Notes

Cyclopentadienyl Ring Methylation and Its Effect on Si-H Bond Activation in $(\eta^5\text{-}C_5H_{5-n}(CH_3)_n)Mn(CO)_2HSiH(C_6H_5)_2$ (n = 0, 1, 5) Complexes

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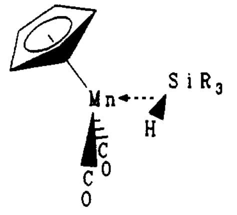
Summary: The He I photoelectron spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiHPh_2$, $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiHPh_2$, and $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_2HSiHPh_2$ (Ph is C_6H_5) are compared to observe the effect of cyclopentadienyl ring methylation on the extent of Si-H bond interaction with the transition metal in these complexes.

Complexes of the general molecular formula $(\eta^5\text{-}C_5R'_5)Mn(CO)(L)HER_3$ (R′ is H, CH_3; L is CO, PMe_3; E is Si, Ge, Sn; R is C_6H_5, Cl) have been studied extensively.[1] The interesting feature of these complexes is the direct interaction of the E-H bond with the transition-metal center. In addition to providing an understanding of the electronic factors of E-H bond activation and oxidative addition to the metal center, these particular complexes are important as models for catalysts in hydrosilation reactions.[2-4] The X-ray and neutron diffraction structures,[1,5-7] ^{29}Si NMR shifts and couplings,[1] reaction chemistry,[8-10] and kinetic studies[11] of these complexes are interpreted in some cases in terms of a three-center two-electron Mn-H-E bond in the complex, as shown in structure A. In other cases, the bonding picture can be interpreted in terms of more complete oxidative addition of the Si-H bond to the metal center to form direct Mn-H and Mn-Si bonds as shown in representation B. The techniques that have been used to study these complexes have not fully characterized the bonding prevalent in the ground state.



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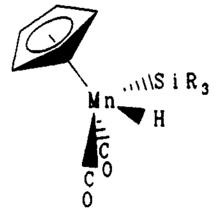

B

Photoelectron spectroscopy studies on these compounds provide more direct information on the bonding.[12] The photoelectron spectra of the trichlorosilyl complexes $CpMn(CO)_2HSiCl_3$ (where Cp is $\eta^5\text{-}C_5H_5$) and $MeCpMn(CO)(PMe_3)HSiCl_3$ (where MeCp is $\eta^5\text{-}C_5H_4CH_3$) have shown these complexes to be most closely represented as Mn(III) species as in representation B.[13,14] This classification is supported by the shifts in the metal-based and ligand-based ionizations from those of the parent tricarbonyl complex and the free ligand, the splitting pattern of the metal ionizations, and the He I/He II ionization intensity characteristics. In contrast, the ionization energy shifts in the case of $MeCpMn(CO)_2HSiPh_3$ (Ph is C_6H_5) and other related phenyl-substituted silyl compounds show these to be best described as Mn(I) systems as in representation A.[15] It is found, as one might expect, that electron-withdrawing groups on silicon and relatively electron donating groups on the metal favor oxidative addition. The substitution of a chlorine for an alkyl on the silicon has a significant effect, driving the addition strongly toward oxidative addition. The substitution of a poor π-accepting phosphine for a carbonyl on the metal is a lesser perturbation, shifting the electron distribution slightly toward oxidative addition but not changing the formal classification of the metal oxidation state.[14]

Methylation of the cyclopentadienyl ring also pushes electron charge density toward the metal center, making it more electron-rich. This might facilitate the breaking of the Si-H bond to give a more complete oxidative addition product as in B. The electronic effects of Cp ring methylation have been studied extensively for $CpMn(CO)_3$.[16] In the photoelectron spectra of these compounds, the Cp e_1'' ring ionizations are destabilized substantially with progressive methylation. The shifts in the valence ionizations are primarily caused by overlap interaction of the e_1'' orbitals of the ring with the methyl group orbitals.[17] For metal ionizations, however, the shift of the ionizations is chiefly due to charge redistribution toward the metal center. Complete methylation of the Cp ring results in a substantial 0.6-eV destabilization of the metal ionizations. Is this destabilization of the metal density sufficient to break the Si-H bond as in representation B in the permethylated complex $C_5Me_5Mn(CO)_2HSiHPh_2$ (C_5Me_5 is $\eta^5\text{-}C_5(CH_3)_5$)?

Structural data[1] and $J_{Si\text{-}H}$ from ^{29}Si NMR[1] on $MeCpMn(CO)_2HSiHPh_2$ and $C_5Me_5Mn(CO)_2HSiHPh_2$

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suggest that three-center two-electron Mn–Si–H bonding as in representation A is retained in these compounds. For instance, the Mn–Si bond lengths in the diphenylsilyl complexes $MeCpMn(CO)_2HSiHPh_2$ and $C_5Me_5Mn(CO)_2HSiHPh_2$ are 0.1 Å longer than the Mn–Si bond length in the trichlorosilyl complex $CpMn(CO)_2HSiCl_3$.[13] This bond length comparison might indicate a weaker metal–silicon bond in the diphenylsilyl complexes, which would tend to classify these as representation A in contrast to the trichlorosilyl complexes, which are best represented as B. However, the additional electron density on the silicon in diphenylsilane in comparison to trichlorosilane may also influence the expectations for normal bond lengths and other properties. The complex $CpMn(CO)_2HSiHPh_2$ is being reported here for the first time, so no similar data for comparison are available for this complex.

The He I photoelectron spectra of $CpMn(CO)_2HSiHPh_2$, $MeCpMn(CO)_2HSiHPh_2$, and $C_5Me_5Mn(CO)_2HSiHPh_2$ are reported here to measure the change in the extent of Si–H bond activation with methylation of the Cp ring. The spectra of the compounds are compared to the spectra of the parent tricarbonyl and the free $HSiHPh_2$ ligand to measure the shift in the metal and ligand-based ionizations. The shift of the ionizations and the splitting pattern of the metal band in the spectra of these compounds give specific information about the extent of Si–H bond activation.

Experimental Section

$MeCpMn(CO)_2HSiHPh_2$ and $C_5Me_5Mn(CO)_2HSiHPh_2$ were prepared by literature methods,[1] and $CpMn(CO)_2HSiHPh_2$ was prepared by an analogous method. All three compounds were characterized by IR spectroscopy. 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.[17-20] The spectrum of $CpMn(CO)_2HSiHPh_2$ was measured at a sample cell temperature of 74 °C. The final step of compound purification was accomplished by fractional sublimation within the instrument, where the identification of volatile components could be monitored. Before the complex sublimed, a spectrum of the free ligand was observed. It was determined that no free ligand was present as the compound itself sublimed, because the peak areas of the ionizations due to this compound are similar to those of $MeCpMn(CO)_2HSiHPh_2$ (where no free-ligand spectrum was observed). The compound sublimes cleanly and is stable in the instrument for a considerable range of temperature. $MeCpMn(CO)_2HSiHPh_2$ was sublimed at a sample cell temperature of 67 °C. At 69 °C, the compound begins to decompose, so care was taken to monitor the temperature. $C_5Me_5Mn(CO)_2HSiHPh_2$ was sublimed at a sample cell temperature of 83 °C. At 84 °C, the compound decomposes, so care should be taken. If one keeps the temperature at 83 °C for a length of time, decomposition slowly begins to build up. It is recommended to take about 40 mg of compound and collect data for 2 h. After that if more data are required, a fresh batch of compound should be loaded. All data collections were repeated at least five times for purposes of examining particular ionization features, and no discernible differences were observed between collections.

The data are represented analytically with the best fit of asymmetric Gaussian peaks (program GFIT).[21,22] 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 a band envelope is about ±5%, with uncertainties introduced from the baseline 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. Although the analytical fits give higher significance to the comparisons that are made, it should be noted that the conclusions of this paper need depend only on features of the ionizations that are observable in the spectra without fitting.

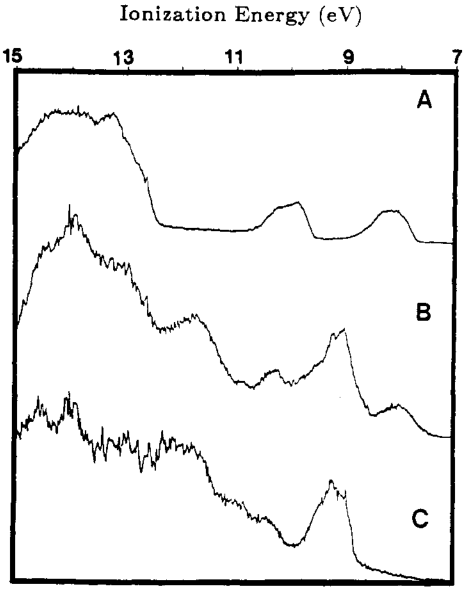

Figure 1. He I photoelectron spectra of (A) $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, (B) $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiHPh_2$, and (C) $HSiHPh_2$.

Results

$CpMn(CO)_2HSiHPh_2$. The HeI valence photoelectron spectrum of $CpMn(CO)_2HSiHPh_2$ is shown in Figure 1. The spectrum is compared to the spectra of $CpMn(CO)_3$ and $HSiHPh_2$. This comparison helps in assigning the ionizations and also in measuring the shift in the metal-based and ligand-based ionizations of this complex compared to the starting tricarbonyl complex and free ligand. The broad band of overlapping ionizations from 12.5 to 15 eV in $CpMn(CO)_2HSiHPh_2$ is due to the carbonyl 5σ and 1π electrons and the Cp a_2'' (π) and σ electrons as well as the ligand σ electrons. Individual assignments in this forest of ionizations are not necessary for the purpose of this study and will not be attempted.

The 7-11-eV region of the spectrum gives specific information on the electron distribution. The ionization at 10.3 eV is due to the Si–C σ electrons and does not shift from its position in the spectrum of the free ligand. The ionizations due to the phenyl π electrons have their most intense ionization peak at 9.0 eV, which is also unshifted from its position in the spectrum of the free ligand. Since the silane ligand-based ionizations of $CpMn(CO)_2HSiHPh_2$ do not shift from their positions for the free ligand, it can be concluded that there is no substantial electron charge shift from the metal to the ligand in this complex.

The Cp e_1'' ring ionizations are observed as a shoulder between 9 and 10 eV on the phenyl π ionization at 9 eV. Because these Cp ionizations are partially masked by the phenyl π ionizations, the shifts in these ionizations will be dealt with only on a semiquantitative basis. It can be said that the Cp ionizations are shifted to lower ionization energy compared to the same ionizations of $CpMn(CO)_3$.

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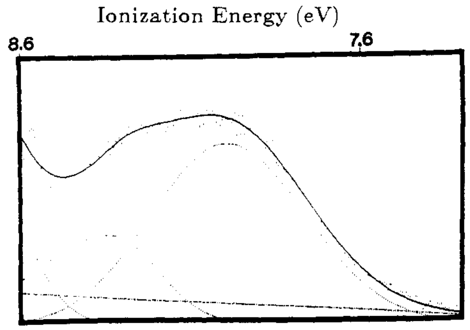

Figure 2. Metal ionization region of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiHPh_2$.

Table I. He I Valence Ionization Features (eV)[a]

complex	position	W_h	W_l	rel area
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	7.99	0.65	0.36	1.00
	8.34	0.65	0.36	0.57
	9.85	0.70	0.33	1.31
	10.25	0.80	0.29	0.56
$(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiHPh_2$	7.99	0.52	0.55	1.00
	8.34	0.52	0.33	0.40
	9.59	0.59	0.34	1.25
	9.95	0.59	0.34	0.62
$(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$	7.90	0.71	0.41	1.00
	8.23	0.71	0.41	0.33
	9.59	0.65	0.42	1.15
	9.99	0.70	0.28	0.61
$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2HSiHPh_2$	7.86	0.41	0.53	1.00
	8.06	0.41	0.53	1.00
	8.36	0.59	0.53	1.19
	9.53	0.42	0.25	3.11
	9.88	0.42	0.25	0.84
$(\eta^5\text{-}C_5Me_5)Mn(CO)_3$	7.52	0.49	0.49	1.00
	7.89	0.55	0.41	0.64
	8.85	0.60	0.40	1.36
	9.26	0.60	0.40	0.53
$(\eta^5\text{-}C_5Me_5)Mn(CO)_2HSiHPh_2$	7.52	0.49	0.49	1.00
	7.92	0.60	0.50	0.48
	8.66	0.60	0.43	1.74
	9.08	0.89	0.40	6.05
	10.36	0.34	0.51	1.22
$HSiHPh_2$	9.03			

[a] Uncertainties are discussed in the Experimental Section.

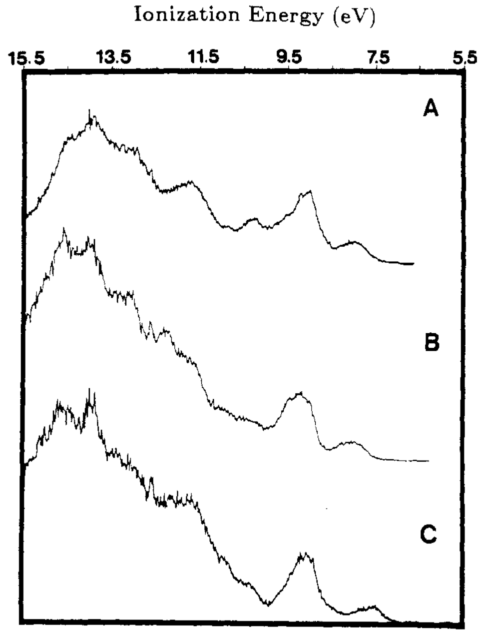

Figure 3. He I 5.5–15.5-eV region of (A) $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiHPh_2$, (B) $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiHPh_2$, and (C) $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_2HSiHPh_2$.

This indicates a more negative metal center than is present in $CpMn(CO)_3$.

The leading edge of the metal ionization band of $CpMn(CO)_2HSiHPh_2$ is destabilized from its position in the spectrum of $CpMn(CO)_3$. Figure 2 shows the analytical representation of the metal close-up region. The metal ionization band is not split to a great extent but is best represented by two peaks in a 1:2 ratio. The vertical ionizations, shapes and relative intensities of the ionizations are compiled in Table I.

$MeCpMn(CO)_2HSiHPh_2$. The He I photoelectron spectrum of $MeCpMn(CO)_2HSiHPh_2$ is shown in Figure 3B. This figure illustrates the comparison of the 5.5–15.5-eV region of all three diphenylsilyl complexes. The Si–C σ ionizations as well as the phenyl π ionizations of $MeCpMn(CO)_2HSiHPh_2$ occur in the same positions as those of the free ligand. The Cp e_1'' ring ionizations are shifted a little to lower binding energy compared to the same ionizations of $CpMn(CO)_2HSiHPh_2$. This small shift is the effect of placing a methyl group on the Cp ring in this complex.

The leading edge of the metal ionization band in $MeCpMn(CO)_2HSiHPh_2$ is shifted 0.13 eV to lower ionization energy compared to that of $CpMn(CO)_2HSiHPh_2$. This is consistent with single methylation of the Cp ring oberved in the tricarbonyl complex. Interestingly, the higher ionization energy edge of the metal band is stabilized 0.03 eV to higher ionization energy compared to that of $CpMn(CO)_2HSiHPh_2$. It is fruitful to compare the metal band widths in $MeCpMn(CO)_2HSiHPh_2$ and $CpMn(CO)_2HSiHPh_2$. The metal band in $CpMn(CO)_2HSiHPh_2$ is 0.65 ± 0.02 eV wide, whereas the metal band in $MeCpMn(CO)_2HSiHPh_2$ is 0.80 ± 0.02 eV wide. Thus the metal ionization band width is 0.15 eV greater for the MeCp complex than for the Cp complex. This is important for interpreting the trend toward donation from the metal to the silyl σ^* and the extent of oxidative addition. The metal ionization band in $MeCpMn(CO)_2HSiHPh_2$ is best represented by the fit of three asymmetric Gaussian peaks. The difference between the highest and lowest ionization energy bands in this region is also 0.15 eV greater for the MeCp complex than for the Cp complex.

In comparison to the parent tricarbonyl complex $MeCpMn(CO)_3$, the Cp e_1'' and metal ionizations of $MeCpMn(CO)_2HSiHPh_2$ are shifted very slightly to lower ionization energy. The metal center is not gaining as much negative charge when $HSiHPh_2$ replaces CO in this case as in $CpMn(CO)_3$ to $CpMn(CO)_2HSiHPh_2$. The leading peak of the metal ionization band in $MeCpMn(CO)_2HSiHPh_2$ is destabilized only 0.04 eV from that of $MeCpMn(CO)_3$. The higher ionization energy peak of the metal band in $MeCpMn(CO)_2HSiHPh_2$, however, is 0.13 eV stabilized from its position in the spectrum of $MeCpMn(CO)_3$.

$C_5Me_5Mn(CO)_2HSiHPh_2$. The He I valence photoelectron spectrum of $C_5Me_5Mn(CO)_2HSiHPh_2$ is shown in Figure 4. It is also compared to the spectra of $C_5Me_5Mn(CO)_3$ and $HSiHPh_2$ for indication of the shifts in the metal-based and ligand-based ionizations in the complex. The region of interest is from 7 to 11 eV, which shows the shifts of the Cp e_1'' ionizations, the Ph π ionizations, and the metal ionizations.

The Si–C σ and phenyl π ionizations of the complex are shifted very slightly to higher ionization energy compared to their positions in the spectrum of the free ligand. The Cp e_1'' ionizations in $C_5Me_5Mn(CO)_2HSiHPh_2$ are assigned to the lower ionization edge of the phenyl π band. The assignment is based on previous studies that show that

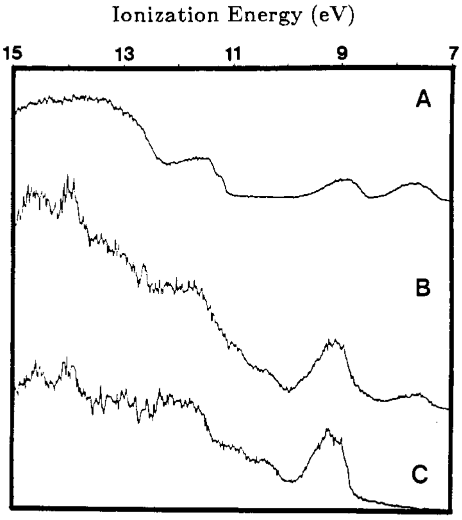

Figure 4. He I photoelectron spectra of (A) (η^5-$C_5(CH_3)_5$)Mn($CO)_3$, (B) (η^5-$C_5(CH_3)_5$)Mn$(CO)_2$HSiHPh$_2$, and (C) HSiHPh$_2$.

these ionizations are destabilized 1.2 eV with permethylation.[17] These ionizations are shifted slightly to lower ionization energy from their position in $C_5Me_5Mn(CO)_3$. This is indicative of a more negative metal center in the complex compared to the parent tricarbonyl complex.

The most significant observations concern the metal-based ionizations. The metal ionization band of the complex can be represented analytically with the fit of two asymmetric Gaussian peaks in a 1:2 ratio. The lower ionization energy peak of the metal band is unshifted from its position in the spectrum of $C_5Me_5Mn(CO)_3$ and the higher ionization energy peak of the metal band is only a little stabilized (0.03 eV) from its position in the spectrum of $C_5Me_5Mn(CO)_3$. Most importantly, the overall width of the metal ionization band is smaller than the widths of the metal bands of the Cp and MeCp derivatives (0.61 ± 0.02 eV in this case). This leads to interesting conclusions as described in the next section.

Discussion

The symmetry interactions of the Si–H bond with the metal have been discussed previously.[13,15] These interactions are commonly presented in terms of the Si–H σ and σ^* orbital interactions with the metal center.[13,23] The donation of electron density from the Si–H σ-bonding orbital into the empty metal orbitals results in the formation of a three-center two-electron bond that is depicted by the valence bond representation A. Studies of systems that involve donation of an E–H bond to the metal center have shown that this interaction produces very little shift of the metal-based ionizations.[15,23] The σ^* interaction involves the donation of electron density from a filled metal orbital into the E–H σ^* orbital. This interaction stabilizes one metal-based ionization with respect to the others. When donation from the metal to the σ^* is extensive, the ionization can become considerably ligand-based. If this is the case, the metal has formally lost an electron pair to the ligand as indicated by the character of the ionizations. For these complexes, the formal d^6 electron count at the metal becomes d^4, and the formal oxidation state at the metal has increased by two. This oxidative addition to the metal corresponds to the formation of direct M–H and M–E bonds as depicted in the valence bond representation B. This interaction also produces a stabilization of the metal-based ionizations and a destabilization of the ligand-based ionizations in the photoelectron spectrum.

Electronic Effects of Permethylation on Si–H Bond Activation. From the information in the photoelectron spectra, CpMn$(CO)_2$HSiHPh$_2$ and MeCpMn$(CO)_2$HSiHPh$_2$ are best described as Mn(I) d^6 systems corresponding to representation A. The extent of donation from the metal to the Si–H σ^* orbital is more in the MeCp complex than in its Cp analogue but not enough to change the general classification of the bonding. These conclusions are supported by the following observations:

1. In the photoelectron spectra of CpMn$(CO)_2$HSiHPh$_2$ and MeCpMn$(CO)_2$HSiHPh$_2$ reported here, the Si–C σ and phenyl π ionizations have not shifted from their positions in the spectrum of the free ligand. In contrast, in our study of CpMn$(CO)_2$HSiCl$_3$, the Cl lone pair ionizations are destabilized 1 eV from their position in free HSiCl$_3$. This was one of the evidences for CpMn$(CO)_2$HSiCl$_3$ being a more complete oxidative addition product.[13] In our previous study of MeCpMn$(CO)_2$HSiPh$_3$, the phenyl π ionizations also were unshifted from their position in the free ligand. This corresponds most closely to a Mn(I) d^6 system.[15] The lack of shift of the silane ligand-based ionizations in the complexes indicates that there is no substantial electron charge shift from the metal to the ligand. There is still some donation from the metal to the Si–H σ^* orbital, because the stabilization of ligand ionizations from donation of electrons from the Si–H σ orbital to the metal and the positive charge at the metal must be balanced by destabilization from electrons accepted by the Si–H σ^* orbital. However, donation into the Si–H σ^* orbital is not dominant.

2. The Cp ring ionizations are destabilized in the metal–silane complexes in comparison to the CpMn$(CO)_3$ system. This indicates a more negative metal center in the silane complexes. If σ donation from CO to the metal is assumed to be similar in magnitude to that from the silane, then the Si–H σ^* orbital is not removing as much electron density as the two CO π^* orbitals that it replaces.

3. The metal ionizations are not significantly split and are not substantially stabilized from their positions in the parent tricarbonyl complexes. In the spectrum of CpMn$(CO)_2$HSiCl$_3$, the metal ionizations are stabilized 0.6 eV from their position in CpMn$(CO)_3$. In CpMn$(CO)_2$HSiHPh$_2$, the lower ionization edge of the metal band is destabilized compared to CpMn$(CO)_3$. This is direct evidence of a more negative metal center in the diphenylsilane complex. The higher ionization energy peak of the metal band in MeCpMn$(CO)_2$HSiHPh$_2$ is 0.13 eV stabilized from its position in MeCpMn$(CO)_3$. This is evidence of some σ^* interaction coming into play. Due to more electron donation from the Cp e_1'' orbitals (because of the methyl group on the Cp ring) there is more negative charge on the metal center. Some of this negative charge is transferred to the Si–H σ^* orbital through the σ^* interaction. This appears in the photoelectron spectrum in the form of a metal ionization stabilized by 0.13 eV as a result of σ^* interaction. The broader metal region observed for the silyl complexes as compared to the metal tricarbonyl complexes indicates that the one Si–H σ^* orbital accepts electron density better than one CO π^* orbital.

4. The width of the metal bands in CpMn$(CO)_2$HSiHPh$_2$ and its MeCp analogue indicates the extent of σ^* interaction in the two complexes. The wider metal band indicates greater σ^* interaction since one of the metal

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ionizations is being more stabilized. The metal band in $MeCpMn(CO)_2HSiHPh_2$ is ≈0.15 eV wider than its Cp analogue, indicating greater σ^* interaction. This is expected because of the more electron-rich metal center in the MeCp complex compared to its Cp analogue.

Steric versus Electronic Effects of Cp Permethylation on Si-H Bond Activation. Permethylation of the Cp ring substantially increases the availability of electron charge density from the metal center and should facilitate donation to the Si-H σ^* orbital. It is found, however, that Si-H σ^* interaction with the metal center is less in $C_5Me_5Mn(CO)_2HSiHPh_2$ than in the Cp and MeCp derivatives. This is evidenced by the following observations in the photoelectron spectrum of $C_5Me_5Mn(CO)_2HSiHPh_2$:

1. The Si-C σ and phenyl π ionizations are stabilized (0.1 ± 0.02 eV) from their position in the spectrum of the free ligand. The slight stabilization of these ionizations is an indication of σ donation of electron density from the Si-H σ orbital to the metal center that is not balanced by back donation from the metal to the ligand as in the Cp and MeCp cases.

2. The C_5Me_5 e_1'' ring ionizations are destabilized from their position in the spectrum of the parent tricarbonyl complex, indicating a more negative metal center. If σ donation from CO to the metal is assumed to be similar in magnitude to that of the silane, then the Si-H σ^* orbital is not removing as much electron density as the two CO π^* orbitals.

3. Most significantly, the metal band in $C_5Me_5Mn(CO)_2HSiHPh_2$ is narrower than those in the Cp and MeCp derivatives. On going from the Cp complex to the MeCp complex, the width of the metal band increases by ≈0.15 eV. This is attributed to the slightly greater σ^* interaction prevalent in the MeCp derivative due to more available electron density on the metal. In the absence of other effects, this trend of increasing width of the metal ionization band with increasing electron richness at the metal center is expected to continue with $C_5Me_5Mn(CO)_2HSiHPh_2$. Instead, $C_5Me_5Mn(CO)_2HSiHPh_2$ has the narrowest metal band (0.61 eV), indicating the smallest interaction with the Si-H σ^* orbital.

Schubert et al. have also concluded that there is a smaller Si-H σ^* interaction in the $C_5Me_5Mn(CO)_2HSiHPh_2$ complex compared to its MeCp derivative. Their conclusion is based partly on measurements of J_{Si-H}, the Si-H coupling constant from ^{29}Si NMR of these complexes. $C_5Me_5Mn(CO)_2HSiHPh_2$ has a 2 Hz higher coupling constant than its MeCp derivative, which is interpreted as a very slightly stronger Si-H bond.[1] $C_5Me_5Mn(CO)_2HSiHPh_2$ also has a 0.03 Å longer Mn-Si length than its MeCp derivative, which is interpreted as a weaker Mn-Si bond. However, as mentioned in the introduction, the lack of knowledge of the direct charge effects on these relative small differences places some uncertainty on the conclusion of weaker Si-H σ^* interaction from these comparisons. In this photoelectron study, the charge effects contribute directly to the trends in the ionizations, and the photoelectron results support the conclusion of decreased metal donation to the Si-H σ^* orbital.

The decreased donation to the Si-H σ^* orbital in the permethylated complex, in spite of increased electron richness at the metal center, is likely due to the steric bulk of the C_5Me_5 ligand. The C_5Me_5 may obstruct the addition of the silane to the metal center from achieving the optimum geometry for donation to the Si-H σ^* orbital. Although some of the key bond distances for structural comparison of the C_5Me_5 complex with the MeCp complex have been reported as cited above, a detailed structural comparison of the two complexes for purposes of identifying the steric interaction is not possible because of disorder in the crystal of the MeCp complex.[24] However, an excellent structure of the closely related $MeCpMn(CO)_2HSiFPh_2$ complex has been reported[6] that shows many similarities to the $MeCpMn(CO)_2HSiHPh_2$ complex. For instance, the Mn-Si distance is 0.04 Å longer in the C_5Me_5 complex than in this particular MeCp complex, and the Si-H distance (by neutron diffraction) is 0.03 Å shorter in the C_5Me_5 complex. Both of these distances can be interpreted as a weaker interaction of the Si-H bond with metal in the C_5Me_5 complex. The greatest difference between the two structures is the Cp(centroid)-Mn-Si angle. This angle increases from 115.6° in the MeCp structure to 124.8° in the C_5Me_5 structure, indicating a strong steric interaction between the diphenylsilyl ligand and the C_5Me_5 ring. The Mn-H-Si angle also increases from 88.2° to 93°. It appears in this case that the steric effect dominates over the electronic effects in determining the extent of Si-H bond addition to the metal center.

The primary results from this study show that methylation of the Cp ring has only a relatively small effect on the extent of the Si-H bond addition to the metal center in these diphenylsilyl complexes. These effects, although subtle, are observed in the photoelectron ionizations. All of the complexes remain classified as formally d^6 Mn(I) complexes with three-center two-electron Mn-H-Si interactions. Donation from the metal to the Si-H σ^* orbital, which is on the path to oxidative addition, is not dominant. In comparison to previous studies on $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_3$[13,14] and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2HSiPh_3$,[15] these studies show that the alkyl and halogen substitutions on silicon have greater control than cyclopentadienyl ring methylation on the extent of addition of the Si-H bond to the metal center.

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