# Photoelectron Spectra of Some Silyl and Germyl Transition-metal Carbonyls and Related Species

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The He I (21·22 eV) photoelectron spectra of six silyl and germyl ($M^1H_3$) derivatives of Mn, Re, and Co ($M^2$) carbonyls show bands attributable to (*a*) transition-metal unshared *d*-electrons ($M^2$ *n'd*) in the range 8—10 eV binding energy; (*b*) to the $M^1H$ σ-bonding levels derived from $M^1$ *np* orbitals (11—12 eV), and (*c*) the carbonyl groups (13—19 eV). Correlation with related hydride and methyl derivatives, where known, suggests that the $M^1M^2$ σ-bonding level gives rise to a band in the 9—10 eV region, where it is obscured by the $M^2$ *n'd* bands. No evidence for any π-interaction between the $M^2$ *n'd* orbitals and the $M^1H_3$ group is observed; it is concluded that the observed shifts in $M^2$ *n'd* reflect the varying σ-acceptor powers of the $M^1H_3$ groups, methyl being a poorer σ-acceptor than silyl or germyl.

SEVERAL $SiH_3$ and $GeH_3$ derivatives of transition-metal carbonyls are known;[1] we report here studies on $M^1H_3Mn(CO)_5$, $M^1H_3Re(CO)_5$, and $M^1H_3Co(CO)_4$ for $M^1$ = Si and Ge. All these compounds obey the 18-electron rule, but it is puzzling that they are comparatively stable at room temperature; of the methyl analogues only $CH_3Mn(CO)_5$ is of comparable stability. It has been suggested[2] that ($d \rightarrow d$) π-bonding might stabilise the Si and Ge compounds relative to the carbon ana-

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[1] B. J. Aylett and J. M. Campbell, *J. Chem. Soc.* (*A*), 1969, 1910, 1916; K. M. Mackay and R. D. George, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 797; 1970, **6**, 289; K. M. Mackay and S. R. Stobart, *ibid.*, p. 687.

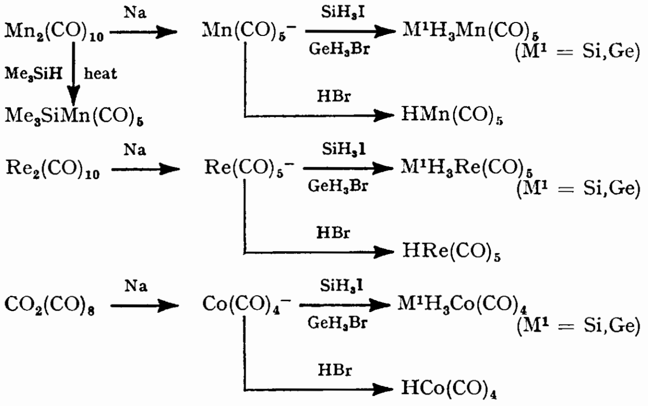
[2] A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. M. Campbell, *J. Organometallic Chem.*, 1968, **14**, 279.

logues, and it has been argued that the exceptionally short Si–M bonds in $SiF_3Co(CO)_4$ and various $SiCl_3$–transition metal derivatives[3] are due to similar $\pi$-donation from transition-metal *d*-levels to Si 3*d*.

We have attempted to study the electronic structures of these compounds using He I photoelectron spectroscopy, which we have used earlier[4] to demonstrate the occurrence of $(p \rightarrow d)$ $\pi$-bonding between Cl and $SiH_3$ or $GeH_3$ groups. We have also recorded the spectra of $HRe(CO)_5$ and $HCo(CO)_4$ for comparison; spectra of $HMn(CO)_5$ and $CH_3Mn(CO)_5$ have already been published.[5] The spectrum of $Me_3SiMn(CO)_5$ was also recorded.

## EXPERIMENTAL

The compounds were prepared by standard routes[1] as shown in the Scheme, purified by vacuum fractionation, and characterised by i.r. spectroscopy. $SiH_3Re(CO)_5$ does not seem to have been reported; full details of the preparation and characterisation will be reported elsewhere.



SCHEME

He I (21·22 eV) photoelectron spectra were recorded by use of a small spectrometer described earlier[5] or a Perkin-Elmer PS16 instrument. The effective resolution achievable with the two instruments was of the order of 50 and 30 meV respectively; no fine-structure attributable to vibration was observed on any band, and all bands were broad. The compounds were introduced into the spectrometers as vapours at room temperature; the low vapour pressures of some of the compounds under these conditions made it necessary to use slow scanning and long integration times to achieve reasonable count rate : noise ratios. Calibration was achieved with rare gases, $N_2$ or $H_2O$ entering the target chamber concurrently with the compound.

## RESULTS

The spectra are illustrated in Figures 1—3 and the vertical ionisation potentials (I.P.s) of the bands collected in Tables 1—3, together with data for some related compounds and for the free transition-metal atoms (Table 4). In each spectrum a set of overlapping bands cover the 13—17 eV region; for these the onset-to-tail ranges are given rather than the vertical I.P. The onset in each case is fairly sharp and well-located; the position of the tail is less well-defined.

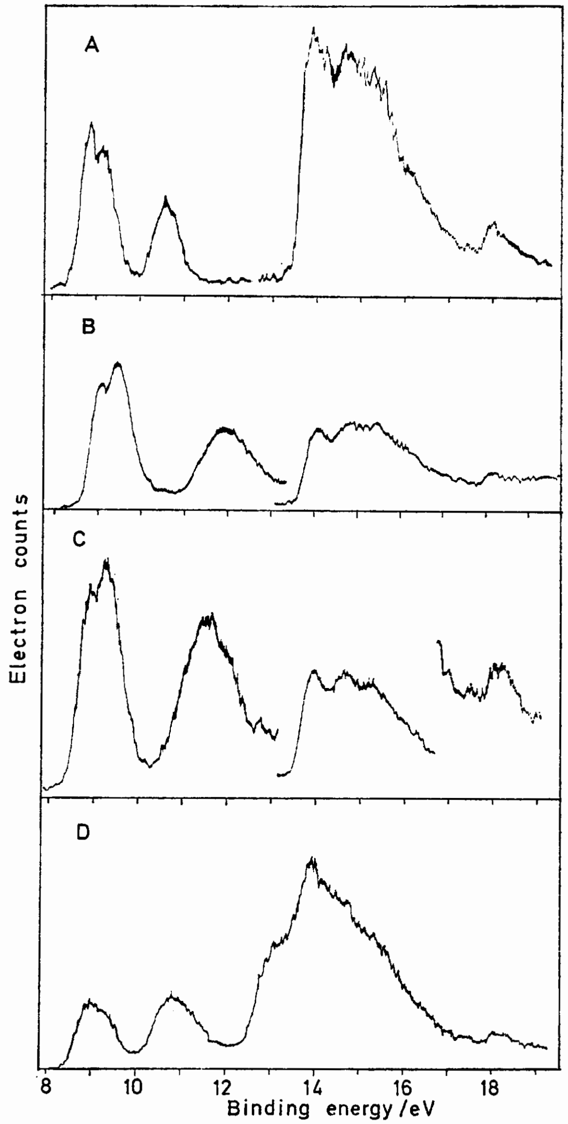


FIGURE 1 Photoelectron spectra of A, $HMn(CO)_5$; B, $SiH_3Mn(CO)_5$; C, $GeH_3Mn(CO)_5$; and D, $Me_3SiMn(CO)_5$. The apparent sharp peaks near 15 eV in A are due to the use of too short an integrating time

TABLE 1

Vertical ionisation potentials/eV for $LMn(CO)_5$

| Region[a] | *A* | | | | *B* | | *C* |
|---|---|---|---|---|---|---|---|
| Levels | Mn 3*d* | | | | Mn–Cσ | C–Oπ | |
| L | *e* | $b_2$ | Mn–H | M¹–H | onset | tail | C–Oσ |
| H[a] | 8·85 | 9·14 | 10·55 | — | 13·4 | 17 | 18·0 |
| $CH_3$[a] | 8·46 | 9·10 | — | 12·6 | 13·5 | 17 | 18·0 |
| $SiH_3$ | 8·99 | 9·38 | — | 11·9 | 13·7 | 17 | 18·0 |
| $GeH_3$ | 8·90 | 9·26 | — | 11·5 | 13·4 | 17 | 18·1 |
| $Me_3Si$ | 9·0 | 9·3 | — | 10·8 Si–C<br>13·1 C–H | 13·5 | 17 | 18·1 |

[a] See ref. 5. Vertical I.P.s ±0·02 or ±0·1 eV depending on number of figures given.

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[3] L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 447.

[4] S. Cradock and R. A. Whiteford, *Trans. Faraday Soc.*, 1971, **67**, 3425.

[5] S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, 1969, **47**, 112.

TABLE 2

Vertical ionisation potentials/eV for $LRe(CO)_5$

| Region | A | | | | B | | C |
|---|---|---|---|---|---|---|---|
| Levels | Re 5*d* | | | | Re–Cσ | C–Oπ | |
| L | *e* | $b_2$ | Re–H | $M^1$–H | onset | tail | C–Oσ |
| H | 8·86,<br>9·15 | 9·53 | 10·5 | — | 13·5 | 17 | n.o. |
| $SiH_3$ | 8·9?,<br>9·1 | 9·5,<br>9·6 | — | 11·6 | 13·6 | 17 | 18·2 |
| $GeH_3$ | 8·9?,<br>9·13 | 9·4,<br>9·6 | — | 11·4 | 13·6 | 17 | 18·1 |

n.o. = Not observed.

TABLE 3

Vertical ionisation potentials/eV for $LCo(CO)_4$

| Region | A | | | | B | | C |
|---|---|---|---|---|---|---|---|
| Levels | Co 3*d* | | | | Co–Cσ | C–Oπ | |
| L | *e* | *e* | Co–H | $M^1$–H | onset | tail | C–Oσ |
| H | 8·90 | 9·90 | 11·5 | — | 13·8 | 17 | 18·2 |
| $SiH_3$ | 8·85 | 9·90 | — | 11·9 | 13·8 | 17 | 18·2 |
| $GeH_3$ | 8·80 | 9·80 | — | 11·9 | 13·5 | 17 | 18·1 |

TABLE 4

First ionisation potentials/eV for metal atoms

| Metal | Mn | Re | Co |
|---|---|---|---|
| I.P. | 7·43 | 7·87 | 7·86 |

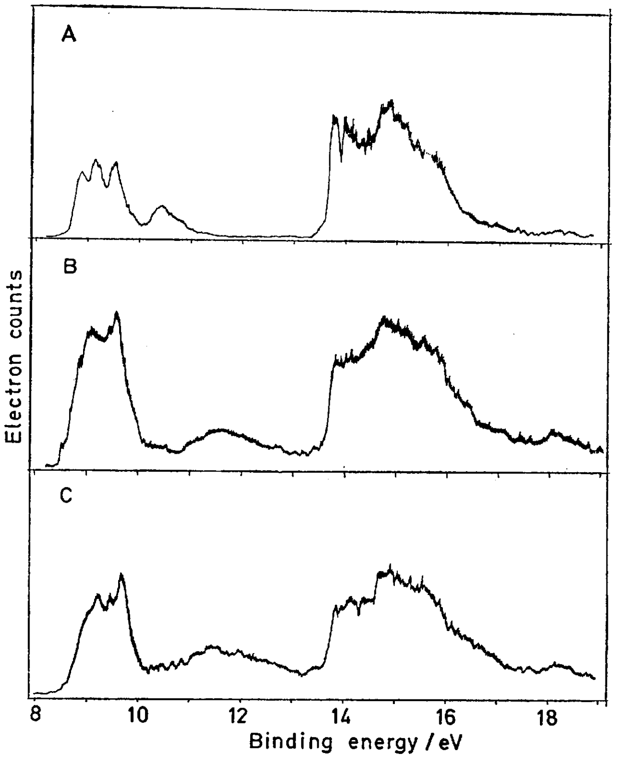

FIGURE 2 Photoelectron spectra of A, $HRe(CO)_5$; B, $SiH_3Re(CO)_5$; and C, $GeH_3Re(CO)_5$

DISCUSSION

In order to analyse our spectra we must establish an approximate scheme to describe the molecular orbitals of the molecules we are studying. Molecules of the form $M^1H_3M^2(CO)_5$ will be assumed to belong to the effective point group $C_{4v}$, the 3-fold symmetry of the $M^1H_3$ group being over-ridden by the four-fold symmetry of the $M^2(CO)_5$ group. The occupied molecular orbitals of the valence shell can be subdivided into four groups: those associated with the CO groups and the $M^2$–C σ-bonds; those associated with the $M^1$–H σ-bonds (symmetry species $a_1$ and $e$); that associated with the $M^1$–$M^2$ σ-bond (symmetry species $a_1$); and those associated with the formally non-bonding metal $M^2$ *d*-orbitals (symmetry species $b_2$ and $e$). The orbitals of molecules $M^1H_3Co(CO)_4$, point-group $C_{3v}$, can be classified in very similar terms; the most important difference is that the formally non-bonding *d*-levels now comprise two doubly-degenerate sets.

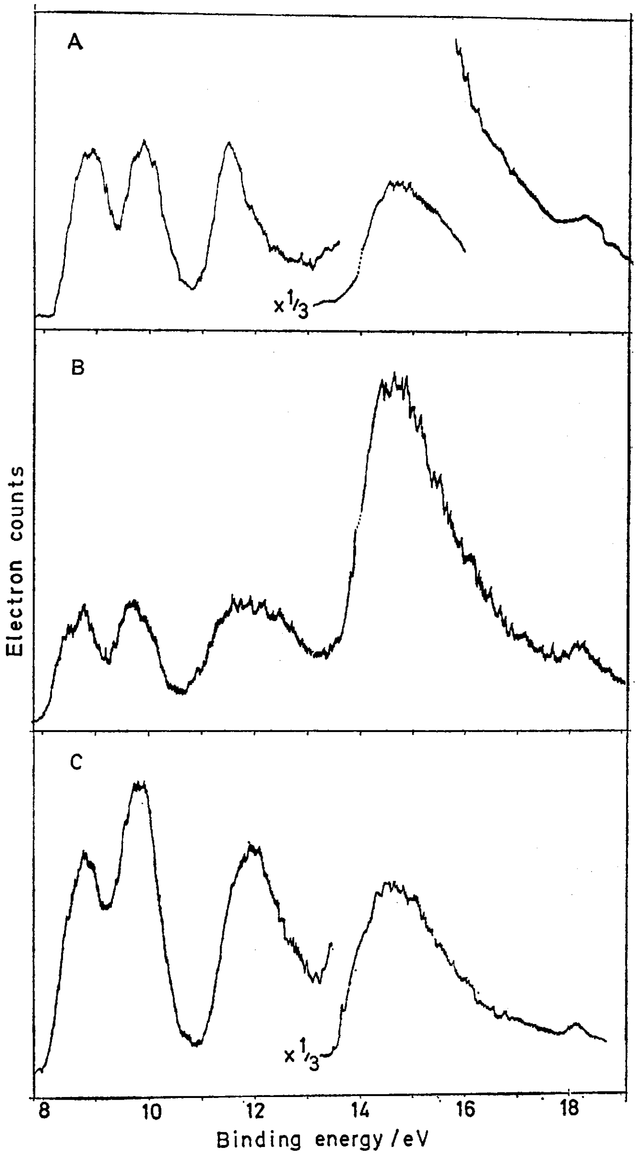

FIGURE 3 Photoelectron spectra of A, $HCo(CO)_4$; B, $SiH_3Co(CO)_4$; and C, $GeH_3Co(CO)_4$

A recent experimental and theoretical study [5] of the photoelectron spectra of compounds containing the $-Mn(CO)_5$ group gives us a valuable basis for our assignment. These spectra were discussed in terms of three regions: *A*, 13—18 eV; *BA*, 8—13 eV; *B* 13—17 eV; and *C* 17—19 eV. In region *C* a broad and relatively weak band is derived from 4σ of CO; region *B* contains a set of overlapping strong bands due to Mn–C σ-bonding and C–O π-bonding levels, while the bands in region *A* were assigned to excitation from the formally non-bonding Mn 3*d*-orbitals, from the sixth σ-bond to Mn and from levels associated mainly with the sixth ligand. Information about the interaction between the transition metal and the $M^1H_3$ group should therefore be obtainable from the bands in region *A*. It seems very probable that the spectra of the cobalt complexes can be analysed in similar terms. In the discussion that follows we shall deal mainly with region *A*.

The spectra of the hydrides $HMn(CO)_5$, $HRe(CO)_5$, and $HCo(CO)_4$ help us to identify the bands due to the metal *d*-levels. In each spectrum there is a set of strong bands between 8 and 10 eV, with a single weaker band near 11 eV; we assign the bands near 9 eV to the non-bonding metal *d*-levels and the band near 11 eV to the $M^2$–H σ-bonding level. This assignment differs from that suggested earlier [5] for $HMn(CO)_5$. For $M^2 =$ Mn and Re the bands at lower binding energy overlap, but in both cases more than one maximum can be distinguished. For $M^2 = Co$ there are clearly two bands of equal intensity separated by 1 eV, assigned to the two expected levels of symmetry species *e*. The spectra of the corresponding $M^1H_3$ derivatives show a superficially similar pattern, a group of strong bands near 9 eV and a broad, weaker band near 12 eV, but while we believe that in these spectra too the bands near 9 eV are due to excitation from the metal *d*-levels, we do not assign the band 12 eV to the $M^1$–$M^2$ σ-bonding level.

Each $M^1H_3$ group has two levels associated with $M^1H$ σ-bonding, derived respectively from *ns* ($a_1$) and *np* (*e*) levels of $M^1$. The former are found in the spectra [4] of simple molecules $MH_3X$ to appear in region *C* or at even higher binding energies. The *e*-levels give bands near 15 eV for methyl halides and near 13 eV for silyl and germyl halides; [4] the bands shift to lower binding energies as the group bound to $M^1H_3$ becomes less electronegative.[6] Thus it is not unreasonable to assign bands near 12 eV in the spectra of $M^1H_3Mn(CO)_5$ to the $M^1H_3$ *e*-symmetry levels shifted greatly to lower binding energies by the very electropositive $-Mn(CO)_5$ group. Similar bands in the spectra of the other silyl and germyl derivatives are assigned in the same way.

We are now left with no resolved bands which we could assign to the $M^1$–$M^2$ σ-bonding levels. From assignments in the spectra of hydrogen, methyl, silyl, and germyl compounds we believe that the binding energies of the $M^1$–$M^2$ σ-bonding level is likely to be 2—3 eV less than that of the corresponding H–$M^2$ level. As in the hydrides we assign the H–$M^2$ bonding level to the band near 11 eV we may expect $M^1$–$M^2$ bonding levels to give bands near 9 eV, where they will be obscured by the $M^2$ non-bonding *d*-levels.

Having made tentative assignments for the bands in region *A* we may attempt to draw some conclusions from the differences in the spectra. Thus for $M^1H_3$-$Mn(CO)_5$ ($M^1 =$ C, Si, and Ge) the Mn 3*d* bands (probably including the Mn–$M^1$ bonding level) near 9 eV shift so that the order of *d*-electron binding energies is Si > Ge > C, rather than C > Si ≈ Ge (as expected on the basis of most electronegativity scales). In the past we [4,6,7] and others [8] have attributed such 'anomalous' shifts in π-levels of groups attached to Si or Ge as being due to π-donation to vacant 3*d* or 4*d* orbitals of Si or Ge respectively. This type of interaction cannot provide the whole explanation here, as one of the Mn 3*d*-levels is of $b_2$ symmetry, which could only δ-bond to Si or Ge [unless the overall interaction between the $C_{3v}$ $M^1H_3$ and $C_{4v}$ $Mn(CO)_5$ groups is rigid enough to reduce the effective symmetry to $C_s$, which seems unlikely].

We believe that the differences in binding energies can be rationalised in terms of differences in σ-accepting power of the $M^1H_3$ groups, which will determine the effective nuclear charge of the Mn atom. The observed order of binding energies implies that the net positive charge on Mn varies in the order Si > Ge > C, so that the order of decreasing σ-accepting power for the $M^1H_3$ groups is $SiH_3 > GeH_3 > CH_3$. This would account for shifts in both the *e* and the $b_2$ Mn 3*d*-levels, whereas ($d \rightarrow d$) π-bonding would produce a shift only in the *e*-level. We conclude that the photoelectron spectra afford no evidence for ($d \rightarrow d$) π-bonding in $SiH_3Mn(CO)_5$ or $GeH_3Mn(CO)_5$. The great similarities of the spectra of the Re derivatives to those of the Mn compounds suggests a similar conclusion in this case also. We are not able to explain why the $SiH_3$ group should act as a better σ-acceptor than the $CH_3$ group; it may be that the larger size of the Si atom or of the $SiH_3$ group allows for more diffusion of charge, or the polarities and polarisabilities of the $M^1$–H bonds may be a determining factor.

The case of $Me_3SiMn(CO)_5$ is interesting. We [4] and others [9] have found that in compounds such as $Me_3SiCl$ the $Me_3Si$ groups interact strongly with neighbouring π-levels (σ–π mixing). In the present compound we find no marked difference in the positions of the Mn 3*d*-levels from those in the silyl compound. The level mainly responsible for the interaction, the *e*-symmetry Si–C bonding level, occurs at 10·8 eV, very close to its position in $Me_3SiH$, where no such interaction can occur.

In $HRe(CO)_5$ the first strong band (assigned in the hydride to the $b_2 + e$ Re 5*d*-levels only) shows three peaks, at 8·86, 9·15, and 9·53 eV, whereas $HMn(CO)_5$

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[6] S. Cradock and R. A. Whiteford, *J.C.S. Faraday II*, 1972, **68**, 281.

[7] S. Cradock, E. A. V. Ebsworth, W. J. Savage, and R. A. Whiteford, *J.C.S. Faraday II*, 1972, **68**, 934.

[8] D. C. Frost, F. G. Herring, A. Katrib, R. A. N. McLean, J. E. Drake, and N. P. C. Westwood, *Canad. J. Chem.*, 1971, **49**, 4033.

[9] C. G. Pitt and H. Bock, *Chem. Comm.*, 1972, 28.

gives only two peaks, at 8·85 and 9·14 eV. As the spin-orbit coupling parameter $\zeta_{5d}$ for Re is of the order of 0·30 eV, while that for Mn, $\zeta_{3d}$, is only 0·03 eV, we assign the extra peak for the Re compound as due to spin-orbit coupling in the $^2E$ state of the ion $HRe(CO)_5^+$. The first atomic I.P. for Re is 0·44 eV greater than that for Mn, so it seems likely that the peaks at 9·14 eV (Mn) and 9·53 eV (Re) can be assigned to the $b_2$ level in each case, while the peak at 8·85 eV (Mn) and the doublet at 8·86 and 9·15 eV (Re) are assigned to the *e*-level. The spectra of $SiH_3Re(CO)_5$ and $GeH_3Re(CO)_5$ are less clearly resolved in this region, probably because of the additional Re–M$^1$ bonding level, but seem to show a first peak near 9·1 eV with a shoulder at 8·9 eV that may well be the two components derived from the *e*-level. In each case there are two further peaks near 9·5 eV that we may assign to the $b_2$ non-bonding and $a_1$ Re–M$^1$ bonding levels.

In summary, we are unable to adduce any evidence for π-interactions between transition-metal *d*-orbitals and $SiH_3$, $GeH_3$, or $Me_3Si$ groups. The changes in binding energy of the transition-metal *d*-electrons seem more probably to be caused by changes in the σ-accepting abilities of the $M^1H_3$ groups.

We thank Drs. A. F. Orchard and S. Evans of the Inorganic Chemical Laboratories, Oxford, for spectra and discussions; the S.R.C. for a grant, and Edinburgh University for a Dewar Scholarship (to A. R.).

[2/1187 *Received, 24th May, 1972*]