presented some indirect evidence for the likelihood that the coordinatively unsaturated Ni cations under discussion are sufficiently electrophilic to abstract H^- from silanes. The fate of the silylium ion is not known yet, but on the basis of the ^{31}P NMR spectrum of a catalytic reaction mixture we have proposed that they might give rise to phosphonium species such as $[Ph_3P\text{-}(SiPhH_2)][BPh_4]$.

(22) We cannot rule out the possibility of a stepwise addition/elimination pathway between $PhSiH_3$ and the phosphine-dissociated species IndNi(Cl), but the requirement in these reactions for Ni(IV) intermediates makes this alternative less likely than the proposed concerted pathway.

Scheme 2



The M-Cl/Si-H exchange proposed above is well-precedented in the reactivities of precursors such as platinic acid or Wilkinson's catalyst and forms the basis of the well-developed catalytic chemistry of these complexes (hydrosilylation, Si−Si bond formation, etc.). More pertinent precedents involving Ni−Cl precursors also exist in the early studies of Kumada and coworkers,[23] which showed that reacting a number of bis(phosphine)$NiCl_2$ complexes with $HSiMe_nCl_{3-n}$ ($n = 0$, 1, 2) leads to Ni(0) species, presumably via Ni-H intermediates. Therefore, we believe that the Ni-Cl precursors under discussion, and in particular the in-situ-generated phosphine-dissociated intermediates, react directly with $PhSiH_3$ to give the analogous Ni-H complexes and $PhSiH_nCl_{3-n}$.[24]

The proposed common intermediate, IndNi(H)L, can then promote either the hydrosilylation reaction (L = styrene) or the silane oligomerization (L = $PhSiH_3$), as illustrated in Scheme 2. An alternative pathway, not shown in Scheme 2, would involve a reductive elimination of Ind-H from the Ni-H intermediate to generate an Ind-free Ni(0) species that could promote both catalytic reactions. This scenario would help rationalize the independence of the hydrosilylation activities from the Ind substituent and is consistent with our preliminary findings that $Ni(PPh_3)_4$ can catalyze these reactions, albeit less efficiently than the indenyl nickel precursors.[7]

Conclusion

The results presented in this report demonstrate that the complexes (R-Ind)Ni(PPh_3)Cl can catalyze the hydrosilylation of styrene in the absence of a cationic initiator and that the steric bulk of the Ind substituent affects the catalytic activities in these reactions. The influence of the R-substituent is likely due to its role in inducing the dissociation of the PPh_3 ligand, a step that was found to be rather facile for complex **3**. The direct reaction of $PhSiH_3$ with **3** is reminiscent of the reaction of (1-Me-Ind)Ni(PPh_3)Me with $PhSiH_3$ to give CH_4 and (by inference) the reactive Ni-SiH_2Ph derivative.[25] Interestingly, while the nature of the Ni-X moiety is important for the relative rate of the direct metathetic reaction between IndNi$(PPh)_3$X and $PhSiH_3$, the Ni-Me derivative being much more reactive than the Ni-Cl derivative, the more important factor seems to be the lability of the PPh_3 ligand, which is significantly dependent on the Ind-substituent. As a result, the sterically bulky Ni-Cl derivatives such as **3** appear to be more reactive toward $PhSiH_3$ than their less bulky Ni-Me counterparts such as (1-Me-Ind)Ni(PPh)Me.

The discovery that bulky Ind ligands can preclude the need for initiators simplifies the protocol for the catalytic reactions and might facilitate other reactions. As mentioned earlier, complex **3** catalyzes the oligomerization of $PhSiH_3$ to $(PhSiH)_n$ in the absence of any initiators/activators; we are currently investigating this reactivity.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques and a glovebox. Dry, oxygen-free solvents were employed throughout. $Ni(PPh_3)_2Cl_2$ was prepared from $NiCl_2 \cdot 6H_2O$ and PPh_3. $PhSiH_3$ was prepared from $PhSiCl_3$ and $LiAlH_4$ according to a published procedure.[26] The preparation of Li[($SiMe_3$)-Ind] has been reported previously (ref 11); the same procedure was used for the preparation of Li[1,3-$(SiMe_3)_2$-Ind]. Styrene was purchased from Aldrich, passed through an alumina column, dried over CaH_2, and distilled under vacuum prior to use. All other chemicals used in the experiments were obtained from commercial sources and used as received. A Bruker ARX 400 spectrometer was used for recording ^1H (400 MHz), $^{13}C\{^1H\}$ (100.56 MHz), and $^{31}P\{^1H\}$ NMR (161.92 MHz). The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal).

1-($SiMe_3$)-IndNi(PPh_3)Cl (2). An Et_2O solution (80 mL) of Li[($SiMe_3$)-Ind] (690 mg, 3.55 mmol) was added dropwise to a stirring suspension of $Ni(PPh_3)_2Cl_2$ (2.575 g, 3.93 mmol) in Et_2O (30 mL) at rt. The reaction mixture was stirred for 30 min after the addition. Filtration and evaporation under vacuum gave a residual solid, which was washed with hexane (2 × 20 mL) and then extracted four times with a 1:5 mixture of ether/hexane (total volume of extracts 120 mL). Evaporation of this solution gave the final product (1.49 g, 77% yield). ^1H NMR (C_6D_6): 7.75 (m, PPh_3), 7.59 (d, $^3J_{H-H} = 8$, H7), 7.21 and 7.03 (m, PPh_3), 7.20 (t, $^3J_{H-H} = 8$, H6), 6.93 (t, $^3J_{H-H} = 8$, H5), 6.65 (d, $^3J_{H-H} = 2$, H2), 6.39 (d, $^3J_{H-H} = 8$, H4), 3.54 (m, H3), 0.66 (s, Si$(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.56 MHz): 134.30 (d, $^2J_{C-P} = 11.1$ Hz, C_{ortho}), 132.00 (d, $^1J_{C-P} = 43.7$ Hz, C_{ipso}), 130.53 (s, C_{para}), 129.08 (s, C_{7a}), 128.50 (d, $^3J_{C-P} = 10.4$ Hz, C_{meta}), 127.31 (s, C6), 126.75 (s, C3a), 125.82 (s, C5), 120.91 (s, C7), 117.73 (s, C4), 109.18 (s, C2), 95.8 (d, $^2J_{C-P} = 13.9$ Hz, C1), 72.74 (s, C3), −0.61 (s, $(CH_3)_3$Si). $^{31}P\{^1H\}$ NMR (C_6D_6): 28.60 (br). Anal. Calcd for $C_{30}H_{30}Cl_1Ni_1P_1Si_1$: C, 66.26; H, 5.56. Found: C, 66.06; H, 5.54.

1,3-$(SiMe_3)_2$-IndNi(PPh_3)Cl (3). An Et_2O solution (100 mL) of Li[1,3-$(SiMe_3)_2$-Ind] (1.07 g, 4.01 mmol) was added dropwise to a stirring suspension of $Ni(PPh_3)_2Cl_2$ (3.42 g, 5.22

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(23) (a) Kiso, Y.; Kumada, M.; Tamao, K.; Umeno, M. *J. Organomet. Chem.* **1973**, *50*, 297. (b) Kiso, Y.; Kumada, M.; Maeda, K.; Sumitani, K.; Tamao, K. *J. Organomet. Chem.* **1973**, *50*, 311.

(24) It is worth noting that the silane-induced reductions of the bis(phosphine)$NiCl_2$ complexes studied by Kumada (ref 23) require high temperatures (90−120 °C) and long induction periods (15−20 h), in contrast to the relatively facile catalysis promoted by complex **3**; this difference is presumably related to the more facile phosphine dissociation from the latter.

(25) Fontaine, F.-G.; Zargarian, D. *Organometallics* **2002**, *21*, 401.

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mmol) in Et_2O (30 mL) at rt. The reaction mixture was stirred for half an hour after the addition and filtered, and the filtrate was evaporated under vacuum. The resulting solid was extracted with a 1:5 mixture of ether/hexane (200 mL), and the extracts were concentrated to approximately 10 mL; this led to the precipitation of a dark red powder, which was isolated by filtration and dried under vacuum (1.48 g, 60% yield). ^1H NMR (C_6D_6): 7.78 (br, PPh_3), 7.19−7.16 (m, aromatic protons of Ind), 6.99−6.95 (m, aromatic protons of Ind and PPh_3), 0.19 (s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ ($CDCl_3$): 134.44 (d, $^2J_{P-C}$ = 11.3 Hz, C_{ortho}), 129.86 (C_{para}), 127.82 (C_{meta}), 125.81 (C3a and C7a), 120.59 and 120.03 (C5, C6, C4, and C7), 115.91 (C1 and C3), 88.18 (C2), −0.71 (−$SiMe_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): 27.84 (br). Anal. Calcd for $C_{33}H_{38}Cl_1Ni_1P_1Si_2$: C, 64.35; H, 6.22. Found: C, 63.45; H, 6.01.

General Procedure for Ni-Catalyzed Hydrosilylation of Styrene. C_6D_6 mixtures of the Ni complex (5 μmol), styrene (500 μmol, ca. 1.0−1.5 M), $PhSiH_3$ (500 or 750 μmol), and $NaBPh_4$ (50 μmol) were agitated in an ultrasonic bath throughout the reaction time and analyzed by ^1H NMR spectroscopy over various time intervals. The yields were determined from a calibration curve prepared as follows. Pure samples of the hydrosilylation product were obtained from large-scale reactions, purified by distillation, and used for making mixtures with styrene and $PhSiH_3$ in proportions corresponding to 5−95% yields. The ^1H NMR spectra of these mixtures were then recorded, and the integrations of the appropriate signals for each component ($PhC(CH_3)H(SiH_2Ph)$, $PhCH{=}CH_2$, and $PhSiH_3$) were plotted against the concentration ratios. The resulting plot was linear in the range corresponding to yields below 70−80%, while the higher yield values seemed to follow a logarithmic function. Fortunately, the entire data set could be fitted to a Lorentzian function that allowed accurate determination of yields ranging from 5 to 95% from NMR integration ratios. The yields obtained from this calibration curve should be considered accurate to ±5%.

X-ray Crystallographic Studies. Crystals suitable for X-ray diffraction were obtained by recrystallization from an ether/hexane solution (for **2**) or by slow evaporation of a hexane solution (for **3**). The crystallographic data were collected on a Bruker AXS SMART 2K diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at 220(2) K, using SMART.[27] Cell refinement and data reduction were done using SAINT.[28] A SADABS[29] absorption correction was applied. The structures were solved by direct methods using SHELXS97[30] and difmap synthesis using SHELXL97;[31] the refinements were done on F^2 by full-matrix least squares. The PPh_3 and Cl groups in **2** are disordered. Details of data collection and refinement are listed in Table 1, while a selection of structural parameters is listed in Table 2. Complete crystallographic data for these structures are included in the Supporting Information.

Acknowledgment. This work was made possible thanks to the financial support provided by the Natural Sciences and Engineering Research Council of Canada (operating grants to D.Z. and graduate scholarships to S.B.) and Université de Montréal (scholarships to C.S.-S.).

Supporting Information Available: Complete details of the X-ray analysis of **2** and **3**, including tables of crystal data, collection and refinement parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atoms. This information is available free of charge via the Internet at http://acs.pubs.org.

OM0494420

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