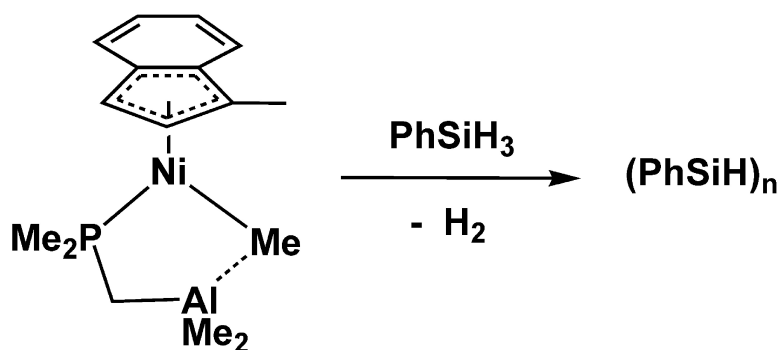


MeAlCHPMe: A New, Bifunctional Cocatalyst for the Ni(II)-Catalyzed Oligomerization of PhSiH

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J. Am. Chem. Soc., **2004**, 126 (28), 8786-8794 • DOI: 10.1021/ja048911m • Publication Date (Web): 25 June 2004

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Me₂AlCH₂PMe₂: A New, Bifunctional Cocatalyst for the Ni(II)-Catalyzed Oligomerization of PhSiH₃

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Abstract: The role of methylaluminumoxane (MAO) in the Ni-catalyzed dehydrogenative homologation of PhSiH₃ has been investigated with a view to designing new cocatalysts possessing well-defined chemical compositions and structures. These studies show that species such as the bifunctional reagent (Me₂PCH₂-AlMe₂)₂, **3**, should act as co-catalyst for the Si–Si bond formation reactions. Thus, it was found that the combination of (1-Me-indenyl)Ni(PPh₃)Me, **2a**, and **3** (Ni/Al ratio of 1:1) converts PhSiH₃ to cyclic oligomers (PhSiH)_n with a turnover frequency (TOF) of >500 h⁻¹, 50 times faster than with **2a** alone. Detailed NMR studies have indicated that this acceleration is due to the formation of the intermediate (1-Me-indenyl)Ni(Me)(Me₂PCH₂AlMe₂), **4**. Coordination of the PMe₂ moiety in this complex to the Ni center allows the tethered AlMe₂ moiety to interact with the Ni–Me moiety in such a way that promotes fairly slow Al–Me–Ni–CD₃ exchange (*t*_{1/2} ca. 12 h) but accelerates the Si–H bond activation and Si–Si bond formation reactions. The catalysis promoted by **2a/3** proceeds even faster in the presence of NEt₃ or THF (TOF > 1600 h⁻¹), because these Lewis bases favor the monomeric form of **3**, which in turn favors the formation of **4**. On the other hand, the much more nucleophilic base quinuclidine suppresses the catalysis (TOF < 300 h⁻¹) by hindering the Ni···R···Al interactions. These observations point to an emerging strategy for using bifunctional reagents such as **3** to place geometrically constrained Lewis acid moieties adjacent to metal centers, thereby activating certain metal–ligand bonds.

Introduction

Polysilanes (RSiR')_n have significant potential as preceramics and in the fabrication of optical devices.¹ The discovery² and development³ of group 4 metallocene-catalyzed routes for the dehydrogenative coupling of hydrosilanes RR'SiH₂ has provided an interesting alternative to the traditional Wurtz coupling of halosilanes for the synthesis of polysilanes. A number of studies have significantly improved our understanding of the way metal-catalyzed dehydrogenative coupling of silanes works⁴ and have resulted in new and increasingly efficient catalytic systems.⁵

Nevertheless, many challenges remain to be overcome, notably in the area of improving product selectivity (cyclic oligomers vs linear polymers) and sustained chain growth.

An emerging strategy for dealing with the above challenges involves the use of Lewis acid-based cocatalysts in conjunction with transition-metal-based catalysts. Thus, Harrod and Dioumaev have reported⁶ that the presence of B(C₆F₅)₃ in reactions catalyzed by the Cp₂ZrCl₂/BuLi system⁷ gives (PhSiH)_n with

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higher M_w . Tilley et al. have also reported that cation-like species generated by the action of B(C₆F₅)₃ or [HNR₃][BAR₄] on metallocenes display higher reactivities toward silanes;^{5d} these authors caution us, however, that the use of these cocatalysts does not always improve the chain growth process and in some cases leads to redistribution reactions involving Si–C bond cleavage.⁸

Our own studies on nickel-catalyzed polymerization of PhSiH₃ have shown that in some cases the presence of methyl aluminumoxane (MAO) can improve the M_w of the resulting (PhSiH)_{*n*}. For instance, the complexes Ind(PR₃)Ni(Me) (Ind = indenyl and its substituted derivatives) react with PhSiH₃ in the absence of cocatalysts to give primarily linear (PhSiH)_{*n*}, with *n* up to 16;⁹ on the other hand, using the analogous Ni–Cl derivatives in combination with excess MAO gives a mixture of (PhSiH)_{*n*} containing longer linear chains (*n* = 20–50).¹⁰ Despite the higher M_w of the products obtained from this Ni/MAO combination, however, the Ni/MAO systems suffer from a number of drawbacks, including slow rates of reaction and the formation of variable mixtures of cyclic and linear products depending on the batch of MAO used. In addition, the need for excess MAO complicates the isolation of the polymeric products and renders mechanistic studies difficult.

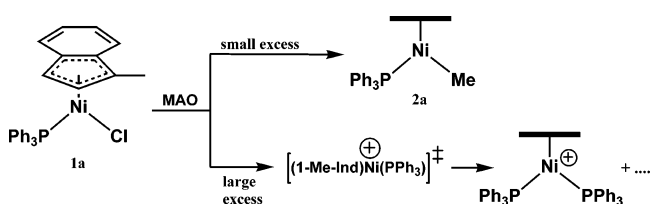
In an effort to address some of these shortcomings, we have investigated the role of MAO in the Ni-catalyzed reactions and are using the knowledge gained from these studies to design new cocatalysts for promoting silane polymerization reactions. The ideal cocatalyst should possess well-defined and readily modifiable structures and should promote our target reaction (i.e., homologation of PhSiH₃) effectively. The present article describes the results of our studies on the reactivities of a new indenyl nickel system featuring an intramolecularly positioned alkyl aluminum cocatalyst.

Results and Discussion

The Role of MAO. NMR monitoring of the reaction of (1-Me-Ind)Ni(PR₃)Cl, **1**, with MAO has shown that methylation and/or ionization of the Ni–Cl bond occur depending on the Ni/MAO ratio. For example, near-stoichiometric quantities of MAO (<5 equiv) convert the precursor (1-Me-Ind)Ni(PPh₃)(Cl), **1a**,¹¹ to the Ni–Me derivative (1-Me-Ind)Ni(PPh₃)(Me), **2a**, while a larger excess of MAO ionizes it to the cationic species [(1-Me-Ind)Ni(PPh₃)]⁺, which is converted to the bis-(PPh₃) derivative in the absence of other ligands or substrates (Scheme 1).¹² The degree of ionization is ca. 35, 60, and 70% in the presence of ca. 20, 30, and 50 equiv of MAO, respectively. We conclude, therefore, that under the conditions of the silane polymerization reactions (i.e., Ni/MAO ≈ 1:10), the precatalyst **1a** is converted to mainly the Ni–Me derivative plus minor amounts of the cationic species.

These observations raised the question of whether MAO is an initiator for the generation of the Ni–Me and the cationic

Scheme 1



complexes, or whether it is a cocatalyst whose action is required throughout the catalytic process. The results of a number of experiments have shown that the catalysis proceeds very differently in the absence of MAO. For instance, we have noted that the reaction of PhSiH₃ with the electronically and coordinatively unsaturated cations [IndNi(PPh₃)]⁺ generated from MAO-free precursors such as IndNi(PPh₃)(OTf)¹³ or [(η³,η¹-Ind-CH₂CH₂NMe₂)Ni(PPh₃)]⁺¹⁴ gives only the dimer (PhSiH₂)₂ in low yields; higher oligomers or polymers are not produced in the absence of MAO. The Ni–Me derivatives are more effective for the homologation of PhSiH₃, but even these give only oligomers in the absence of MAO. Thus, PhSiH₃ is homologated to mostly trimers and tetramers by **2a**, while its PMe₃ analogue gives primarily linear (PhSiH)_{*n*}, with *n* up to 16; in comparison, the **1a**/MAO system converts PhSiH₃ to much longer linear chains (*n* = 20–50).⁹

The above results imply that the role of MAO in the Ni-catalyzed homologation of PhSiH₃ is more than simply methylating the Ni precursors or initiating cationic species. Moreover, neutral Ni–R analogues of **2a** (R = the growing polymer chain) are more likely to be involved in the Ni/MAO-catalyzed process because (a) only a small degree of ionization is expected to take place in the presence of the relatively small excess of MAO used in the catalytic runs (vide supra) and (b) the cationic species do not promote the homologation of PhSiH₃ as effectively as the neutral Ni–Me species. We believe, therefore, that MAO serves to activate the neutral Ni–R moiety during each catalytic cycle through some type of Ni···R···Al(MAO) interaction *not* involving ionization. This idea has precedent in a proposal put forth many years ago¹⁵ that Al compounds can activate transition-metal halide bonds through some type of “polarization” without complete ionization.

The Effect of AlMe₃ on the Catalysis. Since previous studies had shown that AlMe₃ is very effective for methylating the Ni–Cl bond in **1** but does not ionize it, we wondered whether AlMe₃ would promote the PhSiH₃ homologation similarly to MAO. Studying the reaction of PhSiH₃ with **2a** in the presence of AlMe₃ showed, however, that the oligomerization catalysis was *suppressed* completely in the presence of a small excess of AlMe₃ (Ni/Al = 1:5–10). This observation is consistent with our previous findings that MAO promotes the catalytic activity of our Ni system in the polymerization of ethylene, whereas AlMe₃ inhibits this reaction.^{16,17} The different reactivities of MAO and AlMe₃ imply that they interact quite differently with the Ni center in our complexes, and we surmised that a better

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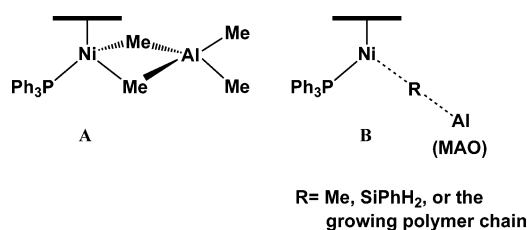
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Scheme 2



understanding of this difference might shed some light on the beneficial role of MAO.¹⁸

To identify the different Ni...Al interactions promoted by MAO and AlMe₃, we studied the ¹H and ³¹P{¹H} NMR spectra of solutions of **2a** containing ca. 10 equiv of MAO or AlMe₃. No spectral change was noted in the presence of these reagents, and in particular the Ni–CH₃ signal was unaffected; however, saturation transfer experiments showed that the Ni–Me moiety undergoes a rapid exchange with the Al–Me moiety in AlMe₃ but not in MAO. It is significant that MAO does not seem to promote the fast exchange process observed for the **2a**/AlMe₃ mixtures.¹⁹ On the basis of literature reports,²⁰ we postulate that bridging interactions of the type Ni(μ-Me)₂Al are promoted by AlMe₃ and that these interactions are responsible for the inhibition of the catalysis in the presence of AlMe₃. Thus, we propose that the interaction of the Ni–Me moiety in **2a** with AlMe₃ leads to the intermediate A (Scheme 2) that inhibits the catalysis by hindering the approach of the substrate; on the other hand, interaction of the Ni–Me moiety in **2a** (or that of Ni–R during the catalysis) with MAO gives intermediate B (Scheme 2) that facilitates the crucial Si–Si bond formation step.

Replacing MAO by a New Cocatalyst. Taken together, the above results confirm that methylation of the Ni–Cl bond in **1** is not the main role of MAO because (a) the independently prepared Ni–Me derivatives **2** alone do not give the same results as the combination of **1**/MAO and (b) Si–Si bond formation is suppressed in the presence of an equally efficient methylating agent such as AlMe₃. In addition, neither the ionizing action of MAO nor the Ni(μ-Me)₂Al-type interactions induced by AlMe₃ is beneficial for the silane oligomerization process. Therefore, to be effective for the Ni-catalyzed homologation of PhSiH₃, a Lewis acid-based cocatalyst should avoid ionizing the Ni–R bond or engaging in bridging-type interactions.

It occurred to us that a system featuring a *pendant* Lewis acid might be less likely to generate solvent-separated ion pairs because of the proximity of the acidic moiety to the Ni center and their 1:1 molar ratio. In addition, simple modeling studies indicated that a short tether might also hinder intramolecular, bridging-type interactions. We wondered, therefore, if bifunc-

tional compounds of the type LCH₂MX_n could coordinate to the Ni center via the Lewis basic moiety L and allow the Lewis acidic moiety MX_n to participate in the catalysis. To test this idea, we set out to evaluate the effectiveness of a bifunctional reagent such as R₂PCH₂AlX₂ as cocatalyst for the Ni-catalyzed dehydrogenative oligomerization of PhSiH₃; the choice of PR₂ and AlX₂ for the Lewis basic and acidic moieties, respectively, was meant to replicate the main features of our Ni/MAO system.

A search of the literature led us to the known compound Me₂-PCH₂AlMe₂ that seemed to have the main requirements for a would-be cocatalyst. The preparation and characterization of this compound, which exists as the dimer (Me₂PCH₂AlMe₂)₂ (**3**) both in the solid state and in solution, have been reported by Karsch et al.,²¹ but to our knowledge its reactivities with transition metals have not been reported previously.²² Therefore, we set out to determine whether the presence of **3** would alter the reactivities of our Ni precursors with PhSiH₃. The main question at the outset was whether the self-dimerization of this species would prevent it from interacting with the Ni complexes; initial tests showed, however, that the PMe₂ moiety in **3** can coordinate to Ni, and the resultant species does indeed promote the dehydrogenative coupling of PhSiH₃, as described below.²³

Reactivities of (Me₂PCH₂AlMe₂)₂ (3**).** In contrast to the very sluggish reaction of PhSiH₃ with **2a** in absence of **3**,⁹ addition of ca. 200 equiv of PhSiH₃ to a 2:1 mixture of **2a** and **3** ([**2a**] = 0.02 M; Ni/Al = 1:1) led to a vigorous evolution of H₂, which lasted for about 15 min until the PhSiH₃ was almost completely consumed (>95% by ¹H NMR); a less vigorous evolution of H₂ continued for many hours afterward. The products of this reaction were analyzed by ¹H NMR²⁴ and GPC analyses of the reaction mixture as a function of reaction time. These analyses indicated that different mixtures of linear oligomers (trimers to hexamers) formed during the initial stages of the catalysis (*t* < 60 min), while allowing the reaction to continue for 10–24 h produced mostly cyclic oligomers (*M*_w = 470;²⁵ *M*_w/*M*_n = 1.03; Scheme 3). Evidently, the presence of **3** accelerates the Ni-catalyzed Si–H bond breaking and Si–Si bond making steps significantly, but this homologation process does not lead to chain growth because the initially formed linear oligomers cyclize over time.

To quantify the effectiveness of **3** in promoting and cocatalyzing the oligomerization of PhSiH₃ catalyzed by **2a**, we carried out manometric measurements of the rate of H₂ evolution during

(17) Many other studies have also shown that the presence of excess AlMe₃ plays a counterproductive role in ethylene and propylene polymerization reactions by converting the active metal catalyst into “deactivated” or “dormant” M(μ-Me)Al-type adducts lacking vacant orbitals suitable for substrate binding. In addition, large excess of AlMe₃ also reduces polymer molecular weights, presumably because of chain-transfer reactions. For a discussion of these phenomena, see: Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(18) It should be pointed out that throughout these studies we have used solid samples of MAO obtained by evaporating the commercially supplied solutions under vacuum for an extensive period of time to remove all but traces of AlMe₃.

(19) It should be pointed out that our experiments cannot rule out a very slow exchange of the Ni–Me and Al–Me moieties in MAO.

(20) Many examples of aluminate complexes bearing M(μ-R)Al moieties have been reported. For a recent report, see: Klimpel, M. G.; Eppinger, J.; Sirsch, P.; Scherer, W.; Anwander, R. *Organometallics* **2002**, *21*, 4021.

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(23) Control experiments have shown that in the absence of our Ni complexes PhSiH₃ does not react with **3**, whether in its dimeric form or as monomer (in the presence of Lewis bases such as NEt₃).

(24) The linear and cyclic oligomers of phenylsilane are readily distinguishable by their respective ¹H NMR signals that appear at ca. 4.4–4.8 ppm and at ca. 5.0–5.5 ppm, respectively. (a) Reference 4f. (b) Reference 4i. (c) Gauvin, F. Ph.D. Thesis, McGill University, Montréal, Canada, 1992.

(25) It should be noted that analyzing polysilanes by GPC techniques using poly(styrene) standards underestimates the molecular weights by ca. 20% compared to values obtained from light scattering techniques: Devaux, J.; Daoust, D.; De Mahieu, A. F.; Strazielle, C. In ref 3g, pp 49–60. In addition, cyclic oligomers are expected to register somewhat smaller molecular weight values because of their smaller hydrostatic volumes compared to linear polymers. Once these considerations are taken into account, the *M*_w values of ca. 470 obtained for our samples using GPC analyses can be assumed to correspond to (PhSiH₂)_n cyclic oligomers having theoretical values of ca. 535 (*n* = 5) and 642 (*n* = 6).

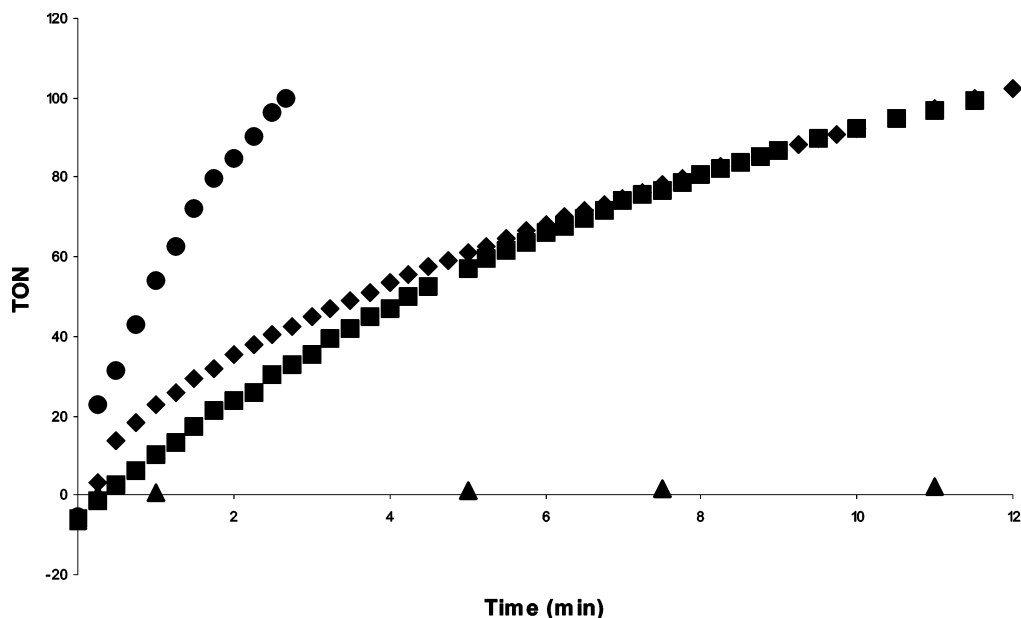
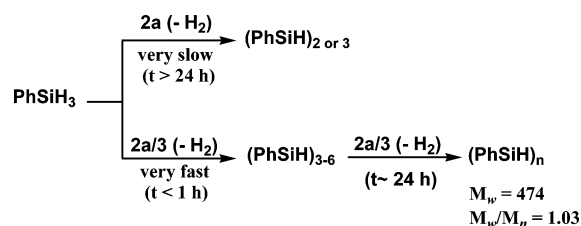


Figure 1. Rate profiles for the evolution of H₂ during the oligomerization of PhSiH₃ catalyzed by **2a** alone (▲), in the presence of **3** (■ first batch of substrate, ◆ second batch of substrate), and in the presence of **3** and 10 equiv of NEt₃ (●). The initial Ni/Al/Si ratio was 1:1:200 in all runs; [Ni] = 0.018 M.

Scheme 3



the initial stages of the catalysis;²⁶ the rate profiles for different catalytic runs are shown in Figure 1. These measurements showed that the dehydrogenative coupling of PhSiH₃ with the **2a/3** combination (Ni/Al = 1:1) proceeded at a turnover frequency (TOF) of 554 h⁻¹ which is ca. 50 times greater than the TOF of the catalysis with **2a** alone (trace b) (Figure 1).²⁷ When the initial batch of monomer had been consumed and the evolution of H₂ had all but stopped (ca. 60 min after the start), a second batch of PhSiH₃ was added to the reaction mixture and the resulting H₂ evolution was measured as before. The rate profile for this reaction (Figure 1) was very similar to that of the initial reaction, implying that the catalytically active species formed initially by the **2a/3** combination remains active during the course of the reaction.

(26) It should be noted that studying the rates of metal-catalyzed dehydrogenative oligomerization of PhSiH₃ using NMR is complicated by the vigorous evolution of gas, and thus manometric measurements are often used for kinetic studies. (For example, see ref 4f.) The appropriateness of the manometric approach is based on the commonly held belief that the initial stage of these reactions is dominated by the dimerization process (2 PhSiH₃ → (PhH₂Si)₂ + H₂); thus, the reaction rate during this period is proportional to the consumption of the monomer, which is, in turn, directly related to the volume of H₂ gas evolved. Therefore, the initial rate of H₂ evolution can be a fairly reliable estimate of initial reaction rate.

(27) The reproducibility of the kinetic data was confirmed by doing the measurements in at least duplicate (triplicate in some cases), and our conclusions pertain to the *relative* rates only. Indeed, a reviewer has pointed out that unless the gas evolved during the catalytic reactions is driven out of the solvent efficiently (e.g., under reduced pressure or by vigorous shaking), the *absolute* values of the experimentally determined gas volumes and the reaction rates derived from them might be underestimated across the board. Since we used only vigorous magnetic stirring under a constant pressure regime to drive off the evolved gas, and since the influence of stirring rates on gas volumes has not been measured, we cannot rule out this possibility.

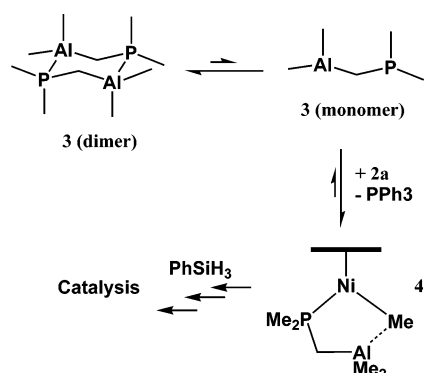
Next, we set out to identify the species responsible for the acceleration of the oligomerization reaction. Monitoring the NMR spectra of a reaction mixture containing **2a**, **3**, and the substrate (Ni/Al/PhSiH₃ ≈ 1:1:20) showed the disappearance of the starting materials and the formation of (PhSiH)_n and free PPh₃ (³¹P NMR signal at ca. -4 to -5 ppm). Evidently, formation of the catalytically active species involves the displacement of the PPh₃ ligand in **2a**, presumably by the phosphine moiety in **3**; the species arising from this substitution was not detected, however, likely because of its fast exchange with other species in the reaction mixture.

In an effort to observe the displacement of PPh₃ prior to the involvement of the resulting species in the catalysis, we monitored the NMR spectra of a mixture of **2a** and **3** in the absence of PhSiH₃. The results of our previous studies^{9,28} on the substitutional lability of the PPh₃ ligand in (1-Me-Ind)(PPh₃)-Ni(X) (X = Cl, Me) would predict that the more nucleophilic phosphine moiety in **3** should readily displace PPh₃ in complex **2a**. Curiously, however, NMR monitoring showed that in the absence of substrate no net reaction takes place between **3** and **2a** (³¹P NMR signals at -39.5 and 48 ppm, respectively); yet, addition of PhSiH₃ to this mixture initiated the catalysis immediately, as signaled by a very vigorous evolution of H₂. These observations can be rationalized by supposing that the displacement of PPh₃ in **2a** by **3** is governed by an initial, unfavorable equilibrium that generates the monomeric form of **3**; the latter reacts with **2a** to give a new Ni complex (**4**) in concentrations that are too small for detection by NMR but sufficient for initiating the catalysis in the presence of PhSiH₃ (Scheme 4).

The apparent reluctance of **3** to react with **2a** in the absence of PhSiH₃ likely stems from the superior stability of the dimeric form of **3**. Karsch has reported²¹ that although the dimeric structure of **3** is very stable, a small amount of the monomer

(28) (a) Fontaine, F.-G.; Dubois, M.-A.; Zargarian, D. *Organometallics* **2001**, *20*, 5145. (b) Fontaine, F.-G.; Ph.D. Thesis, Université de Montréal, Montréal, Canada, 2003.

Scheme 4



exists in solutions of **3**; furthermore, the dimer/monomer equilibrium can be driven toward the monomer in the presence of relatively strong Lewis bases. Accordingly, we found that adding a base such as NEt₃ to the **2a/3** mixture led to the formation of a new compound identified as (1-Me-Ind)Ni(PMe₂-CH₂AlMe₂·NEt₃)Me, **4**·NEt₃ (Scheme 4, L = NEt₃). The spectroscopic characterization of this new adduct and the effect of NEt₃ and other Lewis bases on the oligomerization catalysis are discussed below.

NMR Characterization of (1-Me-Ind)Ni(PMe₂CH₂AlMe₂·NEt₃)Me (4**·NEt₃).** Adding 1 equiv of NEt₃ to a 2:1 mixture of **2a/3** in C₆D₆ caused a 40–50% reduction in the intensities of the ³¹P{¹H} NMR signals for **2a** and **3** and gave rise to two new signals, a broad one due to the exchanging PPh₃ and a sharp singlet at 4.26 ppm. Adding more NEt₃ further reduced the intensities of the **2a/3** signals by ca. 65% with 2 equiv, 75% with 3 equiv, and 85% with 5 equiv. The presence of excess NEt₃ also sharpened the broad signal due to free PPh₃ and increased the intensity of the signal at 4.26 ppm; conversely, evaporation of the reaction mixture to remove NEt₃ regenerated **2a**, implying that the NEt₃-promoted transformation of **2a** is reversible. That this equilibrium involves the displacement of the PPh₃ moiety in **2a** by the Me₂P moiety in **3** to form **4** is supported by the fact that the ³¹P NMR chemical shift of the new product is only a few parts per million downfield of the corresponding signal for (1-Me-Ind)Ni(PMe₃)(Me).²⁹

We have not succeeded in growing single crystals of **4** suitable for X-ray diffraction studies, but additional NMR studies on the **2a/3/NEt₃** mixture (molar ratio of 2:1:8) helped confirm the identity of the new product as (1-Me-Ind)Ni(PMe₂CH₂-AlMe₂·NEt₃)Me. For instance, comparing the ¹H and ¹H{³¹P} NMR spectra of this mixture helped assign the signals for H₃ (ca. 4.7 ppm, dd, ³J_{P-H} = 4.0 Hz, ³J_{H-H} = 4.0 Hz), Ind-CH₃ (ca. 2.0 ppm, d, ⁴J_{P-H} = 4.4 Hz), and Ni-CH₃ (-0.74 ppm, d, ³J_{P-H} = 5.1 Hz); all of these signals are coupled to the ³¹P signal at 4.26 ppm. We also observed ¹H NMR signals for NEt₃, both free and coordinated to Al. Significantly, coordination of the phosphine moiety in **3** to the dissymmetric Ni center renders the symmetry-related nuclei (CH₃)₂PCH₂Al(CH₃)₂·(CH₃CH₂)₃N diastereotopic; as a result, these nuclei are no longer pairwise equivalent and give AA'-type ¹H NMR signals. Finally, TOCSY experiments have allowed us to confirm the connectivities of the various protons in this adduct (Figure 2), and they revealed interactions between (a) free and coordinated NEt₃ and (b) AlMe₂ and Ni-Me moieties.

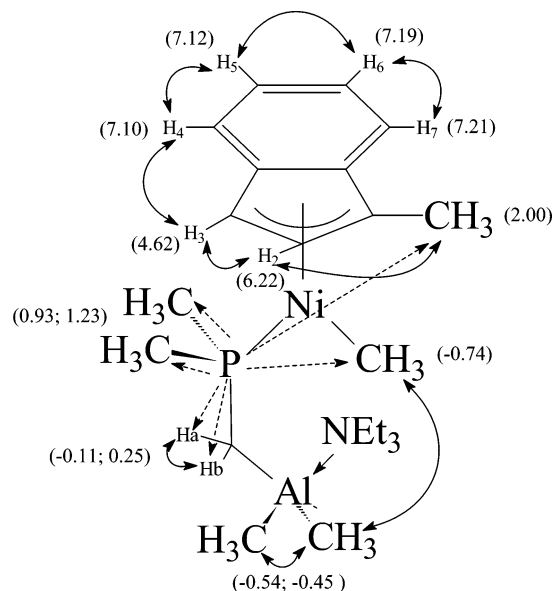


Figure 2. ¹H NMR data for **4**·NEt₃. The dashed arrows indicate the correlations established by selective decoupling of the phosphine resonance (¹H{³¹P}), while the bold arrows indicate the correlations established from the selective TOCSY NMR experiment. The ¹H chemical shifts (in ppm) are given in brackets.

The Effect of Lewis Bases on the Rate of Catalysis. Having established that NEt₃ accelerates the conversion of **2a** to **4**, the question arose whether this would have a favorable influence on the rate of the catalysis. Indeed, we found that the oligomerization of PhSiH₃ catalyzed by **2a/3/NEt₃** (2:1:10) proceeded with a TOF of 1760 h⁻¹ (Figure 1), more than 3 times faster than the rate of catalysis in the absence of NEt₃ and more than 150 times faster than that with **2a** alone. This observation encouraged us to probe the effect of other Lewis bases possessing varying degrees of nucleophilicity toward the Al moiety in **4**,³⁰ as described below.

The influence of the Lewis base on the dimer/monomer equilibrium for **3** was taken as a measure of the base's nucleophilicity. Among the bases studied, quinuclidine was the strongest nucleophile, such that only 1 equiv of it was sufficient to drive the monomer/dimer equilibrium for **3** completely in the direction of the monomeric form. The Lewis bases THF and tmeda were less nucleophilic than quinuclidine, their impact on the monomer/dimer equilibrium being similar to that of NEt₃; the weakest nucleophile, Et₂O, had no effect on the equilibrium. As expected, quinuclidine hindered the rate of catalysis significantly, while tmeda and THF enhanced it much like NEt₃ and Et₂O had little impact (Figure 3, Table 1).

Mechanistic Considerations. The above observations are fully consistent with the direct involvement of adduct **4** in the catalytic oligomerization of PhSiH₃ and support the notion that the AlMe₂ moiety in **4** plays an important role in the promotion of the catalysis. Nevertheless, the following alternative scenarios not involving the formation of **4** have also been considered. First, we have considered the possibility that the catalysis might be promoted as a result of a direct interaction between the AlMe₂ moiety in **3** and the Ni center, without precoordination of the PMe₂ moiety to the Ni center. This seems unlikely, however,

(29) The ³¹P{¹H} NMR signal for (1-Me-Ind)Ni(PMe₃)Me resonates at -3.72 ppm (C₆D₆). (See ref 9.)

(30) It is noteworthy that the O- and N-based Lewis bases used in this study do not coordinate to the Ni center, and thus, their influence on the catalysis can be attributed entirely to their interactions with Al.

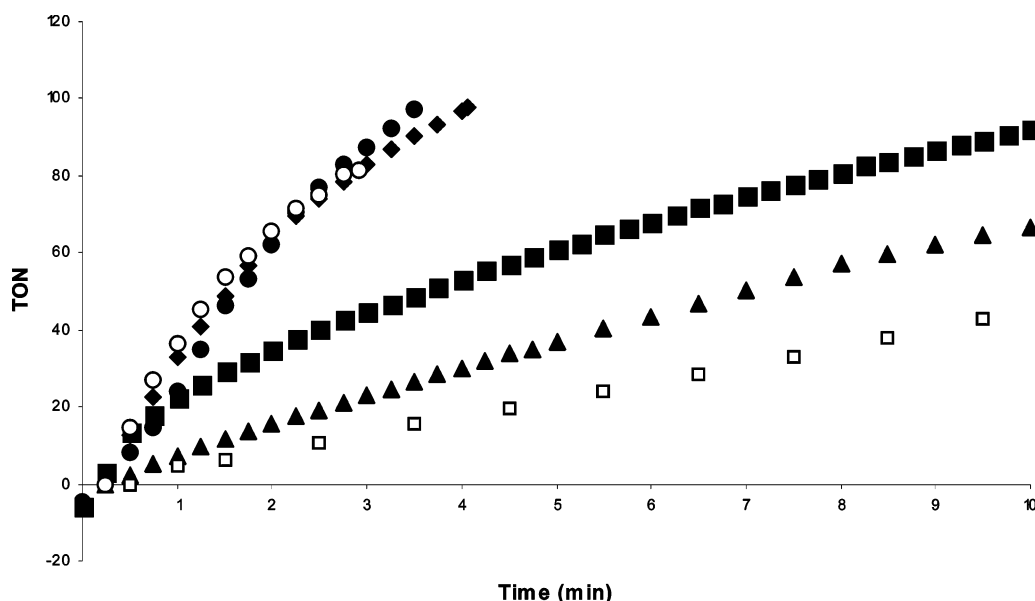


Figure 3. Rate profiles for the evolution of H₂ during the oligomerization of PhSiH₃ catalyzed by a combination of **2a** and **3** without any base (■) and with: 10 equiv of NET₃ (◆), 10 equiv of tmeda (●), 10 equiv of THF (○), 10 equiv of Et₂O (▲), or 2 equiv of quinuclidine (□). The initial Ni/Al/Si ratio was 1:1:200 in all runs; [Ni] = 0.018 M.

Table 1. Catalytic Rates of the Dehydrogenative Oligomerization of PhSiH₃

run	catalytic system ^a	Lewis base ^b	TOF (h ⁻¹) ^c
1	2a		11
2	2a/3		554
3	2a/3^d		552
4	2b		<1
5	2b/3		187
6	2c		141
7	2c/3		53
8	2a/3	NET ₃ ^e	1760
9	2a/3	tmeda ^e	1680
10	2a/3	THF ^e	1655
11	2a/3	Et ₂ O	400
12	2a/3	quinuclidine ^f	280

^a The reaction mixtures consist of a 0.018 M solution of the catalyst in toluene (1 mL), 0.009 mmol of **3** (Ni/Al = 1:1), and 200 equiv (3.6 mmol) of PhSiH₃, mixed and stirred at room temperature. ^b [2a]/[Lewis base] ≈ 1:10 (unless otherwise stated). ^c Average turnover frequency was calculated by dividing the total millimoles of H₂ evolved after 10 min of reaction (unless otherwise stated) by the number of millimoles of **2a** used. ^d For the conversion of a second batch of PhSiH₃ added to the reaction mixture of run 2, one hour after gas evolution had all but ceased. ^e TOF calculated after 3 min of reaction. ^f [2a]/[quinuclidine] ≈ 1:2.

because any Ni–Al interaction involving **2a** and uncoordinated **3** should be similar to that between **2a** and AlMe₃; that is, inhibition rather than acceleration would have resulted from such an interaction. Another conceivable scenario for explaining the beneficial effect of **3** on the catalysis promoted by **2a** would involve the prior reaction of **2a** with PhSiH₃ to generate a Ni–X species (X = hydride or silyl), followed by the interaction of this intermediate with **3**. This scenario can also be discounted in light of our previous results, which showed that the rate-determining step in the oligomerization of PhSiH₃ catalyzed by IndNi(PR₃)₃(Me) is the initial reaction between the monomer and the precatalysts;³¹ thus, the action of **3** on **2a** must precede

the rate-determining step, otherwise it would not be expected to affect the overall rate of the catalysis.

We propose, therefore, that the sequence of steps shown in Scheme 5 depicts a reasonable picture of how the Ni-catalyzed oligomerization catalysis proceeds in the presence of **3**. Thus, the PMe₂ moiety in monomeric **3** (or **3·L**) reacts with **2a** to give the associative displacement of PPh₃ and the formation of **4** (or **4·L**); the presence of the Lewis base L shifts the equilibrium in favor of **4·L**. This sets the stage for the initial reaction with PhSiH₃ to eliminate CH₄ and generate the Ni–SiPhH₂ analogue of **4**, which can react with another monomer to form a Si–Si bond and generate the Ni–H analogue of **4**; the latter reacts with a third molecule of PhSiH₃ to release H₂ and regenerate the Ni–SiPhH₂ analogue of **4**. We envisage that the reactions of the Ni–H and Ni–SiPhH₂ intermediates with PhSiH₃ proceed either via a σ -bond metathesis scheme or through addition–elimination steps.³² It is reasonable to presume that the much more efficient oligomerization of PhSiH₃ by **4** compared to **2a** must be due to the phosphine and Al moieties in **4**. The importance of these moieties for the catalysis has been probed by the experiments outlined in the following sections.

The Influence of the Phosphine Moieties on the Catalysis. Since the rate of PhSiH₃ oligomerization catalyzed by IndNi-(PR₃)Me in the absence of cocatalysts decreases sharply by the increasing size of the phosphine ligand (PMe₃ ≫ PPh₃ > PCy₃),⁹ it is to be expected that displacing the PPh₃ moiety in **2a** by the less bulky Me₂PCH₂R moiety in **4** would accelerate the rate of the catalysis. Accordingly, we noted a dramatic increase in the catalytic activity of (1-Me-Ind)Ni(PCy₃)Me, **2b**, which changed from being virtually inert toward PhSiH₃ in the absence

(31) During the dehydrogenative oligomerization of PhSiH₃ catalyzed by (1-Me-Ind)Ni(PR₃)Me, complete monomer consumption and oligomer formation occur after only small amounts (<10%) of the catalyst precursor has been consumed (ref 9), implying that the initiation step (i.e., reaction of PhSiH₃ with the Ni–Me precursor) is much slower than the propagation step.

(32) According to Tilley's proposal, d⁰ metal centers in group 4 metallocenes promote Si–Si bond formation through σ -bond metathesis reactions; the cyclic oligomers are thought to form via such concerted pathways or by back-biting (ref 4j). We have shown (ref 9) that complex **2c** reacts with PhSiH₃ via a similar mechanism, while the subsequent reactions of PhSiH₃ or the higher oligomers with the Ni–H and Ni–silyl intermediates can also go through addition/elimination reactions involving Ind-free Ni(0) and Ni(II) species.

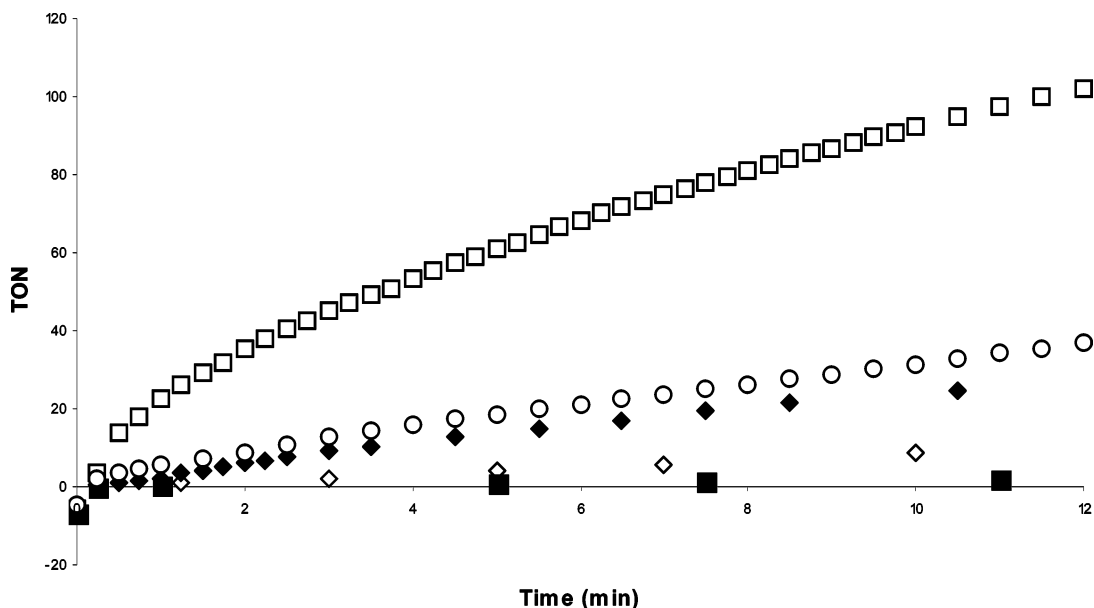
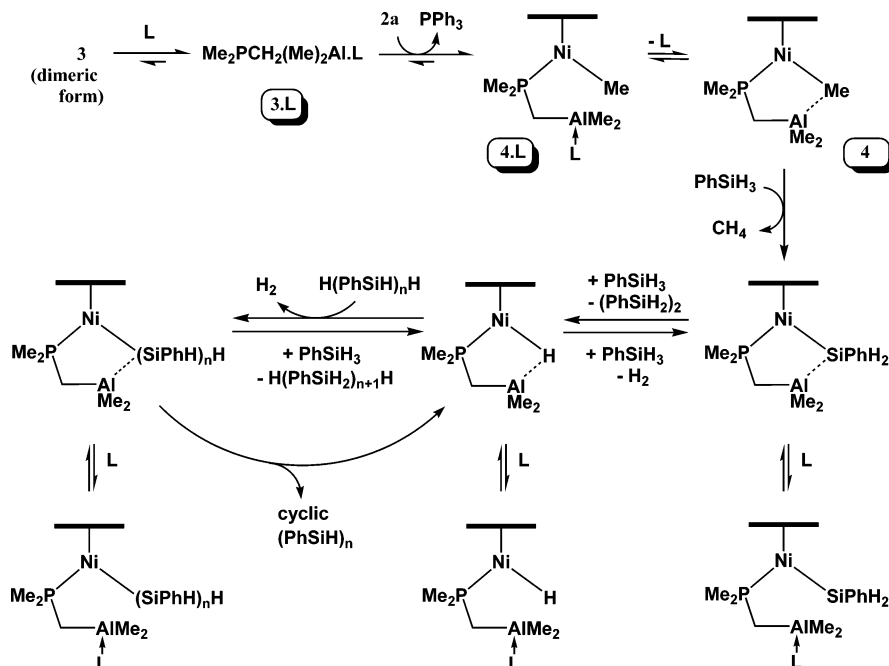


Figure 4. Rate profiles for the evolution of H_2 during the oligomerization of PhSiH_3 catalyzed by **2a** alone (■) and in combination with **3** (□), **2c** alone (◆) and in combination with **3** (◇), and the combination of **2b** and **3** (○). (NB: **2b** is virtually inert toward PhSiH_3 in the absence of **3**.)

Scheme 5



of **3**³³ into a competent catalyst for the oligomerization reaction in the presence of 1 equiv of **3** (TOF = 187 h^{-1} , Figure 4). On the other hand, the oligomerization reaction catalyzed by (1-Me-Ind)Ni(PMe₃)Me, **2c**, was found to proceed *less* efficiently in the presence of **3** (TOF = 53 h^{-1} , Figure 4). In other words, the presence of **3** engenders a rate acceleration of at least 2 orders of magnitude for the reaction catalyzed by **2b**, whereas it *inhibits* the reaction of **2c** with PhSiH_3 !

The above results indicate the net order of reactivity of the Ni–Me complexes **2** toward PhSiH_3 changes from **2c** \gg **2a** > **2b** in the absence of **3** to **2a** > **2b** > **2c** in its presence. The observation that catalytic TOF values vary as a function of Ni–

Me precursor (**2c/3** < **2b/3** < **2a/3**) appears counterintuitive at first, because the reaction of **3** with either **2a**, **2b**, or **2c** should lead to the common intermediate **4**. However, the difference in the reactivities of these systems can be rationalized in terms of the nucleophilicity of the phosphine ligand which is displaced by **3**: since PMe_3 and PCy_3 are more nucleophilic than PPh_3 , they can compete more effectively with the monomer for coordination to Ni, and hence, the catalysis should be less efficient with **2c** and **2b** as precursors.³⁴ Thus, the effectiveness of **3** as a cocatalyst for the Ni-catalyzed oligomerization of PhSiH_3 is inversely proportional to the nucleophilicity of the phosphine ligand displaced from the Ni precursor.

The Nature of the Ni···R···Al Interactions in 4. The above results demonstrate the direct relationship between the significant

(33) The rate of H_2 evolution for the oligomerization reaction catalyzed by **2b** is too small for accurate measurement (ca. less than 1 mL of H_2 evolved over 30 min).

rate accelerations observed in the reactions catalyzed by **2a/3** and **2b/3** and the less bulky phosphine moiety in **4**; however, the nature of the phosphine alone cannot account for the entire rate enhancement brought about by **3**, because precatalyst **2c**, which has a very similar phosphine ligand to the adduct **4** (PMe₃ vs Me₂PCH₂AlMe₂), is less active than **4**. Therefore, the rate enhancement must also be due to the Lewis acidic AlMe₂ moiety in **4**. Although our studies have not established the exact role of the AlMe₂ moiety in **4**, the NMR experiments described below have shown that the Ni···Me···Al interactions present in **4** are quite different from those observed in the presence of AlMe₃.

Monitoring a mixture of (1-Me-Ind)Ni(PPh₃)(CD₃) and **3** (2:1) by ¹H NMR showed that the Ni–CD₃/Al–CH₃ exchange took place with a half-life of about 12 h, significantly slower than the corresponding exchange with AlMe₃ (vide supra) and slower than the rate of oligomerization catalysis. This suggests a link between the Ni–Me/Al–Me exchange and the promotion and inhibition of the catalysis: free AlMe₃ promotes a fast exchange and inhibits the catalysis, whereas the tethered AlMe₂ moiety in **4** promotes a much slower exchange reaction but accelerates the Si–Si bond formation reaction.

Concluding Remarks

The importance of cocatalysts in reactions catalyzed by transition-metal complexes has been recognized for some time, but recent years have witnessed a surge of interest in using Lewis acid-type Al- and B-based cocatalysts to promote organic transformations³⁵ and polymerization reactions.³⁶ In this context, an emerging area of activity is the design of new Lewis acid-type cocatalysts possessing well-defined structures and reactivities.³⁷ The main strategy in these efforts has centered on varying the Al- and B-substituents as a means of modulating the Lewis acidity of the reagents.

In the present study, we have examined a different strategy that seeks to modulate the cocatalytic properties of a simple Lewis acid such as AlR₃ by controlling its approach to the reaction center. Thus, the bifunctional reagent³⁸ Me₂PCH₂AlMe₂ was found to have a great influence on both the rates and the selectivity of Ni-catalyzed Si–Si bond formation reactions, promoting the rapid homologation of PhSiH₃ to mainly cyclic oligomers. Our results indicate that the Lewis basic phosphine

moiety in this reagent serves as an anchor to hold the Lewis acidic AlMe₂ moiety in the proximity of the Ni center; the Ni···R···Al interactions facilitated by this arrangement are responsible for the observed acceleration in the rate of the PhSiH₃ oligomerization reaction. Although we have not uncovered the exact nature of these interactions yet, it is nevertheless remarkable that placing geometrical constraints on the way the Lewis acidic moiety interacts with the reaction center can render an otherwise inhibitor of catalysis (AlMe₃) into a potent cocatalyst (**3**).

The investigations into the cocatalytic properties of Me₂PCH₂AlMe₂ have evolved from our earlier studies on the silane homologation reactions catalyzed by the Ni/MAO system. To be sure, the cocatalytic properties of these reagents are quite different: MAO promotes slow reactions leading to polymers, while Me₂PCH₂AlMe₂ promotes rapid reactions leading to cyclic oligomers. Nevertheless, there may be common features in the way these two systems operate. For instance, the Lewis basic O-moieties present in the oligomeric structures of aluminoxanes can be viewed as potential ligands to metal centers;³⁹ thus, MAO, too, can be considered a bifunctional reagent in which both the Lewis acidic and Lewis basic sites fulfill useful functions. The advantage of bifunctional reagents such as Me₂PCH₂AlMe₂ lies in the fact that their structural simplicity is ideal for NMR monitoring of catalytic reactions, while the ease with which the P- and Al-substituents can be modified should provide easy access to new derivatives. We hope that further mechanistic studies and structural modifications will eventually enable us to prepare a family of bifunctional cocatalysts that promote the formation of linear polysilanes.

Experimental Section

General. All manipulations were performed using dried and distilled solvents in an ultrapure N₂ atmosphere inside a glovebox or using Schlenk techniques. NEt₃ and TMEDA (Aldrich) were dried over CaH₂ and distilled under N₂ atmosphere, quinuclidine (Aldrich) was dried under vacuum for 12 h prior to use, PhSiH₃ (Aldrich) was stored over molecular sieves, AlMe₃ (Aldrich) was used as received, and MAO (Aldrich) was evaporated for several hours to obtain a white solid, which was stored in the glovebox and used in the experiments. Compounds **2a**,¹¹ **2b**,⁹ **2c**,⁹ and **3**¹⁹ were prepared according to previously reported procedures. The Ni–CD₃ analogue of **2a** was prepared following the same procedure as for **2a**, but using CD₃Li instead of CH₃Li; CD₃Li, in turn, was prepared from CD₃I and Li (Aldrich). The ¹H, ¹H{³¹P}, ¹³C{¹H}, and ³¹P{¹H} NMR were recorded on a Bruker ARX-400 spectrometer (400 MHz for ¹H, 162.1 MHz for ³¹P, and 100.6 MHz for ¹³C). 2D experiments (TOCSY, saturation transfer, and HMQC) were recorded on a Bruker DMX-600 spectrometer. The GPC analyses were performed on a Waters GPC system equipped with a refractive index detector calibrated with polystyrene standards in THF.

Reactivities of **1a with MAO and AlMe₃.** ¹H and ³¹P{¹H} NMR spectroscopy (C₆D₆) was used to monitor the transformation of (1-Me-Ind)(PPh₃)Ni(Cl), **1a**, in the presence of various quantities of MAO or AlMe₃. The distinct ³¹P{¹H} NMR signals of **1a** (ca. 31 ppm) and its Ni–Me analogue **2a** (ca. 48 ppm) allowed a convenient monitoring of the methylation reaction. Ionization of **1a** gave primarily the cationic species [(1-Me-Ind)Ni(PPh₃)₂]⁺ that displayed distinct AB signals (ca. 36 and 32 ppm) in their ³¹P{¹H} NMR spectra;¹² integration of these signals against those of the starting materials allowed an evaluation of the extent of ionization under different conditions. In the presence of

- (34) In principle, the different rates of oligomerization might also be attributed to the coordination of the displaced phosphine to the Al center. It should be noted, however, that while formation of such Al·PR₃ adducts can modulate the effectiveness of **3** as a cocatalyst, it should not reduce the overall activity below that of **2c** alone because IndNi(PMe₃)Me and IndNi(Me₂PCH₂AlMe₂·PR₃)Me have similar environments around the Ni center and should have similar reactivities. That this is not the case (i.e., the rate is 4 times slower with **2c/3** compared to **2c** alone) argues in favor of the coordination of the displaced PR₃ to Ni.
- (35) (a) Blackwell, J. M.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1295. (b) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.
- (36) For recent reviews on the various cocatalysts prepared in the context of olefin polymerization catalysis, see: (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (b) Piers, W. E.; Irvine, G. J.; Williams, V. C. *Eur. J. Inorg. Chem.* **2000**, 2131.
- (37) For a few leading references on the preparation of Lewis acid-type cocatalysts for olefin polymerization and other reactions, see: (a) Li, L.; Marks, J. M. *Organometallics* **1998**, *17*, 3996. (b) Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Organometallics* **2000**, *19*, 1619. (c) Zhang, S.; Piers, W. E. *Organometallics* **2001**, *20*, 2088. (d) Elmslie, D. J. H.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1251.
- (38) Bifunctional Lewis acid–Lewis base-type reagents have also been used in catalytic organic transformations: Giles, R. L.; Howard, J. A. K.; Patrick, L. G. F.; Probert, M. R.; Smith, G. E.; Whiting, A. J. *Organomet. Chem.* **2003**, *680*, 257 and references therein.

- (39) (a) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213. (b) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465.

more than 30 equiv of MAO, a new set of AB signals emerged; the very close chemical shift of these signals ($\Delta\delta$ ca. 0.3 ppm) and the virtually identical ${}^2J_{P-P}$ value led us to believe that they represented structurally analogous cations having different MAO-based counteranions. The combined integration values of these signals were used to estimate the extent of ionization.

Catalytic Oligomerization of PhSiH₃. The small-scale catalytic reactions were conducted by syringing PhSiH₃ (ca. 200 equiv) into a septum-capped Schlenk tube (volume ca. 10 mL) containing a vigorously stirring toluene solution (ca. 1 mL) of the Ni(II) precursor and the cocatalyst Me₂PCH₂AlMe₂ (ca. 0.02 M each). The stirring continued for several hours under nitrogen purge to remove the evolved hydrogen. Evaporation of the final reaction mixture gave an oil, which was characterized using ¹H NMR and GPC, as described elsewhere.⁹ These analyses showed that the cyclic oligomers (PhSiH)_n constitute the predominant products of the catalytic runs, while small amounts (<5%) of the linear oligomers also formed. In some cases, the ¹H NMR spectra also signaled the presence of small quantities (<2%) of Ph₂SiH₂, which can arise from a redistribution reaction.⁴⁰

A number of large-scale reactions were also carried out in a similar way using 500 equiv of PhSiH₃ (1.14 mL, 1.00 g). The final mixture was filtered through a plug of Celite and activated charcoal, and evaporated to give (PhSiH)_n as a viscous oil (85% isolated yield).

Kinetic Measurements of the PhSiH₃ Homologation Reaction.

The catalytic reactions were conducted as above by syringing PhSiH₃ (3.6 mmol, 200 equiv) into a septum-capped reaction vessel containing a vigorously stirring toluene solution (1 mL) of the Ni(II) precursor and the cocatalyst Me₂PCH₂AlMe₂ (0.018 M each). The progress of the reaction was monitored by determining the volume of the H₂ gas which evolved during the Si–Si bond formation reactions. The apparatus used for measuring the volume of evolved H₂ consisted of an inverted buret that was filled with water and suspended above a water bath in such a way as to place the bottom of the buret about 2 cm below the water level. The gas evolved during the catalytic runs was allowed to escape from the reaction vessel into the buret through a Teflon tube capped with a gastight needle at each end. Immediately after the PhSiH₃ was added to the reaction mixture, one of these needles was pierced through the gastight septum, sealing the vessel, while the other needle was placed inside the buret in such a way as to ensure that all escaped gases bubbled through the water on their way to the top of the buret. The volume of H₂ liberated was determined by the displacement of the water in the buret as a function of time. The initial reaction rates for the various runs were determined for the first 10 min of each reaction; for runs that were too fast, the monitoring period was reduced to the first 3 min. The rate at $t = 0$ min was adjusted for the initial overpressure caused by (a) the higher-than-atmospheric pressure inside the Schlenk flask that was loaded inside the somewhat

over-pressurized glovebox and (b) the injection of PhSiH₃. The apparatus was calibrated by injecting known volumes of air into the same reaction containing a blank mixture. No deviation of volume has been observed.

Characterization of (1-Me-Ind)Ni(Me₂PCH₂AlMe₂·NEt₃)Me (4·NEt₃). NEt₃ (4 equiv, 46 μ L, 0.34 mmol) were added to a C₆D₆ solution (0.5 mL) of **3** (38.4 mg, 0.083 mmol) and **1** (10.4 mg, 0.083 mmol), and the resulting species (**4**·NEt₃) was characterized by means of the following NMR experiments: ¹H, ³¹P{¹H}, ¹³C{¹H}, selective ¹H{³¹P}, selective TOCSY, HMQC, DEPT, and DEPT {³¹P}. ¹H NMR δ (C₆D₆, 298 K): -0.74 (d, ³J_{H-P} = 5.1, Ni-Me, 3H), -0.54 (br, AlMe, 3H), -0.45 (br, AlMe, 3H), -0.11 (dd, ²J_{H-H} = 12.7 and ²J_{H-P} = 17.7, AlCH₂P, 1H), 0.25 (dd, ²J_{H-H} = 12.7 and ²J_{H-P} = 13.0, AlCH₂P, 1H), 0.62 (br, NCH₂CH₃, 9H), 0.93 (d, ²J_{H-P} = 8.5, PMe, 3H), 1.23 (br, ²J_{H-P} = 8.7, PMe, 3H), 2.0 (d, ³J_{H-P} = 3.6, 1-Me-Ind, 3H), 2.18 (br, NCH₂CH₃, 6H), 4.62 (d, ³J_{H-H} = 2.6, H3, 1H), 6.22 (d, ³J_{H-H} = 2.6, H2, 1H), 7.10 (m, H4), 7.12 (m, H5), 7.19 (m, H6), 7.21 (m, H7). ¹³C{¹H} NMR δ (C₆D₆, 298 K): -19.5 (d, ²J_{C-P} = 23.2, Ni-Me), -5.4 (br, AlMe), 11.0 (d, ³J_{C-P} = 1.6, 1-Me-Ind), 12.5 (br, NCH₂CH₃), 12.8 (s, AlCH₂P), 20.0 (d, ¹J_{C-P} = 26.3, PMe), 20.1 (d, ¹J_{C-P} = 24.0, PMe), 47.6 (br, NCH₂CH₃), 69.5 (s, C3), 86.8 (d, ³J_{C-P} = 12.0, C1), 102.5 (s, C2), 115.7 (s, C7), 116.4 (s, C4), 121.4 (s, C5), 121.4 (s, C6), 121.6 (s, C3a or C7a), 122.3 (s, C3a or C7a). ³¹P{¹H} NMR: δ (C₆D₆, 298 K): 4.26 ppm (s, PMe₂R).

Influence of Lewis Bases on Dimer/Monomer Equilibrium for **3 and on the Oligomerization Catalysis.** Monitoring the ³¹P{¹H} NMR spectra (C₆D₆) of mixtures of **3** and Lewis bases allowed us to establish the dimer/monomer equilibrium by comparing the intensities of the **3**-base adduct (often a broad resonance) to the singlet resonance due to dimeric **3** (-37 ppm). In the case of quinuclidine, the spectrum indicated a complete conversion to the adduct, which displayed a sharp singlet resonance at -49 ppm. The ¹H NMR spectrum of **3** showed the following changes upon addition of quinuclidine: the signal due to Al(CH₃)₂ changed from a doublet (³J_{P-H} = 5.6 Hz) in the absence of quinuclidine to a singlet; the signals for the P-CH₂ nuclei, which are magnetically inequivalent in the dimeric form, changed from two doublets at -0.01 and -0.05 ppm (²J_{P-H} = 6.8 Hz) to one doublet at ca. 0.12 ppm (²J_{P-H} < 2 Hz) for the two equivalent nuclei; the doublet due to P(CH₃)₂ at ca. 0.77 ppm (²J_{P-H} = 7.6 Hz) changed to a broad signal at ca. 1.0 ppm. The influence of the Lewis base on the dehydrogenative oligomerization of PhSiH₃ was determined by means of the manometric measurements described above; the data is given in Table 1.

Acknowledgment. We are grateful to NSERC (Canada), NATEQ (Québec), and Université de Montréal for financial support; Dr. P. V. M. Tan for his help in the NMR characterization of **4**; Wilms Baille and Dr. J. Zhu for the GPC measurements; and Mr. Ralph Flachsbart (Wilmad Labglass) for the gift of the 528-TR-7 NMR tubes.

JA048911M

(40) It is well-known that silane redistribution occurs in many late metal systems to produce R_nSiH_{4-n} and SiH₄; the latter is often incorporated into the polymeric materials because of its high reactivity with the active catalyst. A recent report (Rosenberg, L.; Davis, C. W.; Yao, J. *J. Am. Chem. Soc.* **2001**, *123*, 5120) has described the dramatic effect of H₂ removal on the redistribution reaction.