Electronic Structure Factors of Ge–H Bond Activation by Transition Metals. Photoelectron Spectra of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$, $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$, and $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HGePh_3)]$ †

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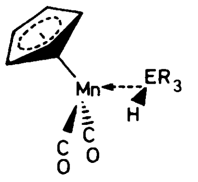
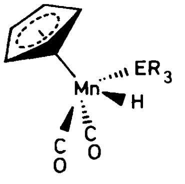
The He I photoelectron spectra of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$, $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$, and $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HGePh_3)]$ have been obtained to measure the nature and extent of Ge–H bond interaction with the transition metal centre in these complexes. The principal electronic structure factors contributing to the addition of the Ge–H bond to the transition metal involve the interaction of the Ge–H σ and σ^* orbitals with the metal. The shape and splitting pattern of the metal-based ionisation band indicates the extent of Ge–H σ^* interaction. The electron distribution between the Ge–H bond and the metal is indicated by the relative stabilities of the metal- and ligand-based ionisations. The electron charge-density shift from the metal to the ligand is negligible in these three complexes and the metal ionisations reflect the formal d^6 electron count at the metal centre. The electronic structure of the Ge–H interaction with the metal is in the initial stages of Ge–H bond addition to the metal, before oxidative addition has become prevalent. The mechanism of interaction of the Ge–H bond with the manganese centre is predominantly through interaction of the filled Ge–H σ-bonding orbital with the empty metal orbitals. It is concluded that the magnitude of Ge–H σ interaction with the metal centre is similar to that of the corresponding Si–H σ interaction.

The activation of C–H bonds by metals is important to synthetic and catalytic processes involving the functionalisation of hydrocarbons[1–4] and likewise activation of Si–H and Ge–H bonds by transition metals is important in a number of industrial processes.[5,6] In addition, an understanding of the electronic factors of E–H bond activation and oxidative addition to the metal centre is important. Complexes of the general molecular formula $[Mn(\eta^5\text{-}C_5R'_5)(CO)L(HER_3)]$ (R′ = H or Me; L = CO or PMe_3; E = Si, Ge, or Sn; R = Ph or Cl) display an interaction of a Si–H, Ge–H, or Sn–H bond with a transition-metal centre.[7–9] Techniques such as *X*-ray and neutron diffraction,[7,10–12] ^{29}Si n.m.r. spectroscopy,[7] reaction chemistry,[8,13–15] and kinetics[16] have been used to illustrate the ground-state bonding and electronic structure of these complexes. The results are interpreted in some cases in terms of a three-centre two-electron Mn–H–E bond as shown in (**A**) where the silane and germane act as neutral two-electron donors. In other cases the results indicate a more complete oxidative-addition product as represented by (**B**). Reaction chemistry has indicated that $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$ is best represented by structure (**A**), while there are no data of any kind on $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$, and $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HGePh_3)]$.



(A)



(B)

E = Si or Ge

Photoelectron spectroscopy on the similar silyl complexes has provided direct information on the electron distribution and bonding with the metal centre.[17–20] The destabilisation of the ligand-based ionisations, stabilisation of the metal-based ionisations, and He I/He II intensity trends observed in the valence photoelectron spectrum of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HSiCl_3)]$[18] and $[Mn(\eta^5\text{-}C_5H_4Me)(CO)(PMe_3)(HSiCl_3)]$[20] showed these complexes to be formally d^4 manganese(III) systems resulting from nearly complete oxidative addition of the Si–H bond to the metal as in (**B**). In contrast, a similar study of $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HSiPh_3)]$, $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HSiHPh_2)]$, and $[Mn(\eta^5\text{-}C_5H_4Me)(CO)(PMe_3)(HSiHPh_2)]$ showed these complexes to be formally d^6 manganese(I) systems where the Si–H bond acts like a two-electron donor as in (**A**).[19,20] The electronegativities of substituents on the silicon atom have a greater control over the addition of the Si–H bond to the metal centre than methylation of the cyclopentadienyl ring or common substitutions of ligands around the metal centre.

Substitution of Ge for Si should have an effect on the extent of E–H bond addition to the metal centre. The electronic structure factors of bond activation have been discussed in terms of σ and σ^* interactions of the E–H bond with the metal centre.[21] The donation of electron density from the E–H σ-bonding orbital into the metal lowest unoccupied molecular orbitals (l.u.m.o.s) is the σ interaction and results in the formation of a three-centre two-electron bond. The σ^* interaction involves the donation of electron density from the filled metal orbitals into the E–H σ^* orbital and finally results in full oxidative addition and formation of direct M–H and M–E bonds. The Si–H and Ge–H bond strengths are 76 and 69 kcal mol^{-1} respectively. The Ge–H σ^* level is anticipated to be at a lower energy than the Si–H σ^* level, therefore the Ge–H σ^* interaction should be greater than that observed in the silane complexes. Is the Ge–H bond completely broken in the metal–germyl complexes?

The reaction chemistry of $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGe$-

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† *Non-S.I. units employed:* cal = 4.184 J, eV ≈ 1.60×10^{-19} J.

Ph_3)] has been studied in detail.[8] Both strong and weak bases abstract the proton from the germyl complexes so the proton is fairly acidic. The co-ordinated silane undergoes substitution by triphenylphosphine according to the reaction (1).[16] The rate of

$$[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HSiR_3)] + PPh_3 \longrightarrow [Mn(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)] + HSiR_3] \quad (1)$$

substitution of the silane by the phosphine is a measure of the extent of Si–H addition to the metal centre. The reaction of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HSiPh_3)]$ with PPh_3 is relatively faster than that of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HSiCl_3)]$ with PPh_3. This difference in reaction rates has been attributed to the retention of Si–H interaction in the metal–$HSiPh_3$ complex. The complex $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$ undergoes elimination of the germane at the same rate as that of the $HSiPh_3$ complex when treated with triphenylphosphine. Since the rates of reaction of the germyl complexes are of the same order of magnitude as those of its silyl analogues, a Mn–H–Ge three-centre two-electron bond [structure (**A**)] is inferred to be present in $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$.

To characterise more completely the nature of the Ge–H bond interaction with the transition metal in the complexes, He I photoelectron spectra of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$, $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$, and $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HGePh_3)]$ have been recorded. The spectra of the compounds are compared to those of the parent tricarbonyl and the free $HGePh_3$ ligand to determine the shifts in the metal- and ligand-based ionisations. The ionisation shifts from complex to complex are compared to observe the effect of cyclopentadienyl ring methylation on the extent of addition of the Ge–H bond to the metal centre.

Experimental

Preparation of Compounds.—The compound $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$ was prepared by photolysis of $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_3]$ in tetrahydrofuran (thf) to form $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(thf)]$, which was later treated with $HGePh_3$.[8] The compounds $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$ and $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HGePh_3)]$ were prepared by an analogous method and all compounds were characterised by i.r. spectroscopy.

Photoelectron Data.—Photoelectron spectra were recorded on an instrument which features a hemispherical analyser (10-cm gap, radius 36 cm), and customised sample cells, excitation sources, detection and control electronics, and data-collection methods that have been described previously.[22–26] The argon $^2P_{\frac{3}{2}}$ ionisation at 15.759 eV was used as an internal calibration lock and the $^2E_{\frac{3}{2}}$ ionisation of MeI at 9.538 eV as an external calibration of the energy scale. The spectra of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$, $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_3]$, and $[Mn(\eta^5\text{-}C_5Me_5)(CO)_3]$ were also collected under these calibration conditions for accurate comparisons of the shifts. The spectrum of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$ was measured at a sample-cell temperature of 102 °C while those of $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$ and $[Mn(\eta^5\text{-}C_5Me_5)(CO)(HGePh_3)]$ were measured at sample-cell temperatures of 88 and 96 °C respectively. Before subliming, the compounds gave off free germane as evidenced by their spectra. All data collections were repeated at least five times for purposes of examining particular ionisation features, and no discernible differences were observed between collections.

The data are represented analytically with the best fit of asymmetric Gaussian peaks (program GFIT).[27,28] The asymmetric Gaussian peaks are defined with the position, the amplitude, the half-width indicated by the high binding-energy side of the peak (W_h), and the half-width indicated by the low binding-energy side of the peak (W_l). The confidence limits of the peak positions and widths are generally ±0.02 eV. The confidence limit of a band envelope is about ±5%, with uncertainties introduced from the baseline subtraction and fitting in the tails of the peaks. The individual positions, shapes, and areas of overlapping peaks are not independent and therefore are more uncertain.

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

Results and Discussion

Metal–germyl complexes have not been characterised as thoroughly as metal–silyl complexes. The reaction chemistry of these complexes indicates a Mn–H–Ge three-centre two-electron bond,[8] but no crystal structure data are available. Therefore, the photoelectron data obtained are especially important to give a measure of the electronic process of Ge–H bond interaction with the metal centre. The photoelectron data on Si–H bond activation[18–20] in similar complexes assists greatly in determining the nature of the Ge–H bond interaction here.

Valence Ionisation Bands and Assignments.—The He I photoelectron spectrum of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$ is shown in Figure 1. This spectrum is compared to those of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ and $HGePh_3$. This comparison helps in observing the shifts of ionisations from the parent tricarbonyl complex and the free germane ligand to the corresponding ionisations of the metal–germyl complex. The broad band of overlapping ionisations from 11 to 15 eV in the spectrum of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$ is due to the carbonyl 5σ and 1π electrons, the cyclopentadienyl a_2'' (π) and σ electrons, as well as the ligand ($HGePh_3$) σ electrons. Individual assignments in this forest of ionisations will not be attempted.

The 7—15 eV region of the spectra of the three complexes is shown in Figure 2. The ionisation features of the three spectra are very similar. The first ionisation correlates with the metal *d* electrons. It shifts to lower ionisation energy on permethylation of the cyclopentadienyl ring. The second ionisation is a broad band featuring the Ph π ionisations and the cyclopentadienyl e_1'' ionisations. This band is at nearly the same position in the spectra of the three complexes. The third ionisation is the Ge–C σ ionisation. It does not shift significantly on permethylation. The photoelectron spectrum of $HGePh_3$ has been assigned previously[29] and it is observed that the ionisation at 9.0 ± 0.05 eV of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(HGePh_3)]$, $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$, and $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HGe$-

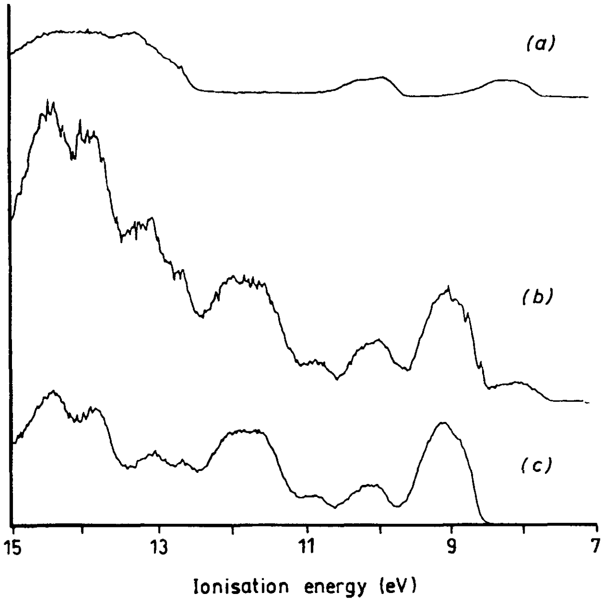

Figure 1. He I valence spectral comparison of (*a*) [Mn(η^5-C_5H_5)(CO)$_3$], (*b*) [Mn(η^5-C_5H_5)(CO)$_2$(HGePh$_3$)], and (*c*) HGePh$_3$. The spectra are plotted so that the metal-based and ligand-based ionisations are the same approximate intensity in each spectrum

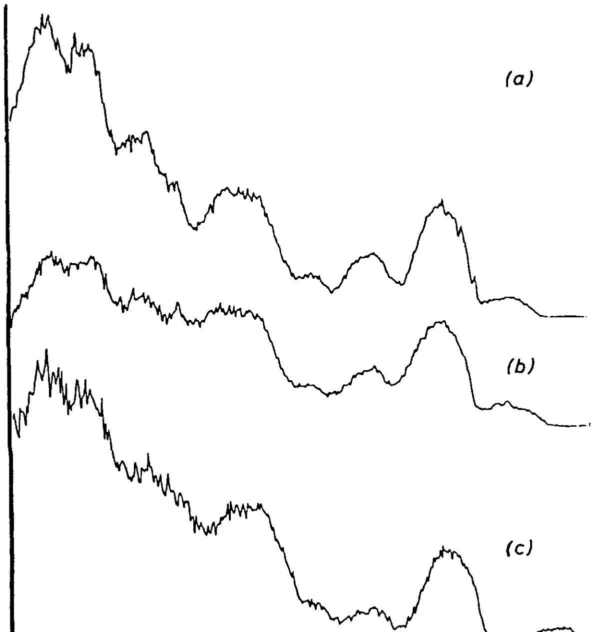

Figure 2. He I full spectral comparison of (*a*) [Mn(η^5-C_5H_5)(CO)$_2$(HGePh$_3$)], (*b*) [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)], and (*c*) [Mn(η^5-C_5Me_5)(CO)$_2$(HGePh$_3$)]

Ph$_3$)], which is due to the phenyl π electrons, does not shift from its position for the free ligand. All positions are given in the Table. Virtually no electron-charge shift from the metal to the ligand in these complexes is therefore indicated.

Since the germane-based ligand ionisations in the complexes do not shift from their positions in the free ligand, spectral subtraction was performed. Subtraction of the free-ligand spectrum from that of the complex leaves the metal-based and cyclopentadienyl ionisations. This subtraction is most helpful in locating the position of the cyclopentadienyl ring ionisations which lie in the region of the phenyl π band. It also helps isolate the metal ionisations, the higher binding-energy edge of which is also near the phenyl π band. The spectral subtraction does not leave accurate peak areas, but the positions and band profiles are more clearly observed.

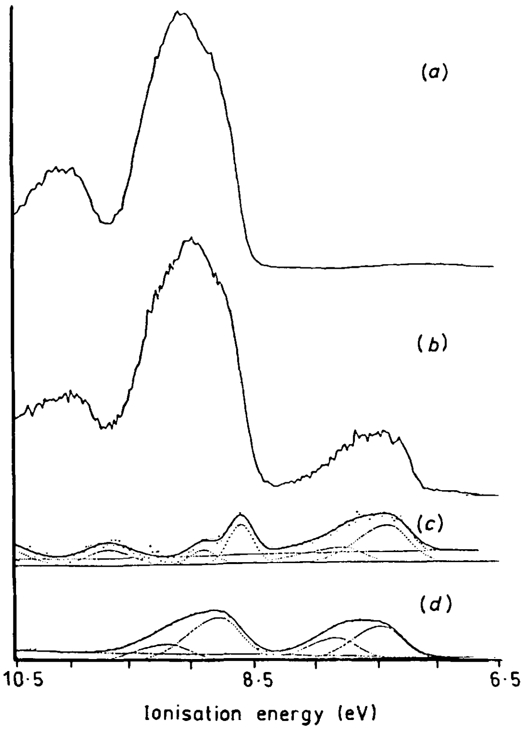

Figure 3. Spectral comparison of (*a*) HGePh$_3$, (*b*) [Mn(η^5-C_5Me_5)(CO)$_2$(HGePh$_3$)], (*c*) subtracted spectrum, and (*d*) [Mn(η^5-C_5Me_5)(CO)$_3$]

Figure 3 shows in a stepwise fashion the effect of ligand subtraction in the spectrum of [Mn(η^5-C_5Me_5)(CO)$_2$(HGePh$_3$)]. Figure 3(*a*) is the free-ligand spectrum which is subtracted from the complex spectrum [Figure 3(*b*)] resulting in the spectrum shown in Figure 3(*c*). The leading ionisation band is the metal band which can be analytically represented by the fit of two asymmetric Gaussian peaks in a 1:2 ratio. The metal band remains at nearly the same position as the metal band of [Mn(η^5-C_5Me_5)(CO)$_3$] [Figure 3(*d*)]. The ionisation at 9.7 eV of [Mn(η^5-C_5Me_5)(CO)$_2$(HGePh$_3$)] is present in all reasonable subtractions and is assigned to the Mn–H–Ge three-centre two-electron bond ionisation.

Figure 4 features the close-up ionisation region of the three complexes following spectral subtraction as above. The cyclopentadienyl e_1'' ring ionisations of [Mn(η^5-C_5H_5)(CO)$_2$(HGePh$_3$)] are shifted 0.2 eV to lower ionisation energy compared to the corresponding ionisations of [Mn(η^5-C_5H_5)(CO)$_3$]. Similarly, the cyclopentadienyl e_1'' ring ionisations of [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)] are 0.1 eV destabilised from those of [Mn(η^5-C_5H_4Me)(CO)$_3$]. The cyclopentadienyl e_1'' ring ionisations have been assigned to the lower ionisation-energy edge of the phenyl π band in [Mn(η^5-C_5Me_5)(CO)$_2$(HGePh$_3$)]. The interaction of five methyl group orbitals with the cyclopentadienyl e_1'' ring orbitals can destabilise them as much as 1.2 eV.[23] These ionisations are also 0.2 eV destabilised from their position in [Mn(η^5-C_5Me_5)(CO)$_3$]. The shift of the cyclopentadienyl ionisations to lower binding energy from their position in the parent tricarbonyl indicates a slightly more negative metal centre in the germyl complexes.

Table. He I valence ionisation features *

Complex	Position (eV)	W_h (eV)	W_l (eV)	Relative area
[Mn(η^5-C_5H_5)(CO)$_3$]	7.99	0.65	0.36	1.00
	8.34	0.65	0.36	0.57
	9.85	0.70	0.33	1.31
	10.25	0.80	0.29	0.56
[Mn(η^5-C_5H_5)(CO)$_2$(HGePh$_3$)]	7.88	0.50	0.31	1.00
	8.11	0.50	0.31	0.96
	8.37	0.50	0.31	0.98
	9.72	0.46	0.40	2.54
	10.12	0.46	0.40	1.35
HGePh$_3$	9.03	0.36	0.43	
[Mn(η^5-C_5H_4Me)(CO)$_3$]	7.90	0.71	0.41	1.00
	8.23	0.71	0.41	0.33
	9.59	0.65	0.42	1.15
	9.99	0.70	0.28	0.61
[Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)]	7.82	0.33	0.38	1.00
	8.13	0.33	0.38	1.48
	8.41	0.33	0.38	1.38
	9.53	0.38	0.58	2.37
	9.91	0.38	0.58	2.17
[Mn(η^5-C_5H_4Me)(CO)$_2$(HSiPh$_3$)]	7.85	0.32	0.34	1.00
	8.10	0.32	0.34	0.97
	8.36	0.32	0.34	1.15
	9.54	0.57	0.35	1.76
	9.94	0.57	0.35	0.43
[Mn(η^5-C_5Me$_5$)(CO)$_3$]	7.52	0.55	0.41	1.00
	7.89	0.55	0.41	0.64
	8.85	0.60	0.40	1.36
	9.26	0.60	0.40	0.53
[Mn(η^5-C_5Me$_5$)(CO)$_2$(HGePh$_3$)]	7.45	0.60	0.39	1.00
	7.82	0.80	0.36	0.47
	8.67	0.25	0.23	0.50
	8.97	0.25	0.23	0.19
	9.74	0.42	0.43	0.37

* Uncertainties are discussed in the Experimental section.

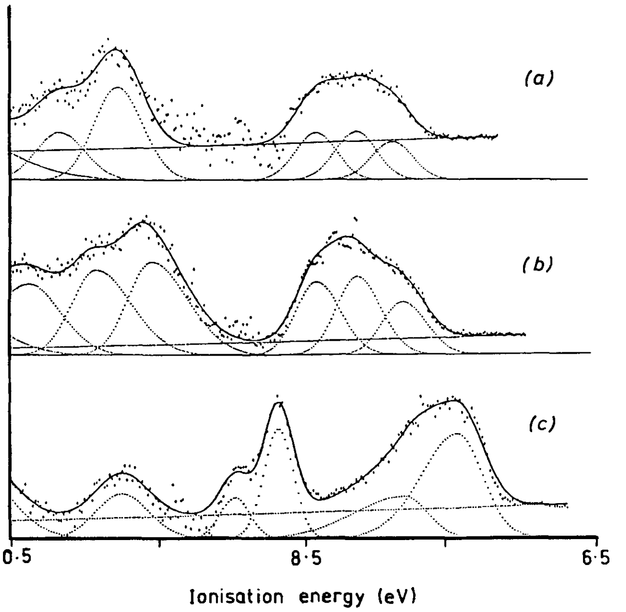

Figure 4. Ligand-subtracted and fitted spectra of (*a*) [Mn(η^5-C_5H_5)(CO)$_2$(HGePh$_3$)], (*b*) [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)], and (*c*) [Mn(η^5-C_5Me$_5$)(CO)$_2$(HGePh$_3$)]

The leading peaks of the metal ionisation bands in [Mn(η^5-C_5H_5)(CO)$_2$(HGePh$_3$)], [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)], and [Mn(η^5-C_5Me$_5$)(CO)$_2$(HGePh$_3$)] are destabilised from their positions in the parent tricarbonyls by 0.1 eV. This destabilisation of the metal orbitals also denotes a more negative metal centre compared to the parent tricarbonyls. The metal ionisation bands are not split to a very great extent and can be represented analytically by the fit of three asymmetric Gaussian peaks in a nearly 1:1:1 ratio in the C_5H_5 and C_5H_4Me complexes and a 2:1 ratio in the case of the C_5Me$_5$ complex mentioned above.

It is important to note the width of the metal bands in the spectra of the germyl complexes. The metal ionisation band of [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)] is 0.69 ± 0.05 eV wide. This is ≈0.2 eV wider than the metal band in [Mn(η^5-C_5H_5)(CO)$_2$(HGePh$_3$)] (0.51 ± 0.05 eV). The metal band in [Mn(η^5-C_5Me$_5$)(CO)$_2$(HGePh$_3$)] is 0.55 ± 0.05 eV wide and therefore is ≈0.15 eV narrower than the metal band in [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)]. The significance of these observations will be discussed shortly.

Figure 5 compares the spectral features of [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)] and [Mn(η^5-C_5H_4Me)(CO)$_2$(HSiPh$_3$)]. The cyclopentadienyl ionisations and the metal ionisations are at nearly the same positions in the spectra of both compounds. The higher ionisation-energy peak of the metal band in [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)] is stabilised a little to higher binding energy than the same peak in [Mn(η^5-C_5H_4Me)(CO)$_2$(HSiPh$_3$)]. This indicates that σ^* interaction in the germyl complexes may be greater than in the silyl complexes (see below).

E–H *Orbital Interactions with the Metal.*—The shifts in ionisation energies that occur when one ligand is substituted for another in a metal complex provide specific information about

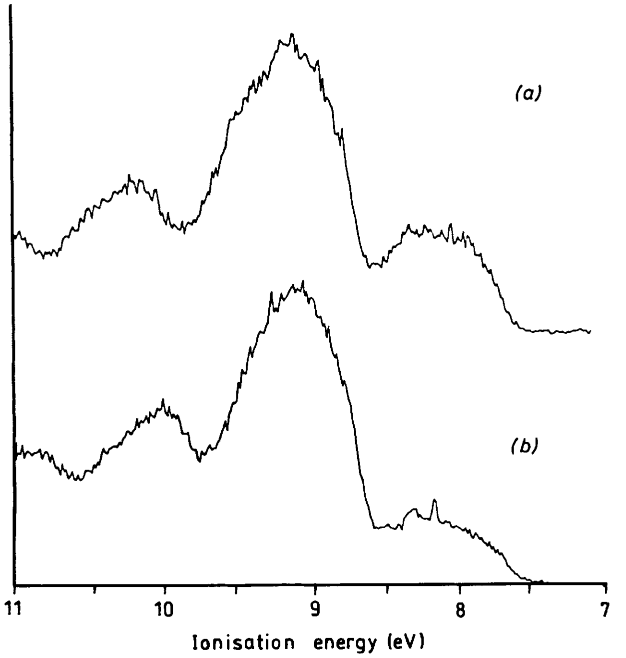

Figure 5. He I spectral comparison of (*a*) [Mn(η^5-C_5H_4Me)(CO)$_2$(HSiPh$_3$)] and (*b*) [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)]

the electronic structure interactions of the ligands with the metal. The interactions of several different ligands with the metals in d^6 'piano-stool' [Mn(η^5-C_5H_5)(CO)$_2$L] complexes have been summarised in recent reviews.[30,31] One focus of the present study is the evaluation of the interaction of the Ge–H bond with the transition metal by comparing the ionisations of the germyl complexes to those of the parent tricarbonyl complexes and the free germane.

The symmetry interactions of the Si–H bond with the metal have been presented previously.[18,19] The Ge–H bond interaction with the metal is similar. The donation of electron density from the E–H σ-bonding orbital into the empty metal orbitals results in the formation of a three-centre two-electron bond. Studies of systems involving this kind of interaction show that it produces very little shift of the metal-based ionisations.[19] The σ^* interaction involves the donation of electron density from a filled metal orbital into the E–H σ^* orbital. This interaction produces a stabilisation of one metal-based ionisation with respect to the others, and is the reason that the total width of the metal ionisation band is significant. The limit of this interaction can be described as oxidative addition with the formation of direct M–H and M–E bonds. This interaction produces a considerable stabilisation of the metal-based ionisations and a corresponding destabilisation of the ligand-based ionisations.[18] The ionisation-energy shifts and splittings observed for the germyl complexes characterise the nature of the interactions of the Ge–H bonds with the metal centres. The Ge–H bond is the σ-donating orbital. The single accepting orbital is the Ge–H σ^* orbital. In [Mn(η^5-C_5H_5)(CO)$_2$(HGePh$_3$)] and [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)] one metal orbital (lowest ionisation energy) is back bonding to one carbonyl, one metal orbital is back bonding to two carbonyls, and the third metal orbital (highest ionisation energy) is back bonding to one carbonyl and germane. This results in the splitting pattern observed in the ionisations of these complexes. For [Mn(η^5-C_5Me_5)(CO)$_2$(HGePh$_3$)] the two lower ionisation energy peaks in the metal band are accidentally degenerate.

Substitution of HGePh$_3$ *for* CO *in* [MnX(CO)$_2$(HGePh$_3$)] *Complexes* (X = η^5-C_5H_5, η^5-C_5H_4Me, *or* η^5-C_5Me_5.—The photoelectron ionisations in these complexes show that they can be described best as manganese(I), d^6 complexes where the germane acts as a neutral two-electron donor. The Ge–H σ interaction with the metal is the predominant electronic process in all three complexes, although some Ge–H σ^* interaction is also present. These conclusions are based on the following observations from the photoelectron experiments.

(1) The phenyl π ionisations in the complexes occur at the same ionisation potential (i.p.) as those in free HGePh$_3$. In [Mn(η^5-C_5H_5)(CO)$_2$(HSiCl$_3$)] the chloride lone-pair ionisations were destabilised 1 eV from their position in HSiCl$_3$. This amount of destabilisation indicates a formal -1 charge for the $SiCl_3^-$ unit, and [Mn(η^5-C_5H_5)(CO)$_2$(HSiCl$_3$)] is described best as a manganese(III) complex [structure (**B**)].[18] On the other hand, [Mn(η^5-C_5H_4Me)(CO)$_2$(HSiPh$_3$)] has the phenyl π ionisations at the same position as those of HSiPh$_3$,[19] and is described best as a manganese(I) species. Therefore, the manganese centres in the germyl complexes are also described best as Mn^I, d^6. The Ge–H σ^* interaction is not predominant since this process entails substantial electron-charge shift from the metal to the ligand. Stabilisation of ligand ionisations from electrons donated from the Ge–H σ bond and the net positive charge at the metal are balanced by the destabilisations from electrons accepted by the Ge–H σ^* orbital which leads to no shift of the phenyl π ionisations in the complexes.

(2) The cyclopentadienyl ring ionisations in all three compounds are destabilised from their positions in the parent tricarbonyl complex. This indicates a more negative metal centre in the germyl complexes since the cyclopentadienyl e_1'' ring orbitals are donating electrons into the empty metal levels, and a more negative metal centre destabilises these levels. If one assumes the germane and carbonyl σ donation to be of similar magnitude, then the germane σ^* orbital is not removing as much electron density as do two CO π^* orbitals.

(3) The leading ionisation band in all three complexes is predominantly metal in character and is well separated from the phenyl-based ionisations. This band is best represented by three asymmetric Gaussian peaks in the C_5H_5 and C_5H_4Me derivatives and two asymmetric Gaussian peaks (2:1 ratio) in the C_5Me_5 derivative, which is consistent with the six electrons of a manganese(I) centre.

(4) The ionisation at 9.74 eV in [Mn(η^5-C_5Me_5)(CO)$_2$(HGePh$_3$)] is attributed to the Mn–H–Ge three-centre two-electron bond ionisation. One of the reasons for this assignment is that the Ge–H bond in the free ligand has an ionisation at 10.8 eV.[29] It is reasonable that the weaker Ge–H bond due to the interaction of the Ge–H bond with the metal will have an ionisation in this region. This ionisation is actually buried under the phenyl π ionisations and is located by ligand subtraction.

Comparison of Si–H *and* Ge–H *Bond Interactions.*—The complexes [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)] and [Mn(η^5-C_5H_4Me)(CO)$_2$(HSiPh$_3$)] are analogous and can be used to compare the extent of E–H bond interaction with the metal (see Figure 5). Both compounds fail to show substantial electron-charge shift from the metal to the ligand indicating that σ^* interaction of the Si–H and Ge–H bonds with the manganese centre is not predominant. The cyclopentadienyl ionisations are at nearly the same position in both compounds indicating that the charge on the metal in both compounds is similar. The metal band is also at the same position for both compounds. The highest-energy metal orbital in [Mn(η^5-C_5H_4Me)(CO)$_2$(HGePh$_3$)] is a little stabilised from the same orbital in the silyl analogue. Thus the magnitude of the Ge–H σ^* orbital interaction with the metal is a little more than that of the Si–H σ^* interaction. This is to be expected since the Ge–H

σ^* level is anticipated to be at a lower energy than that of the corresponding Si–H σ^* orbital. The Si–H and Ge–H σ interactions with the metal are nearly the same in magnitude, resulting in small shifts in the positions of the metal and cyclopentadienyl ionisations.

Cyclopentadienyl Ring Methylation Effect on Bond Activation.—The metal band in $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$ is $\approx$0.2 eV wider than that in the C_5H_5 analogue. Due to the greater electron density at the metal centre in the C_5H_4Me compound, more σ^* interaction comes into play as evidenced by the relative stabilisation of the metal orbital which is interacting with the Ge–H σ^* orbital and subsequent widening of the metal band is observed. The complex $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HGePh_3)]$ has a metal centre which is even more electron-rich. However, instead of the metal band being wider, it is narrower than that in $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$ by $\approx$0.15 eV. The steric bulk of the C_5Me_5 ligand probably obstructs the addition of a germane and prevents significant σ^* interaction. This result was also observed in the case of $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HSiHPh_2)]$ and $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HSiHPh_2)]$. Other techniques, such as ^{29}Si n.m.r. spectroscopy, kinetics, and *X*-ray diffraction also point to the σ^* interaction being less in $[Mn(\eta^5\text{-}C_5Me_5)(CO)_2(HSiHPh_2)]$ than in $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HSiHPh_2)]$.[32] A detailed study of cyclopentadienyl ring methylation and its effect on bond activation in these metal–silyl systems is reported elsewhere.[33] Thus once again, for the same substituents on E (where E is Si or Ge), the E–H orbital interactions, electron distribution, and bonding with the metal centre are very similar between silyl and germyl complexes.

Acknowledgements

We acknowledge support by the Petroleum Research Fund (PRF No. 20408-AC3), U.S. Department of Energy (Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, DE-FG02-86ER13501), the National Science Foundation (CHE8519560), and the Materials Characterisation Program, Department of Chemistry, University of Arizona.

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Received 2nd *January* 1990; *Paper* 0/00003E