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Electronic Structure Control of Si–H Bond Activation by Transition Metals. 2. Valence Photoelectron Spectra of (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiPh_3$, (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiHPh_2$, and (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiFPh_2$ (Ph = C_6H_5)

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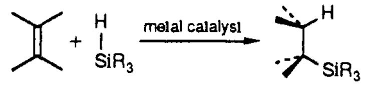
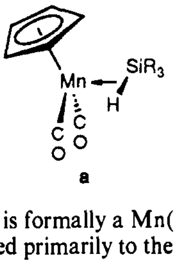
Abstract: The He I photoelectron spectra of (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiHPh_2$, (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiPh_3$, and (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiFPh_2$ (Ph = C_6H_5) have been obtained in order to measure the nature and extent of Si–H bond interaction with the transition-metal center in these complexes. The principal electronic structure factors contributing to the addition of the Si–H bond to the transition metal involve the interaction of the Si–H σ and σ^* orbitals with the metal. The extent of Si–H σ^* interaction with the metal is obtained from the shape and splitting pattern of the metal-based ionization band. The electron distribution between the Si–H bond and the metal is indicated by the relative stabilities of the metal-based and ligand-based ionizations. It is found that the metal-based ionizations of these complexes reflect the formal d^6 electron count at the metal center. Also, the small shifts of the valence ionizations reveal that the extent of electron charge density shift from the metal to the ligand is negligible. These observations show that the electronic structure of the Si–H interaction with the metal is in the initial stages of Si–H bond addition to the metal, before oxidative addition has become prevalent. The mechanism of interaction of the Si–H bond with the Mn center is predominantly through interaction of the filled Si–H σ-bonding orbital with empty metal orbitals. This contrasts with our previous photoelectron studies on (η^5-C_5H_5)$Mn(CO)_2HSiCl_3$, where the experimental data showed this compound to be a nearly complete oxidative addition product with formation of discrete Mn–H and Mn–Si bonds. The combination of the present study with the previous results demonstrates that complexes can be obtained that stabilize different stages of activation of the Si–H bond. These stages range from weak coordination of the Si–H bond to the metal to complete oxidative addition, depending on the substituents on the silicon atom.

The activation of C–H bonds by metals is important to synthetic and catalytic processes involving functionalization of hydrocarbons.[1-4] Likewise, activation of Si–H bonds by transition metals is important to industrial processes such as hydrosilation, as shown below. The mechanism of hydrosilation reactions catalyzed by transition metals is not well understood.[5-7] The mechanism is presumed to proceed through interaction of the Si–H bond with the metal to form the metal silyl, followed by olefin insertion and reductive elimination.[6] Model compounds for the catalysts are essential for understanding the factors that stabilize possible intermediates and favor different mechanisms of these reactions.

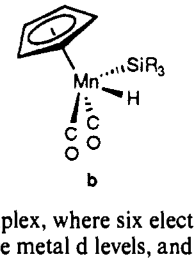


The complexes examined here are members of a class of molecules that display the interaction of a Si–H, Ge–H, or Sn–H bond with a transition-metal center.[8-10] The general molecular formula is $CpMn(CO)_2HER_3$ where E is Si, Ge, or Sn; R is Ph or Cl; and Cp is η^5-C_5H_5. In valence-bond terms, one wishes to know which of the valence-bond structures shown below more appropriately represents the ground state of each complex.



a

versus



b

Structure **a** is formally a Mn(I) complex, where six electrons have been assigned primarily to the valence metal d levels, and the Si–H bond is acting as a neutral two-electron donor. Structure **b** is formally a Mn(III) complex, with a d^4 configuration assigned to the metal. This is the product of complete oxidative addition with formation of primarily direct bonds to the formally anionic ligands H^- and $SiCl_3^-$. It should be remembered that these two structures are limiting descriptions of the bonding prevalent in these compounds and do not represent the partial delocalization of charge and orbital mixing that are present in a more detailed description of the electronic structure and bonding.

In molecular orbital terms, the electronic structure factors of bond activation have been discussed in the literature in terms of σ and σ^* interactions of the E–H bond with the metal center.[11] The donation of electron density from the E–H σ-bonding orbital into the empty metal LUMO's is the σ interaction and results in the formation of a 3-center–2-electron bond. The σ^* interaction involves the donation of electron density from the filled metal orbitals into the E–H σ^* orbital. If the donation of electron density from the metal into the σ^* orbital is predominant, the direct E–H bond is effectively broken and the coordinated E and H atoms take on a net negative charge. This electron distribution represents

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the approach to full oxidative addition and formation of direct M–H and M–E bonds.

We have found that photoelectron spectroscopy can provide specific experimental information on the principles of E–H bond interaction with the transition-metal center. In an earlier work, the σ interaction of the C–H bond with the metal center, corresponding to valence-bond structure **a**, was seen to be predominant in cyclohexenylmanganese tricarbonyl by photoelectron spectroscopy.[11] In the case of silyl complexes, several observations from the He I/He II photoelectron studies on $CpMn(CO)_2HSiCl_3$ have shown that this compound is most correctly classified as a Mn(III), d^4 system represented by structure **b**.[12] For one, only two of the valence ionizations of this complex displayed the characteristics of metal-based ionizations, and thus the formal assignment of electrons gives the d^4 configuration. The third valence ionization was observed at 0.7-eV greater ionization energy than the metal-based ionizations and showed the He I/He II intensity characteristics of the Mn–Si bond with primary density on the $SiCl_3^-$ ligand. The destabilization of the other ligand-based ionizations and the stabilization of the metal-based ionizations also demonstrate the charge redistribution from the metal to the ligand that takes place with nearly complete oxidative addition and formation of direct Mn–H and Mn–Si bonds. The Si–H σ^* orbital of $HSiCl_3$ is clearly sufficiently low in energy and interacts strongly with the metal to withdraw density from the metal center. The important question is whether the result of this study on the $HSiCl_3$ complex is characteristic of the Si–H bond only or is dependent on the substitutions on the silicon and on the metal. Can the extent of interaction of the Si–H bond with the metal be significantly perturbed by chemical substitutions?

The evidence of the bonding mode from X-ray studies, ^{29}Si NMR, and reaction chemistry studies[8-10,13,14] of $MeCpMn(CO)_2HSiPh_3$ (where MeCp is η^5-$C_5H_4CH_3$) indicates the presence of a 3-center–2-electron bond in this complex and little progress toward a full oxidative addition product. In order to compare the electron distribution and bonding in these different complexes, we have obtained the photoelectron spectra of $MeCpMn(CO)_2HSiPh_3$, $MeCpMn(CO)_2HSiHPh_2$, and $MeCpMn(CO)_2HSiFPh_2$. It is anticipated that the different group electronegativities of the Ph-substituted silyl complexes may be significant in comparison to the trichlorosilyl complex. As in previous studies, the spectra of the compounds will be compared to the spectra of starting materials and free ligand to determine the shifts in the metal- and ligand-based ionizations. These ionization energy shifts are sensitive to the electron charge shift from the metal to the ligand. $MeCpMn(CO)_2HSiFPh_2$ represents a complex where the group electronegativity of the silicon substituents is intermediate between the phenylsilyl complexes and the trichlorosilyl complex. Photoelectron studies on this complex are undertaken to observe whether the extent of electron charge redistribution between the metal and the bonding and antibonding orbitals of Si–H is also intermediate. This work demonstrates how the extent of Si–H bond addition and activation in the complexes is influenced by the substituents on silicon.

Experimental Section

Preparation of Compounds. $MeCpMn(CO)_2HSiHPh_2$ and $MeCpMn(CO)_2HSiPh_3$ were prepared by photolysis in hexane of $MeCpMn(CO)_3$ with $HSiHPh_2$ (Strem Chemicals) and $HSiPh_3$ (Aldrich), respectively.[8,15] $MeCpMn(CO)_2HSiFPh_2$ was prepared by reacting $MeCpMn(CO)_2HSiHPh_2$ with $[Ph_3C]^+BF_4^-$.[8] All compounds were characterized by IR spectroscopy and ^1H NMR.

Photoelectron Data. Photoelectron spectra were recorded on an instrument that features a 36 cm radius hemispherical analyzer (10-cm gap) and customized sample cells, excitation sources, detection and control electronics, and data collection methods that have been described previously.[16-20] The spectrum of $MeCpMn(CO)_2HSiPh_3$ was measured with a sample cell temperature at 85 °C. Care was taken to ensure that the temperature of sublimation did not exceed 87 °C. Beyond this temperature, appreciable decomposition of the compound occurred. The decomposition was evidenced in the photoelectron spectrum by the observation of free ligand $HSiPh_3$ ionizations. $MeCpMn(CO)_2HSiHPh_2$ was sublimed at a sample cell temperature of 67 °C. At 69 °C, the compound similarly begins to decompose so appropriate care was taken. Again, the spectrum of the free ligand $HSiHPh_2$ indicated the decomposition of the compound. $MeCpMn(CO)_2HSiFPh_2$ was sublimed at a sample cell temperature of 113 °C. All data collections were repeated at least 5 times for purposes of examining particular ionization features, and no discernible differences were observed between collections.

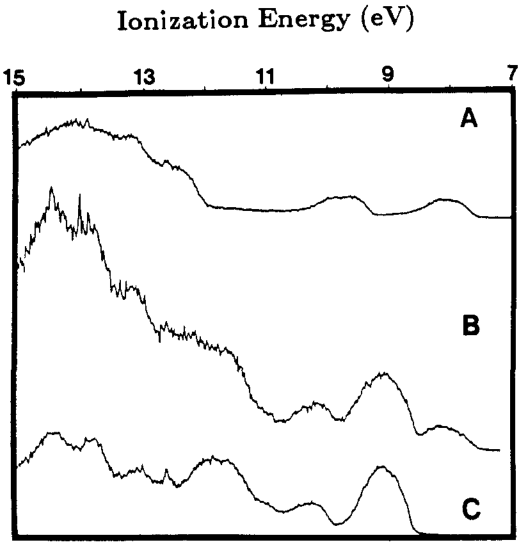

Figure 1. Comparison of the He I photoelectron spectra of (A) (η^5-$C_5H_4CH_3$)$Mn(CO)_3$, (B) (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiPh_3$, and (C) $HSiPh_3$ (Ph = C_6H_5).

The data are represented analytically with the best fit of asymmetric Gaussian peaks (program GFIT).[21] The asymmetric Gaussian peaks are defined with the position, the amplitude, the half-width indicated by the high binding energy side of the peak (W_h), and the half-width indicated by the low binding energy side of the peak (W_l). The confidence limits of the peak positions and widths are generally ±0.02 eV. The confidence limit of the area of a band envelope is about ±5%, with uncertainties introduced from the base-line subtraction and fitting in the tails of the peaks. The individual positions, shapes, and areas of overlapping peaks are not independent and, therefore, are more uncertain.

Spectral Subtraction. In the spectra of some compounds, a key ionization of the complex is obscured by overlap with ionizations of the ligands. For example, in the complexes reported here the Cp ionizations are obscured under the phenyl π ionizations of the silyl. Since the phenyl π ionizations do not change significantly on coordination of the silyl to the metal, the spectrum of the free ligand could be subtracted from the spectrum of the complex to more clearly observe the Cp ionizations. In order to minimize the noise introduced by spectral subtractions, the spectrum of the free ligand was first fit with asymmetric Gaussian peaks and the fit sum was subtracted from the complex spectrum. In the analytical representation of the residual spectrum, an additional uncertainty is introduced into the relative peak intensities because of uncertainty in weighting the ligand ionizations that are subtracted. However, the band profiles and the peak positions (±0.05 eV) in the residual spectrum remain significant. Since the conclusions are not based on the relative intensities, the spectral subtraction technique is very useful.

Results

The He I photoelectron spectrum of $MeCpMn(CO)_2HSiPh_3$ from 7 to 15 eV is shown in Figure 1. The assignment of the

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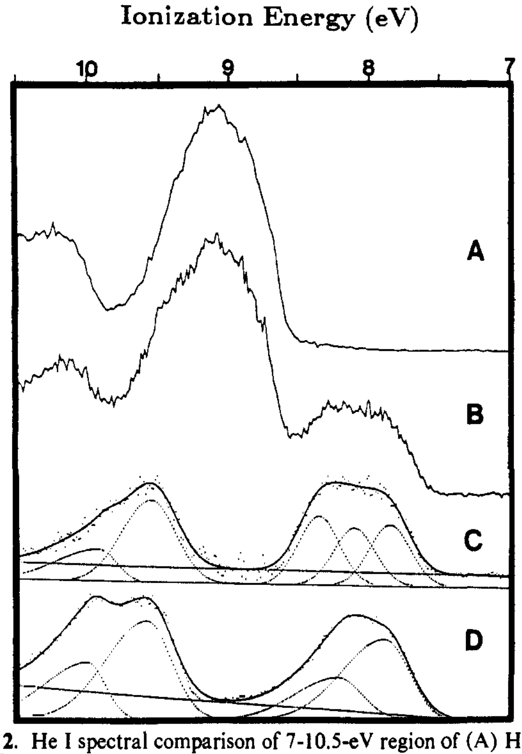

Figure 2. He I spectral comparison of 7-10.5-eV region of (A) $HSiPh_3$, (B) (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiPh_3$, (C) subtracted spectra, and (D) (η^5-$C_5H_4CH_3$)$Mn(CO)_3$ (Ph = C_6H_5).

valence ionizations of this complex is aided by comparison to the spectrum of the free $HSiPh_3$ molecule (Figure 1C) and the spectrum of $MeCpMn(CO)_3$ (Figure 1A). The broad band of overlapping ionizations from 12 to 15 eV in both $MeCpMn(CO)_2HSiPh_3$ and $MeCpMn(CO)_3$ is due to the carbonyl 5σ and 1π ionizations and the Cp a_2'' (symmetric π) and valence σ ionizations.[17] Some of the ionizations in $MeCpMn(CO)_2HSiPh_3$ in the 12–15-eV region are due to the ligand ($HSiPh_3$) σ and phenyl π ionizations, as can be seen from the spectrum of the free ligand. Individual assignments in this forest of ionizations will not be attempted.

It is helpful to focus on the ionizations of the free ligand $HSiPh_3$ before the ionizations in the low-energy region of $MeCpMn(CO)_2HSiPh_3$ are assigned. The photoelectron spectrum of $HSiPh_3$ has been reported previously,[22] and the assignments of the valence ionizations are straightforward. The band at 9.1 eV is assigned to the phenyl π ionizations while the band at 10.4 eV is assigned to the Si–C σ ionizations. These same ionizations observed in the spectrum of the free silane are also present in the spectrum of $MeCpMn(CO)_2HSiPh_3$. The shift of these ionizations on complexation gives specific information about the electron distribution.

The valence ionization features of $MeCpMn(CO)_2HSiPh_3$ in the 7–10.5-eV region are shown in Figure 2B. The leading ionization band is broad and flattened at the top compared to the metal band in $MeCpMn(CO)_3$ (Figure 2D). This band represents ionization of the metal-based 3d electrons. The second leading ionization band (8.6–9.8 eV) is broad and comprises the phenyl π ionizations and the predominantly Cp e_1'' ring π ionizations, on the basis of comparisons with the free silane and $MeCpMn(CO)_3$. The third ionization band (10–11 eV) is probably due to the Si–C σ ionizations. In order to illustrate the relationships of these ionizations more clearly, the free-ligand spectrum (Figure 2A) is subtracted from the spectrum of the complex (Figure 2B) as described in the Experimental Section. The result of the subtraction is shown in Figure 2C. The phenyl π ionization band is only shifted 0.03 eV from its location in the free ligand to match the same band in the complex. This is the extent that the silane ligand ionizations shift on complexation. The third ionization band is definitely due to the Si–C σ ionizations as seen from the spectral comparison. From ligand subtraction, it is seen that the shift of the ligand ionizations in the spectrum of the complex from their position in the spectrum of the free ligand is very small.

Table I. He I Valence Ionization Features

compound	posn	W_h	W_l	rel area
$MeCpMn(CO)_3$	7.90	0.71	0.41	1.0
	8.23	0.71	0.41	
	9.59	0.65	0.42	1.76
	9.99	0.70	0.28	
$MeCpMn(CO)_2HSiPh_3$	7.86	0.34	0.35	1.0
	8.11	0.34	0.35	
	8.36	0.34	0.35	
	9.56	0.47	0.42	0.83
	9.91	0.70	0.28	
$MeCpMn(CO)_2HSiHPh_2$	7.86	0.41	0.53	1.0
	8.06	0.41	0.53	
	8.36	0.59	0.53	
	9.53	0.42	0.25	1.24
	9.88	0.42	0.25	

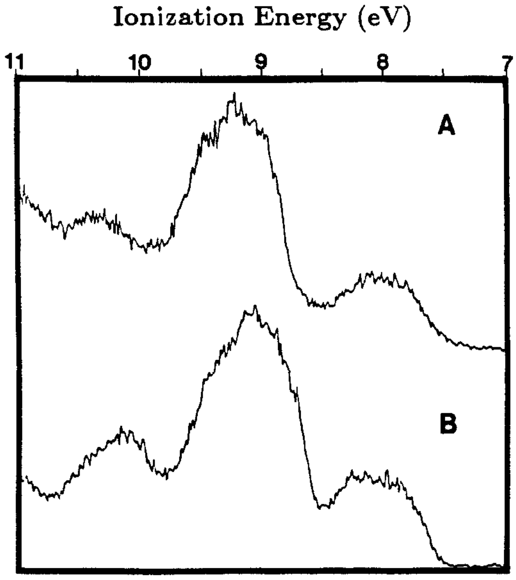

Figure 3. He I spectral comparison of 7-11-eV region of (A) (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiHPh_2$ and (B) (η^5-$C_5H_4CH_3$)$Mn(CO)_2HSiPh_3$ (Ph = C_6H_5).

The positions of the predominantly Cp e_1'' ring π ionizations are very clearly seen in Figure 2C after ligand subtraction. The Cp e_1'' ionization in the spectrum of $MeCpMn(CO)_3$ and in the spectra of a large number of $MeCpMn(CO)_2L$ complexes[17] has a characteristic shoulder on the high binding energy side. It is necessary to include the shoulder on the Cp ionization in the analytical representation of $MeCpMn(CO)_2HSiPh_3$, and this shoulder is constrained to have the same splitting as was observed in $MeCpMn(CO)_3$. The positions of the ionizations of both $MeCpMn(CO)_3$ and $MeCpMn(CO)_2HSiPh_3$ are given in Table I. It is important to note that the Cp-based ionizations in $MeCpMn(CO)_2HSiPh_3$ do not shift significantly from their position in $MeCpMn(CO)_3$.

The low-energy metal-based ionizations are shown most clearly in Figure 2C. The broad flat top of the metal band (cf. $MeCpMn(CO)_3$ in Figure 2D) indicates the presence of more than two peaks in this region. Representation of the broad band by two asymmetric Gaussian peaks was attempted, but this analytical representation did not produce peaks with reasonable half-widths for these complexes. Therefore, the broad band is represented by three asymmetric Gaussian peaks as shown in the figure. The peaks were constrained to have the same shapes to minimize the number of parameters. The peak positions are given in Table I. The leading edge of the ionization is shifted slightly to lower binding energy compared to $MeCpMn(CO)_3$, while the higher

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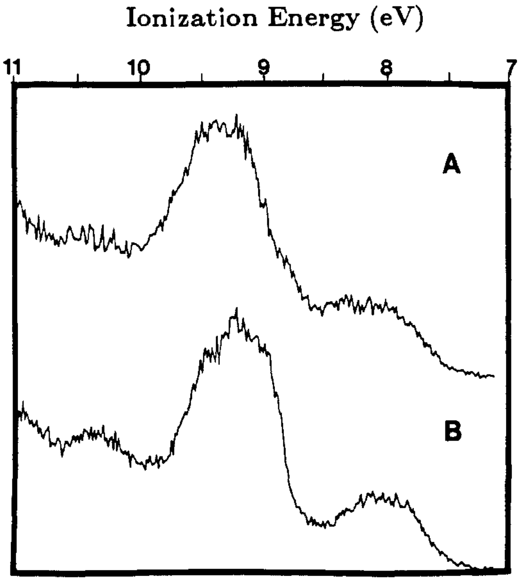

Figure 4. He I spectral comparison of 7-11-eV region of (A) (η^5-$C_5H_4CH_3$)Mn(CO)$_2$HSiFPh$_2$ and (B) (η^5-$C_5H_4CH_3$)Mn(CO)$_2$HSiHPh$_2$ (Ph = C_6H_5).

binding energy edge is shifted 0.13 eV to higher ionization energy compared to MeCpMn(CO)$_3$.

The valence ionization features of MeCpMn(CO)$_2$HSiHPh$_2$ in the 7–11-eV region are shown in Figure 3A. The valence photoelectron spectrum of MeCpMn(CO)$_2$HSiPh$_3$ is also shown in Figure 3B to demonstrate the similarity in the ionization features of the two compounds. The broadness of the metal ionization band in MeCpMn(CO)$_2$HSiHPh$_2$ indicates that it can be represented analytically by three asymmetric Gaussian peaks as was done in MeCpMn(CO)$_2$HSiPh$_3$. The peak positions are given in Table I. Independent of the fit, the leading and trailing ionization edges of the metal-based ionization band are in the same position in both compounds. The splitting and width of the metal-based ionizations are important to the interpretation of the electronic structure and bonding. Rather than compare the positions of the fit peaks in the metal-based ionization bands, it is more significant to compare the combined widths of the metal bands. The parameters of the fit peaks are not completely independent because of overlap of the peaks in the bands, but the total band widths are direct experimental observables. The width of the metal band in MeCpMn(CO)$_2$HSiPh$_3$ is 0.69 ± 0.05 eV while that in MeCpMn(CO)$_2$HSiHPh$_2$ is 0.67 ± 0.05 eV. Following the metal-based ionizations are the phenyl π ionizations and the predominantly Cp e_1'' ring ionizations in the region from about 8.5 to 10 eV. The third ionization band (10–11 eV) is due to the Si–C σ ionizations. The Cp e_1'' ionization shoulder in MeCpMn(CO)$_2$HSiHPh$_2$ is shifted slightly to lower ionization energy (cf. MeCpMn(CO)$_2$HSiPh$_3$). The similarity in ionization features suggests that the electronic structure factors of the Si–H bond interaction with the metal are similar in both compounds.

The valence ionization features of MeCpMn(CO)$_2$HSiFPh$_2$ in the 7–11-eV region are shown in Figure 4A. The valence photoelectron spectrum of MeCpMn(CO)$_2$HSiHPh$_2$ is also shown in Figure 4B for visual comparison of the ionization features. The leading edge of the metal ionization band is shifted slightly to higher ionization energy, and the leading edge of the phenyl π ionizations is shifted slightly to lower ionization energy in MeCpMn(CO)$_2$HSiFPh$_2$ compared to MeCpMn(CO)$_2$HSiHPh$_2$. The width of the metal band in MeCpMn(CO)$_2$HSiFPh$_2$ is 0.79 ± 0.05 eV. Other than slight shifts in ionizations, the ionization features of the two compounds are very similar.

Discussion

Information from X-ray crystallographic, ^{29}Si NMR, and neutron diffraction techniques have been interpreted in terms of a Mn, H, Si 3-center-2-electron (3c–2e) bond in MeCpMn(CO)$_2$HSiHPh$_2$, MeCpMn(CO)$_2$HSiFPh$_2$, and MeCpMn(CO)$_2$HSiPh$_3$.[8,9,23,24] The definition of the 3c–2e bond in this case is that some Si–H bonding is retained while the Si–H σ bond is acting as a two-electron donor in the formation of a dative bond with the metal center. The same structural and NMR techniques have also suggested to previous workers the presence of a 3c–2e bond in MeCpMn(CO)$_2$HSiCl$_3$, but our gas-phase photoelectron studies on this compound reveal it to be best represented by direct Mn–Si and Mn–H bonds and little direct Si–H bonding interaction. This result is in agreement with Fenske–Hall calculations, although the Fenske–Hall (and to a much greater extent the extended Hückel calculations) underestimated the amount of charge transferred to the Si atom that was shown by the experiment.[12]

We have also carried out Fenske–Hall calculations on model silyls coordinated to CpMn(CO)$_2$ to see what the calculation could tell us about the effects of changing the electronegativities of the groups bound to the silicon. Structural studies have shown that the coordinated Si–H and Mn–H bond distances are relatively invariant from the HSiCl$_3$ complex through the complexes that are the focus of the present study.[8] The greatest structural effect is on the Mn–Si distance, which varies from 2.25 Å for the HSiCl$_3$ complex to 2.46 Å for the HSiPh$_3$ complex, partly as a result of the charge effect on the size of the silicon atom. Calculations on HSiMe$_3$ and SiH$_4$ model complexes with the same structural and calculational parameters as previously[12] showed that the Fenske–Hall calculations are largely insensitive to these chemical perturbations. The population of the Si–H σ^* orbital remained 0.51 ± 0.03 e without any trend in group electronegativities. This remained true despite artificially changing the 1s basis function on the three uncoordinated hydrogen atoms in the HSiH$_3$ calculation to remove a full electron from the silicon center. The limitations of the approximate calculations in giving a quantitative estimate of the charge distribution between the metal and the silyl are understandable because the distribution critically depends on the energy and interaction of a virtual orbital (the Si–H σ^*) with the metal, and it is difficult to accurately place a virtual orbital with a minimal basis set approximate method. The limitations of the approximate calculations underscore the importance of obtaining independent indications of the Si–H interactions with the metal from photoelectron spectroscopy. The photoelectron results show that the bonding picture and electron distribution in the phenyl-substituted compounds are substantially different from that of the Cl-substituted complex.

The ionization information from MeCpMn(CO)$_2$HSiPh$_3$ does not indicate any net shift of electron charge from the metal to the ligand. The Si–C σ and phenyl π ionizations are shifted no more than 0.03 eV from their positions in the free ligand HSiPh$_3$. This is in contrast to the results from the photoelectron spectrum of CpMn(CO)$_2$HSiCl$_3$, in which the Cl lone-pair ionizations are shifted 1 eV to lower binding energy compared to the corresponding ionizations in the free HSiCl$_3$ ligand. The destabilization of the ligand-based ionizations in the Cl complex indicates extensive negative charge on the ligand as would be expected with oxidative addition. In molecular orbital terms, the charge donated from the Si–H σ bond to the metal is exceeded by back-donation from the metal to the Si–H σ^* orbital. The absence of this destabilization of the ligand ionizations of the HSiPh$_3$ complex is one indication that the electron distribution in this complex is much different from that in the HSiCl$_3$ complex. The stabilization of ligand ionizations from donation of electrons from the Si–H σ-bonding orbital to the metal and net positive charge at the metal are just balanced by destabilization from electrons accepted by the Si–H σ^* orbital. In simple terms, the HSiPh$_3$ ligand has not proceeded as far in oxidative addition to the Mn center as the HSiCl$_3$ ligand.

The ionizations that correlate with the Cp e_1'' electrons in MeCpMn(CO)$_2$HSiPh$_3$ also are not shifted from the corresponding ionizations of MeCpMn(CO)$_3$. The filled Cp e_1'' levels

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are involved in donation to empty metal levels to form the primary bonding between the ring and the metal.[17] The lack of shift in the Cp-based ionizations between the two complexes shows that the net σ donation and π acceptance of the silane is similar to that of CO (vide infra). This is another indication that the triphenylsilyl complex has not advanced to full oxidative addition. In comparison, the ionizations due to the Cp e_1'' electrons in $CpMn(CO)_2HSiCl_3$ are shifted 0.4 eV to higher binding energy compared to their position in $CpMn(CO)_3$, indicating a more positively charged metal center in $CpMn(CO)_2HSiCl_3$.

The leading ionization band in $MeCpMn(CO)_2HSiPh_3$ is predominantly metal in character and is well separated from the phenyl-based ionizations as is well shown by the ligand-subtracted spectrum in Figure 2. This band is best represented by three asymmetric Gaussian peaks, which are consistent with the formal assignment of six electrons to the Mn(I) center. Further evidence of a formally d^6 center is provided by the integrated peak areas of the Cp and metal ionization bands shown in Table I. Even with the uncertainty in the integrated peak areas introduced by the overlap of the silane ionizations with the Cp ionizations, there is sufficient intensity in the first ionization band to account for six metal-based electrons. The profile and intensity of the first ionization band are the third indication of incomplete oxidative addition for the phenyl complexes.

The leading edge of the metal ionization band is destabilized by 0.04 eV compared to $MeCpMn(CO)_3$ while the higher ionization energy edge of the metal band is stabilized by 0.13 eV. The observation that the metal band as a whole does not shift from its position in $MeCpMn(CO)_3$ also signifies that the σ-donor/π-acceptor properties of the silane balance out in comparison to CO. The metal orbital that is stabilized to higher binding energy (cf. $MeCpMn(CO)_3$) is interacting with the empty Si–H σ^* orbital (π back-acceptance) while the Si–H σ orbital is donating to the empty metal LUMO's. The extent of π back-acceptance in $MeCpMn(CO)_2HSiPh_3$ is not as large as was observed in $CpMn(CO)_2HSiCl_3$. In the latter compound, the metal d_{yz} orbital interacts with the Si–H σ^* orbital to such an extent that the Si–H bonding provided by the Si–H σ orbital is essentially canceled, leaving primarily direct Mn–H and Mn–Si bonds. The Mn–Si ionization is observed at 9.3 eV in the spectrum of $CpMn(CO)_2HSiCl_3$, which is 0.6 eV separated from the other metal ionizations. The two metal-based ionizations (d^4) of $CpMn(CO)_2HSiCl_3$ are shifted 0.7 eV to higher binding energy compared to the metal band in $CpMn(CO)_3$. This shift indicates stabilization of the metal orbitals as would be expected with a higher positively charged metal center. The metal band in $MeCpMn(CO)_2HSiPh_3$ is not stabilized overall from that of $CpMn(CO)_3$. In $MeCpMn(CO)_2HSiPh_3$, the silane is primarily acting as a neutral two-electron-donor ligand through the Si–H σ bond and donating electron density into the empty metal levels. The extent of σ^* interaction that is present in $MeCpMn(CO)_2HSiPh_3$ (as evidenced by the stabilization of one of the metal orbitals by 0.13 eV) is substantially smaller than that present in $CpMn(CO)_2HSiCl_3$. The density accepted by the Si–H σ^* is just sufficient to keep the net charge on the metal essentially the same as in the parent tricarbonyl complex. As in $MeCpMn(CO)_3$, the metal in $MeCpMn(CO)_2HSiPh_3$ is best considered to be formally in the +1 oxidation state.

The photoelectron spectrum of $MeCpMn(CO)_2HSiHPh_2$ is very similar to that of the triphenylsilane complex. The lack of significant shifts of the coordinated silyl, cyclopentadienyl, and metal-based ionizations from those of $MeCpMn(CO)_3$ and the small spread of the metal-based ionization all give evidence that oxidative addition of the Si–H bond to the metal is not as complete in these complexes as in the $HSiCl_3$ complex.

The primary difference between the phenyl- and chlorosilyl complexes is the group electronegativity of the substituents on the silicon. The replacement of one phenyl group with a fluorine atom to give $MeCpMn(CO)_2HSiFPh_2$ provides a complex with mixed substituents on Si and a group electronegativity intermediate between the phenyl- and chlorosilyl complexes. The photoelectron spectrum of this F complex shows stronger interaction of the Si–H bond with the metal center than the Ph complex but does not indicate full oxidative addition. The ionization features of $MeCpMn(CO)_2HSiFPh_2$ are most similar to those of $MeCpMn(CO)_2HSiHPh_2$ and $MeCpMn(CO)_2HSiPh_3$. The metal band in $MeCpMn(CO)_2HSiFPh_2$, however, is wider than in the two other compounds by ≈0.1 eV. The relative increase in width of the metal band indicates more Si–H σ^* interaction with the metal in $MeCpMn(CO)_2HSiFPh_2$ compared to $MeCpMn(CO)_2HSiHPh_2$ and $MeCpMn(CO)_2HSiPh_3$. The complex is best represented as a Mn(I), d^6 system but has proceeded to a more advanced stage of oxidative addition than the other complexes reported in this paper. Thus, the electronegative fluorine atom on silicon helps drive the compound toward oxidative addition by making the $HSiFPh_2$ ligand a better π acceptor than the $HSiPh_3$ and H_2SiPh_2 ligands.

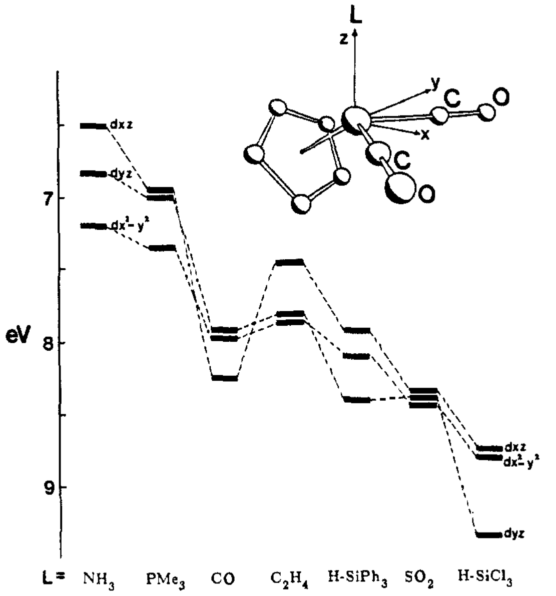

Figure 5. Correlation diagram of experimental ionization energies of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2L$ complexes where L = NH_3, PMe_3, CO, C_2H_4, $HSiPh_3$, SO_2, and $HSiCl_3$.

Comparison of Silyl Ligands with Other Common Ligands. We have previously studied the electron distribution in numerous other $MeCpMn(CO)_2L$ complexes (where L = NH_3, PMe_3, C_2H_4, and SO_2) by photoelectron spectroscopy.[16,25-27] The photoelectron spectra reported here provide the opportunity to compare the electron donating and back-accepting powers of the silyl ligand to other neutral two-electron-donor ligands. Figure 5 shows the observed ionization energies that correlate with the three predominantly metal orbitals for different $MeCpMn(CO)_2L$ complexes. The reference compound is $MeCpMn(CO)_3$ where the metal ionizations are split by 0.3 eV in a 2:1 pattern by the 3-fold symmetry of the three carbonyls.[17] When a ligand L is substituted along the z-axis for one of the carbonyls, the stability and splitting pattern of the metal orbitals reveal the σ-donor and π-acceptor properties of L in relation to CO. The foundations of this analysis have been thoroughly discussed previously.[28] The x-axis for the following discussion bisects the two carbonyl ligands as shown in Figure 5. The first effect of replacing a CO ligand along the z-axis with another ligand L is to shift the predominantly d_{xz} and d_{yz} orbitals according to the relative amount of stabilization that they

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receive from π back-bonding into the ligand. The ligand L donates its σ electrons into the empty metal orbitals, and although a direct observation of this metal-based orbital ionization is not possible by photoelectron spectroscopy, observation of the corresponding ligand ionizations and the total shift of the occupied metal orbital ionizations gives an indication of the net donor/acceptor properties of the ligand. The metal $d_{x^2-y^2}$ ionization senses the relative charge at the metal center without direct π overlap effects from the ligand on the z-axis.

As an example, NH_3 is a good σ donor through its nitrogen lone pair, and the strength of donation is such that the metal orbital is destabilized by 0.7 eV.[25] There is no π acceptance by the ligand to stabilize the metal orbitals, and the metal-based ionizations are split over a wide range. The ligand PMe_3 (Me = CH_3) is also an effective σ donor, and the metal orbital is destabilized by 0.6 eV. The P lone pair in $MeCpMn(CO)_2PMe_3$, which is responsible for σ donation, is stabilized by 1.2 eV from its position in free PMe_3.[16] Both NH_3 and PMe_3 have little or no π acceptance as observed from the spread of the metal-based ionizations (vide infra).

The ethylene in $MeCpMn(CO)_2C_2H_4$ has a σ-donating orbital and a single π-accepting orbital. The d_{xz} orbital is orthogonal to the π-accepting orbital of ethylene, and the corresponding ionization is destabilized by 0.4 eV[26] relative to the $d_{x^2-y^2}$ ionization when the back-bonding of the CO ligand is replaced by the ethylene. The destabilization of the metal orbitals is smaller than that observed for $MeCpMn(CO)_2NH_3$ and $MeCpMn(CO)_2PMe_3$. The net transfer of charge to the metal from σ donation/π acceptance is obviously not as great for ethylene as for NH_3 and PMe_3. This is partly because of the π-acceptor capability of ethylene. The empty π^* orbital of the olefin interacts with the d_{yz} orbital of the metal, which is the most effective donor orbital on the metal.[29] The stabilizing influence of this ethylene acceptor orbital is similar to that of a single CO π-acceptor orbital as shown by the observation that the d_{yz} orbital ionization remains degenerate with the $d_{x^2-y^2}$ orbital ionization.

The Si–H bond (with Ph as substituents on the Si) in $MeCpMn(CO)_2HSiPh_3$ is the σ-donating orbital. Like ethylene, the Si–H bond has a single accepting orbital. In this case the single accepting orbital is the Si–H σ^*. The d_{yz} orbital is stabilized about 0.1 eV relative to the other metal levels since it has some interaction with the Si–H σ^* orbital. The metal orbital involved in back-bonding to silane is slightly more stabilized than this same orbital, which was back-bonding to the ethylene π^* orbital. Therefore, the π-accepting power of this single silane orbital is more than that of one CO or ethylene π^* orbital. In $MeCpMn(CO)_2HSiPh_3$, one metal orbital (lowest ionization energy) is back-bonding to one carbonyl, one metal orbital is back-bonding to two carbonyls, and the third metal orbital (highest ionization energy) is back-bonding to one carbonyl and the silane. This explains the splitting pattern of the metal band in the PES of $MeCpMn(CO)_2HSiPh_3$. The net σ-donor/π-acceptor properties of CO and silane are similar. Since the total acceptor ability of the phenylsilanes is less than the total acceptor ability of CO, the phenylsilanes are also weaker σ donors than CO. The trichlorosilane is therefore an even weaker donor.

The Si–H bond (with Cl as substituent on the Si) in $MeCpMn(CO)_2HSiCl_3$ has π acceptance by the Si–H σ^* orbital to such an extent that the ionization that correlates with the d_{yz} is substantially stabilized with respect to the other metal-based ionizations. The stability of the Si–H σ^* orbital and its overlap interaction with the d_{yz} orbital results in an orbital with extensive Si character rather than metal character. It is best described as a Mn–Si bond ionization that is stabilized by as much as 1.3 eV from the metal-based ionization with which it correlates in $MeCpMn(CO)_3$. This corresponds to the breaking of the Si–H bond and the formation of an oxidative addition product. In addition, the d_{xz} and $d_{x^2-y^2}$ metal ionizations in this case are stabilized by as much as 0.7 eV as a result of the electron transfer from the metal to the ligand.

As a final comment, it is appropriate to compare the results of these studies on Si–H bonds with our previous studies of the C–H bond interaction with the metal. The C–H bond is also a weak σ donor as illustrated in the case of cyclohexenylmanganese tricarbonyl.[11] There is no destabilization of the metal orbitals in this case because the negative charge on the metal due to donation of electron density from the C–H bond is compensated by the positive protic charge of the hydrogen. In the case of the Si–H bond, it is a better σ donor than the C–H bond since a slight destabilization of the metal orbitals is observed in this case. The most important factor is that the Si–H σ^* orbital is a much better π acceptor than the C–H σ^* orbital. This leads to complete oxidative addition of the Si–H bond to the manganese center in these complexes if the Si–H σ^* is sufficiently stabilized by electronegative substituents on the Si.

The substitution of Ph for Cl on the Si in these complexes drastically changes the extent of Si–H interaction with the metal center, going from a nearly complete oxidative addition product (for Cl) to a weak interaction of the Si–H bond with the metal (for Ph). The valence photoelectron results clearly distinguish between these limiting classifications of the interaction. The presence of two or three Ph rings on the Si atom is of little consequence to the extent of σ and σ^* interaction. The $HSiFPh_2$ complex shows somewhat more charge redistribution to the Si–H σ^* orbital than the $HSiPh_3$ and $HSiHPh_2$ complexes, as evidenced by the slight shifts of the ligand and metal ionizations, and the slightly increased splitting in the metal ionizations. The valence photoelectron ionizations presently are not able to give a more quantitative measure of the charge redistribution. Other studies, such as high-precision XPS measurements, are needed for more information. In any event, the studies in this paper demonstrate that the extent of oxidative addition of the Si–H bond to the metal center is sensitive to the nature of the Si substituents.

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