Hydrosilylation of alkenes and ketones catalyzed by nickel(II) indenyl complexes[1]

Frédéric-Georges Fontaine, René-Viet Nguyen, and Davit Zargarian

Abstract: Abstraction of Cl^- from the complexes (indenyl)Ni(PPh_3)Cl generates cationic species that are effective precatalysts for the hydrosilylation of some olefins and ketones. For instance, the mixture of (1-Me-indenyl)Ni(PPh_3)Cl and $NaBPh_4$ (or methylaluminoxane) reacts at room temperature with ca. 100 equiv. each of $PhSiH_3$ and styrene to produce [1-phenyl-1-ethyl](phenyl)silane, $PhCH(CH_3)(SiPhH_2)$, in 50%–80% yield. The same system can also catalyze the hydrosilylation of 1-hexene and norbornene, but the products arising from these substrates consist of mixtures of regio- and stereoisomers. On the other hand, ketone hydrosilylation is regiospecific, giving the corresponding silyl ethers in high yields. A number of experimental observations have indicated that the initially generated Ni-based cation is not the catalytically active species. Indeed, the cationic initiators may be replaced by $LiAlH_4$ or $AlMe_3$, which generate the corresponding Ni-H or Ni-Me derivatives, respectively. Moreover, the observed regioselectivity for the addition of $PhSiH_3$ to styrene (i.e., predominant addition of the silyl fragment to the α-C) is opposite of what would be expected if the reaction mechanism involved carbocationic intermediates. A new mechanism is proposed in which the active species is a Ni-H species originating from the transfer of H^- from $PhSiH_3$ to the initially generated Ni cation.

Key words: hydrosilylation, nickel indenyl complexes, cationic complexes, hydride intermediates.

Résumé : L'abstraction des ions chlorures des complexes (indényle)Ni(PPh_3)Cl génère des espèces cationiques qui sont des précatalyseurs efficaces pour la réaction d'hydrosilylation de certaines oléfines et de certaines cétones. Par exemple, le mélange de (1-Me-indényle)Ni(PPh_3)Cl et de $NaBPh_4$ (ou de méthylaluminoxane) réagit à la température de la pièce avec environ 100 équivalents de $PhSiH_3$ et 100 équivalents de styrène pour donner le [1-phényl-1-éthyl](phényl)silane, $PhCH(CH_3)(SiPhH_2)$ avec un rendement allant de 50 % à 80 %. Le même système peut également catalyser l'hydrosilylation du 1-hexène et du norbonène, mais on obtient dans ces conditions des mélanges de régio- et de stéréo-isomères. Par ailleurs, l'hydosilylation des cétones est régiospécifique, et conduit aux éthers silylés correspondants avec des rendements élevés. Plusieurs observations expérimentales ont révélé que le cation à base de nickel généré initialement n'est pas l'espèce active catalytiquement. Effectivement l'initiateur cationique peut-être remplacé par le $LiAlH_4$ ou par le $AlMe_3$ qui génèrent respectivement les dérivés Ni-H ou Ni-Me correspondants. De plus, la régiosélectivité observée lors de l'addition du $PhSiH_3$ sur le styrène (i.e. l'addition prédominante du fragment silylé sur le carbone en α) est à l'opposé de ce à quoi on pourrait s'attendre si le mécanisme réactionnel impliquait un carbocation intermédiaire. On propose un nouveau mécanisme dans lequel l'espèce réactive est le Ni-H provenant du transfert de H^- à partir du $PhSiH_3$ vers le cation nickel généré initialement.

Mots clés : hydrosilylation, complexes indényle-nickel, complexes cationiques, hydrures intermédiaires.

[Traduit par la Rédaction]

Introduction

Based on their pioneering studies on the mechanism of the olefin hydrosilylation reaction, Harrod and Chalk proposed, in 1965, a general mechanistic scheme involving hydrido(silyl) intermediates of the type $L_nM(H)(SiR_3)$ (Scheme 1) (1). According to this scheme, insertion of the olefin into the M—H bond generates an alkyl intermediate that undergoes reductive elimination to give the final product. The main elements of the Chalk–Harrod mechanism have served as useful guiding principles for the development of numerous hydrosilylation catalysts over the past four decades (2–4).

We became interested in the hydrosilylation reaction during our studies on the oligomerization of $PhSiH_3$ catalyzed by Ni(II) indenyl precursors (5). The presumed involvement of Ni-H or Ni-SiR_3 intermediates in these reactions suggested that the same Ni-indenyl systems might also promote the hydrosilylation of olefins or ketones if these unsaturated substrates were present in the reaction mixture. This assertion was borne out by a series of tests, which indicated that the presence of certain olefins effectively inhibited the Si—Si bond formation step in favour of the hydrosilylation reaction. These initial results prompted us to carry out a literature survey, which revealed that a number of related Ni complexes are known to promote the hydrosilylation of ole-

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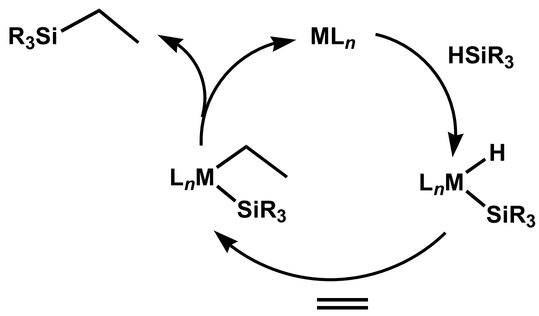
Scheme 1.



fins, as follows: the dimeric complex $\{CpNi(\mu\text{-}CO)\}_2$ catalyzes the addition of $HSiCl_3$ to styrene to give $PhCH(SiCl_3)Me$ (6); $CpNi(PPh_3)Ph$ reacts with butadiene and Me_3SiH to give a mixture of products arising from 1,4-hydrosilylation ($MeCH{=}CHCH_2SiMe_3$), coupling–hydrosilylation (2,6-octadienyltrimethylsilane), and dimerization–cyclization (1,5-cyclooctadiene) (7); $CpNi(PR_3)R'$ reportedly catalyzes the hydrosilylation of methyl acrylate and allyl formate with $HSiCl_3$ (8). Although little is known about the way these systems work, their mechanisms might involve intermediates similar to those operating in our systems.

Thus, we undertook to investigate the effectiveness of our Ni(II) indenyl complexes in the hydrosilylation reaction and examine the mechanism of these reactions. The present report describes the hydrosilylation of alkenes and ketones catalyzed by the precursors $IndNi(PR_3)X$ (Ind = indenyl ligand and its substituted derivatives; R = Ph, Me; X= Cl, alkyl, or positive charge).

Results and discussion

Our initial experiments focused on the reaction of $PhSiH_3$ and styrene with a catalytic system based on the combination of $IndNi(PR_3)Cl$ and methylaluminoxane (MAO); the selection of this Ni–MAO system was based on the knowledge that it promotes the dehydrogenative polymerization of $PhSiH_3$ (5*a*). A typical experiment was carried out as follows: to the toluene mixture of $(1\text{-Me-Ind})Ni(PPh_3)Cl$ (**1**), styrene, and $PhSiH_3$ (1:100:100 ratio) was added a toluene solution of MAO (10 equiv. with respect to Ni); the wine-red mixture darkened immediately, but no gas evolution was observed, implying that the Si—Si bond formation reaction (and its concomitant formation of H_2 gas) had been circumvented by the presence of styrene.

The reaction mixture was stirred for 8 h and worked-up; analysis of the nonvolatile products by GC–MS confirmed that styrene had been hydrosilylated.[3] Distillation gave a colourless oil, which was shown to consist, almost exclusively, of the α-isomer ((1-phenyl)ethylphenylsilane). This assignment was based on the following features of the ^1H NMR spectrum of the final product (Fig. 1): the multiplet due to the benzylic methyne proton at 2.55 ppm ($PhC\mathit{H}(Me)SiH_2Ph$), the signals due to the diastereotopic $Si\mathit{H}_2$ protons and their ^{29}Si satellites at 4.35 ppm, and the doublet at ca. 1.4 ppm assigned to the methyl protons ($^3J_{H\text{-}H}$ = 7 Hz); the benzylic protons of the minor isomer ($PhC\mathit{H}_2CH_2SiPhH_2$) were barely perceptible at ca. 2.7 ppm. These assignments are consistent with the reported data for these products (9).

Subsequent experiments showed that the hydrosilylation of styrene promoted by $IndNi(PPh_3)Cl$–MAO is fairly sluggish, requiring several hours of reaction time for ca. 70% yield (see runs 1–4 of Table 1). Curiously, using more catalyst or a higher temperature did not accelerate the catalysis (compare runs 5 to 2, and 6 to 4); on the other hand, combining these two variations did increase the rate, but did not affect the yield (compare run 7 to runs 6 and 5). It should be noted here that the higher temperature reactions tend to give higher proportions of the β-isomer (ca. 5%–10%); the significance of this observation for the probable mechanism of the catalytic reaction will be discussed later. The reaction rate also improved upon using the 1-*i*-Pr-Ind analogue of **1** as precatalyst (compare run 8 to run 2), whereas using the PMe_3 analogue of **1** did not offer any advantage (compare run 9 to run 5).

Although the precise role of MAO in the present system is not known yet, our previous studies (10) have shown that a small excess of MAO (ca. 5 equiv.) serves primarily to methylate the Ni—Cl bond, while a large excess (>10 equiv.) leads to both methylation and ionization in varying proportions. For example, $^{31}P\{^1H\}$ NMR analysis of a 1:25 mixture of **1** and MAO showed the formation of an approximately 50:50 mixture of the Ni-Me analogue of **1** ($(1\text{-Me-Ind})Ni(PPh_3)Me$) and the cationic complex $[(1\text{-Me-Ind})Ni(PPh_3)_2]^+$. Previous studies have shown that the latter complex forms when the highly electrophilic cation $[IndNi(PPh_3)]^+$ is generated in the absence of suitable ligands or nucleophilic substrates (11). We conclude, therefore, that the MAO:Ni ratios used in our studies (ca. 10:1) convert the Ni-Cl precursor to a mixture of the analogous Ni-Me derivative and $[IndNi(PPh_3)]^+$. To determine which, if any, of these in situ generated derivatives is crucial for the hydrosilylation reaction, we tested the catalytic effectiveness of each species separately, as follows.

Tests with the complex $(1\text{-Me-Ind})Ni(PPh_3)Me$, either preformed (12) or prepared in situ from **1** and $AlMe_3$, showed that it was less than half as effective as the combination of **1**–MAO (compare runs 10 and 11 to run 4). The weak activity of the Ni-Me derivative is perhaps not surprising since this compound is inert toward styrene insertion and reacts only very sluggishly with $PhSiH_3$ (5*b*). On the other hand, the Ni-(*i*-Pr) derivative, which reacts faster with $PhSiH_3$ than the Ni-Me analogue (10*b*), showed a better level of activity (run 12). Interestingly, the catalytic activity of the Ni-Me complex improves somewhat when MAO is added to the reaction medium (compare runs 10 and 11 to run 13); this result implies that the main role of MAO in this system is not simply methylating the Ni—Cl bond. We concluded, therefore, that the reactivity of the Ni-Me complex alone could not account for the activity levels shown by the combination of **1** and MAO, and set out to assess the importance of ionization in the **1**–MAO-catalyzed reactions.

To examine the reactivity of the cationic species $[IndNi(PPh_3)]^+$ in the absence of the Ni-Me derivative, we

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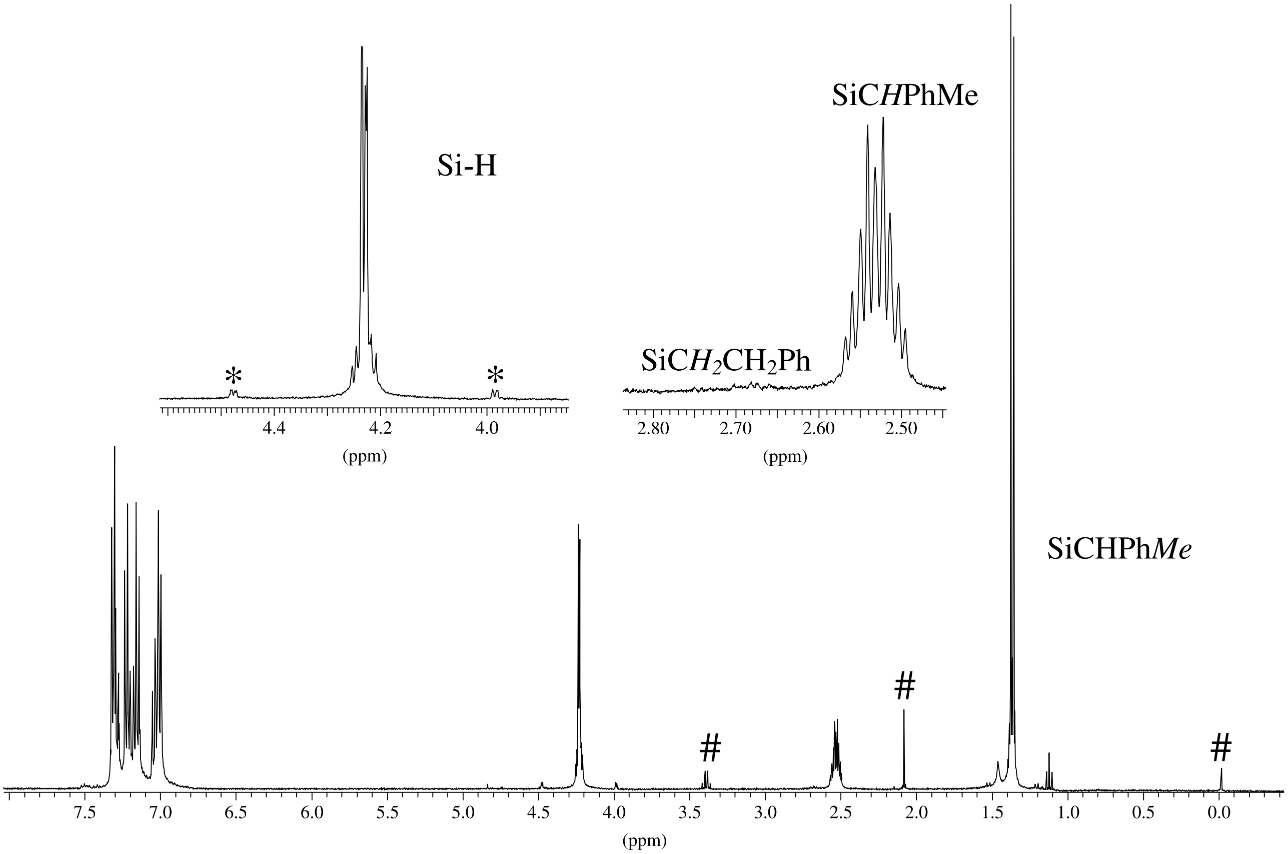
[3] Control experiments have shown that neither the Ni-Cl complexes nor the initiators used in this study (MAO, $AlMe_3$, $NaBPh_4$, $LiAlH_4$) can promote the hydrosilylation reaction when used alone.

Fig. 1. ^{1}H NMR (C_6D_6) of the product obtained from the Ni-catalyzed hydrosilylation of styrene with $PhSiH_3$. The peaks denoted by * represent the satellites due to the $J_{29Si\text{-}H}$ coupling, while the peaks denoted by the # represent the internal standard (ca. 2.1 ppm), residual Et_2O (ca. 3.4 and 1.1 ppm), and $SiMe_4$.



generated this species in situ by the direct abstraction of Cl^- from **1** by $NaBPh_4$;[4] this approach gave results comparable to those obtained with MAO (compare run 14 to run 4). To our surprise, even the cation $[(1\text{-Me-Ind})Ni(PPh_3)_2]^+$, which is normally quite inert in ligand substitution and other catalytic reactions (10*b*), showed some reactivity in the absence of MAO (run 15). These observations suggested that the electronically and coordinatively unsaturated species $[IndNi(PPh_3)]^+$, which is generated in situ by the abstraction of Cl^- by $NaBPh_4$ or MAO, can initiate the hydrosilylation reaction. Thus, during the second round of the optimization tests we focused our efforts on finding the best conditions for the catalytic hydrosilylation of styrene using $NaBPh_4$ as a cationic initiator, as described below.

The initial experiments showed that the ratio of **1**:$NaBPh_4$ used in the catalytic runs has a direct effect on the yield, excess of $NaBPh_4$ giving higher yields (Table 2, runs 1–4). Since only one equivalent of the initiator should be sufficient for generating the cationic species, the need for a large excess (run 4) is presumably due to the limited solubility of $NaBPh_4$. Even though a [Ni]:$NaBPh_4$ ratio of 1:50 gave the best yield, using such a large excess of the initiator is not practical, and so we adopted a 1:10 ratio as a reasonable compromise. As before, a higher reaction temperature does not seem to improve the catalytic activity (run 5), but gave a higher proportion of the β-isomer. Using the 1-*i*-Pr-Ind derivative does not offer any advantages (runs 6 and 7), while using the PMe_3 analogue of **1** led to considerably lower activities (runs 8 and 9). The latter observation is interesting: that the more active precatalyst is the one bearing the less nucleophilic phosphine ligand might imply that the hydrosilylation reaction involves a PR_3 dissociation. Consistent with this possibility, the presence of added PPh_3 ([Ni]:PPh_3 = 1:2) hindered the catalysis significantly (run 10). This point will be elaborated further during the discussion of the mechanism of these reactions (vide infra).

The scope of the hydrosilylation reactions promoted by **1**–$NaBPh_4$ has been explored briefly, as follows. Norbornene and 1-hexene were hydrosilylated with $PhSiH_3$ to ca. 1:1 mixtures of regio- (for 1-hexene) and stereoisomers (endo- and exo-products from norbornene), while *trans*-β-Me-styrene gave the α-isomer in ca. 10:1 ratio (ca. 50% overall yield). On the other hand, cyclohexene, indene, and *trans*-stilbene gave no hydrosilylation products; for the latter two olefins, the reaction mixtures displayed broad signals in the NMR spectra implying poly(olefin) formation, but no further analyses were performed to confirm this possibility. Although $PhSiH_3$ has been used in almost all of our studies,

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[4] The abstraction of Cl^- from **1** by $NaBPh_4$ is clean but generally sluggish, especially in nonpolar solvents such as toluene, in which $NaBPh_4$ has a very limited solubility. Although $AgBF_4$ is much more efficient for Cl^- abstraction, its higher cost and the possibility of secondary reactions (e.g., electron transfer with the Ni complex and redistribution with $PhSiH_3$) render it less practical than $NaBPh_4$ for our purposes.

Table 1. Catalytic addition of $PhSiH_3$ to styrene.*

Run	Catalyst[$]–co-catalyst	[Ni] (%)	Time (h)	Temperature (°C)	Yield (%)
1	**1**–MAO (1:10)	1	3	25	28
2	**1**–MAO (1:10)	1	5	25	39
3	**1**–MAO (1:10)	1	7	25	42
4	**1**–MAO (1:10)	1	16	25	69
5	**1**–MAO (1:10)	2	5	25	38
6	**1**–MAO (1:10)	1	16	65	61
7	**1**–MAO (1:10)	2	5	65	66
8	(1-(*i*-Pr)-Ind)(PPh_3)Ni(Cl)–MAO (1:10)	1	5	25	58
9	(1-Me-Ind)(PMe_3)Ni(Cl)–MAO (1:10)	2	5	25	36
10	**1**–$AlMe_3$ (1:1.1)	1	16	25	29
11	(1-Me-Ind)(PPh_3)Ni(Me)/—	1	24	25	26
12	(1-Me-Ind)(PPh_3)Ni(*i*-Pr)/—	1	72	25	60
13	(1-Me-Ind)(PPh_3)Ni(Me)–MAO (1:10)	1	16	25	40
14	**1**–$NaBPh_4$ (1:10)	1	16	25	73
15	$[(1\text{-Me-Ind})Ni(PPh_3)_2]^+$/—	2	5	25	13

*The reactions were carried out under anaerobic conditions on NMR-scale (C_6D_6), and the yields were determined relative to an internal standard. The detailed procedure is described in the *Experimental* section.

[$] **1** = (1-Me-Ind)($PPh_3$)Ni(Cl).

Table 2. Addition of $PhSiH_3$ to styrene catalyzed by (1-R-Ind)Ni(PR_3')Cl–$NaBPh_4$.*

Run	Pre-catalyst	[Ni]:$NaBPh_4$:styrene:$PhSiH_3$	Yield (%)
1	**1**	1:1:50:50	27
2	**1**	1:2:50:50	50
3	**1**	1:10:50:50	69
4	**1**	1:50:50:50	86
5	**1**	1:10:50:50[$]	64
6	(1-(*i*-Pr)-Ind)Ni(PPh_3)Cl	1:10:100:100	50
7	(1-(*i*-Pr)-Ind)Ni(PPh_3)Cl	1:10:50:50	61
8	(1-Me-Ind)Ni(PMe_3)Cl	1:10:100:100	10
9	(1-Me-Ind)Ni(PMe_3)Cl	1:10:50:50	36
10	**1** + 2PPh_3	1:10:50:50	19

*Unless otherwise indicated, all runs were carried out under anaerobic conditions in benzene at 25 °C for 5 h. Details of the procedure and yield determination are given in the *Experimental* section.

[$] This run was carried out at 65 °C.

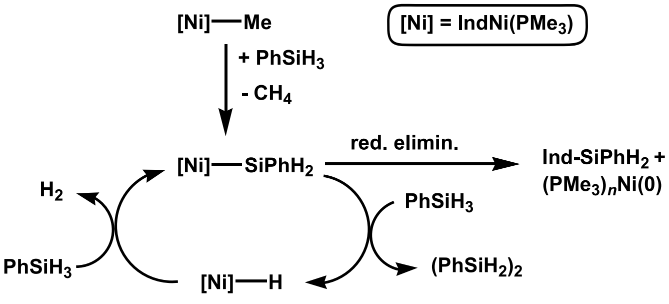
the reactivity of other silanes was also examined briefly. Thus, we found that tri-substituted silanes such as Et_3SiH and $(EtO)_3SiH$ are inactive in the hydrosilylation of styrene, but Ph_2SiH_2 does add to styrene to give the products $PhCH(CH_3)(Ph_2SiH)$ and $PhCH_2CH_2(Ph_2SiH)$ in ca. 60:40 ratio (ca. 28%–48% overall yield). The inertness of tri-substituted silanes is presumably due to steric hindrance. Finally, acetophenone and 2-nonanone were hydrosilylated very efficiently to the corresponding PhH_2Si–ethers, giving nearly quantitative conversions by NMR.

Mechanistic considerations

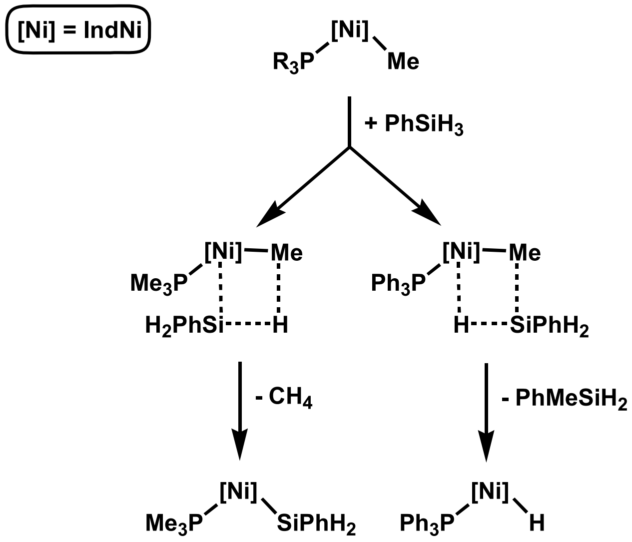
The results described above show that the hydrosilylation reactions can be promoted by the in situ generated species (Ind)(PPh_3)Ni(Me) or $[(Ind)(PPh_3)Ni]^+$, the latter being more effective in most cases. This section considers the various ways in which these two species can initiate the catalysis. It should be emphasized at the outset that whereas $[(Ind)(PPh_3)Ni]^+$ can, in principle, react with either the olefin or the silane, the Ni-alkyl derivatives are known to be inert towards the insertion of olefins and must, therefore, react first with $PhSiH_3$. For simplicity, we begin the mechanistic discussion with the latter systems.

The complexes (1-Me-Ind)(PR_3)Ni(Me) are known to convert $PhSiH_3$ (without a co-catalyst) to $(PhSiH)_n$ (R = Me, Ph; n = 3–16) (5*b*). Whereas the reactions involving the PPh_3 analogue were quite sluggish, those of the PMe_3 analogue proceeded at a conveniently rapid rate and were, therefore, subjected to detailed kinetic and D-labeling studies. On the basis of these studies, we have proposed that the oligomerization of $PhSiH_3$ is initiated by a concerted, σ-bond metathesis reaction as opposed to an oxidative addition – reductive elimination sequence. Analysis of the side products of this reaction pointed to the formation of methane and 1-($SiPhH_2$)-3-Me-Ind, but not $PhMeSiH_2$, suggesting that the initial reaction leads to a Ni-silyl intermediate, as shown in Scheme 2. The putative Ni-$SiPhH_2$ intermediate would then react further with $PhSiH_3$ to initiate the oligomerization process, while its decomposition (by reductive elimination) could form 1-($SiPhH_2$)-3-Me-Ind (Scheme 2) (5*b*).

Scheme 2.



Scheme 3.



To determine if the pathway depicted in Scheme 2 is also followed by the PPh_3 analogue, we did a similar analysis (by TOCSY ^1H NMR) of the products of the reaction of (1-Me-Ind)(PPh_3)Ni(Me) with $PhSiH_3$. This study revealed the presence of traces of $PhMeSiH_2$ and 3-Me-Ind, but not 1-($SiPhH_2$)-3-Me-Ind. We infer from these observations that, unlike its PMe_3 analogue, the precursor (1-Me-Ind)(PPh_3)Ni(Me) reacts with $PhSiH_3$ to eliminate $PhSiMeH_2$ (instead of methane) and form the hydride derivative (eq. [1]; [Ni] = (1-Me-Ind)Ni(PPh_3)). The latter could then react with styrene to initiate the hydrosilylation catalysis, while its decomposition (by reductive elimination) would produce 3-Me-Ind (instead of 1-($SiPhH_2$)-3-Me-Ind) (eq. [2]). The precise reasons for this difference in reactivity between the PMe_3 and PPh_3 derivatives are not known with certainty. Modeling studies suggest that the greater steric bulk of the PPh_3 derivative might favour the transfer to the Ni centre of the less-hindered side of PhH_2Si-H (i.e., the H, see Scheme 3), but electronic factors cannot be ruled out (the more electron-rich PMe_3 analogue might stabilize the Ni—Si bond).

[1] $PhSiH_3 + [Ni]\text{-}Me \rightarrow PhMeSiH_2 + [Ni]\text{-}H$

[2] $\text{3-Me-Ind} + (PPh_3)_nNi(0) \leftarrow [Ni]\text{-}H \rightarrow \text{hydrosilylation}$

To test the likelihood that a Ni-H derivative is involved in the hydrosilylation catalysis promoted by the present system, we tested the effectiveness of $LiAlH_4$ as co-catalyst (or initiator, (instead of MAO or $NaBPh_4$) in the hydrosilylation of styrene. Thus, stirring a toluene solution of styrene–$PhSiH_3$–**1**–$LiAlH_4$ (100:100:1:2.5) at room temperature for 16 h resulted in the usual product ($PhCH(CH_3)(PhSiH_2)$) in 41% yield. This result establishes that the hydrosilylation reaction can be catalyzed by a Ni-H intermediate generated either from **1**–H^- or by the reaction of the Ni-Me precursor and $PhSiH_3$.

Let us now turn to discussing the mechanism of the hydrosilylation reactions initiated by the in situ generated cationic species $[IndNi(PPh_3)]^+$. Given the highly electrophilic nature of this species and the fact that various Lewis acids can catalyze hydrosilylation of olefins (13), we considered the likelihood of our Ni cations acting as Lewis acids to promote the observed hydrosilylation reactions. A recent example of such Lewis-acid-catalyzed hydrosilylation has been reported by Gevorgyan and co-workers (14) who have shown that 5–10 mol% of $B(C_6F_5)_3$ can catalyze the hydrosilylation of a range of olefins with various aryl- or alkylsilanes. These authors have drawn on the findings of Lambert et al. (15) and Piers and co-workers (16) to argue, quite convincingly, that these $B(C_6F_5)_3$-catalyzed reactions are initiated by the formation of $[R_3Si]^+[HB(C_6F_5)_3]^-$. The silylium cation R_3Si^+ is believed to add to the C=C to generate a carbocationic intermediate, which abstracts a hydride from the anion $[HB(C_6F_5)_3]^-$ to release the final product. The regiochemistry of the hydrosilylation products obtained by Gevorgyan and co-workers is consistent with a carbocationic mechanism; for instance, styrene is converted to the $PhCH_2CH_2SiR_3$, presumably via the intermediate $[PhC^+HCH_2SiR_3]$.

By analogy to Gevorgyan's proposed abstraction of H^- by $B(C_6F_5)_3$, we considered a scenario involving the abstraction of H^- from $PhSiH_3$ by $[IndNi(PPh_3)]^+$ to give IndNi(PPh_3)H and a silylium species; the main question is whether the aptitude of the species $[IndNi(PPh_3]^+$ for abstracting H^- from $PhSiH_3$ can be assumed to be comparable to that of $B(C_6F_5)_3$. This question was investigated by the following NMR experiments that allowed some measure of the relative Lewis acidities of these electrophiles. First, monitoring mixtures of IndNi(PPh_3)Cl and $B(C_6F_5)_3$ (1:5) showed that the ionization of the Ni—Cl bond is very slow (<ca. 20%–30% ionization in 30–60 min). Next, adding $B(C_6F_5)_3$ to solutions of IndNi(PPh_3)Me (1:2) did not lead to ionization, forming instead what we believe is a species featuring a Ni•••Me•••B moiety.[5] Hence, it appears that $[IndNi(PPh_3)]^+$ and $B(C_6F_5)_3$ have similar Lewis acidities and should have similar aptitudes for abstracting H^- from $PhSiH_3$. Unfortunately, it has not been possible to find direct evidence for the formation of

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[5] NMR evidence supporting this assertion includes the observation of a broad signal in the upfield region of the ^1H NMR spectrum, slightly downfield of the original Ni-Me signal at ca. –0.7 ppm, and the absence of the characteristic AB signals for the formation of the species $[IndNi(PPh_3)_2]^+$. Significantly, none of the B- or Al-based Lewis acids tested in our study abstract the Ni-bound phosphine ligands, implying that the Ni centre is a strong Lewis acid.

Ni-H intermediates in the mixtures of $PhSiH_3$ and in situ generated $[IndNi(PPh_3)]^+$, because the putative Ni-H species reacts with $PhSiH_3$ at a faster rate than it is produced. However, we have obtained indirect evidence for the generation of such a Ni-H species, as described below.

Given that a number of late transition metal hydride bonds react with C—Cl bonds, especially those of chloroform, we reasoned that if the Ni-H species could be generated in a chlorinated solvent, chlorination might give the Ni-Cl derivatives, which could be easily detected. Thus, we monitored the NMR spectra of two $CDCl_3$ samples, one containing the independently prepared cationic complex $[(1\text{-Me-Ind})Ni(PPh_3)_2][BPh_4]$ alone, the other containing the same complex in addition to ca. 10 equiv. of $PhSiH_3$. The NMR spectra showed that the cationic complex is stable in $CDCl_3$ for at least 24 h in the absence of the silane (no new peaks in the $^{31}P\{^1H\}$ NMR spectrum), whereas the sample containing $PhSiH_3$ displayed many new $^{31}P\{^1H\}$ NMR signals, including that of the complex $(1\text{-Me-Ind})Ni(PPh_3)Cl$ (31.1 ppm). We believe that the latter compound likely arises from the reaction of the Ni-H intermediate with $CDCl_3$. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture also showed signals at 16–20 ppm, which is close to the spectral region associated with the signals for phosphonium salts such as $Ph_3MeP^+I^-$ (ca. 22 ppm); these signals might be due to phosphonium species such as $[Ph_3P(SiR_3)][BPh_4]$. Finally, the ^1H NMR spectrum of this sample showed traces of 3-Me-Ind, which could originate from the reductive elimination of a Ni-H intermediate.

The above observations provide indirect support for the proposal that the in situ generated Ni cations react first with $PhSiH_3$ (as opposed to styrene)[6] to form Ni-H and silylium species. The next question that arises is which one of these intermediates would react with the olefin to initiate the hydrosilylation reaction. On this question, the regioselectivity of the Ni-catalyzed reactions can help rule out the possibility that these reactions proceed by the same reaction pathway proposed for the $B(C_6F_5)_3$ system above, i.e., the addition of R_3Si^+ to the olefin. Thus, Ni-catalyzed hydrosilylation of styrene gives α-silylation, which is the opposite of that observed with the $B(C_6F_5)_3$ system discussed above; moreover, the hydrosilylation of 1-hexene gives a 50:50 mixture of α- and β-silylation instead of the exclusive α-silylation expected from a carbocationic path. On the other hand, the regioselectivities observed in our system are consistent with a Chalk–Harrod type mechanism involving M-H intermediates. These considerations favour the insertion of the olefinic substrate into the Ni—H bond over reaction with the silylium species. The latter is presumably stabilized by $[BPh_4]^-$ and (or) the solvent (17), but our results do not shed any light on the fate of this species.

Therefore, we envisage the following sequence of steps for the hydrosilylation reactions promoted by the present system: (*a*) the Ni-H analogue of **1** is generated by the reaction of $PhSiH_3$ with the in situ formed $[IndNi(PPh_3)]^+$ or the Ni-Me analogue;[7] (*b*) insertion of the olefin (or ketone) into the Ni—H bond of the intermediate generates a new Ni-alkyl (or Ni-alkoxy) derivative, which reacts subsequently with another molecule of silane to form the C—Si (or O—Si) bond and regenerate the Ni-H intermediate.[8] The regiochemistry of the hydrosilylation reaction is determined at the insertion step; in the case of styrene, this gives the alkyl intermediates $Ni\text{-}CH_2CH_2Ph$ and (or) Ni-CH(Me)Ph. Although the latter intermediate should, in principle, be more susceptible to β-H elimination, we propose that it is in fact more stable because of the possibility of reverting to an η^3-benzyl derivative, as shown in Scheme 4. It is worth noting that Brookhart and co-workers (18) have proposed such η^3-benzyl intermediates for the addition of $HSiR_3$ (R = Et, *i*-Pr) to styrene catalyzed by the cationic complexes $[(1,10\text{-phenanthroline})Pd(Me)L][BAr_4]$.[9] The likelihood of such intermediates being involved in our system is supported by the following observations: (*a*) Monitoring a catalytic run by $^{31}P\{^1H\}$ NMR spectroscopy showed that the initial signal of the precatalyst **1** (ca. 31 ppm) is replaced by the signal for free PPh_3 (ca. –4 ppm) and a number of new signals at ca. 43–45 ppm. The latter region is associated with the $^{31}P\{^1H\}$ signals for complexes $(1\text{-Me-Ind})Ni(PPh_3)R$, wherein R is a secondary alkyl such as *i*-Pr or cyclohexyl (45 ppm), and *sec*-Bu or neopentyl (42–43 pm) (5*b*). The presence of free PPh_3 is also consistent with the earlier observation that the PMe_3 precursors are less effective for promoting the hydrosilylation reaction; (*b*) Recall that using higher reaction temperatures or Ph_2SiH_2 resulted in somewhat higher proportions of the minor regioisomer, $PhCH_2CH_2SiPhRH$ (R = H, Ph). Higher temperatures should accelerate the β-H elimination from Ni-CH(Me)Ph, thus favouring the $Ni\text{-}CH_2CH_2Ph$ intermediate; on the other hand, the more bulky Ph_2SiH_2 might be expected to react more readily with the less bulky $Ni\text{-}CH_2CH_2Ph$ intermediate.

Conclusions

The present study has shown that combining the complexes $IndNi(PPh_3)Cl$ with suitable cationic initiators gives rise to an efficient catalytic system for the hydrosilylation of olefins and ketones. This system is particularly attractive for styrene because it gives, almost exclusively, one regioisomer; this regioselectivity is comparable to that reported for organolanthanide-catalyzed hydrosilylation reaction (9). On the other hand, Pd(II){bis(imine)} complexes give the opposite regioselectivity (18), while similar Ni precursors bearing Cp ligands give complicated mixtures of products (6, 7). Future studies will be aimed at expanding the scope of these hydrosilylation reactions.

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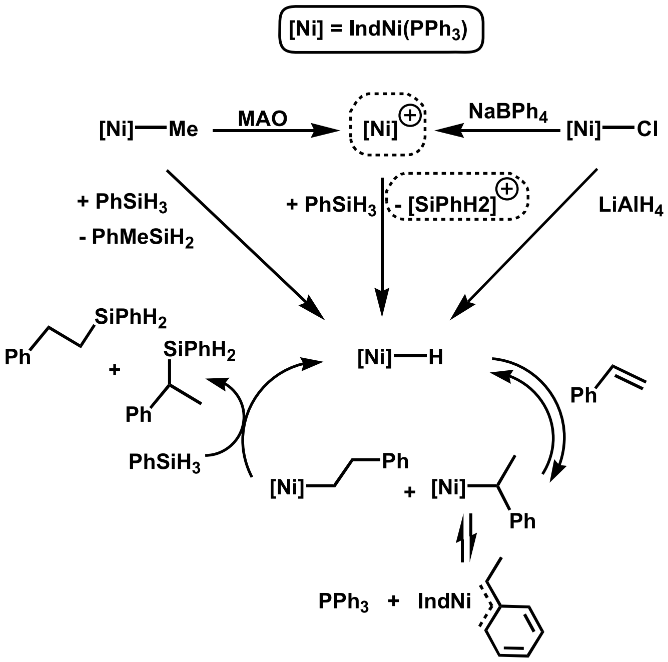
[6] The direct reaction of Ni-based cations with styrene would be expected to result in the oligo- or polymerization of styrene.

[7] One of the reviewers of our manuscript proposed the following alternative mechanism: the redistribution reaction involving the intermediate $[IndNi(PR_3)]^+$ might take place to produce $[IndNi(PR_3)_2]^+$ and phosphine-free species such as “IndNiCl” or $[IndNi]^+$; the latter might react with the hydrosilane to generate a Ni-H species. This alternative scenario is consistent with our observations and merits consideration.

[8] The latter step likely proceeds by a concerted, σ-bond metathesis pathway as opposed to an oxidative addition – reductive elimination route involving Ni(IV) intermediates.

[9] This Pd-based system leads to various mixtures of products arising from hydrosilylation and dehydrogenative silylation. The proposed mechanism involves the insertion of styrene into the $Pd—SiR_3$ bond as opposed to the Pd—H bond.

Scheme 4.



A number of observations, including the fact that $LiAlH_4$ can be used instead of $NaBPh_4$ and MAO to activate the Ni-Cl precursor, have pointed to the involvement of the corresponding Ni-H derivative (X = H) as the active intermediate in these reactions. In the case of the reactions involving cationic initiators, we have proposed that this Ni-H intermediate is generated via the transfer of H^- from the silane to the coordinatively unsaturated and highly electrophilic species $[IndNi(PPh_3)]^+$. This $Si \rightarrow Ni^+$ hydride transfer process is very interesting because it provides a convenient route to the reactive Ni-H intermediate.[10] Studies are currently underway with the objective of elucidating the main parameters controlling this reactivity and investigating the feasibility of catalytic hydroboration reactions with the same system (i.e., transfer of hydride from R_2BH).

Experimental

General

Unless otherwise specified, all manipulations were performed under an inert atmosphere of N_2 or argon using standard Schlenk techniques and a dry box. Dry, oxygen-free solvents were employed throughout. The complexes $(1\text{-Me-Ind})Ni(PPh_3)Cl$ (**1**) (12), $(1\text{-Me-Ind})Ni(PMe_3)Cl$ (19), $(1\text{-}i\text{-Pr-Ind})Ni(PPh_3)Cl$ (20), $(1\text{-Me-Ind})Ni(PPh_3)Me$ (12), and $[(1\text{-Me-Ind})Ni(PPh_3)_2][BPh_4]$ (12) were prepared according to previously published procedures. $PhSiH_3$ was either purchased from Aldrich and used as received, or prepared from $PhSiCl_3$ according to a previously published procedure (21). Styrene was purchased from Aldrich and treated by (*a*) passing it through a plug of alumina, and (*b*) storing over 4 Å molecular sieves prior to use. All other reagents, including MAO, $AlMe_3$, $LiAlH_4$, and $NaBPh_4$, were purchased from Aldrich and used as received. The NMR spectra were recorded using the following spectrometers: Bruker DMX600 (2D ^1H-^{29}Si), Bruker AMX400 (^1H at 400 MHz, $^{13}C\{^1H\}$ at 100.56 MHz, and $^{31}P\{^1H\}$ at 161.92 MHz), and Bruker AV300 (^1H at 300 MHz for TOCSY). GC–MS analyses were carried out on a Hewlett Packard 6890 series gas chromatograph equipped with a split mode capillary injector and a HP 5973 mass selective detector. The following operating parameters were used: the injector and detector temperatures were 250 °C; the carrier gas was hydrogen (2 mL/min); the column used was HP-5MS, 5% phenyl methyl siloxane; temperature program: 40 °C for 2 min, 10 °C/min up to 140 °C, 20 °C/min up to 280 °C.

Details of catalytic runs

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere. The catalytic runs were conducted as NMR-scale experiments or on a larger scale in Schlenk vessels. For the NMR-scale reactions, the following general procedure was followed. The Ni-Cl precursor complex (ca. 8 mg, 0.016 mmol) and the internal standard (hexamethyl benzene, ca. 15 mg, 0.09 mmol) were dissolved in C_6D_6 (0.8 mL); styrene and $PhSiH_3$ (100–200 μL, 50–100 equiv. of each) were then added to the resultant red solution. Prior to initiating the catalysis, a ^1H NMR spectrum was recorded to register the integral ratios for the signals of the internal standard and the reactants (Si-H of $PhSiH_3$ and vinylic protons of styrene). The NMR sample was then taken inside the dry box to add the initiator. For the room temperature experiments, the sample was kept in an ultrasonic bath throughout the reaction time to ensure agitation and homogeneity; for the high-temperature experiments, the sample was kept in a 65 °C water bath. If required, the progress of the catalysis was monitored periodically by ^1H NMR spectroscopy. The final yields were determined by comparing the intensities of the CH_3 signals of the product and the internal standard. The final values were checked against a calibration curve prepared by plotting the integral ratios obtained for various mixtures of the internal standard (C_6Me_6) and the main product ($PhCH(PhSiH_2)CH_3$) (slope = 1.069, R^2 = 0.9997).

The larger-scale catalytic runs were conducted as follows. Inside the dry box, the Ni precursor (ca. 10 mg) and the initiator were weighed into a Schlenk vessel containing a stirring bar; the capped vessel was then taken out of the dry box. The reactants and the solvent (benzene, unless otherwise specified) were then added under nitrogen in rapid succession (<1 min), and the mixture was stirred at room temperature or 65 °C. The work-up consisted of removing the volatiles on a rotoevaporator, extracting the residues with water–Et_2O, and evaporating the combined organic layers. The resulting yellow oil was distilled under vacuum to give the product(s) as a clear oil. When little product was obtained, the yield was determined based on the ^1H NMR spectrum of a carefully prepared mixture of the product and hexamethyl benzene as internal standard, according to the protocol described above.

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[10] The same Ni-H intermediate might also be accessible from the reaction of $PhSiH_3$ with $Ind(PPh_3)Ni(Me)$, but this reaction is generally sluggish.

Control experiments

To ascertain that the initiators used in our studies (MAO, $NaBPh_4$, $LiAlH_4$, and $AlMe_3$) do not promote the hydrosilylation reactions in the absence of Ni complexes, we prepared mixtures of styrene, $PhSiH_3$, and the initiator (in a molar ratio of 1:1:0.2) and analyzed them by ^1H NMR spectroscopy. No hydrosilylation product was detected in any of the experiments, and the ratio of styrene and $PhSiH_3$ remained unchanged. When AgOTf was tested with the substrates, gas evolution was observed and analysis of the sample showed that a small degree of silane redistribution had taken place (e.g., PhH_2Si-$SiPhH_2$ was detected by ^1H NMR).

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