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THE GAS PHASE MOLECULAR STRUCTURES OF METHYL-, SILYL- AND GERMYL-RHENIUM PENTACARBONYL, DETERMINED BY ELECTRON DIFFRACTION *

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Summary

The molecular structures of the title compounds in the gas phase have been determined by electron diffraction. The C(methyl)—Re, Si—Re and Ge—Re bond lengths (r_a) are 230.8 ± 1.7, 256.2 ± 1.2 and 262.8 ± 0.6 pm respectively. The $Re(CO)_5$ groups in the molecules have almost identical structures, with r(Re—C) 200-201 pm, r(C—O) 113 pm, and the equatorial carbonyl groups bent towards the MH_3 group away from the regular octahedral positions by 4-7°.

Introduction

Studies of the structures of methyl-, silyl- and germyl-manganese pentacarbonyl [1,2] have shown that the Mn—Si and Mn—Ge bonds are about 11 pm shorter than would be expected on the basis of covalent radii. This may be attributed to π-bonding between silicon or germanium and the metal, or to differences of σ-acceptor properties of the methyl, silyl and germyl substituents, but the differences seem to be rather large to be purely electronegativity effects.

There are some surprising differences between manganese and rhenium carbonyl derivatives. For example, the metal carbonyls not only have different conformations, one having D_{4d} symmetry, and the other D_{4h}, but also the Re—Re bond length in $Re_2(CO)_{10}$ is about twice the covalent radius of rhenium [3], whereas the Mn—Mn bond in $Mn_2(CO)_{10}$ [4] is 10-20 pm longer than twice the mangenese covalent radius (depending on how the radius is defined). These observations are consistent with estimates of the metal—metal bond dissociation energies, which are reported as 104 and 187 kJ mol^{-1} for Mn—Mn and Re—Re respectively [5]. Morevoer, the dissociation energies for the metal—carbon (methyl) bonds in methyl-manganese and -rhenium carbonyls have been reported as being 117-129 and 222 kJ mol^{-1} respectively [6], and the Si—metal and Ge—metal stretching force constants for silyl- and germyl-rhenium pentacar-

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* No reprints available.

bonyls are considerably greater than those for the manganese derivatives [7]. As all this evidence implies that bonds from rhenium to carbon, silicon and germanium are all stronger than those from mangenese, we have determined the structures of three rhenium pentacarbonyl derivatives, to see whether the bond lengths are consistent with the other evidence.

Experimental

Samples of methyl-, silyl- and germyl-rhenium pentacarbonyl were prepared by reaction of methyl iodide, silyl bromide or germyl bromide with sodium rhenium pentacarbonyl [7,8], and purified by fractional condensation in vacuo.

Scattering intensities were recorded photographically on Agfa Gevaert Replica 23 plates using a Balzers' KD.G2 gas diffraction apparatus, and were converted to digital form with a Joyce-Loebl microdensitometer. During exposures the samples were maintained at 333 K, and the inlet nozzle at 340 K. For each compound, three nozzle-to-plate distances (250, 500 and 1000 mm) were used, (usually two plates at each distance), giving scattering intensities over a range of s from about 10 to 280 nm^{-1}. The electron wavelength used, 5.660(5) pm, was determined from diffraction patterns for gaseous benzene.

Calculations were carried out on an ICL 4-75 computer at the Edinburgh Regional Computing Centre with data reduction and least squares refinement programs described elsewhere [9,10]. The refinement program uses an off-diagonal weight matrix: weighting points used in setting it up are given in Table 1, together with scale factors and correlation parameters.

In early refinements, the scattering factors of Schäfer, Yates and Bonham [11] were used. However, both the real and imaginary parts of the scattering factor for rhenium were found to be inadequate, and were modified in the light of the experimental data. The real part was observed to have an oscillation of frequency about 80 nm^{-1} at high *s* values. This oscillation, which has been noticed before [12] was removed by smoothing the appropriate part of the scattering factor, resulting in a considerable improvement of the fit of experimental and calculated scattering, both atomic and molecular. The original and modified forms are shown in Fig. 1.

For the imaginary part of the scattering factor, we normally use cubic func-

TABLE 1

WEIGHTING FUNCTIONS, CORRELATION PARAMETERS AND SCALE FACTORS

Compound	Camera height (mm)	del *s* (nm^{-1})	s_{min} (nm^{-1})	s_1 (nm^{-1})	s_2 (nm^{-1})	s_{max} (nm^{-1})	*p/h*	scale factor
$CH_3Re(CO)_5$	250	4	68	104	220	260	0.3975	0.864 ± 0.021
	500	2	26	55	138	158	0.4822	0.978 ± 0.021
	1000	1	11	21	62	72	0.1314	0.749 ± 0.012
$SiH_3Re(CO)_5$	250	4	100	140	240	284	0.1369	0.813 ± 0.046
	500	2	26	50	130	154	0.4722	0.762 ± 0.021
	1000	1	12	20	61	71	0.4555	0.713 ± 0.024
$GeH_3Re(CO)_5$	250	4	68	128	230	276	0.3737	0.962 ± 0.039
	500	2	22	40	124	144	0.4283	0.865 ± 0.027
	1000	1	13	23	61	72	0.3954	0.664 ± 0.029

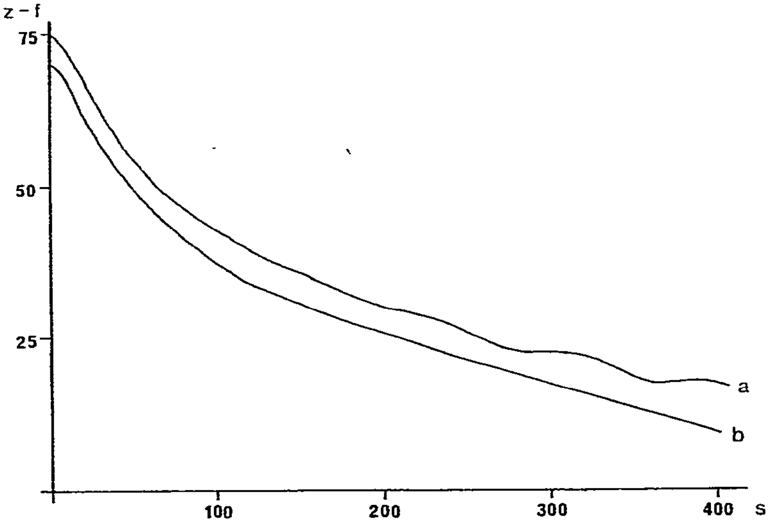


Fig. 1. Scattering factor, $z - f$, for rhenium, (a) derived from data by Schäfer et al. [11] and (b) as modified and used in this work. The second curve is displaced 5 units downwards, for clarity.

tions fitted to the tabulated phase angles [11]. Thus for the atom pair i—j the phase shift is given by:

$$\eta_i - \eta_j = a_i - a_j + (b_i - b_j)s + (c_i - c_j)s^2 + (d_i - d_j)s^3.$$

This may be rewritten as:

$$\Delta\eta = \pi/2 + \Delta b'(s - s_c) + \Delta c'(s - s_c)^2 + \Delta d'(s - s_c)^3,$$

where s_c is the "beat-out" point, where $\cos(\Delta\eta) = 0$. Using tabulated values for $\eta(s)$, the beat-out points for Re—C, Re—O, Re—H, Re—Si and Re—Ge atom pairs were calculated to be 140, 147, 117, 179 and 333 nm^{-1} respectively. In all three structure determinations, the values for Re—C and Re—O were allowed to refine. Optimum values in each case were close to 131 and 138 nm^{-1} for Re—C and Re—Re—O: in subsequent refinements they were fixed at these values, with those for Re—H, Re—Si and Re—Ge adjusted to 108, 170 and 324 nm^{-1} respectively.

Approximate shrinkage corrections, as listed in Table 2, were applied to non-bonded distances.

Refinements

Molecular model

For each compound, the model used was the same as that used for manganese carbonyl derivatives [2]. This assumed C_{4v} symmetry for the $Re(CO)_5$ group, C_{3v} for the $ReMH_3$ group, and free rotation about the Re—M bond. In view of the problems caused by inadequate scattering factors, and the correla-

(continued on p. 336)

TABLE 2

MOLECULAR PARAMETERS FOR $MH_3Re(CO)_5$

	$CH_3Re(CO)_5$		$SiH_3Re(CO)_5$		$GeH_3Re(CO)_5$		Shrinkage correction
	Distance (pm)	Amplitude	Distance (pm)	Amplitude	Distance (pm)	Amplitude	
(a) Independent distances							
r_1(C—O)	113.0(4)	4.5(9)	113.6(4)	5.0(7)	112.0(5)	5.8(7)	—
r_2(Re—C)	200.0(4)	5.6(4)	201.0(4)	6.2(4)	200.2(5)	6.4(5)	—
r_3(Re—M)	230.8(17)		256.2(12)	6.7(16)	262.8(6)	9.1(7)	—
r_4(M—H)	110.0(fixed)	5.0(fixed)	151.4(37)	8.0(fixed)	152.1(fixed)	10.0(fixed)	—
(b) Dependent distances							
$d_5(Re\cdots O_{ax})$	312.2(9)	7.2(4)	313.8(9)	5.7(4)	311.3(9)	7.2(6)	0.6
$d_6(Re\cdots O_{eq})$	312.2(9)		313.7(9)		311.2(9)		0.6
$d_7(C_{eq}\cdots C_{eq})$	395.6(13)	9.5(fixed)	399.2(12)	9.5(fixed)	395.0(10)	9.5(fixed)	1.3
$d_8(C_{eq}\cdots O_{eq})$	506.6(17)		511.0(16)		505.1(14)		2.3
$d_9(O_{eq}\cdots O_{eq})$	617.1(24)		622.2(23)		614.6(21)		3.4
$d_{10}(C_{eq}\cdots C_{ax})$	280.7(9)	14.7(18)	283.3(9)	13.0(fixed)	280.3(7)	16.8(30)	0.3
$d_{11}(C_{eq}\cdots C_{eq})$	298.2(7)		292.9(7)		300.9(8)		0.3
$d_{12}(C_{eq}\cdots O_{eq})$	388.6(8)	19.1(13)	382.5(8)	18.2(12)	390.8(8)	21.0(13)	0.8
$d_{13}(C_{eq}\cdots O_{ax})$	368.2(14)		371.3(13)		366.9(11)		0.8
$d_{14}(C_{ax}\cdots O_{eq})$	388.6(7)		384.8(8)		389.3(8)		0.8
$d_{15}(O_{eq}\cdots O_{eq})$	464.6(10)	30.7(40)	459.4(10)	30.0(fixed)	465.1(11)	30.0(fixed)	1.4
$d_{16}(O_{eq}\cdots O_{ax})$	437.8(16)		441.4(16)		436.0(15)		1.4
$d_{17}(M\cdots C_{ax})$	428.7(18)	9.5(fixed)	455.1(15)	11.1(fixed)	460.9(10)	10.0(fixed)	1.4
$d_{18}(M\cdots O_{ax})$	540.3(20)	10.0(fixed)	567.3(17)	11.0(fixed)	571.4(13)	11.0(fixed)	2.4
$d_{19}(M\cdots C_{eq})$	287.7(16)	14.7[a]	315.3(14)	20.0(fixed)	308.6(11)	22.4[a]	0.3
$d_{20}(M\cdots O_{eq})$	366.2(18)	19.1[b]	388.8(17)	24.2[b]	381.6(15)	28.0[b]	0.9
$d_{21}(Re\cdots H)$	286.7(16)	10.0(fixed)	335.4(34)	10.0(fixed)	346.7(8)	12.0(fixed)	0.6
$d_{22}(C_{ax}\cdots H)$	476.3(18)	18.0(fixed)	521.7(38)	18.0(fixed)	533.2(11)	18.0(fixed)	2.3
$d_{23}(O_{ax}\cdots H)$	583.1(21)	18.0(fixed)	627.3(42)	18.0(fixed)	637.8(13)	18.0(fixed)	3.4
$d_{24}(H\cdots H)$	178.9(fixed)	9.0(fixed)	248.8(45)	10.0(fixed)	246.6(fixed)	10.0(fixed)	0.1
$(C_{eq}\cdots H)$	265-387		299-448		299-445		
$(O_{eq}\cdots H)$	314-471		330-531		329-527		
(c) Angles (°)							
∠1(Re—M—H)	110(fixed)		108(fixed)		111(fixed)		
$\angle 2(C_{ax}—Re—C_{eq})$	96(2)		94(2)		97(2)		
$\angle 3(Re—C_{eq}—O_{eq})$	180(fixed)		182(2)[c]		178(2)[d]		

[a] Tied to $u10$. [b] Tied to $u12$. [c] Bent towards Si. Not included in final refinement. [d] Bent away from Ge.

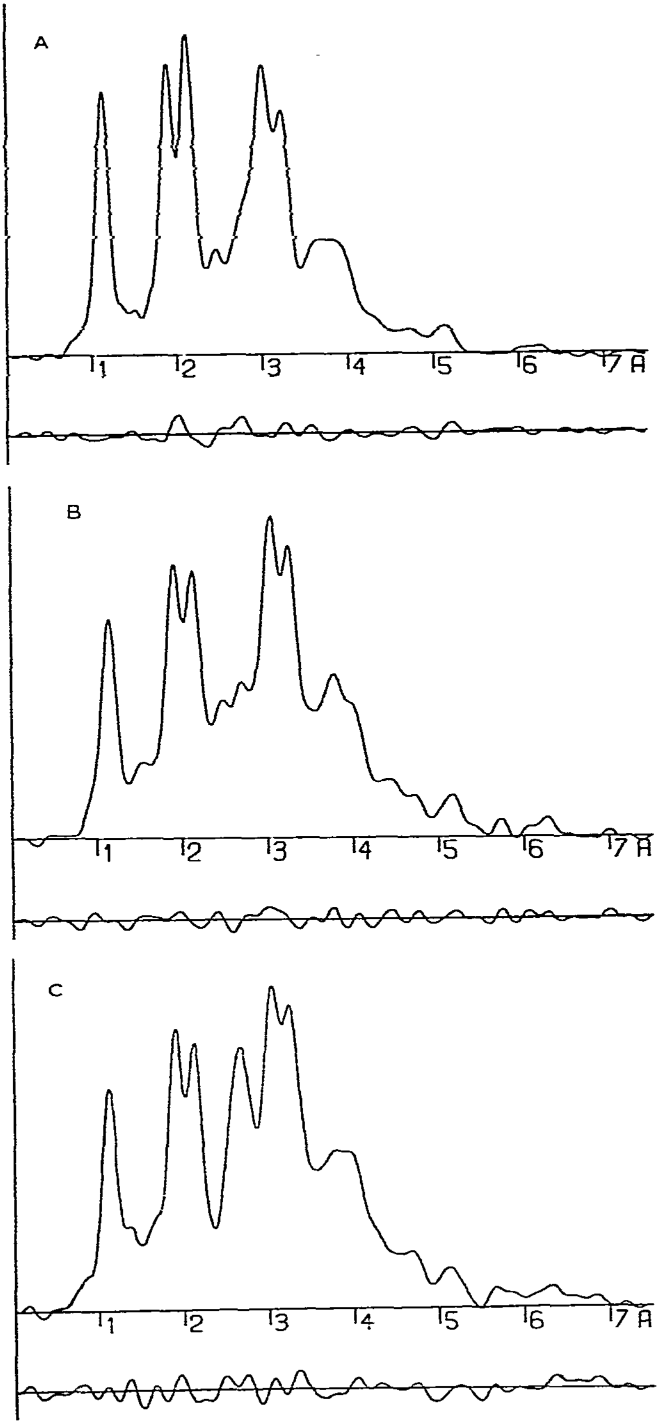


Fig. 2. Radial distribution curves, $P(r)/r$, and difference curves, for (a) $CH_3Re(CO)_5$, (b) $SiH_3Re(CO)_5$ and (c) $GeH_3Re(CO)_5$. In each case, before Fourier inversion, the data were multiplied by: $s \times \exp(-d \times s^2)/(z_{Re} - f_{Re})(z_C - f_O)$, where the damping factor, d, was 0.000015 nm^{-2} for $SiH_3Re(CO)_5$, and otherwise 0.00001 nm^{-2}.

TABLE 3

LEAST SQUARES CORRELATION MATRIX FOR $CH_3Re(CO)_5$, MULTIPLIED BY 100

r1	r2	r3	∠2	u1	u2	u5	u10	u12	u15	k1	k2	k3	
100	7	−2	−4	7	1	9	2	−3	−3	12	9	23	r1
	100	−30	3	19	19	−2	−24	1	4	24	−12	−21	r2
		100	11	−5	−28	−1	2	−11	−13	−27	24	49	r3
			100	−1	1	0	−71	−66	−31	7	−10	−17	∠2
				100	16	5	1	3	2	25	−4	7	u1
					100	0	−4	3	4	36	−16	−3	u2
						100	7	5	−2	11	6	19	u5
							100	43	23	−14	19	27	u10
								100	54	11	−7	−19	u12
									100	9	2	−13	u15
										100	−51	−20	k1
											100	16	k2
												100	k3

tion of refined "beat-out" parameters for Re—C and Re—O with the amplitudes of vibration for these distances, no attempt was made to differentiate between axial and equatorial Re—C distances. Such a difference would in any case be small.

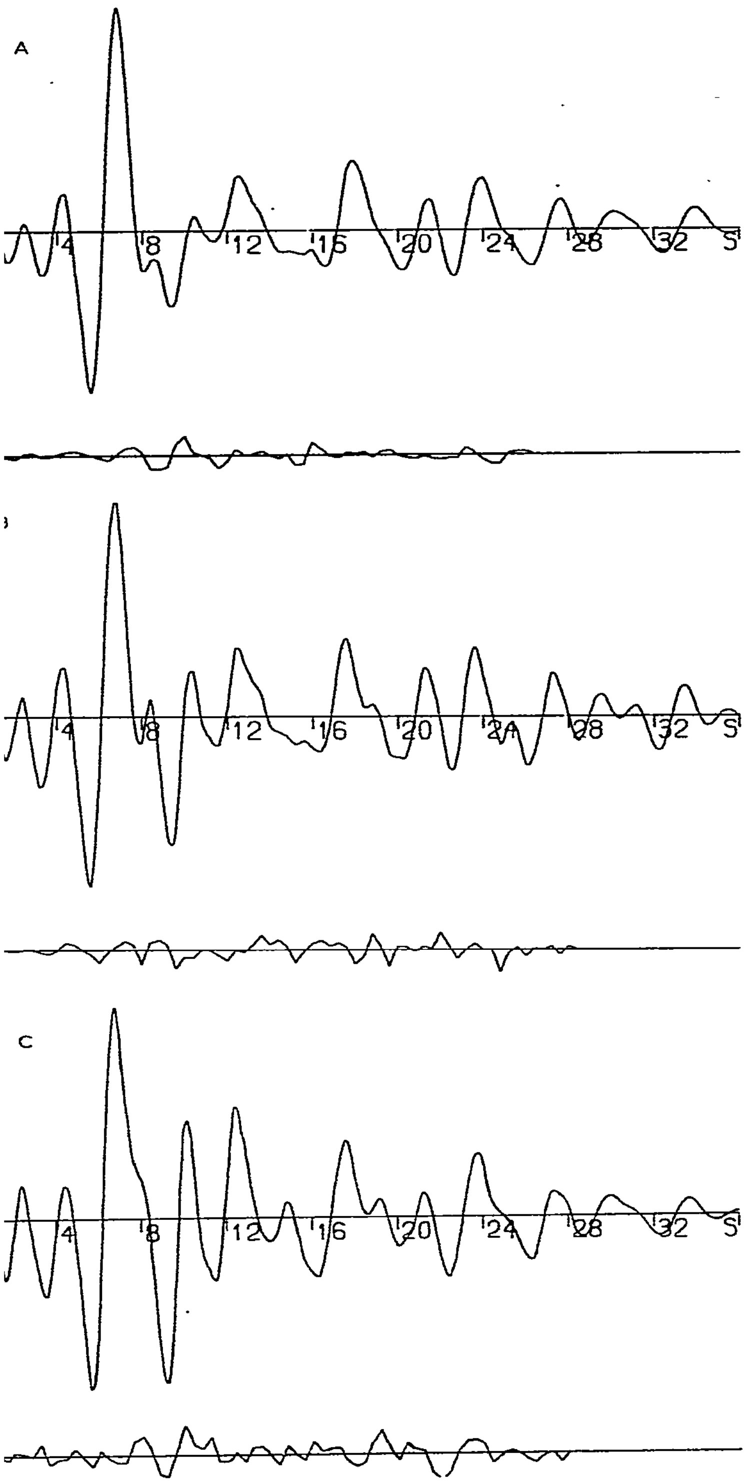
Methyl-rhenium pentacarbonyl

The bond lengths Re—C(methyl), Re—C(carbonyl) and C—O, and their amplitudes of vibration, and the angle C_{ax}—Re—C_{eq}, all refined satisfactorily. In the radial distribution curve (Fig. 2a) there is much overlapping of peaks due to non-bonded pairs of atoms, and groups of amplitudes of vibration were refined together, as shown in Table 2. All parameters involving hydrogen, and one group of vibration amplitudes, were fixed at reasonable values, as they were not well enough defined to be included in refinements. The parameters from the final refinement, for which R_G was 0.12, are given in Table 2. The least squares

TABLE 4

LEAST SQUARES CORRELATION MATRIX FOR $SiH_3Re(CO)_5$, MULTIPLIED BY 100

r1	r2	r3	r4	∠2	u1	u2	u3	u5	u12	k1	k2	k3	
100	1	0	−12	−1	12	9	5	12	−1	17	7	9	r1
	100	−4	3	−4	12	12	6	7	−1	11	5	2	r2
		100	−10	0	−3	−3	2	5	9	−3	1	−3	r3
			100	0	−5	−7	−1	−9	1	−11	−1	−4	r4
				100	0	3	−11	4	−20	1	−12	−5	∠2
					100	41	19	43	3	67	14	2	u1
						100	−3	46	2	65	14	8	u2
							100	5	4	28	2	−15	u3
								100	3	64	17	7	u5
									100	4	15	−15	u12
										100	14	1	k1
											100	−2	k2
												100	k3



. 3. Combined molecular scattering intensity and difference curves for (a) $CH_3Re(CO)_5$, (b) $SiH_3Re(CO)_5$ (c) $GeH_3Re(CO)_5$. In regions where the sum of the weights for the 250, 500 and 100 mm data sets was than 1, theoretical intensity has been included.

correlation matrix is presented in Table 3. It should be noted that the errors quoted included those derived from the least squares analysis, and an allowance for systematic errors. The use of an off-diagonal weight matrix takes care of the problem of correlation between observations.

The combined molecular intensity curves for the three molecules are shown in Fig. 3. Intensity data may be obtained from the authors on request.

Silylrhenium pentacarbonyl

The four bond lengths Re—Si, Re—C, C—O and Si—H, their amplitudes of vibration (except that for Si—H) and the angles C_{ax}—Re—C_{eq} and Re—C_{eq}—O_{eq}, were refined, with some amplitudes of vibration for non-bonded atom pairs. The results of a refinement for which R_G was 0.21, are shown in Table 2, together with details of constraints on vibrational parameters. The least squares correlation matrix is given in Table 4. The values of R_G for this compound and for the germyl analogue are larger than usual, mainly because the scattering intensities due to atom pairs involving rhenium are reduced by the phase shift term discussed earlier. The poor rhenium scattering factor adds to the problem.

Germylrhenium pentacarbonyl

The results of a refinement with R_G equal to 0.22 are given in Table 2, and the least squares correlation matrix is in Table 5. In this case it was found to be possible to refine the Re—C, Re—Ge and C—O distances and vibrational amplitudes, the angles C_{ax}—Re—C_{eq}, Re—C_{eq}—O_{eq} and three groups of amplitudes of vibration for non-bonded distances. As with the other compounds, the Re—C and Re—O "beat-out" points were included in early refinements, but subsequently fixed.

Discussion

It is not easy to define a covalent radius for a metal such as manganese or rhenium, but the best estimates available for these atoms are 139 [13] and 153

TABLE 5

LEAST SQUARES CORRELATION MATRIX FOR $GeH_3Re(CO)_5$, MULTIPLIED BY 100

*r*1	*r*2	*r*3	∠2	*u*1	*u*2	*u*3	*u*5	*u*10	*u*12	*k*1	*k*2	*k*3	
100	2	−2	−3	0	−2	1	−1	7	0	−3	8	15	*r*1
	100	−4	−6	9	9	−2	6	−3	2	5	11	7	*r*2
		100	3	6	9	26	−18	25	4	17	7	−4	*r*3
			100	−12	−13	−5	0	−39	−45	−18	−29	−25	∠2
				100	27	28	15	24	11	47	35	22	*u*1
					100	29	17	23	11	51	35	25	*u*2
						100	1	48	9	55	43	21	*u*3
							100	−13	2	33	15	11	*u*5
								100	27	33	54	50	*u*10
									100	17	22	7	*u*12
										100	42	30	*k*1
											100	34	*k*2
												100	*k*3

TABLE 6

BOND LENGTHS INVOLVING Mn OR Re

	Mn	Ref.	Re	Ref.	Difference
$M'H_3M(CO)_4—CO$[a]	184.9(3)	1,2	200.4(4)	this work	15.5
$(CO)_5M—CH_3$	218.5(11)	1	230.8(17)	this work	12.3
$(CO)_5M—SiH_3$	240.7(5)	2	256.2(12)	this work	15.5
$(CO)_5M—GeH_3$	248.7(2)	2	262.8(6)	this work	14.1
$(CO)_5M—M(CO)_5$	297.7(11)	4	304.0(5)	3	6.3/2 = 3.2
Covalent radius	139	12	153	13	14

[a] Mean of values in CH_3, SiH_3 and GeH_3 derivatives.

pm [14] respectively. The difference between these values, 14 pm, is close to the difference between average metal—carbonyl distances, as shown in Table 6, and so this difference may be taken as being reliable, even if the absolute values are not. Using these covalent radii, and 76.7 pm for carbon, we predict Mn—C and Re—C distances of 215.7 and 229.7 pm. Thus the Mn—C bond in methylmanganese pentacarbonyl does seem to be anomalously long, consistent with estimates of its bond dissociation energy [6]. The Mn—Mn bond in dimanganese decacarbonyl is even more remarkably long. In contrast, Table 6 shows that the bonds in silyl- and germyl-rhenium pentacarbonyls are 14-15 pm longer than the bonds in the manganese derivatives. These bonds are still short compared to those to a methyl group carbon, which may reflect some multiple bond character in the silicon and germanium bonds, but there is no evidence that the extent of this is different for the two metals, rhenium and manganese. This is not consistent with results based on metal—metal stretching force constants [7], but those estimates depended on some assumptions and simplifications that could lead to large errors.

On the other hand, there are estimates of the manganese covalent radius up to 146 pm (based on a value for cobalt [15]), and using this we find our results to agree with all the earlier work, except that concerning bond dissociation energies in methyl derivatives.

The structures of the $—Re(CO)_5$ groups are exactly as would be expected. The parameters seem to depend very little on the substituent, although small variations in the $Re—C_{ax}$ distance would not be easily detected by electron diffraction.

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