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Thermochemistry of Silane Substitution of CO on Metal Carbonyl Complexes. Interaction of Silanes with Metal Centers

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Abstract: By using photoacoustic calorimetry, the enthalpy of CO substitution by triethylsilane for $M(CO)_6$ (M = Cr, Mo, W), $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, and $\eta^5\text{-}CpMn(CO)_3$ (Cp = cyclopentadienyl) in neat triethylsilane was found to be 16, 19, 18, 17, and 31 kcal/mol, respectively. The enthalpy of CO substitution by alkane solvent for $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (in heptane) and $\eta^5\text{-}CpMn(CO)_3$ (in cyclohexane) was found to be 33 and 45 kcal/mol, respectively. By using these data and metal–CO bond energies, the enthalpies of the metal–silane and metal–alkane binding in the adducts were estimated to be in the range of 21–28 and 9–13 kcal/mol, respectively. Thus, the variation in the binding energies is 7 and 4 kcal/mol, respectively, while the variation for the corresponding metal–CO bonds is 18 kcal/mol. These results suggest the metal–silane interactions are more like the corresponding metal–alkane interactions than metal–CO bonds. It is concluded that for the cases studied the silane undergoes an incomplete oxidative addition to the metal, and the metal–silane interaction is a three-center two-electron bond. Silane adducts from $Cr(CO)_6$ and $W(CO)_6$ have been detected by UV–vis and IR spectroscopy. The results suggest the $M(CO)_5(HSiEt_3)$ may be more stable than previously presumed.

Introduction

The addition of a silane to a metal complex normally involves the loss of a ligand, providing a coordination site for interaction with the silane. The extent of reaction between the metal center and the silane can vary. Complete oxidative addition of the silane to the metal occurs for some silane adducts where the metal inserts into the Si–H bond. Here the SiH bond is completely broken and two localized σ bonds are formed, i.e., metal–hydrogen and metal–silicon bonds (Scheme Ia). Incomplete oxidative addition occurs for other silane adducts where a three-center two-electron bond is formed. Such σ complexes have significant interaction between the silicon and hydrogen atoms (Scheme Ib).[1-6] Interest in the reaction of silanes with metal carbonyls stems from our investigation of the activation of alkanes by transition-metal complexes. Although alkanes are less reactive than silanes, the same variety of bonding interactions exists for alkanes. Indeed, complete oxidative addition of alkanes has been observed for some metal complexes (Scheme Ic) and incomplete oxidative addition for others.[7-14] Analogous intramolecular reactions with a ligand alkyl are well documented: the extreme cases are represented by cyclometalated and agostic bonded complexes.[15] The similar reactivity of alkanes and silanes toward metal centers suggests

Scheme I
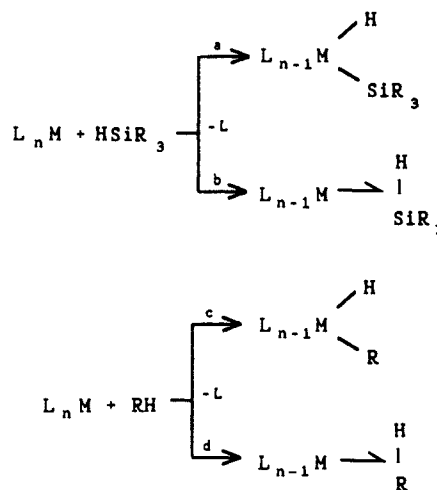
that studies leading to the understanding of the chemistry of metal–silane interactions may be extended to that of metal–alkane interactions.

Little is known about the magnitude of the energy associated with these interactions, and this information should be useful in understanding the factors that favor the formation of alkane and silane adducts, whether they are σ complexes or insertion products. For Cr–, Mo–, and $W(CO)_5$(alkane), insertion into a CH bond does not occur, and the metal–alkane binding has been found to be on the order of 10 kcal/mol.[12,13] It is almost certain that σ complexes are formed (with three-center two-electron bonds) in these cases. For more reactive complexes where insertion into CH bonds does occur, the net interaction (enthalpy of bonds formed minus that of bonds broken) will certainly be much greater than 10 kcal/mol. In one case, the enthalpy of insertion into cyclohexane by a $Cp^*Ir(PMe_3)$ complex has been estimated to be ≥ 29 kcal/mol.[16] For this reaction, there is evidence that σ complexes are formed prior to insertion.[10] With metal centers of intermediate reactivity that do not insert into CH bonds, a σ complex with metal–alkane binding stronger than 10 kcal/mol

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might be expected; in other words, the strength of the metal–alkane binding of the σ complex should vary with complex composition, but how the binding strength varies is not certain. The strength of the metal–alkane binding in a σ complex that precedes the insertion product may not necessarily parallel the extent of oxidative addition of the alkane to the metal center since the structure of the σ complex and the resultant insertion product may be very different. For example, the Cr–H–C bond angle in $Cr(CO)_5(CH_4)$ and similar complexes is believed to be linear.[17] In such cases, the metal–carbon interaction is small compared to that in the insertion product. If the structures of a σ complex and corresponding insertion product are very different, i.e., the σ complex must undergo substantial rearrangement to form the insertion product, then factors that enhance alkane binding may not necessarily enhance insertion. Investigation of the energetics of metal–alkane interactions will help clarify the relationship between σ complexes and insertion products.

Like the metal–alkane interaction, the strength of a metal–silane interaction should also vary with the composition of the metal complex. NMR, X-ray structure, and photoelectron spectral studies show that the interaction between the Si–H bond and a metal is affected by changes in the silicon substituents or the composition of the metal complex.[1-6] For example, recent photoelectron spectroscopy studies of η^5-$CpMn(CO)_2HSiR_3$ by Lichtenberger's group indicate nearly complete oxidative addition to manganese for R = Cl and incomplete oxidative addition (three-center two-electron bonding) for less electron withdrawing R such as phenyl groups.[2] The photoelectron studies show the extent of electron density donation to or from a metal center or a bound ligand; nevertheless, these and other studies do not provide binding energies.

The present paper is an investigation of the heat of addition of $HSiEt_3$ (triethylsilane) to metal centers that are less reactive than or as reactive as η^5-$CpMn(CO)_2$. Since the triethylsilyl group is less electron withdrawing than the triphenylsilyl group, incomplete oxidative addition with the formation of three-center two-electron bonds is expected in these cases (vide supra). Photoacoustic calorimetry (PAC) can be used to determine bond energies and has been used widely to study biochemical, organic, inorganic, and organometallic species.[12,13,18,19] Using PAC, we have determined the enthalpy of CO substitution by $HSiEt_3$ on metal carbonyl complexes (ΔH_1, eq 1). The compounds $M(CO)_6$ (M = Cr, Mo, and W), $(\eta^6$-$C_6H_6)Cr(CO)_3$, and η^5-$CpMn(CO)_3$

$$ML_nCO + HSiEt_3 \xrightarrow{\Delta H_1} ML_n(HSiEt_3) + CO \qquad (1)$$

were studied in neat $HSiEt_3$. From an M–CO bond energy and ΔH_1, the enthalpy of the net interaction between the metal and silane can be calculated. The heat evolved after pulsed photolysis of a sample is detected by PAC; therefore, the photochemistry of a complex must be sufficiently characterized to assign the heat to particular processes. Each of these complexes is known to undergo ligand substitution of a carbonyl upon photolysis.[20] Flash photolysis and/or matrix isolation studies show that photolysis of each of the metal carbonyls initially leads to CO dissociation, and in an alkane solvent, the initial intermediate is solvent coordinated.[7,9,21-23] In the presence of $HSiEt_3$, a silane adduct

should form. In fact, silane adducts have been observed upon photolysis of $(\eta^6$-$C_6H_6)Cr(CO)_3$ and η^5-$CpMn(CO)_3$ in the presence of a silane,[1,5,6,24] whereas no evidence of silane adduct formation from $M(CO)_6$ has been reported previously. In this study, we present spectral and PAC evidence of silane adduct formation from $M(CO)_6$.

Experimental Section

Materials. All compounds were obtained from Aldrich unless otherwise noted. (Benzene)chromium tricarbonyl and molybdenum hexacarbonyl were obtained from Strem. The metal carbonyls were sublimed under vacuum two or more times. Triethylsilane was dried over molecular sieves overnight and distilled immediately before use. Distilled water was further purified with a Millipore Milli-Q water system. Tetrahydrofuran (Baker, reagent grade), alkanes (hplc or spectrophotometric grade), and di-*n*-butylamine were distilled from sodium or potassium before use. Gases were zero grade (Air Products). Solvents and di-*n*-butylamine were refluxed overnight with respective drying agents before distilling.

Sample Preparation. The preparation of metal carbonyl solutions and the operation of the photoacoustic calorimeter have been described previously and will only be discussed briefly.[12] All solutions containing metal carbonyls were prepared and used in the dark in foil-covered, septum-sealed vessels, purged with helium, and cannulated to avoid contamination by air. Concentrated metal carbonyl solutions were cannulated into a graduated reservoir and diluted with additional silane to the desired optical density. The graduated reservoir had a fritted bubbler that was used to pressurize and purge the reservoir with helium. The reservoir was connected to a flow cuvette via a glass manifold with Teflon stopcocks.

Measurements. Solutions in the flow cuvette were photolyzed with a pulsed nitrogen laser (337.1 nm, 1 ns, 20–30 mJ/pulse). The signal from a transducer clamped to the cuvette was obtained after each pulse and averaged on a digital oscilloscope. The flow of solution was increased until the transducer signal became independent of changes in the solution flow rate. The signal from the transducer was calibrated before and after each measurement of a metal carbonyl solution with use of a reference solution of *o*-hydroxybenzophenone or ferrocene which deposits all the absorbed light energy as heat.[25,26] Absorbances of metal carbonyl solutions were typically between 0.09 and 0.11 for a 1-cm path length. The absorbances of reference solutions were within 2% of that of metal carbonyl solutions. As before, the absorbances of solutions were determined from PAC measurements, and the observed heats were corrected for differences in absorptions of reference solutions and laser pulse energies.[12] If the reactions occurring after the laser pulse are much faster and/or much slower than the response of the transducer (1 MHz), then the amplitude of the transducer signal is proportional to the amount of heat released by the fast reactions.[19] The amplitude of the transducer signal is therefore a measure of the heat of the fast reactions. The enthalpy of a reaction can be calculated from eq 2, where E_r is the energy of a mole of photons (84.8 kcal/mol for 337.1 nm), α is the observed heat expressed as a fraction of the light energy absorbed, and Φ is the quantum yield

$$\Delta H = E_r(1 - \alpha)/\Phi \qquad (2)$$

of photosubstitution. The magnitude of α is dependent on the thermal expansion of the solvent that results from the heat released in the reaction. The contribution to α by reaction volume changes is expected to be insignificant for eq 1, since reactions described by eq 1 are analogous to the dissociation of CO from metal carbonyls in an alkane solvent (eq 3). In the latter case, reaction volume changes were found to have a negligible contribution to α.[12,27] Since the coefficient of thermal expansion of $HSiEt_3$ is approximately that of alkanes, for eq 1 the con-

$$ML_nCO + RH \xrightarrow{\Delta H_3} ML_n(RH) + CO \qquad (3)$$

tribution of reaction volume change to α is likely to be small compared to that by thermal expansion. Assuming the limiting rate conditions mentioned above are met, α should be a good measure of the heat released in $HSiEt_3$ for eq 1.

Quantum yields for photosubstitution of CO were assumed to be the same in neat $HSiEt_3$ as in alkane solvents. The quantum yield for Mo-

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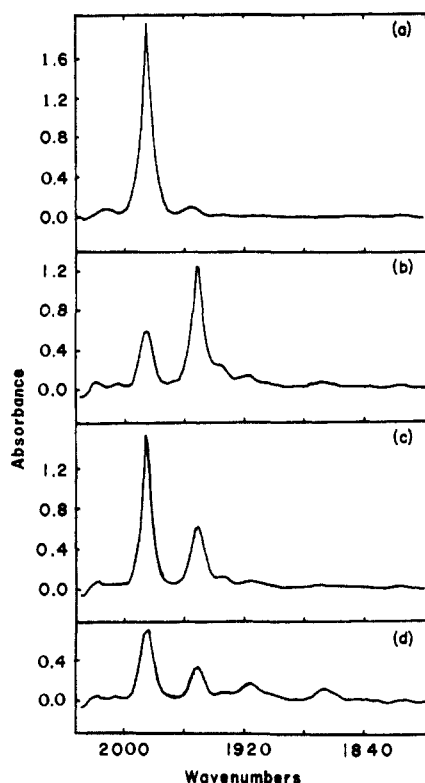
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Figure 1. Infrared spectra of the carbonyl region of 3 mM $Cr(CO)_6$ in $HSiEt_3$ (a) before photolysis, (b) after 2 min photolysis, (c) 15 min later without further photolysis, and (d) after 15 min of photolysis.

$(CO)_6$ was assumed to be the same as for $Cr(CO)_6$ due to similar electronic structure and photochemistry.[28-30] The quantum yields for $Cr(CO)_6$ (0.67 ± 0.02), $W(CO)_6$ (0.72 ± 0.05), and η^6-$C_6H_6Cr(CO)_3$ (0.72 ± 0.07) are independent of wavelength in the near-UV, and this is assumed to be the case for $Mo(CO)_6$.[31-33] The value for η^5-$CpMn(CO)_3$ (0.65 ± 0.15) is the same used previously for PAC measurements at 337 nm.[18,34,35] The emission for 337-nm excitation was determined with use

(28) The dynamics of the hexacarbonyls of Cr, Mo, and W after photolysis have been extensively studied in low-temperature matrices (see ref 30 for leading references). Upon photolysis, a CO is ejected, and an excited metal pentacarbonyl is formed that rearranges to a trigonal-bipyramidal geometry. The trigonal bipyramid relaxes to a ground-state square-pyramidal geometry via one of three equally probable pathways, each involving two equatorial CO's opening to nearly 180°. Each pathway provides a vacant octahedral site facing a different direction, but only in one direction is the vacant site facing the ejected CO. In this case, the CO promptly recombines with the metal pentacarbonyl to form the hexacarbonyl. For the other two pathways, the pentacarbonyl reacts with solvent adjacent to the vacant octahedral site. For solvents as reactive as or more reactive than alkanes, cage escape of CO is much faster than solvent displacement by CO. The solvent-coordinated metal pentacarbonyl eventually reacts with a dispersed nucleophile resulting in an overall yield for photosubstitution. Careful quantum yield studies have confirmed within experimental error a value of $^2/_3$ for $Cr(CO)_6$ and $W(CO)_6$.[29,33,31] A value of 0.93 was recently reported for $Mo(CO)_6$ without experimental detail (Wieland, S.; Van Eldik, R. *Coord. Chem.* **1990**, *97*, 155). Historically, erroneously high values have been reported for photosubstitution of metal carbonyls particularly if the photosubstitution is monitored indirectly by CO evolution. Until further details are provided, $^2/_3$ appears to be the most reliable value for the quantum yield of $Mo(CO)_6$ photosubstitution in organic solvents.

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Table I. Enthalpies of Reaction of Metal Carbonyls with Triethylsilane (ΔH_1) and Alkanes $(\Delta H_3)^a$

	ΔH_1	ΔH_3
$Cr(CO)_6$	15.7 ± 1.1	27.2 ± 1.2
$Mo(CO)_6$	18.5 ± 0.5	31.8 ± 1.3
$W(CO)_6$	18.2 ± 0.5	32.6 ± 0.4
$(\eta^6$-$C_6H_6)Cr(CO)_3$	17.1 ± 2.5	32.8 ± 0.3
η^5-$CpMn(CO)_3$	30.9 ± 1.0	44.7 ± 1.4

^{a} kcal/mol, errors are 1σ. See ref 38.

of quinine sulfate as a standard with a Perkin-Elmer MPF-3 spectrofluorimeter. The quantum yield for emission was found to be negligible ($<10^{-3}$) for each compound.

Infrared Spectra. Spectra were obtained with a Mattson Polaris NU 10000 FTIR (16–64 scans, 2-cm^{-1} resolution). The $Cr(CO)_6$ and $W(CO)_6$ solutions (ca. 4 mM in neat silane) for FTIR spectra were prepared and helium purged in a 1-mL syringe and transferred to a helium-purged 0.5-mm path length NaCl cell. The solutions in the cell were photolyzed with a 150-W high-pressure xenon lamp (PTI housing and power supply). The light was filtered with a 10-cm water filter.

Results

The photochemical reaction of $M(CO)_6$ with $HSiEt_3$ was characterized by IR and to a lesser extent by UV–vis spectroscopy. Upon steady-state photolysis of $Cr(CO)_6$ in neat $HSiEt_3$, a 414-nm absorption is observed. The 414-nm absorption persists at room temperature even an hour after photolysis. Infrared spectra, shown in Figure 1, reveal that after 2 min of photolysis of $Cr(CO)_6$ in neat $HSiEt_3$ a peak at 1951 cm^{-1} is formed as the 1985-cm^{-1} peak of $Cr(CO)_6$ decreases. When a spectrum was recorded about 15 min later, the 1951-cm^{-1} peak decreased about 50% and the 1985-cm^{-1} peak increased. Eventually the 1985-cm^{-1} peak nearly regained its prephotolysis intensity. Other peaks, particuarly at 1916 and 1866 cm^{-1}, are observed at longer irradiation times, but their intensities do not change with time or photolysis as the 1951-cm^{-1} peak does. No 414-nm absorption or 1951-cm^{-1} peak is observed when $Cr(CO)_6$ is photolyzed in cyclohexane in the absence of $HSiEt_3$. The assignment of the 1951-cm^{-1} peak to the $\nu_e(CO)$ of $Cr(CO)_5(HSiEt_3)$ is consistent with these results. The $\nu_{a1}(CO)$ peaks, whose intensities are expected to be considerably weaker, could not be identified. This was probably due to overlap with the large $HSiEt_3$ peak near 2100 cm^{-1} and the peaks of the other photoproduct(s). Similar results were observed for $W(CO)_6$: a peak assigned to the silane adduct (1949 cm^{-1}) appeared upon photolysis and decayed slowly (50% decay in ca. 1 day). It can be concluded that the photolysis of $Cr(CO)_6$ (or $W(CO)_6$) in the presence of $HSiEt_3$ leads to the formation of $Cr(CO)_5(HSiEt_3)$ (or $W(CO)_5(HSiEt_3)$), and based on analogous photochemistry, a silane adduct should also form from $Mo(CO)_6$. As noted earlier, the other metal carbonyl complexes, in the presence of a silane, are known to form stable silane adducts upon photolysis.[1,5] These results establish that silane adducts are formed in each case and are stable on a time scale much longer than the response time of a 1-MHz transducer.

The heats observed after photolysis of metal carbonyls in neat $HSiEt_3$ were more exothermic (by 12 kcal/mol or more) than those in an alkane solvent in the absence of silane. This indicates that the observed heats are dependent on a reaction with the silane. "Coordinatively unsaturated" species have been reported to react with alkane solvent faster than diffusion control.[21,36] When a silane is the solvent the reaction with silane likewise will be faster than diffusion control. Taken together, these results indicate that in neat silane the rate of the reaction with silane will be much faster than the response of the 1-MHz transducer. Therefore the observed heat is assigned to the heat of the reaction in eq 1 (after correction for the light energy absorbed and quantum yield, see eq 2). The enthalpies calculated from eq 2 are listed in Table I and are the average of at least three experiments, each from

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Table II. Enthalpy of Metal–Silane and Metal–Alkane Binding[a]

	$-\Delta H_{\text{M-SiH}}$	$-\Delta H_{\text{M-RH}}$	$-\Delta H_{\text{M-CO}}$[b]
Cr(CO)$_6$	21.1 ± 2.3	9.6 ± 2.3	36.8 ± 2
Mo(CO)$_6$	22.0 ± 2.1	8.7 ± 2.7	40.5 ± 2
W(CO)$_6$	27.8 ± 2.1	13.4 ± 2.0	46.0 ± 2
(η^6-C$_6$H$_6$)Cr(CO)$_3$	28	12	45[c]
η^5-CpMn(CO)$_3$	24.4	10[d]	55[d]

[a] kcal/mol, errors are 1σ. [b] Reference 44. [c] Reference 45.
[d] References 46 and 47.

a freshly prepared metal carbonyl solution.[37,38]

The heats observed after photolysis of η^5-CpMn(CO)$_3$ and (η^6-C$_6$H$_6$)Cr(CO)$_3$ in cyclohexane and heptane, respectively, were found to be independent of changes in ligand concentration (tetrahydrofuran and di-n-butylamine, respectively) in the range of 0.001–0.01 M ligand. The observed heat was more exothermic at ligand concentrations above 0.01 M ligand. This indicated that in the range of 0.001–0.01 M ligand no significant amount of heat from the reaction with the ligand was being detected, and only the reaction of eq 3 was being measured.[39] The enthalpies for CO dissociation in an alkane solvent are listed in Table I for (η^6-C$_6$H$_6$)Cr(CO)$_3$ and η^5-CpMn(CO)$_3$. The values for the other metal carbonyl complexes in heptane have been reported previously.[12]

Discussion

There are two kinds of sites at which a metal can attack a silane: an alkyl CH or the SiH bond. Two pieces of evidence confirm that we are observing an interaction with the SiH bond. First, the strength of the interaction with HSiEt$_3$ is much stronger than what is observed for alkanes. Second, the intramolecular rearrangement of metal–alkyl complexes is very rapid. Simon and Xie studied the photolysis of Cr(CO)$_6$ in octanol and smaller alcohols and found that an alkyl and a hydroxy complex are formed, but the alkyl complex rearranges to the more stable hydroxy complex in less than 10 ns.[7,40] Likewise, one would expect a silane–alkyl complex to rearrange to a more stable interaction with the silicon–hydrogen moiety. A similar rearrangement has been proposed for iridium–alkane complexes.[10]

A comparison of the enthalpies of CO substitution by silane (ΔH_1) and by alkane (ΔH_3) reveals a parallel reactivity toward the different metal complexes. In each case the reaction is endothermic, indicating that the metal–silane and metal–alkane binding is weaker than the corresponding metal–CO bond. If the solvation of products and reactants is nearly the same, as is the case for other organometallic reactions of neutral species in hydrocarbon solvents,[41–43] then ΔH_1 is a measure of the difference in the magnitudes of the metal–silane and metal–CO bonding. An analogous argument applies to ΔH_3. The variation in ΔH_1 and ΔH_3 is similar and large (15 and 18 kcal/mol, respectively). Unlike ΔH_1 and ΔH_3, the difference between ΔH_3 and ΔH_1 is rather constant and varies by only 4 kcal/mol (12–16 kcal/mol).

The difference is equal to the difference in the enthalpy of metal–silane and metal–alkane binding, and its lack of variation from complex to complex suggests similar bonding in the metal–silane and metal–alkane adducts. The enthalpy for metal–silane binding ($\Delta H_{\text{M-SiH}}$) can be calculated from eq 4 if the M–CO bond enthalpy ($\Delta H_{\text{M-CO}}$) is known. Similarly, the enthalpy of the analogous metal–alkane binding ($\Delta H_{\text{M-RH}}$) can be determined from eq 5. Note that the absolute values of the binding enthalpies are equivalent to bond dissociation energies (eqs 6 and 7). These

$$\Delta H_{\text{M-SiH}} = \Delta H_1 + \Delta H_{\text{M-CO}} \qquad (4)$$

$$\Delta H_{\text{M-RH}} = \Delta H_3 + \Delta H_{\text{M-CO}} \qquad (5)$$

$$\text{ML}_n(\text{HSiEt}_3) \xrightarrow{-\Delta H_{\text{M-SiH}}} \text{ML}_n + \text{HSiEt}_3 \qquad (6)$$

$$\text{ML}_n(\text{RH}) \xrightarrow{-\Delta H_{\text{M-RH}}} \text{ML}_n + \text{RH} \qquad (7)$$

values are listed in Table II, and for comparison, $\Delta H_{\text{M-CO}}$ values have been included from the literature.[44–48] The variation in the net metal–silane binding (7 kcal/mol) resembles that of metal–alkane binding (4 kcal/mol) more than that of the M–CO bonds (18 kcal/mol).

For the complexes examined, the change in the binding enthalpies indicates that HSiEt$_3$ tends to behave more like an alkane than CO. This is consistent with the current understanding of the metal bonding to these compounds. The M–CO bond strengths depend greatly on the ability of the metal to backbond, and the low oxidation states of these complexes favor backbonding. So the M–CO bond strengths are very sensitive to the composition of the complex. For metal–alkane σ complexes, backbonding is believed to be of secondary importance where σ donation to the metal dominates.[49] For silane adducts, both σ donation to the metal and backbonding to the silane can be important,[2] but the parallel behavior between HSiEt$_3$ and alkanes suggests that σ donation to the metal may play a larger role than backbonding. Therefore the silane adducts formed in this study are expected to be σ complexes with two-electron three-center bonds. This is in agreement with studies that indicate three-center two-electron bonding occurs for η^5-CpMn(CO)$_2$(HSiR$_3$) and (η^6-C$_6$H$_6$)Cr-(CO)$_2$(HSiR$_3$) (R = H, alkyl, or aryl).[4,6,50] In particular, photoelectron spectroscopy studies show that the metal center of η^5-CpMn(CO)$_2$(HSiPh$_3$) is at the same oxidation state as in η^5-CpMn(CO)$_3$, indicating the balance of σ donor and π acceptor characteristics of HSiPh$_3$ is the same as for CO.[51] To the extent

(37) The reaction with HSiEt$_3$ in perfluorodecalin has also been investigated. The results are similar, however, the heats of reaction have not been quantitated since the quantum yields are not known for this solvent. In the case of Cr(CO)$_6$, Φ = 0.35 ± 0.03; Nayak, S.; Burkey, T. J. Manuscript in preparation.

(38) Uncertainties in quantum yields are not included in the error analysis. In general, the results are not very sensitive to the uncertainty in the quantum yields; for example, a decrease in the quantum yield for photosubstitution of Mo(CO)$_6$ of 0.04 (Φ = 0.63) results in a change of 1.2 kcal/mol in ΔH_1(19.7) and $\Delta H_{\text{M-SiH}}$(20.8). An analysis of the propagated error which includes an uncertainty of 0.04 in the quantum yield results in an overall error of 0.9 and 2.2 kcal/mol, respectively. An error of 0.04 in a the quantum yield for the other compounds will produce similar uncertainties in the enthalpies.

(39) The ligands are added to scavenge the alkane-coordinated complex to inhibit reaction with the parent complex. Without this precaution, deposits on the cuvette sometimes result.

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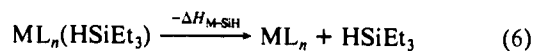
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(45) Theoretical calculations indicate the average M–CO bond strength for (η^6-C$_6$H$_6$)Cr(CO)$_3$ should be 8 kcal/mol stronger than that of Cr(CO)$_6$: Calhorda, M. J.; Frazao, C. F.; Martinho Simoes, J. A. *J. Organomet. Chem.* **1984**, *262*, 305.

(46) The M–CO bond strength for η^5-CpMn(CO)$_3$ has been calculated from the enthalpy of CO dissociation in cyclohexane (Table I) and Mn-alkane binding. The Mn-alkane binding was estimated from the enthalpy of heptane substitution on η^5-CpMn(CO)$_2$(heptane) by *cis*-cyclooctene (ΔH = –24.5 kcal/mol, ref 18) and the enthalpy of activation for cyclooctene substitution on η^5-CpMn(CO)$_2$(*cis*-cyclooctene) by PPh$_3$ in methylcyclohexane (ΔH^* = 34.9 kcal/mol, ref 47). The activation enthalpy corresponds to a dissociative process where the rate-determining step involves the formation of a metal-alkane complex. Therefore the difference in the magnitude of these values (ΔH^* + ΔH = 10.4) equals the activation energy for alkane displacement. This value would be a lower limit for alkane binding since the displacement may be an associative process with respect to the alkane. Alkane binding of 10 kcal/mol or more for η^5-CpMn(CO)$_2$(cyclohexane) is consistent with other results. A greater alkane binding for η^5-CpMn(CO)$_2$(cyclohexane) versus Cr(CO)$_5$(cyclohexane) might be expected since CO displacement of cyclohexane is an order of magnitude faster for Cr(CO)$_5$(cyclohexane) than for η^5-CpMn(CO)$_2$(cyclohexane).[24,48] The binding of cyclohexane in Cr(CO)$_5$-(cyclohexane) is at least 10 kcal/mol.[12]

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(51) This does not indicate the contribution of each kind of bonding to the overall magnitude of the bond strength, since other factors such as orbital overlap effect the bond strength.

that $HSiEt_3$ is a better σ donor and poorer π acceptor than $HSiPh_3$, σ donation will become more important, and σ complexes will be formed with $HSiEt_3$ since the metal centers are as reactive as or less reactive than η^5-$CpMn(CO)_2$.[52] It can be concluded that incomplete oxidative addition is occurring in the $HSiEt_3$ adducts of the present study and that the extent of oxidative addition is less than that of previous studies of silane adducts.

Little, if any, spectroscopic evidence for silane adducts of the $M(CO)_5$ (M = Cr, Mo, or W) has been previously reported,[53] and the ΔH_{M-SiH} values suggest that these silane adducts may be more stable than previously supposed.[20] The ΔH_{M-SiH} generally follows the observed kinetic lability of the silane adducts.[5] For example, our IR results show that $W(CO)_5(HSiEt_3)$ decomposes more slowly than $Cr(CO)_5(HSiEt_3)$, consistent with stronger metal–silane binding. This trend may not be general for all silane adducts since the mechanism of silane adduct decomposition may vary and may not involve simple elimination of silane. Clarification will require further mechanistic studies of silane adduct decomposition and binding.

With the results of previous studies, the activation enthalpy for $HSiEt_3$ elimination from η^5-$CpMn(CO)_2(HSiEt_3)$ can be estimated. The addition of $HSiEt_3$ to η^5-$CpMn(CO)_2$ has been studied recently by Wrighton's group,[5] who measured the rates at low temperature for the reaction with $HSiEt_3$ in methylcyclohexane or neat $HSiEt_3$ (eq 8). The manganese forms a σ complex with CH from the silane–alkyl group or methylcyclohexane. Thus the reaction involves the disruption of a Mn–alkyl interaction when the silane adduct is formed. The enthalpy of this reaction should be equal to the difference in the enthalpies of the Mn–silane and Mn–alkyl binding, as well as the difference between the forward and reverse activation enthalpies (eq 9). Hill and Wrighton obtained a value of 7.2 ± 1.0 kcal/mol for ΔH^*_{for}, ΔH_8 is -13.8 ± 1.7 kcal/mol ($\Delta H_1 - \Delta H_3$), and from eq 9, 21.0 ± 2.0 kcal/mol can be calculated for ΔH^*_{rev} (silane elimination). This value is consistent with 29.2 ± 0.3 kcal/mol obtained by

$$\eta^5\text{-}CpMn(CO)_2(RH) + HSiEt_3 \xrightarrow{\Delta H_8}$$
$$\eta^5\text{-}CpMn(CO)_2(HSiEt_3) + RH \quad (8)$$
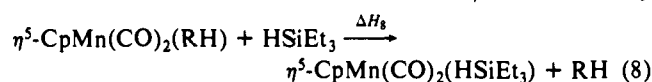
$$\Delta H_8 = \Delta H_{Mn-SiH} - \Delta H_{Mn-RH} = \Delta H^*_{for} - \Delta H^*_{rev} \quad (9)$$

Hart-Davis and Graham from their kinetic studies of the substitution of $HSiPh_3$ adduct in heptane (eq 10). They observed dissociative kinetics indicating that the incoming phosphine does not participate in the rate-determining step and concluded that the rate-determining step is probably silane elimination. Therefore

$$\eta^5\text{-}CpMn(CO)_2(HSiPh_3) + PPh_3 \xrightarrow{heptane}$$
$$\eta^5\text{-}CpMn(CO)_2(PPh_3) + HSiPh_3 \quad (10)$$
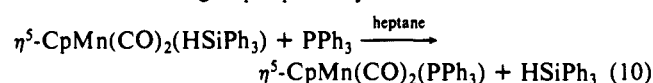
the activation enthalpy of eq 10 should be similar to ΔH^*_{rev}, which involves $HSiEt_3$. The lower value for $EtSi_3H$ is expected since the $HSiPh_3$ adduct is more stable then the $HSiEt_3$ adduct (vide supra).

The magnitude of ΔH_{Mn-SiH} exceeds that of ΔH^*_{rev} by 3 kcal/mol, indicating that the displacement of the silane is not a simple dissociation of the silane.[54] The low activation enthalpy is consistent with a stabilization of the transition state which can be attributed to Mn–alkyl bonding in the transition state. Similar stabilization energies in transition states by metal–alkyl interaction have been reported.[13] Thus the displacement of the silane by an alkyl may involve bond formation to the alkyl as the Mn–silane interaction is broken, i.e. an associative process.[55] Not coincidentally, the magnitude of ΔH_{Mn-RH} exceeds ΔH^*_{for} by 3 kcal/mol as well, as must be the case by microscopic reversibility. These results and interpretation are in agreement with the suggestion by Hill and Wrighton that the solvent participates in the transition state. In particular, they report that the activation entropy for silane addition is -6.7 ± 2.4 eu, consistent with an associative process.[56,57]

Conclusions. The enthalpies of metal–silane binding, which have been determined for the first time, are less sensitive to changes in the metal complex than M–CO bonds and somewhat more sensitive than the enthalpies of corresponding metal–alkane binding. The trends in the enthalpies of the metal–silane binding are consistent with incomplete oxidation addition, i.e., three-center two-electron bonding between the metal and Si–H. The M-$(CO)_5(HSiR_3)$ (M = Cr, Mo, W) are more stable than previously supposed, and further room temperature investigation of these compounds should be possible. These compounds may prove to be the best "silane" models for alkane σ complexes.

(52) The ionization for $HSiEt_3$ attributed to Si–H electrons is lower than that for $HSiPh_3$: Distefano, G.; Pignataro, S.; Szepes, L.; Borossay, J. *J. Organomet. Chem.* **1976**, *104*, 173. Beltram, G.; Fehlner, T. P.; Mochida, K.; Kochi, J. K. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 153.

(53) A UV–vis spectrum has been reported for a transient generated by the photolysis of $Cr(CO)_6$ and SiH_4 in the gas phase; however, the identity of the transient is uncertain. Breckenridge, W. H.; Stewart, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 364.

(54) The error for ΔH_{Mn-SiH} is uncertain due to the estimate of the quantum yield for photosubstitution, and 24.4 is likely to be within experimental error of ΔH^*_{rev}. On the other hand, 24.4 is likely to be a lower limit for $-\Delta H_{Mn-SiH}$ since the magnitude of ΔH_{Mn-SiH} is expected to be significantly larger than that of ΔH_{Cr-SiH} where the quantum yield is well established.

(55) One reviewer pointed out it seems unlikely that an associative process occurs for such a bulky silane. A silane with three alkyls may indeed be to sterically hindered at the silicon for an associative displacement of an alkyl at the metal center. It may be that the metal attacks the silane at a less hindered alkyl chain and then "walks" down the chain to the silicon. Such rearrangements have been reported previously.[40]

(56) It should be noted that most of Hill and Wrighton's experiments were in neat silane, and a unimolecular rearrangement may account for their results. Only two experiments were in methylcyclohexane, and although these results fit nicely on a Arrhenius plot, they are close together and are at the extreme end of the plot. It seems unlikely that the unimolecular and bimolecular processes would have the same activation parameters. Thus it is possible the methycyclohexane data belong on a different plot. Using Hill and Wrighton's activation parameters, the room temperature rate constant for eq 8 is greater than 10^9 M^{-1} s^{-1} (using the Eyring equation and assuming the activation parameters are temperature independent). This value is unexpectedly high since it exceeds the rate by about 10^2 of other known bimolecular reactions of $CpMn(CO)_2(RH)$ where RH must be displaced,[24] suggesting they are observing an intramolecular reaction. In an analogous reaction, the unimolecular rearrangement of $Cr(CO)_5(EtOH)$ to $Cr(CO)_5(HOEt)$ is also much faster than the bimolecular displacement of alkane from $Cr(CO)_5(RH)$.[13,40,57] If Hill and Wrighton's activation parameters do apply to a unimolecular rearrangement, then eq 9 (RH = CH) is still applicable, and the difference in the magnitude of ΔH_{Mn-RH} and ΔH^*_{for} can still be attributed to an Mn–alkyl interaction in the transition state.

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