Spectroscopic Properties of Compounds with Group 4B–Transition-metal Bonds. Part 2.[1] Pentacarbonylrhenium and Tetracarbonylcobalt Complexes †

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Established synthetic routes have been used to obtain the new complexes $[Re(CO)_5(MMe_3)]$ [M = Si (1) or Ge (2)]. Infrared and Raman spectra for (1), (2), and $[Re(CO)_5(SnMe_3)]$ (3) have been recorded and assigned, with ν(M–Re) at 297 (1), 175 (2), and 151 cm^{-1} (3). Mass-spectral fragmentation data are consistent with (*i*) increased metal–metal bond strength and (*ii*) increased transition-metal–carbonyl-carbon bond strength in (1)—(3) as compared with the manganese analogues. Appearance-potential measurements for ions $[MMe_3]^+$ provide bond-dissociation energies $D(M^1–M^2)$ for (1)–(3) and for $[Co(CO)_4(MMe_3)]$ [M = Si (4), Ge (5), or Sn (6)] as follows: (1), 3.1; (2), 3.2 (3), 3.7; (4), >2.4; (5), 3.2; (6), 2.8 eV; that for complex (3) well exceeds any related datum and its significance is discussed.

WE have previously [1] delineated the basis for our interest in the spectroscopic properties of complexes embodying bonds between transition metals and the Group 4B elements. Since the publication of our results for trimethylsilyl-, trimethylgermyl-, and trimethylstannyl-pentacarbonylmanganese,[1] and a preliminary account [2] of analogous data for corresponding pentacarbonylrhenium and tetracarbonylcobalt complexes, comparable measurements for the iron complexes $[Fe(\eta\text{-}C_5H_5)(CO)_2(EMe_3)]$ (E = Si, Ge, Sn, or Pb) have appeared.[3] Here we enlarge on earlier outline remarks.[2]

EXPERIMENTAL

Synthesis of Complexes.—(*a*) *Pentacarbonyl*(*trimethylsilyl*)*rhenium*. Excess of $SiMe_3H$ (*ca*. 7.0 mmol) and $[Re_2(CO)_{10}]$ (281 mg, 0.40 mmol) were heated (135 °C) in a sealed tube for 7 d. Vacuum-line fractionation afforded in 10% yield the *complex*, condensed in a trap at −23 °C, as a colourless solid, m.p. 51—52 °C (Found: C, 24.4; H, 2.50. Calc. for $C_8H_9O_5ReSi$: C, 24.05; H, 2.25%). The ^1H n.m.r. spectrum in cyclohexane consisted of a singlet at τ 9.73 (relative to internal $SiMe_4$).

(*b*) *Pentacarbonyl*(*trimethylgermyl*)*rhenium*. To a solution of $Na[Re(CO)_5]$ prepared from $[Re_2(CO)_{10}]$ (227 mg, 0.35 mmol) in dry tetrahydrofuran (thf) (5 cm^3) was added $GeBrMe_3$ (201 mg, 1.02 mmol). Removal of solvent followed by sublimation *in vacuo* (40 °C) gave the colourless air-stable *complex* (156 mg, 0.35 mmol), m.p. 53—55 °C (Found: C, 21.45; H, 1.80. Calc. for $C_8H_9GeO_5Re$: C, 21.65; H, 2.05%). The ^1H n.m.r. shift measured as in (*a*) was at τ 9.70.

(*c*) *Pentacarbonyl*(*trimethylstannyl*)*rhenium*. This complex was prepared in 32% yield as described previously;[4] physical and analytical data were identical with published values.

(*d*) *Tetracarbonylcobalt derivatives*. The complexes

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† No reprints available

[1] Part 1, R. A. Burnham and S. R. Stobart, *J.C.S. Dalton*, 1973, 1269.

[2] R. A. Burnham and S. R. Stobart, *J. Organometallic Chem.*, 1975, **86**, C45.

[3] G. Innorta, A. Foffani, and S. Torroni, *Inorg. Chim. Acta*, 1976, **19**, 263.

[4] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2217.

$[Co(CO)_4(MMe_3)]$ (M = Si, Ge, or Sn) were isolated as reported earlier.[5]

Infrared, Raman, and 70-eV mass spectra were recorded *using* methods and instrumentation identical to those used earlier:[1,2] appearance-potential data were also determined as before using repeated determinations on carefully purified samples.*

TABLE 1

Vibrational spectra (cm^{-1}) of $[Re(CO)_5(MMe_3)]$ (M = Si, Ge, or Sn)

$[Re(CO)_5(SiMe_3)]$		$[Re(CO)_5(GeMe_3)]$		$[Re(CO)_5(SnMe_3)]$		Approximate description
I.r.	Raman	I.r.	Raman	I.r.	Raman	
2 952m	2 952m	2 965m	2 960w	2 975w	2 980m	$\nu_{asym}(CH_3)$
2 897m	2 914m 2 894m	2 914m	2 915w	2 910w	2 908m	$\nu_{sym}(CH_3)$
			2 133m (p)			
2 112m	2 118s (p)	2 110w	2 118m (p)	2 107m	2 110m (p)	$\nu(CO)[a_1^{(2)}]$
	2 072m	2 071w			2 065w (sh)	
	2 037vs (dp)		2 037vs (dp)		2 030vs (dp)	$\nu(CO)(b_1)$
		2 014m (sh)	2 020w (sh)			
1 997vs	1 996vs (dp)	1 999vs	1 990s (dp)	1 997vs	1 990vs (dp)	$\nu(CO)(e)$
1 975m 1 965w (sh)	1 974s	1 984m	1 978s	1 983m (sh) 1 975m	1 978w	$\nu(CO)[a_1^{(1)}]$
1 438w	1 440w, br					
1 401m	1 400w, br	1 400w, br				$\delta_{asym}(CH_3)$
	1 271m, br					
1 260w		1 240w	1 240m	1 192w	1 189s	$\delta_{sym}(CH_3)$
1 239m	1 244w	1 227w	1 227m	1 180w	1 180s	$\delta_{asym}(CH_3)$
1 091w, br	1 116w	1 095w, br		1 090w, br		
1 025w, br		1 023w		1 020w		
960w		962vw		960w		
942w	949s	942vw		932w, br		
830s	832w	818m		759s		$\rho(CH_3)$
748m	755w	746w		696w		$\rho(CH_3)$
679m	682m (dp)			518s	522s	$\nu_{asym}(MC_3)$
605s (sh)		602m (sh)	597w (sh)	597s (sh) 586s		$\delta(ReCO)$
590s 581s	593w, br	590s	582m			
	627m (p)	558m	560m (p)	507s	506s (p)	$\nu_{sym}(MC_3)$
513m	507w	519m	520w 510w			
	463s (p)		465s (p)		461s (p)	$\nu(ReC)(a_1)(eq)$
			453w (sh)	447m		
429m	435w	435w 428w		429w	412w	
400s	395m (p)	397m	397w (p)	394s	397w	$\nu(ReC)(a_1)(ax)$
291m	297w (p)		175s (p)		151s (p)	$\nu(MRe)$
	197m (p)		201w			$\delta(MC_3)$
	164m 137m		124m (dp)			$\rho(MC_3)$
	117m 97m (dp)		104m (dp)		103s (dp)	Skeletal deformations

RESULTS

Trimethylsilyl-, trimethylgermyl-, and trimethylstannyl-derivatives of pentacarbonylmanganese have been known for several years[1] but only one of the analogous rhenium complexes, $[Re(CO)_5(SnMe_3)]$, has been reported.[4] Synthesis of the corresponding complexes of silicon and germanium was a prerequisite of this study, and was readily achieved either by reaction of decacarbonyldirhenium with trimethylsilane [equation (1)] or by utilizing the nucleophilic character of the pentacarbonylrhenium anion [equation (2)]. The colourless volatile products possessed the physical and analytical properties described in the Experimental section, and further characterization was provided by the mass and vibrational spectra discussed below.

Pentacarbonylrhenium Complexes.—Vibrational spectra. The i.r. and Raman spectra for the three complexes are listed in Table 1, and closely resemble one another and those for the manganese analogues.[1] Features attributable to the vibrations of the MMe_3 unit can be readily distinguished and in the low-wavenumber range (MC_3 stretching and deformation) show the expected decrease in energy with increasing mass of the M atom. The general assignment of bands due to the $Re(CO)_5$ vibrations is likewise straightforward by analogy with that proposed for the manganese complexes[1]

$$[Re_2(CO)_{10}] + 2SiMe_3H \longrightarrow 2[Re(CO)_5(SiMe_3)] + H_2 \quad (1)$$

$$Na[Re(CO)_5] + GeBrMe_3 \longrightarrow [Re(CO)_5(GeMe_3)] + NaBr \quad (2)$$

and further discussion is therefore confined to specific aspects of the data.

The carbonyl-stretching region is dominated in the i.r. by bands which are sufficiently intense to be observed in the vapour phase at ambient temperature and which show depolarized Raman shifts in solution. These clearly correspond to the *e* mode predicted on the basis of ' local ' C_{4v} symmetry at the central metal atom. Further very strong, depolarized, Raman lines near 2 037 cm^{-1} have no i.r. counterparts and belong to the corresponding b_1 component. These observations confirm assignments made earlier,[1,6,7]

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* Throughout this paper: 1 eV $\approx$ 1.60 $\times$ 10^{-19} J; 1 dyn = 10^{-5} N.

[5] G. F. Bradley and S. R. Stobart, *J.C.S. Dalton*, 1974, 264.

[6] R. D. George, K. M. Mackay, and S. R. Stobart, *J.C.S. Dalton*, 1972, 1505.

[7] K. M. Mackay and S. R. Stobart, *J.C.S. Dalton*, 1973, 214.

and the fact that the energies of both vibrations are virtually invariant with M implies near-identical electronic character for the metal–metal bond in all the three complexes. Weak splittings in the solid state give rise to detection of a fifth band in each spectrum, consistent with deviations from the 'local-symmetry' approximation which are rather more pronounced than for [1] the manganese analogues.

Two of the Re–C–O bending components (probably $a_1 + e$) appear in the i.r. as a characteristic strong doublet,[1,7] while at lower energy the two a_1 Re–C stretching modes are assigned to bands near 460 (equatorial: strongly Raman active, polarized) and 395 cm^{-1} (axial: strongly i.r.-active, Raman polarized). Elsewhere [7] we have emphasized the apparent cross-over in relative energy of these M–C fundamentals between M = Mn and Re in the spectra of $[M(CO)_5(GeH_3)]$, and here a parallel relation is distinguishable with the $[Mn(CO)_5(MMe_3)]$ species for which axial and equatorial components were assigned respectively at 480 and 417 cm^{-1}.

The metal–metal bond-stretching vibration (a_1 for C_{nv} symmetry) gives rise to a conspicuous polarized Raman shift at 175 cm^{-1} for $[Re(CO)_5(GeMe_3)]$ and at 151 cm^{-1} for $[Re(CO)_5(SnMe_3)]$. Calculation of bond-stretching force constants from a simple diatomic-oscillator approximation [1,5–7] gives $F_{M\text{-}M}(DA) = 0.94$ mdyn Å^{-1} for M = Ge and 0.97 mdyn Å^{-1} for M = Sn, both substantially higher than for the manganese analogues [1] implying an increase [7] in metal–metal bond strength between Mn and Re. Like the situation encountered [1,8] for its manganese and cobalt relatives, ν(SiRe) for $[Re(CO)_5(SiMe_3)]$ is uncharacteristically weak in the Raman effect but a polarized contour at 297 cm^{-1} corresponding to a medium-intensity i.r. band at 291 cm^{-1} is assigned to this vibration. Thus, there is no decrease in ν(SiM) between M = Mn [1] and Re, comparable with $[M(CO)_5(SiH_3)]$ where [7] ν(SiRe) was at higher energy (308 cm^{-1}) than ν(SiMn) (304 cm^{-1}) despite the effect of the increased mass of the transition-metal atom.

TABLE 2

Fragment-ion abundances for $[Re(CO)_5(MMe_3)]$ (M = Si, Ge, or Sn) [a]

Ion family [b]	M = Si	M = Ge	M = Sn
$[Re(CO)_5(MMe_x)]^+$	13	25	33
$[Re(CO)_4(MMe_x)]^+$	11	14	13
$[Re(CO)_3(MMe_x)]^+$	14	15	19
$[Re(CO)_2(MMe_x)]^+$	12	16	9
$[Re(CO)(MMe_x)]^+$	15	16	12
$[Re(MMe_x)]^+$	8	10	9
$[Re(CO)_y(MMe_3)]^+$	13	3	2
$[Re(CO)_y(MMe_2)]^+$	30	56	42
$[Re(CO)_y(MMe)]^+$	19	22	29
$[MMe_3]^+$	18	3	1

[a] Expressed as a percentage of the total metal-containing ions. [b] $x = 0$—3, $y = 0$—5.

Mass spectra. Fragmentation data are collected in Table 2, expressed as summed relative abundances for important categories of ion species. When compared with corresponding results [1] for the manganese analogues two differences can be distinguished which are consistent with enhancement of metal–carbonyl-carbon bond strength on replacing Mn by Re. On the one hand there is a marked increase in abundances for ions having high CO content (notably those with five, four, or three CO groups); on the other, an increased proportion of ion current is carried by fragments formed by loss of methyl groups (rather than CO). A rough measure of the variation in metal–metal bond strength may be provided through examination of the total abundances for ions in which this bond nominally remains intact: such a comparison is made in Table 3 between analogous manganese,[1] cobalt,[5] and rhenium complexes, and offers supporting evidence for the conclusions reached below.

TABLE 3

Abundances * of ions with metal–metal bonds

		M^1		
		Si	Ge	Sn
M^2	Mn	37	52	59
	Co	50	66	66
	Re	76	97	95

* Expressed as a percentage of the total metal-containing ions.

Appearance-potential Measurements: Pentacarbonylrhenium and Tetracarbonylcobalt Complexes.—Experimental methods, derivation of bond-dissociation energies *D*, uncertainties, and potential complications due to secondary fragmentation processes have been evaluated elsewhere by us [1] and other workers.[3,9] Results are collected in Table 4. Extremely long 'tails' in the ionization-efficiency curves for $[Co(CO)_4(SiMe_3)]^+$ and its daughter ion $[SiMe_3]^+$ made it impossible to apply the Warren method to the cobalt–silicon complex, and at best only an estimate of a lower limit to the *D*(Co–Si) bond energy could be arrived at. This problem was undoubtedly due to the presence of hexamethyldisiloxane, which is a decomposition product of the material,[10] as an alternative source of the $[SiMe_3]^+$ ion but was not encountered for $[Mn(CO)_5(SiMe_3)]$ or the rhenium complex.

TABLE 4

Ionization potentials, appearance potentials, and derived bond-dissociation energies *

Complex	I.p.	A.p. (MMe_3^+)	*D* (M^1-M^2)	$D[Me_3M^1M^2\text{--}(CO)_5{}^+]$
$[Co(CO)_4(SiMe_3)]$	>9.0	>9.6	>2.4	
$[Co(CO)_4(GeMe_3)]$	8.8	10.2	3.2	1.4
$[Co(CO)_4(SnMe_3)]$	8.5	9.7	2.8	1.1
$[Re(CO)_5(SiMe_3)]$	9.6	10.3	3.1	0.7
$[Re(CO)_5(GeMe_3)]$	8.6	10.3	3.2	1.7
$[Re(CO)_5(SnMe_3)]$	8.8	10.5	3.7	1.7

* All values in eV, ±0.1. For a discussion of estimated uncertainties, see refs. 1, 3, and 9. All the values were derived assuming i.p.(Ar) and i.p.$(Me_3M\cdot)$ as given in ref. 1.

DISCUSSION

Various difficulties are inherent in applying calorimetric methods to the determination of bond-dissociation energies in complexes of the type under discussion. It seems likely, therefore, that in spite of the fact that values derived from mass-spectroscopic measurements represent upper limits [1] and are not very precise (± 0.1 eV, *ca.* 10 kJ mol^{-1} at best), the data presented here and previously [1,3,9] will continue for some time to be the best available estimates of strengths of bonds between transition- and non-transition-metal atoms. It therefore seems appropriate to comment briefly on the conclusions which can currently be drawn in this area.

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[10] F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 1970, **92**, 2324.

(1) The bond-dissociation energies in question are quite large, generally exceeding 200 kJ mol^{-1} and in the range first established by Lappert and his co-workers.[9] (2) There is clear evidence from the present and earlier [1,9] results that a substantial increase in bond energy accompanies exchange of a first-row transition metal for its third-row congener. (3) Although not so well established as (2), there seems to be a correlation with position in the first transition series, bond energy increasing from Cr through Co. This is in accord with our earlier tentative remarks [7] based on force-constant data. (4) The effect of varying the main-group element is not easy to identify. Uncertainties remain in the case of silicon, while our data (all for complexes of simple carbonyls) suggest that bonds from either germanium or tin to the same transition metal have rather similar dissociation energies. By contrast, other reported data [3,9] (all for complexes embodying η-cyclopentadienyl as well as carbonyl ligands) indicate an increase in bond energy on exchanging germanium for tin. Additional evidence adduced from vibrational spectroscopy and mass-spectral fragmentation behaviour is in complete agreement with points (1)—(4).

The *D* value of 3.7 eV (*ca.* 360 kJ mol^{-1}) calculated for $[Re(CO)_5(SnMe_3)]$ is indicative of a very strong rhenium–tin bond, and this is reflected in the data of Tables 2 and 3. The metal–metal interaction in this complex is thus significantly stronger than in Sn_2Me_6 [*D*(Sn–Sn) 260 kJ mol^{-1}] [11] or $[Re_2(CO)_{10}]$ [*D*(Re–Re) 214 kJ mol^{-1}].[12] While it is tempting to ascribe such enhancement to existence of (*d*–*d*) π overlap involving unoccupied 5*d* orbitals at the tin atom, unambiguous direct evidence for such bonding has not been forthcoming although widely sought,[13] and the $SnMe_3$ group is notionally a rather poor π acceptor (compared [5] with say $SnCl_3$).

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