Electronic Structure of Transition Metal–Silicon Bonds. Valence Photoelectron Spectra of (η^5-C$_5$H$_5$)Fe(CO)$_2$L Complexes (L = SiCl$_3$, Si(CH$_3$)$_3$)

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Abstract: The HeI and HeII photoelectron spectra of (η^5-C$_5$H$_5$)Fe(CO)$_2$SiCl$_3$ and (η^5-C$_5$H$_5$)Fe(CO)$_2$Si(CH$_3$)$_3$ have been obtained in order to examine the bonding of silyl ligands to transition metals. The chemistry of both complexes has been studied previously in relation to models for catalytic intermediates in hydrosilation reactions. The nature of the metal–silicon σ bond and the possibility of π back-bonding from the metal to empty silicon d orbitals are of particular interest to the understanding of this chemistry. Previous observations of unusually short Fe–Si bond lengths in this class of complexes have led to the proposal that silane ligands are good π-acceptors. However, the splitting pattern of the "t$_{2g}$-based" metal ionizations of (η^5-C$_5$H$_5$)-Fe(CO)$_2$Si(CH$_3$)$_3$ shows no evidence of stabilization of metal d orbitals as would occur with π-back-bonding to the silane. The splitting is essentially the same as observed in the spectrum of (η^5-C$_5$H$_5$)Fe(CO)$_2$H, where the hydride clearly has no π-acceptor capability. This same splitting is also observed in the spectrum of (η^5-C$_5$H$_5$)Fe(CO)$_2$CH$_3$. A reduced splitting is observed in the spectrum of (η^5-C$_5$H$_5$)Fe(CO)$_2$SiCl$_3$. Evaluation of these ionizations shows that SiCl$_3$ is a better π-acceptor than CN and is about half as effective as CO at π stabilization of the metal ionizations. The π-back-bonding to SiCl$_3$ probably involves significant portions of the Si–Cl σ^* orbitals. The short Fe–Si bond in the SiCl$_3$ complex is a combination of π-back-bonding and ionic bonding contributions. The ionizations of (η^5-C$_5$H$_5$)Fe(CO)$_2$SiCl$_3$ are also compared with the ionizations of the "isoelectronic" (η^5-C$_5$H$_5$)Mn(CO)$_2$-HSiCl$_3$ complex. The manganese complex is related to the iron complex by a "hydride shift" from the iron nucleus, and the ionization shifts help to reveal the extent of oxidative addition of the Si–H bond to the manganese center. The strength of the Mn–SiCl$_3$ bond contributes to the nearly complete oxidative addition of the Si–H bond to the metal. The implications of these results to the proposed mechanisms of hydrosilation reactions are discussed. The ionization trends in these complexes favor olefin insertion into the metal–silyl bond in the case of trialkylsilyl complexes.

Introduction

The chemistry of (η^5-C$_5$H$_5$)Fe(CO)$_2$SiR$_3$ complexes (R = CH$_3$, Cl) is of interest in relation to the hydrosilation reaction,[1] shown below. As recently discussed by Wrighton, different mechanisms
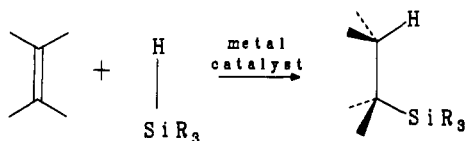
for the stepwise course of hydrosilation reactions appear viable on the basis of model studies.[2] Chalk and Harrod originally proposed that the olefin inserts into the metal–hydride bond of the catalyst, followed by the reductive elimination of the alkyl group and the silyl group to form the alkylsilane.[1] Wrighton has shown that olefin insertion into the metal–silicon bond can be facile and reversible, and has demonstrated all the steps necessary for hydrosilation initiated by this insertion. Wrighton first illustrated these steps through the photochemistry of (η^5-C$_5$(CH$_3$)$_5$)Fe-(CO)$_2$SiCl$_3$ and (η^5-C$_5$(CH$_3$)$_5$)Fe(CO)$_2$Si(CH$_3$)$_3$ as model systems and more recently through the photochemistry of (CO)$_4$CoSiR$_3$, which is known to be an active hydrosilation catalyst under irradiation.[3]

A central issue in understanding the relative stability of possible species along the reaction coordinate concerns the strength of the metal–silyl bond. The nature of the metal–silyl bond has been a source of controversy for over 25 years. Structural data have shown that the metal–silicon distances are shorter than expected for single covalent bonds. For instance, the Fe–Si bond lengths in Cp(CO)FeH(SiCl$_3$)$_2$ (Cp is η^5-C$_5$H$_5$) (2.3 Å),[4] [N(C$_2$-H$_5$)$_4$][(CO)$_4$FeSiCl$_3$] (2.2 Å),[5] and CpFe(CO)$_2$SiCl$_3$ (2.2 Å)[6] are substantially smaller than the predicted value of a single Fe–Si bond length of 2.43 Å.[7] These short bond lengths have been attributed to dπ–dπ π-bonding involving donation of d-electron density from the metal center to empty Si d orbitals or perhaps into Si–R$_3$ σ^* orbitals of the appropriate symmetry.[8] The structures of early transition metal–silyl complexes appear con-

sistent with the proposal of π-back-bonding when metal d$_\pi$ electrons are present. In the d^0 cases, where there are no metal d electrons to back-bond to the silicon, the M–Si bond lengths are generally longer than expected from simple predictions based on covalent radii.[9–15] However, it is also recognized that covalent single-bond distances depend on the ionic character of the bond, the substituent effects, the coordination number, and the oxidation state of the metal.[10,16] The shortening of the Fe–Si bond is greatest with electronegative substitutents on Si (Fe–Si bond in CpFe(CO)$_2$SiCl$_3$ is 2.21 Å compared to 2.28 Å in CpFe(CO)$_2$-(SiF(C$_6$H$_5$)$_2$).[6] The more electronegative substituents would also favor π-back-bonding, so the source of the bond shortening is not clear.

An alternative explanation for these short bond distances is based on σ effects alone. This has been discussed most clearly in the case of the analogous stannyl derivatives.[17] The enhanced

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s character in the tin–transition metal bond is reflected in the tendency for short M–Sn distances and high bond stretching force constants. Likewise, the larger residue of p character in the orbitals directed toward the remaining ligands on Sn leads to smaller than tetrahedral C–Sn–C or X–Sn–X angles and to the tendency for long Sn–C and Sn–X distances.

Numerous spectroscopic studies have addressed the role of π-back-bonding in metal–silyl bonds, with many differences of opinion.[10,16,18] From a combined Mossbauer and carbonyl stretching frequency study of $CpFe(CO)_2L$ complexes (L = alkyl, silyl), it was concluded that $d\pi$–$d\pi$ back-bonding to the trialkylsilyls is minimal.[19] The Mossbauer results revealed greater s-electron density at the metal center, which was attributed to an excellent σ-donor ability of alkyl silyl ligands. Thus some investigators emphasize $d\pi$–$d\pi$ interactions, while others emphasize high σ-donor ability of the SiR_3 group. As stated in a review of metal–silicon chemistry, "no decision can yet be made as to which is the more realistic of these approaches."[18]

The difficulty with the physical and spectroscopic methods which have been used until now to characterize the metal–silyl bond is that these methods do not cleanly separate the π effects from the σ effects of the bonding. The potential hazards of interpreting carbonyl stretching frequencies in tems only of π effects are well-known.[10] Even in the case of the Mossbauer studies, the increase in s-electron density at the metal center may be attributed simply to better direct σ-donor ability from the silyl, or alternatively to increased π-back-bonding from the metal to the silyl that is compensated by a synergistic flow of σ density back to the metal.[19] The separation of the σ- and π-bonding effects requires measurement of properties which are independently sensitive to the different symmetry interactions. Valence photoelectron spectroscopy is especially valuable in this regard. The technique measures ionization to the different symmetry states, and thus allows a clear separation of the electronic π effects from the σ effects. The technique has been used to show the relative σ-donor and π-acceptor capabilities of a wide variety of ligands.[20,21]

Specifically, the π-acceptor capability of a ligand is experimentally characterized in photoelectron spectroscopy by observing the relative stabilization of the ionizations of the occupied metal donor orbitals which have overlap interaction with the ligand acceptor orbitals. When two different ligands are simultaneously bound to the same metal, the competitive π-acceptor stabilization of the different metal ionizations by the two ligands may be compared directly in a single photoelectron spectrum. In the complexes of this study, the bonding of the silyls may be compared with the bonding of the common carbonyl ligand. When one ligand substitutes for another in the bonding to a common metal fragment, the ionizations of the two complexes may be compared to determine the relative σ-donor and π-acceptor abilities of the ligands. In the case of the complexes studied here, the common fragment is $CpFe(CO)_2$, and the ligands whose bonding abilities are compared are $SiCl_3$, $Si(CH_3)_3$, CN, and CH_3. The analogous hydride complex is an important addition to this series, because the hydride has no π-acceptor capability. We have not yet been able to obtain a quality photoelectron spectrum of this hydride complex.[22] However, we have found that the related pentamethylcyclopentadienyl complex, $Me_5CpFe(CO)_2H$ (Me_5Cp is η^5-$C_5(CH_3)_5$), gives a high-quality gas-phase photoelectron spectrum that allows characterization of the effects of a strictly non-π-acid ligand, the hydride, on the valence ionizations.[23]

Photoelectron spectroscopy has also been used in the study of the isoelectronic $CpMn(CO)_2HSiR_3$ complexes (R = Cl, Ph) to

show the extent of electron charge shift from the manganese center to the silyl ligand.[24,25] It was concluded that the electronegative chlorine substituents on the silicon in $CpMn(CO)_2HSiCl_3$ help to drive the Si–H bond to essentially full oxidative addition to form a Mn(III) metal with discrete bonds to the hydride and the silyl anions. Phenyl substituents on Si result in a $MeCpMn$-$(CO)_2HSiPh_3$ complex ($MeCp$ is η^5-$C_5H_4CH_3$) which is best described as a Mn(I) species where the Si–H bond of the silane remains primarily a two-electron donor ligand. Therefore, the electron charge density shift from the metal to the ligand is dependent on the substituents on silicon. The charge density shifts primarily involved σ bonding, with the π-acceptor ability of the silanes appearing negligible compared to carbonyl in these compounds. However, because of the reduced symmetry of these complexes, detailed evaluation of the π-acceptor ability of the silyl was more difficult. Comparisons of the electronic characteristics of the silyls with alkyls or other ligands also were not possible at that time. Now, the ionization features of $CpMn(CO)_2HSiCl_3$ can be compared with those of $CpFe(CO)_2SiCl_3$ since the d^6 Fe(II) center can be thought of as a hydride (2 electrons, 1 proton) added to a Mn(III) center. This relationship, which is called a "hydride shift", has been used in the study of other systems.[21,26,27] The comparison of the Mn and Fe complexes is useful because the position of the ligand group ionizations indicate the electron charge shift from the metal to the silyl ligand and thus an additional indication of the extent of oxidative addition of the Si–H bond to the metal is obtained.

Experimental Section

$CpFe(CO)_2SiCl_3$ and $CpFe(CO)_2Si(CH_3)_3$ were prepared by literature methods.[28,29] Photoelectron spectra were recorded on an instrument which 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.[30-34] The spectrum of $CpFe(CO)_2SiCl_3$ was measured at a sample cell temperature of 55 ± 3 °C for He I and He II measurements, and $CpFe(CO)_2Si(CH_3)_3$ was measured at a sample cell temperature at 18 ± 5 °C for He I and He II measurements. The compounds sublime cleanly in the instrument with no decomposition. All data collections were repeated about five times for purposes of examining particular ionization features, and no discernible differences were observed between collections.

The data are represented analytically with asymmetric Gaussian peaks (program GFIT).[35-37] 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). Because of the several overlapping ionizations of these complexes, the reproducibility of the positions is only about 0.02 eV, and that of the widths is about 0.05 eV. These uncertainties in the individual parameters arise primarily because the parameters of overlapping peaks in a band are not completely independent. It is important to note that the results which lead to the conclusions of this paper are observed directly in the data and do not require the analytical representations. The value of the analytical representations is in providing a quantitative measure (that can be statistically evaluated)[36,37] of the key observations and their implications. For the analytical representations of the He II spectra, the peak positions and widths are fixed

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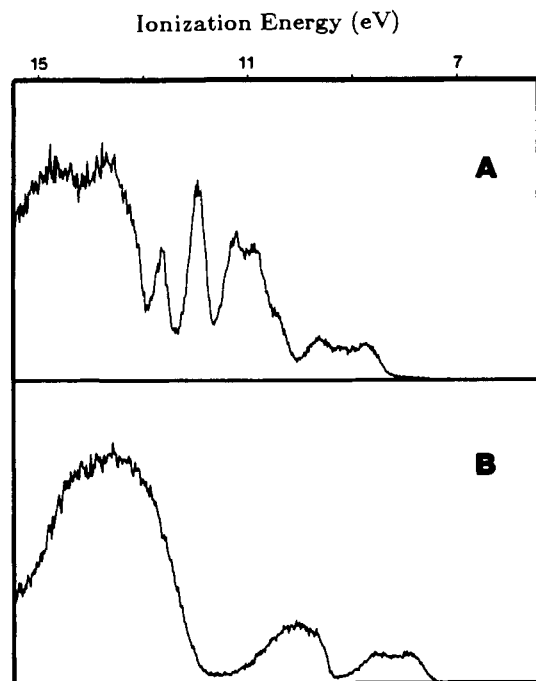(23) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, M. Work in progress.

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$(\eta^5$-$C_5H_5)Fe(CO)_2L$ *Complexes*

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Ionization Energy (eV)

Figure 1. He I full spectra of (A) $(\eta^5$-$C_5H_5)Fe(CO)_2SiCl_3$ and (B) $(\eta^5$-$C_5H_5)Fe(CO)_2Si(CH_3)_3$.

at the values obtained from the He I spectra, and only the relative intensities are allowed to vary.

Assignments of the Photoelectron Ionizations

The He I valence photoelectron spectra of $CpFe(CO)_2SiCl_3$ and $CpFe(CO)_2Si(CH_3)_3$ are shown in Figure 1. The general assignments follow from correlations with previously investigated $CpM(CO)_2L$ complexes,[21,20,35] and from correlations with the related silanes $HSiCl_3$[24,38] and $HSi(CH_3)_3$.[39,40] The region of overlapping ionizations from 13.5 to 15.5 eV consists of the carbonyl 5σ and 1π ionizations, the Cp a_2'' (symmetric) π ionizations and ring σ ionizations, and certain silyl σ ionizations. Individual assignments in this region will not be attempted for either compound. The lowest energy valence ionizations are generally metal-based, followed by certain metal–ligand σ ionizations and ligand π and lone-pair ionizations. The assignments and characteristics of these ionizations are most important for understanding the valence electronic structure.

PES of $CpFe(CO)_2SiCl_3$. A close-up of the lower ionization energy region of $CpFe(CO)_2SiCl_3$ is shown in Figure 2. The intense ionizations at 10.9, 11.2, and 11.9 eV are due primarily to the Cl lone-pair electrons. The pattern of these ionizations (spacing and relative intensities) is very similar to that of the ionizations observed in $HSiCl_3$ and $CpMn(CO)_2HSiCl_3$.[24] The Cl lone-pair ionizations of $CpFe(CO)_2SiCl_3$ are only 0.1 eV destabilized from the corresponding ionizations in the spectrum of $CpMn(CO)_2HSiCl_3$, and these ionizations of both complexes are about 1 eV destabilized from the similar lone-pair ionizations of $HSiCl_3$. The Cp e_1'' ring ionizations of $CpFe(CO)_2SiCl_3$, at 10.5 eV, are 0.1 eV stabilized from their position in the spectrum of $CpMn(CO)_2HSiCl_3$. The ionizations at 8.7 eV and 9.3 eV are identified as metal-based. They correlate with the metal-based ionizations of $CpFe(CO)_2CN$ which occur at 8.8 eV and 9.3 eV.[34] The two metal-based ionizations have a 2:1 intensity pattern. This pattern is consistent with the expected electronic symmetry at the metal center. Previous studies have shown that the electronic symmetry at the d^6 metal in $CpMn(CO)_3$ is near octahedral, with nearly degenerate metal ionizations, and the replacement of one
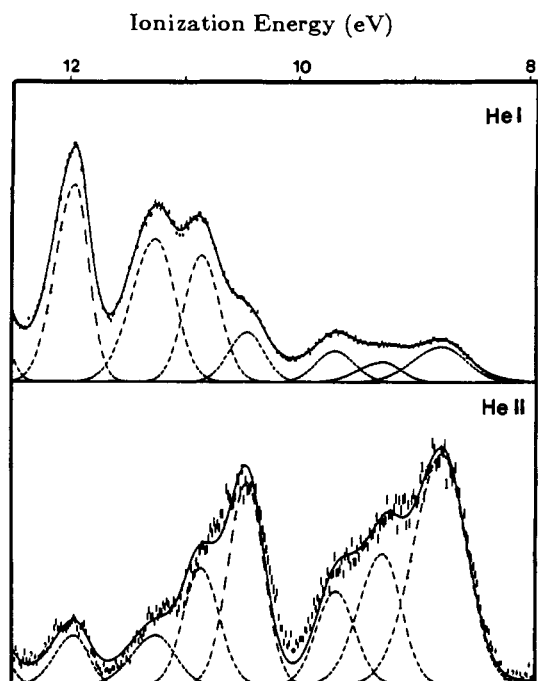
Ionization Energy (eV)

Figure 2. He I/He II intensity trends in $(\eta^5$-$C_5H_5)Fe(CO)_2SiCl_3$.

carbonyl with a heteroligand to form $CpM(CO)_2X$ reduces the symmetry to near C_{4v} and a 2:1 pattern of metal levels.[20,21,35] The remaining ionization at 9.7 eV is assigned to the Fe–Si σ bond electrons.

The relative intensity changes which are demonstrated in the He II spectrum of this compound confirm the He I assignments based on ionization energy correlations. The first two ionizations are predominantly metal-based and show the characteristic increase in relative intensity with He II excitation. The Fe 3d photoionization cross sections are predicted to rise by a factor of 1.6[41] on going from He I to He II excitation while photoionization cross sections of C 2p, Cl 3p, and Si 3p ionizations decrease on going from He I to He II excitation. The third ionization peak is not as intense and falls by a factor of 2 relative to the first ionization on going from He I to He II, so it is more ligand-based and reasonably assigned to the Fe–Si σ ionization. The peak at 10.5 eV, previously identified as the Cp ionization, falls by a factor of 1.5 on going from He I to He II. The C 2p photoionization cross sections fall by a factor of 3 on going from He I to He II. The relative intensity of the Cp ionizations falls by a lower factor than expected for a pure carbon 2p ionization because of mixing with metal character. The Cl 3p photoionization cross sections are predicted to fall by a factor of 20 on going from He I to He II. The sixth and seventh ionization peaks decrease considerably from He I to He II excitation as shown in Figure 2, consistent with expectations for the Cl lone-pair ionizations. The fifth ionization band falls by a lesser amount on going from He I to He II excitation according to this analysis. However, it is recognized that the characteristic shoulder of the Cp ionization[31] is in the same position as this Cl lone-pair ionization, thus enhancing the intensity in this position of the He II spectrum and complicating the fit analysis of relative areas.

PES of $CpFe(CO)_2Si(CH_3)_3$. As seen in Figure 1, the characteristic ionization regions of $CpFe(CO)_2Si(CH_3)_3$ are all shifted to lower ionization energy by about 1 eV from the corresponding ionizations of $CpMn(CO)_2HSiCl_3$. This is expected from the relative electronegativity and electron inductive effects of the methyl groups relative to the chlorides. A close-up of the lower ionization energy region of $CpFe(CO)_2Si(CH_3)_3$ is shown in Figure 3. Two broad regions of ionizations are observed. One spans from about 7 to 9 eV and the other from about 9 to 11 eV. The observed shoulders and changes in overall band contours from He

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Table I. He I Valence Ionization Features

compound	orbital character	position	W_h	W_l	He I peak area	He II peak area
CpFe(CO)$_2$SiCl$_3$	M	8.75	0.59	0.49	1.00	1.00
	M	9.27	0.49	0.38	0.46	0.46
	M–Si	9.68	0.38	0.39	0.64	0.29
	Cp	10.45	0.37	0.35	0.95	0.59
	Cl	10.85	0.35	0.38	0.68	0.34
	Cl	11.24	0.49	0.40	0.94	0.18
	Cl	11.95	0.39	0.29	1.00	0.14
CpFe(CO)$_2$SiMe$_3$	M	7.89	0.59	0.45	1.00	1.00
	M–Si	8.36	0.59	0.45	0.50	0.31
	M	8.68	0.56	0.49	0.65	0.66
	Cp	9.68	0.42	0.29	1.01	0.59
	Si–C	10.07	0.70	0.41	1.53	0.74
	Si–C	10.56	0.81	0.77	1.47	0.43

Ionization Energy (eV)
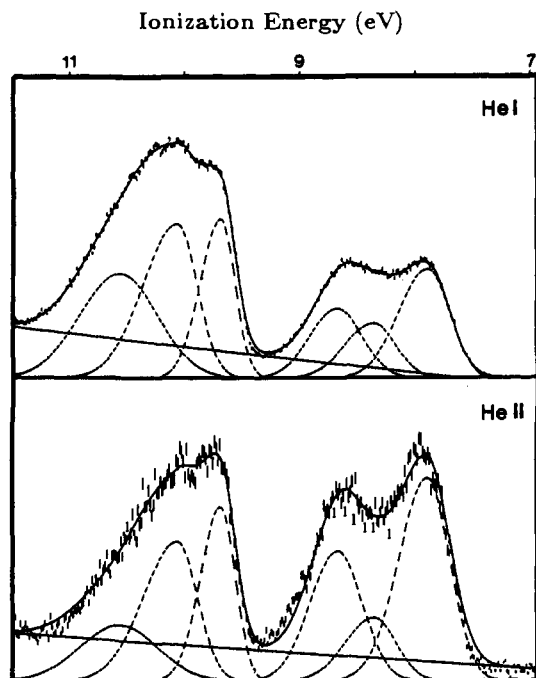
Figure 3. He I/He II intensity trends in (η^5-C$_5$H$_5$)Fe(CO)$_2$Si(CH$_3$)$_3$.

I to He II excitation show that several ionizations are overlapping in each of these regions. Correlations with the ionizations of related complexes can determine which ionizations contribute to each region, but are not sufficient to confidently assign each individual ionization contributing to each region. The metal-based ionizations of the d^6 metal are expected to contribute to the lower energy band by comparison with the metal ionizations in CpFe-(CO)$_2$CH$_3$, which occur at 7.8 eV and 8.0 eV.[35] The ionization of the Fe–Si σ electrons is also expected to be here by correlation with Co–Si ionizations of (CO)$_4$CoSiCl$_3$ which appear in the same energy vicinity.[42] As can be seen in Figure 3, the ionization contour of the overall band is accurately represented by three Gaussian components. Attempts to model the band contour with less than three components gave severe discrepancies. As in the case of the other CpFe(CO)$_2$L complexes, the d^6 metal ionizations are expected to be in two bands with an approximate 2:1 intensity pattern. The leading edge of the ionization envelope is therefore probably metal-based as indicated by its relative intensity to the He I spectrum. It is not possible on the basis of the He I intensities to determine which of the remaining contributions to this band is the other metal-based ionization and which is the Fe–Si σ bond ionization.

The ionization at 9.7 eV is assigned to the Cp e$_1''$ ring ionizations by correlation with these same ionizations of CpFe-(CO)$_2$CH$_3$ (9.9 eV).[35] The remaining ionizations at 10.1 eV and

10.6 eV are assigned to the Si–C σ ionizations. These same ionizations appear at 10.7 eV and 11.0 eV in the spectrum of (CH$_3$)$_3$SiH.[40] In comparison, the Si–C σ ionizations of CpFe-(CO)$_2$Si(CH$_3$)$_3$ are 0.5 eV destabilized from the corresponding ionizations of the free ligand. The peak positions and areas of the bands are given in Table I.

The He II spectrum of the compound shown in Figure 3 clarifies the assignment of the ionizations in the band between 7 and 9 eV. It is visually apparent that the ionization intensity in the middle of the band diminishes in comparison to the ionizations near the edges of the band, creating a deeper saddle in the middle of the band. From the fit analysis in Table I, the ionization at 7.9 eV grows in relative intensity in He II so it is predominantly metal-based as mentioned above and can be assigned to four d electrons (d^4) from integrated peak area. The second ionization at 8.4 eV falls by a factor of 1.6 on going from He I to He II. The third ionization grows in intensity in He II compared to the second one. The ionization intensity in the vicinity of 8.4 eV (in the middle of the band) is assigned to the Fe–Si electrons, while the ionization intensity in the vicinity of 8.7 eV is assigned to the remaining two d electrons of the six d electrons at the metal center.

In comparison, the ionization at 9.7 eV, which has been assigned to the Cp electrons, falls by a factor of 1.7 on going from He I to He II. The ionizations at 10.1 eV and 10.6 eV fall by a factor of 2.1 and 3.4 on going from He I to He II. These ionizations are predominantly due to Si–C σ electrons with the band at 10.1 eV overlapping with the tail of the Cp peak, thus making it fall by a lesser factor in He II.

Discussion

Photoelectron studies of a variety of CpM(CO)$_2$L complexes have been carried out previously for comparison of the σ-donating and π-accepting ability of ligands. These studies have generally involved neutral two-electron donating ligands L such as CO, N$_2$, NH$_3$, alkenes, alkynes, SO$_2$, and silanes, and the metal in the complex most often has been manganese.[20,21,25] In this study the ligands are formally minus one charged anions and the metal is iron. The formal charge of the ligands will not be designated when referring to these ligands, but it is often implied in the discussion. The focus of this discussion will be the CpFe(CO)$_2$Si(CH$_3$)$_3$ and CpFe(CO)$_2$SiCl$_3$ complexes. An attractive feature of this class of iron complexes is the possibility of including the hydride complex in the comparisons, because the hydride ligand clearly has no significant π-acceptor capability. A comparison of the ionization features of these metal–silyl complexes to other CpFe(CO)$_2$L compounds, such as with L equal to CH$_3$ and CN, further reveals the ligating characteristics of the silyl ligand relative to other common ligands.

Orbital Interactions of the Silyl with the CpFe(CO)$_2$ Fragment. The symmetry interactions of a ligand L with a CpM(CO)$_2$ fragment have been discussed previously.[43] The coordinate system which has been most useful for this discussion is shown in Figure 4. The metal is located at the origin with the z axis pointed

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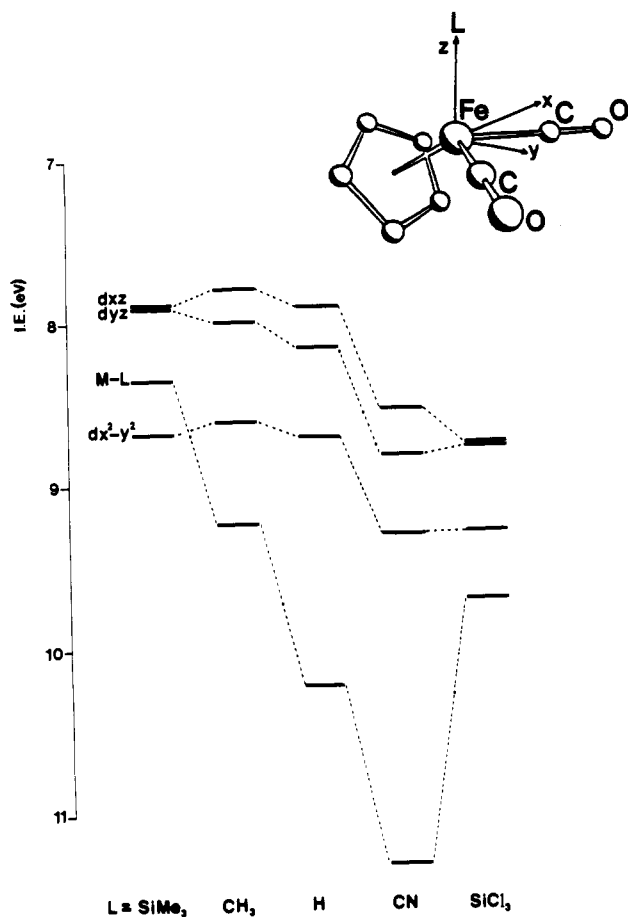(43) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

Figure 4. Stepwise correlation of the ionizations in (η^5-C$_5$H$_5$)Fe(CO)$_2$L systems where L is Si(CH$_3$)$_3$, CH$_3$, H, CN, and SiCl$_3$.

directly at the silyl ligand and with the y axis bisecting the carbonyls. The Fe–Si σ bond is formed from the empty metal d_{z^2} orbital interacting with the silane ligand. These complexes have pseudo-octahedral electronic symmetry.[43] The "t_{2g}" metal-based orbitals are the d_{xz}, d_{yz}, and $d_{x^2-y^2}$ orbitals in this coordinate system. Electrons occupying these orbitals account for the formal d^6 electron configuration at the metal center, and the ionizations corresponding to these orbitals are most often the lowest energy ionizations of the complexes. The pseudo-octahedral electronic symmetry of this class of complexes is demonstrated most clearly in the photoelectron spectrum of CpMn(CO)$_3$, where the d_{xz}, d_{yz}, and $d_{x^2-y^2}$ ionizations overalp to form the single "t_{2g}" ionization band.[31] The deviation from true octahedral electronic symmetry is observed only as a small shoulder ionization which corresponds to a split of about 0.3 eV in the ionizations of the "t_{2g}" band. This splitting is less than the vibrational envelope of the band. The CpFe(CO)$_2$L complexes in this study have pseudo-C_{4v} electronic symmetry at the metal center, and the metal-based ionizations split into the "e" and "b$_2$" bands. The lack of true C_{4v} symmetry results in a splitting of less than 0.3 eV in the "e" ionization band, and, as is the case in this study, the two separate ionizations are often not resolved in this band.[34]

According to this coordinate system, the "e" ionization band is comprised of the d_{xz} and d_{yz} metal orbitals. Each orbital has π symmetry with respect to the silyl ligand and each also effectively π back-bonds to one carbonyl. The $d_{x^2-y^2}$ orbital of the metal π back-bonds to two carbonyls. Thus the primary difference between the energy of the d_{xz}, d_{yz} ionizations and the energy of the $d_{x^2-y^2}$ ionization lies in the difference between the π-back-bonding stabilization of a ligand L compared to that of a carbonyl. This energy measure of the π-back-bonding ability is important for understanding the relative stability and bond strengths of the complexes, which is most important in relation to chemical behavior.[37,44]

The shift of charge with ligand substitution is reflected in the overall shift of the metal-based and ligand-based ionizations. For instance, the $d_{x^2-y^2}$ orbital has δ overlap with the ligand L, and since these ligands have no significant δ interactions with the metal, the shift of this ionization when one ligand L is replaced by another is primarily a consequence of the change in charge potential at the metal center.[21] The change in charge potential at the metal is a result of the combined difference in σ-donor and π-acceptor abilities of the ligands. The change in charge potential at the metal is also reflected in the shifts of the ionizations of other ligands coordinated to the metal. Most significant here are the Cp e$_1''$ ionizations, which follow the shift of the metal $d_{x^2-y^2}$-based ionization.

π-Acceptor Ability of Silane Ligands in CpFe(CO)$_2$L Systems. As mentioned in the Introduction, there is controversy about the π-accepting ability of the silyl ligands in the CpFe(CO)$_2$L systems (where L is Si(CH$_3$)$_3$, SiCl$_3$). Figure 4 shows the relative stabilities of the metal ionizations in a series of CpFe(CO)$_2$L complexes. In the center of the figure are the ionizations of CpFe(CO)$_2$H. These are estimated by shifting the ionizations of Me$_5$CpFe-(CO)$_2$H[23] 0.5 eV to higher binding energy. This shift is based on the 0.5-eV shift which is consistently observed between the ionizations of other CpFe(CO)$_2$L and Me$_5$CpFe(CO)$_2$L complexes.[34] The important observation is the average split between the d_{xz},d_{yz} ionizations and the $d_{x^2-y^2}$ ionization, which does not significantly change with methylation of the Cp ring. The observed splitting is 0.67 (2) eV. This represents the magnitude of the splitting expected for a ligand L that has no π-back-bonding capability. As a ligand approaches the π-acceptor ability of CO, the stabilization of the d_{xz},d_{yz} ionizations will approach that of the $d_{x^2-y^2}$ ionization, and the splitting will become less. When the π-acceptor ability of the ligand equals that of CO, the splitting will be approximately that observed in the spectrum of CpMn-(CO)$_3$, about 0.3 eV.

To the left of the ionizations of the hydride complex in Figure 4 are the ionization energies of the CpFe(CO)$_2$CH$_3$ complex.[35] As can be seen, the metal-based ionization energies of the hydride complex and the methyl complex are very similar. The average separation in energy between "e" and "b$_2$" ionizations is again 0.70 (2) eV. As expected,[45] the methyl ligand is not a significant π-acceptor.

On the far left of the diagram are the metal-based ionization energies of the Si(CH$_3$)$_3$ complex. These energies are also very similar to those of the methyl and the hydride complexes. The splitting between the "e" and "b$_2$" ionizations is 0.79 (6) eV. The magnitude of this splitting may be overestimated by as much as 0.1 eV by the band fitting because the two peaks are on the outer edges of the overlapping band, and the reduced symmetry splitting of the "e" ionization is not observed as it is in the hydride and methyl complexes. Nonetheless, it is clear from this splitting that the trialkylsilyl is not effective at stabilizing the bonding through π interactions with the metal center.

The photoelectron spectrum of CpFe(CO)$_2$CN shows the stabilizing effect of the weakly π-accepting CN ligand.[34] The difference in energy between the $d_{x^2-y^2}$ ionization and the average of the d_{xz}/d_{yz} ionizations is 0.60 (2) eV, which is just less than observed for the hydride complex.

The metal ionizations of the CpFe(CO)$_2$SiCl$_3$ complex are split by 0.52 (6) eV. Thus the π-accepting ability of the SiCl$_3$ ligand is slightly better than that of the CN ligand. Using the observation that the splitting for a non-π-accepting ligand such as a hydride or a methyl is about 0.7 eV and the splitting for a π-accepting carbonyl ligand is about 0.3 eV, it follows that the SiCl$_3$ ligand is about half as effective as a carbonyl ligand at stabilizing the metal-based ionizations through π-back-bonding. This will have an influence on the bond strength and bond distances as discussed later. The ionizations do not indicate whether this back-bonding

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(45) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351.

is into the silicon d orbitals or into the Si–Cl σ^* orbitals. Based on our recent studies of π bonding of second-row main group atoms, we suspect that the π-back-bonding is dominantly to the Si–Cl σ^* orbitals (which may also contain d_π character).[8,46] This is supported by the Si–Cl bond distances in the CpFe(CO)$_2$SiCl$_3$ complex, which at 2.07 Å are 0.05 Å longer than standard Si–Cl distances in molecules where π-back-bonding is not possible.[47]

σ-**Donor Abilities and Net Electron Distributions.** The most significant shifts of the metal-based ionizations are due to the different σ-donor abilities of the Si(CH$_3$)$_3$ and SiCl$_3$ ligands. The ionization energies of the iron–ligand σ bonds are also shown in Figure 4. The Fe–ligand σ ionization energy decreases from L equals H to CH$_3$ to Si(CH$_3$)$_3$. The metal-based ionizations are the lowest energy ionizations except in the case of the CpFe-(CO)$_2$Si(CH$_3$)$_3$ complex, where the Fe–Si σ ionization occurs at a lower energy than the metal ionization corresponding to the $d_{x^2-y^2}$ orbital (as shown from He I/He II intensity trends). This is an important observation for discussion later.

The decreasing stability of the ligand σ levels would normally result in an increasing transfer of σ-electron density from the ligand to the metal, assuming that metal–ligand σ overlap is the same. There is no significant shift of the metal-based ionizations between these complexes, showing that the effect of decreasing stability of ligand σ levels is compensated by poorer metal–ligand overlap as the ligands come from lower rows in the periodic table. The relatively constant metal-based ionization energies of these complexes, as shown most clearly by the $d_{x^2-y^2}$ ionization, is consistent with the nearly equal electronegativity and the lack of π-back-bonding by these atoms and groups. The group electronegativities of CH$_3$ and Si(CH$_3$)$_3$ are both reported to be 2.27 in comparison to 2.28 for H.[48]

The metal-based ionizations of the CN complex are substantially stabilized from those of the three complexes discussed above. The splitting of the metal-based ionizations showed that the CN is only a weak π-acceptor in this complex, and it is not possible to attribute the total shift of the metal-based ionizations to the withdrawal of π electron density. More importantly, the σ lone pair of CN which donates to the metal is significantly more stable (at 11.27 eV)[34] than the lone pairs of the other ligands, and the overlap is not expected to be significantly better than the overlap of the CH$_3$ σ donor with the metal. Thus CN is a significantly poorer σ donor than the three ligands to the left in Figure 4, and this accounts for the stabilization of the metal-based ionizations. This stabilization is also related to the much higher group electronegativity of the CN ligand, which ranges from 3.1 to over 4.0 depending on the method of determination.[49]

The metal-based ionizations of the SiCl$_3$ complex are similar to those of the CN complex. The SiCl$_3$ group is a poor σ donor in comparison to Si(CH$_3$)$_3$, because of the higher electronegativity of the Cl groups which serve to stabilize the σ-donor orbital. The group electronegativity of SiCl$_3$ is 2.78, or about 0.5 greater than the electronegativity of H, CH$_3$, and Si(CH$_3$)$_3$. The σ-donor ionization is 1.3 eV more stable than that of the Si(CH$_3$)$_3$ complex, the metal-based ionizations are in turn stabilized by about 1 eV, and the Cp e_1'' ring ionizations are stabilized about 0.8 eV from those of CpFe(CO)$_2$Si(CH$_3$)$_3$.

The $d_{x^2-y^2}$ ionization energy of the SiCl$_3$ complex is essentially the same as that of the CN complex, even though the group electronegativity of the SiCl$_3$ ligand is much smaller. This points to the additional stabilization and withdrawal of electron density from the metal-based levels by the π-back-bonding of the SiCl$_3$ ligand.

In the spectrum of CpFe(CO)$_2$SiCl$_3$, the Cl lone-pair ionizations are destabilized 1.2 eV from their position in HSiCl$_3$, signifying a larger electron charge shift from the metal to the ligand. In comparison, in the spectrum of CpFe(CO)$_2$Si(CH$_3$)$_3$, the Si–C

σ ionizations are destabilized only 0.5 eV from those of HSi(CH$_3$)$_3$. The SiCl$_3$ bond to the metal has a much greater ionic contribution than the Si(CH$_3$)$_3$ bond to the metal.

Bond Lengths and Bond Strengths in Metal–Silyl Complexes. It is now possible to discuss the bond lengths in terms of the inherent single bond covalent radii and contributions from ionic bonding and π-back-bonding. First, the methyl complex is shown to have no π-back-bonding contribution to the Fe–CH$_3$ bond, and by analogy with the hydride and the Si(CH$_3$)$_3$ complexes, is not expected to have much contribution from ionic terms. The sum of the single bond covalent radii for carbon and iron is 2.02 Å. CpFe(CO)$_2$CH$_3$ is a waxy solid and the low-temperature crystal structure has not been done. The closest analogy is CpFe-(CO)$_2$CH$_2$CO$_2$H, where the Fe–alkyl bond length has been determined to be 2.06 (2) Å.[50] Thus the single bond covalent radii are a reasonable approximation for this class of complexes in the absence of ionic contributions and π-back-bonding. The observed bond length may be slightly longer than the estimated length because of slight electronic repulsive interactions between the CH$_3$ σ bonds and the occupied metal orbitals.[45]

The sum of single bond covalent radii for the Fe–silyl complexes is 2.43 Å, but the distance in CpFe(CO)$_2$SiCl$_3$ has been determined to be 2.21 Å. The ionic contribution to the bond shortening may be estimated from a combination of the ionization information and the group electronegativities of the silyl groups. As mentioned above, the electronegativities of the H, CH$_3$, and Si(CH$_3$)$_3$ groups are all about 2.27, and the electronegativity of the SiCl$_3$ group is 2.78. There is apparently no significant ionic contribution to the bond length in the methyl complex, so the electronegativity of the CpFe(CO)$_2$ fragment may be assumed to be slightly less than 2.27. Schomaker and Stevenson have related the bond shortening in the absence of multiple bonding and rehybridization to about 0.09 Å times the difference in electronegativities.[51] Thus even if the difference in electronegativities of the CpFe(CO)$_2$ and SiCl$_3$ groups were as large as one unit, this would still account for only less than half of the bond shortening. The remaining 0.13-Å shortening is attributed to the π-back-bonding to the SiCl$_3$ group.

It would be desirable to have the Fe–Si distance from the CpFe(CO)$_2$Si(CH$_3$)$_3$ complex, because here there would be no bond shortening due to π-back-bonding on the basis of the photoelectron studies, and the shortening from ionic contribution would be small on the basis of comparison with the ionizations of the methyl complex and the structure of the alkyl complex cited above. This complex is also a waxy solid at room temperature and the structure at low temperature has not been reported. The closest analogy is cis-(CO)$_4$Fe(Si(CH$_3$)$_3$)$_2$. The Fe–Si bond distance in this complex is 2.456 (2) Å, which is in good agreement with the expectations from single bond covalent radii.

It is interesting to compare the bond shortening due to π-back-bonding with the amount of stabilization of the metal d orbital ionizations. The π-back-bonding of a carbonyl shortens the Fe–C distance by about 0.3 Å (to about 1.76 Å from the 2.06 Å Fe–C distance of the metal-alkyl). The photoelectron ionizations show that the SiCl$_3$ group is about half as effective as a carbonyl at stabilizing the metal ionizations, and the Fe–Si distance is also shortened by about half as much as the Fe–C distance.

All of these factors which contribute to the short Fe–Si bond length in the SiCl$_3$ complex also relate to a stronger Fe–Si bond in this complex than in the Si(CH$_3$)$_3$ complex. We have previously published an account of the relationships between ionization energies and bond energies.[44] In general, the more stable ionizations relate to stronger bond formation. The complete relationships to obtain a quantitative comparison of the bond energies cannot be applied in this case until more information on the ionization energies of the CpFe(CO)$_2$ and silyl fragments is developed. However, it is clear from the higher ionization energy of the Fe–Si bond and the stabilization of the metal ionizations by π-back-

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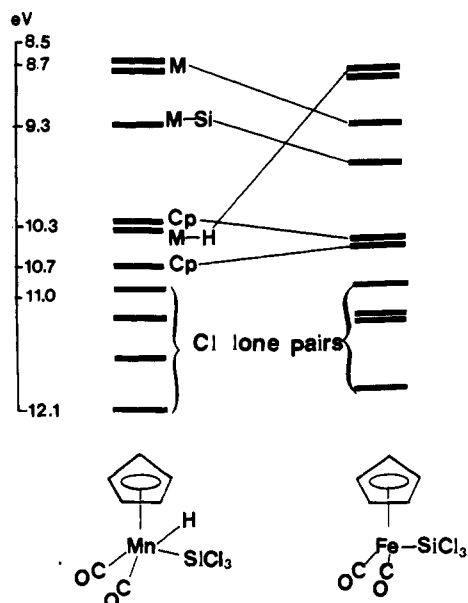
Figure 5. Ionization correlation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_3$.

bonding that the Fe–Si bond is stronger for the SiCl₃ complex.

The "Hydride Shift". We have previously studied by photoelectron spectroscopy the electronic structure factors of Si–H bond activation by the Mn center in $CpMn(CO)_2HSiCl_3$.[24] Some properties of this complex had been interpreted in terms of the Si–H bond acting as two-electron donor to the d⁶ manganese center, while other techniques had suggested that the complex should be more correctly described as a full oxidative addition product which results in a d⁴ metal center and direct Mn–hydride and Mn–silyl bonds. We obtained the He I and He II spectra of this complex and from the intensity trends were able to determine that the complex has advanced to essentially complete oxidative addition. In comparison, the photoelectron spectra of the trialkylsilyl complexes showed that the Si–H bond addition to the metal center was much less complete, and the complexes were best considered as d⁶ Mn(I) species. The greater electronegativity of the SiCl₃ group was cited as one reason for the more complete oxidation addition to the Mn center. It is clear now that the stronger Mn–Si bond for the SiCl₃ complex compared to the trialkylsilyl complexes is also important in proceeding toward oxidative addition.

The $CpMn(CO)_2HSiCl_3$ complex is related to the $CpFe(CO)_2SiCl_3$ complex by the concept of the "hydride shift". The d⁶, Fe(II) center can be thought of as a hydride (2 electrons, 1 proton) added to a d⁴, Mn(III) center (see below). The structures
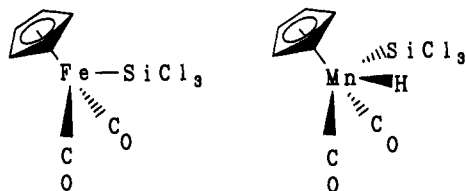
of the Mn complex and $CpFe(CO)_2SiCl_3$ have been compared in the hope of determining if the Mn–Si bond is a direct bond, without influence by the hydride, as is the case for the Fe–Si bond.[6] The structural comparison shows that the Mn–Si bond length in $CpMn(CO)_2HSiCl_3$ is only 0.02 Å longer than the Fe–Si bond in $CpFe(CO)_2SiCl_3$, and this small lengthening may be attributed only to change in metal atomic radii.

As further evidence of the similarity of these bonds, an ionization correlation diagram in Figure 5 shows how the ionization features of the Mn and Fe complexes compare. The predominantly metal ionizations and the Fe–Si ionization in the Fe complex are stabilized relative to the Mn complex because of the increased nuclear charge at the metal center. The electrons associated with
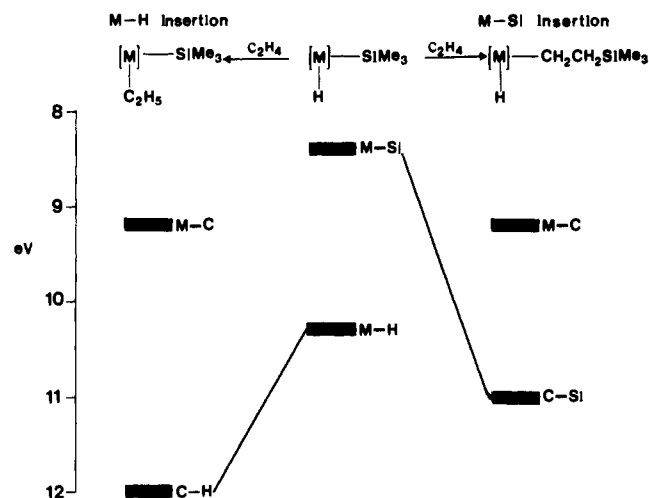

Figure 6. Ionization correlation for insertion of ethylene into metal–hydride and metal–silyl bonds.

the transfer of two electrons and a proton in proceeding from Mn–H to Fe give rise to an additional ionization at the low energy of 8.75 eV. In $CpMn(CO)_2HSiCl_3$, these electrons are in the Mn–H bond which ionizes in the region of ≈10.2 eV.[24] Most importantly, the other ligand ionizations are sensing essentially the same charge distribution in the complexes. The Cp ionizations are not significantly shifted. The Cl lone-pair ionizations of the two complexes are also very similar. In $CpFe(CO)_2SiCl_3$, these ionizations are only 0.1 eV destabilized from the same ionizations in $CpMn(CO)_2HSiCl_3$. Therefore, the extent of electron charge density shift from the metal to the silyl is nearly the same in both complexes. Nearly complete oxidative addition has occurred to form the $CpMn(CO)_2HSiCl_3$ complex.

Insertion of Ethylene into the Metal–Hydride or Metal–Silyl Bonds. As mentioned in the Introduction, Chalk and Harrod originally proposed that the next step of the hydrosilation reaction involves insertion of ethylene into the metal–hydride bond. Wrighton later showed that ethylene insertion into the metal–silyl bond is viable. The ionization energies give an indication of the factors that favor insertion into either of these bonds. Figure 6 shows an ionization correlation diagram for both of these processes. In the center of the figure are the M–L ionization energies determined for the $CpFe(CO)_2Si(CH_3)_3$ and $CpFe(CO)_2H$ complexes. Insertion of ethylene into the metal–hydride bond forms a metal–alkyl. The approximate ionization energies of the new metal–alkyl bond and the new C–H bond are shown on the left of the figure. The metal–alkyl bond energy is taken from the M–L bond energy of the $CpFe(CO)_2CH_3$ complex. Insertion of ethylene into the metal–silyl bond forms the species on the right of the figure, where the new metal–alkyl and C–Si bond ionization energies are shown. The C–Si ionization energy is taken from the first ionization of H_3CSiH_3,[40] and the C–H ionization energy is taken from the first ionization of H_3CCH_3.[52] The difference in these ionization energies is about 1 eV (23 kcal/mol), which compares well with the difference in bond energies (C–H ≈ 98 kcal/mol, C–Si ≈ 76 kcal/mol).[48]

The diagram shows that, for these complexes, ethylene insertion is favored into the Fe–Si(CH₃)₃ bond rather than into the Fe–H bond. This traces primarily to the instability of the Fe–Si(CH₃)₃ ionization and the greater stabilization that is gained by formation of the C–Si bond. Note also that the diagram strongly favors insertion into a metal–alkyl bond over insertion into a the metal–hydride bond, as is well-known in organometallic chemistry.[53] The M–C bond ionization is much less than the M–H bond ionization, and the C–C bond ionization that is formed from

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insertion into the alkyl is greater than the C–H bond ionization. Insertion into the Fe–SiCl$_3$ bond is not as favorable as into the Si(CH$_3$)$_3$ bond, because the Fe–Si bond ionization is much greater, and the stabilization of the metal ionizations by π-back-bonding to SiCl$_3$ would also be lost.

Summary

For a metal to assist a chemical reaction in proceeding at a reasonable rate under reasonable conditions of temperature and pressure, the interactions of the metal with the starting molecules must be sufficiently strong to activate the bonds of interest, but not so strong that subsequent bond-forming and product-elimination processes are significantly hindered. Otherwise the reaction falls into a thermodynamic "hole" which is difficult to escape. Successful catalytic processes involve a fine balance of these forces of interaction and stabilization of intermediates along the reaction pathway. The studies presented here give an indication of the extent that different factors such as the electron richness of the metal, the substitutions on the silyls, and the d-electron count may influence the different steps of the hydrosilation reaction.

It has been shown in this and our previous studies of Si–H bond activation that the substituents on the silicon atom have a large effect on the extent of oxidative addition of the Si–H bond to the metal center. The electronegative chlorine substituents favor oxidative addition over alkyl substituents. The present study shows that if the metal has d electrons which can back-bond to the silyl, this can be an additional factor in the stabilization of the intermediate. The trichlorosilyl ligand is approximately half as effective as a carbonyl ligand at stabilizing the complex through π-back-bonding, and this additional strengthening and shortening of the M–Si bond further favors oxidative addition to form direct metal–silyl and metal–hydride bonds. This factor is not significant

for trialkylsilyl ligands, which are negligible as π-back-bonding ligands in these complexes. The Si–H bond of the trialkylailanes does not completely add to the metal in the manganese complexes referred to in this study.

The ionization correlations indicate that ethylene insertion is thermodynamically favored into the metal–silyl bond rather than into the metal-hydride bond in these complexes. This traces primarily to the instability of the metal–silyl σ bond ionization relative to the metal–hydride σ bond ionization. Insertion is favored somewhat more for the trialkylsilyl than for the trichlorosilyl because of the stronger M–Si bond in the latter species due to π-back-bonding and ionic bonding contributions. The final step to product is the reductive elimination of the new alkylsilane. The electronic factors that favor reductive elimination are the reverse of those that favor oxidative addition, and can be influenced by similar changes in ligand and metal substituents and d-electron count.

Dynamics of Water Protons in Concentrated Ga^{3+}, Al^{3+}, Fe^{3+}, and Dy^{3+} Aqueous Solutions: A Study Using Incoherent Quasi-Elastic Neutron Scattering

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Abstract: The method of high-resolution incoherent quasi-elastic neutron scattering (IQENS) is applied to investigate the translational diffusive motion of water protons and the cation to water proton binding time in concentrated Ga^{3+}, Al^{3+}, Fe^{3+}, and Dy^{3+} aqueous solutions. The IQENS data for the Ga^{3+}, Al^{3+}, and Fe^{3+} solutions are consistent with the model for slow exchange wherein the dynamic hydration number $n_h = 6$. This gives a limit of $\tau_1 \gtrsim 5 \times 10^{-9}$ s for the binding time of protons in the hexa-aquo metal ion species. The IQENS data for the Dy^{3+} aqueous solution show that the water protons are in intermediate or slow exchange, which sets a lower limit of $\tau_1 > 10^{-10}$ s. The second-shell water protons in the Ga^{3+}, Al^{3+}, and Fe^{3+} solutions are not observed to be in slow exchange with the cation which gives a binding time for these protons of $\tau_1^{(2)} < 5 \times 10^{-9}$ s. A reduced limit of $\tau_1^{(2)} \lesssim 10^{-10}$ s is, however, argued for. Although the IQENS data for the Ga^{3+} and Fe^{3+} solutions are, within the experimental uncertainties of the method, consistent with $n_h = 6$, the data are better represented if a degree of hydrolysis is assumed. This gives $n_h < 6$, a lower limit of $\tau_1 \gtrsim 5 \times 10^{-9}$ s for protons in any metal ion hydrolysis products, and an upper limit of $\tau_1 < 5 \times 10^{-9}$ s for any dissociated protons.

1. Introduction

The object of this paper is to present new results on the proton dynamics in concentrated Ga^{3+}, Al^{3+}, Fe^{3+}, and Dy^{3+} aqueous solutions. The results are obtained by using the method of

high-resolution incoherent quasi-elastic neutron scattering (IQENS), which is described by Hewish et al.[1] and Salmon.[2] The merits of the method for the study of ionic solution dynamics are as follows.

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