

between atoms in bonds.³² Orbital σ_3 has nodes between atom pairs 1 and 2 and pairs 3 and 4, and the 2-3 interaction is bonding, again different from the 5c scheme. Thus we would expect the 4c hypervalent bond to be significantly weaker than the 3c or 5c hypervalent bonds. In the 4c bond, nodes occur between atoms in the occupied orbitals whereas, in the 3c and 5c bond, nodes occur at atoms in these orbitals.

The above simple model assumes that the atoms are of equal electronegativity. However, in $[\text{FKrNCH}]^+$ the atoms are clearly not of equal electronegativity. Furthermore, the C-H bond is of the right energy for mixing, which complicates the analysis. The presence of a triple bond between C and N is also a complicating factor, as this increases the s component (sp hybridization) in the C-N σ bond, which would be part of the 4c hypervalent bond. Examination of Figure 1 shows that the orbitals do not delocalize as extensively as suggested by our model for the 4c hypervalent bond due to the large electronegativity differences. Furthermore, the s and p orbitals are clearly mixed. The highest occupied σ orbital, σ_6 , is similar to orbital σ_2' of the 4c bond with the largest population on N and the next highest population on F. Because of the large s character in the CN σ bond, this orbital is very low in energy and the C-H σ bond mixes with the Kr-F σ bond instead of mixing with the C-N σ bond as one would expect from the 4c hypervalent bond. The CN σ bond is mixing, instead, with the

Kr valence s orbital. Thus the bonding of the σ_1' orbital of the 4c bond is dispersed over a range of σ orbitals.

Another model for this bonding would involve considering both the C-N and C-H bonds as "spectators" and dealing only with a normal 3c,4e hypervalent bond centered at Kr based on the Kr-F σ bond and the lone pair on N. In this case, σ_6 of $[\text{FKrNCH}]^+$ is like σ_2'' of the 3c,4e bond. There is essentially a node at Kr, and the population is not equally distributed between N and F. The σ_4 orbital of the complex then corresponds to σ_1'' of the 3c,4e bond. A complication for this model is that the 3c,4e bond preferentially places the least electronegative atom in the center. Clearly, Kr^{+4} is not the least electronegative atom. In order for it to lower its electronegativity in order to participate in the hypervalent bond, charge transfer occurs from the C-H region to the Kr to lower its positive charge and hence its electronegativity. This is actually observed in the population analysis and is consistent with the resonance structure shown above.

All of our results are consistent with some type of covalent bonding interaction in $[\text{FKrNCH}]^+$ being present. However, as the above discussion points out, there is no clear choice between the 3c and 4c hypervalent bond models. Rather, the bonding description for the interaction of $[\text{FKr}]^+$ with NCH has components of both models present. The results do show that the bonding between Kr and N is not a simple covalent σ bond between two centers but rather is best described in terms of hypervalent bonds.

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Electronic Structure Factors of Si-H Bond Activation by Transition Metals. Valence Photoelectron Spectra of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ (Me = CH₃, Ph = C₆H₅)

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The valence photoelectron spectra of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{L})\text{HSiCl}_3$ and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{L})\text{HSiHPh}_2$, where L is CO or $\text{P}(\text{CH}_3)_3$, are compared to determine the effect of ligand substitution at the metal center on Si-H bond activation. Metal centers that are more electron rich may promote more complete oxidative addition of the Si-H bond to the metal. The shifts in the metal and ligand ionization energies and the relative intensities of ionizations in the He I and He II photoelectron experiments show that the metal in $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ is best represented by a formal oxidation state of III (d⁴ electron count). This indicates nearly complete oxidative addition of the Si-H bond to the metal center and results in independent Mn-H and Mn-Si bonds. In contrast, the splitting and intensity pattern of the metal-based ionizations of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ reflect the formal d⁶ electron count of a metal corresponding to oxidation state I. The extent of electron charge density shift from the metal to the ligand is also small, as evidenced by the negligible shifts of these ionizations from those of the related $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2(\text{PMe}_3)$ complex. These observations indicate that the electronic structure of the Si-H interaction with the metal in this complex is in the initial stages of Si-H bond addition to the metal, before oxidative addition has become prevalent. Comparison with the previously reported photoelectron spectra of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{HSiCl}_3$ and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2\text{HSiHPh}_2$ shows that the Si-H bond interaction with the transition metal is affected more by alkyl and halogen substitutions on silicon than by substitution of a carbonyl with typical two-electron donor ligands at the metal center.

Introduction

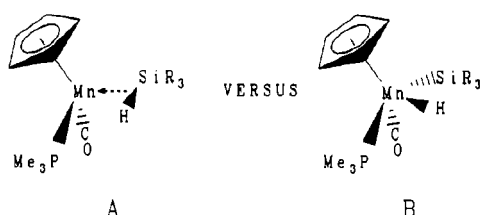
Studies of complexes with the general molecular formula $(\eta^5\text{-C}_5\text{R}'_5)\text{Mn}(\text{CO})(\text{L})\text{HER}_3$ (R' = H, CH₃; L = CO, PMe_3 ; E = Si, Ge, Sn; R = Ph, Cl) have provided a wealth of information on different stages of interaction of an E-H bond with a metal center.¹ In addition to contributing to an understanding of the electronic factors of general E-H bond activation and oxidative addition to a metal center, the complexes are important as models for catalysts in hydrosilation reactions.² The X-ray and neutron diffraction structures,^{1,3-5} ²⁹Si NMR shifts and couplings,¹ and

reaction chemistry⁶⁻⁸ and rates⁹ of these complexes are interpreted in some cases in terms of a three-center-two-electron Mn←H-E

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bond in the complex, as represented schematically in A. In other



cases an interpretation 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, is more consistent with the observations. The implications from these techniques are in many instances ambiguous or confusing because the observations are not directly and solely related to the ground-state bonding and electronic structure.

Photoelectron spectroscopy of these compounds provides more direct information on the electron distribution and bonding with the metal center.¹⁰ For example, the destabilization of the ligand-based ionizations, stabilization of the metal-based ionizations, and He I/He II intensity variations observed in the valence photoelectron spectrum of CpMn(CO)₂HSiCl₃ (Cp = η⁵-C₅H₅) showed this complex to be a formally d⁴ Mn(III) system resulting from nearly complete oxidative addition of the Si-H bond to the metal, as in representation B.¹¹ In contrast, a similar study of CpMn(CO)₂HSiHPh₂, MeCpMn(CO)₂HSiHPh₂, MeCpMn(CO)₂HSiPh₃, and MeCpMn(CO)₂HSiFPh₂ showed these complexes to be formally d⁶ Mn(I) systems in which the Si-H bond acts more like a two-electron donor to the metal as in representation A, with strong synergistic back-bonding into the Si-H σ* orbital.¹² The nature of the Si substituents plays a large role in controlling the extent of Si-H bond addition to the transition-metal center in these complexes. Electron-withdrawing substituents on silicon tend to favor more complete oxidative addition.

Substitutions of ligands around the metal center should also have some effect on the extent of Si-H bond addition to the metal center. It is anticipated that metal centers that are more electron rich should favor more complete oxidative addition. Substitution of a carbonyl on the metal with a trialkylphosphine ligand is one way to increase the availability of electron density on the metal center, because the phosphine is a poorer π-electron acceptor than carbonyl. We and others have studied the effects of this substitution on the photoelectron spectra of metal carbonyl complexes.¹³ In the case of phosphine substitution into the CpMn(CO)₃ system, the metal orbitals are substantially destabilized by the reduced back-bonding to the ligand and the additional electron density on the metal center.¹⁴ To what extent does this phosphine substitution influence the oxidative addition of the Si-H bond to the metal center?

The complexes MeCpMn(CO)(PMe₃)HSiCl₃ and MeCpMn(CO)(PMe₃)HSiHPh₂ have been studied by X-ray crystallography and ²⁹Si NMR spectroscopy. X-ray crystallographic studies on MeCpMn(CO)(PMe₃)HSiHPh₂ and MeCp(CO)₂MnHSiHPh₂ show that the structures are very similar in all details,¹ including the length of the coordinated Si-H bond and its orientation with respect to the Mn(CO)₂ and Mn(CO)(PMe₃) bonds. The only possibly significant difference is the 3.7 pm shorter Mn-Si bond length in the phosphine complex, but Schubert points out that the influence of the PMe₃ ligand on the bonding radius of Mn and how this affects the Mn-Si bond length are not known, so the actual Si-H bonding interaction cannot be estimated from

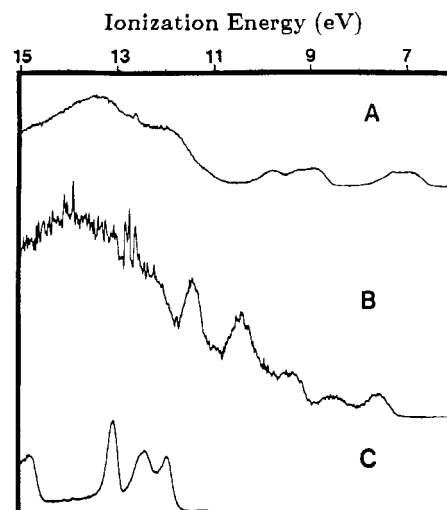


Figure 1. He I valence photoelectron spectra of (A) (η⁵-C₅H₄CH₃)Mn(CO)₂PMe₃, (B) (η⁵-C₅H₄CH₃)Mn(CO)(PMe₃)HSiCl₃, and (C) HSiCl₃.

structural studies. The Si-H coupling constants, *J*_{Si-H}, obtained from ²⁹Si NMR spectra are smaller in the phosphine complexes compared to their dicarbonyl derivatives.¹ This has been interpreted as an indication that the Si-H bond has proceeded to a greater extent of oxidative addition in the phosphine complexes than in the dicarbonyl derivatives. Kinetic investigations on MeCpMn(CO)(PMe₃)HSiHPh₂ reveal that H₂SiPh₂ is substituted readily by a phosphine as in MeCpMn(CO)₂HSiHPh₂ systems, suggesting the presence of a relatively weak three-center-two-electron Mn←H-E bond. However, substitution in MeCpMn(CO)(PMe₃)HSiHPh₂ is 10³ times slower than in MeCpMn(CO)₂HSiHPh₂,¹⁵ another indication that oxidative addition has proceeded to a greater extent in the phosphine compound.

To characterize more directly the nature of the Si-H bond interaction with the transition metal in the phosphine complexes, the He I and He II spectra of MeCpMn(CO)(PMe₃)HSiCl₃ and the He I spectrum of MeCpMn(CO)(PMe₃)HSiHPh₂ are reported. The metal and ligand valence ionizations of these complexes are compared to those of CpMn(CO)₂HSiCl₃ and MeCpMn(CO)₂HSiHPh₂ to obtain a measure of the effect of the phosphine ligand on the extent of interaction of the Si-H bond with the transition metal.

Experimental Section

MeCpMn(CO)(PMe₃)HSiCl₃ and MeCpMn(CO)(PMe₃)HSiHPh₂ were prepared by literature methods.¹⁵ 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.¹⁶⁻¹⁹ The spectrum of MeCpMn(CO)(PMe₃)HSiCl₃ was measured at a sample cell temperature of 108 °C for He I measurements and 114 °C for He II measurements. The compound sublimates cleanly in the instrument with no decomposition. MeCpMn(CO)(PMe₃)HSiHPh₂ was sublimed at a sample cell temperature of 99 °C. A small amount of decomposition over time was evidenced by the observation of free ligand ionizations. In the close-up spectrum of the metal band, there is also some evidence of a decomposition product on the lower binding energy side of the band. This is most likely due to the complex decomposing to give MeCpMn(CO)₂PMe₃ and free silane. The small amount of decomposition evident in the spectrum is not sufficient to influence the conclusions. He II studies on this compound were not attempted because of the moderate signal-to-noise ratio in the He I spectrum of this compound and also because of this tendency of the compound to decompose after some time. All data collections were

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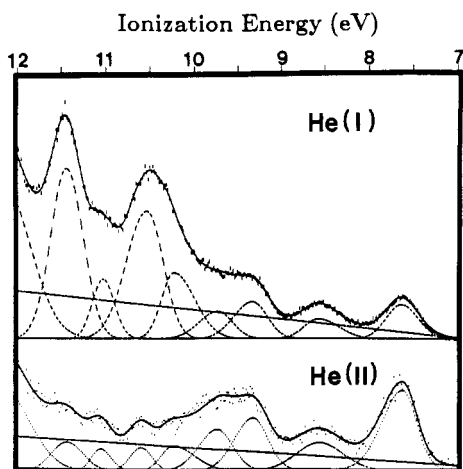


Figure 2. He I/He II spectral comparison of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$.

repeated at least five times for purposes of examining particular ionization features, and no discernable differences were observed between collections.

The data are represented analytically with asymmetric Gaussian peaks (program GFIT).²⁰ The asymmetric Gaussian peaks are defined by 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 $\pm 5\%$, with uncertainties introduced from subtracting the base line 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.

Results

MeCpMn(CO)(PMe₃)HSiCl₃. The He I photoelectron spectrum of MeCpMn(CO)(PMe₃)HSiCl₃ is shown in Figure 1. It is compared to the photoelectron spectra of MeCpMn(CO)₂PMe₃ and HSiCl₃, the free ligand, to help illustrate the assignments and shifts of the metal-based and ligand-based ionizations. The ionizations from 12 to 15.5 eV are due to the carbonyl 5σ and 1π electrons and the Cp a_2'' (symmetric π) and valence σ electrons. Individual assignments in this forest of ionizations of these complexes will not be attempted.

Figure 2 shows the low binding energy valence ionizations of MeCpMn(CO)(PMe₃)HSiCl₃ in greater detail. The analytical representations of the valence ionizations of all the complexes in this study are collected in Table I. Table I also lists the primary metal or ligand character associated with each ionization, as indicated by the photoelectron data. The identification of these characters is clarified in the following discussion.

It is helpful first to examine the ionizations of the free HSiCl₃ molecule. An assignment of the valence ionizations of the HSiCl₃ molecule has been reported previously.¹¹ The ionizations of HSiCl₃ in the region from 12 to 13 eV are due primarily to the ionizations of the Cl lone pairs, as is observed in the photoelectron spectrum of SiCl₄.²¹ The six chlorine ($p\pi$) lone pairs form symmetry combinations that are comprised of a_2 , a_1 , and two e sets. The a_2 combination has been assigned to the ionization at 11.95 eV, the first e set has been assigned to the 12.39-eV ionization, and the second e set has been assigned to the ionization at 13.07 eV. The a_1 combination has been assigned to a shoulder at 12.6 eV on the first e ionization. The ionizations in the range 14–15 eV correspond to the Si–Cl σ ionizations. The position of the Si–H ionization is not certain but most likely contributes to the high binding energy side of the Si–Cl σ ionizations at 14.8 eV, with some mixing into the a_1 ionization at 12.6 eV.

The relative intensity pattern and splitting of the chlorine lone pair ionizations of MeCpMn(CO)(PMe₃)HSiCl₃ are very similar

Table I. He I Valence Ionization Features

complex	primary character	position	W_h	W_l	rel area
MeCpMn(CO) ₂ PMe ₃	M1	6.94	0.67	0.49	1.00
	M2	7.32	0.67	0.24	0.44
	Cp	8.87	0.54	0.37	1.02
	Cp	9.30	0.54	0.37	0.71
CpMn(CO) ₂ HSiCl ₃	P	9.79	0.58	0.35	0.85
	M1	8.69	0.55	0.51	1.00
	ML	9.32	0.55	0.51	0.59
	Cp	10.27	0.59	0.34	1.33
	Cp	10.66	0.59	0.34	0.79
	Cl	10.95	0.33	0.41	2.40
MeCpMn(CO)(PMe ₃)-HSiCl ₃	Cl	11.59	0.33	0.41	2.30
	Cl	12.04	0.46	0.37	4.39
	M1	7.64	0.41	0.46	1.00
	ML	8.57	0.39	0.54	0.62
	Cp	9.34	0.50	0.41	1.12
	Cp	9.74	0.50	0.41	0.83
	P	10.24	0.32	0.56	1.93
	Cl	10.54	0.55	0.43	4.14
	Cl	11.04	0.28	0.31	1.17
	Cl	11.44	0.43	0.42	4.86
HSiCl ₃	Cl	11.95	0.37	0.21	0.73
	Cl	12.39	0.32	0.33	0.72
	Cl	12.62	0.32	0.33	0.37
	Cl	13.07	0.28	0.18	1.00
MeCpMn(CO) ₂ HSiHPh ₂	M1	7.86	0.41	0.53	1.00
	M2	8.06	0.41	0.53	1.00
	M3	8.36	0.59	0.53	1.19
	Ph	9.01	0.40	0.34	4.77
MeCpMn(CO)(PMe ₃)-HSiHPh ₂	M1	6.90	0.49	0.55	1.00
	M2	7.38	0.49	0.55	0.50
HSiHPh ₂	Ph	8.8 ^a			
	Ph	9.03 ^a			

^aUncertainty 0.05 eV.

to those of HSiCl₃. However, they are shifted ≈ 1.6 eV to lower ionization energy in the metal complex. The a_2 ionization overlaps with the e ionization in the band at 10.54 eV. The second e combination is observed at 11.44 eV. The a_1 combination is observed as a weak ionization at 11.04 eV in the He I spectrum. This ionization is observed more clearly in the He II spectrum, where its intensity relative to the other chlorine lone pair ionizations is slightly enhanced.

The band at 9.3 eV is labeled "Cp" in Table I because it correlates with the predominantly Cp e_1'' ring ionizations. The shoulder on the high binding energy side of this band is characteristic of Cp e_1'' ionizations, as has been discussed in previous studies of similar complexes.¹⁶ The numbers in Table I show that the Cp ionizations in MeCpMn(CO)(PMe₃)HSiCl₃ are shifted 0.4 eV to higher binding energy compared to the Cp ionizations in MeCpMn(CO)₂PMe₃. This shift to higher binding energy is indicative of a more positive metal center in the metal–silyl complex compared to MeCpMn(CO)₂PMe₃. The ionization at 10.2 eV is probably due to the metal–phosphorus σ electrons (labeled "P" in Table I). The corresponding ionization of MeCpMn(CO)₂PMe₃ occurs at 9.79 eV. Thus, this ionization shifts the same amount as the Cp ionizations between these two complexes. The position of the Mn–H ionization cannot be exactly ascertained but probably occurs in the 9.5–10.5-eV region.

The first ionization band (labeled M1 in Table I) of MeCpMn(CO)(PMe₃)HSiCl₃ is well separated from the second ionization (labeled ML) and is approximately twice as intense. The "M" designation is used in the label because these ionizations derive from the formal d^6 configuration of the parent tricarbonyl complex, with four metal-based electrons represented by the first ionization and the other two electrons represented by the second ionization. The second ionization is labeled "ML" because our previous studies have shown that this ionization may be associated with predominant ligand character in these complexes, depending on the silane.^{11,12} The determination of predominant ligand or metal character in the second ionization is important to the un-

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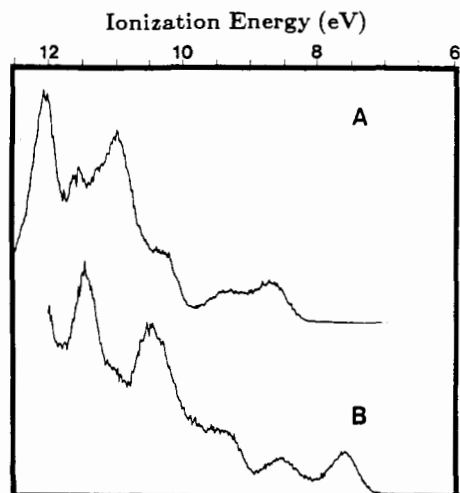


Figure 3. He I photoelectron spectra in the 6–12.5-eV region of (A) $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{HSiCl}_3$ and (B) $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$.

Understanding of the electron distribution and bonding in these complexes. The large separation between the M1 and ML ionizations of this complex is one indication of strong ligand effects. The leading ionization band in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ (M1) occurs 0.7 eV higher binding energy compared to its position in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$ (M1), indicating a more positive metal center in the silyl complex. The second ionization band (ML) is stabilized more (1.25 eV) from the corresponding ionization of $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$ (M2), indicating that the silyl substitution is providing additional stabilization to this level beyond a simple charge effect.

Figure 2 shows the He I/He II comparison of the 7–12-eV region of $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$. The bands due to the Si–Cl and Cl lone pair electrons (10–12 eV) show negligible intensity in the He II spectrum. This is because of the relatively low He II ionization cross sections of the Cl orbitals. According to calculations, the Cl 3p photoionization cross section falls by a factor of 20, while carbon falls by a factor of 3 on going from He I to He II.²² The Cp ionization band therefore gains intensity relative to the Cl lone pair ionizations in the He II spectrum. The Mn 3d photoionization cross section is calculated to increase from He I to He II excitation,²² and the first ionization band (M1) grows substantially relative to all other ionizations with He II excitation. The intensity of this band indicates that it represents predominantly 3d electrons. The second ionization band (ML) shows relatively little growth from He I to He II excitation compared with the leading metal band and is therefore ligand-based.

The valence photoelectron spectra of $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ and $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$ are compared in Figure 3. All of the valence ionizations are shifted to lower binding energy when a phosphine replaces a CO on the metal. The magnitudes of the shifts approximately follow the proximity of the ionizations to the metal centers. The leading ionization band (M1) occurs 1.1 eV to lower binding energy from its position in $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. The Cp ionizations are shifted about 1 eV to lower ionization energies from their positions in $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. The metal and Cp ionizations generally shift by nearly the same amount with substitutions at the metal center,²³ and the shifts observed here indicate that $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ has a more negative metal center than $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. The Cl lone pair ionizations in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ are shifted by ≈ 0.6 eV to lower ionization energies from their position in CpMn -

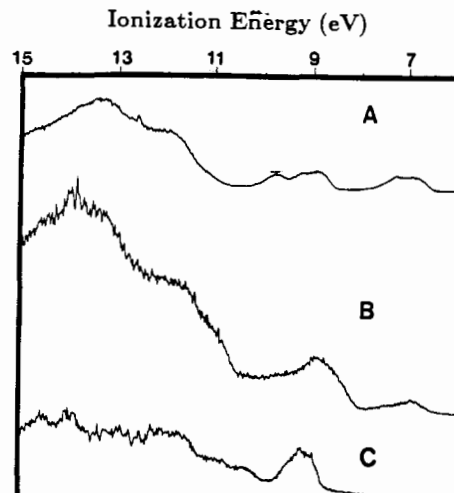


Figure 4. He I valence photoelectron spectra of (A) $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2\text{PMe}_3$, (B) $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$, and (C) HSiHPh_2 .

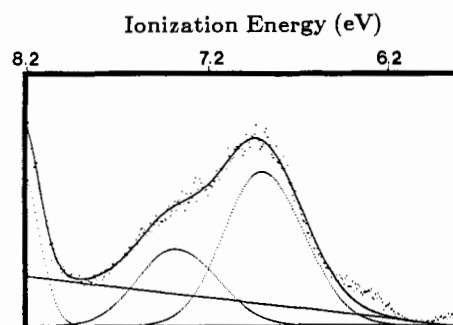


Figure 5. "Metal" ionization region of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$.

$(\text{CO})_2\text{HSiCl}_3$. The second leading ionization band (ML) is 0.8 eV destabilized from its position in $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. The observation that the second ionization band (ML) shifts less than the first (M1) shows again that the second ionization is more ligand-based.

$\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$. The He I valence photoelectron spectrum of $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ is shown in Figure 4. As before, the spectrum is compared with the spectra of $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$ and HSiHPh_2 , the free ligand. The Si–C σ ionizations are buried under a broad band of overlapping ionizations from 9.5 to 11 eV. The most intense peak of the silane ionizations is the phenyl π ionizations (Ph), which occur at 8.8 ± 0.05 eV. This ionization is ≈ 0.2 eV destabilized from its position in the free ligand and indicates some electron charge transfer from the metal to the ligand but not to as great an extent as was observed in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$. The ionizations due to the Cp e_1'' ring electrons also lie in the region of overlapping ionizations from 9 to 11 eV and are not clearly observed.

The metal ionization region is most informative. The metal ionization region does not show two well-separated peaks as in the case of the HSiCl_3 complexes. Instead, a broad asymmetric band is observed that is most simply represented by two asymmetric Gaussian peaks that have areas in the ratio 2:1 (first: second), as shown in Figure 5. This band conforms to expectations for the ionization of six metal-based electrons. The low ionization energy side of the metal band (M1) is slightly destabilized from its position in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$ while the higher ionization energy side of the metal band (M2) is slightly stabilized. As a result, the overall band in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ is about 0.1 eV wider than the band in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$, but it has not shifted significantly.

Figure 6 compares the 6–15-eV spectral region of $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$ and $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ in order to gauge the effect of CO/PMe₃ substitution on the valence ioni-

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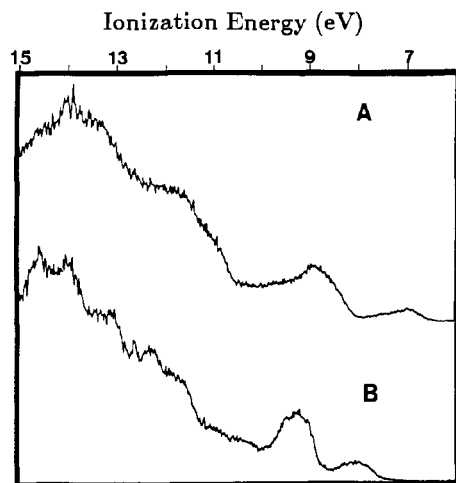


Figure 6. He I valence spectral comparison of (A) $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ and (B) $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2\text{HSiHPh}_2$.

zations. The phenyl π ionizations in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ are also 0.2 eV destabilized from their position in $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$. The leading metal band in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ is shifted 1 eV to lower ionization energy from its position in $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$.

Si-H Orbital Interactions with the Metals

The shifts in ionization energies and changes in character that occur when one ligand is substituted for another in a metal complex provide specific information about the electronic structure interactions of the ligands with the metal. In a sense, the metal fragment orbitals and ionizations act as probes of the bonding capabilities and electron distributions of the ligands. The ionization energy shifts are separated into different orbital symmetry effects and specific changes in electron distribution. The interactions of several different ligands with the metals in d^6 "piano-stool" $\text{CpM}(\text{CO})_2\text{L}$ complexes have been summarized in recent reviews.^{23,24} One focus of the present study is to evaluate the interaction of the Si-H bond with the transition metal by comparing the ionizations of the $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiR}_3$ complexes ($\text{R} = \text{Ph}, \text{Cl}$) with the ionizations of the dicarbonyl complex, $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$, and the free silanes.

Before summarizing the information from these comparisons, it is pertinent to briefly review the basic orbital interactions in these complexes. One attractive feature of these systems is the approximate electronic symmetry at the metal center. For instance, the electronic symmetry about the metal in the parent $\text{CpMn}(\text{CO})_3$ complex is nearly octahedral. The angles between the carbonyl ligands are close to 90° , and the three ionizations from the formal d^6 configuration of the metal occur in a single " t_{2g} " ionization band.¹⁶ When a CO in $\text{CpMn}(\text{CO})_3$ is substituted by a phosphine, the electronic symmetry at the metal becomes approximately C_{4v} .¹⁴ The d^6 metal t_{2g} ionization clearly splits into a 2:1 intensity pattern. The most intense ionization represents four of the d^6 electrons and corresponds to the degenerate "e" combination of symmetry orbitals in C_{4v} . In this case each of these degenerate orbitals is basically π in symmetry with respect to the phosphine and one carbonyl. The other, higher energy ionization has π symmetry with respect to both carbonyls and basically has δ symmetry with respect to the phosphine. The 2:1 splitting pattern occurs because the most stable of the three metal-based ionizations is back-bonding into both carbonyls while each of the other two are only stabilized by back-bonding to one carbonyl. From the ligand additivity model, the splitting is a measure of the back-bonding stabilization provided by one CO π -acceptor orbital in comparison to a phosphine.¹³ The increased density on the metal center when the poor π -accepting ligand PMe_3 replaces CO is evidenced by the overall destabilization of the metal-based ionizations.

The symmetry interactions of the Si-H bond with the metal have been presented previously.^{11,12} These are most simply considered in terms of the Si-H σ and σ^* orbital interactions with the metal center.²⁵ 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. Previous studies of systems that are described primarily in terms of donation of an E-H bond to a metal center have shown that this interaction, in contrast to donation from a normal lone electron pair, produces very little shift of the metal-based ionizations.^{12,25} The σ^* interaction involves the donation of electron density from a filled metal orbital into the E-H σ^* orbital. This interaction serves to stabilize one metal-based ionization with respect to the others. When donation from the metal to σ^* is extensive, the ionization can become more ligand-based than metal-based. At this stage, the interaction is more appropriately described in terms of oxidative addition and formation of direct M-H and M-E bonds. This interaction produces a substantial stabilization of the metal-based ionizations and a corresponding destabilization of the ligand atom E-based ionizations.¹¹ These ionization energy shifts and splittings, as observed for the complexes in this study, characterize the nature of individual interactions of the Si-H bonds with the metal centers.

HSiCl₃ Substitution for CO in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$. The photoelectron ionizations of $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ show that this complex is best described as a Mn(III), d^4 complex with individual Mn-Si and Mn-H bonds. This conclusion is based on the following observations from the photoelectron experiment:

1. The Cl lone pair electrons in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ ionize at over 1 eV lower ionization energy compared to the corresponding ionizations of free HSiCl_3 . This destabilization of the silane-based levels follows from extensive negative charge delocalization from the metal onto the Si. The amount of destabilization corresponds to expectations for formation of a SiCl_3^- ligand anion from oxidative addition to the metal center.

2. The metal-phosphorus electrons in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$ ionize at 9.8 eV. In $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$, this ionization is in the vicinity of 10.2 eV. Stabilization of this ionization indicates a more positive metal center in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ than in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$.

3. The ionizations due to the donation from filled Cp e_1'' levels to empty metal levels in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ are also shifted to higher binding energy compared to those in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$. The shift of these ionizations to higher binding energy also indicates a more positively charged metal center in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$, favoring the +3 oxidation state description of the complex.

4. The leading ionization of $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ is predominantly metal-based (from the He I/He II intensities) and is shifted to higher binding energy compared with the corresponding metal band in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$. This increased ionization energy indicates a stabilization of the metal orbitals as expected for a higher positive charge on the metal. Thus, there is a destabilization of the SiCl_3 -based ionizations and stabilization of the metal-based and other ligand-based ionizations. This observation supports an electron distribution tending toward oxidative addition to give a Mn(III) species.

5. The peak at 8.6 eV (ML) is a ligand-based ionization, as indicated by the relative He I/He II intensities and the shift with CO/ PMe_3 substitution. Since this ionization is ligand-based, the formal electron count at the metal is d^4 (from the leading ionization band), consistent with Mn(III). The ionization at 8.6 eV can be attributed to the Mn-Si bond electrons, since the He I/He II intensity trends show this to be a Mn-Si rather than a Mn-H ionization.

HSiHPh₂ Substitution for CO in $\text{MeCpMn}(\text{CO})_2(\text{PMe}_3)$. In contrast to the case for the chlorosilane complex just described, the photoelectron ionizations show that $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ is best described as a Mn(I), d^6 complex with a three-center Mn-H-Si bond arising from donation of the Si-H

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bond to the metal center. There is also appreciable donation from the metal to the Si-H σ^* orbital but not sufficient donation to represent formal oxidation of the metal center. These conclusions are based on the following observations from the photoelectron experiment:

1. The Ph π ionizations of $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ are only slightly destabilized from their position in free HSiHPh_2 . This destabilization, though not large, denotes some negative charge redistribution to Si. It is not large enough to designate silyl as a SiHPh_2^- anion. The shift of the phenyl π ionizations to lower binding energy corroborates the presence of some Si-H σ^* interaction.

2. The metal ionization as a whole does not shift from its position in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$. This indicates that the charge at the metal center is similar to that in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$. Some σ^* interaction is present as evidenced by the stabilization of the higher binding energy side of the metal band relative to the first ionization.

Effect of CO/PMe₃ Substitution on Bond Activation. The second focus of this study is to compare these results on the $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiR}_3$ complexes with the previous results from the $\text{MeCpMn}(\text{CO})_2\text{HSiR}_3$ complexes (R = Ph, Cl). The purpose is to determine the effect of replacing a carbonyl ligand with a phosphine ligand on the Si-H interaction with the metal. Competition for π -back-bonding electrons from the metal is diminished when a phosphine is substituted for a carbonyl, and the Si-H σ^* orbital should be able to accept additional electron density. The relative ionization energy shifts give a measure of the significance of this interaction.

MeCpMn(CO)(PMe₃)HSiCl₃ versus CpMn(CO)₂HSiCl₃. Both $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ and $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$ are best described as Mn(III) complexes where oxidative addition of the Si-H bond to the metal center is nearly complete. The phosphine complex however shows a greater electron charge shift from the metal to the ligand, as expected from the greater electron richness of the metal center. This conclusion is drawn from the following observations:

1. The Cl lone pair ionizations in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ are shifted to a 0.6–1.0 eV lower ionization energy from their positions in $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. This indicates greater negative charge delocalization onto the Si atom in the phosphine-substituted compound.

2. The Cp ring ionizations in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ are destabilized 0.9 eV from their position in $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. The methyl substitution on the Cp ring is known to destabilize the Cp ionizations by 0.3 eV.¹⁶ Thus, the net effect of the phosphine substitution is to destabilize the Cp ring ionizations by 0.6 eV. This is the same amount that the Cp e_1'' ring ionizations in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$ are shifted to lower ionization energy from their position in $\text{MeCpMn}(\text{CO})_3$.

3. The leading metal band is shifted about 1.1 eV to lower ionization energy from its position in $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. Again, this is essentially the same amount that the leading metal band in $\text{MeCpMn}(\text{CO})_2\text{PMe}_3$ shifts from its position in $\text{MeCpMn}(\text{CO})_3$. This destabilization is the effect of a more negatively charged metal center created by substituting carbonyl with a phosphine. The second leading metal band in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ is the Mn-Si ionization and is 0.7 eV destabilized from its position in $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. This destabilization occurs because of the greater negative charge at the metal center due to the CO/PMe₃ substitution, but its magnitude is less than the destabilization of the pure metal levels because this ionization is mostly ligand-based in this complex.

MeCpMn(CO)(PMe₃)HSiHPh₂ versus MeCpMn(CO)₂HSiHPh₂. Both $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ and its dicarbonyl derivative are incomplete oxidative addition products and are best described as Mn(I) systems. Oxidative addition is more advanced in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$, as evidenced by the following observations:

1. The phenyl π ionizations in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ are destabilized from their positions in $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$. This destabilization indicates that there is more negative charge

on the silane ligand, and $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ has advanced to a greater degree of oxidative addition than $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$. The greater electron density at the metal center due to the σ donation of a phosphine can now be dissipated by back-bonding to only one carbonyl. The silane ligand is in a position to act as a π acceptor, since there is Si-H σ^* interaction present in $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$, as seen previously.¹² Due to the substitution of a phosphine for a carbonyl, back-bonding to the silane increases and $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ has a greater degree of Si-H σ^* interaction than does $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$.

2. The leading metal band in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ is ≈ 1 eV destabilized from its position in $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$. The second leading metal ionization band in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ is also ≈ 1 eV destabilized from the higher binding energy metal band in $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$. This shows that the second leading metal band in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ is predominantly metal-based and not ligand-based as in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$, although some back-bonding to the silane is still present.

Discussion

These results show that the chloro and phenyl substitutions on the Si atom have more effect on the M-Si bond formation than carbonyl and phosphine substitutions on the metal in these complexes. Both $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ and its dicarbonyl derivative are basically Mn(III), d^4 species, while $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ and its dicarbonyl derivative are basically Mn(I), d^6 systems. The electronegative Cl on Si drives the complexes to more complete oxidative addition, while Ph substituents on the Si result in a weak interaction of the Si-H bond with the metal.

There are subtle effects on bond interaction in these compounds due to the CO/PMe₃ substitution. The nature of the bond interaction in the compounds does not change but the substitution of PMe₃ for CO results in a more negative metal center. This shows up in the photoelectron spectra as shifts of the ligand and metal ionizations. The electron charge transfer from the metal to the ligand is greater in both $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ and $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ compared with their dicarbonyl derivatives. Although both are formally Mn(I) species, $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ has reached a greater stage of oxidative addition than $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$. This is supported by the 0.03 Å shorter Mn-Si bond length in $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ compared to that in $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$ ¹ and by the slower substitution rate of the silane in the phosphine complex.

The $J_{\text{Si-H}}$ NMR coupling constants have often been examined as an indication of Si-H interaction in the complexes. These coupling constants can be useful for closely related molecules. For instance, the 38-Hz $J_{\text{Si-H}}$ NMR coupling constant of $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiHPh}_2$ compared to the 65-Hz coupling of $\text{MeCpMn}(\text{CO})_2\text{HSiHPh}_2$ correctly indicates that the Si-H bond is more completely broken in the Si-H addition to the phosphine complex. Likewise, the 20-Hz $J_{\text{Si-H}}$ coupling of $\text{MeCpMn}(\text{CO})(\text{PMe}_3)\text{HSiCl}_3$ is less than the 55-Hz coupling of $\text{CpMn}(\text{CO})_2\text{HSiCl}_3$. The $J_{\text{Si-H}}$ of 20 Hz is the same value as that found for $(\text{CO})_4\text{FeHSiPh}_3$, a compound known to have no direct Si-H bond.¹

However, the reduction of the $J_{\text{Si-H}}$ coupling constant does not reflect solely the extent of oxidative addition of the Si-H bond. In addition to the amount of Si-H bonding interaction, the coupling constants are also affected by the electronegativity of the $\text{MeCp}(\text{CO})\text{LMn}$ fragment and the silicon substituents. This is most clearly illustrated by the HSiHPh_2 complexes, in which one of the Si-H bonds is coordinated to the metal and the other is in a terminal position. The bridging $J_{\text{Si-H}}$ and the terminal $^1J_{\text{Si-H}}$ in $\text{MeCpMn}(\text{CO})\text{LHSiHPh}_2$ are both sensitive to the change in charge at the silicon with substitution of CO by PMe₃. Only the bridging $J_{\text{Si-H}}$ is additionally influenced by the change in Si-H bonding with coordination to the metal. On going from $\text{MeCp}(\text{CO})_2\text{MnHSiHPh}_2$ to $\text{MeCp}(\text{CO})(\text{PMe}_3)\text{MnHSiHPh}_2$, the ter-

minal $^1J_{\text{Si-H}}$ falls by 20 Hz. A lower value of $J_{\text{Si-H}}$ is expected in the phosphine-substituted compounds simply because of the basic nature of the phosphines. The bridging $J_{\text{Si-H}}$ falls by 27 Hz on going from $\text{MeCp}(\text{CO})_2\text{MnHSiHPh}_2$ to $\text{MeCp}(\text{CO})(\text{PMe}_3)\text{MnHSiHPh}_2$. Since at least 20 Hz of this change is expected due to the charge redistribution from the phosphine in place of a carbonyl, the decreased coupling due to a decrease in Si-H bonding interaction on going from the dicarbonyl complex to the phosphine complex is no more than 7 Hz. This slight change in the Si-H interaction with the metal from phosphine substitution is consistent with the photoelectron results.

It is evident that the phosphine ligand with its electron density and low π -back-bonding capabilities is not responsible for changing the general nature of the bond interaction in these complexes. The valence photoelectron measurements show that PMe_3 does change the degree of interaction to a small extent, resulting in a slightly stronger Si-H bond interaction with the metal in both phosphine compounds as compared to their dicarbonyl derivatives. The extent

of oxidative addition of the Si-H bond to the manganese center in these complexes is strongly favored by electron-withdrawing substituents on the silicon atom and is less improved by substitution of a carbonyl with typical two-electron donor ligands, which increase the electron density at the metal center.

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Studies of Mixed-Valence Linear-Chain Complexes Crystallized at Elevated Pressures. Crystal Structures of $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{X}_2](\text{ClO}_4)_4$ ($\text{X} = \text{Br}, \text{I}$)

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The structures of the complexes $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Br}_2](\text{ClO}_4)_4$ (**1**) and $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{I}_2](\text{ClO}_4)_4$ (**2**) grown at elevated pressures (7 kbar) have been determined. The bromide is monoclinic with cell dimensions $a = 8.307$ (2) Å, $b = 5.460$ (2) Å, $c = 8.307$ (2) Å, and $\beta = 109.01$ (3)°, in space group $P2_1/m$ with one formula unit of $[\text{Pt}(\text{en})_2\text{Br}(\text{ClO}_4)_2]$ per cell. The iodide is monoclinic with cell dimensions $a = 16.908$ (2) Å, $b = 5.818$ (1) Å, $c = 7.436$ (1) Å, and $\beta = 98.55$ (1)°, in space group $C2$ with one formula unit per cell. The structure of the bromide complex has a more symmetrical packing arrangement of the chains with respect to the structure grown under ambient-pressure conditions. The degree of trapped-valence character and the disorder in the position of the bridging bromine ligand are similar to those features of the ambient-pressure structure. The iodide complex has a very similar spatial arrangement compared with its ambient-pressure structure; however the ethylenediamine ligands appear to pack in a more conventional staggered arrangement.

Introduction

Mixed-valence linear-chain complexes have been studied extensively over the last decade. In general, these materials exhibit anisotropic optical and electronic behavior that can be observed with numerous spectroscopic techniques including electronic absorption and resonance Raman spectroscopy.¹⁻³ Complexes such as those described herein exhibit a Peierls distortion from a delocalized chain of formally Pt(III) metal centers to a trapped-valence chain structure with alternating Pt(II) and Pt(IV) metal centers, resulting in a charge density wave system.^{4,5} Associated with these chains are small but noticeable concentrations of local gap states (polarons, bipolarons, excitons, and kinks) that have been characterized by Peierls-Hubbard and other many-body models.⁶ These defect states typically have absorption maxima at longer wavelengths with respect to the intervalence charge-transfer band associated with the Pt(II)-Pt(IV) moiety. The defect states can be observed in resonance Raman spectroscopy with vibrational features distinctly different from those in the remainder of the chain.^{7,8}

Structural characterization is extremely important in the elucidation of the degree of trapped-valence character along the chains, prediction of the effects of neighboring chains and any counterions on the optical and electronic properties of the material, and the generation and stability of the observed gap states.^{9,10}

Many reported crystal structures of these linear-chain complexes show disorder due to a stacking fault perpendicular to the chain axis, as shown in Figure 1.¹¹⁻¹³ Also, counterions and waters of hydration often are disordered with respect to their orientation as well as position in the lattice. The structure along the chain usually can be resolved by locating two bridging ligand positions on either side of the centroid position with half-occupancy. However, the possible effects of neighboring chains and counterions

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