Table I. Iron(III) and Cobalt(III) Porphyrin Reduction Rates by Chromium(II)

Porphyrin[a,b]	k_1, $M^{-1}\,s^{-1}$	k_2, $M^{-1}\,s^{-1}$	k, s^{-1}	pK_1
Fe^{III}DPDME	0	5.5×10^5	11.0	4.7
Fe^{III}MPDME	0	1.7×10^5	1.6	5.0
Fe^{III}TPyP[c]	270	4×10^5	8.0	4.7[e]
Co^{III}TPyP[d]	49	3.2×10^5	0.4	5.9[f]
Co^{III}TMPyP[c]	16	13×10^5	1.6	5.9[f]
$Co^{III}TPPS_4$[d]	0	24×10^5	4.9	5.7[g]
$Co^{III}TPPC_4$[d]	0	753×10^5	3.0	7.4[h]

[a] Rate = $[k_1(M^{III}P) + k_2(HO\text{–}M^{III}P)](Cr(II))$, $k = k_2K_1$. [b] Key: DPDME and MPDME, deutero- and mesoporphyrin IX dimethyl esters; TPyP, tetrakis(4-pyridyl)porphine; TMPyP, tetrakis(4-*N*-methylpyridyl)porphine; $TPPS_4$, tetrakis(4-sulfonatophenyl)porphine; $TPPC_4$, tetrakis(4-carboxyphenyl)porphine. [c] Reference 6. [d] Reference 3. [e] While this pK_1 is for Fe^{III}TMPyP, it is assumed to be similar to that of Fe^{III}TPyP, which is insoluble above pH 4. [f] Reference 22. [g] Reference 18. [h] Reference 19.

Our postulated mechanism assumes that these $Cr^{2+}/Fe^{III}P$ reactions take place through the hydrolyzed $HO\text{–}Fe^{III}P$ form. Studies on the Cr^{2+} reductions of the synthetic water soluble tetrakis(4-carboxyphenyl)porphine- and tetrakis(4-sulfonatophenyl)porphinecobalt(III) complexes are also found to proceed exclusively by the inverse (H^+) pathway.[3] Although the species $HO\text{–}Co^{III}P$ was present,[18,19] the inverse hydrogen ion pathway was ascribed[3] to deprotonation of sulfonic acid and carboxylic acid functional groups present in the para positions of these metalloporphyrins. Reduction of the cobalt(III) center was assumed to proceed via an inner-sphere mechanism with a demonstrated incorporation of chromium(III) at the remote functional groups and electron transfer through the porphyrin ring.[3,4] The iron porphyrin esters that we have studied are without peripheral substituents capable of ionization, and since $CrOH^+$ is not generally invoked as a reactant, $HO\text{–}Fe^{III}P$ is our suggested oxidant.

In the $Cr^{2+}/[(NH_3)_5CoOH_2]^{3+}$ system, it has been demonstrated[20] that $[(NH_3)_5CoOH]^{2+}$ is the sole reactant. One explanation was that –OH was a better bridging group with Cr^{2+} than $-OH_2$ and that an inner-sphere pathway was involved. A similar mechanism could be followed in the present case, with a Cr(OH)FeP bridged intermediate. If this hydroxy-bridged species is the activated complex in our reaction, and since $H_2O\text{–}Fe^{III}P$ is unreactive, the implication is that electron transfer with these natural porphyrin derivatives does not occur via a remote attack at the porphyrin edge with Cr^{2+}, as has been suggested[11] for certain pathways with oxidized cytochrome *c*.

Preliminary results[23] indicate that the rate law for SCN^- addition to the water-soluble cobalt(III) complexes of $TPPS_4$ and TMPyP is the same in the presence and absence of the neutral detergent Triton X-100 (2% solution). In addition, the anation rate constants and equilibrium constants increased by only a factor of 2 when going from water to the neutral detergent media. Thus, the indication is that this detergent does not strongly alter porphyrin reactivity parameters.

Table I shows results for several Cr^{2+}/iron(III) or -cobalt(III) porphyrin reductions. The rates are factored such that the inverse hydrogen ion dependence is ascribed to $HO\text{–}M^{III}P$ as the reactant. With the exception of the cobalt(III) tetrakis(4-carboxyphenyl)porphyrin, the rates by the assumed k_2 pathway are surprisingly similar to one another, irrespective of the porphyrin type or the coordinated metal ion. Since the reported pK_1 values show some apparent inconsistencies, similar conclusions are reached by consideration of k $(=k_2K_1)$.

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Strength of Metal–Metal Interactions in Some Substituted Dimetal Carbonyls

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The strengths of metal–metal bonds in dinuclear metal carbonyls can be defined and inferred in a number of ways. The length of the Mn–Mn bond in $Mn_2(CO)_{10}$ was originally thought to imply that the bond was weak[1a] and the lengths of metal–metal bonds have recently been used to provide estimates of metal–metal bond orders and strengths.[1b] Force constants for metal–metal stretching vibrations have also been used to provide qualitative estimates of relative bond strengths.[2] Thermochemical[3] and mass spectrometric[4] measurements can, in principle, provide numerical estimates of metal–metal bond strengths. Not many values have been obtained in these ways and those that have suffer, in practice, from imprecision,[3] dependence on arbitrary assumptions,[4] or ambiguities of definition.[4,5] A substantial number of values of activation enthalpies, ΔH_{hf}^{*}, have recently been assigned to homolytic fission of metal–metal bonds in the complexes $M_2(CO)_{10-n}L_n$ (M_2 = Mn_2, MnRe, Tc_2, Re_2; n = 1 or 2; L = P- or As-donor ligand).[6] These are the energies needed to stretch the bonds to the breaking point and they provide a very useful quantitative measure of the metal–metal bond strengths and of the dependence of the strengths on the nature of M and L. Thus, for example, a pronounced steric effect is observed in substituted dimanganese complexes.[6]

A very readily made measurement that is related quantitatively to the strength of these metal–metal bonds has been demonstrated by Gray et al.[7] The band at 343 nm in the electronic spectrum of $Mn_2(CO)_{10}$ was assigned to the $\sigma \rightarrow \sigma^*$ transition involving orbitals along the metal–metal bond axis. Corresponding bands were assigned by analogy to the same transitions in several closely related complexes. The

Table I. Energies Assigned to $\sigma \rightarrow \sigma^*$ Transitions in Some Axially Substituted Dimanganese and Dicobalt Carbonyls

		$[Mn(CO)_4L]_2$[a]		$[Co(CO)_3L]_2$[a]			
No.	L	kJ mol^{-1}	cm^{-1}	kJ mol^{-1}	cm^{-1}	Δ(hnp),[b] mV	Cone angle,[c] deg
1	$P(OPh)_3$	338	28 300	323	27 000	875	128
2	$P(OCH_2)_3CEt$			335[d]	28 000	650	101
3	$P(OMe)_3$	342	28 600	330	27 600	520	107
4	$PPh(OMe)_2$	337[e]	28 200			537	120
5	$PPh_2(OMe)$	329[e]	27 500			555	132
6	PPh_3	318	26 500	304[f]	25 400	573	145
7	$P(p\text{-}MeOC_6H_4)_3$	319[e]	26 700			439	145
8	PPh_2Et	324	27 100	311	26 000	400	141
9	$PPhEt_2$	329	27 500	318	26 600	300	136
10	PEt_3	337	28 200			111	132
11	PBu_3	337	28 200	322	26 900	131	132
12	$P(C_6H_{11})_3$	327	27 300	316	26 400	33	179

[a] At room temperature in cyclohexane, except where indicated. [b] Reference 11. [c] References 12 and 13. [d] In CH_2Cl_2. [e] In decalin. [f] In CH_2Cl_2; ref 7c.

excitation energy, $h\nu(\sigma \rightarrow \sigma^*)$, is an approximation of the energy required to move each of the two electrons from the bonding σ MO into the atomic orbitals, on the metals, from which the MO was constructed. $h\nu(\sigma \rightarrow \sigma^*)$ is therefore a measure of the strength of the σ interaction between the two metals. Since none of the atoms in the complex moves during the transition, the process is equivalent to destroying the metal–metal interaction without affecting any of the other attractions or repulsions between the two $M(CO)_4L$ moieties. The energy of the transition in $Mn_2(CO)_{10}$ (29 200 cm^{-1}, 349 kJ mol^{-1}) is much greater than the energy required to stretch the Mn–Mn bond to the breaking point (154 kJ mol^{-1}).[6] This difference must be made up of interligand repulsion energies released during the stretching of the bond, a gain in strength of the Mn–CO bonds as each metal approaches the five-coordinate form, and also, perhaps, a decrease in repulsion between d_π electrons on each metal. In spite of these contributions to $\Delta H_{hf}^\ddagger$ there is a close correlation between the values of $\Delta H_{hf}^\ddagger$ and $h\nu(\sigma \rightarrow \sigma^*)$ for the decacarbonyls and also for some substituted complexes.[6,8]

The extreme ease of measuring these $\sigma \rightarrow \sigma^*$ transition energies and the close relationship between them and the attractive σ interactions between the two metals make their systematic measurement a matter of considerable interest. Relatively few energies have been reported for substituted carbonyls[7,10] and no systematic picture has emerged that enables the various electronic and steric effects due to the substituents to be inferred. We report here the electronic spectra, in what might be called the metal–metal bonding region, of a substantial number of Mn_2 and Co_2 carbonyls that contain axially positioned substituents. The energies of the $\sigma \rightarrow \sigma^*$ transitions depend on the nature of the substituent in ways that enable the importance of σ basicity, π acidity, and steric effects to be distinguished with some degree of clarity. Quantitative estimates of the effects can also be made.

Experimental Section

The complexes were prepared and purified by standard methods and characterized by their IR spectra.[6,9] The complexes $[Mn(CO)_4PPh_2(OMe)]_2$ and $[Mn(CO)_4PPh(OMe)_2]_2$ were a gift from Dr. E. Singleton of the National Chemical Research Laboratory, Pretoria, South Africa. Spectra of solutions (usually in cyclohexane) were measured with a Cary 16K recording spectrophotometer calibrated by means of a holmium oxide filter.

Results and Discussion

The spectra of all the complexes were identical in form with those that have been published,[7,10] and assignment by analogy of the $\sigma \rightarrow \sigma^*$ transition to the first intense band in the near-UV was quite straightforward. The values obtained were in excellent agreement with those that have already been published, the values in acetonitrile[10] being slightly higher than those in cyclohexane. The value for $[Mn(CO)_4P(OEt)_3]_2$, however, was substantially higher than the published value.[10] Since our value is consistent with a systematic trend along the series $[Mn(CO)_4PPh_n(OEt)_{3-n}]_2$ (n = 0–3), we believe our value to be correct.

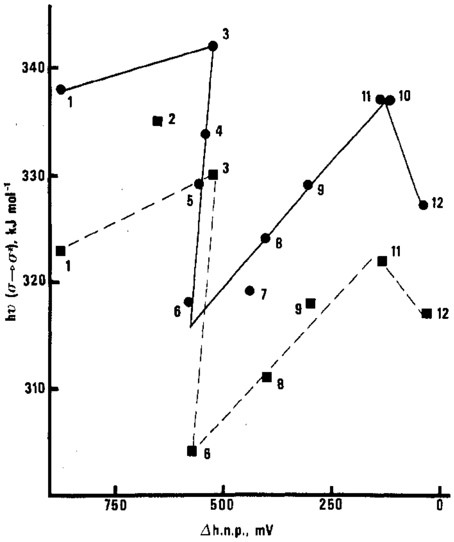

Figure 1. Dependence of $h\nu(\sigma \rightarrow \sigma^*)$ for $[Mn(CO)_4L]_2$ (●) and $[Co(CO)_3L]_2$ (■) on the basicity of L (numbering taken from Table I). Basicity increases with decreasing Δ(hnp).

The energies of the $\sigma \rightarrow \sigma^*$ transitions are shown in Table I. Values of $h\nu(\sigma \rightarrow \sigma^*)$ are plotted in Figure 1 against the relative half-neutralization potentials, Δ(hnp), of the substituents, the latter being a useful measure of the substituents' σ basicity,[11] the value decreasing with increasing basicity. When L is a phosphine, $h\nu(\sigma \rightarrow \sigma^*)$ for $[Mn(CO)_4L]_2$ increases linearly with decreasing Δ(hnp) from L = PPh_3 to L = PEt_3 and P-n-Bu_3 and then decreases sharply to L = $P(C_6H_{11})_3$. When L is a phosphite the more basic substituent is associated with a higher value of $h\nu(\sigma \rightarrow \sigma^*)$. The deviation of $h\nu(\sigma \rightarrow \sigma^*)$ for L = $P(C_6H_{11})_3$ from the regular linear behavior shown by the other phosphines is ca. 14 kJ mol^{-1} and this can be associated with its exceptionally large cone angle.[12,13] Comparison of the values of $h\nu(\sigma \rightarrow \sigma^*)$ for L = $P(C_6H_{11})_3$ and PPh_3 shows that the effect of the higher basicity of $P(C_6H_{11})_3$ in strengthening the interaction is greater than its steric weakening effect. The steric effect can be quantified as follows. The cone angle of $P(C_6H_{11})_3$ is 47° larger than that of PEt_3 or PBu_3 and its steric weakening effect is ca. 14 kJ mol^{-1} larger. The cone angle of PPh_3 is 13° larger than that of PEt_3 or PBu_3. If the relative steric deviations are proportional to the cone angles, the deviation for PPh_3 will be (14 kJ mol^{-1}) × (13°/47°) = 3.9 kJ mol^{-1}; i.e., of the increase of 19 kJ mol^{-1} in $h\nu(\sigma \rightarrow \sigma^*)$ from L = PPh_3 to L = PEt_3 or

PBu_3, only 3.9 kJ mol^{-1} or ca. 20% is due to the decreasing cone angle, the remaining 15 kJ mol^{-1} being due to the increasing basicity. Although a linear dependence of thermodynamic and kinetic parameters on cone angle is not infrequently observed,[6,12] one would expect, in general, that such steric effects would increase with cone angle more rapidly at large cone angles than at small ones, e.g., a change from 90 to 100° would have a smaller effect than a change from 170 to 180°. This implies that the steric contribution of 3.9 kJ mol^{-1} calculated above is an upper limit, the change in steric effect from PEt_3 to PPh_3 probably being proportionately less (per unit cone angle change) than that from PPh_3 to $P(C_6H_{11})_3$.

The 24 kJ mol^{-1} increase in $h\nu(\sigma \rightarrow \sigma^*)$ along the series L = PPh_3, $PPh_2(OMe)$, $PPh(OMe)_2$, and $P(OMe)_3$ cannot be due solely to an increase in σ basicity which is very small. Assuming a similar dependence on σ basicity to that found for the phosphines, only ca. 2 kJ mol^{-1} of the increase can be due to this. The increase can, therefore, most reasonably be ascribed to increasing π acidity and/or decreasing size of L. The decrease in cone angle from PPh_3 to $PPh_2(OMe)$ is 13°, the same as from PPh_3 to PEt_3, and the same steric effect of $\lesssim$3.9 kJ mol^{-1} should operate; i.e., of the 11 kJ mol^{-1} increase in $h\nu(\sigma \rightarrow \sigma^*)$ from L = PPh_3 to L = $PPh_2(OMe)$, the amount that can be due to the decrease in size is $\lesssim$3.9 kJ mol^{-1}. Alternatively (by comparison with the effect of $P(C_6H_{11})_3$) of the 24 kJ mol^{-1} increase in $h\nu(\sigma \rightarrow \sigma^*)$ from L = PPh_3 to L = $P(OMe)_3$ (a decrease of 24° in cone angle), not more than $(14\ \mathrm{kJ\ mol^{-1}}) \times (24°/47°) = 7.1\ \mathrm{kJ\ mol^{-1}}$, i.e., $\lesssim$30%, is due to the decrease in size. A clear enhancement of at least $24 - 7 - 2 = 15$ kJ mol^{-1} in the strength of the Mn–Mn σ interaction can therefore be associated with increasing π acidity. The increase in $h\nu(\sigma \rightarrow \sigma^*)$ from L = $P(OPh)_3$ to $P(OMe)_3$ is less than would be expected simply from the increase in σ basicity. This is consistent with a greater π acidity of $P(OPh)_3$ compared with $P(OMe)_3$. The value (349 kJ mol^{-1}) of $h\nu(\sigma \rightarrow \sigma^*)$ for L = CO must lie well above the line through L = $P(OPh)_3$ and $P(OMe)_3$ because the basicity of CO is much lower, and this is another indication of the association of high values of $h\nu(\sigma \rightarrow \sigma^*)$ with π-acid character.

The data for the $[Co(CO)_3L]_2$ complexes show exactly the same form of dependence of $h\nu(\sigma \rightarrow \sigma^*)$ on L. The quantitative nature of the effects is also very similar but with all the values lying ca. 14 kJ mol^{-1} below the corresponding ones for the Mn_2 complexes. The steric deviation for L = $P(C_6H_{11})_3$ is smaller, possibly because the threefold axis of the phosphine can mesh more easily with the three equatorial carbonyls in $[Co(CO)_3L]_2$ than with the four in $[Mn(CO)_4L]_2$. Also the value for L = $P(OCH_2)_3CEt$ is not intermediate between those for L = $P(OPh)_3$ and $P(OMe)_3$ as expected from its σ basicity. Similarly, the value[12] of ν_{CO} in $Ni(CO)_3[P(OCH_2)_3CEt]$ is substantially higher than expected from the σ basicity of the ligand and this is not due to steric effects. This enhancement of $h\nu(\sigma \rightarrow \sigma^*)$ and ν_{CO} by $P(OCH_2)_3CEt$ may, therefore, be due to its being a stronger π acid than $P(OPh)_3$ or $P(OMe)_3$. Values for the monosubstituted complexes $Mn_2(CO)_9L$ show the same trend; viz., L = $P(OPh)_3$, PPh_3, PBu_3, and $P(C_6H_{11})_3$ have $h\nu(\sigma \rightarrow \sigma^*)$ = 341, 331, 341, and 335 kJ mol^{-1}, respectively. The size of the variations is roughly half that shown by the disubstituted complexes.

The increase of $h\nu(\sigma \rightarrow \sigma^*)$ with increasing basicity of the axial substituents can be explained tentatively on the basis of a simple quasi-ligand field approach.[14] An electron in the σ^* orbital will have a relatively much greater probability of being found closer to the substituent ligands than one in the σ orbital. The stronger the σ donor character of L the greater will be the splitting between the σ and σ^* orbitals—exactly what is observed.

The effect of the π acidity of L may simply be due to a reduction of electron density between the two metal atoms and an increase between M and L. This would lower the energy of an electron in the M–M σ-bonding orbital and increase that of one in the σ^* orbital. (This is a rather different effect from the reduction in d_π–d_π electron repulsions suggested previously.[7b]) The decrease in $h\nu(\sigma \rightarrow \sigma^*)$ due to large substituents could be associated with an increase of the Mn–Mn or Mn–P bond lengths.[15] Substitution has not been found to increase the Mn–Mn bond length in such complexes[18] but the amount of lengthening needed to produce the quite small effects observed may be itself very small and no structures of compounds with such large substituents as $P(C_6H_{11})_3$ appear to have been measured.

Thus we may conclude that: (i) the energies of the $\sigma \rightarrow \sigma^*$ transitions in these axially substituted Mn_2 and Co_2 complexes are a measure of the σ-bonding interactions between the metals, (ii) these bonding interaction energies in the Mn_2 complexes are substantially greater than the energies needed for the complex to undergo homolytic fission because of favorable changes in ligand–ligand and metal–ligand interactions as the Mn–Mn bond is stretched, (iii) the interaction energies increase as the axial substituents increase in σ basicity and π acidity and these effects can be established quantitatively and can be qualitatively understood in terms of a simple quasi-ligand field approach, (iv) steric weakening of the interactions occurs and limiting values for it can be obtained. It is substantial only for particularly large ligands such as $P(C_6H_{11})_3$.

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Registry No. $[Mn(CO)_4P(OPh)_3]_2$, 15228-70-3; $[Mn(CO)_4P(OMe)_3]_2$, 15529-61-0; $[Mn(CO)_4PPh(OMe)_2]_2$, 61943-30-4; $[Mn(CO)_4PPh_2(OMe)]_2$, 61943-35-9; $[Mn(CO)_4PPh_3]_2$, 51435-59-7; $[Mn(CO)_4P(p\text{-}MeOC_6H_4)_3]_2$, 15662-85-8; $[Mn(CO)_4PPh_2Et]_2$, 15444-76-5; $[Mn(CO)_4PPhEt_2]_2$, 15444-75-4; $[Mn(CO)_4PEt_3]_2$, 15529-60-9; $[Mn(CO)_4PBu_3]_2$, 15609-33-3; $[Mn(CO)_4(C_6H_{11})_3]_2$, 15662-81-4; $[Co(CO)_3P(OPh)_3]_2$, 21118-36-5; $[Co(CO)_3P(OCH_2)_3CEt]_2$, 66731-93-9; $[Co(CO)_3P(OMe)_3]_2$, 21407-15-8; $[Co(CO)_3PPh_3]_2$, 10170-27-1; $[Co(CO)_3PPh_2Et]_2$, 66731-92-8; $[Co(CO)_3PPhEt_2]_2$, 21279-33-4; $[Co(CO)_3PBu_3]_2$, 14911-28-5; $[Co(CO)_3P(C_6H_{11})_3]_2$, 32875-65-3.

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ESCA Investigations of Group 4 Derivatives. 4. Binding Energies of Hydrido(methyl)germanes and -silanes and of Hydrido(halo)methylgermanes and -silanes

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We have reported[1,2] the core-level binding energies of all atoms in series of halo(methyl)germanes and -silanes of the type Me_nMX_{4-n}, where M = Ge or Si, X = F, Cl, Br, or I, and $n = 0–4$. In general, all of the observed binding energies increase in a stepwise fashion as methyl groups are replaced by halogen atoms, as expected if the latter have a greater electron-withdrawing capacity than the methyl groups. Thus, as the degree of substitution increases, so the central atoms (and any remaining carbon atoms) become relatively more positively charged and the binding energies (C 1s, Ge 3d, Si 2p) all increase. Further, as the "competition" from the other halogen atoms increases, so each halogen is relatively *less* negatively charged and so the binding energies (F 1s, Cl 2p, Br 3d, I 3d) also progressively increase. In conjunction with these studies, calculations were carried out which related the partial charges on atoms to the observed binding energies. The simple calculations were based on the electronegativity-equalization method of Huheey[3] with the added concept that the bonding orbitals of the halogen utilize varying degrees of s-orbital participation.[4] These EESOP (electronegativity equalization involving s-orbital participation) calculations "explain" the similar effective electronegativities of the halogens as arising from an increasing s-orbital participation along the series Cl < Br < I, which differs for germanium and silicon. (A similar concept has been employed in NQR studies[5] while other calculations have suggested 0 and 20% s character respectively for fluorine and chlorine.[6]) The implicit assumption that contributions from "relaxation energy" are at least consistent within these related compounds[7] seems to be supported, because the calculated partial charges correlate exceptionally well with the observed binding energies indicating that the changes in binding energies are reflecting changes in electronic distribution. With this background, we turn to a study of the hydrido(halo)methylgermanes and -silanes.

Experimental Section

Core-electron binding energies were determined on a McPherson ESCA-36 photoelectron spectrometer, using magnesium Kα X radiation (1253.6 eV) for photoelectron excitation. Samples were introduced in the vapor phase at pressures close to 5×10^{-5} Torr. Argon gas was bled in to form 20% of total sample. Binding energies were referenced to the argon $2p_{3/2}$ level at 248.63 eV (C 1s, F 1s, Cl $2p_{3/2}$, I $3d_{5/2}$) or to the neon 2s level at 48.47 eV (Ge 3d, Si 2p, Br $3d_{5/2}$).[4] Details of the data-accumulation procedures and the curve-fitting program are given in part 1.[1]

Table I. Core-Electron Binding Energies (BE) for the Hydrido(methyl)- and Hydrido(halo)methyl Derivatives of Germanium and Silicon

	Binding energy,[a] eV					
			C 1s		X[b]	
Compd	Ge 3d	Si 2p	Ge	Si	Ge	Si
Me_4M	36.11	106.02	289.82	289.78		
Me_3MH	36.35	106.18	289.88	289.90		
Me_2MH_2	36.68	106.71	290.04	290.14		
$MeMH_3$	36.98	106.95	290.26	290.31		
MH_4	37.32	107.31				
Me_2HMF[c]	37.74	107.63	290.30	290.33	690.81	692.25
MeH_2MF[c]	37.65	108.01	290.70	290.53	691.29	692.51
$MeHMF_2$	39.03	109.04	291.03	290.80	691.80	692.96
Me_2HMCl	37.52	107.38	290.38	290.24	205.26	205.68
MeH_2MCl	37.80	107.76	290.74	290.45	205.66	205.97
$MeHMCl_2$	38.47	108.54	290.89	290.68	205.81	206.23
Me_2HMBr	37.49	107.27	290.34	290.16	75.34	75.58
MeH_2MBr	37.83	107.70	290.52	290.55	75.48	75.86
$MeHMBr_2$	38.35	108.27	290.75	290.66	75.68	76.12
Me_2HMI	37.62	107.12	290.20	290.28	625.74	626.02
MeH_2MI	37.48	107.37	290.55	290.42	626.12	626.34
$MeHMI_2$	38.24	107.95	290.76	290.37	626.26	626.29

[a] Values corrected relative to Ar $2p_{3/2} = 248.63$ eV;[11] uncertainty ±0.5 eV, except that Ge 3d, Si 2p, and Br $3d_{5/2}$ are reported relative to Ne 2s at 48.47 eV.[11] [b] X corresponds to F 1s, Cl $2p_{3/2}$, Br $3d_{5/2}$, and I $3d_{5/2}$. [c] Partial overlap of F 2s peak with Ge 3d peak occurs resulting in a larger error in the assignment of the Ge 3d peak.

Materials. The hydrido(methyl)germanes and -silanes and the halo(hydrido)methylgermanes and -silanes were either obtained commercially (Laramie Chemical Co., Ventron Corp., Alfa Products, Matheson Gas Products, Petrarch Systems) or prepared by standard methods. In all cases, the materials were purified by vacuum techniques and identified by their ^1H NMR and vibrational spectra.

Charge Calculations. The previously described[1] mode of EESOP calculation is based on the relationship $\chi_M = a + b\delta_M$ relating the orbital electronegativity of an element, χ_M, to the partial charge δ_M, on that element.[3] As in our work on bromo- and iodo(methyl)germanes and -silanes, we obtain a and b values for the halogens for varying orders of s-orbital participation by interpolating between the limiting values.[2] The literature value of $\chi_H = 7.17 + 12.85\delta_H$[3] was used in the initial calculations to obtain the partial charges listed in part a of Tables II–VII,[8] along with the values of χ_M (M = Si, Ge, F, Cl, Br, I) shown in the tables which are in all cases identical with those values quoted earlier.[2] In subsequent calculations the value of $\chi_H = 8.7 + 12.85\delta_H$ was used to obtain the values for partial charge in part b of Tables II–VII.[8]

Results and Discussion

The experimentally observed core-level binding energies for the halo(hydrido)methylgermanes and -silanes, Me_2MHX, $MeMH_2X$, and $MeMHX_2$ (M = Ge, Si; X = F, Cl, Br, I), are given in Table I, along with those of the hydrido(methyl)germanes and -silanes, Me_nMH_{4-n} (M = Ge, Si; n = 0, 1, 2, 3). For the hydrido(methyl)germanes and -silanes it is clear that the observed binding energies increase in a stepwise fashion as the methyl groups are replaced by hydrogen atoms, in an analogous fashion to that observed with the halogens[1,2] but with lesser increments. The progression is as expected if hydrogen is acting as a "weakly electronegative" halogen but still with *more* electron-withdrawing power than the methyl group. Such a concept rationalizes, in qualitative terms, the general trends within all of the hydrido(halo)methylgermane and -silane series and is consistent with the fact that the polarity of the bonds has been shown to be Si(δ+)–H(δ−) in alkylsilanes.[9] Also, reactions of germanium