stantial π,η^4-character, more so than is present in the $(\eta^5\text{-}C_5H_5)_2M(\text{diene})$ (M = Zr, Hf) complexes. This in turn suggests that the M(II) oxidation state contributes significantly to the bonding scheme of the derivatives M-$(\eta^4\text{-}C_4H_6)R'[N(SiMe_2CH_2PR_2)_2]$.

These new group 4 butadiene complexes display fluxional behavior that is best described as diene rotation rather than the envelope-flipping mechanism normally associated with early metal diene derivatives. That this fluxional process is more akin to that found for an electron-rich, late-transition-metal complex provides further support for the proposal that phosphine donors can stabilize lower oxidation states of the early transition metals.[31]

(31) For recent examples of this strategy, see: (a) Wielstra, Y.; Gambarotta, S.; Roedelof, J. B.; Chiang, M. Y. *Organometallics* 1988, 7, 2177. (b) Wielstra, Y.; Gambarotta, S.; Chiang, M. Y. *Organometallics* 1988, 7, 1866.

Supplementary Material Available: Tables of calculated hydrogen atom parameters, anisotropic thermal parameters, and bond lengths and angles involving refined hydrogen atoms (Tables S1–S4) (5 pages); listings of structure factors (Tables S5 and S6) (50 pages). Ordering information is given on any current masthead page.

A Survey of Catalytic Activity of η^5-Cyclopentadienyl Complexes of Groups 4–6 and Uranium and Thorium for the Dehydrocoupling of Phenylsilane

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The effectiveness of a variety of metallocene, metallocene alkyl, and metallocene hydride complexes of group 4–6 metals and of U and Th as catalysts for the dehydrocoupling of phenylsilane was studied. Among the d-block complexes only those of Ti and Zr showed high activity for the production of higher oligomers (degree of polymerization 10–20). Vanadocene is an effective catalyst for the synthesis of 1,2-diphenyldisilane and 1,2,3-triphenyltrisilane from phenylsilane but under much more forcing condition than necessary with the group 4 catalysts. The metallocene hydrides of Mo, W, Nb, and Ta react slowly with phenylsilane to give relatively stable metallocene silyl hydrides or other decomposition products that show no catalytic activity. The synthesis and characterization of a number of new hydridosilylmolybdenocene complexes are described. Although the organouranium and -thorium complexes show some catalytic activity for dehydrocoupling of phenylsilane in ether solution, their instability and the complexity of the chemistry involved mitigates against their usefulness as practical catalysts. An explanation of the unique activity of Ti and Zr complexes is proposed that invokes the necessity for an empty nonbonding orbital on the metal to facilitate an α-hydrogen elimination from coordinated silyl ligand.

Introduction

A number of promising applications of polysilanes has recently aroused considerable interest in their synthesis and the study of their physical and chemical properties.[1] The only known route to poly(organosilanes) of high molecular weight is the condensation of diorganodihalosilanes through reaction with a group 1 metal (the Wurtz–Fittig reaction).[2,3] Although this method is highly versatile and can give linear polymers with molecular weights up to ca.

10^6, it suffers from the fact that it is difficult to control and usually gives large amounts of cyclic oligomers and/or a low molecular weight fraction.

The discovery of catalysts for the facile dehydrocoupling of primary organosilanes aroused hopes that such reactions might provide another, and perhaps superior, synthesis of polysilanes.[4–6] The first class of catalysts explored by us were compounds of the type Cp$_2$MR$_2$, where Cp is an

(1) West, R.; Maxka, J. In *Inorganic and Organometallic Polymers*; Zeldin, M.; Wynne, K. J.; Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 2 and references therein.

(2) Burkhard, C. A. *J. Am. Chem. Soc.* 1949, 71, 963. Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* 1968, 6, 19. West, R. *Pure Appl. Chem.* 1982, 54, 1041. Hengge, E. *Top. Curr. Chem.* 1974, 51, 1. Yajima, S.; Hayashi, J.; Omori, M. *Chem. Lett.* 1975, 931.

(3) West, R.; David, L. D.; Djurovic, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* 1981, 103, 7352. Trujillo, R. E. *J. Organomet. Chem.* 1980, 198, C27. Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* 1979, 17, 2833.

(4) (a) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* 1985, 279, C11. (b) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* 1986, 108, 4059. (c) Aitken, C. T.; Samuel, E.; Harrod, J. F. *Can. J. Chem.* 1986, 64, 1677. Harrod, J. F.; Yun, S. S. *Organometallics* 1987, 6, 1381.

(5) Harrod, J. F. *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 7. Harrod, J. F. *The Design, Activation and Transformation of Organometallics into Common and Exotic Materials*; Laine, R. M., Ed.; NATO ASI Series E, 141; Martinus Nijhoff: Amsterdam, 1988; p 103.

(6) Aitken, C. T.; Harrod, J. F.; Gill, U. S. *Can. J. Chem.* 1987, 65, 1804.

Table I. Summary of Screening Reaction for Catalytic Dehydrocoupling of Phenylsilane[a]

reactant	temp, °C	time, h	cat. concn, M	[cat.]/[silane]	metallocene product	silane product (yield, %)
CpTiMe$_3$	−80 to 20	6	0.02	0.1	e	oligomer (trace)
CpZrMe$_3$	−80 to 20	6	0.02	0.1	e	oligomer (trace)
Cp*TiMe$_3$	c	6	0.02	0.1	e	oligomer (trace)
Cp*ZrMe$_3$	c	6	0.02	0.1	e	oligomer (trace)
(MeCp)$_2$TiMe$_2$	c	6	0.02	0.01	f	oligomer (85)
(MeCp)$_2$ZrMe$_2$	c	6	0.02	0.01	f	oligómer (100)
CpCp*TiMe$_2$	c	40	0.02	0.1	g	oligomer (80)
CpCp*ZrMe$_2$	c	40	0.02	0.1	g	oligomer (100)
Cp$_2$HfmE$_2$	20–90	12	0.10	0.5	h	none
Cp*$_2$TiMe$_2$	−60 to 20	12	0.10	0.5	e	oligomer (trace)
Cp*$_2$ZrMe$_2$	−60 to 20	12	0.10	0.5	e	oligomer (trace)
Cp$_2$V	100–120	40	0.125	0.025	e	dimer (40) trimer (20)
Cp$_2$VMe$_2$	100–120	40	0.125	0.025	e	dimer (40) trimer (20)
Cp$_2$NbH$_3$	100–120	12	0.10	0.5	i	none
Cp$_2$TaH$_3$	100–120	12	0.10	0.5	i	none
Cp$_2$Cr	c	12	0.02	0.1	h	none
Cp$_2$MoH$_2$	d	12	0.10	0.5	j	none
Cp$_2$WH$_2$	d	12	0.10	0.5	h	none
Cp*$_2$UMe$_2$[b]	c	6	0.02	0.1	e	oligomer (30)
Cp*$_2$ThMe$_2$[b]	c	6	0.02	0.1	e	dimer (70)

[a] All reactions run in toluene unless otherwise indicated. [b] Reactions run in diethyl ether. [c] Ambient temperature. [d] UV photolysis at ambient temperature. Low-pressure Hg lamp. [e] Reactant completely transformed. No product identified. [f] Products analogous to those formed with Cp$_2$MMe$_2$ (M = Ti or Zr). [g] Completely transformed to unidentified products. Not same as [f]. [h] Starting material recovered unchanged. [i] Stable silyl hydrides detected by NMR. [j] Stable silyl hydride isolated and characterized.

η^5-cyclopentadienyl or a substituted cyclopentadienyl ligand, M = Ti or Zr, and R was a hydrocarbyl ligand. While these catalysts are easy to prepare and use and in some cases show high reactivity, the poly(organosilanes) produced had maximum degrees of polymerization of ca. 20, well below what is required for a polymer with useful mechanical properties and well below the chain length at which electronic properties level off. A systematic search among related organometallic compounds was therefore initiated to find superior catalysts, particularly with regard to their ability to give high molecular weight polymers. The results of this survey are the subject of this paper.

Results and Discussion

The results of a survey of the catalytic reactivity of all of the complexes used in the present study are summarized in Table I.

Mono(cyclopentadienyl) and Bis(alkylcyclopentadienyl) Complexes of Group 4. Studies on dialkylbis(cyclopentadienyl)titanium and -zirconium complexes indicated that the rate of silane polymerization was strongly dependent on steric factors.[4] It was therefore of interest to study the reactions of a primary organosilane with less sterically congested trialkyl(cyclopentadienyl)-titanium and -zirconium compounds. Trimethyl(η^5-cyclopentadienyl)titanium underwent rapid reaction with phenylsilane at 20 °C to give unidentified products that showed no catalytic activity for the polymerization of phenylsilane. A similar result was obtained with the zirconium analogue, synthesized in situ by addition of methyllithium to CpZrCl$_3$ at low temperature. The trimethyl η^5-pentamethylcyclopentadienyl complexes were found to be similarly inactive as catalysts, and no identifiable reaction products were isolated from their reactions with phenylsilane.

Dimethylbis(methylcyclopentadienyl)titanium and -zirconium both had similar activities to the cyclopentadienyl analogues and gave poly(phenylsilanes) with the same degrees of polymerization. This was also true of the dimethyl η^5-cyclopentadienyl η^5-pentamethylcyclopentadienyl complexes, although the reactions were much slower. Also, with these catalysts, after long polymerization times, a white precipitate was observed to settle to the

bottom of the reactor. Although the precipitate appeared visually to be substantial, it actually only accounted for about 1% of the product. This highly insoluble white material was shown to be identical with the all-trans isomer of hexaphenylcyclohexasilane, previously reported by Hengge and co-workers.[7]

The dimethyl bis(η^5-pentamethylcyclopentadienyl) complexes showed no catalytic activity but did show evidence of undergoing a reaction with phenylsilane. A freshly prepared 2% (w/w) solution of dimethylbis(η^5-pentamethylcyclopentadienyl)titanium in phenylsilane gave an ^{1}H NMR spectrum in which sharp signals for both components of the mixture were clearly evident. After the solution was left standing for 4 h at room temperature, the phenyl and Si–H signals had considerably broadened, while no change in the line widths of the resonances of the metal complex protons was observed. Cooling the solution to −60 °C reversibly restored the original line width. Similar behavior was observed with dimethylbis(η^5-pentamethylcyclopentadienyl)zirconium. We attribute this selective line broadening of the silane protons to a dynamic process which involves all of the silane and only a small fraction of the catalyst complex. A likely candidate for the titanium case is the transformation of a small part of the starting complex to permethyltitanocene, which then participates in a rapid, reversible oxidative addition reaction with the silane, as shown in eq 1. Such a reaction is analogous to the previously observed, reversible oxidative addition of H$_2$ to permethyltitanocene[8] (Cp* = η^5-pentamethylcyclopentadienyl).

$$\text{Cp*}_2\text{Ti} + \text{PhSiH}_3 \rightleftharpoons \text{Cp*}_2\text{TiH(SiH}_2\text{Ph)} \qquad (1)$$
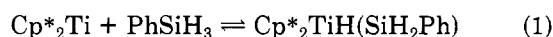
Similar reactions could account for the results with the zirconium system.

Attempts to isolate silane-containing oxidative addends by letting the reactions proceed for extended periods gave only intractable paramagnetic products.

Reactions of phenylsilane with dimethylhafnocene at room temperature and at 90 °C gave only starting materials after a 12-h reaction.

(7) Hengge, E.; Lunzer, F. *Monatsh. Chem.* **1976**, *107*, 371.
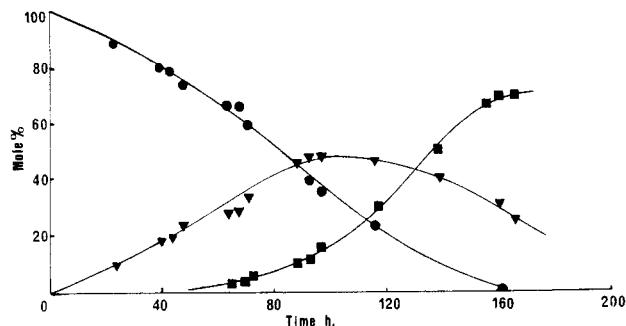(8) Bercaw, J. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

Figure 1. Conversion of PhSiH$_3$ into dimer and trimer under the influence of a vanadocene catalyst. In toluene (1:2 v/v) at 100 °C (catalyst concentration = 3 mol %): ●, phenylsilane; ▼, dimer; ■, trimer.

Some Reactions of Group 5 Metallocene Complexes with Phenylsilane.

Vanadocene does not undergo any evident reaction with phenylsilane under ambient conditions. In refluxing toluene solutions, vanadocene catalyzes the stepwise oligomerization of phenylsilane at a modest rate. The monomer is converted to about 50% dimer before significant amounts of trimer begin to accumulate. Subsequently, trimer builds up to about 70% of total product before significant accumulation of higher oligomers begins. The results of such an oligomerization are summarized in Figure 1. This behavior contrasts with that of the titanocene system where only small amounts of dimer and trimer are detected during the polymerization reaction. The vanadocene-catalyzed dimerization is a good synthetic route to diphenyldisilane and to triphenyltrisilane. The behavior of dimethylvanadocene was essentially the same as that of vandocene itself.

Neither niobocene nor tantalocene is available as a stable compound under ambient conditions. We therefore studied the reactions of the readily available trihydride derivatives with phenylsilane. Neither of the compounds Cp$_2$MH$_3$ (M = Nb or Ta) showed any activity as catalysts, under ambient conditions, under photolysis, or in refluxing phenylsilane. Extended reflux of these complexes in neat phenylsilane resulted in the disappearance of the hydride ^{1}H NMR resonances of the starting materials and the appearance of new hydride resonances at a slightly lower field. These new hydrides were almost certainly the analogues of the tertiary silyl complexes previously reported by Curtis et al.[9]

Some Reactions of Group 6 Metallocene and Metallocene Hydride Complexes with Group 4 Hydrides.

Chromocene was unreactive with phenylsilane and did not catalyze dehydrocoupling under mild reaction conditions.

Molybdenocene dihydride reacted readily with a variety of alkyl- and aryl-substituted silanes and with triphenylgermane, under UV photolysis, to give the compounds listed in Table II. These compounds are analogous to those recently reported by Berry et al.,[10b] prepared by trapping dimethylsilylene with Cp$_2$MoH$_2$. The frequencies of the Si–H vibrations of the PhSiH$_2$ and Ph$_2$SiH ligands are unusually low, as observed by Berry for Mo and Ta silyl complexes.[10]

All of the complexes listed in Table II were air sensitive and underwent slow decomposition at room temperature. Their characterization rests on spectroscopic data, since satisfactory chemical analyses were not obtained. All of the complexes containing an Si–H bond decomposed to

Table II. Spectral Data for Some Hydrido Silyl and Hydrido Germyl Derivatives of Molybdenocene (Cp$_2$MoH(R))

R	mp, °C	MS parent, m/e	IR, cm^{-1} MoH	IR, cm^{-1} SiH	^{1}H NMR,[a] ppm Mo–H	^{1}H NMR,[a] ppm Cp	^{1}H NMR,[a] ppm Si–H
SiH$_2$Ph	121–123	334 (M$^+$ – 3H)	1820	2005	–8.17	4.19	5.06
SiHMePh	115–118	346 (M$^+$ – 4H)	1810	2035	–7.99	4.09	5.08
SiHPh$_2$	109–111	410 (M$^+$ – 2H)	1820	1985	–7.90	4.18	5.65
SiPh$_3$	118–121	487 (M$^+$ – H)	1820		–7.43	4.08	
GePh$_3$	132–135	532 (M$^+$ – H)	1802		–7.71	4.08	

[a] Measured in toluene-d_8.

give Cp$_2$MoH$_2$ and unidentified silicon-containing products. No evidence for dehydrocoupled silicon derivatives was observed. This decomposition reaction prevented the preparation of these complexes completely free of contaminants.

Attempts to duplicate the above reactions with Cp$_2$WH$_2$ were not successful. In all cases the starting complex proved to be unreactive and was quantitatively recovered after irradiation.

Reactions of Cp*$_2$MMe$_2$ (M = U and Th) with Phenylsilane.

The synthesis and reactions of pentamethylcyclopentadienyl complexes of uranium and thorium have been extensively studied by Marks and co-workers.[11] These compounds exhibit extraordinarily high rates for hydrogenation and polymerization of olefins.[11d] It was therefore of interest to determine whether they had any special catalytic activity with respect to silane polymerization. To this end the reactions of Cp*$_2$MMe$_2$ (M = U and Th) with phenylsilane were studied.

The paramagnetism of Cp*$_2$UMe$_2$ causes large shifts in the ^{1}H NMR resonances of the compound, but they remain sharp and easily observable.[11a] Addition of 2 equiv of PhSiH$_3$ to a solution of this complex in deuteriotoluene leads to rapid and complete disappearance of its NMR spectrum, suggestive of rapid reduction to a U(III) species. The spectrum of the phenylsilane remains normal but is supplemented by the appearance of some phenylmethylsilane (ca. 0.2 equiv). Subsequently a large number of peaks slowly appear in the methyl region, characteristic of the decomposition products of Cp* actinide complexes. Attempts to work up a product from either the initial or final reaction mixtures were uniformly unsuccessful.

The behavior described in the previous paragraph was also observed in the presence of a large excess of phenylsilane. No evident gas evolution occurred, but small amounts of a low molecular weight oligosilane were obtained. However, when ether was used as a solvent, rather than toluene, a fairly rapid and complete catalytic dehydrocoupling of the silane to oligomers occurred.

The reaction of Cp*$_2$ThMe$_2$ with phenylsilane is very rapid and extremely complex. In a reaction of this compound with 2 equiv of phenylsilane in toluene, no starting complex was left after 5 min at room temperature. At this point 80% of the original thorium-bonded methyl groups were accountable by ^{1}H NMR as phenylmethylsilane and most of the remainder as methane. The disappearance of

(9) Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701.

(10) (a) Berry, D. H.; Mistifer, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 3777. (b) Berry, D. H.; Jiang, Q. *J. Am. Chem. Soc.* **1987**, *109*, 6210.

(11) (a) Fagan, P. J.; Manriquez, J. M.; Maata, E. A.; Seyam, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650. (b) Marks, T. J. *Science (Washington, DC)* **1982**, *217*, 989. (c) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (d) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 641.

the starting complex was also accompanied by the appearance of a large number (at least seven) of peaks in the ligand methyl region and of several peaks in the low-field Th–H region (δ ca. 19 ppm[11a]). Five minutes later, most of the ligand methyl resonances had greatly diminished and been replaced by a singlet at 2.2 ppm. Little is to be gained from this data beyond the knowledge that the reaction is of a daunting complexity.

In ether solvent, the thorium complex is an effective catalyst for the dimerization of phenylsilane to 1,2-diphenyldisilane but does not effect the production of higher oligosilanes. In addition, this reaction leads to the formation of the known hydride complex $[Cp*_2ThH(\mu\text{-}H)]_2$[11a] in about 10% yield.

The reaction of the uranium complex resembles the behavior of dimethyltitanocene, particularly with respect to the fact that a pronounced induction period is observed in both cases, followed by reduction of most of the metal species to a lower oxidation state. The thorium system parallels the dimethylzirconocene system to some degree in that these reactants both remain predominantly in the oxidation state IV. They differ in the fact that the thorium complex is a specific catalyst for phenylsilane dimerization while the zirconocene complex gives oligomers of ca. 15–20 Si atoms. Dimethylzirconocene also differs from the thorium complex in that it does not give the dimer hydride complex or phenylmethylsilane. $[Cp*_2ZrN_2]_2N_2$,[12] however, is rapidly and quantitatively converted to the hydride $Cp*_2ZrH_2$[13] on reaction with phenylsilane.

The Relationship between Catalytic Activity and Catalyst Structure. From the foregoing results it is quite evident that the catalytic activities of the dialkylmetallocenes of titanium and zirconium for dehydrocoupling of silanes are uniquely high among the complexes of the transition metals that have been so far investigated.

The failure of the heavier congeners of groups 5 and 6 to efficiently catalyze the reaction is readily attributed to two experimentally observed features of their chemistry with phenylsilane. In the first place, the starting hydride complexes react, at best, only sluggishly with the silane, and secondly, relatively stable silyl hydride complexes are formed when the reaction does take place.

It is important to stress that the overall catalytic process may be impaired by a failure of the starting complex to be transformed into an active species or by the intermediates being too stable. Both of these factors operate in the Mo, W, and Nb, Ta cases. In the cases of Ti and Zr, the observed induction periods are due to primary reactions of the dialkylmetallocenes that are relatively slow, but once reactive intermediates accumulate, the overall reaction becomes very fast. This is particularly evident in the case of titanium, where the primary reaction seems to be a branched chain reaction. In the titanium case, the primary reaction leads to the reduction of all of the observable titanium to Ti(III), whereas the zirconium remains predominantly in the oxidation state IV. It is likely that the reduction of the titanium is not per se a necessary condition for catalytic activity but rather a means of generating the true catalytic intermediate, which we believe is a titanium(IV) species.[4,5] On the other hand, even though the major observable zirconium species are Zr(IV), it is possible that the primary reactions of the zirconium complex may involve reduction to Zr(III), since para-

Chart I. α-Hydride Migration in a Silylhydridotitanium(IV) Complex[a]

| 1 | 2 | 3 |
| Ti: 16e | Ti: 18e | Ti: 16e |
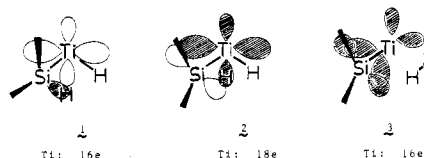
[a]The Cp ligands are omitted for clarity.

magnetic species are observed in the reaction medium by ESR. The failure of dimethylhafnocene to react with phenylsilane supports the possibility that a branched chain reduction is a key step in the activation of the group 4 complexes. The length of the induction period in such a reaction is potentially very sensitive to small changes in the rate constants for the initiation steps and can easily become very long. This explanation seems more plausible than any that requires a dramatic difference between zirconium and hafnium in their simple bimolecular reactions.

The failure of either dimethylvanadocene or vanadocene to catalyze dehydrocoupling efficiently is particularly remarkable and points to some very severe constraint on the ability of compounds to catalyze this reaction. In addition to the dialkyltitanocenes, a number of other titanium species, such as $[Cp_2Ti]_2$, $Cp_2Ti(CO)_2$, and $[Cp_2TiH]_2$, are also active.[4b] Thus, even if the reduction of V(IV) were slow, at least the free vanadocene should show activity. The nonreactivity of the vanadium points to a unique electronic feature of the group 4 compounds, and this in turn leads to the conclusion that the empty, relatively nonbonding, a_1 frontier orbital that is characteristic of only the group 4 metallocenes[14] in oxidation state IV is the key to their exceptional catalytic activity in dehydrocoupling.

In Chart I we show the manner in which the empty nonbonding orbital of the Cp_2Ti^{IV} entity can facilitate the α-hydrogen elimination from a primary or secondary silyl ligand. In this scheme, the energy of the transition state is lowered by spreading of the nonbonding orbital from the titanium to the silicon as the hydride ligand is transferred from the silicon to the titanium; i.e., the transition state contains a large contribution of the structure 2. If the starting metal silyl hydride complex has more than 16 electrons, this process produces a metal center with more than 18 electrons and would be expected to be less favorable.

In addition to the electronic factor, Chart I is also sterically demanding. The lowest energy conformation for the transfer in Chart I to occur is that in which the Si–H bond is coplanar with the H–Ti–Si atoms and with the nonbonding a_1 orbital of the Ti. This conformation forces the other two substituents on the silicon into closest contact with the Cp rings. The steric bulk of those substituents is therefore expected to have a profound influence on the rate, as observed experimentally. Similar arguments would apply to the steric encumbrance introduced by methyl substitution at the Cp rings.

The reactions of the organoactinide complexes, while not inconsistent with a model in which coordination unsaturation at the metal atom is the key feature, are too complicated to seriously offer a mechanism at this point. One factor that is undoubtedly important in the case of the organoactinides is their excessive activity. It has already been shown by Marks and co-workers that these complexes can undergo reactions with C–H bonds.[11] It is likely that

(12) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* 1974, *96*, 6229. Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* 1982, *104*, 4712.

(13) Manriquez, J. M.; McAllister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* 1978, *100*, 2716.

(14) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* 1976, *98*, 1729.

this is a complication when hydrocarbons are used as solvents or when reactions are run in neat phenylsilane. The use of ether as solvent reduces the overall reactivity of the system and gross decomposition of the catalyst, thereby allowing catalytic dehydrocoupling of phenylsilane to occur. In view of the failure of these catalysts to give results significantly different from those of the group 4 catalysts and their much greater difficulty of preparation and handling, it was not considered worthwhile to pursue their study further.

Under forcing conditions, many transition-metal complexes catalyze the slow oligomerization of silanes by dehydrocoupling.[15,16] It is likely that these reactions proceed by different mechanisms from that operating in the case of the group 4 metallocene derivatives. Even in the case of the group 4 catalysts, it is likely that more than one mechanism is involved.

Conclusions

The ability to rapidly catalyze dehydrocoupling of primary silanes appears to be a highly restricted phenomenon. The metallocene derivatives of titanium and zirconium exhibit a unique activity among the d group metallocenes and readily give polymers of 10–20 silicon atoms. No other d group shows activity in the same range, although the ability to catalyze slow oligomerization under forcing conditions is a fairly common property. Dimethylbis-(pentamethylcyclopentadienyl)actinide complexes (U and Th) show high catalytic activities for dehydrocoupling under ambient conditions, but the difficulty in preparing and handling these compounds mitigates against their use as practical catalysts.

Experimental Section

All reactions were carried out under argon by using standard inert atmosphere techniques. Solvents were freshly distilled and degassed before use. Vanadocene and chromocene were purchased from Strem Chemical Co. and used as received. Phenylsilane was prepared by a literature method.[17] The following complexes were prepared by literature methods: (cyclopentadienyl)trimethyltitanium[18] ((pentamethylcyclopentadienyl)trimethyltitanium was made by using the same method); (pentamethylcyclopentadienyl)trimethylzirconium;[19] dimethyltitanocene[20] and -zirconocene[21] (the bis(methylcyclopentadienyl) compounds were made by the same methods); dimethyl(cyclopentadienyl)(pentamethylcyclopentadienyl)titanium and dimethylbis(pentamethylcyclopentadienyl)titanium;[22] dimethyl(cyclopentadienyl)(pentamethylcyclopentadienyl)zirconium;[19] dinitrogenbis[dinitrogenbis(pentamethylcyclopentadienyl)zirconium];[12] (cyclopentadienyl)dimethylvanadium;[23] (cyclopentadienyl)trihydridoniobium[9] and -tantalum;[9] dihydridobis-(cyclopentadienyl)molybdenum and -tungsten;[24] dimethylbis-(pentamethylcyclopentadienyl)uranium and -thorium.[11a]

(Pentamethylcyclopentadienyl)trimethylzirconium has not been reported in the literature and appears to be extremely unstable in solution. For the purposes of the present study it was generated in situ at -78 °C by the addition of 3 equiv of methyllithium to

a suspension of CpZrCl₃[25] in toluene and phenylsilane.

Polymerization Reactions. All polymerizations catalyzed by titanium, zirconium, and organoactinide complexes were carried out at, or below, room temperature in 20-mL Schlenk tubes. Typically, the tubes were charged with catalyst, degassed solvent, and phenylsilane. The reaction mixture was periodically sampled and the course of the reaction was followed by ¹H NMR. The resonances of both the metal complexes and the silanes were followed. The nature of the polymers was determined by previously described procedures.[6] The 1,2-diphenyldisilane produced with the organothorium catalyst was identified by comparison with an authentic sample produced by using a vanadocene catalyst (see below) and by comparison with literature data.[7] A summary of all the reactions studied together with the conditions used for screening for catalytic activity is given in Table I.

Vanadium-Catalyzed Oligomerizations. A solution of PhSiH₃ (2 mL; 16 mmol) in toluene (4 mL) was injected into an argon-filled reflux apparatus. Following addition of vanadocene (200 mg, 1.1 mmol) the reaction mixture was heated to 110 °C with stirring for 5 days. The reaction was followed by periodic sampling and measurement of the relative amounts of monomer, dimer, and trimer by the three distinct Si–H resonances in their ¹H NMR spectra. When the product had reached the desired composition, the reaction mixture was cooled, exposed to air, and passed down a short Florisil column to remove the catalyst. After the solvent and residual phenylsilane were flash-distilled, the product was subject to microdistillation under high vacuum (65 °C/10⁻³ mm) to give pure dimer (0.8 g, 45%). Although the trimer can be distilled under reduced pressure (85 °C/10⁻³ mm), it is essential to pass it over a Florisil column again since residual traces of catalyst cause extensive decomposition during distillation. Even after further removal of catalyst, a considerable amount of trimer is lost due to polymerization and redistribution. If care is taken not to allow the original reaction to proceed to the point where higher oligomers are formed, the residue after distillation of the *dimer* consists of trimer of >90% purity, a material that is useful for further study. Both dimer and trimer were characterized by NMR spectroscopy. ¹H NMR: dimer (4.49 ppm, s); trimer (4.61 ppm, m) (the resonances due to the internal and terminal Si–H are not resolved at 200 MHz). ²⁹Si NMR: dimer (61.2 ppm, $J_{Si–H}$ = 192 Hz); trimer (58.5 and 67.9 ppm, $J_{Si–H}$ = 198 and 186 Hz).

Synthesis of Hydridosilylmolybdenocene Complexes. The following is a typical procedure. Dihydridomolybdenocene (0.30 g, 1.3 mmol) was suspended in hexane (30 mL) in a quartz Schlenk tube. A sample of organosilane (2.6 mmol) was then syringed into the tube, and the well-stirred solution was irradiated for 4 h with a 100-W Hanovia low-pressure mercury lamp. During irradiation the mixture changed color from pale yellow to brown and the molybdenum complex slowly went into solution. After the reaction was complete, the product was filtered through Celite and evaporated to give a yellow solid that was recrystallized by cooling a concentrated hexane solution. Spectroscopic data for all of the prepared complexes are listed in Table II.

Registry No. PhSiH₃ (homopolymer), 80731-82-4; PhSiH₃ (SRU), 95584-36-4; CpTiMe₃, 38386-55-9; CpZrMe₃, 120666-08-2; Cp*TiMe₃, 107333-47-1; Cp*ZrMe₃, 81476-64-4; (MeCp)₂TiMe₂, 78169-38-7; (MeCp)₂ZrMe₂, 68193-38-4; CpCp*TiMe₂, 95402-77-0; CpCp*ZrMe₂, 81476-76-8; Cp*₂TiMe₂, 11136-41-7; Cp*₂ZrMe₂, 67108-80-9; Cp₂V, 1277-47-0; Cp₂VMe₂, 62363-03-5; Cp*₂UMe₂, 67605-92-9; Cp*₂ThMe₂, 67506-90-5; Cp₂MoHSiH₂Ph, 120666-09-3; Cp₂MoHSiHMePh, 120666-10-6; Cp₂MoHSiHPh₂, 120666-11-7; Cp₂MoHSiPh₃, 120666-12-8; Cp₂MoHGePh₃, 120685-63-4; PhSiH₃ (dimer), 120666-01-5; PhSiH₃ (trimer), 120666-02-6.

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