Phenylsilane dehydrocoupling and addition to styrene catalyzed by (R-indenyl)Ni(phosphine)(methyl) complexes¹

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Abstract: This report describes the synthesis and characterization of the Ni–Me complexes (R-indenyl)Ni(PR'₃)Me (R = 1-*i*-Pr, 1-SiMe₃, and 1,3-(SiMe₃)₂; R'= Me, Ph) and outlines their catalytic reactivities in the dehydrogenative oligomerization of PhSiH₃ and its addition to styrene in the absence of initiators/activators. Observation of higher hydrosilylation activities for PPh₃-based compounds featuring bulky substituents on the indenyl ligand confirms earlier suggestions that phosphine dissociation is an important component of the catalytic cycle for this reaction. In contrast, oligomerization of PhSiH₃ is more facile with PMe₃-based precursors and independent of the steric bulk of the indenyl ligand, implying that this reaction does not involve phosphine dissociation. These conclusions are consistent with the variable-temperature ¹H NMR spectra of {1,3,-(SiMe₃)₂-indenyl}Ni(PR'₃)Me and various structural parameters observed in the solid-state structures of {1,3,-(SiMe₃)₂-indenyl}Ni(PPh₃)Me, {1,3,-(SiMe₃)₂-indenyl}Ni(PMe₃)Cl, and {1-SiMe₃-indenyl}Ni(PMe₃)Me.

Key words: nickel-indenyl complexes, hydrosilylation, hydrosilane oligomerization.

Résumé : Ce rapport présente la synthèse et la caractérisation des complexes (R-indényle)Ni(PR'₃)Me (R = 1-*i*-Pr, 1-SiMe₃ et 1,3-(SiMe₃)₂; R'= Me et Ph) ainsi que la réactivité catalytique de ces composés dans l'oligomérisation déshydrogénative du PhSiH₃ et dans son addition au styrène en absence d'un initiateur ou d'un activateur. L'observation des plus grandes activités d'hydrosilylation chez les composés à base de PPh₃ et portant des substituants volumineux sur le ligand indényle indique que le cycle catalytique implique la dissociation de la phosphine. D'ailleurs, l'oligomérisation du PhSiH₃ est plus facile avec les composés à base de la PMe₃ et indépendante de la taille des substituents de l'indényle, ce qui semble indiquer que cette réaction n'implique pas la dissociation de la phosphine. Ces conclusions sont concordantes avec d'autres observations tirées des spectres RMN ¹H à températures variables des composés {1,3,-(SiMe₃)₂-indényle}Ni(PPh₃)Me, {1,3,-(SiMe₃)₂-indényle}Ni(PMe₃)Cl et {1-SiMe₃-indényle}Ni(PMe₃)Me.

Mots-clés : composés nickel-indényles, hydrosilylation, oligomérisation des hydrosilanes.

[Traduit par la Rédaction]

Introduction

Recent reports have shown that the complexes IndNi(L)X (Ind= indenyl and its substituted derivatives; L= neutral ligands such as phosphines or *N*-heterocyclic carbenes; X= anionic ligands such as halides, alkyls, triflate, and so forth) (1) promote the polymerization of ethylene (2), alkynes (3), or PhSiH₃ (4) in the presence of activators such as methyl-

Received 1 May 2008. Accepted 7 July 2008. Published on the NRC Research Press Web site at canjchem.nrc.ca on 24 October 2008.

This paper is dedicated to Professor Richard Puddephatt for his great contributions in Organometallic Chemistry.

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¹This article is part of a Special Issue dedicated to Professor R. Puddephatt.

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aluminoxanes. The in situ activation of these precursors can also be done using cationic initiators, such as AgBF₄, NaBPh₄, or AlCl₃, all of which generate the electronically unsaturated and highly electrophilic cations [IndNi(PR₃)]⁺ (5); these intermediates 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(PPh₃)(OSO₂CF₃) (8) or [(η^5 , η^1 -Ind^NR₂)Ni(PR₃)]⁺ (^ = various side chains tethering the amine moiety to the Ind ligand) (9), or by heating the complexes [IndNi(PR₃)₂]⁺ bearing bulky phosphine ligands (10).

A number of recent studies have shown that of the reactions promoted by $IndNi(PR_3)X$, only those involving hydrosilanes can proceed in the absence of activators/initiators. Thus, the Ni–Me complexes (1-Me-Ind)Ni(PR₃)Me (R = Me, Ph, Cy) act as single-component precursors for the dehydrogenative oligomerization of PhSiH₃ (11), whereas the Ni–Cl complexes (R-Ind)Ni(PPh₃)Cl promote the addition of PhSiH₃ to styrene in the absence of any activator/initiator (12). The available mechanistic information indicates that these reactions are sensitive to the steric bulk and (or) Scheme 1.



nucleophilicity of the phosphine ligand, the rates following the order $PMe_3 > PPh_3 > PCy_3$ for silane oligomerization (11) and $PPh_3 > PMe_3$ for the hydrosilylation (7). The latter reaction is also favoured by compounds featuring bulkier indenyl ligands (1,3-(SiMe_3)_2-Ind > 1-SiMe_3-Ind > 1-Me-Ind) (13). These and a number of other observations led us to propose that the hydrosilylation requires the dissociation of the phosphine ligand (12).

As a continuation of our studies on the structure–activity relationships in Ni–indenyl complexes, we have prepared a new series of IndNi(PR₃)Me complexes and studied their structures and reactivities in the oligomerization of PhSiH₃ and its addition to styrene as a function of Ind substituents and the phosphine ligands. This report presents the synthesis, characterization, and reactivity studies for the complexes $(1-\text{SiMe}_3-\text{Ind})\text{Ni}(\text{PPh}_3)\text{Me}$ (1), $\{1,3-(\text{SiMe}_3)_2-\text{Ind}\}\text{Ni}(\text{PPh}_3)\text{Me}$ (2), $\{1,3-(\text{SiMe}_3)_2-\text{Ind}\}\text{Ni}(\text{PMe}_3)\text{Cl}$ (3), $(1-\text{SiMe}_3-\text{Ind})\text{Ni}(\text{PMe}_3)\text{Me}$ (4), $\{1,3-(\text{SiMe}_3)_2-\text{Ind}}\text{Ni}(\text{PMe}_3)\text{Me}$ (5), and $\{1-i-\text{Pr-Ind}\}\text{Ni}(\text{PMe}_3)\text{Me}$ (6), including the X-ray diffraction studies for 2–4.

Results and discussion

Syntheses

Reaction of (R-Ind)Ni(PPh₃)Cl with MeMgCl gave the corresponding Ni–Me complexes in moderate yields (Scheme 1; R = 1-SiMe₃ (1, 73%), 1,3-(SiMe₃)₂-Ind (2, 66%)), but this approach did not work well for the preparation of the analogous PMe₃ complexes because of the difficult purification of the analogous Ni–Cl precursors. For instance, reacting equimolar quantities of Li[1,3-(SiMe₃)₂-Ind] and Ni(PMe₃)₂Cl₂ gave the desired {1,3-(SiMe₃)₂-Ind}Ni(PMe₃)Cl (3) in ~50% crude yield. As noted previously, however, the main challenge in the synthesis of Ni–indenyl compounds bearing PMe₃ is avoiding a side reaction that generates Ni(PMe₃)₄ and reducing the yield of the de-

sired product (14). Removal of the PMe₃ released during the synthesis by periodic pumping of the reaction mixture helps minimize this decomposition pathway, but does not eliminate it altogether. In the case of **3**, the presence of small quantities of Ni(PMe₃)₄ in the reaction mixture complicated the purification, since both species appear to be highly soluble in most solvents, including hexane. However, solution NMR spectra and X-ray analysis of crystals obtained by removal of the oily impurities helped establish the identity of this compound unambiguously (vide infra).

The difficult purification of **3** encouraged us to seek an alternative pathway to the desired Ni–Me compounds. We found that the direct reaction of Li[R-Ind] with $(PMe_3)_2NiCl(Me)$ gave reasonable yields of $(R-Ind)Ni(PMe_3)Me$ (Scheme 1; R = 1-SiMe₃ (**4**, 87%), 1,3-(SiMe_3)_2-Ind (**5**, 64%), *i*-Pr (**6**, 77%)). The purification of **5** was also challenging, but **4** and **6** were obtained in good purity. The characterization of compounds **1**–**6** by solution NMR spectra and, in the case of **2**–**4**, by X-ray diffraction studies was straightforward, as described below.

NMR characterization

All of the complexes showed a single resonance in their ${}^{31}P{}^{1}H$ NMR spectra at chemical shifts that are characteristic of each type of complex. Thus, **1** and **2** gave singlets at ~47 and 44 ppm, respectively (cf. 48 ppm for (1-Me-Ind)Ni(PPh₃)Me) (15), **3** gave a singlet at ~ -18 ppm (cf. -11 ppm for (1-Me-Ind)Ni(PMe₃)Cl) (14), and **4–6** gave singlets at ~ -9 (**5**) and -4 ppm (**4** and **6**) (cf. -3.7 ppm for (1-Me-Ind)Ni(PMe₃)Me) (11).

The ¹H NMR spectra showed a number of characteristic signals for the Ni–Me moiety (~ -0.7 ppm), the SiMe₃ substituents (~0.3-0.5 ppm), the PMe₃ ligand (~0.6-0.8 ppm), and H2 of the Ind ligands (~6.1-6.7 ppm). It is interesting to note that methylation of the Ni–Cl bond shifts δ H2 upfield in {1,3-(SiMe₃)₂-Ind}Ni(PMe₃)X (from 6.72 to 6.13 ppm), {1,3-(SiMe₃)₂-Ind}Ni(PPh₃)X (from ~7 to 6.33 ppm), and (1-SiMe₃-Ind)Ni(PPh₃)X (from 6.65 to 6.42 ppm). This upfield shift likely arises from the greater delocalization induced in the five-membered ring moiety of the Ind ligands in Ni–alkyl vs. Ni–halide derivatives (1, 15). Finally, the phenyl rings of the PPh₃ ligand exert some shielding influence on H3 of the Ind ligand that is evident from a comparison of the δ H3 in **1** (4.23 ppm) vs. **4** (4.62 ppm) and **6** (4.44 ppm).

We studied the variable-temperature ¹H NMR spectra of 2 and 5 (Fig. 1) and compared them to those of $\{1,3-(SiMe_3)_2-$ Ind Ni(PPh₃)Cl to probe the issue of phosphine lability in the Ni-Me derivatives. It is worthwhile to recall that the low-temperature spectra of {1,3-(SiMe₃)₂-Ind}Ni(PPh₃)Cl showed a gradual sharpening of the ³¹P{¹H} signal as well as the splitting of the ¹H singlet due to the Si(CH₃)₃ protons (Fig. 1*a*). The relatively small ΔG^{\ddagger} value of ~10 kcal/mol (1 cal = 4.184 J) calculated for this exchange process, as well as a number of parameters from the solid-state structure of {1,3-(SiMe₃)₂-Ind}Ni(PPh₃)Cl, convinced us that the dynamic exchange observed for this compound was caused by a rapid dissociation/re-association of the PPh₃ ligand as opposed to the hindered rotation of the 1,3-(SiMe₃)₂-Ind ligand (12). The lability of the PPh₃ ligand was ascribed to the significant steric interaction with the SiMe₃ substituents.

Fig. 1. The variable-temperature ¹H NMR spectra (toluene- d_8 , 400 MHz) for {1,3-(SiMe_3)₂Ind}Ni(PPh_3)Cl (*a*), {1,3-(SiMe_3)₂Ind}-Ni(PPh_3)Me (**2**, *b*), and {1,3-(SiMe_3)₂Ind}Ni(PMe_3)Me (**5**, *c*).



In contrast to the above discussed temperaturedependence of the $\{1,3-(SiMe_3)_2-Ind\}Ni(PPh_3)Cl$ spectra, low-temperature spectra of the Ni–Me derivatives **2** and **5** showed no change in the linewidths of the ³¹P signals or the multiplicities of the Si(CH₃)₃ singlets (Figs. 1*b* and 1*c*)

down to -70 °C. These observations can be understood when we consider that methylation of the Ni–Cl bond is anticipated to reinforce the Ni–P bond strength and increase the delocalization of bonding in the five-membered-ring moiety of the Ind ligands; these changes would, in turn, lead to less facile phosphine dissociation and a less hindered Ind rotation. Since the NMR spectra indicate that the exchange process responsible for the equivalence of the SiMe₃ substituents in **2** and **5** is faster than the corresponding process in the Ni–Cl complex {1,3-(SiMe₃)₂-Ind}Ni(PPh₃)Cl, we conclude that these observations are more consistent with the rapid rotation of the 1,3-(SiMe₃)₂-Ind ligand as opposed to a dissociation/re-association of PR₃. The lower lability of their phosphine ligands should influence the hydrosilylation activities of the Ni–Me compounds (vide infra).

Solid-state structures

Single crystals obtained for 2-4 allowed us to examine their solid-state structures, which were found to be free of disorder and refined to a good degree of precision, as reflected in the *R* values of 3.77% (2), 4.16% (3), and 3.62%(4). The ORTEP diagrams for these compounds are shown in Fig. 2, and a selection of structural parameters is listed in Table 1; the full list of structural refinement parameters and the crystal data are provided as Supplementary data.⁴

In all three 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 of ~67°. As commonly observed in this family of complexes (1), the Ind–Ni interaction in **2–4** is primarily through the allylic carbons, while the Ni–C bond distances for the benzo carbons are longer. This "slippage" away from an ideal η^5 hapticity is attributed to the tendency of Ni(II) to favour forming 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) and caused by the unequal trans influences of the PR₃ and X ligands (X= halides, phthalimidato, thiolato, triflato, and so forth). Little or no 'sideways slippage" is evident in the PMe₃ compounds 3 and 4 (Δ Ni-C(1,3) is within 6 esd values), which is consistent with the similar trans influences of PR₃ and Me ligands (1). On the other hand, complex 2 exhibits fairly different Ni–C bond lengths (Δ Ni–C(1,3) = 50 × esd). We suspect that this anomalous elongation of the Ni-C3 bond in 2 is due primarily to the steric repulsion between PPh₃ and its neighbouring SiMe₃ group. This repulsion is also manifested in the greater C3-Ni-P angle in 2 (111°) compared with 3 (106°) and 4 (104°) . Similar observations have been noted for the analogous complexes $\{(SiMe_3)_n - Ind\}Ni(PPh_3)Cl (n =$ 1 or 2) (12).

Finally, the shorter Ni–P bond distance in 4 relative to 2 is consistent with both the greater nucleophilicity of PMe_3 and the larger Tolman cone angle for PPh₃, whereas the shorter

⁴ Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3832. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 686331, 686332, and 686333 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 2. ORTEP diagrams for complexes 2 (*a*), 3 (*b*), and 4 (*c*). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.



Ni–P bond in 4 relative to 3 reflects the tendency of the Ni–alkyl compounds to form stronger Ni–P interactions compared to their Ni–Cl counterparts (17). To the extent that solid state bond distances can correlate with the kinetic labilities of phosphines, the shorter Ni–P distance in 4 signals lower hydrosilylation activities for this complex (vide infra).

Table 1. Structural parameters for complexes 2–4.

	2 (X= C8)	3 (X= Cl)	4 (X= C8)
Ni—C(1)	2.1013(14)	2.108(3)	2.0999(15)
Ni-C(2)	2.0910(14)	2.056(2)	2.0812(16)
Ni—C(3)	2.1763(14)	2.097(3)	2.1098(16)
Ni—C(3a)	2.3015(14)	2.308(3)	2.3075(16)
Ni—C(7a)	2.2700(15)	2.313(3)	2.2887(15)
Ni—X	1.9591(16)	2.1915(8)	1.9456(19)
Ni—P	2.1343(4)	2.1671(8)	2.1129(5)
Si(1) - C(1)	1.8634(15)	1.873(3)	1.8662(16)
Si(2)—C(3)	1.8684(16)	1.883(3)	
C(1)—C(2)	1.428(2)	1.412(4)	1.431(2)
C(2)—C(3)	1.423(2)	1.418(4)	1.404(2)
C(1)—C(7a)	1.466(2)	1.470(5)	1.463(2)
C(3)—C(3a)	1.457(2)	1.469(4)	1.440(3)
C(3a)—C(7a)	1.434(2)	1.422(5)	1.428(2
X-Ni-C(1)	93.82(6)	96.64(8)	98.66(8)
X–Ni–P	88.07(5)	90.85(3)	90.05(7)
C(1)–Ni–P	173.24(5)	165.21(10)	170.21(5)
X-Ni-C(3)	160.13(6)	163.36(8)	165.32(8)
P-Ni-C(3)	111.60(4)	105.71(8)	104.47(5)
C(1)–Ni–C(3)	66.98(6)	67.63(11)	66.70(6)
$\Delta Ni - C^a$ (Å)	0.15	0.21	0.19

Catalytic reactivities

The hydrosilylation activities of the Ni-Me complexes were examined for comparison with those of the corresponding Ni–Cl precursors. In addition, we hoped to determine the influence of factors such as nature of the phosphine ligand and the Ind substituents on these reactivities. The addition of PhSiH₃ to styrene was selected as a model system to allow comparison to our previous studies. The catalysis is initiated by the direct reaction of PhSiH₃ with the Ni–Me moiety, obviating the need for an activator/initiator. The main product of this reaction, PhCH(Me)(SiPhH₂), arises from regioselective (>95%) α -addition of the silvl moiety (eq. [1]); as will be discussed later, appreciable quantities of silane oligomers, $(PhSiH)_n$, are also produced in some cases (vide infra). The catalytic runs were carried out at room temperature with Ni/styrene/PhSiH₃ ratios of 1:50:75 or 1:100:125; the excess of PhSiH₃ was meant as a compensation for its possible loss in the competitive silane oligomerization side reaction, thus ensuring the availability of sufficient quantities of silane for the desired hydrosilylation reaction. Analysis of the products and quantification of the yields were done according to previously published procedures (12).

$$[1] Ph \longrightarrow + PhSiH_3 \xrightarrow{IndNi(PR_3)Me} Ph \xrightarrow{SiPhH_2}$$

The results of the catalytic hydrosilylation reactions are shown in Table 2. The main point arising from the data is that the Ni–Me derivatives studied display more or less the same level of hydrosilylation activity as their analogous IndNi(PPh₃)Cl complexes when the latter are used in the absence of any initiators (18). For instance, the addition of PhSiH₃ to styrene using the complexes {1,3-(SiMe₃)₂-Ind}Ni(PPh₃)X under the same conditions proceeded with an 82% yield with X = Cl (12) vs. 79% with X = Me (Run 4). The similar catalytic activities of the Ni–Me and Ni–Cl pre-

Run	Ind	PR ₃	Ni:Styrene:PhSiH ₃	Time (h)	Conversion (%)
1	1-Me-Ind	PPh ₃ ^a	1:50:75	5	37
2	1-SiMe ₃ -Ind	PPh ₃	1:50:75	5	26
3	1,3-(SiMe ₃) ₂ -Ind	PPh ₃	1:50:75	5	74
4	1,3-(SiMe ₃) ₂ -Ind	PPh ₃	1:100:125	5	79
5	1-Me-Ind	PMe ₃ ^b	1:100:125	3	18
				5	22
6	1-i-Pr-Ind	PMe ₃	1:100:125	3	29
				5	31
7	1-SiMe ₃ -Ind	PMe ₃	1:100:125	3	11
				5	14
8	$1,3-(SiMe_3)_2-Ind$	PMe ₃	1:100:125	3	35
				5	36

Table 2. Hydrosilylation of Styrene with PhSiH₃ catalyzed by IndNi(PR₃)Me.

Note: Unless otherwise specified, the catalytic runs were conducted at room temperature in 394 mL of benzene using 5 μ mol of the Ni precursor.

^aThe runs using PPh₃-based precursors gave traces only of cyclic and linear (PhSiH)_n oligomers.

^bThe runs using PMe₃-based precursors gave variable quantities of cyclic and linear (PhSiH)_n oligomers.

catalysts can be rationalized by noting that both of these precursors generate the same catalytically active intermediates beyond the initiation step.

Inspection of the data listed in Table 2 indicates that the PPh₃ derivatives are more active than their corresponding PMe₃ counterparts (Runs 1–3 vs. 5, 7, and 8), particularly for the precursors featuring the bulky 1,3-(SiMe)₃-Ind ligand, the most effective pre-catalyst being complex **2** (Runs 3 and 4). These observations confirm that hydrosilylation activity correlates with steric bulk of the Ind ligand (1,3-SiMe₃-Ind > 1-*i*-Pr-Ind > 1-Me-Ind) and phosphine lability (PPh₃ > PMe₃; Ni–Me < Ni–Cl). Interestingly, the Ni:substrate ratio does not appear to have a significant impact on the reactivities (Run 3 vs. 4).

As mentioned above, the PMe₃-based precursors exhibit lower hydrosilylation activities because of the less labile Ni- PMe_3 (12). On the other hand, the PMe_3 -based complexes are efficient promoters of the competitive dehydrocoupling of PhSiH₃ (eq. [2]), whereas their PPh₃ counterparts are nearly inactive for this reaction; this implies that the dehydrocoupling does not require phosphine dissociation. Upon a closer examination of the silane dehydrocoupling reaction with the IndNi(PMe₃)Me precursors, we found that the outcome of the catalysis was virtually independent of the specific Ind ligand used (Table 3). This implies that all of the IndNi(PMe₃)Me precursors generate the same intermediate (e.g., $Ni^0(PMe_3)_n$) that acts as the active catalyst for the Si-Si bond formation reaction. It is worth noting that previous studies in our group have shown that most $Ni^{0}(PR_{3})_{n}$ react with PhSiH₃ to produce mixtures of cyclic and linear oligomers (19), but the involvement of in situ generated Ni^0 species in the present studies has not been confirmed.

[2] PhSiH₃
$$\xrightarrow{\text{IndNi}(PMe_3)Me}$$
 (PhSiH)_n

Conclusion

This study supports our earlier observation that phosphine dissociation is an important step in the addition of PhSiH₃ to styrene catalyzed by IndNi(phosphine)X. It follows that PPh₃

Table 3.	Deh	ydrocoup	ling c	of	PhSiH ₃	catalyz	zed b	y I	IndNi(PMe ₃)Me.
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	(PhSiH) _n							
Ind	$M_{ m w}$	M _n	$M_{\rm w}/M_{\rm n}$	% lin				
1-Me-Ind	1197	1172	1.02	79				
1-i-Pr-Ind	1206	1180	1.02	87				
1- SiMe ₃ -Ind	1362	1283	1.06	82				
	1439 ^{<i>a,b,c</i>}	1331	1.08	66				
	1283 ^{<i>a</i>,<i>c</i>}	1223	1.05	82				
	$1354^{b,c}$	1272	1.06	67				
	1318 ^c	1252	1.05	87				
1,3-(SiMe ₃) ₂ -Ind	1254	1216	1.03	88				

Note: Unless otherwise indicated, the catalytic runs were conducted by stirring the Ni precursor (18 μ mol) and PhSiH₃ (200 equiv.) in toluene (0.25 mL) at -35 °C for 7 day.

"This experiment was run in THF.

^bThis experiment was run at 25 °C.

^cThis experiment was run for 4 days.

derivatives are better catalyst precursors compared to their PMe₃ counterparts, and that bulky indenyl ligands facilitate the catalysis, presumably by favouring the phosphine dissociation step. Contrary to our expectation that stronger Ni–P interactions in the Ni–Me derivatives (supported by both solution and solid-state data) should mean a less facile phosphine dissociation step and hence lower hydrosilylation activities in these complexes, reactivity data showed that the nature of the ligand X (Cl or Me) has no significant impact on the catalysis. Studies are in progress to elucidate the intimate mechanisms of hydrosilylation and silane oligomerization reactions as catalyzed by indenyl–nickel complexes.

Experimental section

General

All manipulations were performed under nitrogen atmosphere using standard Schlenk techniques and a glovebox. Dry, oxygen-free solvents were employed throughout. The Ni precursors Ni(PR₃)₂Cl₂ were prepared from NiCl₂·6H₂O and PPh₃ or NiCl₂ and PMe₃, respectively. The syntheses of 1-SiMe₃-IndH and 1,3-(SiMe₃)₂-IndH and their Ni derivatives (1-SiMe₃-Ind)Ni(PPh₃)Cl and $\{1,3-(SiMe_3)_2-$ Ind Ni(PPh₃)Cl have been described previously;12 1-*i*-Pr-IndH and Li[i-Pr-Ind] were prepared as described previously (3b, 6a). Ni(PMe₃)₂MeCl (21) was prepared by reacting $Ni(PMe_3)_2Cl_2$ with 1 equiv. of MeMgCl in THF at -30 °C, and characterized by ¹H NMR and ³¹P NMR spectroscopy. All other reagents 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), ${}^{13}C{H^1}(100.56 \text{ MHz})$, and ${}^{31}P{H^1}(161.92 \text{ MHz})$. Unless otherwise noted, the NMR spectra were recorded at 25 °C. The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal). The molecular masses of $(PhSiH)_n$ oligomers were measured by a Waters 1525 GPC system with a refractive-index detector, using THF as eluent and polystyrene standards.

(1-SiMe₃-Ind)Ni(PPh₃)Me (1)

MeMgCl (0.43 mL of a 3 mol/L solution in THF, 1.30 mmol) was added dropwise to a stirring solution of (1-SiMe₃-Ind)Ni(PPh₃)Cl (0.64 g, 1.18, in 40 mL of Et₂O) at room temperature. The reaction mixture was stirred for 30 min after the addition was completed, the solution was concentrated to about 5 mL under vacuum, and the resulting residue was extracted into hexane (40 mL). The extracts were concentrated to about 8 mL and cooled to -30 °C to give a brown solid (0.45 g, 73% yield).

¹H NMR (C₆D₆): 7.38 (d, ${}^{3}J_{H-H} = 8.0$ Hz; H4 or H7), 7.35 (m; aromatic protons of PPh₃), 7.28 and 7.05 (t, ${}^{3}J_{H-H} = 7.6$ Hz; H5 and H6), 7.00 (m; aromatic protons of PPh₃), 6.81 (d, ${}^{3}J_{H-H} = 8.0$ Hz; H4 or H7), 6.42 (s; H2), 4.23 (s; H3), 0.53 (s; Si(CH₃)₃), -0.52 (d, ${}^{3}J_{P-H} = 6.0$ Hz; Ni–CH₃). ${}^{13}C{H^{1}}$ NMR (CDCl₃): 134.2 (d, ${}^{1}J_{P-C} = 43$ Hz; C_{ipso}), 133.9 (d, ${}^{2}J_{P-C} = 11$ Hz; C_{ortho}), 128.9 (C_{para}), 128.1 (d, ${}^{3}J_{P-C} = 10$ Hz; C_{meta}), 125.0, 124.0, 122.9, 121.5, 118.9, and 117.7 (C3A, C4, C5, C6, C7and C7A), 106.3 (d, ${}^{2}J_{C-P} = 6$ Hz; C2), 82.0 (d, ${}^{2}J_{C-P} = 9$ Hz; C3), 82.0 (d, ${}^{2}J_{C-P} = 12$ Hz; C1), 0.2 (–SiMe₃), -24.4 (d, ${}^{2}J_{P-C} = 27$ Hz; Ni–CH₃). ${}^{31}P{H^{1}}$ NMR (C₆D₆): 47.1 (s). Anal. calcd. for C₃₁H₃₃Ni₁P₁Si₁: C, 71.14; H, 6.36. Found: C, 70.29; H, 6.62.

$\{1,3-(SiMe_3)_2-Ind\}Ni(PPh_3)Me(2)$

MeMgCl (0.35 mL of a 3 mol/L solution in THF, 1.05 mmol) was added dropwise to a stirring solution of $\{1,3-(SiMe_3)_2-Ind\}Ni(PPh_3)Cl$ (0.59 g, 0.95 mmol, in 30 mL of Et₂O) at room temperature. The reaction mixture was stirred for 30 min after the addition was complete, the solvent was removed under vacuum, and the residue was extracted with hexane (~60 mL). The extracts were concentrated to ~5 mL and allowed to stand at room temperature, which gave a brown solid (0.41 g, 66% yield). Single crystals of this compound were grown from cold, concentrated hexane solutions and subjected to X-ray diffraction studies.

¹H NMR (C₆D₆): 7.49–7.41 (m; PPh₃), 7.06–6.98 (m; aromatic protons of Ind and PPh₃), 6.33 (s; H2), 0.28 (s; Si(CH₃)₃), -0.70 (d, ${}^{3}J_{P-H} = 7.0$ Hz; Ni–CH₃). ${}^{13}C{H^{1}}$ (CDCl₃): 134.4 (d, ${}^{2}J_{P-C} = 11$ Hz; C_{ortho}), 134.3 (d, ${}^{1}J_{P-C} = 43$ Hz; C_{ipso}), 129.8 (C_{para}), 128.0 (d, ${}^{3}J_{P-C} = 10$ Hz; C_{meta}), 125.8, 121.9 and 120.7 (C3A, C7A, C5, C6, C4 and C7), 112.1 (C2), 87.9 (C1 and C3), 0.5 (SiMe₃), -24.4 (d, ${}^{2}J_{P-C} = 10$

28 Hz; Ni–CH₃). ${}^{31}P{H^1}$ NMR (C₆D₆): 44.0 (s). Anal. calcd. for C₃₄H₄₁Ni₁P₁Si₂: C, 68.57; H, 6.94. Found: C, 67.94; H, 7.13.

$\{1,3-(SiMe_3)_2-Ind\}NiPMe_3Cl (3)$

A THF solution (100 mL) of Li[1,3-(SiMe₃)₂-Ind] (0.611 g, 2.29 mmol) was added dropwise to a stirring solution of Ni(PMe₃)₂Cl₂ (0.646 g, 2.29 mmol, in 30 mL of THF) at room temperature. The reaction vessel was placed under vacuum for 30 s at regular intervals (following the addition of each 15 mL aliquot of the Li[1,3-(SiMe₃)₂-Ind] solution) to remove the free PMe₃ released from the reaction (inefficient removal of PMe₃ results in the decomposition of the product and the formation of side-products such as $Ni(PMe_3)_4$). The reaction mixture was stirred for 10 min after the addition was complete, then the solvent was removed under vacuum, and the resulting residue was extracted with hexane (~15 mL). The extracts were concentrated to about 3 mL and allowed to stand at room temperature, which gave red crystals that were covered with a viscous oil (0.457 g, 51% crude yield). Repeated attempts to purify this product were not successful due to the high solubility of the desired product and the main impurity $(Ni(PMe_3)_4)$.

¹H NMR (C_6D_6): 7.02–6.91 (m; H4, H5, H6 and H7), 6.72 (s; H2), 0.83 (d, ² J_{P-H} = 9.0 Hz; P–CH₃), 0.33 (s; Si(CH₃)₃). ¹³C{H¹} NMR (C_6D_6): 134.4, 125.8 and 120.1 (C3A, C7A, C5, C6, C4 and C7), 116.0 (C2), 86.0 (C1 and C3), 15.3 (d, ¹ J_{P-C} = 28 Hz; P–CH₃), 0.4 (Si(CH₃)₃). ³¹P{H¹} NMR (C_6D_6): –18.1 (s).

(1-SiMe₃-Ind)Ni(PMe₃)Me (4)

A THF solution (30 mL) of Li[1-(SiMe₃)Ind] (0.232 g, 1.19 mmol) was added dropwise to a stirring THF (30 mL) solution of Ni(PMe₃)₂MeCl (0.297 g, 1.13 mmol) at RT. The reaction vessel was placed under vacuum for 30 s at regular intervals (following the addition of each ~7 mL aliquot of the Li[1-(SiMe₃)Ind] solution) to remove the free PMe₃ released from the reaction (inefficient removal of PMe₃ results in the decomposition of the product and the formation of side-products such as Ni(PMe₃)₄). The reaction mixture was stirred for 10 min after the addition was complete, the solvent was removed under vacuum, and the residue was extracted with 20 mL hexane. The solution was concentrated to about 5 mL and cooled to -78 °C to yield a dark red solid (0.332 g, 87% yield).

¹H NMR (C₆D₆): 7.51 (d, ${}^{3}J_{H-H}$ = 7.6 Hz; H4 or H7), 7.14–7.12 (m; aromatic protons of Ind), 7.04 (t, ${}^{3}J_{H-H}$ = 7.0 Hz; H5 or H6), 6.27 (bs; H2), 4.62 (b s; H3), 0.60 (d, ${}^{2}J_{P-H}$ = 9.1 Hz; P–CH₃), 0.50 (s; Si(CH₃)₃), –0.64 (d, ${}^{3}J_{P-H}$ = 6.4 Hz; Ni–CH₃). ¹³C{H¹} NMR (C₆D₆): 126.6, 125.4, 123.1, 122.0, 119.6 and 117.4 (C3A, C7A, C5, C6, C4 and C7), 106.6 (C2), 81.7 (d, ${}^{2}J_{C-P}$ = 11 Hz; C1), 76.9 (C3), 16.5 (d, ${}^{1}J_{P-C}$ = 28 Hz; P–CH₃), 0.6 (SiMe₃), –28.4 (d, ${}^{2}J_{P-C}$ = 28 Hz; Ni–CH₃). ³¹P{H¹} NMR (C₆D₆): –3.5 (s). Anal. calcd. for C₁₆H₂₇Ni₁P₁Si₁: C, 57.00; H, 8.07. Found: C, 57.37; H, 8.06.

$\{1,3-(SiMe_3)_2-Ind\}Ni(PMe_3)Me(5)$

The procedure used for preparation of complex **4** was used here with $Li[1,3-(SiMe_3)_2-Ind]$ (0.351 g, 1.32 mmol) and $Ni(PMe_3)_2MeC1$ (0.328 g, 1.25 mmol). The reaction

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this work.

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- 13. For instance, the addition of PhSiH₃ to styrene catalyzed by IndNi(PPh₃)Cl in the absence of any activator/initiator gives yields of 7% (1-Me-Ind), 56% (1-SiMe₃-Ind), and 82% (1,3,-(SiMe₃)₂-Ind) (see ref. 12). It is important to emphasize, however, that for reactions run in the presence of initiators/activators, the steric bulk has little or no favourable influence on the reactivities unless the Ind ligand is substituted at both 1- and 3-positions. For instance, the addition of PhSiH₃ to styrene catalyzed by the combination of (1-R-Ind)Ni(PPh3)Cl and NaBPh₄ is no more effective with R = i-Pr (61%) than Me (69%) (see ref. 7). This can be understood by recalling that the complexes (1-R-Ind)Ni(PPh₃)X always adopt a configuration that places the PPh₃ ligand away from the more bulky Ind substituent to avoid steric congestion (see ref. 1); hence, placing a substituent at the 1-position has no advantage for increasing the lability of the phosphine ligand or the catalytic activities.
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(1-*i*-Pr-Ind)Ni(PMe₃)Me (6)

(0.301 g, 64% yield).

53.83; H. 8.85.

The procedure used for preparation of complex **4** was used here with Li[1-*i*-Pr-Ind] (0.214 g, 1.30 mmol) and Ni(PMe₃)₂MeCl (0.310 g, 1.18 mmol) to give the target complex as a dark red solid (0.277 g, 77% yield).

ucts are highly soluble in non polar solvents such as toluene

and hexane. The residue was sublimated at 85-95 °C at 3 Torr (1 Torr = 101 325/760 Pa), and the initially obtained oily solid ((Ni(PMe₃)₄)) was cleaned and the sublimation restarted to collect the target product as a dark brown solid

¹H NMR (C_6D_6): 7.45–7.43 and 6.99–6.96 (m; aromatic

protons of Ind), 6.13 (s; H2), 0.64 (d, ${}^{2}J_{P-H} = 9.2$ Hz; P–CH₃), 0.42 (s; Si(CH₃)₃), -0.71 (d, ${}^{3}J_{P-H} = 7.2$ Hz; Ni– CH₃). ${}^{13}C{H^{1}}$ NMR (C₆D₆): 126.4, 122.2 and 121.4 (C3A,

C7A, C5, C6, C4 and C7), 111.2 (C2), 87.1 (C1 and C3),

16.3 (d, ${}^{1}J_{P-C} = 29$; P-CH₃), 1.2 (SiMe₃), -29.6 (d, ${}^{2}J_{P-C} =$

31 Hz; Ni– \widetilde{CH}_3). ³¹P{H¹} NMR (C₆D₆): -8.6 (s). Anal.

calcd. for C₁₉H₃₅Ni₁P₁Si₂: C, 55.75; H, 8.62. Found: C,

¹H NMR (C₆D₆): 7.21–7.00 (m; aromatic protons of Ind), 6.15 (b s, H2), 4.44 (b s; H3), 2.87 (septet, ${}^{3}J_{H-H} = 6.8$ Hz; CHMe₂), 1.39 and 1.35 (d, ${}^{3}J_{H-H} = 6.8$ Hz, CH(CH₃)₂), 0.65 (d, ${}^{2}J_{P-H} = 9.0$ Hz; P–CH₃), -0.77 (d, ${}^{3}J_{P-H} = 6.4$ Hz; Ni–CH₃). ${}^{13}C{H^{1}}$ NMR (C₆D₆): 122.4, 122.1, 121.5, 120.2, 116.8 and 116.8 (C3A, C7A, C5, C6, C4 and C7), 100.8 (d, ${}^{2}J_{C-P} = 12$ Hz; C1), 97.3 (C2), 70.2 (C3), 25.3 (*i*Pr–CH), 23.8 (*i*Pr–CH₃), 21.1 (*i*Pr–CH₃), 16.5 (d, ${}^{1}J_{P-C} = 28$ Hz; P–CH₃), -22.2 (d, ${}^{2}J_{P-C} = 25$ Hz; Ni–CH₃). ${}^{31}P{H^{1}}$ NMR (C₆D₆): -4.0 (s). Anal. calcd. for C₁₆H₂₅Ni₁P₁: C, 62.59; H, 8.21. Found: C, 61.93; H, 8.20.

General procedure for catalytic runs

The catalytic runs were carried out by stirring the substrates and the Ni precursors in benzene (hydrosilylations) or toluene (dehydrogenative oligomerizations) at the specified temperatures. The characterization of the products and yield determinations were done on the basis of NMR and GC– MS, as described in our previous report (12).

X-ray crystallographic studies

Crystals suitable for X-ray diffraction studies were obtained by recrystallization of the purified solids (for 2 and 4) or crude material (for 3) from hexane solutions. The crystallographic data were collected on a Bruker AXS SMART 2K diffractometer with graphite-monochromated Cu Ka radiation ($\lambda = 1.54178$ Å) at 220(2) K, using SMART (20). Cell refinement and data reduction were done using SAINT (21). A SADABS (22) absorption correction was applied. The structures were solved by direct methods using SHELXS97 (23) and difmap synthesis using SHELXL97 (24); the refinements were done on F^2 by full-matrix least squares. The PPh₃ 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 Supplementary data.4

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- 17. Ni–PR₃ interactions in IndNi(PR₃)X compounds can be understood in the following terms. Relatively soft X ligands like alkyls result in more effective interactions and shorter Ni–P bonds, whereas harder X ligands such as halides give less effective and longer Ni–P bonds. An alternative explanation for the less effective Ni–X bonds is in terms of cis-labilizing interactions between the occupied d_{z2} orbital on Ni and the lone pair of electrons on ligands X (halide, OR, NR₂, and so forth).
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