# Transition-metal Carbonyl Derivatives of the Germanes. Part IV.[1] Germylpentacarbonylrhenium

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Physical and spectroscopic properties of germylpentacarbonylrhenium, $GeH_3Re(CO)_5$, (I) prepared through reaction of germyl bromide with $NaRe(CO)_5$, are reported and compared with those of the manganese analogue and other related complexes. A further product, isolated in very low yield during the formation of (I), is tentatively identified as bis(pentacarbonylrhenium)germane, $GeH_2[Re(CO)_5]_2$ (II). Ions arising from transfer of hydrogen from Ge to Re are of unusually high abundance in the mass spectrum of (I).

UNTIL our preliminary report of germylpentacarbonylrhenium,[2] exploration of the properties of metal carbonyl derivatives of the hydrides of the Group IVB elements was restricted to complexes of first-row transition metals with the single exception of $SiH_3Mo(C_5H_5)(CO)_3$, first reported [3] in 1969 by Russo and Hagen but not studied in any detail until more recently.[4] By comparison with $GeH_3Mn(CO)_5$,[5] the properties of the rhenium compound indicate the effect on the germanium–metal bond of progressing from a light transition metal to its heavy congener.

## EXPERIMENTAL

Manipulations and spectroscopic measurements were carried out as reported previously.[5] Sodium pentacarbonylrhenate(−1) was prepared by reduction of $Re_2(CO)_{10}$ (Strem Chemicals) using 5% sodium amalgam in tetrahydrofuran solution under an atmosphere of dry nitrogen.

*Reaction of Bromogermane with Sodium Pentacarbonylrhenate.*—Typically, bromogermane (299 mg, 1·93 mmol) was condensed onto a solution in tetrahydrofuran (*ca.* 5 ml) of $NaRe(CO)_5$ prepared from $Re_2(CO)_{10}$ (639 mg, 0·98 mmol). On warming to room temperature, the golden-yellow colour of the solution was slowly discharged with the precipitation of a white solid. After *ca.* 4 h the solution was pale yellow and no further change could be discerned; pumping through a fractionation line yielded *germylpentacarbonylrhenium* (331 mg, 0·83 mmol), held as large colourless crystals in a trap cooled to −25 °C. Germane (21 mg, 0·27 mmol) was recovered in the head fraction.

At 80 °C and $10^{-2}$ mmHg pressure, there sublimed from the yellow reaction residues, a small amount of a white, rhenium carbonyl derivative (*ca.* 30 mg), m.p. 100—101 °C, with i.r. absorptions (Nujol mull) at 2155w, 2080w, 2050s, 2040s,br, 1980w, 1950w, 835m, 740w, 600m,sh, 590m. Raman: 2158s, 2083vs, 2030s, 1998s, 1955w, 820w, 500s, 467s, 370m $cm^{-1}$ (not observed below 250 $cm^{-1}$ due to size of sample).

*Germylpentacarbonylrhenium.*—*Characterisation.* Determination of exact masses of peaks due to parent-family ions $^{12}C_5{}^{1}H_n{}^{16}O_5{}^{76}Ge^{187}Re$ ($n = 1$, 2, or 3) gave agreement between observed and calculated values of *ca.* 8 p.p.m. as reported previously.[2] The $^1H$ n.m.r. resonance was a singlet at $\tau$ 7·09 (cyclohexane solution), $\tau$ 6·81 (benzene solution).

*Handling properties.* $GeH_3Re(CO)_5$ is a colourless, crystalline solid, m.p. 53—54 °C, which sublimes readily *in vacuo* and may be handled using vacuum manipulation. The solid shows no sign of decomposition when exposed to the atmosphere for relatively long periods: almost complete recovery was made by resublimation of a sample kept in air for 80 h. A sample sealed under vacuum was unaffected by heating at 100 °C for 48 h but after 5 h at 140° a dark brown mirror formed although *ca.* 50% of the original could be resublimed unchanged.

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[4] A. P. Hagen, C. R. Higgins, and P. J. Russo, *Inorg. Chem.*, 1971, **10**, 1157.

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*Reaction with* HBr. $GeH_3Re(CO)_5$ (41·3 mg, 0·10 mmol) was sealed with an excess of dry HBr and allowed to react at 20° for 48 h. After removal of HBr, the white powdery product (64·2 mg; m.p. 145—146 °C) was recovered by recrystallization from diethyl ether (Found: C, 9·9; H, 0·4; Br, 25·7. Calc. for $C_5H_2BrGeReO_5$: C, 12·5; H, 0·4; Br, 16·6. Calc. for $C_5HBr_2GeReO_5$: C, 10·7; H, 0·2; Br, 28·4%). I.r. (KBr disc): 2140w, 2100vw, 2030vs,br, 940vw, 820vw, 684s, 679s, 601s, 586s, 525w, 435w, 420w, 384s. Raman (solid): 2154s, 2097w, 2081vs, 2056w, 2040vs, 2028vw, 684s, 461s, 266s, 208vs $cm^{-1}$.

*Reaction with chloroform.* Initially the $^1H$ n.m.r. spectrum of a dilute solution in $CDCl_3$ of $GeH_3Re(CO)_5$ showed only a singlet at $\tau$ 7·15. After 1 h, a singlet at $\tau$ 4·74 attributable to $CHDCl_2$ was observed, together with a singlet at $\tau$ 4·2, and the $\tau$ 7·15 signal had markedly diminished. After 24 h, only the $\tau$ 4·74 singlet remained.

## RESULTS AND DISCUSSION

*Vibrational Spectrum.*—I.r. and Raman frequencies are listed in Table 1 with approximate descriptions of observed fundamentals. The spectra closely resemble those of the manganese analogue and may similarly be discussed,[5] mainly in terms of local symmetries of $C_{3v}$ at Ge and $C_{4v}$ for the $Re(CO)_5$ group.

Most of the assignments indicated in Table 1 follow from those proposed [5] for $GeX_3Mn(CO)_5$ (X = $^1H$ or $^2H$) but several features are worthy of further discussion. In the carbonyl stretching region, where marked shifts of some bands with change of phase is noticeable as observed for the related cobalt [6] and manganese [5] compounds, the Raman spectrum in cyclohexane solution confirms that the order of CO stretches is the same as that in $GeH_3Mn(CO)_5$. The i.r.-inactive $b_1$ mode gives rise to a very strong, depolarised Raman band between the two $a_1$ modes, with the corresponding $e$ mode at lowest frequency, of lowest Raman intensity and separating into a distinct contour in the solid state.

TABLE 1

Vibrational spectrum of $GeH_3Re(CO)_5$ ($cm^{-1}$)

| I.r. | | Raman | | Tentative description |
|---|---|---|---|---|
| gas [a] | solid | solid | $C_6H_{12}$ soln.[b] | |
| 2126m | 2124m | 2131vs | 2134vs,pol | νCO(eq), $a_1$ |
| 2051m,sh | 2028vs,sh | 2050vs | 2058vs,dp | νGeH(*I.r.*) + νCO, $b_1(R)$ |
| 2024vvs | 2015vvs | 2035s,br | 2025s,pol | νCO, $a_1$ |
| 1998w | 1995s,sh | 1998s | 2015m,sh,dp | νCO, $e$ |
| 1985w | 1974vw | | | $\nu^{13}CO$ |
| 1966vw | | | | |
| | | 891w | 886w,dp | $\delta GeH_3$, $e$ |
| 821R<br>817Q s<br>814P | 810s | 815vw | | $\delta GeH_3$, $a_1$ |
| 600<br>592 s | 598<br>588 s | | | δReCO, $a_1 + e$ |
| 539w | 535vw | | | $\rho GeH_3$, $e$ |
| | | 462s | 463s,pol | νReC(eq), $a_1$ |
| 399s | 392m | 390vw | | νReC(ax), $a_1$ |
| | | 210vs | 209vs,pol | νGeRe, $a_1$ |
| | | | 100vs,br,dp | skeletal deformations |

[a] Spectrometer cell compartment warmed to 35 °C. [b] polarised bands, pol; depolarised bands, dp.

The most significant differences between the spectra of the germyl-manganese and -rhenium complexes are found in the relative positions of M–C–O bending and M–C stretching modes. The drop in frequency from *ca.* 670 $cm^{-1}$ in the Mn compound to *ca.* 595 $cm^{-1}$ in the Re analogue of the two bands attributed to two M–C–O deformations (either $a_1 + e$ or $2e$) parallels a similar frequency-change for these modes in $M(CO)_5X$ (M = Mn or Re; X = Cl, Br, or I) where respective values of *ca.* 640 and 590 $cm^{-1}$ have been observed.[7] The other major change is the apparent reversal of relative energy of the two $a_1$ M–C stretches, assigned at 473 (axial) and 409 $cm^{-1}$ (equatorial) for $GeH_3Mn(CO)_5$. By analogy with the latter, the strong, polarised Raman band at 463 $cm^{-1}$ in the spectrum of the Re compound is attributable to the $a_1$ (eq) mode, the strong i.r. absorption with a very weak Raman counterpart at lower frequency (399 $cm^{-1}$) accounting for the axial vibration. As emphasised earlier,[5] substantial mixing of fundamentals may be occurring in this region so that these assignments are tentative. However, a recent study of the Raman spectra of $M_2(CO)_{10}$ (M = Mn or Re) has indicated [8] features similar to those described above: a decrease in frequency of *ca.* 50 $cm^{-1}$ in δ(MCO) modes on going from Mn to Re was accompanied by changes in axial and equatorial M–C stretches, respectively from 486, 409 to 475, and 458 $cm^{-1}$.

The intense, polarised band in the Raman spectrum assigned to the $a_1$ GeRe stretch has a frequency of 209 $cm^{-1}$ and this is compared with values for some related molecules in Table 2. Also in this Table are listed approximate metal–metal stretching force-constants, calculated either by assuming a diatomic model involving only the masses of the two metal atoms [$F_{M-M}$(DA) values] or derived from a pseudodiatomic model whereby the effective mass of each pseudoatom is taken as the sum of that of the metal atom plus those of

TABLE 2

Metal–metal stretching frequencies/$cm^{-1}$ and force-constants/mdyn $Å^{-1}$

| Compound | $\nu_{obs}$(M–M) | $F_{M-M}$(DA) [a] | $F_{M-M}$(PDA) [b] |
|---|---|---|---|
| $SiH_3Co(CO)_4$ | 310 [c] | 1·07 | 1·49 |
| $GeH_3Co(CO)_4$ | 228 [d] | 1·00 | 1·60 |
| $GeH_3(H)Fe(CO)_4$ | 226 [e] | 0·95 | 1·57 |
| $GeH_3Mn(CO)_5$ | 219 [f] | 0·88 | 1·54 |
| $GeH_3Re(CO)_5$ | 209 | 1·34 | 1·58 |
| $Ge_2H_6$ | 268 [g] | 1·60 | 1·60 |
| $Mn_2(CO)_{10}$ | 157 [h] | 0·40 | 1·42 |
| $Re_2(CO)_{10}$ | 128 [i] | 0·90 | 1·35 |

[a] Value calculated assuming a diatomic model. [b] Value calculated assuming a pseudodiatomic model, ligand masses summed to those of the metal atoms (see text). [c] B. J. Aylett and J. M. Campbell, *J. Chem. Soc.* (*A*), 1969, 1910. [d] Ref. 6. [e] Ref. 1. [f] Ref. 5. [g] Ref. 11. [h] H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Comm.*, 1966, 616. [i] J. Lewis, A. R. Manning, J. R. Miller, M. J. Ware, and F. Nyman, *Nature*, 1965, **207**, 142.

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[8] D. M. Adams, M. A. Hooper, and A. Squire, *J. Chem. Soc.* (*A*), 1971, 71.

the attached ligands [$F_{\text{M-M}}$(PDA) values]. While the latter approach gives values for $F_{\text{M-M}}$ in the range 1·35—1·60 mdyn Å$^{-1}$ for all the intermetallic compounds included in Table 2, the simple diatomic approximation leads to values which increase significantly with increasing atomic number either on traversing the transition series or on descending a group. Other workers who have compared the results of this type of simplified calculation with those of more rigorous force-constant analyses have concluded [9,10] that of the two approximations the simple diatomic model provides much the more realistic values. Comparison of the $F_{\text{M-M}}$(DA) results shown in Table 2 for digermane and for dimanganese and -rhenium decacarbonyls with those of 1·60, 0·59, and 0·82 mdyn Å$^{-1}$ respectively derived [10,11] from more sophisticated calculations lends credence to this view. Thus while the approximate nature of the solutions included in Table 2 must be borne in mind, they nevertheless provide reasonable evidence for a monotonic increase in force-constant from Ge–Mn ($F = 0{\cdot}88$ mdyn Å$^{-1}$) through Ge–Fe ($F = 0{\cdot}95$ mdyn Å$^{-1}$) to Ge–Co ($F = 1{\cdot}00$ mdyn Å$^{-1}$), together with a much bigger increase * between Ge–Mn and Ge–Re (0·88 to 1·34 mdyn Å$^{-1}$). These results also seem reasonable on chemical grounds when compared with the very similar pattern of values obtained [10] for polynuclear metal carbonyls. Regarding possible mixing of the metal–metal stretching modes with other fundamentals, it has been proposed [10] that interaction with vibrations of carbonyl groups is of relatively minor importance, and it has been demonstrated [12] that mixing between heavy-atom stretching modes and GeH vibrations is negligible.

TABLE 3

Mass spectrum of $GeH_3Re(CO)_5$

| $m/e$ | Assignment [a] | Relative [b] intensity |
|---|---|---|
| 406—396 | $GeH_xRe(CO)_5^+$ | 28·6 |
| 378—367 | $GeH_xRe(CO)_4^+$ | 39·7 |
| 348—339 | $GeH_xRe(CO)_3^+$ | 43·7 |
| 329—325 | $HRe(CO)_5^+$ | 10·3 |
|  | $Re(CO)_5^+$ | 5·6 |
| 320—311 | $GeH_xRe(CO)_2^+$ | 100 |
| 301—297 | $HRe(CO)_4^+$ | 9·5 |
|  | $Re(CO)_4^+$ | 14·3 |
| 292—283 | $GeH_xRe(CO)^+$ | 90·5 |
| 275—269 | $HRe(CO)_3^+$ | 20·6 |
|  | $Re(CO)_3^+$ | 40·5 |
| 264—255 | $GeH_xRe^+$ | 98·4 |
| 244—241 | $HRe(CO)_2^+$ | 40·0 |
|  | $Re(CO)_2^+$ | 40·0 |
| 228—225 | $HRe(CO)C^+$ | *ca.* 1 |
|  | $Re(CO)C^+$ | 4·8 |
| 216—213 | $HRe(CO)^+$ | 9·5 |
|  | $Re(CO)^+$ | 24·6 |
| 203—197 | $HReC^+$ | 4·8 |
|  | $ReC^+$ | 27·0 |
| 188—185 | $HRe^+$ | 7·1 |
|  | $Re^+$ | 89·7 |
| 77—70 | $GeH_x^+$ | 61·1 |

[a] Weak doubly charged ions $Re(CO)_n^{2+}$ ($n = 0$, 1, 2, 3, or 4) and $Re(CO)C^{2+}$ also observed. [b] Summed over $x =$ 0, 1, 2, 3 and over Ge and Re isotopes where appropriate.

*Mass Spectrum.*—The mass spectrum of $GeH_3Re(CO)_5$ is summarised in Table 3. Fragmentation appears to follow a broadly similar course [5] to that of $GeH_3Mn(CO)_5$ although ion-families containing both metal atoms account for a slightly lower percentage of the total ion-current and abundances of $M^+$ and $GeH_x^+$ ions are higher. A novel feature however is the very high abundance observed for ions $HRe(CO)_n^+$, arising from transfer of hydrogen from Ge to Re. The ratio $HRe(CO)_n^+/Re(CO)_n^+$ is equal to 1·84 for $n = 5$, 1·00 for $n = 2$ and greater than 0·5 for $n = 3$ or 4. Analogous ions were detected in the mass spectra of the corresponding Mn and Co compounds, but in much lower abundance. Related to this, the relative abundances of ions arising by loss of hydrogen is significantly different from that found for the light-metal analogues. Thus for $GeH_xRe(CO)_5^+$ the relative abundances for $x = 3$, 2, 1 are 10 : 7 : 8 while the corresponding figures for the manganese [5] compounds were 10 : 2·2 : 0·4 and for the cobalt [6] one, 10 : 0·2 : 0. While the nature of the rearrangement processes is uncertain, these high relative abundances may be compared with those for hydrogen-containing ions in the mass spectra of rhenium carbonyl hydrides,[13] which were again higher than for the manganese analogues, and may indicate a stronger metal–hydrogen bond to Re than to Mn.

*Other Properties.*—Use of a well established preparative route [5,6,14] affords $GeH_3Re(CO)_5$ (I), a crystalline, volatile, colourless solid possessing significantly greater stability towards oxidation and thermal decomposition than its manganese analogue.[5]

The second product from the synthesis may be tentatively identified as $GeH_2[Re(CO)_5]_2$ (II), which may arise by disproportionation of (I) into (II) + $GeH_4$. The germyl bromide used in the preparation of (I) was free of the dibromide. The i.r. spectrum and volatility of the second complex are similar to those of the known [15] $GeH_2[Mn(CO)_5]_2$ supporting its tentative formulation as (II).

Reaction of (I) with HBr gives an involatile solid whose Br content indicates it to be mainly $GeHBr_2Re(CO)_5$. No germyl bromide was found, thus (I) parallels the manganese compound [5] in reacting according to (1) whereas HCl cleaves the GeCo bond in

$$H_3GeM(CO)_5 + nHX \longrightarrow X_nH_{3-n}GeM(CO)_5 + nH_2 \quad (1)$$

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* *Note added in proof:* A similar increase in $F_{\text{M-M}}$(DA) is found for the compounds $H_3SiMn(CO)_5$ and $H_3SiRe(CO)_5$, values of 1·02 and 1·36 mdyn Å$^{-1}$ being determined from the Raman frequencies νSiMn at 304 and νSiRe at 308 cm$^{-1}$ (B. J. Aylett, personal communication).

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the cobalt analogue.[6] In the i.r. spectrum the band at 684 cm$^{-1}$ may be assigned as a bending mode involving the single GeH bond; the 266 cm$^{-1}$ Raman band is νGeBr, and that at 208 cm$^{-1}$ is assigned as νGeRe, very close to the value observed for (I). The reaction of (I) with chloroform similarly gives progressive chlorination at germanium.

TABLE 4

Relationship between $\delta_{sym}(GeH_3)$ and Ge*H* chemical shift data

| Compound | $\delta_{sym}(GeH_3)$/ cm$^{-1}$ | τ(Ge*H*) [a] | Effective electronegativity [b] |
|---|---|---|---|
| $GeH_3Co(CO)_4$ | 810 | 6·95 | 2·14 |
| $GeH_3Re(CO)_5$ | 817 | 6·81 | 2·34 |
| $GeH_3Mn(CO)_5$ | 818 | 6·72 | 2·38 |
| $GeH_3(H)Fe(CO)_4$ | 821 | 6·65 | 2·47 |
| $(GeH_3)_2Fe(CO)_4$ | 823 [c] | 6·50 | 2·53 |

[a] Benzene solution. [b] See Ref. 16 and text. [c] Mean of two $a_1$ band frequencies: see Ref. 1.

The Ge*H* chemical shift measured for $GeH_3Re(CO)_5$ is compared in Table 4 with those for related complexes.[1,5,6] It is interesting to note that a plot of τ(Ge*H*) against $\delta_{sym}(GeH_3)$ is linear as predicted by Jolly's[16] relationship, which additionally gives the 'effective electronegativity' values for the (carbonyl)metal groups shown in Table 4. These data also suggest a shift of the Ge*H* resonance to low field with increasing substituent electronegativity, as has been established previously for both $GeH_3$ and $SiH_3$ derivatives.[17]

Thus $GeH_3Re(CO)_5$, while broadly similar in properties to the manganese analogue, has probably a substantially stronger Ge–M bond as reflected in the stretching force-constant, the increased thermal and chemical stability, and the changes in the fragmentation pattern.

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