UPS Study of Compounds with Metal−Silicon Bonds: $M(CO)_nSiCl_3$ (M = Co, Mn; *n* = 4, 5) and $Fe(CO)_4(SiCl_3)_2$

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Received August 13, 1996[⊗]

The (trichlorosilyl) (and -germyl)metal carbonyls $Co(CO)_4SiCl_3$, $Co(CO)_4GeCl_3$, $Mn(CO)_5SiCl_3$, and *cis*-$Fe(CO)_4(SiCl_3)_2$ have been synthesized in high yields. He I photoelectron spectra (UPS) of the complexes have been measured and interpreted on the basis of empirical arguments and density functional theory (DFT) calculations. For *cis*/*trans*-$Fe(CO)_4(SiCl_3)_2$ isomers the calculations predict the *trans*-isomer to be more stable than *cis* by 15.2 kJ mol^{-1}. The *cis*-isomer is exclusively present in the solid state and in the gas phase. UPS results suggest the importance of charge polarization effects and the lack of π-back-donation along TM−Si bonds. The calculated M−Si bond distances amounted to 2.34 Å (Co−Si), 2.43 Å (Co−Ge), 2.47 Å (Mn−Si), 2.41 Å (*trans*-Fe−Si), and 2.45 Å (*cis*-Fe−Si). For $Co(CO)_4SiCl_3$, the DFT calculated Co−Si bond dissociation energy was 317.7 kJ mol^{-1}, compared to 222.2 kJ mol^{-1} for Co−C energy in $Co(CO)_4CCl_3$.

Introduction

Complexes with metal−silicon bonds have attracted much attention. In particular, the recently synthesized compounds with metal−silicon multiple bonds have great synthetic potential and may contribute toward extending the scope of modern organometallic silicon chemistry beyond the chemistry of singly bonded species.[1]

Metal−silicon single bonds are unique and often display unusual properties, such as unexpectedly short bond distances or high bond energies, which are not yet fully understood.[2] A straightforward comparison of the properties of metal−silicon versus metal−carbon bonds is often misleading. One example may be given as an illustration: In $CpFe(CO)_2SiCl_3$ the iron−silicon bond distance (2.21 Å) is considerably shorter than the sum of van der Waals radii (VDW, 2.43 Å). The UPS study by Lichtenberger et al.[3] used He I and He II radiation to address this problem in depth. The result suggested that a combination of π-back-bonding and ionic bonding contributions is responsible for metal−silicon bond shortening.

π- or δ-back-bonding effects can only be expected for transition metals (TM) with a d^n electron configuration ($n > 1$). As a consequence, no TM−Si bond shortening should occur in the case of d^0 transition metals, which is exactly what had been observed in many cases.[1b] It must be pointed out that similar bond shortening effects had also been observed in some metal carbon complexes,[4] especially those with fluorinated substituents such as *trans*-$HCF_2CF_2Co(CO)_3P(C_6H_5)_3$ (exptl C−Co 1.95 Å, calcd 2.10 Å) or *cis*-(CFH═CF)$Mn(CO)_5$ (exptl C−Co 1.95 Å, calcd 2.10 Å).

Particularly suitable targets for the study of metal−silicon bonding interactions are the highly volatile silylmetal complexes of the type $Cl_3SiM(CO)_n$ (M = Co, Mn) and *cis*-$(Cl_3Si)_2Fe(CO)_4$. The unusually short metal−silicon bonds in these compounds have stimulated discussion about $d_\pi p_\pi$- and even δ-bonding effects between metal and silicon.

The He I/He II photoelectron study of complexes $L_3MCo(CO)_4$ (M = Si, Ge, Sn, Pb; L = Cl, Br, CH_3) has been performed and used to discuss $p_\pi d_\pi$ and $p_\delta d_\delta$ effects. The study focused on the electronic structure trends induced by variation of M (Si, Ge, Sn, Pb).[5] In contrast to the expected electronegativity trends, bands due to ionization from metal d (2e) orbitals are stabilized on going from M = Si to M = Sn. This effect was rationalized by the assumption of δ-back-bonding from the 2e orbitals at Co to vacant Si 3d orbitals. Partial multiple bonding is seen as a basis for the short metal−silicon bond distances. This conclusion was at variance with the results of UPS study by Ebsworth et al.,[6] who

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

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S0276-7333(96)00692-9 CCC: $14.00

could find no evidence for π-interactions between transition metal and SiH_3 or CH_3 groups.

The particularly high M–Co bond dissociation energies of $R_3M{-}Co(CO)_4$, M = Si, Ge, Sn, and Pb, complexes[7] do seem to support the notion of partial multiple bonding between silicon and transition metals.

MacDiarmid et al.[4] addressed the question of TM → Si π-back-bonding by a careful survey of structural and spectroscopic data of selected complexes. According to an extended Hückel theory (EHT) calculation for $Cl_3Si{-}Co(CO)_4$, 97% of the Co–Si bond energy is accounted for by σ-bonding, involving mainly 3s and 3p orbitals at Si (calculation of overlap energy). π-Bonding overlap is found to account for only 3% of the total bond energy. In $F_3Si{-}Co(CO)_4$, 84% of the total Co–Si bonding energy arises from σ-bonding, the rest being derived from $(d \rightarrow p)\pi$ (8%) and $(d \rightarrow s^*)\pi$ (6%) bonding.

π-Back-bonding effects in metal silyl complexes have been investigated by various spectroscopic studies, including Mössbauer spectroscopy, IR spectroscopy (ν_{CO} stretching vibrations), and ^{13}C and ^{29}Si NMR.[2] Nonetheless, the distinction between σ- and π-effects has not always been unambiguous. M–E σ-bonding effects have also been investigated and were shown to be particularly significant for heavier elements (E), e.g. in transition metal stannyl complexes.[8] We shall attempt to shed more light on the (presently) large and somewhat confusing array of theoretical, structural, and thermodynamic data related to transition metal–silicon bonds. We shall do so by studying and comparing the electronic structures in a series of compounds containing TM–M bonds (TM = Co, Mn, Fe; M = Si, Ge, Sn). The observed variations along the series can then be used to deduce information about TM–M bonds.

Experimental and Theoretical Methods

Instrumental Measurements. IR spectra were obtained on a Perkin-Elmer 1725 instrument. ^1H, ^{13}C, and ^{29}Si NMR spectra were measured on a Jeol FX 900, a Bruker ACF 300, or a Bruker AMX 500 spectrometer. Mass spectra were recorded on a VG 7035 double-focusing spectrometer equipped for the EI technique. The He I photoelectron spectra were measured on a Leybold-Heraeus UPG-200 spectrometer with a specially designed inlet system using Ar^+ $^2P_{3/2}$ (15.759 eV) and CH_3I $^2E_{1/2}$ (9.54 eV) as calibration lines. The same lines were used to check the linearity of the kinetic energy scale. The resolution of the spectrometer was 18–25 meV (fwhm) when measured on the $^2P_{3/2}$ Ar^+ line. The assignment of the spectra was based on empirical arguments: relative band intensities, comparison with spectra of related compounds, and DFT calculations.

Theoretical Methods. Density functional theory (DFT) has proved to be very useful for study of various transition metal complexes and their properties.[9,10] DFT calculations were performed on a Cray T94 computer using the UniChem 3.0 program package.[11] The DFT method is implemented in the DGauss program, which forms part of the UniChem package. Our calculations used nonlocal density approximation, the DZVP basis set, and the Becke–Lee–Yang–Parr (BLYP) functional.[12] All the molecular geometries were fully optimized, and the geometries obtained were established to be genuine minima on potential energy surfaces as indicated by the absence of imaginary vibrational frequencies. Metal–silicon bond dissociation energies were calculated for $Co(CO)_4(CCl_3)$ and $Co(CO)_4(SiCl_3)$ and amount to 222.2 and 317.7 kJ mol^{-1} for the Co–C and Co–Si bonds, respectively. They were obtained from total energies of products and reactants in the heterolytic dissociation reaction $Co(CO)_4MCl_3 \rightarrow Co(CO)_4 + MCl_3$ (M = C, Si).

Synthesis. Unless otherwise stated, manipulations of starting materials and products were carried out in Ar atmosphere using standard Schlenk techniques. The compounds were prepared in round bottom flasks, Carius tubes with Teflon valves, or sealed tubes. Alternatively, an autoclave may be applied. The reaction vessels were immersed approximately half-volume in silicone-oil baths at the desired temperature and the solutions magnetically stirred. In the case of $Co_2(CO)_8$, the reaction vessel was cooled upon the addition of $SiHCl_3$. Reaction vessels should be placed behind a safety shield when low boiling silanes are heated up to 135 °C in a glass apparatus or a sealed tube. However, we experienced no difficulties in handling such reactions.

Hexane was refluxed over $LiAlH_4$, distilled, and stored on 4 Å type molecular sieves under Ar prior to use. $Fe_3(CO)_{12}$ was prepared according to the literature. Cl_3SiH was obtained in sealed ampules and used without further purification. Sublimations were carried out in a standard vacuum system at a pressure of ca. 5.0×10^{-2} mmHg. Microanalyses were performed by the Analytical Laboratories of The National University of Singapore.

Tetracarbonyl(trichlorosilyl)cobalt, $Co(CO)_4SiCl_3$ (1). The original prescription by Harrod and Chalk[13] was slightly modified to a one-pot procedure. A 3.0 g (8.77 mmol) amount of $Co_2(CO)_8$ was dried in a high vacuum. To this solid, 13.5 g (100 mmol) of freshly distilled Cl_3SiH was added at −40 °C. The mixture was stirred for 2 h and allowed to warm slowly to room temperature. Excess trichlorosilane was removed in vacuo. The residual, gray-brown powder was purified by repeated sublimation at 45 °C, 0.1 mbar. The procedure yielded about 1.2 g of $Cl_3SiCo(CO)_4$ (**1**) as large, pale yellow crystals (23% yield). Anal. Calcd for $C_4Cl_3CoO_4Si$ (245.4): C, 19.58; H, 0.00; Si, 11.44. Found: C, 19.40; H, 0.00; Si, 11.51. IR (Nujol, ν_{CO}, cm^{-1}): 2118 (m), 2063 (s), 2036 (s). Mp: 65 °C. ^{29}Si NMR ($CDCl_3$, 25 °C): δ 36.1. ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ 192.5 (CO_{ax}), 198.1 (CO_{eq}). The vapor pressure curve of $Co(CO)_4SiCl_3$ has been measured in the range between 10.4 and 30.1 °C. The vapor pressure at 22.0 °C amounts to 0.41 mbar.

Tetracarbonyl(trichlorogermyl)cobalt, $Co(CO)_4GeCl_3$ (2). A 1.5 g (5.6 mmol) amount of $NaCo(CO)_4{\cdot}Et_2O$ was dissolved in 50 mL of THF and cooled to −30 °C. Then, 1.2 g (5.6 mmol) of $GeCl_4$ dissolved in 20 mL of THF was added dropwise with stirring. The reaction mixture turned deep orange. After filtration and removal of the solvent in vacuo, the crude material was sublimed at 60 °C and 10^{-2} Torr. The sublimation process was performed twice, to separate the product from impurities of $GeCl_2\{Co(CO)_4\}_2$ and $GeCl\{Co(CO)_4\}_3$. Yield of **2**: 1.07 g (66%). The reaction can also be done on a larger scale. Anal. Calcd for $C_4Cl_3CoGeO_4$ (289.9): C, 16.57; H, 0.00; Ge, 25.04. Found: C, 16.58; H, 0.00; Ge, 25.01. Mp: 98–101 °C. IR (Nujol): 2120 (m), 2068 (s), 2040 (vs).

Pentacarbonyl(trichlorosilyl)manganese, $Mn(CO)_5SiCl_3$ (3).[14] A 1.0 g (2.6 mmol) amount of $Mn_2(CO)_{10}$ was placed in a tube with N_2 inlet and evacuated for 15 min to remove traces of water. Then, 10 mL (100 mmol) of pure trichlorosilane

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$SiHCl_3$ was added, and a magnetic stir bar was placed inside the tube. The tube was sealed, packed into an iron jacket, and heated for 60 h to 120 °C in an oil bath with stirring. During this time, the color of $Mn_2(CO)_{10}$ disappeared. After being cooled to room temperature, the glass tube was opened in a glovebox and its contents transferred to a 50 mL flask with N_2 inlet. Any excess $SiHCl_3$ was condensed off into a separate cold trap. The crude product was then transferred into a sublimation device and sublimed (4 h) at 75 °C, 0.1 Torr. A 0.9 g amount of $Mn(CO)_5(SiCl_3)$ was obtained as white crystals which corresponds to a yield of 52%. Anal. Calcd for $C_5Cl_3O_5Mn$ (329.43): C, 18.23; H, 0.00; Si 8.53. Found: C, 18.23; H, 0.00; Si 8.61. Mp: 119 °C. IR (Nujol, ν_{CO}, cm^{-1}): 2124 (s), 2033 (s). The vapor pressure curve has not been measured; however, the compound is only slightly less volatile than **1** and sublimes at 75 °C/10^{-1} Torr.

***cis*-Tetracarbonylbis(trichlorosilyl)iron, *cis*-Fe(CO)$_4$(SiCl$_3$)$_2$ (4).**[15] A 1.0 g (2.0 mmol) amount of $Fe_3(CO)_{12}$ was placed in a Carius tube (stir bar) and dried in vacuum, and 10 mL (100 mmol) of $SiHCl_3$ was added. The closed vessel was heated for 36 h to 120 °C with stirring. The intense green color of the iron dodecacarbonyl disappeared during the reaction. Although no accidents occurred, it is advisable to place the glass tube behind a safety shield. After the reaction was completed and the vessel cooled to room temperature, excess $SiHCl_3$ was removed by condensation into a separate cold trap. The crude product was transferred into a sublimation device and sublimed (24 h) at 85 °C, 0.1 Torr. A 0.5 g (20% yield) amount of slightly greenish crystals was obtained. Anal. Calcd for $C_4Cl_6Si_2Fe$ (436.78): C, 11.00; H, 0.0. Found: C, 11.14; H, 0.0. Mp: 93−96 °C. *cis*-Isomer IR (Nujol, ν_{CO}, cm^{-1}): 2125 (m), 2077 (m), 2070 (vs), 2060 (s). The *trans*-isomer was not present. ^{13}C NMR ($CDCl_3$, 400 MHz): δ (*cis*) 199.44 (CO_{ax}), 197.30 (CO_{eq}). ^{29}Si NMR ($CDCl_3$): δ 21.5. **4** is slightly less volatile than **3** and sublimes at 85 °C/10^{-1} Torr. Above 90 °C, *cis*−*trans* isomerization may occur.

Results and Discussion

General Reactivity. Various methods are known for the synthesis of transition metal−silicon bonds.[16] For instance, the insertion of 16e transition metal species into Si−H bonds (Si−H activation) has been investigated widely.[17] Further synthetic methods include silylene trapping and displacement reactions. We have followed an approach utilizing the direct combination of trichlorosilane with transition metal carbonyls in a sealed tube or Carius tube reaction. Trichlorosilane is one of the most active reagents in Si−H activation reactions. Furthermore, the products are sufficiently volatile for PE-spectroscopic investigations.

The reactions of octacarbonyldicobalt with trichlorosilane was performed as a one-pot synthesis for the sake of simplicity, following a scheme outlined by Harrod et al.[13]

$$Co_2(CO)_8 + 2Cl_3SiH \rightarrow HCo(CO)_4 + Cl_3Si(CO)_4$$

$$HCo(CO)_4 + Cl_3SiH \rightarrow Cl_3SiCo(CO)_4 + H_2$$

$$2HCo(CO)_4 \rightarrow Co_2(CO)_8 + H_2$$

The mechanism involves an oxidative addition of silane to the metal accompanied by cleavage of the cobalt−cobalt bond. The related germyl complex was synthesized by combination of sodium tetracarbonylcobaltate with germanium tetrachloride.

Table 1. Physical Properties of (Trichlorosilyl)metal Carbonyls

compd	microanal. calcd (found) C	microanal. calcd (found) H	IR data^a (cm^{-1})
$Co(CO)_4(SiCl_3)$ (**1**)	19.58 (19.40)	0.00	2118 (m), 2063 (s), 2036 (vs)^b
$Co(CO)_4(GeCl_3)$ (**2**)	16.57 (16.58)	0.00 (0.00)	2180 (m), 2068 (s), 2040 (vs)^b
$Mn(CO)_5(SiCl_3)$ (**3**)	18.23 (18.23)	0.00 (0.00)	2124 (s), 2033 (s)^c
$Fe(CO)_4(SiCl_3)_2$ (**4**)	11.00 (11.14)	0.00 (0.00)	*cis:* 2125 (m), 2077 (m), 2070 (m), 2060 (s)^d

^{a} IR spectrum taken in Nujol. ^{b} $A_1 + E + E$. ^{c} $A_1 + B_1 + B_2 + E$. ^{d} $A_1 + A_2 + B_1 + B_2$.

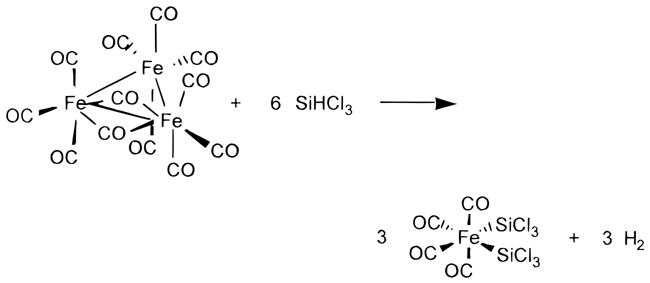
$$Co_2(CO)_8 + 2Na \rightarrow 2NaCo(CO)_4$$

$$NaCo(CO)_4 + GeCl_4 \rightarrow Cl_3Ge{-}Co(CO)_4 + NaCl$$

For the synthesis of pentacarbonyl(trichlorosilyl)manganese, decacarbonyldimanganese has been combined directly with trichlorosilane in the absence of any solvent.

$$Mn_2(CO)_{10} + 2SiHCl_3 \rightarrow 2Mn(CO)_5(SiCl_3) + H_2$$

Finally, the synthesis of tetracarbonylbis(trichlorosilyl)iron involved the reaction of dodecacarbonyltriiron with trichlorosilane at elevated temperatures in a Carius tube.



Alternatively, an autoclave with an inside coating of Hostaflon (Teflon) is suitable. In all cases, the reactions produced *cis*-Fe(CO)$_4$(SiCl$_3$)$_2$ in the absence of any solvent (Table 1). The isomerization between *cis*/*trans*-Fe(CO)$_4$ has been studied by ^{13}C NMR spectroscopy.[18] At 90 °C, coalescence was observed in the ^{13}C NMR spectrum of axial and equatorial CO signals of the *cis*-isomer (in a mixture of *cis* and *trans*) which corresponds to a free energy of activation of $\Delta G^{\ddagger} = 17.5$ kcal mol^{-1}. The isomerization is believed not to involve any dissociative mechanism.[18]

Electronic Structure. The He I photoelectron spectra recorded are shown in Figure 1. Vertical ionization energies for $Co(CO)_4SiCl_3$ measured in this work are systematically higher than the values reported by Oskam et al.[5] by 0.2−0.4 eV. We suggest that the shift could have arisen due to charging effects (contamination) or the nonlinearity of the kinetic energy scale. The latter explanation seems more likely, since Oskam et al.[5] did mention that they had not performed any corrections for analyser dependence.

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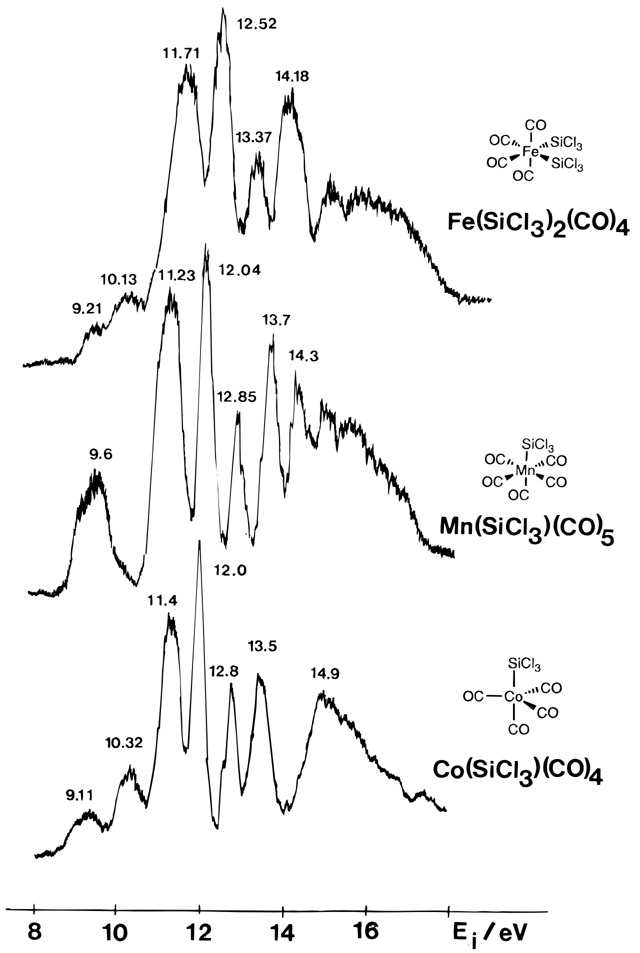

Figure 1. He I photoelectron spectra of $Co(CO)_4SiCl_3$, $Mn(CO)_5SiCl_3$, and *cis*-$Fe(CO)_4(SiCl_3)_2$.

The initial analysis of the spectra in Figure 1 can be obtained by comparison with spectra of related complexes[5,6,19] $Mn(CO)_5H$, $Fe(CO)_4H_2$, and $Co(CO)_4H$ and the spectrum[20] of $SiHCl_3$. The ionization energy region below 13.5 eV contains bands arising from ionization of five transition metal 3d orbitals and Cl 3p (lone pair) orbitals. The bands immediately following these, at higher ionization energies, correspond to ionizations from π orbitals of −CO ligands. The next important question (and the purpose of this work) concerns the character of transition metal−silicon bond. We can deduce some interesting details about it from the careful analysis of band shapes and ionization energy shifts of metal 3d and Cl 3p bands.

We shall discuss spectra[6] of manganese complexes first, $Mn(CO)_5H$, $Mn(CO)_5SiH_3$, and $Mn(CO)_5SiCl_3$. The comparison of ionization energies and band profiles of Mn 3d bands shows that there is a bonding interaction with silyl substituents, because the Mn 3d band changes shape on going from hydrogen to silyl derivatives. In addition there is an inductive shift toward higher ionization energy upon silylation ($-H \rightarrow -SiH_3$). Replacing the $-SiH_3$ group with $-SiCl_3$ (chlorination) induces a further small (0.2 eV) inductive shift in Mn 3d band.

Next, we shall compare spectra[5,6] of $Co(CO)_4H$, $Co(CO)_4SiH_3$, and $Co(CO)_4SiCl_3$. The results indicate no change in energy or shape of two Co 3d bands upon silylation. Chlorination leads to sizable (0.4 eV) inductive shift of Co 3d bands.

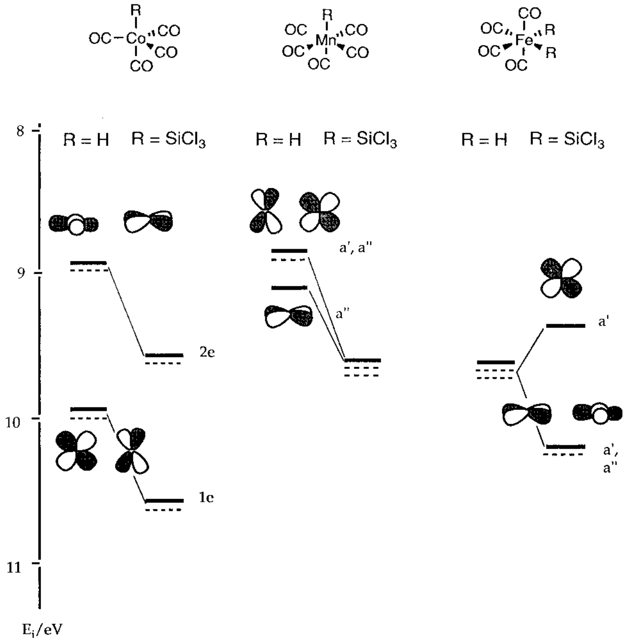

Figure 2. Comparison of TM 3d-ionization energies in $Co(CO)_4H$, $Co(CO)_4SiCl_3$; $Mn(CO)_5H$, $Mn(CO)_5SiCl_3$; and *cis*-$Fe(CO)_4H_2$, *cis*-$Fe(CO)_4(SiCl_3)_2$ (experimental He I data).

Finally, we shall compare the spectra[19] of $Fe(CO)_4H_2$ and $Fe(CO)_4(SiCl_3)_2$. (The spectrum of $Fe(CO)_4(SiH_3)_2$ has not yet been reported.) This complex can conceivably exist in two isomeric forms, *cis* and *trans*. The DFT total energies (ZPE corrected) for *cis* and *trans* isomers of $Fe(CO)_4(SiCl_3)_2$ predict the *trans* isomer to be more stable by 15.2 kJ mol^{-1}. In order to establish which isomer predominates in the gas phase, we have simulated the He I spectra of the two isomers by calculating (via 1st order time-dependent perturbation theory implemented in DGauss[11]) differential photoionization cross sections for different single particle electronic states.[21] The bands were represented by Gaussians (0.1 eV width). The photoelectron was approximated by the plane wave which, although not the best approximation available, is sufficient for the purpose of distinguishing qualitatively the spectra of two isomers. The simulated spectra of the two isomers are shown in Figure 2. Comparison of experimental and simulated spectra suggests that *cis* isomer is predominant in the gas phase. The same is true of the condensed phase as indicated by our IR and NMR data (see Experimental and Theoretical Methods section).

The Fe 3d bands in $Fe(CO)_4(SiCl_3)_2$ are partially overlapped by Cl 3p bands, but nonetheless we can see that they have significantly lower ionization energies (by 0.4−0.9 eV) than $Fe(CO)_4H_2$. This is an interesting result which can be explained by the strong bonding interactions between Si and Fe. We shall examine next the ionization energies of Cl 3p bands. The rationale is that a shift of Cl 3p bands toward lower energies gives a qualitative indication of electron density transfer from the silicon to chlorine atom. If we use the spectrum of $SiHCl_3$ as a reference,[20] it appears that in Mn and Co

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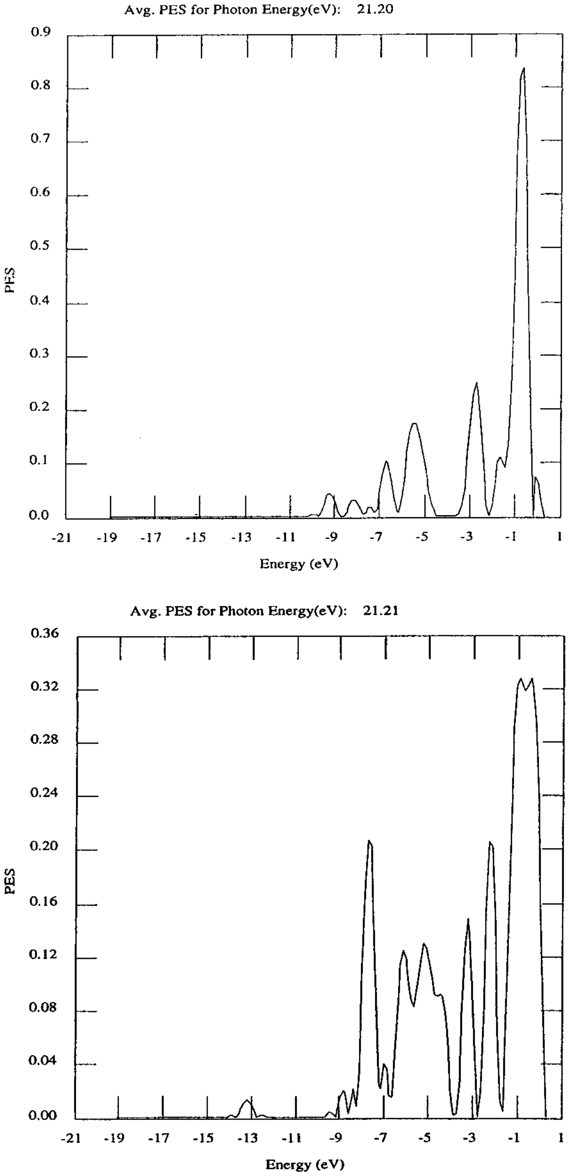

Figure 3. Simulation of He I photoelectron spectra for (a, top) *trans*-$Fe(CO)_4(SiCl_3)_2$ and (b, bottom) *cis*-$Fe(CO)_4(SiCl_3)_2$.

complexes some electron density is transferred to chlorine, while in the Fe complex little "electron flow" can be detected. Furthermore, TM−Si interactions seem to be strong in Mn and Fe complexes but weaker in Co complexes. The arguments used so far are empirical and as such have an advantage of not being dependent on a particular model.

However, experimental observations concerning transition metal complexes are often rationalized within frameworks of qualitative models, one of the most widely used being the Dewar−Chatt−Duncanson (DCD) model.[22] In this model the electronic structure is expressed via three parameters: σ-donation from ligands (L) to transition metal, π-back-donation from metal to L, and charge polarization. In MO language these terms correspond to the following fragment orbital interactions: interaction between vacant *n*d and occupied L orbitals, interaction between vacant L orbitals and occupied *n*d orbitals, interaction between occupied *n*d and L orbitals. The model has recently been put on a more quantitative basis by the method of charge decomposition analysis (CDA).[23] There is no unique way of mapping our experimental data onto model parameters (which are not observables), but we shall try to interpret our results in terms of these parameters. The two questions in particular are of special interest within the framework of the DCD model: (1) What are the ionization and dissociation energies of TM−Si bond in title compounds? (2) What are the corresponding charge distributions along the TM−Si bond?

Table 2. Ionization Energies (E_i/eV) and Assignments of UPS Bands[a]

compd	band	E_i	assgnt
$Co(CO)_4SiCl_3$	X̃−Ã	9.11	Co 3d
	B̃−D̃	10.32	Co 3d, Co−Si
	Ẽ−G̃	11.4	Cl 3p
	H̃−Ĩ	12.0	Cl 3p
	J̃	12.8	Cl 3p
$Mn(CO)_5SiCl_3$	X̃−D̃	9.6	Mn 3d, Mn−Si
	Ẽ−G̃	11.23	Cl 3p
	H̃−Ĩ	12.04	Cl 3p
	J̃	12.8	Cl 3p
$Fe(CO)_4(SiCl_3)_2$	X̃−Ã	9.21	Fe 3d, Fe−Si
	B̃−D̃	10.13	Fe 3d
	Ẽ−J̃	11.71	Cl 3p
	K̃−Ñ	12.52	Cl 3p
	Õ−P̃	13.37	Cl 3p

[a] Most bands whose ionization energies are quoted in this table comprise several ionizations, and the numerical values refer to the maxima of each band cluster.

The ionization and dissociation energies of a particular bond are strictly speaking not observables and can thus only be estimated from experimental data. The dissociation energies were estimated as described in the Experimental and Theoretical methods section. The TM−Si bond ionization energies (or, more precisely, ionization energies of orbitals strongly localized along the TM−Si bond) can be estimated by comparison of quantum mechanical calculations with UPS data. DFT calculations are not suitable for the purpose, because there is no Koopmans' theorem equivalent for DFT (Kohn−Sham) orbitals. On the other hand, *ab initio* calculations must be of very high (post HF) quality because of the well-established presence of Koopmans' defects in transition metal complexes.[24] We can however deduce TM−Si orbital ionization energies of the title compounds by comparing UPS data for Fe−H, Mn−H, and Co−H bonding orbitals in hydrides[6,19] and ionization energies[3,5] of Fe−Si and Co−Si bonding orbitals in $CpFe(CO)_2SiCl_3$ and $Co(CO)_4SiCl_3$. The general conclusion is that ionization energies of TM−H localized orbitals are approximately 1.3 eV higher than that of TM−Si. The band assignments are summarized in Table 2. The TM−Si orbital ionization energies suggest that the bonding interactions are stronger between Fe−Si and Mn−Si than between Co−Si. This result emphasizes the fact that not all transition metal−silicon bonds are similar. The second important parameter concerns the electron distribution (transfer) between silicon and transition metal. Once again, no unambiguous answer is possible based solely on experimental results, since electron transfer is not an observable. However, one can compare ionization energies and bond lengths to get some insight into charge distribu-

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Table 3. Available Structural Data for TM−Si Bonds (in Å)

bond	DFT	X-ray	VDW
Co−Si	2.341	2.254	2.51
Mn−Si	2.473	2.50	2.54
cis-Fe−Si	2.447		2.56
trans-Fe−Si	2.412	2.326	2.56

tions along TM−Si bonds. The low E_i values for Fe 3d and Mn 3d ionizations (compared to Co 3d) tend to suggest that higher electron distributions can be expected on Fe and Mn atoms than on the Co atom. We also note that (vide infra) Cl 3p ionization energies in Mn complex are lower than in Fe or Co complexes. The two observations can be rationalized by assuming that the polarization effect is significant along the TM−Si bond while π-back-donation is not. If the latter were important, one would expect to observe an increase in metal *n*d ionization energies and decrease in Cl 3p energies. Ebsworth et al.[6] reached a similar conclusion regarding the lack of π-back-donation effects.

On the other hand, a decrease in both energies suggests that metallic and chlorine atoms both gain some electron density upon TM−Si bond formation. The electron density gain by Cl is accompanied by a slight decrease of density on Si, the final result being generation of partial (and opposite) charges on TM and silicon centers. In the DCD model this corresponds to a charge polarization effect. The electrostatic attraction of opposite charges then contributes to the observed bond shortening. We have already mentioned (see Introduction) that measured TM−Si internuclear distances are shorter than the sum of van der Waals radii. We have performed Löwdin's population analysis (LPA) on DFT orbitals. Despite the fact that Löwdin's population analysis partitions the electron density in a somewhat arbitrary manner (as does Mulliken's) and that better ways of describing the charge density are available,[23] the LPA results are interesting. The calculated partial charges on Co, Mn, and Fe are −0.82, −1.21, and −1.00, respectively. The silicon carries a positive partial charge +0.4, approximately. LPA results support our conclusion deduced from UPS data concerning charge polarization effects. The strength of dipolar effects is highest in Mn and weakest in Co complexes. The UPS is not the most direct method available which can help in unraveling the complexities of electron distribution along TM−Si bonds. However, the difficulties associated with measuring Si and TM NMR spectra means that UPS results are very useful. The available NMR data for TM−Si complexes[2] show high-field ^{13}C NMR shifts of equatorial carbons. This had been interpreted as evidence of σ-donation from −CO groups to metal.

Structural data (Table 3) reveal that DFT and X-ray bond lengths, when available, are consistently shorter than the sum of van der Waals radii, which can be explained by strong dipolar effects which favor shorter bonds.

Finally, it is interesting to compare the bond strengths of TM−C and TM−Si bonds. Once again we used the DFT method, and for $Co(CO)_4(SiCl_3)$, the calculated Co−Si bond dissociation energy was 317.7 kJ mol^{-1}, compared to 222.2 kJ mol^{-1} for the Co−C bond in $Co(CO)_4(CCl_3)$. This suggests a high σ-bonding contribution (overlap) in the case of silicon.

Conclusion

We have used primarily experimental results and empirical deductions in order to illuminate the nature of transition metal−Si bonds in some complexes. The results can be interpreted by assuming the presence of charge polarization effects and the lack of π-back-donation. The former effects do vary from metal to metal. The strength of polarization effects is reflected in TM−Si bond lengths. The TM−Si bond is considerably stronger than its organometallic counterpart TM−C bond. Further NMR and X-ray studies may help to broaden the conclusions reached in this work.

Acknowledgment. The work has been supported by The National University of Singapore by the Research Grants RP940634 and RP900624. We thank Professors How Gee Ang and Hsing Hua Huang for support and the National Supercomputer Research Centre for giving us a generous allocation of computer time. Ms. Francis Lim performed the elemental analyses with never ending patience and accuracy, and Ms. Fang Ying Lee measured the NMR spectra. Finally, we thank Meng Ooi Kwan (National JC) and Ooi Zi En (Raffles JC) for assistance.

OM960692T