supports the formulation of the paramagnetic product as the dinuclear Zr(III) phosphine adduct $[SiMe_2(C_5H_4)_2][CpZrCl(PMe_3)]_2$ (eq 7). Unfortunately, this species shows limited stability in solution.

$$[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2 + 2PMe_3 \rightarrow [SiMe_2(C_5H_4)_2][CpZrCl(PMe_3)]_2 \quad (7)$$

Whereas the reactions of 2 with THF and PMe_3 occur with the gradual formation of paramagnetic Zr(III) adducts, the corresponding reaction of 2 with CN-*t*-Bu proceeds quite differently. This reaction occurs with the consumption of 1 equiv of CN-*t*-Bu, giving a bright orange product. Its NMR and IR spectra[36] are compatible with the formation of a dinuclear complex containing a semibridging isocyanide ligand similar to that observed in the fulvalene-bridged complex $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrCl]_2(\sigma,\pi\text{-CN-}t\text{-Bu})$, reported by Herrmann and co-workers.[29]

Although the reaction of 2 with various Lewis bases results in the cleavage of the chloro bridges, two different types of dinuclear products are observed. For PMe_3 and THF, metal coordination to each Zr center leads to the formation of dinuclear zirconocenophane species containing two mechanically linked paramagnetic zirconocene fragments. Alternatively, the unsaturation introduced by the CN triple bond of CN-*t*-Bu enables it to coordinate in both a σ and π fashion.

The presence of two Zr(III) centers in $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$ suggests that this compound should behave as a two-electron reductant. Evidence of this behavior is provided by the reactions of 2 with stoichiometric amounts of either Ph_3PO or CO_2. Heating the corresponding reaction mixture in a sealed NMR tube at 75 °C similarly proceeds with O atom abstraction and complete conversion of 2 to $[SiMe_2(C_5H_4)_2][CpZrCl]_2(\mu\text{-}O)$[14] within several days. For Ph_3PO, the formation of Ph_3P is readily apparent from the NMR spectrum. The formation of two strong Zr–O bonds provides the thermodynamic driving force for cleavage of the P=O bond (130 kcal/mol)[37] in Ph_3PO and a C=O bond (127 kcal/mol)[38] of CO_2. The formation of the oxo-bridge compound clearly requires the participation of both Zr(III) centers.

Future work will focus on modifying the structures of 1 and 2 in an effort to make the Zr–(μ-X)–Zr (X = S, Cl) linkages more susceptible to cleavage and thereby enhance the reactivity. By replacing Cp with Cp*, the additional steric bulk of Cp* should increase the Zr···Zr separation and reduce the ability of the bridging atoms to interact symmetrically with both zirconium centers.

Acknowledgment. Support for this research was provided in part by the West Virginia Energy and Water Research Center and the Petroleum Research Fund, administered by the American Chemical Society. Computer time for the X-ray structural analyses was made available by the West Virginia Network for Educational Telecomputing.

Registry No. 1, 138234-09-0; **2**, 118920-58-4; $[SiMe_2(C_5H_4)_2][CpZrCl_2]_2$, 118920-56-2; $[SiMe_2(C_5H_4)_2][CpZrMe_2]_2$, 138234-10-3; $[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2$, 118920-55-1; $[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2$, 118920-54-0; $[SiMe_2(C_5H_4)_2][CpZrCl(THF)]_2$, 138234-11-4; $[SiMe_2(C_5H_4)_2][CpZrCl(PMe_3)]_2$, 138234-12-5; $[SiMe_2(C_5H_4)_2][CpZrCl]_2(\mu\text{-}O)$, 118920-57-3.

Supplementary Material Available: Tables of thermal parameters, interatomic distances and bond angles, and least-squares planes for the X-ray structural analyses of $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}X)]_2$ (X = S, Cl) (15 pages); listings of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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[36] Spectroscopic data for $[SiMe_2(C_5H_4)_2][CpZrCl]_2(\sigma,\pi\text{-CN-}t\text{-Bu})$: ^1H NMR (C_6D_6) δ 6.59, 6.58, 5.93 (2 H), 5.83, 5.78, 5.68, 4.68 (m, C_5H_4), 5.97, 5.64 (s, C_5H_5), 1.38 (s, CMe_3), 0.44, 0.16 (s, SiMe); $^{13}C\{^1H\}$ NMR (C_6D_6) 129.5, 127.1, 126.3, 122.5, 115.9, 115.4, 114.6, 107.7, 106.7, 106.2 (C_5H_4), 110.2, 109.7 (C_5H_5), 66.9 (*C*Me), 29.7 (C*Me*$_3$), 0.36, 0.02 (SiMe); IR $\nu_{C\equiv N}$ = 1600 cm^{-1}.

[37] Cobridge, D. E. C. *Phosphorous*; Elsevier Scientific Publishing: Oxford, 1978; p 24.

[38] Atkins, P. W. *Physical Chemistry*, 3rd ed.; W. H. Freeman: New York, 1986; p 821.

Reactions of Hydrosilanes and Olefins in the Presence of Cp_2MCl_2/nBuLi

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The Cp_2MCl_2/nBuLi (M = Ti, Zr, Hf) catalyzed reactions of $PhMeSiH_2$ in the presence of near-stoichiometric quantities of cyclic and acyclic olefins have demonstrated a range of reactions including hydrosilylation of the olefin, isomerization/hydrosilation of internal olefins, dehydrocoupling of the silane to silicon oligomers, and dehydrocoupling of the silane with the olefin to form vinylsilanes. The product which dominates is a function of the metal and the nature of the olefin. Hydrosilation of terminal acyclic olefins and isomerization/hydrosilylation of internal olefins occur with M = Zr. Cyclic olefins promote the formation of silicon oligomers, and cyclooctene and norbornene with M = Ti provide the highest conversion and highest rates, respectively. Dehydrocoupling of the vinyl hydrogen in cyclooctene and the hydrosilane occurs when M = Zr or Hf. The variations in chemistry can be rationalized through the silylmetal, $Cp_2M(H)SiPhMeH$, and plausible mechanisms for formation of the various products are discussed.

Introduction

We have demonstrated recently that the combination Cp_2MCl_2/nBuLi (M = Ti, Zr, Hf) provides a catalyst system effective for the condensation of secondary silanes to oligomers.[1] In the case of $PhMeSiH_2$, disilane through octasilane are obtained in the presence of Cp_2ZrCl_2 and 2 equiv of *n*BuLi when the reaction is conducted at 90 °C

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[1] Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D. *Organometallics* 1991, *10*, 924.

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Table I. Reaction of $PhMeSiH_2$ with Olefins in the Presence of Cp_2MCl_2/*n*BuLi

olefin	Si/olefin[a] (mole ratio)	time (h), conversion[b] (%)	Si product distribn[c]: HSi addn[d]	SiH/HSi coupling[e]	SiH/HC coupling[f]	PhMeBuSiH
		Cp_2ZrCl_2/*n*BuLi				
none		1, 24		91		9
1-tetradecene	1.2	1, 70	92	5 (2–3)		2
		3, 78	92	6 (2–4)		2
	2.6	1, 34	77	19 (2–3)		4
		4.5, 47	73	23 (2–4)		4
1-octene	1.3	1, 74	92	4 (2)		3
	0.7	0.5, 99	91		6	1
cis-4-octene	1.0	1, 97[g]	97	1 (2)		2
trans-4-octene	1.0	1, 95	95	3 (2)		2
cyclooctene	0.9	1, 32	6	29 (2–3)	60	4
		24, 74	23	6 (2–3)	69	2
1-methylcyclohexene[h]	0.9	1, 19		86 (2)		14
		24, 57		92 (2–4)		8
4-methylcyclohexene[h]	0.9	1, 32		82 (2–3)	12	7
		24, 71	5	73 (2–4)	15	6
norbornene[h]	0.9	1, 34	18[i]	75 (2–3)		6
		24, 93	39[i]	58 (2–5)		3
	2.9	1, 45	14[j]	81 (2–3)		5
		24, 62	15[j]	81 (2–5)		4
		Cp_2TiCl_2/*n*BuLi				
none		1, 15		100 (2–3)		
		24, 39		100 (2–3)		
		48, 47		100 (2–3)[k]		
1-octene	0.95	1, 85	65	28 (2–4)	7	
cis-4-octene	1.4	1, 88	64	33 (2–4)	3	
cyclooctene	0.9	1, 67		100 (2–5)		
		24, 98		100 (2–5)		
norbornene[h]	1.1	0.5, 89	12	88 (2–5)		
		Cp_2HfCl_2/*n*BuLi				
none		1, 10		81 (2–3)		19
		24, 44		95 (2–3)		5
		48, 54		95 (2–3)[l]		5
1-octene	1.1	1, 1				1
		24, 18	44		50	6
4-methylcyclohexene[h]	1.0	1, 14		71 (2–3)	7	22
		24, 69		79 (2–4)	13	9
		48, 79		78 (2–5)	14	8
cyclooctene	1.0	1, 9	17	11 (2–3)	68	5
		24, 70	9	5 (2–3)	84	2
		48, 83	12	4 (2–3)	82	2

[a] Reactions run at 90 °C with 2 mL of toluene/g of $PhMeSiH_2$; Si/Zr = 30–40. [b] Determined by GC measurements: $[(PhMeSiH_2)_i - (PhMeSiH_2)_t]/[PhMeSiH_2]_i \times 100$. [c] Determined by GC measurements: GC percent of individual silicon-containing product divided by sum of silicon-containing products × 100. [d] Hydrosilylation product. [e] Silicon oligomer products; values in parentheses correspond to *x* in $H(PhMeSi)_xH$. [f] Vinylsilane products. [g] No reaction at room temperature after 7 h. [h] Olefin masked by toluene. [i] Includes $HPhMeSiC_7H_{11}$, $(HPhMeSi)_2C_7H_{10}$, and $H(PhMeSi)_2C_7H_{11}$ (see text). [j] $HPhMeSiC_7H_{11}$. [k] Contains 5% of $x = 4$. [l] Contains 0.5% of $x = 4$.

in toluene. Since reaction periods are generally from 2 to 4 days, we wished to develop an approach that would allow rapid high conversions of secondary silanes to oligomers and also to promote the reaction of dialkylsilanes which provide only small quantities of oligomers even under the optimum coupling conditions found for $PhMeSiH_2$.

The enthalpy for the dimerization reaction of organosilanes may be nearly thermodynamically neutral, and evolution of the dihydrogen byproduct could tip the balance in favor of silicon–silicon bond formation.[2] The addition of a hydrogen acceptor such as an olefin may improve the conversion of monosilanes. Only a few studies were found in which mixtures of olefins and arylsilanes were reacted with Cp_2TiMe_2, Cp_2TiPh_2, and Cp_2ZrMe_2 with some success at improving oligomer formation and/or increasing chain length.[3,4] The hafnium analogue, Cp_2HfMe_2, does not appear to be effective for the dehydrocoupling of primary silanes,[5] and the influence of olefin coreactants has not been reported.

In this report the effect of the presence of olefin on the reactions of $PhMeSiH_2$ with catalytic quantities of Cp_2MCl_2/*n*BuLi (M = Ti, Zr, Hf) is described. Our original objective was to improve conversion of secondary silanes, but a surprising diversity of reaction products was observed which depended on the nature of the olefin (cyclic vs acyclic) and the nature of the metal.

Results

Reactions were performed in toluene at 90 °C on 1–2 g of $PhMeSiH_2$ with approximately 1 equiv of olefin and a molar ratio of silane to Cp_2MCl_2 between 30 and 40. The course of the reaction was monitored by removing aliquots at periodic intervals and analyzing the reaction mixtures by gas chromatography and by GC–MS. Selected results are reported in Table I. In addition to dehydrocoupling

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(2) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239.

(3) (a) Harrod, J. F.; Yun, S. S. *Organometallics*, **1987**, *6*, 1381. (b) Harrod, J. F. *ACS Symp. Ser.* **1988**, *No. 360*, 89.

(4) Nakano, T.; Nakamura, H.; Nagai, Y. *Chem. Lett.* **1989**, 83.

(5) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rosseau, D. *Organometallics* **1989**, *8*, 1732.

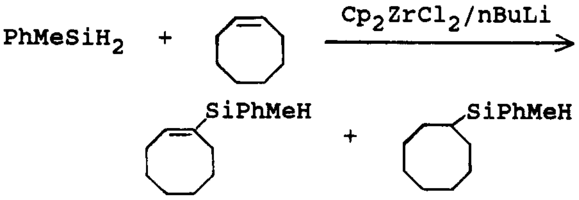
of the hydrosilane, three other reaction processes are observed which involve addition or coupling of the starting silane with the olefin. An additional process involves hydrogenation of the olefin which is observable in reactions that involve tetradecene, octenes, and cyclooctene. In all, four acyclic and four cyclic olefins were studied. Three of the cyclic olefins and their hydrogenated products were coincident with toluene or the solvent front; therefore, conversions listed in the tables are based on the silane. In cases where one major product was formed, the product was isolated and characterized by spectroscopic methods.

$PhMeSiH_2$/Olefin/Cp_2ZrCl_2/*n*BuLi. In the absence of olefins, $PhMeSiH_2$ condenses in the presence of the catalyst precursor Cp_2ZrCl_2/*n*BuLi to give oligomers with Dp values from 2 to 8 after 4 days at 90 °C. In this system the weight percent of starting silane in the reaction mixture appears to level off at about 20%. When reactions are conducted in the presence of terminal olefins, the rate of reaction of the starting silane increases but instead of improved conversion to oligomers the major condensation product is that which arises from hydrosilylation of the olefin to give the β product, $HPhMeSiCH_2CH_2R$, which was isolated and characterized. Results for four acyclic olefins are summarized in Table I.

Hydrogenated olefins are formed from tetradecene and the octenes listed in Table I but are minor components of the reaction mixtures. The dehydrocoupling products (silicon oligomers) and saturated olefin products were determined by GC–MS. The monosilane PhMeBuSiH is always observed in reactions of $PhMeSiH_2$ in the presence of Cp_2ZrCl_2/*n*BuLi.[1] Although PhMeBuSiH is still observed when olefin is present, the amounts are lower than when condensation reactions are run in the absence of olefins. When the reactions are conducted in the presence of excess olefin, the starting silane is consumed within 0.5 h. As the ratio of silane/olefin increases, the rate of conversion of silane decreases and dehydrocoupling of the silane to oligomers becomes more competitive.

Internal olefins also react rapidly with $PhMeSiH_2$, and the major product (>90%) is the hydrosilylation product. All three olefins, $CH_2{=}CHR$ (R = *n*-C_6H_{13}) and *cis*- and *trans*-$RCH{=}CHR$ (R = *n*-C_3H_7), give the same *n*-octylsilane product with the silicon substituent on the terminal carbon atom as verified by the presence of only two resonances of reversed phase in the attached proton test (APT) NMR spectrum. These results show that isomerization of an internal olefin occurs rapidly under the conditions provided by the Cp_2ZrCl_2/*n*BuLi catalyst system.

When the condensation of $PhMeSiH_2$ is conducted in the presence of cyclic olefins, the results were found to vary with each olefin and these results are also summarized in Table I. In addition to oligomers, the reaction of cyclooctene and $PhMeSiH_2$ produced two products which incorporate the olefin as shown in eq 1. The major product, (C_8H_{13})PhMeSiH, formed in the early stages of the reaction corresponds to a formal dehydrocoupling of SiH with a vinyl proton of cyclooctene. The second product, (C_8H_{15})PhMeSiH, which increases with time is the equivalent of hydrosilylation of the cyclooctene. The ratio of (C_8H_{13})PhMeSiH to (C_8H_{15})PhMeSiH decreases from about 9 after 1 h to about 3 after 24 h. After 5 days these two products were isolated by Kugelrohr distillation as a mixture in a 1/1 ratio. The ^{1}H NMR spectrum exhibits two sets of doublets in the SiMe region and two sets of signals in the SiH region. A triplet centered at 6.2 ppm is assigned to the vinyl proton in (C_8H_{13})PhMeSiH. The ^{13}C APT data exhibit three peaks with a reversed phase, two of which are upfield of TMS, consistent with two SiMe groups, and a third which corresponds to the CH group bearing the silicon substituent in (C_8H_{15})PhMeSiH.



(1)

The reactions of methyl-substituted cyclohexenes with $PhMeSiH_2$ were studied, but in this case the starting olefin could not be distinguished from toluene during the GC analyses; the products were identified by GC–MS. The results in the presence of 1-methylcyclohexene are similar to those obtained in the absence of olefin, and only silicon oligomers were observed. Although silicon oligomers are the major products with added 4-methylcyclohexene, minor products due to SiH/HC dehydrocoupling, $PhMeHSi(C_7H_{11})$ (three isomers), and to the equivalent of hydrosilylation, $PhMeHSi(C_7H_{13})$, are observed. Attempts to isolate these minor products provided only a crude mixture for which the ^{1}H NMR spectrum was too complicated to assign resonances to specific products.

With norbornene, the reaction of $PhMeSiH_2$ also produced several products. The major process involves condensation of the starting silane to oligomers but reaction of norbornene with silane competes to a greater extent than in the 4-methylcyclohexene case. The GC–MS data for the products that incorporate olefin show that three hydrosilylation products, $PhMeHSi(C_7H_{11})$, and $(PhMeSiH)_2C_7H_{10}$, and/or $H(PhMeSi)_2(C_7H_{11})$, are produced. The $(PhMeSiH)_2C_7H_{10}$ could be formed by SiH/CH coupling or norbornene with $PhMeSiH_2$ followed by hydrosilylation of the SiH/CH coupling product with another 1 equiv of $PhMeSiH_2$, and $H(PhMeSi)_2C_7H_{11}$ would be formed from hydrosilylation of norbornene by HPhMeSiSiPhMeH.

With acyclic olefins, hydrosilylation ultimately dominates for both terminal or internal olefins, but with cyclic olefins, three processes can compete in the $PhMeSiH_2$/Cp_2ZrCl_2/*n*BuLi system: dehydrocoupling of SiH/HSi, dehydrocoupling of SiH/HC, and hydrosilylation of the olefin. The process which dominates is a function of the olefin. The highest consumption of starting material was observed with norbornene, but hydrosilylation is a competitive process in this system. In all cases studied, the reactions that occur in the presence of cyclic olefins are slower than those observed with acyclic olefins at similar silicon/olefin ratios.

$PhMeSiH_2$/Olefin/Cp_2TiCl_2/*n*BuLi. The reactions of $PhMeSiH_2$ with *cis*-4-octene and 1-octene in the presence of Cp_2TiCl_2/*n*BuLi are similar to those observed with the zirconium catalyst except that a higher percentage of oligomer products is formed (Table I). However, the major product is still that which corresponds to hydrosilylation of the olefin with the silicon substituent on the terminal carbon atom (β product). The hydrosilylation products arise not only from the starting monomer but from the disilane that is formed initially. Both $HPhMeSiPhMeSi(C_8H_{17})$ and $(C_8H_{17})PhMeSiSiMePh(C_8H_{17})$ are observed, although these two products are seldom found in greater than 10% of the product mixture. Such products can arise from dehydrocoupling of $HPhMeSi(C_8H_{17})$ with $PhMeSiH_2$; however, failure to dehydrocouple the tertiary silane, $PhMe_2SiH$, makes this route less likely. The isolated products exhibit spectroscopic properties identical to those

Scheme I

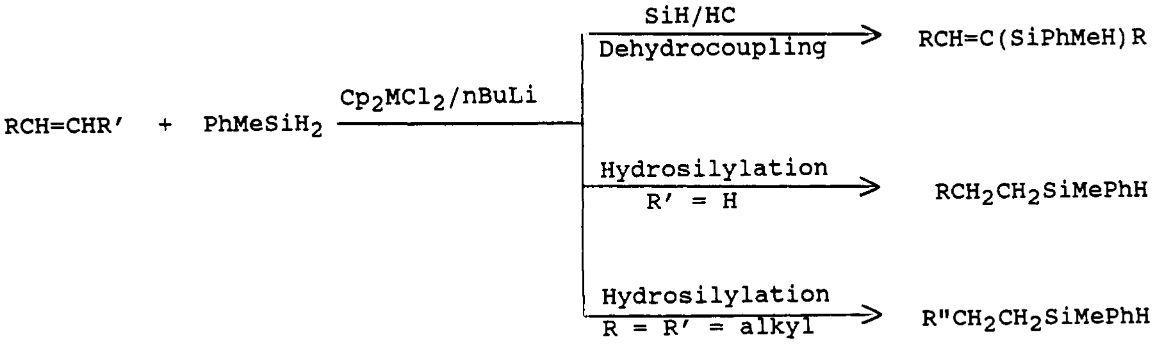


Table II. Comparison of the Reactions of $PhMeSiH_2$ with 1-Octene and Cyclooctene Catalyzed by $Cp_2MCl_2/nBuLi$

				Si product distribn[c]		
				coupling		
olefin	Cp_2MCl_2 (M)	Si/olefin[a]	% conversion[b] (h)	SiH/HSi	SiH/CH	hydrosilylation
1-octene	Ti	0.95	85 (1)	28	7	65
	Zr	0.7	99 (0.5)			91
	Hf	1.1	18 (24)		50	44
cyclooctene	Ti	0.9	98 (24)	100		
	Zr	0.9	74 (24)	6	69	23
	Hf	1.0	70 (24)	5	84	9

[a] Mole ratio. [b] Calculations based on starting silane. See footnote *b*, Table I. [c] Calculations based on silicon-containing products; see footnote *c*, Table I. PhMeBuSiH values are not indicated.

isolated from the zirconium catalyst.

In contrast, cyclic olefins promote the formation of oligomers (Table I). With cycloctene no products involving hydrosilylation or dehydrocoupling of the olefin are observed. After 24 h, 98% of the starting silane has been consumed and the ratio of cyclooctane to cyclooctene is 2.5 (olefin was in excess). The oligomers formed range from disilane through pentasilane in contrast to only disilane and trisilane obtained in the absence of olefin for the same time period. Although dehydrocoupling reactions are faster in the presence of norbornene, hydrosilylation products are also formed.

$PhMeSiH_2/Cp_2HfCl_2/nBuLi$. The addition of the acyclic olefin 1-octene appears to suppress the reaction of $PhMeSiH_2$ in the presence of $Cp_2HfCl_2/nBuLi$, with less than 20% conversion after 24 h (Table I), and no oligomer formation is observed. The cyclic olefins 4-methylcyclohexene and cyclooctene both improve the conversion of starting monosilane, but the major products differ for the two olefins. Cyclohexene provides oligomers of longer chain length than are formed in the absence of olefin plus minor cyclohexenylsilanes products. However, the vinylsilane $(C_8H_{11})SiPhMeH$ is the major product with cyclooctene, and oligomers are only minor products.

Discussion

When olefins are added to $PhMeSiH_2$ in the presence of $Cp_2MCl_2/nBuLi$, three reaction processes are observed in addition to the dehydrocoupling of the monosilane to form silicon oligomers. These general processes are summarized in Scheme I. The process which dominates is a function of both olefin and metal. With Zr and Ti and acyclic olefins, hydrosilylation occurs preferentially, and in the presence of most cyclic olefins, dehydrocoupling and of hydrosilane is promoted except for cyclooctene where the equivalent of another dehydrocoupling between SiH/CH occurs especially with Zr and Hf. A comparison of the results for 1-octene and cyclooctene with all three catalyst systems is illustrated in Table II and demonstrates this variation in the chemistry. When 4-octene is used in place of 1-octene, rapid isomerization/hydrosilylation occurs to give the same product as observed from 1-octene with both Zr and Ti. In most of the cases studied, the rate of one of the reaction processes shown in Scheme I is faster than the others and one major product is ultimately formed. The systems where processes are sufficiently competitive to produce two or more products in greater than 25% by GC analysis are zirconium with cyclooctene and norbornene (at longer reaction times) and titanium and hafnium with acyclic olefins.

Table III. Comparison of Dehydrocoupling of $PhMeSiH_2$ in the Presence of Selected Cyclic Olefins

M in Cp_2MCl_2	olefin	conversion[a] (%) (Time (h))	$H(PhMeSi)_xH$[b] (% *x*)
Ti	none	52 (48)	100 (2–4)
	cyclooctene	98 (24)	100 (2–5)
	norbornene	89 (0.5)	88 (2–5)[c]
Zr	none	48 (24)	93 (2–4)[d]
	4-methylcyclohexene	52 (3)[e]	81 (2–4)[f]
	norbornene	45 (1)[g]	81 (2–3)[h]
Hf	none	56 (72)	95 (2–3)[i]
	4-methylcyclohexane	52 (8)	79 (2–3)

[a] Calculated as described in footnote *b* of Table I. [b] Calculated as described in footnote *c* of Table I. [c] Remainder are hydrosilation products. [d] Remainder is PhMeBuSiH. [e] $PhMeSiH_2$/olefin = 2. [f] Remainder contains PhMeBuSiH + HSi/HC coupling products. [g] $PhMeSiH_2$/olefin = 2.9. [h] Remainder contains PhMeBuSiH and hydrosilation and HSi/HC products. [i] Contains 0.6% of tetramer.

Promotion of Oligomer Formation. Although there is a variation in chemistry as a function of olefin, the original objective of improving the rate of conversion of starting silane to oligomer products was realized and the best cases observed for each catalyst system are summarized in Table III. The choice of olefin to promote the formation of oligomers is a balance between the rate of conversion of the starting silane and the minimization of the byproducts produced by incorporation of the olefin. The cleanest system for highest conversion of $PhMeSiH_2$ to oligomers is cyclooctene with $Cp_2TiCl_2/nBuLi$. With cyclic olefins and zirconium or hafnium catalysts, bypro-

Table IV. Distribution of Oligomers Produced in the Presence of Olefins[a]

M in Cp_2MCl_2	olefin	$PhMeSiH_2$[b] (%)	x in $H(PhMeSi)_xH$[c]				
			2	3	4	5	6
Ti	none	53	1	0.77	0.10		
	norbornene	4.5	1	3.5	4.4	2.0	0.35
	cyclooctene	0	1	6.4	5.7	0.32	
Zr	none	40	1	1.1	0.43		
	4-methylcyclohexene	18	1	2.2	1.3	0.54	
Hf	none	46	1	0.30	0.24		
	4-methylcyclohexene	20	1	1.21	0.13	0.05	tr

[a] Reactions performed at 90 °C for 48 h with 2 mL of toluene/g of $PhMeSiH_2$; Si/M = 30. [b] GC percent of starting material remaining after 48 h. [c] Proportions of oligomers relative to the disilane determined from GC.

ducts from competitive processes occur at longer reaction times. Some balance in conversion of starting material and production of byproducts can be achieved by increasing the silicon/olefin ratio as observed with the zirconium catalyst (compare Tables I and III). With silicon in excess, the byproducts which incorporate the olefin are suppressed but not eliminated. The fastest rate of conversion of silane occurs with norbornene and the titanium catalyst with about 90% of the starting silane consumed within 0.5 h, but hydrosilylation byproducts are also formed.

In all cases studied longer reaction times promote the formation of longer chain lengths. The oligomer distribution observed after 48 h for selected systems is given in Table IV. The increased chain length can occur stepwise and/or by redistribution. Redistribution is demonstrated in the norbornene/Cp_2TiCl_2/*n*BuLi system where 90% of the starting material is consumed after 0.5 h and the ratio of oligomers, $H(PhMeSi)_xH$, relative to the disilane is 1/3.7/1.3/0.12 (x = 2/3/4/5) compared to 1/2.4/2.1/0.7 after 24 h. It is this redistribution that reduces the possibility of obtaining a specific chain length through dehydrogenative coupling at least with the Cp_2MCl_2/*n*BuLi catalyst precursors. It is, however, possible to target shorter chain lengths with the hafnium catalyst and improve the quantities of longer chain lengths with titanium in combination with cyclooctene.

Dialkylsilanes and Tertiary Silanes. Although aryl-substituted secondary silanes condense in the absence of olefins (Cp_2MCl_2/*n*BuLi catalyst precursor), dialkylsilanes give only traces of oligomers.[1] Since oligomer formation is promoted in the presence of cyclic olefins, the condensation of di-*n*-propylsilane was conducted in the presence of such olefins. With Cp_2ZrCl_2/*n*BuLi and 4-methylcyclohexene only traces of tetra-*n*-propyldisilane were obtained. However, condensation occurs in the presence of Cp_2TiCl_2 and added cyclooctene and norbornene. Although the starting silane is coincident with the solvent peak, it is possible to observe the slow formation of cyclooctane over several days as well as the formation of both disilane and trisilane. After 5 days, catalyst and volatile materials were removed. A GC analysis of the remainder showed that the mixture contained $H(Pr_2Si)_xH$ (x = 2, 65%; 3, 10%), $(C_8H_{13})Pr_2SiH$ (12%), a product of SiH/HC coupling, and five unidentified products (totaling 13%). In contrast to cyclooctene the reaction with norbornene occurs rapidly to give $H(Pr_2Si)_xH$ (x = 2, 3), the hydrosilylation products, $(C_7H_{11})Pr_2SiH$ and $(C_7H_{11})_2SiPr_2$, $C_7H_{11}C_7H_{11}$, and three minor unidentified products. The ratio between oligomers and hydrosilylation products is about 3 and remains so from 1 h after mixing through 4 days. However, the ratio between disilane and trisilane changes from 5.0 to 2.2, and the initially formed hydrosilylation product $(C_7H_{11})_2SiPr_2$ slowly isomerizes. The ratio of oligomers to silicon products that contain olefin appear to be approximately the same with the two olefins. Although contaminated with byproducts this represents the first successful condensation of a dialkylsilane with a titanium triad catalyst.

The coupling reaction of the tertiary silane $PhMe_2SiH$ with cyclooctene or norbornene catalyzed by Cp_2TiCl_2/*n*BuLi was also examined. In the presence of cyclooctene, less than 4% reaction occurred after 48 h at 90 °C and products were not identified. With norbornene, about 25% of $PhMe_2SiH$ is consumed after 45 h at 90 °C. Only the hydrosilylation product $PhMe_2Si(C_7H_{11})$ was identified by GC/MS.

Comparison of Cp_2MMe_2 and Cp_2MCl_2/*n*BuLi. Only a few other studies of the condensation of silanes in the presence of olefins have been reported, and the published results seem to differ for primary and secondary silanes. In the condensation of primary silanes with Cp_2TiMe_2, the presence of an internal olefin suppresses the evolution of dihydrogen and increases the rate of polymerization of $RSiH_3$ but produces oligomers of the same chain length as in the absence of olefin.[3] In a related study with Cp_2TiPh_2 as catalyst, it was shown that the percent conversion of $PhMeSiH_2$ to disilanes and trisilanes is improved when cyclooctene is present, and in this case the formation of the trisilane is considerably enhanced (the ratio of disilane/trisilane is 2.3 in absence of olefin and 0.08 in the presence of cyclooctene).[4] Thus, Cp_2TiPh_2 and the catalyst generated from Cp_2TiCl_2/*n*BuLi are similar in enhancing the formation of longer chain lengths in the presence of cyclooctene.

With Cp_2TiMe_2 and phenylsilane, the major fate of the olefin is hydrogenation in the case of 2-pentene (internal olefin) and isomerization of 1-pentene (terminal olefin) to 2-pentene. The minor hydrosilylation products produced from 1-pentene include $RSiH_2Ph$ (R = *n*-pentyl) from the monosilane starting material and three hydrosilylation products produced from the disilane, PhH_2SiSiH_2Ph, $R(H_2PhSi)_2H$ (R = 1-pentyl, 2-pentyl), and RHPhSiSiPhHR (R = pentyl). The combination of Cp_2TiPh_2 and $PhMeSiH_2$ isomerizes 1-octene to 2-octene at 90–120 °C.[6]

In the case of Cp_2TiCl_2/*n*BuLi and $PhMeSiH_2$, hydrosilylation of both internal and terminal olefins occurs to give the β product although two minor hydrosilylation products from the disilane are also observed. Although the combination of Cp_2TiCl_2/*n*BuLi is reported to be a good isomerization catalyst for converting terminal olefins to internal olefins,[7] addition of hydrosilane to the mixture suppresses the isomerization of the olefin and instead hydrosilylation is favored. Although octane and 1-octene could be distinguished by GC and GC–MS analysis, if 2-octene is formed, it is not distinguished from 1-octene and therefore the possibility of some isomerization of the olefin cannot be eliminated.

In the system $Cp_2TiMe_2/PhSiH_3$/norbornene hydro-

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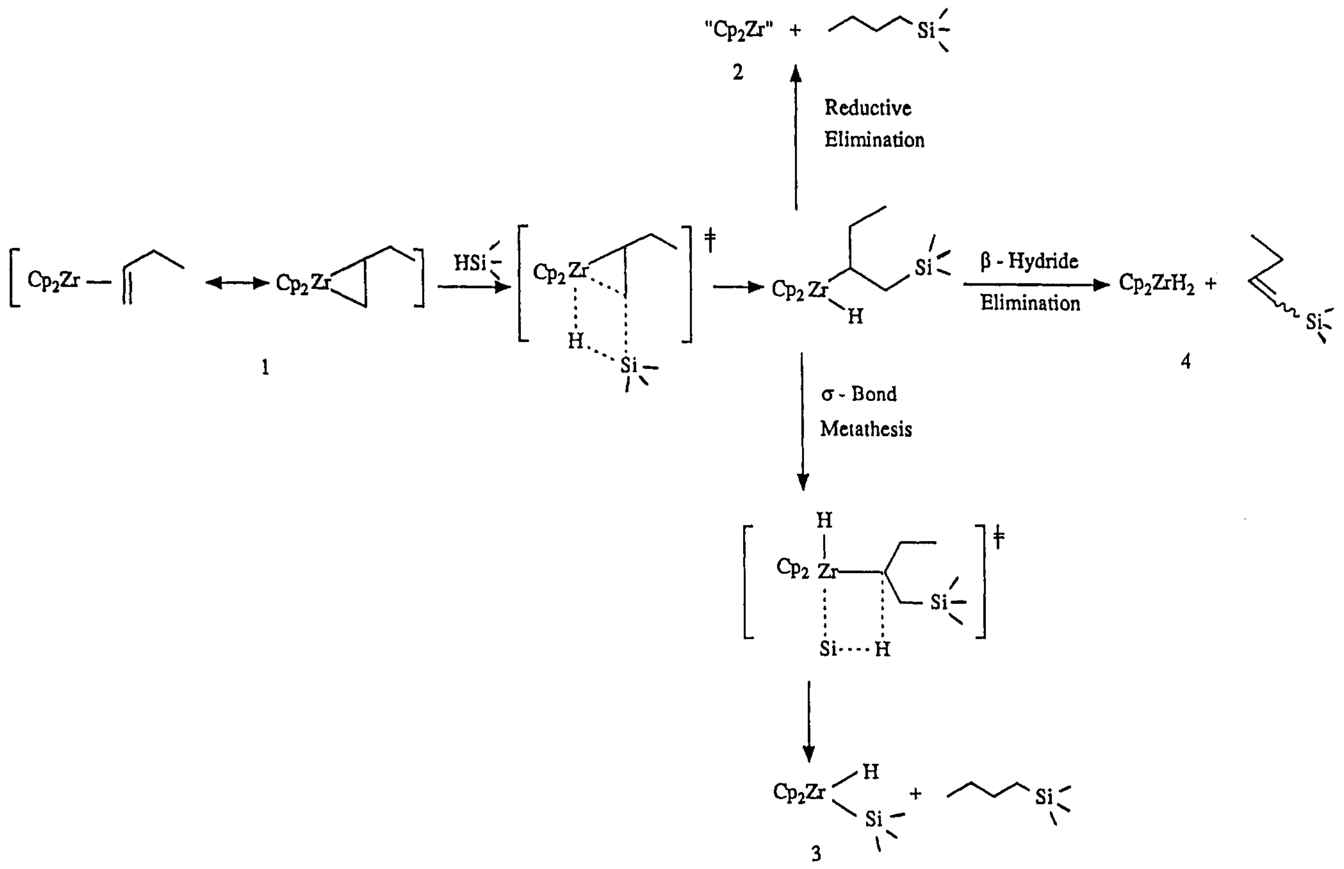
(6) Nakano, T.; Nagai, Y. *Chem. Lett.* **1988**, 481.

(7) Akita, M.; Yasuda, H.; Nagasuna, K.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 554.

Scheme II



genation of norbornene occurs at high catalyst concentrations, and at low catalyst concentrations norbornane and norbornyl-terminated oligosilanes, $C_7H_{11}(SiHPh)_nSiH_2Ph$ and $C_7H_{10}[(SiHPh)_nSiH_2Ph]_2$, are formed. Although norbornane could not be measured in the Cp_2TiCl_2/nBuLi/$PhMeSiH_2$/norbornene system, the high percentage of oligomers formed suggests that the results are similar to those of the $Cp_2TiMe_2/PhSiH_3$/norbornene at high catalyst concentrations but includes a feature of the results with low catalyst concentration, that is, the formation of minor portions of the norbornyl-terminated oligosilanes $C_7H_{11}(SiPhMe)_nSiMePhH$ ($n = 0, 1$).

When olefins are added to phenylsilane in the presence of catalytic quantities of Cp_2ZrMe_2, hydrosilylation of the acyclic olefin (styrene) occurs faster than polymerization, but in the presence of the cyclic olefin cyclohexene, polymerization of the hydrosilane occurs.[3b] In the latter case, after completion of the polymerization the equivalent of slow hydrosilylation results in the incorporation of a cyclohexyl group at about 50% of the SiH sites.[3b] The results of the present study parallel those observed by Harrod for related olefins. However, neither rapid isomerization of internal olefins nor the formation of the equivalent of SiH/HC coupling products has been reported for Cp_2ZrMe_2 as described here for Cp_2ZrCl_2/nBuLi.

The hafnium analogue, Cp_2HfMe_2, does not appear to be effective for the dehydrocoupling of primary silanes,[5] and the effect of olefin coreactants has not been reported. The major difference therefore between Cp_2HfMe_2 and Cp_2HfCl_2/nBuLi is that the latter does indeed promote the coupling of hydrosilanes although the oligomers formed are of shorter chain length than for the titanium and zirconium systems.

Mechanism. With mixtures of olefins and secondary silanes, the catalyst system Cp_2MCl_2/nBuLi promotes not only two types of dehydrocoupling reactions but also hydrosilylation and/or isomerization/hydrosilylation. All of these processes could occur from the same intermediate although that intermediate need not be the same for all three metals (Ti, Zr, Hf).

There are two aspects that ultimately need to be considered in rationalizing the observed results. The first concerns the species formed in the combination of Cp_2MCl_2/nBuLi, and the second relates to how this species either functions in the catalytic cycle or is converted to the reacting species in the presence of silane and/or olefin. In the case of zirconium there is some evidence for Cp_2Zr(butene) (1) generated from the combination Cp_2ZrCl_2/nBuLi. The structure of the adduct $Cp_2Zr(CH_2{=}CHEt)PMe_3$, which forms when PMe_3 is added to the reaction mixture, has been reported.[8] Since rapid transfer of a butyl group to $PhMeSiH_2$ occurs with Cp_2ZrCl_2/nBuLi/$PhMeSiH_2$, a possible conversion of 1 to various reactive species by the hydrosilane through reductive elimination, β-hydride elimination, and/or σ-bond metathesis is depicted in Scheme II.

In our previous report[1] which surveyed the self-coupling of secondary silanes, we suggested the equivalent of hydrosilylation of the coordinated butene and release of a reactive zirconocene equivalent, 2, which should insert into an SiH bond to form the silylzirconium, 3. A σ-bond metathesis reaction of 3 with a second molecule of silane would generate a silicon–silicon bond and produce 4. Thus, all three species shown in Scheme II were involved in the proposed cycle leading to oligomers. We proposed that 3 was required for the formation of oligomers and the additional chemistry observed when olefins are present can also be rationalized through 3 as illustrated in Scheme III.

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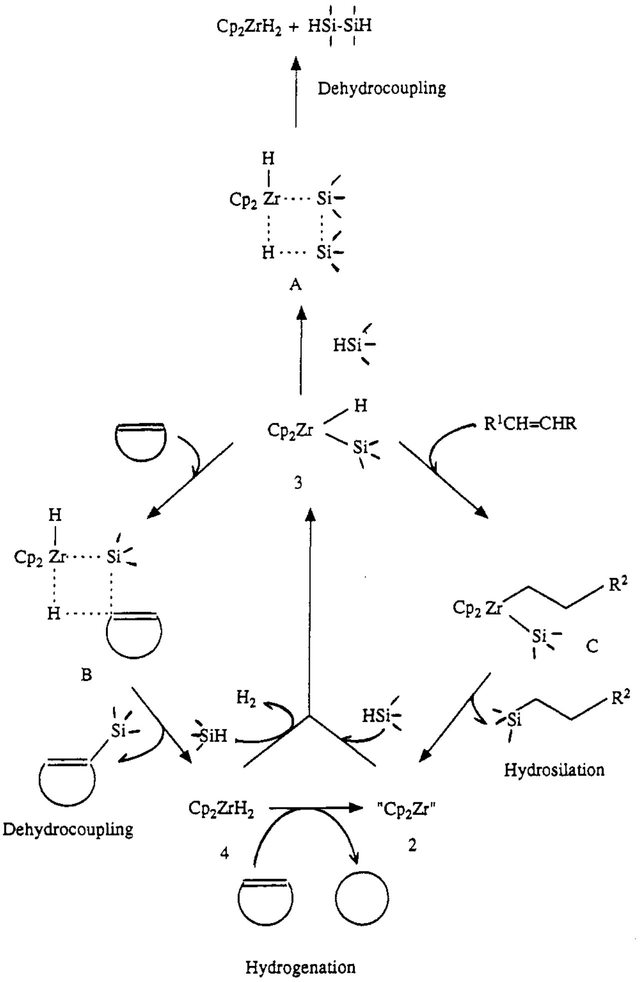
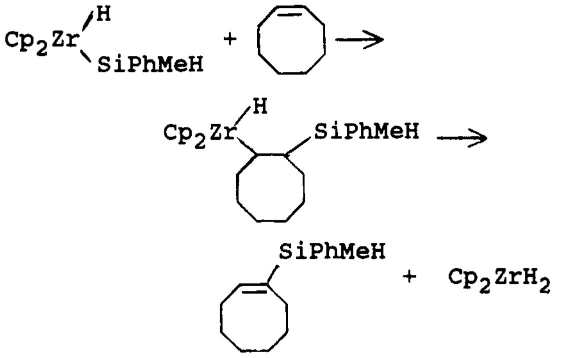
[8] (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C., *J. Am. Chem. Soc.* **1987**, *109*, 2544. (b) Goddard, R.; Binger, P.; Hall, S. R.; Muller, P. *Acta Crystallogr., C* **1990**, *46*, 998.

Scheme III



A certain parallel exists between the chemistry observed with Cp_2ZrCl_2/nBuLi/silane/olefin and "hydrozirconation" reported by Schwartz and co-workers.[9] In hydrozirconation, 1-octene and *cis*- and *trans*-4-octene are converted by $[Cp_2Zr(H)Cl]_x$ to $Cp_2Zr(n\text{-}C_8H_{17})Cl$ but additional reagents are required to remove the organic group from the zirconium center. A rapid rearrangement of internal olefins with Cp_2ZrCl_2/nBuLi/silane is also observed although in this case the organic group produced from the olefin is transferred to the silicon without the need for additional reagents. The coupling of the organic group and the silicon center could occur through the reductive elimination shown in Scheme III. To provide support for this parallel in the chemistry, the reaction of *cis*-4-octene and $PhMeSiH_2$ was conducted in the presence of $Cp_2Zr(H)Cl$ and 1 equiv of nBuLi. Rapid production of $PhMeSiH(n\text{-}C_8H_{17})$ was observed. The hydrosilylation product was identical to that observed from reactions of $PhMeSiH_2$ and *cis*-4-octene or 1-octene with Cp_2ZrCl_2/nBuLi.

Hydrozirconation of a cyclic olefin is much slower than that observed for an acyclic olefin. Neither 1-methylcyclohexene nor cyclooctene reacts with $Cp_2Zr(H)Cl$ even when heated to 40 °C overnight.[9] The factors which distinguish between reaction of acyclic vs cyclic olefins are not clear, but 1-methylcyclohexene, a trisubstituted olefin, should be the least reactive toward a sterically crowded metal center. This suggests that, in the presence of cyclic olefin, other reaction processes could at least compete with the hydrozirconation of the olefin. In addition to the SiH/SiH coupling a σ-bond metathesis of **3** with the sp^2-CH bond of the olefin could occur as shown in Scheme III to provide the SiH/CH coupling product. An alternative to the formation of the vinylsilane could be insertion of the cyclic olefin into the Zr–Si bond of **3** followed by a β-hydride elimination as shown in eq 2. Although only



(2)

the vinylsilane shown in eq 2 was observed from cyclooctene and not the allylsilane which could also be obtained from β-hydride elimination, three cyclohexenylsilanes were observed in the reaction of 4-methylcyclohexene/$PhMeSiH_2$, one of which must be an allylsilane. The insertion of ethylene into the Zr–Si bond in $CpCp^*Zr[Si(SiMe_3)_3]Cl$ and in $Cp^*Cl_2ZrSi(SiMe_3)_3$ has been observed by Tilley, but photochemical activation of the Zr–Si bond was required.[10]

Since most of the reactions are expected to involve **3**, the process which predominates will depend on the stability of intermediates A, B, or C (Scheme III). The steric effect of the substituents on silane and the cyclic olefin is one of the factors which could influence the stability of intermediates A or C. For the substituted cyclic olefin, when the substituent is located on the double bond (e.g., 1-methylcyclohexene), interaction of the olefin with **3** is expected to be weak and dehydrocoupling should dominate. Even when the substituent is removed (4-methylcyclohexene), intermediate B appears to be unfavorable and dehydrocoupling dominates. Although a mechanism was not formulated for the enhanced conversion of secondary silanes to oligomers by olefins in the presence of Cp_2TiPh_2[4] and side products were not described, there are some indications that there are steric requirements for whatever process operates. In the condensation of $MePhSiH_2$, 1-decene has essentially no effect on the product distribution or percent conversion but cyclooctene increases conversion and more than 90% of the oligomer product is trisilane. However, in the condensation of Ph_2SiH_2, cyclooctene has no effect on either the percent conversion or the product distribution whereas 1-decene increases the percent conversion but not oligomer formation (disilane is the only oligomer formed).

The hydrogenation of olefin probably originates from **4** and not **3** since the catalytic hydrogenation of olefins with Cp_2ZrH_2 has been previously reported.[11] Hydrogenation products of olefins were observed in cyclooctene, octene, and 1-tetradecene cases.

Although the previous discussion has focused on a silylzirconium formed from the butene complex of zirconocene, another route exists in the presence of olefin

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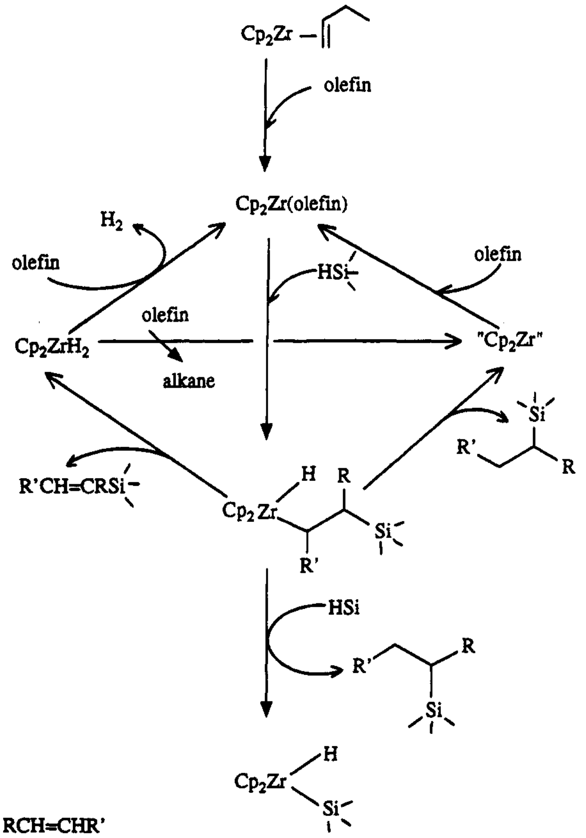
[9] Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.*, **1974**, *96*, 8115.

[10] Arnold, J.; Ergeler, M. P.; Elsner, F. H.; Heny, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284.

[11] (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *43*, C32. (b) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M.; *J. Am. Chem. Soc.* **1982**, *104*, 1846.

Scheme IV



through the displacement of coordinated butene in 1 with the added olefin. Subsequent chemistry similar to that outlined in Scheme II would generate the variation of products and is summarized in Scheme IV. Negishi and co-workers have provided some evidence that a coordinated olefin in the complex $Cp_2Zr(olefin)PMe_3$ does not exchange with free olefin.[12] However, their studies did not include systems in which phosphines were absent.

The mechanisms for the reactions catalyzed by $Cp_2TiCl_2/nBuLi$ are less clear. Reacting solutions are nearly black in the presence or absence of olefin in contrast to those reported for Cp_2TiMe_2[13] which are usually described as royal blue. The royal blue color is maintained in the cohydrogenation of 1-pentene by $PhSiH_3$, but the color is orange-brown with styrene and green with norbornene.[13] Although with cyclic olefins cohydrogenation (observed for cylooctene and presumed for norbornene) and thus oligomer formation predominate at similar Si/Ti ratios for both Cp_2TiMe_2 and $Cp_2TiCl_2/nBuLi$, hydrosilylation and hydrosilylation–isomerization occur for $Cp_2TiCl_2/nBuLi$ with acyclic olefins, whereas this process is minor for Cp_2TiMe_2 and, in addition, isomerization of terminal to internal olefin is observed as the major process for the latter catalyst. The catalytic species generated from $Cp_2TiMe_2/PhSiH_3$ was presumed to be $Cp_2Ti(H)SiH_2Ph$ or a hydridic decomposition product. With the exception of cyclooctene, the chemistry observed for $PhMeSiH_2$/olefin combinations is similar for both titanium and zirconium ($Cp_2MCl_2/nBuLi$) and thus the observed products could arise from $Cp_2Ti(H)(SiPhMeH)$ although the origin of the silyltitanium is unlikely to be similar to that for zirconium since PhMeBuSiH is not observed in titanium-catalyzed reactions. Even though there are differences in the chemistry observed for $Cp_2TiMe_2/PhSiH_3$ and $Cp_2TiCl_2/nBuLi$, the reactions for the former are conducted at room temperature and those for the latter at 90 °C and this may account for the differences. The possibility that lower valent titanium species are responsible for the reaction processes cannot be discounted since Harrod and co-workers also found that the metastable titanocene[14] as well as Cp_2TiH also reacts rapidly with $PhSiH_3$ to form polysilane and H_2.[15]

The reaction processes observed in the presence of $Cp_2HfCl_2/nBuLi$ and $Cp_2ZrCl_2/nBuLi$ for cyclic olefins are similar, but the hafnium system does not promote hydrosilylation to any significant extent. The reactions promoted by hafnium are slower, which may infer that there is an induction period for catalyst formation although rate studies would be required to resolve this question. The rapid dehydrocoupling of $Cp^*_2HfH_2$ and $HPPh_2$ at room temperature has been reported.[16] Therefore, if Cp_2HfH_2 is formed from $Cp_2HfCl_2/nBuLi$, it is not unreasonable to expect a similar condensation reaction with $PhMeSiH_2$ which would then provide the silylhafnium similar to those discussed for zirconium and titanium.

An additional process occurs in the systems that contain oligomers that is not described in Schemes III or IV, and that is redistribution of chain lengths in the presence of the catalyst. This was described earlier for the titanium-catalyzed condensation of $PhMeSiH_2$ in the presence of norbornene/$Cp_2TiCl_2/nBuLi$. Redistribution would occur if in the σ-bond metathesis shown in intermediate A (Scheme III) involves the reaction of a silicon–silicon bond instead of a SiH bond. This redistribution is also demonstrated in the reaction of HPhMeSiSiPhMeH in the presence of freshly prepared $Cp_2ZrCl_2/nBuLi$. The disilane reacts within 0.5 h to generate both $PhMeSiH_2$ and PhMeBuSiH as well as trisilane and tetrasilane. The redistribution process may not necessarily be the same for both titanium and zirconium.

Summary. This study has shown that the combination $Cp_2MCl_2/nBuLi$ is an effective catalyst for hydrosilylation of olefins, isomerization/hydrosilylation of internal olefins, dehydrocoupling of hydrosilanes, and in certain cases the formation of vinylsilanes. The products are a function of the metal and the olefin. The combination $Cp_2ZrCl_2/nBuLi/PhMeSiH_2$ reacts with acyclic olefins in a manner similar to hydrozirconation except that the final product contains silicon on the terminal carbon atom. The presence of an additional functional group on silicon allows for further elaboration at silicon or for removal of the silyl substituent. The combination $Cp_2TiCl_2/nBuLi$/norbornene is the fastest oligomerization system found thus far for $PhMeSiH_2$, but the cleanest conversion of $PhMeSiH_2$ to oligomers occurs in the presence of cyclooctene. The dehydrocoupling of cyclooctene and silane occurs to the highest degree with $Cp_2HfCl_2/nBuLi$. It is proposed that the variations in chemistry occur through the silylmetal, $Cp_2M(H)SiPhMeH$, through a σ-bond metathesis of either a hydrosilane or a cyclic olefin or insertion of an olefin into either the MH or MSi bonds leading eventually to hydrosilylation or to HC/SiH coupling. Thus, the tactic of using a dihydrogen "sponge" is an effective way to produce silicon oligomers, but other reactions can occur and in some cases take precedence over silicon–silicon bond formation.

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[12] Negishi, E.; Swanson, D. R.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1254.

[13] Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381.

[14] Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brinzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

[15] Aitken, C.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

[16] Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 1760.

Experimental Section

General Procedures. All reactions were carried out under an inert atmosphere of dry nitrogen or argon. Solvents were dried by standard techniques, and all glassware was dried in an oven at 120 °C prior to use. Toluene was purified by distillation and stored over molecular sieves.

The GC data were collected on a Varian Aerograph Series 1400 gas chromatograph with a 15 m × 0.54 mm (i.d.), 1.5-μm film DB-5 column (J & W Scientific) (column A) at a flow rate of 6 mL/min helium and temperature programming at 50–320 °C (20 °C/min) and recorded on a HP3394 A integrator. The injection temperature was 200 °C, and the detector was set at 320 °C. Alternatively data were collected on a Shimadzu GC-14A gas chromatograph with column A at a flow rate of 6 mL/min helium or a DB-5 capillary column (column B) at a flow rate of 4 mL/min helium and the same temperature programming but injector and detector temperatures at 275 and 350 °C, respectively, and the output recorded on a Shimadzu CR601 integrator. Mass spectral data were collected on a Hewlett-Packard 5988A GC/MS instrument with an RTE-A data system with gas chromatographic separations in split injection mode using a 12.5-m (HP-1) capillary column.

^{1}H, ^{13}C, ^{13}C APT, and ^{29}Si NMR spectra were collected on a Varian XL-300 multinuclear spectrophotometer in CDCl$_3$. For ^{1}H and ^{13}C data, the characteristic solvent peaks were used as internal reference unless otherwise specified. Infrared spectra were determined on a Perkin-Elmer Model 1600 FT-IR spectrophotometer as thin films. Liquid chromatography was performed on a Perkin-Elmer Series 3B liquid chromatograph equipped with a C-18 reversed-phase analytical column and a Perkin-Elmer LC-95 UV/visible spectrophotometric detector set at a wavelength of 270 nm. Analyses were recorded on a Hewlett-Packard 3394A integrator. The eluting solvent was HPLC-grade acetonitrile at 2 mL/min.

The following compounds are commercially available: PhMeSiCl$_2$, *n*Pr$_2$SiCl$_2$, Cp$_2$ZrCl$_2$, Cp$_2$TiCl$_2$, Cp$_2$HfCl$_2$, Cp$_2$Zr(H)Cl, LiAlH$_4$, 1-octene, 1-tetradecene, *cis*-4-octene, *trans*-4-octene, cyclooctene, norbornene, 1-methylcyclohexene, 4-methylcyclohexene. Commercial *n*-BuLi (1.6 M in hexanes) was titrated periodically to determine the concentration of the active *n*-BuLi. Unless specified otherwise, 1.6 M solutions were used.

The hydrosilanes PhMeSiH$_2$ and *n*Pr$_2$SiH$_2$ are prepared by literature methods from the chlorosilanes.[17] The oligomer products, H(PhMeSi)$_x$H, have been previously described.[1]

Elemental analyses were performed by Galbraith Laboratories, and the high-resolution mass spectrum was recorded by Dr. Robert Orth (Monsanto Chemical Co.).

Reaction of PhMeSiH$_2$ with Olefins Catalyzed by Cp$_2$ZrCl$_2$/*n*BuLi. General Procedure. Degassed toluene was injected into a flask which contained Cp$_2$ZrCl$_2$ under a nitrogen atmosphere, and the slurry was cooled in an ice bath. The *n*BuLi was injected by syringe whereupon the colorless mixture turned yellow immediately and darkened to yellow-red after being stirred for 5 min at 0 °C. The PhMeSiH$_2$ and olefin were injected into the reaction flask, whereupon a bright yellow clear solution formed. The ice bath was removed and the flask placed in a 90 °C oil bath. The solution changed to dark-brown within a few minutes. Aliquots were removed periodically and added to hexanes followed by filtration through a small plug of Celite prior to injection of samples into the gas chromatograph, and uncorrected GC integration data were recorded. The reaction mixture was stirred for the indicated time at 90 °C before removal of the volatile material under vacuum. Hexanes (5–10 mL) were added, and the resultant slurry was filtered through Celite. After removal of the solvent, an oily material was obtained. The results with various olefins follow. Product analyses by GC–MS were performed on aliquots removed during the course of reaction and/or on oils obtained after workup and are provided in Table I.

1-Tetradecene. Cp$_2$ZrCl$_2$ (0.062 g, 0.21 mmol) and *n*BuLi (0.26 mL, 0.42 mmol) in 1.5 mL of toluene were reacted with PhMeSiH$_2$ (1.01 g, 8.3 mmol) and 1-tetradecene (1.31 g, 6.7 mmol) at 90 °C. Aliquots removed periodically showed the following weight percent of PhMeSiH$_2$ [time (h), %]: 0.0 (38), 1.0 (11), 3.0 (8.1), 8.0 (6.7), 24 (4.7), 45.5 (3.5). After 1 h the GC ratio of HPhMeSi(C$_{14}$H$_{29}$) to C$_{14}$H$_{30}$ was 4.9. Workup after 120 h provided a brown-yellow oily material (1.67 g). Kugelrohr distillation of 1.05 g of the oil gave PhMeSiH(C$_{14}$H$_{29}$) as the major product (0.86 g, 94% by GC): bp 145–152 °C (0.07 mmHg); IR 2115 cm^{-1} (SiH, strong); mass spectrum, *m/e* (relative intensities) 318 (M$^+$, 0.2), 121 (PhMeSiH$^+$, 100), 113 (74), 99 (14); high-resolution mass spectrum (HRMS) 318.2734, calcd for C$_{21}$H$_{38}$Si 318.2733; ^{1}H NMR, δ (J, Hz) (CDCl$_3$) 0.35 (d, SiMe, $^{3}J_{\mathrm{CHSiH}}$ = 3.6, 2.6 H), 0.8–0.9 (br m, SiCH$_2$ + CH$_3$, 4.7 H), 1.2–1.4 (br m, CH$_2$, 23.8 H), 4.38 (sextet, SiH, $^{3}J_{\mathrm{SiHCH}}$ = 3.6, 1.0 H), 7.3–7.6 (m, arom, 5.9 H); ^{13}C NMR, δ (CDCl$_3$) −5.64 (SiMe), 13.39, 14.14, 22.73, 24.35, 29.33, 29.40, 29.60, 29.71, 31.96, 33.22 (Si(CH$_2$)$_{13}$CH$_3$), 127.81, 129.12, 134.30, 136.80 (arom); ^{13}C APT (CDCl$_3$) −5.64, 14.14 (reversed phase).

Reaction of PhMeSiH$_2$ (1.17 g, 9.6 mmol) and tetradecene (0.73 g, 3.7 mmol) in 2.2 mL of toluene catalyzed by Cp$_2$ZrCl$_2$ (0.088 g, 0.30 mmol) and *n*BuLi (0.38 mL, 0.60 mmol) at 90 °C was also monitored by GC [time (h), wt % starting silane in mixture]: 0.0 (52.2), 1.0 (34.7), 4.5 (27.8), 22 (21.5), 48.5 (14.6). Workup after 120 h gave a yellow oil (1.60 g) which contained hydrosilylation product (72% by GC) and oligomers (up to pentamer, 27% by GC).

1-Octene. Cp$_2$ZrCl$_2$ (0.090 g, 0.31 mmol) and *n*BuLi (0.62 mL, 0.62 mmol) in 2.2 mL of toluene were reacted with PhMeSiH$_2$ (1.31 g, 10.7 mmol) and 1-octene (0.94 g, 8.4 mmol) at 90 °C. Aliquots removed periodically showed the following weight percent of PhMeSiH$_2$ [time (h), %]: 0.0 (45.2), 0.5 (5.6), 1.0 (5.6), 3.0 (6.0). Workup after 24 h provided a yellow oil (1.75 g). Distillation provided the product PhMeSiH(C$_8$H$_{17}$): bp 75–85 °C (0.02 mmHg) (lit.[18] bp 156–158 °C (5 mmHg)) (center cut, 0.71 g, 94% by GC); mass spectrum, *m/e* (relative intensities) 234 (M$^+$, 0.2), 156 (M$^+$ − C$_6$H$_6$, 13), 127 (17) 121 (PhMeSiH$^+$, 100), 113 (60), 107 (PhSiH$_2$$^+$, 13), 105 (PhSi$^+$, 11); ^{1}H NMR, δ (J, Hz) (CDCl$_3$) 0.32 (d, SiMe, $^{3}J_{\mathrm{CHSiH}}$ = 3.75), 0.8–0.9 (br m, SiCH$_2$ + CH$_3$), 1.2–1.5 (br m, CH$_2$), 4.35 (sextet, SiH, $^{3}J_{\mathrm{SiHCH}}$ = 3.6), 7.3–7.6 (m, arom); ^{13}C APT NMR, δ (CDCl$_3$) −5.65 (SiMe), 13.38, 14.11 (reversed phase).

***cis*-4-Octene.** Cp$_2$ZrCl$_2$ (0.14 g, 0.46 mmol) and *n*BuLi (0.58 mL, 0.92 mmol) in 3.4 mL of toluene were reacted with PhMeSiH$_2$ (1.75 g, 14.3 mmol) and *cis*-4-octene (1.55 g, 13.8 mmol) at 90 °C. Aliquots removed periodically showed the following weight percent of PhMeSiH$_2$ [time (h), %]: 0.0 (44), 1.0 (7.9), 3.0 (6.0), 24 (5.5). Workup after 46 h gave a yellow cloudy oil (2.99 g) which contained the hydrosilylation product PhMeSiH(C$_8$H$_{17}$) (86% by GC). Repeated distillation provided a purified sample of PhMeSiH(C$_8$H$_{17}$): bp 88–90 °C (0.07 mm Hg) (0.16 g). IR 2114 cm^{-1} (SiH, strong); mass spectrum, *m/e* (relative intensities) 234 (M$^+$), 121 (base); ^{1}H NMR, δ (J, Hz) (CDCl$_3$) 0.40 (d, SiMe, $^{3}J_{\mathrm{CHSiH}}$ = 3.8, 2.5 H), 0.8–1.0 (br m, SiCH$_2$ + CH$_3$, 4.8 H), 1.3–1.5 (br m, CH$_2$, 12 H), 4.43 (sextet, SiH, $^{3}J_{\mathrm{SiHCH}}$ = 3.6, 1 H), 7.3–7.6 (m, arom, 5.5 H); ^{13}C NMR, δ (CDCl$_3$) −5.62 (SiMe), 13.46, 14.13, 22.73, 24.40, 29.31, 31.99, 33.26 (Si(CH$_2$)$_7$CH$_3$), 127.84, 129.14, 134.33, 136.82 (arom); ^{13}C APT NMR, δ (CDCl$_3$) −5.62, 14.13 (reversed phase). Anal. Calcd for C$_{15}$H$_{26}$Si: C, 76.36; H, 11.12. Found: C, 77.10; H, 11.82.

***trans*-4-octene.** Cp$_2$ZrCl$_2$ (0.122 g, 0.42 mmol) and *n*BuLi (0.53 mL, 0.82 mmol) in 3.1 mL of toluene were reacted with PhMeSiH$_2$ (1.55 g, 12.7 mmol) and *trans*-4-octene (1.40 g, 12.5 mmol) at 90 °C. Analysis of the aliquots showed the following weight percent of PhMeSiH$_2$ [time (h), %]: 0.0 (56), 1.0 (9.4), 3.0 (6.2), 8.0 (6.1), 24 (5.1). Workup after 46 h provided a light yellow oil (2.94 g) which contained PhMeSiH(C$_8$H$_{17}$) (90% by GC) as the major product: mass spectrum, *m/e* 234 (M$^+$), 121 (100); ^{1}H and ^{13}C NMR data, identical to those for the product obtained from *cis*-4-octene.

Cyclooctene. Cp$_2$ZrCl$_2$ (0.153 g, 0.52 mmol) and *n*BuLi (0.65 mL, 1.04 mmol) in 3.8 mL of toluene were reacted with PhMeSiH$_2$ (1.71 g, 14.0 mmol) and cyclooctene (1.74 g, 15.8 mmol) at 90 °C. Analysis of the aliquots showed the following weight percent of PhMeSiH$_2$ [time (h), %]: 0.0 (42), 1.0 (28), 3.0 (21) 24 (11), 48 (4.5). After 24 h the ratio of unreacted cyclooctene to cyclooctane was 2/1. Workup after 120 h provided a yellow, oily material (2.26

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g). Kugelrohr distillation gave a fraction with boiling point 115–135 °C (0.3 mmHg) which contained two products, $PhMeSiH(C_8H_{13})$ (48%) and $PhMeSiH(C_8H_{15})$ (52%). $PhMeSiH(C_8H_{13})$: mass spectrum, *m/e* (relative intensities) 230 (M^+, 3.8), 215 ($M^+ - 15$, 2.7), 187 (5.0), 152 ($M^+ - C_6H_6$, 10), 121 ($PhMeSiH^+$, 100), 105 ($PhSi^+$, 25); ^1H NMR, δ (J, Hz) ($CDCl_3$) 0.37 (d, SiMe, $^3J_{CHSiH} = 3.8$), 1.4–1.9 (br m, CH_2), 4.60 (q, SiH, $^3J_{SiHCH} = 3.8$), 6.22 (t, C=CH, $J_{CH} = 7.8$ Hz), 7.3–7.6 (m, arom). $PhMeSiH(C_8H_{15})$: mass spectrum, *m/e* (relative intensities) 232 (M^+, 0.3), 217 ($M^+ - 15$, 0.3), 154 ($M^+ - C_6H_6$, 18), 121 ($PhMeSiH^+$, 100); ^1H NMR, δ (J, Hz) ($CDCl_3$) 0.47 (d, SiMe, $^3J_{CHSiH} = 3.8$), 1.4–1.8 (br m, CH_2), 2.2–2.4 (br m, CH), 4.28 (2 overlapping q, SiH, $^3J_{SiHCH} = 3.8$), 7.3–7.6 (m, arom). Mixture of these two products: IR 2109.7 (SiH, strong), 1611.9 cm^{-1} (C=C, weak); ^{13}C NMR, δ (mixture in $CDCl_3$) −7.37, −5.52 (SiMe), 21.77, 26.01, 26.35, 26.40, 27.05, 27.10, 27.49, 27.58, 27.84, 27.96, 28.25, 28.90, 29.39 ($Si(C_8H_{13})$ and $Si(C_8H_{15})$), 127.70, 127.74, 129.07, 129.11, 134.67, 136.20, 136.24, 138.06, 143.34 (arom); ^{13}C APT NMR, δ ($CDCl_3$) −7.37, −5.52, 21.77 (reversed phase).

Reaction of $PhMeSiH_2$ (1.55 g, 12.7 mmol) with cyclooctene (0.60 g, 5.5 mmol) catalyzed by Cp_2ZrCl_2 (0.160 g, 0.55 mmol) and *n*BuLi (0.68 mL, 1.10 mmol) in 4.0 mL of toluene at 90 °C was also monitored by GC [time (h), wt % of $PhMeSiH_2$ in initial mixture]: 0.0 (95.0), 4.5 (56.3), 22.0 (32.8). Workup after 120 h gave a yellow oil (0.98 g) which is a mixture of oligomers (up to trimer) (28% by GC/MS), $PhMeSiH(C_8H_{13})$ (40% by GC/MS), and $PhMeSiH(C_8H_{15})$ (10% by GC/MS).

1-Methylcyclohexene. Cp_2ZrCl_2 (0.063 g, 0.21 mmol) and *n*BuLi (0.27 mL, 0.43 mmol) in 1.6 mL of toluene were reacted with $PhMeSiH_2$ (0.85 g, 7.0 mmol) and 1-methylcyclohexene (0.75 g, 7.8 mmol) at 90 °C. Analysis of the aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), % (1-methylcyclohexene occurs in the solvent front)]: 0.0 (100), 0.5 (81), 1.0 (75), 3.0 (71), 24 (43). Workup after 24 h provided a bright yellow oil (0.65 g) which contained oligomers (up to tetramers) and unknown products in about 50/1 ratio.

4-Methylcyclohexene. Cp_2ZrCl_2 (0.054, g, 0.185 mmol) and *nBuLi* (0.23 mL, 0.37 mmol) in 1.4 mL of toluene were reacted with $PhMeSiH_2$ (0.75 g, 6.2 mmol) and 4-methylcyclohexene (0.69 g, 7.2 mmol) at 90 °C. Analysis of aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), % (4-methylcyclohexene occurs in the solvent front)]: 0.0 (98), 0.5 (76), 1.0 (68), 3.0 (54), 8.0 (38), 24 (19), 48 (18). After 48 h, the GC trace shows that the major products are disilane through tetrasilane, but at least three additional components with retention times shorter than the oligomers are present. Workup after 48 h gave a clear yellow oil (0.65 g). An attempt was made to isolate the monosilane products which incorporated olefin by distillation. A fraction (0.07 g) with bp 75–85 °C (0.05 mmHg) was obtained which contained several components. GC/MS analysis was consistent with the presence of $PhMeSiH(C_7H_{13})$ [[*m/e* (relative intensities)] 218 (M^+, 9.2), 140 ($M^+ - C_6H_6$, 36), 121 ($PhMeSiH^+$, 100), 96 (18), 95 (17), 94 (10)] and at least three isomers of $PhMeSiH(C_7H_{11})$ [[*m/e* (relative intensities) 216 (M^+, 7), 138 ($M^+ - C_6H_6$, 11), 121 (100), 94 (44)]. ^1H NMR and ^{13}C NMR spectra were too complex to analyze.

Reaction of $PhMeSiH_2$ (1.31 g, 10.7 mmol) with 4-methylcyclohexene (0.53 g, 5.5 mmol) catalyzed by Cp_2ZrCl_2 (0.102 g, 0.35 mmol) and *n*BuLi (0.54 mL, 0.70 mmol) in 2.6 mL of toluene at 90 °C was monitored by GC [time (h), wt % of $PhMeSiH_2$ (olefin occurs in the solvent front)]: 0.0 (97), 0.5 (72), 1.0 (46), 8.0 (37), 24 (830), 48 (18), 120 (17). Workup after 120 h gave a cloudy yellow oil (1.37 g): IR 2102.1 cm^{-1} (SiH, strong). A combination of GC and HPLC showed that the sample contained oligomers (94% by GC), from dimer through hexamer, and a small amount of other products.

Norbornene. Cp_2ZrCl_2 (0.076 g, 0.26 mmol) and *n*BuLi (0.32 mL, 0.52 mmol) in 1.5 mL of toluene were reacted with $PhMeSiH_2$ (1.06 g, 8.7 mmol) and norbornene (0.74 g, 7.9 mmol, dissolved in 0.4 mL of toluene) at 90 °C. Analysis of aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), % (olefin is coincident with the solvent front)]: 0.0 (97), 0.5 (77), 1.0 (64), 3.0 (32), 8.0 (7.8), 24 (7.1), 48 (6.4), 72 (3.0). Workup after 72 h provided yellow oil (1.05 g) which contained SiH/SiH coupling products (dimer through hexamer, 57%) and several hydrosilylation products (a total of 43%). Mass spectral data of the hydrosilylation products [*m/e* (relative intensities)]: $PhMeSiH(C_7H_{11})$, 216 (M^+, 5.8), 201 ($M^+ - 15$, 0.7), 173 (2.8), 138 ($M^+ - C_6H_6$, 22), 121 ($PhMeSiH^+$, 100), 110 (29), 105 ($PhSi^+$, 11), 95 (9); $(PhMeSiH)_2(C_7H_{10})$ and/or $H(PhMeSi)_2C_7H_{11}$ (three isomers), 336 (M^+, 0.9), 258 ($M^+ - C_6H_6$, 6.7), 243 (1.4), 197 (Ph_2MeSi^+, 12.9), 121 (100)]; 336 (7.9, M^+), 258 ($M^+ - C_6H_6$, 4.0), 241 ($M^+ - C_7H_{11}$, 6.0), 215 (M^+ − PhMeSiH, 32), 197 (Ph_2MeSi^+, 20), 121 ($PhMeSiH^+$, 100); and 336 (M^+, 5.8), 241 (5.3), 215 (38), 197 (18), 187 (7.5), 121 (100).

Reaction of $PhMeSiH_2$ (1.04 g, 8.5 mmol) with norbornene (0.27 g, 2.9 mmol) catalyzed by Cp_2ZrCl_2 (0.077 g, 0.26 mmol) and *n*BuLi (0.33 mL, 0.52 mmol) in 1.9 mL of toluene at 90 °C was monitored by GC [time (h), wt % $PhMeSiH_2$]: 0.0 (97), 0.5 (56), 1.0 (53), 3.0 (48), 8.0 (44), 24 (37), 48 (29), 72 (26). Workup after 72 h gave a yellow oil (0.83 g) which contained oligomers (85% by GC, up to hexamer) and the hydrosilylation product $PhMeSiH(C_7H_{11})$ (15%).

Reaction of $PhMeSiH_2$ with Olefin Catalyzed by Cp_2TiCl_2/*n*BuLi. General Procedure. A sample of Cp_2TiCl_2 was transferred to a preweighed 10-cm^3 round-bottom flask and degassed toluene, and *n*BuLi were added with cooling at 0 °C. A dark, brown-red slurry formed. Addition of $PhMeSiH_2$ and olefin produced a brown-green solution which changed to almost black when heated to 90 °C. Aliquots were removed periodically, added to hexanes, and filtered through Celite before being monitored by GC and uncorrected integration data recorded. After the specified time, volatile material was removed under vacuum and hexanes (about 5 mL) were added to the residue. The slurry was then filtered through Celite to produce a dark brown filtrate. Evacuating the filtrate at room temperature for 15–20 min gave a brown oily material. Results for selected olefins are described below.

***cis*-4-Octene.** Cp_2TiCl_2 (0.063 g, 0.26 mmol) and *n*BuLi (0.32 mL, 0.52 mmol) in 1.9 mL of toluene were reacted with $PhMeSiH_2$ (1.05 g, 8.6 mmol) and *cis*-4-octene (0.76 g, 6.8 mmol) at 90 °C. Analysis of the aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), %]: 0.0 (49.9), 0.5 (11.0), 1.0 (8.4), 3.0 (6.4), 24 (6.4). Workup after 48 h gave a brown oil (1.31 g) which contained hydrosilylation product $PhMeSiH(C_8H_{17})$ (70%), SiH/SiH coupling products (dimer through pentamer) (20%), and the SiH/CH coupling product $PhMeSiH(C_8H_{15})$ (6%). Isolation of the major product by Kugelrohr distillation provided $PhMeSiH(C_8H_{17})$: fraction bp 100–102 °C (0.06 mmHg) (0.36 g, 86% by GC); ^1H NMR, δ (J, Hz) ($CDCl_3$) 0.37 (d, SiMe, $^3J_{CHSiH} = 3.8$), 0.8–1.0 (br m, $SiCH_2 + CH_3$), 1.3–1.5 (br m, CH_2), 4.4 (sextet, SiH, $^3J_{SiHCH} = 3.6$ Hz), 7.3–7.6 (m, arom); ^{13}C NMR, δ ($CDCl_3$) −5.65 (SiMe), 13.38, 14.11, 22.68, 24.34, 29.24, 29.27, 31.92, 33.20 [$Si(CH_2)_7CH_3$], 127.79, 129.10, 134.29, 136.79 (arom); ^{13}C APT NMR, δ ($CDCl_3$) −5.65, 14.11 (reversed phase).

1-Octene. Cp_2TiCl_2 (0.088 g, 0.36 mmol) and *n*BuLi (0.44 mL, 0.70 mmol) in 2.4 mL of toluene were reacted with $PhMeSiH_2$ (1.27 g, 10.4 mmol) and 1-octene (1.26 g, 11 mmol) at 90 °C. Analysis of the aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), %]: 0.0 (54.8), 0.5 (17.4), 1.0 (12.2), 3.0 (8.3), 8.0 (7.9), 24 (7.8). Workup after 48 h gave a reddish-brown clear oil (1.35 g) which contained hydrosilylation product $PhMeSiH(C_8H_{17})$ (72%), SiH/SiH coupling products (dimer through tetramer, 20%), and the SiH/CH coupling product $PhMeSiH(C_8H_{15})$ (8%). Isolation of the major product by distillation provided a fraction (0.44 g) with bp up to 100 °C (0.05 mmHg) which contained $PhMeSiH(C_8H_{17})$ (87% by GC): mass spectra, *m/e* (relative intensities) 234 (M^+, 0.3), 156 ($M^+ - C_6H_6$, 16), 121 ($PhMeSiH^+$, 100), 113 (61); ^1H NMR, δ (J, Hz) ($CDCl_3$) 0.37 (d, SiMe, $^3J_{CHSiH} = 3.8$), 0.8–1.0 (br m, $SiCH_2 + CH_3$), 1.2–1.5 (br m, CH_2), 4.39 (sextet, SiH, $^3J_{SiHCH} = 3.6$), 7.3–7.6 (m, arom); ^{13}C NMR, δ ($CDCl_3$) −5.65 (SiMe), 13.38, 14.11, 22.68, 24.34, 29.24, 29.27, 31.92, 33.20 ($Si(CH_2)_7CH_3$), 127.81, 129.11, 134.29, 134.85, (arom); ^{13}C APT NMR, δ $CDCl_3$) −5.65, 14.11 (reversed phase).

Cyclooctene. Cp_2TiCl_2 (0.088 g, 0.36 mmol) and *n*BuLi (0.44 mL, 0.71 mmol) in 2.6 mL of toluene were reacted with $PhMeSiH_2$ (1.27 g, 10.4 mmol) and cyclooctene (1.26 g, 11.5 mmol) at 90 °C. Analysis of aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), %] 0.0 (43.8), 0.5 (18.7), 1.0 (14.4), 3.0 (7.8), 8.0 (3.7), 24 (1.0), 48 (0.3). Workup after 48 h provided a brown, slightly cloudy oil (1.76 g) which contained cyclooctene (11%), cyclooctane (40%), and SiH/SiH coupling products (dimer to hexamer, 49%) as determined by a combination of GC and HPLC.

Norbornene. Cp_2TiCl_2 (0.075 g, 0.30 mmol) in toluene (2.2 mL) and *n*BuLi (0.46 mL, 0.60 mmol) were reacted with $PhMeSiH_2$ (1.19 g, 9.7 mmol) and norbornene (0.80 g, 8.5 mmol, dissolved in 0.25 mL toluene) at 90 °C. Analysis showed the following consumption of starting silane [time (h), wt % of $PhMeSiH_2$]: 0.0 (96), 0.5 (7.4), 1.0 (7.5), 3.0 (9.8), 8.0 (11.9), 24 (13.3), 48 (4.5). Workup after 48 h provided a brown oil (1.07 g) which contained SiH/SiH coupling products, dimer through hexamer (86%), and hydrosilylation product $PhMeSiH(C_7H_{11})$ (14%).

Reaction of $PhMeSiH_2$ with Olefin Catalyzed by Cp_2HfCl_2/*n*BuLi. General Procedure. In the same manner Cp_2HfCl_2 was transferred into a preweighed 10-cm^3 flask, and toluene (degassed) and *n*BuLi were added with cooling. The $PhMeSiH_2$ and olefin were injected separately by syringe. A light yellow slurry was obtained which changed to a cream-colored, cloudy solution after heating to 90 °C. Slow bubbling occurred. Aliquots were removed periodically to monitor the consumption of starting material by GC. The reaction was stopped after a certain time, and workup in the same manner provided a light yellow oil. The results with selected olefins are described below.

1-Octene. Cp_2HfCl_2 (0.17 g, 0.45 mmol) and *n*BuLi (0.56 mL, 0.90 mmol) in 3.3 mL of toluene were reacted with $PhMeSiH_2$ (1.58 g, 12.9 mmol) and 1-octene (1.33 g, 11.9 mmol) at 90 °C. Analysis of the aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), %]: 0.0 (46.1), 1.0 (41.7), 3.0 (33.2), 8.0 (21.4), 24 (13.8), 48 (8.1). Workup after 48 h provided a light yellow oil (0.89 g) which was a mixture of hydrosilylation product (41% by GC), SiH/CH coupling product (54%), and PhMeSiBuH (5%). GC/MS shows the presence of $PhMeSiH(C_8H_{17})$ ([*m/e* (relative intensities)] 234 (M^+, 0.3), 156 ($M^+ - C_6H_6$, 14), 121 ($PhMeSiH^+$, 100), 113 (59)] and two isomers of $PhMeSiH(C_8H_{15})$ ([*m/e* (relative intensities)] 232 (M^+, 1.2), 189 (6.6), 161 (7.0), 154 (3.5), 147 (11), 134 (15), 121 (100); 232 (M^+, 0.7), 189 (6.7), 161 (8.7), 154 (9.0), 147 (16), 134 (17.7), 121 (100)). An attempt to isolate the major products by distillation provided a fraction (0.37 g) with bp up to 100 °C (0.05 mmHg) which contained $PhMeSiH(C_8H_{17})$ as well as $PhMeSiH(C_8H_{15})$ in about a 2/1 ratio. The ^1H NMR spectrum is complicated, but the ^{13}C APT NMR showed four peaks with reversed phase (δ, $CDCl_3$): −5.47, −4.94 (SiMe), 14.22, 14.25 (CH_3). Thus, the silyl substituents must be attached to the terminal carbon for both hydrosilylation and SiH/CH coupling products.

Cyclooctene. Cp_2HfCl_2 (0.189 g, 0.50 mmol) and *n*BuLi (0.62 mL, 1.0 mmol) in 3.6 mL of toluene were reacted with $PhMeSiH_2$ (1.82 g, 14.9 mmol) and cyclooctene (1.69 g, 15.4 mmol) at 90 °C for 48 h. The ratio of unreacted cyclooctene to cyclooctane was 2.4/1. After workup, a light yellow oillike material (2.38 g) was obtained. The GC and GC/MS data indicated the presence of SiH/CH coupling product $PhMeSiH(C_8H_{13})$ (87%), hydrosilylation product (7%), and SiH/SiH coupling product (6%, up to trimer). Isolation of the major product by Kugelrohr distillation provided a purified sample of $PhMeSiH(C_8H_{13})$ with bp 100–115 °C (0.05 mmHg) (1.88 g): ^1H NMR, δ (*J*, Hz) ($CDCl_3$) 0.49 (d, SiMe, $^3J_{CHSiH}$ = 3.8, 2.3 H), 1.4–1.6 and 2.2–2.4 (2 br m, CH_2, 8.0 H + 3.9 H), 4.62 (q, SiH, $^3J_{SiHCH}$ = 3.8, 0.9 H), 6.24 (t, C=CH, J_{CH} = 7.9, 1.0 H), 7.4–7.7 (m, arom, 5.9 H) (the data match those for $PhMeSiH(C_8H_{13})$ which was obtained from Cp_2ZrCl_2/*n*BuLi system); ^{13}C NMR, δ ($CDCl_3$) −5.51 (SiMe), 26.03, 26.37, 27.06, 27.11, 27.85, 28.91, 29.40 ($(CH_2)_6$), 127.71, 127.75, 129.12, 134.69, 136.07, 136.18, 143.34 (arom + vinyl); ^{13}C APT NMR, δ ($CDCl_3$) −5.51 (SiMe) (reversed phase).

4-Methylcyclohexene. Cp_2HfCl_2 (0.148 g, 0.39 mmol) and *n*BuLi (0.78 mL, 1.0 M, 0.78 mmol) in 2.8 mL of toluene were reacted with $PhMeSiH_2$ (1.55 g, 12.7 mmol) and 4-methylcyclohexene (1.21 g, 12.6 mmol) at 90 °C. Analysis of the aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), % (olefin is coincident with the solvent front)]: 0.0 (96.5), 0.5 (87.3), 1.0 (82.8), 3.0 (65.2), 8.0 (46.3), 24 (30) 48 (20). Workup after 48 h gave a yellow, cloudy oil (1.33 g) which contained oligomers (up to pentamer) (86%) and at least two isomers of the SiH/CH coupling product $PhMeSiH(C_7H_{11})$ (14%): mass spectra, *m/e* (reversed phase) 216 (M^+, 4.1), 138 (2.9), 121 (100), 94 (37.5); 216 (M^+, 1.9), 138, (6.0), 121 (100), 94 (53).

Reaction of $(nPr)_2SiH_2$ with Norbornene Catalyzed by Cp_2TiCl_2/*n*BuLi. Cp_2TiCl_2 (0.10 g, 0.41 mmol) and *n*BuLi (0.68 mL, 1.2 M, 0.82 mmol) in 2.8 mL of toluene were reacted with $(nPr)_2SiH_2$ (1.44 g, 12.4 mmol) and norbornene (0.96 g, 10.2 mmol) at 90 °C. Aliquots were removed periodically to monitor the reaction. Both silane and olefin starting material appeared in the solvent front, but dimer and trimer formed and their ratio changed with time [time (h), wt % of dimer/wt % of trimer]: 0.5 (58.5/10), 3.0 (53.8/14.5), 8.0 (51/16.7), 24 (49.6/18), 48 (47/19), 96 (45/20). Workup in the same manner after 96 h gave a brown oil (1.47 g) which is a mixture of several products. According to GC and GC/MS analysis, the mixture showed the presence of the following components.

Disilane $H[(nPr)_2Si]_2H$ (42%) [*m/e* (relative intensities)]: 230 (M^+, 18), 187 ($M^+ - C_3H_7$, 10.6), 145 ($Pr_2Si_2H_3^+$, 18), 144 ($Pr_2Si_2H_2^+$, 10), 115 (Pr_2SiH^+, 38), 114 ($C_6H_{14}Si^+$, 100).

Trisilane $H[(nPr)_2Si]_3H$ (19%) [*m/e* (relative intensities)]: 344 (M^+, 1.4), 301 ($M^+ - C_3H_7$, 1.1), 259 ($M^+ - C_3H_7 - C_3H_6$, 4.7), 228 ($Pr_4Si_2^+$, 100), 187 ($Pr_3Si_2H_2^+$, 72), 186 ($Pr_3Si_2H^+$, 90), 145 ($Pr_2Si_2H_3^+$, 73), 144 ($Pr_2Si_2H_2^+$, 61), 115 (Pr_2SiH^+, 8.5).

$[(nPr)_2Si(C_7H_{11})_2$ (at least two isomers, 19% by GC) [*m/e* (relative intensities)]: 304 (M^+, 1.7), 261 ($M^+ - C_3H_7$, 25), 209 ($M^+ - C_7H_{11}$, 30), 195 (100), 153 (67), 125 (29), 115 (16), 95 (25)]; 304 (M^+, 1.0), 261 (20), 209 (91), 195 (100), 153 (92), 125 (49), 115 (25), 95 (58).

$(C_7H_{11})_2$ (<3% by GC) [*m/e* (relative intensities)]: 190 (15), 95 (100).

Kugelrohr distillation provided purified disilane (0.41 g, 87% by GC) with bp 70 °C (0.05 mmHg): ^1H NMR, δ ($CDCl_3$) 0.7–0.8 (m, $SiCH_2$, 6.5 H), 0.9–1.0 (m, CH_3, 11.6 H), 1.3–1.5 (m, CH_2, 8.4 H), 3.60–3.66 (complex m, SiH, 1.6 H); ^{13}C NMR, δ ($CDCl_3$) 13.21, 17.98, 19.79 (C_3H_7); ^{29}Si NMR, δ ($CDCl_3$/TMS) −33.01.

Reaction of $(nPr)_2SiH_2$ and Cyclooctene with Cp_2TiCl_2/*n*BuLi. In the same manner, Cp_2TiCl_2 (0.100 g, 0.40 mmol) and *n*BuLi (0.50 mL, 0.80 mmol) in 2.8 mL of toluene were reacted with nPr_2SiH_2 (1.14 g, 9.8 mmol) and cyclooctene (1.26 g, 11.5 mmol) at 90 °C. Workup after 120 h gave a brown oil (1.14 g) which contained cyclooctene (7%), cyclooctane (16%), disilane (45%), and trisilane (7%) as well as the SiH/CH coupling product $nPr_2SiH(C_8H_{13})$ (8%) [*m/e* (relative intensities)]: 224 (M^+, 16), 181 (45), 153 (29), 139 (72), 115 (13), 111 (100) 108 (31). Kugelrohr distillation provided a purified disilane (0.40 g, 74% by GC) with bp 70–78 °C (0.08 mmHg). ^1H NMR spectra match those for the disilane produced in the presence of norbornene.

Reaction of $PhMe_2SiH$ with Cyclooctene Catalyzed by Cp_2TiCl_2/*n*BuLi. In a similar fashion, Cp_2TiCl_2 (0.081 g, 0.33 mmol) and *n*BuLi (0.47 mL, 1.4 M, 0.65 mmol) in 2.7 mL of toluene (degassed) were reacted with $PhMeSiH_2$ (1.03 g, 8.4 mmol) and cyclooctene (1.08 g, 9.8 mmol) at 90 °C. Analysis of aliquots showed that only minor reaction occurred [time (h), wt % of cyclooctene, $PhMe_2SiH$)]: 0.0 (52.5, 45.1), 1.0 (51.7, 41.5), 24 (51.7, 41.9), 48 (51.7, 42.0). Several minor products were observed but not identified.

Reaction of $PhMe_2SiH$ with Norbornene Catalyzed by Cp_2TiCl_2/*n*BuLi. In the same manner, Cp_2TiCl_2 (0.08 g, 0.30 mmol) and *n*BuLi (0.50 mL, 1.2 M, 0.60 mmol) in 2.5 mL of toluene (degassed) were reacted with $PhMe_2SiH$ (0.93 g, 7.6 mmol) and norbornene (0.86 g, 9.1 mmol) at 90 °C. Analysis of aliquots indicated that approximately 25% of the silane was consumed, but the only product that could be identified was $PhMe_2Si(C_7H_{11})$ (11% by GC): mass spectrum, *m/e* (relative intensities) 230 (M^+, 2.4), 135 ($PhMe_2Si^+$, 100), 121 ($PhMeSiH^+$, 11).

Reaction of $PhMeSiH_2$ with *cis*-4-Octene Catalyzed by $Cp_2Zr(H)Cl$/*n*BuLi. In a similar fashion, $Cp_2Zr(H)Cl$ (0.026 g, 0.10 mmol) was transferred in a drybox into a preweighed 10-cm^3 round-bottom flask which was wrapped with aluminum foil. Toluene (1.1 mL, degassed) and *n*BuLi (0.06 mL, 0.10 mmol) were added with cooling to 0 °C. Then, $PhMeSiH_2$ (0.57 g, 4.7 mmol) and *cis*-4-octene (0.49 g, 4.4 mmol) were injected separately by syringe. A cloudy cream-colored slurry was obtained which changed to dark brown after heating to 90 °C. Analysis of the aliquots showed the following weight percent of $PhMeSiH_2$ [time (h), %]: 0.0 (100), 0.5 (9.9), 1.0 (8.9), 3.0 (7.8), 24 (6.3). Workup in the same manner after 24 h gave a light yellow cloudy oil (0.81 g) which contained one major product $PhMeSiH(C_8H_{17})$ (90%). Kugelrohr distillation provided a purified sample of PhMeSiH-

(C_8H_{17}) (0.61 g) with bp 100 °C (0.07 mmHg), which had spectroscopic data identical to that observed for the product obtained with Cp_2ZrCl_2/nBuLi.

Reaction of $H(PhMeSi)_2H$ with Cp_2ZrCl_2/nBuLi. In the same manner as performed for the coupling reaction of $PhMeSiH_2$, Cp_2ZrCl_2 (0.042 g, 0.14 mmol) and nBuLi (0.22 mL, 1.3 M, 0.28 mmol in 1 mL of toluene (degassed)) were reacted with $H(PhMeSi)_2H$ (0.63 g, 2.6 mmol, 95% by GC) at 90 °C. A dark brown solution formed, and bubbling was observed for a few minutes. Aliquots were removed to determine the distribution of products [time (h), wt % $PhMeSiH_2$/PhMeBuSiH/disilane/trisilane/tetrasilane/pentasilane/hexasilane]: 0.0 (–/0.6/94/0.7/–/–/–), 0.50 (13/4.1/59/8.6/11/–/–), 1.0 (18/4.3/46/12/15/0.9/–), 24 (17/4.4/14/25/20/3.8/0.5).

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Synthesis, Structure, and Reactivity of Chiral Rhenium Carboxylic and Carbonic Acid Ester Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(X)X')]^+X''^-$

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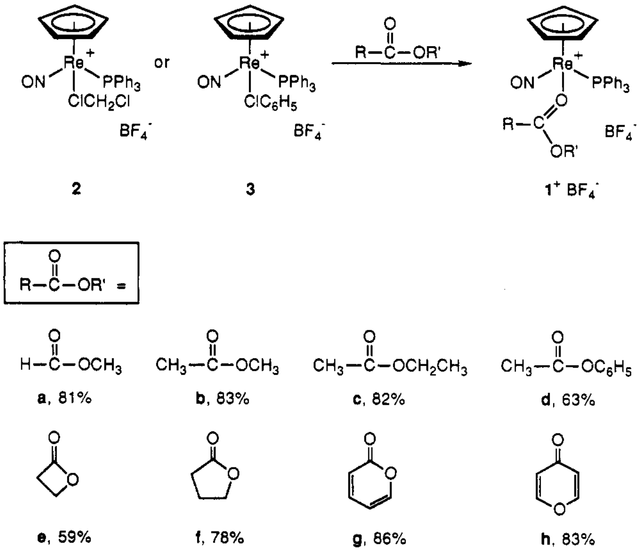
Reactions of chlorocarbon complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClX)]^+BF_4^-$ (X = CH_2Cl, C_6H_5) with (**a**) methyl formate, (**b**) methyl acetate, (**c**) ethyl acetate, (**d**) phenyl acetate, (**e**) propiolactone, (**f**) γ-butyrolactone, (**g**) 2*H*-pyran-2-one, (**h**) 4*H*-pyran-4-one, (**i**) dimethyl carbonate, (**j**) ethylene carbonate, and (**k**) imidazolidone give the corresponding σ complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(X)X')]^+BF_4^-$ ($\mathbf{1a}$–$\mathbf{k}^+BF_4^-$; 87–42% after workup). Reactions of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$, $Ph_3C^+PF_6^-$, and esters **b**,**f** give $\mathbf{1b},\mathbf{f}^+PF_6^-$ (83–88%). Crystal structures of $\mathbf{1b},\mathbf{f}^+PF_6^-$ show similar ON—Re—O=C torsion angles (27.6 (9)°, 12.1 (6)°) and C=O bond lengths (1.23 (1), 1.236 (7) Å), but the ester oxygen is *E* to the rhenium in the former and *Z* in the latter. Spectroscopic, structural, and dynamic properties of $\mathbf{1a}$–$\mathbf{k}^+X^-$ are analyzed in detail. The ester ligands in $\mathbf{1c},\mathbf{f},\mathbf{i}^+BF_4^-$ are readily displaced by acetone and propionaldehyde at room temperature (Lewis basicity order: propionaldehyde > acetone > **c**,**f**,**i**). Analogous substitutions occur with alcohols.

The synthesis, structure and reactivity of Lewis acid/base adducts of transition-metal fragments and organic carbonyl compounds have been receiving increasing attention.[1] In particular, *chiral* transition-metal Lewis acid fragments offer numerous potential applications in chiral recognition and asymmetric organic synthesis. Remarkably, there have been few if any systematic studies of complexes of *nonchelated* carboxylic and carbonic acid ester functionalities.[1-4] This is surprising in view of the variety of metalloenzyme-catalyzed biological transformations of such compounds[5] and the many commercial transesterification processes that use metal catalysts.[6]

Scheme I. Syntheses of Ester Complexes $\mathbf{1a}$–$\mathbf{h}^+BF_4^-$



We have conducted an extensive study of complexes of the chiral rhenium moiety $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) and organic aldehydes and ketones O=CRR'.[7-10] These

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