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Article

Silane Complexes of Electrophilic Metal Centers

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Photolysis of solutions of $M(CO)_6$ (M = Cr, Mo, and W) in the presence of Et_3SiH affords the silane complexes $Cr(CO)_5(\eta^2\text{-}HSiEt_3)$, $Mo(CO)_5(\eta^2\text{-}HSiEt_3)$, and $W(CO)_5(\eta^2\text{-}HSiEt_3)$. Observed values of J_{SiH} in these complexes are consistent with modest elongation of the Si–H bond. With Ph_3SiH, complexes of $Cr(CO)_5$ and $W(CO)_5$ were obtained, but no complex with Mo was observed. When Ph_2SiH_2 was employed, only one Si–H bond interacts with the metal center. A dynamic exchange process observable on the magnetic resonance time scale exchanges the pendant and coordinated Si–H bonds of the coordinated diphenylsilane. Silanes bound to $M(CO)_5$ are activated with respect to reaction with nucleophiles. With methanol, catalytic methanolysis of $HSiEt_3$ has been observed in the presence of $Cr(CO)_5(\eta^2\text{-}HSiEt_3)$, affording Et_3SiOMe.

Introduction

Activation of Si–H bonds is a key step in hydrosilation, a reaction widely employed for the derivatization of olefins.[1] Silane complexes are thought to be intermediates on the pathway to oxidative addition of Si–H bonds, analogous to other σ-bond complexes such as alkane complexes and dihydrogen complexes. Since the first observation of a mononuclear silane complex by Hart-Davis and Graham,[2] complexation and activation of Si–H bonds has become an active area of research that has been thoroughly reviewed.[3] Kubas has pointed out the many similarities between complexation of Si–H bonds and the related chemistry of C–H and H–H bonds.[4] This aspect has also been emphasized in reviews by Crabtree[5] and by Schneider.[6]

Kubas and co-workers have studied the interaction of Si–H bonds with various group 6 carbonyl-containing complexes. For example, $Mo(CO)(Et_2PCH_2CH_2PEt_2)_2$ binds silanes such as H_2SiPh_2. The closely related but less basic $Mo(CO)(Ph_2PCH_2CH_2PPh_2)_2$ only binds primary silanes and does so more weakly.[7] Sterically less congested but highly electrophilic Re and Mn cations such as $[(PPh_3)Re(CO)_4]^+$ and $[mer\text{-}Mn(CO)_3\{P(OCH_2)_3CMe\}_2]^+$ bind silanes such as Et_3SiH more strongly than H_2.[8,9]

Examples of highly electrophilic, carbonyl-rich metal centers that bind silanes are rare, indeed Kubas has suggested that the "electron-poor group 6 species such as M(silane)-$(CO)_5$ are not stable".[4] While such complexes may not be isolable at room temperature, there is precedent for their observation in solution. For example, Brown and co-workers reported that photolysis of $Cr(CO)_6$ in the presence of Et_3SiH transiently formed $Cr(CO)_5(\eta^2\text{-}HSiEt_3)$.[10] Burkey has employed photoacoustic calorimetry (PAC) to estimate the binding enthalpy for complexation of Et_3SiH to $M(CO)_5$ (M = Cr, Mo, and W) to be 21, 22, and 28 kcal/mol, respectively, and suggests that these complexes may be reasonably stable with respect to silane dissociation.[11]

We have recently reported that moderately stable dihydrogen complexes $(H_2)Cr(CO)_5$ and $(H_2)W(CO)_5$ can be prepared by photoextrusion of CO from the hexacarbonyls in the presence of H_2.[12] Here we report our extensions of these methods to the observation of silane coordination to these highly electrophilic metal centers. We also report the

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chemical preparation of a silane complex of the very electrophilic cation $[Re(CO)_5]^+$.

Experimental Section

General Procedures. Standard vacuum-line and drybox techniques were employed in the manipulation of samples and in the vacuum transfer of solvents. NMR spectra were acquired on a Bruker Avance 500-MHz spectrometer running xwinnmr version 2.6. ^1H and ^{13}C NMR chemical shifts are referenced to the solvent and are reported in ppm (δ) relative to tetramethylsilane. ^{31}P NMR chemical shifts are referenced to PMe_3, which was located at δ −61 relative to 85% H_3PO_4. Magnetization transfer experiments were conducted using the double-pulsed field-gradient spin−echo to achieve selective magnetization prior to standard pulse sequence components to detect exchange.[13] IR spectra were recorded on a Bruker tensor 27 Fourier transform IR (FTIR) spectrometer.

Reagents. $M(CO)_6$ (M = Cr, Mo, and W; Aldrich or Strem) were sublimed twice prior to use. CD_2Cl_2 (CIL) was distilled, placed over activated silica, and then stored over CaH_2 under vacuum. $HSiEt_3$ (Strem) and H_2SiPh_2 (Aldrich) were stored over $LiAlH_4$ under Ar in a Teflon-stopcock-fitted glass bomb. $HSiPh_3$, Cl_2SiPh_2, $LiAlH_4$, and $LiAlD_4$ were used as received from Aldrich. $Ph_3B(C_6F_5)_4$ (Strem) was used as received. $Cr(CO)_5(PMe_3)$ was made by minor modifications to a published procedure[14] in 50-mg batches and purified by sublimation prior to use.

Preparation of $HDSiPh_2$. A glass bomb fitted with a Teflon stopcock was charged in the glovebox with a Teflon-coated stir bar and equimolar amounts of $LiAlH_4$ and $LiAlD_4$ (250 mg, 276.5 mg, 6.59 mmol). The stopcock was fitted and the bomb removed from the glovebox. The bomb was pump-cycled onto a vacuum line. and under a flow of Ar, Cl_2SiPh_2 (4.0 mL, 17.6 mmol) was added by syringe. The bomb was then evacuated by three freeze−pump−thaw cycles and heated in an oil bath to 350 K for 3 days with stirring. Upon cooling, hexane (10 mL) was added under a flow of Ar to precipitate LiCl. The solution was filtered by a cannula filter into a second Teflon-stopcock-fitted glass bomb, where hexane was removed under vacuum. ^1H NMR spectroscopy confirms the identity of the product and shows that the signals due to Ph_2SiH_2 and Ph_2SiHD are of approximately equal intensity, confirming that the mole ratio of Ph_2SiH_2/Ph_2SiHD is 1:2, as expected for ca. 50% deuteration. A precise integration cannot be obtained because of the small chemical shift separation. The level of deuteration was also measured by mass spectroscopy, which indicated 55% deuteration.

^{13}CO Enrichment of $Cr(CO)_6$ and $W(CO)_6$. A glass bomb fitted with a Teflon stopcock was charged with $M(CO)_6$ (M = Cr and W) in the glovebox. The bomb was pumped onto a vacuum line, evacuated briefly, and tetrahydrofuran (THF) was vacuum-transferred at 77 K. The solution was subjected to photolysis at room temperature for 3 h and evacuated every 30 min by a freeze−pump−thaw cycle. After the last freeze−pump−thaw cycle, the bomb was backfilled with $^{13}CO(g)$ (760 mmHg) and left to stand overnight. The orange color of the solution of $M(CO)_5(THF)$ fades to colorless, reforming $M(^{13}CO)(CO)_5$. This cycle was repeated to form enriched $M(CO)_6$, which was recrystallized from pentane prior to use. Isotope incorporation was checked by IR and ^{13}C NMR spectroscopy.

$[Re(CO)_5(\eta^2\text{-}HSiEt_3)][B(C_6F_5)_4]$ (4). A screw-cap NMR tube was charged with $Ph_3CB(C_6F_5)_4$ (10 mg, 10.8 mmol). After the addition of Et_3SiH (ca. 1−2 mL; excess) via vacuum transfer, the resulting yellow mixture was sonicated for 24 h. The volume of Et_3SiH was reduced under vacuum to leave a white solid in a small quantity of $HSiEt_3$. $(CO)_5ReCl$ (3 mg, 8.25 mmol) was added under Ar, and after evacuation, C_6H_5F was vacuum-transferred into the tube. The sample was then backfilled with Ar. ^1H NMR (250 K, C_6H_5F): δ −10.73 (Re−H−Si, J_{SiH} = 55 Hz).

Photolysis Reactions. A typical sample preparation is as follows: An NMR tube modified to fit a Teflon stopcock was heated to 430 K overnight and pumped into an Ar-filled drybox while still hot. The tube was charged with $M(CO)_6$ (3−5 mg), and the stopcock was fitted before being removed from the glovebox. The tube was pump-cycled onto a vacuum line and evacuated briefly. Approximately 0.5 mL of CD_2Cl_2 (or other solvent) was vacuum-transferred into the tube at 77 K. Addition of the various silanes was achieved either by a gastight syringe under a flow of Ar or by vacuum transfer where possible. Addition of $HSiPh_3$ was performed in an Ar-filled glovebox. Photolysis (water-jacketed 450-W Hg−arc lamp) was conducted at 195 K in a quartz Dewar. The sample was removed to a separate Dewar that was precooled to 195 K using a dry ice slush for transportation. The sample was then inserted into a precooled NMR probe for analysis. IR spectra of the triethylsilane complexes were recorded on a Bruker tensor 27 FTIR spectrometer using 0.02 M solutions of $M(CO)_6$ in cyclopentane and an 8-fold excess of silane.

$Cr(CO)_5(\eta^2\text{-}HSiEt_3)$ (1). ^1H NMR (CD_2Cl_2, 240 K): δ −13.58 (1H, Cr−H−Si, J_{HH} = 1.9 Hz, J_{SiH} = 95.2 Hz), 1.00 (9H, CH_3, J_{HH} = 7.5 Hz), 0.88 (6H, Si−CH_2, J_{HH} = 1.9 and 7.5 Hz). ^{13}C NMR (CD_2Cl_2, 233 K): δ 223.3 (1C, *trans*-CO, J_{CH} = 2.3 Hz), 215.1 (4C, *cis*-CO, J_{CH} = 2.9 Hz), 7.70 (CH_2), 5.41 (CH_3). IR (ν_{CO}, cyclopentane): 1951 cm^{-1}.

$Mo(CO)_5(\eta^2\text{-}HSiEt_3)$ (2). ^1H NMR (CD_2Cl_2, 240 K): δ −8.36 (1H, Mo−H−Si, J_{HH} ~ 1.9 Hz, J_{SiH} = 96 Hz), 0.98 (9H, CH_3, J_{HH} = 7.9 Hz), 0.85 (6H, Si−CH_2, J_{HH} = ~1.9 and 7.9 Hz). ^{13}C NMR (CD_2Cl_2, 233 K): δ 203.96 (*cis*-CO), 7.86 (CH_2), 5.26 (CH_3). IR (ν_{CO}, cyclopentane): 1957 cm^{-1}.

$W(CO)_5(\eta^2\text{-}HSiEt_3)$ (3). ^1H NMR (CD_2Cl_2, 240 K): δ −8.55 (1H, W−H−Si, J_{HH} ~ 1.5 Hz, J_{SiH} = 86 Hz), 0.99 (9H, CH_3, J_{HH} = ~7.5 and 1.5 Hz), 0.98 (6H, Si−CH_2, J_{HH} = ~7.5 and 1.5 Hz). ^{13}C NMR (CD_2Cl_2, 233 K): δ 200.3 (1C, *trans*-CO, J_{CH} unresolved), 196.8 (4C, *cis*-CO, J_{CH} = 1.3 Hz), 4.88 (CH_2), 6.12 (CH_3). IR (ν_{CO}, cyclopentane): 1951 cm^{-1}.

$Cr(CO)_5(\eta^2\text{-}HSiPh_3)$ (5). ^1H NMR (CD_2Cl_2, 220 K): δ −11.65 (1H, Cr−H−Si, J_{SiH} = 111 Hz).

$W(CO)_5(\eta^2\text{-}HSiPh_3)$ (6). ^1H NMR (CD_2Cl_2, 230 K): δ −6.38 (1H, W−H−Si, J_{SiH} = 101 Hz, J_{WH} = 36 Hz).

$Cr(CO)_5(\eta^2\text{-}H_2SiPh_2)$ (7). ^1H NMR (CD_2Cl_2, 220 K): δ −11.17 (1H, Cr−H−Si, J_{SiH} = 108 Hz, $^2J_{HH}$ = 10.3 Hz), 6.02 (1H, Cr−Si−H, J_{SiH} = 234 Hz, $^2J_{HH}$ = 10.3 Hz). When complex **7** was prepared with a 1:2 mixture of Ph_2SiH_2 and Ph_2SiHD, integration of the bound silane resonance at δ −11.2 versus the pendant silane resonance at δ 6.0 showed that the bound silane resonance was slightly more intense, with a ratio of 1.08:1.

$Mo(CO)_5(\eta^2\text{-}H_2SiPh_2)$ (8). ^1H NMR (CD_2Cl_2, 185 K): δ −6.49 (1H, Mo−H−Si, J_{SiH} = 111 Hz, $^2J_{HH}$ = 11.8 Hz), 6.04 (1H, Mo−Si−H, J_{SiH} = 232 Hz, $^2J_{HH}$ = 11.8 Hz).

$W(CO)_5(\eta^2\text{-}H_2SiPh_2)$ (9). ^1H NMR (CD_2Cl_2, 220 K): δ −6.40 (1H, W−H−Si, J_{SiH} = 98 Hz, $^2J_{HH}$ = 11.0 Hz, $^1J_{WH}$ = 39 Hz), 6.50 (1H, W−Si−H, J_{SiH} = 236 Hz, $^2J_{HH}$ = 11.0 Hz).

***trans*-$Cr(CO)_4(PMe_3)(\eta^2\text{-}HSiEt_3)$ (10).** ^1H NMR (CD_2Cl_2, 210 K): δ −12.47 (1H, Cr−H−Si, J_{SiH} = 102 Hz, J_{PH} = 16.8 Hz). ^{31}P NMR (CD_2Cl_2, 210 K): δ 21.4.

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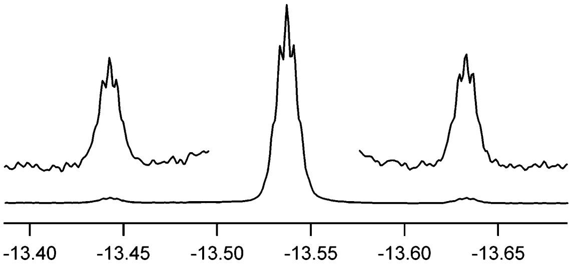

Figure 1. Partial (hydride region) ^{1}H NMR spectra (CD_2Cl_2, 500 MHz, 220 K) of **1**. Inset: ×24 magnefication.

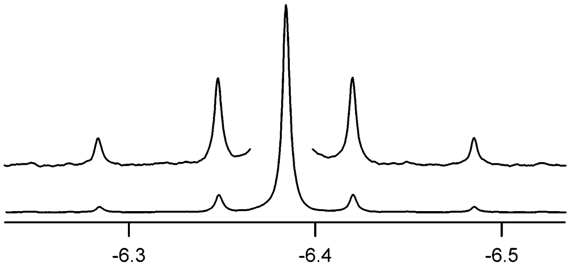

Figure 2. Partial (hydride region) ^{1}H NMR spectra (CD_2Cl_2, 500 MHz, 230 K) of **6**. Inset: ×5 magnefication.

***cis*-Cr(CO)$_4$(PMe$_3$)(η^2-HSiEt$_3$) (11).** ^{1}H NMR (CD_2Cl_2, 210 K): δ −14.18 (1H, Cr−H−Si, J_{SiH} = 99 Hz, J_{PH} = 8.2 Hz). ^{31}P NMR (CD_2Cl_2, 210 K): δ 9.4.

Catalytic Methanolysis. In a 50-mL Schlenk tube connected to a bubbler, 5.0 mg (23 μmol) of $Cr(CO)_6$ was dissolved in 10.0 mL (62 mmol) of Et_3SiH. After photolysis for 30 min, 5.0 mL (123 mmol) of MeOH was added. Vigorous evolution of H_2 was observed, diminishing gradually over several hours. After 12 h, analysis of the mixture by gas chromatography (GC)−mass spectrometry (MS) revealed the formation of Et_3SiOMe and consumption of 50% of the starting Et_3SiH. If the photochemical preparation of $Cr(CO)_5(\eta^2\text{-}HSiEt_3)$ is 100% efficient, the turnover number (TON) calculated from these data would be 1350. Separate studies demonstrate that the photolytic preparation of $Cr(CO)_5(\eta^2\text{-}HSiEt_3)$ has a yield of ca. 50%; thus, a better estimate of the TON would be 2700. Similar methanolysis activity was observed when preformed $Cr(CO)_5(THF)$ was added to a 1:1 mixture of MeOH and Et_3SiH.

Results

All photolysis reactions were carried out at 195 K. Initial studies were carried out in toluene and alkane solvents. Low-temperature solubility of the precursor complexes is quite limited under these conditions, limiting the accessible concentration of silane complexes. Attempts to isolate the silane adducts were frustrated by incomplete photochemical conversion to the desired complex. It was found that methylene chloride provided much increased low-temperature solubility. The stability of the complexes is somewhat reduced in methylene chloride, but more satisfactory NMR spectra were obtained.

Photolysis of methylene chloride solutions of the metal hexacarbonyl complexes $M(CO)_6$ in the presence of Et_3SiH (1 equiv) produces pale-yellow solutions of the σ silane complexes **1**−**3**. The ^{1}H NMR spectrum of each solution (Figure 1) exhibits a new hydridic signal at δ −13.54 (Cr), −8.36 (Mo), and −8.55 (W). The hydride resonances are partially resolved heptets due to a small three-bond coupling to the methylene protons of the silane. The value of $^3J_{HH}$ in **1** is observed to be 1.9 Hz, reduced from that in the free silane (3.1 Hz). Coupling to ^{29}Si ($I = -{}^1/_2$, 6%) is clearly visible in the hydride resonances for all three complexes and allows the direct measurement of $^1J_{SiH}$ = 95 (**1**), 96 (**2**), and 86 (**3**) Hz. In addition, **3** also exhibits coupling to ^{183}W ($I = {}^1/_2$, 14%) with $^1J_{WH}$ = 36 Hz.

In the ^{13}C NMR spectrum, the carbonyl signals for **1**−**3** are weak, but the use of ^{13}CO-enriched $Cr(CO)_6$ and $W(CO)_6$ allows the observation of the ^{13}C NMR signals for the carbonyl groups of **1** and **3**. These are observed in an approximate intensity ratio of 1:4 at δ 223.3 and 215.1 (**1**) and δ 200.3 and 196.8 (**3**). These resonances are assigned to the *trans*- and *cis*-carbonyl groups in these molecules, respectively. In both **1** and **3**, a two-bond coupling $^2J_{CH}$ between the metal-bound ^{13}CO and a ^{1}H nucleus is detected in the fully ^{1}H-coupled ^{13}C NMR spectra. The coupling of the *cis*-^{13}CO in **1** is $^2J_{CH}$ = 2.9 Hz, larger than that of the *trans*-^{13}CO, where $^2J_{CH}$ is ∼2 Hz. This is also true for **3**, where the cis coupling $^2J_{CH}$ is ∼1.3 Hz and the trans coupling is unresolved. The bound Si−H proton was confirmed as the source of these couplings using a ^{1}H−^{13}C heteronuclear multiple-quantum coherence (HMQC) experiment. Further verification of the structures of **1**−**3** was provided by IR spectroscopy in an alkane solution, where the CO stretching vibrations can be readily observed. Consistent with previous reports, only the strong E mode could be conclusively assigned as a result of the overlap of other modes with starting materials.[11]

Yields estimated for these reactions by NMR spectroscopy are between 50% and 75%. Attempts to drive the reactions to completion using longer irradiation times resulted in decomposition. The complexes are persistent for hours in toluene and alkanes at room temperature, with some gradual regeneration of $M(CO)_6$ observed along with decomposition to unidentified products. More rapid decay was observed in methylene chloride below room temperature.

The rhenium complex **4** can be generated by the reaction of $Re(CO)_5Cl$ with $[SiEt_3][B(C_6F_5)_4]$ in the presence of $HSiEt_3$ in a fluorobenzene solvent. A hydridic resonance is observed at δ −10.73 as an unresolved heptet with satellites due to coupling to ^{29}Si with $^1J_{SiH}$ = 55 Hz.

Similar low-temperature irradiation experiments carried out with $HSiPh_3$ produces the complexes **5** and **6**. Binding of $HSiPh_3$ to $Mo(CO)_5$ has not been detected under these conditions. The hydride signal for **5** is observed at δ −11.65 (J_{SiH} = 111 Hz), and the corresponding signal for **6** is observed at δ −6.38 (J_{SiH} = 101 Hz). In the case of complex **6**, additional satellites due to coupling to ^{183}W with J_{WH} = 36 Hz are also observed (Figure 2).

Complexes **7**−**9** are obtained similarly in the presence of diphenylsilane. In this case, ^{1}H NMR resonances due to both coordinated (denoted H_A) and pendant Si−H moieties (denoted H_B) are observed (with $^2J_{HH}$ = 10−12 Hz), with the former exhibiting diminished values of J_{SiH} of 108 (**7**), 111 (**8**), and 98 (**9**) Hz. The hydridic resonance for complex **8** also exhibits coupling to ^{183}W, J_{WH} = 39 Hz. For **7**−**9**,

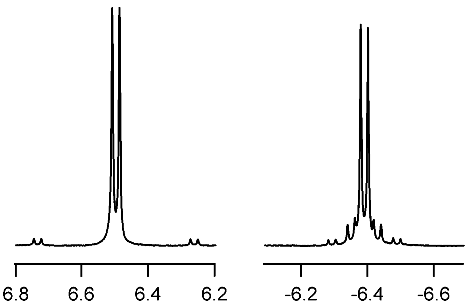

Figure 3. Partial ^1H NMR spectra (CD_2Cl_2, 500 MHz, 215 K) of **9**.

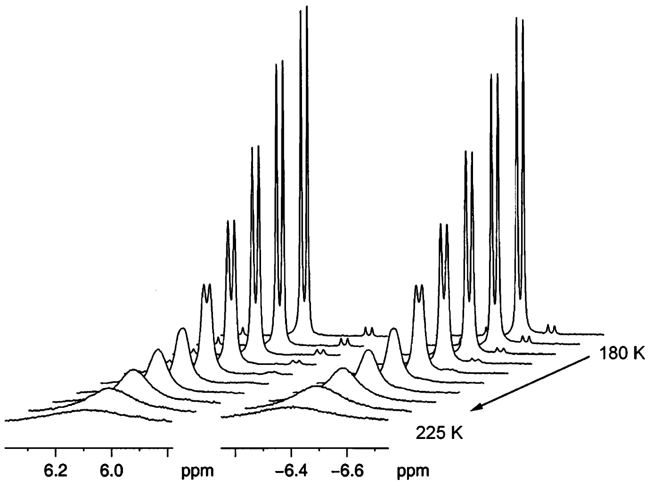

Figure 4. ^1H NMR spectra (CD_2Cl_2, 500 MHz) of **8** for pendant and bound Si−H resonances at 180−225 K.

the pendant Si−H resonance is observed between δ 6 and 6.5, with J_{SiH} significantly increased from that in the free silane (Figure 3). Values of J_{SiH} for the pendant SiH are 234 (**7**), 232 (**8**), and 236 (**9**) Hz, which are much greater than $J_{SiH} = 200$ Hz observed in free diphenylsilane.

An interesting dynamic process is observed in complexes **7**−**9**, which exchanges the coordinated and pendant Si−H on the NMR time scale. At low temperatures, two sharp resonances are observed. Upon an increase in the temperature, line broadening is observed as a result of the exchange process (Figure 4). Coalesecence of the resonances could not be observed because of decomposition at higher temperatures. The resonance due to free Ph_2SiH_2 remains sharp at all temperatures. The selective magnetization of the protons in the H_B environment allowed their exchange to be monitored using spin saturation transfer. Exchange was observed only between the H_A and H_B environments and not with the free silane. This remained true even with the longest mixing periods of up to 4 s.

Line-shape analysis over the temperature range 200−260 K allows the extraction of rate data for this exchange process in complexes **7**−**9**, which was used in an Eyring analysis. Activation parameters are $\Delta H^{\ddagger} = 9.9 \pm 1.8$ kcal/mol and $\Delta S^{\ddagger} = -5 \pm 7$ eu (**7**); $\Delta H^{\ddagger} = 8.0 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -4 \pm 2$ eu (**8**); and $\Delta H^{\ddagger} = 9.7 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -5 \pm 2$ eu (**9**).

A small equilibrium isotope effect is seen in the coordination of $HDSiPh_2$ to $Cr(CO)_5$. A 1:2:1 mixture of H_2SiPh_2-d_0/H_2SiPh_2-d_1/H_2SiPh_2-d_2 was prepared by reaction of Cl_2SiPh_2 with 1:1 $LiAlH_4/LiAlD_4$. Irradiation of $Cr(CO)_6$ with 1 equiv of this isotopically labeled silane affords a mixture of complex **7**, **7**-d_1, and **7**-d_2. Integration of the resonances for protons of H_A and H_B in **7** and **7**-d_1 separately is not possible because of overlap in the ^1H NMR spectrum, but because no isotope effect is expected in the H_2SiPh_2 complex, both resonances can be integrated together. The ratio of integrated intensity of the coordinated SiH resonance to the pendant resonance is 1.08:1.

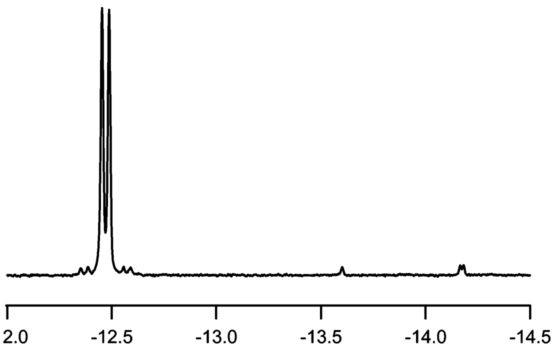

Figure 5. Partial (hydride region) ^1H NMR spectrum (CD_2Cl_2, 500 MHz, 210 K) of the products of photolysis of $(PMe_3)Cr(CO)_5$ with Et_3SiH.

A phosphine-substituted derivative of $Cr(CO)_6$ was investigated to provide a direct comparison to the $[(PR_3)Re(CO)_4]^+$ system reported by Kubas and co-workers. Thus, photolysis of $(PMe_3)Cr(CO)_5$ in the presence of Et_3SiH was found to afford both *cis*- and *trans*-silane complexes, along with a small amount of complex **1** formed by phosphine loss (Figure 5).

The major product exhibits a hydridic resonance at δ −12.47 with $J_{PH} = 16.8$ Hz and $J_{SiH} = 102$ Hz. This resonance is attributed to **10**. The minor product gives a resonance at δ −14.18 with $J_{PH} = 9.4$ Hz and $J_{SiH} = 99$ Hz. This signal is assigned to **11**.

Catalytic Silane Alcoholysis. When solutions of **1** are treated with methanol, the formation of $MeOSiEt_3$ was observed, identified by ^1H and ^{13}C NMR spectroscopy,[15] and confirmed by GC−MS. H_2 gas was evolved, and the presence of $Cr(CO)_5(MeOH)$ was noted. The methanol complex was independently prepared by photolysis of toluene solutions of $Cr(CO)_6$ in the presence of methanol. Bound methanol in this Cr complex has characteristic resonances in the ^1H NMR spectrum at δ 2.69 (3H) and 5.68 (1H). After generation of complex **1** photochemically in neat Et_3SiH, the addition of MeOH to the pale-yellow solution turns it bright yellow and H_2 evolution was observed. The process is catalytic in Cr, with ca. 2700 turnovers observed at room temperature over 12 h before catalyst deactivation occurs. Preformed $Cr(CO)_5(THF)$ was also an effective catalyst precursor. H_2 evolution and formation of $MeOSiEt_3$ were observed upon the addition of $Cr(CO)_5(THF)$ to a 1:1 Et_3SiH/MeOH mixture.

Discussion

Complexation of Si−H bonds to a variety of transition-metal fragments has been reported in the literature, usually

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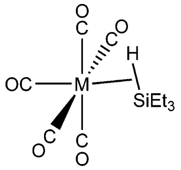
with a mixture of Cp, arene, and phosphine coligands. Highly electrophilic, carbonyl-rich metal centers are rarely observed to bind silanes. Indeed, Kubas has suggested that such molecules are not stable.[4] While such complexes may not be isolable at room temperature, there is precedent for their observation in solution, as noted above.

The preparation of $M(CO)_5(L)$ complexes by photoextrusion of CO in the presence of ligand L is well precedented in the literature. We have previously demonstrated that this procedure can be extended to the preparation of complexes with L being a σ-bond donor such as H_2.[12] Similar to our experience with H_2, we find that silane complexes are formed in sufficient yield by this procedure to allow for their observation by ^{1}H NMR spectroscopy. Because the silane ligands are weakly bound, we have been unable to isolate these complexes in a pure state, partly because of contamination with the starting material $M(CO)_6$. Prolonged irradiation leads to increased formation of unidentified decomposition products.

Triethylsilane Complexes. Complexes **1**−**3** are indeed observable in solution below room temperature. Formulation as silane σ complexes is based upon the observation of large values of J_{SiH} = 95 (**1**), 96 (**2**), and 86 (**3**) Hz. This formulation as six-coordinate silane adducts is confirmed by the C_{4v} geometry of the carbonyl ligands indicated by the ^{13}C NMR spectra.



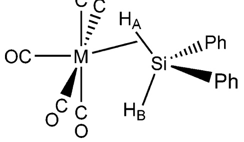
These values of J_{SiH} are substantially reduced from the value of 175 Hz observed in Et_3SiH. In comparison, some other reported values of J_{SiH} in Et_3SiH complexes are 62 Hz[16] in cationic $[CpFe(PEt_3)(CO)(\eta^2\text{-}HSiEt_3)]^+$ and 61 Hz[8] in cationic $[cis\text{-}Re(CO)_4(PPh_3)(\eta^2\text{-}HSiEt_3)]^+$. Because the reduction of J_{SiH} is much less than that observed in other Et_3SiH complexes, we conclude that the interaction with the metal center is relatively weak. In particular, because the presence of five CO ligands renders the metal center highly electron-deficient, back-donation from the metal d orbitals into the Si−H σ* orbital is limited. This result is similar to the reported observations in the case of dihydrogen complexes such as $Cr(CO)_5(H_2)$ and $W(CO)_5(H_2)$, where the properties of the molecules were found to be consistent with limited back-donation from the metal center to the bound H_2.[12]

The observation of **1**−**3** provides a unique opportunity to compare Si−H bond coordination in a homologous series spanning the group 6 metals. If we assume that Si−H bond elongation is inversely proportional to J_{SiH} within a homologous series, we can correlate the observed couplings to bond elongation and use this as a probe for the strength of the interaction with the metal. On the basis of the observed values of J_{SiH}, the interaction with Cr and Mo is seen to be quite similar, while the interaction in the W complex **3** is somewhat stronger. This is quite consistent with the PAC data of Burkey, where the binding enthalpies of Et_3SiH to $Cr(CO)_5$ and $Mo(CO)_5$ were quite similar (21 and 22 kcal/mol) but the binding to $W(CO)_5$ was significantly stronger (28 kcal/mol).

The rhenium complex **4** allows an opportunity to investigate the effect of charge on the activation of a coordinated silane. We observe the Si−H bond to be lengthened considerably (J_{SiH} = 55 Hz) with respect to the neutral $W(CO)_5$ analogue upon an increase in the charge of the molecule. The activation of the bond is mostly due to σ donation to a vacant metal orbital with a minimal contribution from back-donation. Interestingly, complex **4** has a value for J_{SiH} very similar to that reported by Kubas in $[cis\text{-}(PPh_3)\text{-}Re(CO)_4(\eta^2\text{-}HSiEt_3)]^+$ (J_{SiH} = 61 Hz). If back-donation from metal to bound silane were significant, the more electron-rich metal center in the phosphine-substituted cation would be expected to exhibit greater bond elongation and correspondingly lower J_{SiH}.

Triphenylsilane Complexes. In the case of Ph_3SiH, complexation affording **5** and **6** was observed, but no Mo analogue could be obtained. Similar to the Et_3SiH complexes, the values of J_{SiH} are diminished substantially from that of the free silane (J_{SiH} = 200 Hz) upon coordination. Complex **5** has J_{SiH} = 111 Hz, and complex **6** exhibits J_{SiH} = 101 Hz. For both $HSiEt_3$ and $HSiPh_3$, the Si−H bond is more activated for W versus Cr. A small number of examples of Ph_3SiH coordination have been previously reported. In comparison to these examples, the extent of activation of the Si−H bond in **5** and **6** is quite modest. For example, in $(MeCp)Mn(CO)_2(HSiPh_3)$, J_{SiH} = 65 Hz.[17] We conclude that complexes **5** and **6** represent examples of relatively weak silane complexation, presumably due to steric congestion in Ph_3SiH, which may also be responsible for our failure to observe the Mo analogue. It is interesting to note that a prior report of prolonged photolysis of $W(CO)_6$ in the presence of Ph_3SiH led to a tricarbonyl species $W(CO)_3(\eta^6\text{-}C_6H_5\text{-}SiHPh_2)$ with a coordinated phenyl group.[18] It seems plausible that complex **6** is an intermediate in the formation of this tricarbonyl species, which we do not observe under our conditions.

Diphenylsilane Complexes. Coordination of Ph_2SiH_2 was observed for all of the group 6 metals, affording **7**−**9**. As expected, only one of the Si−H bonds coordinates, with J_{SiH_A} = 108 (**7**), 111 (**8**), and 98 (**9**) Hz. Again, the W complex exhibits the greatest degree of Si−H bond elongation.



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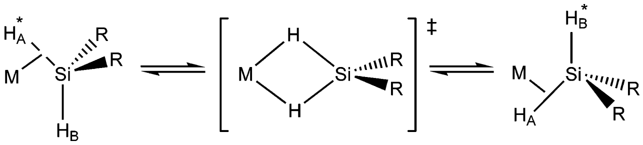
Interestingly, J_{SiH_B} *increases* slightly upon complexation to 234 (**7**), 232 (**8**), and 236 (**9**) Hz. This large perturbation in the coupling in the pendant SiH moiety has been previously observed only in complexes of R_2SiH_2 with highly electrophilic cationic metal centers, where the bound silane is also activated toward reaction with nucleophiles. In the case of $[(PPh_3)Re(CO)_4(\eta^2\text{-}HSiEt_3)]^+$, liberation of $[SiEt_3]^+$ and formation of products consistent with the formation of $(PPh_3)Re(CO)_4H$ has been observed.[8] Thus, the increase in J_{SiH_B} may indicate an increase in the s character of the Si−H bond because of the increased polarization of the bound Si−H bond and incipient formation of the silyl cation, which would have sp^2 hybridization.

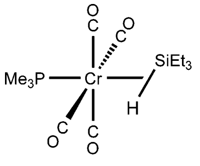
In comparison to other reported complexes of Ph_2SiH_2, complexes **7**−**9** have high values of J_{SiH}, consistent with relatively limited back-donation from the metal center to the Si−H σ^* orbital. Previously reported examples from the Cr triad include $J_{SiH} = 71$ Hz in $(\eta^6\text{-}Me_6C_6)Cr(CO)_2(\eta^2\text{-}HSiPh_2H)$[19] and $J_{SiH} = 50$ Hz in $(CO)Mo(dppe)_2(\eta^2\text{-}HSiPh_2H)$.[7]

Complexes **7**−**9** exhibit a very interesting intramolecular dynamic process, observable by NMR line broadening and magnetization transfer. The coordinated SiH_A is observed to exchange rapidly with the pendant SiH_B, with enthalpies of activation of 9−10 kcal/mol. Dissociation of the bound silane is not involved because no line broadening is observed in free silane. The entropies of activation are slightly negative, consistent with an intramolecular process with an ordered transition state. We suggest a mechanism for this process proceeding via a species with both Si−H bonds coordinated to the metal, as depicted in the following. Such a rapid exchange of free and coordinated Si−H bonds in metal complexes of SiH_2R_2 has not been previously observed. Slow exchange of this type was detected using deuterium labeling in the manganese complex $CpMn(CO)_2(\eta^2\text{-}DSiHRR')$.[20] In the ruthenium silyl hydride $Ru(P^tBu_2Me)(CO)H_A(SiH_BPh_2)$, exchange of H_A and H_B was detectable by spin saturation transfer.[21] We suggest that the rapid exchange observed in **7**−**9** is a further manifestation of the highly electrophilic nature of these metal centers. The coordination of a second Si−H bond to form the η^3-H,Si,H structure is lowered in energy with respect to the η^2-Si,H structure in these electrophilic complexes, which enables the exchange to happen more rapidly than has been observed previously.



Equilibrium isotope effects were probed by preparing complex **6** with partially deuterated diphenylsilane using a mixture of H_2SiPh_2 and $HDSiPh_2$. On the basis of extensive precedent with agostic C−H bonds, it was expected that there would be a nonstatistical occupancy of the bound and pendant site by deuterium. We anticipated that H would concentrate in the metal-bound environment because this bond is weakened and elongated by coordination. Thus, deuterium is expected to concentrate around the pendant site. Integration of the ^1H NMR signals verifies this expectation in that the intensity of the hydridic resonance is slightly greater (1.08:1) than that for the pendant SiH. In a study of alkane σ complexes of $CpRe(CO)_2$, Ball and co-workers have made similar observations and report a slight preference for H to concentrate in the metal-bound environment.[22]

$Cr(CO)_4(PMe_3)(\eta^2\text{-}HSiEt_3)$. Photolysis of $(PMe_3)Cr(CO)_5$ in the presence of Et_3SiH gives two isomeric silane adducts **10** and **11** in a 20:1 ratio. The major product, complex **10**, is assigned to the trans structure based on the larger coupling to ^{31}P. This assignment was verified by a $^1H-^{31}P$ HMQC experiment, which also confirmed the assignment of the ^{31}P NMR resonances at δ 21.4 (**10**) and 9.4 (**11**). The starting material $(PMe_3)Cr(CO)_5$ exhibits a ^{31}P NMR signal at δ 9.0. Complexation of Et_3SiH cis to PMe_3 has very little effect on the ^{31}P NMR chemical shift, while replacement of a *trans*-CO group with Et_3SiH in **10** leads to a significant chemical shift change to δ 21.4.



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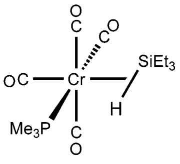

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Surprisingly, both isomers exhibit nearly identical values of J_{SiH} of 102 (**10**) and 99 (**11**) Hz, which are also quite similar to the value for **1** of 95 Hz. This outcome is unexpected because it is generally believed that the identity of the trans ligand controls the degree of bond activation in σ complexes. In these very electrophilic metal centers, the interaction with the Si−H bond is dominated by donation from the Si−H bond to an acceptor orbital on Cr, with minimal contributions from back-donation. Thus, the strong π-acid CO trans to bound silane versus the phosphine ligand leads to a very similar degree of Si−H bond elongation. A similar outcome was recently reported for coordination of H_2 to these Cr centers.[23] The increase in J_{SiH} upon inclusion of a phosphine ligand in the metal coordination sphere is similar to that observed between $[Re(CO)_5(\eta^2\text{-}HSiEt_3)]^+$ and $[Re(CO)_4(PPh_3)(\eta^2\text{-}SiEt_3)]^+$. Because the electronic nature of the Cr−HSi interaction is very similar in **10** and **11**, the observed product ratio of 20:1 versus the statistical ratio of 1:4 must arise from other factors. We suspect either that there is a steric influence to the preferred structure or that the products are themselves photoactive, and the observed product ratio represents that from a photostationary state attained during photosynthesis.

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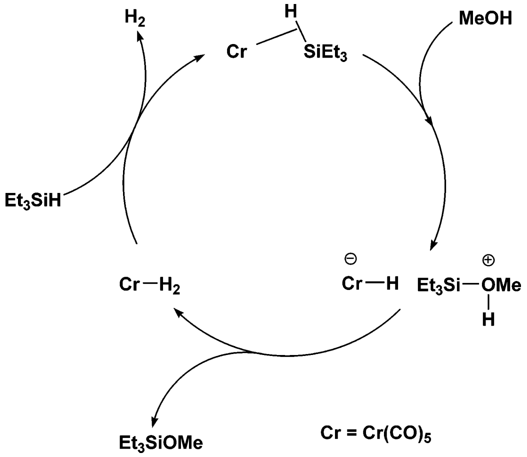
Catalytic Methanolyis. Binding of silanes to transition metals is well-known to lead to enhanced reactivity with nucleophiles. Particularly important in this respect is the use of alcohols as the nucleophile, which affords silyl ethers. This is a useful reaction in organic synthesis for reversible protection of OH functionalities.

We find that $Cr(CO)_5(\mathbf{L})$ complexes ($\mathbf{L}$ = THF and Et_3SiH) are effective catalysts for methanolysis of Et_3SiH. We have not optimized the conditions but find that $MeOSiEt_3$ can be efficiently formed from MeOH and Et_3SiH, with 2600 turnovers prior to catalyst deactivation, which occurs after about 12 h. These results are comparable to those reported by Brookhart and co-workers[24] using $[CpFe(CO)_2]^+$ but slower than those of Luo and Crabtree's catalyst $[IrH_2(PPh_3)_2(THF)_2]^+$.[25] We suggest the mechanism depicted below for the catalytic reaction, which is similar to that suggested by Brookhart and co-workers.[24]



Conclusions. Silanes bind weakly to electrophilic $M(CO)_5$ fragments, with modest activation of the Si−H bond. An unusual rapid exchange between bound and pendant Si−H bonds has been observed in Ph_2SiH_2 complexes. Replacement of one CO ligand with PMe_3 has surprisingly little effect on the activation of Et_3SiH on Cr. The electronic basis of the SiH/metal interaction is relatively insensitive to the coligands, suggesting a minor role for back-donation from metal to ligand. Both cis and trans isomers are observed in a nonstatistical ratio.

Increasing the charge on the complex is seen to increase the extent to which the coordinated bond is elongated on coordination, consistent with dominant σ donation from silane to the metal center and minor contributions to the interaction from back-donation. Complexation activates silanes toward reaction with nucleophiles, which has been applied to catalytic methanolysis.

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