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GROUP IVB DERIVATIVES OF THE IRON TRIAD CARBONYLS

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CONTENTS

A. INTRODUCTION

This review deals with complexes of the type $[R_xM'_yM_n(CO)_m]$, where $M' = Si$, Ge, Sn or Pb and $M = Fe$, Ru or Os. No restriction is placed on the other group IV ligands (R_x), but derivatives with mixed ligands on the iron triad metal (e.g. C_5H_5, PR_3) are beyond the scope of this article.

Earlier reviews [1—7] have recognised the complexity of group IV—iron triad carbonyl systems, but have been concerned with the broader area of group IV—transition metal derivatives. Thus this is the first review to concentrate on iron triad carbonyl complexes. Data have been collected from over thirty years of literature, beginning with the reports of Hein and Pobloth [8].

Part B is concerned with tabulations of the numerous complexes now known, with notes on the synthetic methods employed. Part C presents data from single crystal x-ray diffraction studies, and Parts D—F deal with the vibrational, nmr and mass spectral data reported. Part G discusses the Mössbauer and photoelectron spectral data available for these types of complex.

B. THE TYPES OF COMPLEX AND THEIR SYNTHESES

The complexes reported to date are divided into three main categories; those containing one, two and three or more iron triad metals. A compromise has been necessary between attempting to deal with the different types of complex in such a manner as to reflect proportionately the amount of study which has been carried out with each type, and on the other hand to explore the wide variety of systems now known in the area. To emphasize the two types of derivative most widely studied, the $(R_3M')_2M(CO)_4$ and $[R_2M'M(CO)_4]_2$ compounds are collected separately in Tables 1 and 2. Table 3 then lists the remaining derivatives with two iron triad metals, and Table 4 lists higher molecular weight species.

(i) General notes regarding syntheses

The preparative methods used for the large number of $(R_3M')_2M(CO)_4$ complexes reported conveniently fall into three major categories; reactions of (1) metal carbonyls themselves, (2) metal carbonyl anions and (3) metal carbonyl hydrides. These three basic routes are then broken down, depending upon the group IV precursor used (mainly hydrides and halides, see footnote (a) in Table 1). Arbitrarily, a fourth preparative system is distinguished where an exchange type of reaction is used (examples of this type could conceivably be classified under the three mentioned above, e.g. the reaction of $Hg(SiMe_3)_2$ with $Fe(CO)_5$ could be listed in category 1).

After this very general approach in Table 1 to the syntheses of the complexes, mention is made of several specific reactions in the text (section (iii)), with details of reaction conditions, yields (which are generally good), and the methods of manipulation, separation and purification of compounds.

A general approach is also made to the syntheses of the second major class, the $[R_2M'M(CO)_4]_2$ complexes which are also typically obtained in reasonable yields as illustrated in the specific examples given in section (iv) a.

The majority of complexes listed in Tables 3 and 4 were isolated from systems which again fall into the categories distinguished for the other compounds. However, the yields reported for these higher complexes vary considerably (and in some cases a variety of products resulted). Thus, to be consistent in approach, percentage yields are given in Tables 3 and 4 in those cases where complexes were isolated as minor by-products. In instances where different types of reagent were employed, these are specifically noted in the Tables.

Where chemical rearrangements of examples in the different groups have been examined, these are noted briefly at the end of discussion relating to that compound type. The rearrangement products are also listed in the later Tables.

(ii) The iron triad carbonyl anion systems

The transition metal precursors $Fe(CO)_5$ and $M_3(CO)_{12}$, and their hydride derivatives are all well-established. However, a note is now required to examine briefly the data available for the anion systems formed by the iron triad carbonyls, which have been used in many of the syntheses of complexes discussed in sections (iii)—(vi).

The earliest workers reacted alkali with $Fe(CO)_5$ to obtain salts formulated (in the case when $Ca(OH)_2$ was used) as $2\,CaFe(CO)_4 \cdot H_2Fe(CO)_4$, from which the first group IV—iron complexes were derived [8].

Anions formally referred to as $M(CO)_4^{2-}$ are produced through sodium reduction in liquid ammonia of $M_3(CO)_{12}$ compounds (9—11) or of $Fe(CO)_5$ [9]. The solids have been described as mixtures of $Na_2M(CO)_4$ and $Na(H)M(CO)_4$ [10,11], and complexes of the type $R_3M'(H)M(CO)_4$ are commonly isolated from reactions of the anions with halides of the type $R_3M'X$ (see footnote (c) of Table 1). In the case of iron, reaction beyond the stage at which the blue metal—ammonia colour is discharged results in coloured polynuclear anions, identifiable from their visible spectra [12]. The complex $[Me_3SnRu(CO)_4]_2$ was isolated in small yield from reaction of Me_3SnCl with the ruthenium anion [13], indicating that there may commonly be reaction beyond the mononuclear anion stage in this case also.

TABLE 1

$(R_3M^1)_2M(CO)_4$ complexes

Configuration %ages		Complex	Preparative routes [a]	Characterization [b]	Refs.
cis	*trans*				
100	0	$(H_3Si)_2Fe(CO)_4$ [c]	2a	ea, ir, pmi, ^1H nmr (ME ref. 18)	16, 17
100	0	$(Me_3Si)_2Fe(CO)_4$	4	ea, ir, pmi, ^{13}C & ^1H nmr (XD ref. 21)	19, 20 21
100	0	$(Me_2SiCl)_2Fe(CO)_4$	1a?	ea, ir, pmi, ^{13}C & ^1H nmr	20
92	8 (253 K)	$(MeSiCl_2)_2Fe(CO)_4$	1a?	ea, ir, pmi, ^{13}C & ^1H nmr	20
81	19 (308 K)	$(Cl_3Si)_2Fe(CO)_4$ [c]	1a	ea, ir, pmi, ^{13}C & ^1H nmr (XD for *trans*, ref. 25)	20, 22 23, 24
100?	0	$(Cl_3Si)(Cl_3Sn)Fe(CO)_4$ [d]	2a	ea, ir	26
100?	0	$(Cl_3Si)(PhSnCl_2)Fe(CO)_4$ [d]	2a	ea, ir	26
100	0	$(Et_3Si)_2Fe(CO)_4$	1a	ir,	22
100	0	$(OC)_4FeSiMe_2(CH_2)_2SiMe_2$	1a	ea, ir, pmi, ^{13}C & ^1H nmr	27
100	0	$(H_3Ge)_2Fe(CO)_4$ [c,e]	2a	ea, ir, R, *m/s*, ^1H nmr	28, 29
100	0	$(MeGeH_2)_2Fe(CO)_4$ [c,e]	2a	ir, R, *m/s*, ^{13}C & ^1H nmr	30
100	0	$(Me_2GeH)_2Fe(CO)_4$ [c]	2a	ir, ^1H nmr	31
100	0	$(Me_3Ge)_2Fe(CO)_4$ [c]	2a	ea, ir, R, *m/s*, ^{13}C & ^1H nmr	20, 32
100	0	$(Et_3Ge)_2Fe(CO)_4$	1a	ir	22
cis and *trans* separated		$(Cl_3Ge)_2Fe(CO)_4$ [f]	1b	ea, ir, R (pmi for *trans*)	33, 34
0	100	$(Br_3Ge)_2Fe(CO)_4$ [f]	1b	ea, ir	33
0	100	$(I_3Ge)_2Fe(CO)_4$ [f]	1b	ea, ir pmi	33
100	0	$(Me_3Sn)_2Fe(CO)_4$	1a & f, 2a, 3a	ea, ir, pmi, ^{13}C & ^1H nmr	20, 22, 35—37
100	0	$(Et_3Sn)_2Fe(CO)_4$	2a	ea, ir, pmi, ^{13}C nmr	37
100	0	$(Pr^n{}_3Sn)_2Fe(CO)_4$	2a	ea, ir, pmi, ^{13}C nmr	37
100	0	$(Bu^n{}_3Sn)_2Fe(CO)_4$	2a	ea, ir, pmi, ^{13}C nmr	37
100	0	$(Ph_3Sn)_2Fe(CO)_4$	1e, 2a & b	ea, ir, pmi, ^{13}C nmr (XD ref. 37)	37—41
100	0	$(Bu_2SnCl)_2Fe(CO)_4$	1b	ea, ir	35, 42
100	0	$(Et_2SnCl)_2Fe(CO)_4$	1b	ea, ir	35, 42
100	0	$(BuSnCl_2)_2Fe(CO)_4$	1b	ea, ir	41

				(ME ref. 43)	
100	0	$(Br_3Sn)_2Fe(CO)_4$ [f]	1b	ea, ir (ME ref. 43) (for *trans* isomer see ref. 43)	33
100	0	$(Et_3Pb)_2Fe(CO)_4$	2a	ir	22
—		$(C_6H_{11})_3Pb_2Fe(CO)_4$	2b	ea, mw	44
—		$(Ph_3Pb)_2Fe(CO)_4$	2a & b	ea, mw	39, 44
100	0	$(Me_3Si)_2Ru(CO)_4$	1a	ea, ir, pmi, ^{13}C & ^1H nmr	20, 45
100	0	$(OC)_4RuSiMe_2(CH_2)_2SiMe_2$	1a	ea, ir, pmi ^{13}C & ^1H nmr	27
100	0	$(Me_2SiCl)_2Ru(CO)_4$	1a?	ea, ir, pmi, ^{13}C & ^1H nmr	20
88 (305 K)	12	$(MeSiCl_2)_2Ru(CO)_4$	1a	ea, ir, pmi, ^{13}C & ^1H nmr	20
100	0	$(F_3Si)_2Ru(CO)_4$	1a	ea, ir, R, pmi, ^{19}F nmr	34
cis and *trans* separated		$(Cl_3Si)_2Ru(CO)_4$ [c]	1a	ea, ir, ^{13}C & ^1H nmr (R & *m/s* for both isomers ref. 34)	20, 46
100	0	$(Me_3Ge)_2Ru(CO)_4$	1a	ea, ir, pmi, ^{13}C & ^1H nmr	20, 47
0	100	$(Ph_3Ge)_2Ru(CO)_4 \cdot CH_2Cl_2$	1a	ea, ir, pmi (for $(Ph_3Ge)_2Ru(CO)_4^+$) ^1H nmr	34
cis and *trans* separated		$(Cl_3Ge)_2Ru(CO)_4$	1a	ea, ir, R $(P—Cl)^+$ in *m/s* (XD both isomers ref. 48)	34, 47
0	100	$(Br_3Ge)_2Ru(CO)_4$	1b	ea, ir, R, pmi	34
100	0	$(Me_3Sn)_2Ru(CO)_4$	1a	ea, ir, pmi, ^{13}C & ^1H nmr	20, 45
cis and *trans* inseparable		$(Me_3Sn)(R_3Si)Ru(CO)_4$ [d] R = Me, Et	2a	ea, ir, pmi	45
0	100	$(Ph_3Sn)(Me_3Si)Ru(CO)_4$ [d]	2a	ea, ir, pmi	45
cis and *trans* inseparable		$(Bu_3Sn)(Me_3Si)Ru(CO)_4$ [d]	2a	ea, ir, *m/s*	45
		$(Me_3Sn)(Bu_3Sn)Ru(CO)_4$	4	ea, ir, pmi	45
100 for R = Me to 0 R = Ph, $PhCH_2$	0 100 for	$(R_3Sn)_2Ru(CO)_4$ (R = Me, Et, Pr, Bu, Ph, $PhCH_2$)	1a, 2a	ea, ir (*m/s* for R = Me, Et; mw for R = Ph)	10, 40, 49

Table 1 (continued)

Configuration %ages		Complex	Preparative routes [a]	Characterization [b]	Refs.
cis	*trans*				
0	100	$(Cl_3Sn)_2Ru)_2Ru(CO)_4$	1b	ea, ir, R, pmi	34, 93
0	100	$(Br_3Sn)_2Ru(CO)_4$	1b	ea, ir, R, pmi	34
100	0	$(Me_3Pb)_2Ru(CO)_4$	2a	ea, ir, pmi, ^{13}C & ^{1}H nmr	20, 40
37	63 (303 K)	$(Me_3Si)_2Os(CO)_4$	1a	ea, ir, pmi, ^{1}H nmr	20, 50, 51
40	60 (303 K)	$(Me_2SiCl)_2Os(CO)_4$	1a	ea, ir, pmi, ^{13}C & ^{1}H nmr	20
cis and *trans* separated		$(MeSiCl_2)_2Os(CO)_4$	1a	ea, ir, pmi, ^{13}C & ^{1}H nmr	20, 52
cis and *trans* separated		$(F_3Si)_2Os(CO)_4$	1a	ea, ir, pmi, ^{19}F nmr (R for *cis*)	34
0	100	$(Cl_3Si)_2Os(CO)_4$ [c]	1b	ea, ir, R, pmi	34
0	100?	$(Et_3Si)_2Os(CO)_4$ [c]	1a	ea, ir, pmi, ^{1}H nmr	51
0	100	$(Cl_3Si)_2Os(CO)_4$	1a	ea, ir, pmi, ^{13}C nmr	20, 53
0	100?	$(SiMe_2Ph)_2Os(CO)_4$	1a	ea, ir, pmi, ^{1}H nmr	52
100	0	$(OC)_4\overline{OsSiMe_2(CH_2)_2SiMe_2}$	1a	ea, ir, pmi, ^{13}C & ^{1}H nmr	27
100	0	$(H_3Ge)_2Os(CO)_4$ [c]	2a	ea, ir, pmi, ^{1}H nmr	11
80	20 (293 K)	$(Me_3Ge)_2Os(CO)_4$ [c]	1a	ea, ir, pmi, ^{13}C & ^{1}H nmr	20, 47
0	100	$(Cl_3Ge)_2Os(CO)_4$	1a & b	ea, ir, R, pmi	34
80	20 (293 K)	$(Me_3Sn)_2Os(CO)_4$	1a	ea, ir, pmi, ^{1}H nmr	11, 51
50	50 (RT)	$(Me_3Sn)(Me_3Si)Os(CO)_4$ [d]	2a	ea, ir, pmi, ^{1}H nmr	51
0	100	$(Bu_3Sn)_2Os(CO)_4$	2a, 3b	ir, R, ^{1}H nmr	54
0	100	$(PhBu_2Sn)_2Os(CO)_4$	2a	ir, R, ^{1}H nmr	54, 55
0	100	$(Ph_3Sn)_2Os(CO)_4$ [c]	2a, 3b	ea, ir, R, pmi, ^{1}H nmr (XD ref. 54)	11, 54
0	100	$(PhSnCl_2)_2Os(CO)_4$	[g]	ir, R, ^{1}H nmr	54

0	100	$(Bu_2SnCl)_2Os(CO)_4$	[g]	ir, R, ^1H nmr	54
0	100	$(Cl_3Sn)_2Os(CO)_4$ [c]	1b	ea, ir, R pmi	34
0	100	$(Br_3Sn)_2Os(CO)_4$	[g]	ir, R	54
100	0	$(Me_3Pb)_2Os(CO)_4$	2a	ea, ir, pmi, ^{13}C & ^1H nmr	11, 20

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[a] Divided into categories: 1. Reactions of metal carbonyls with (a) group IV-hydrides (M'—H), (b) halides (M'—X), (c) bivalent derivatives [$R_2M'(II)$], (d) M'—Y species (Y = O, S, Se), (e) derivatives of the type $(E)_nM'R_{4-n}$ (E = vinyl, alkynyl), (f) derivatives of the type R_3M'—$M'R_3$. 2. Reactions of metal carbonyl anions with (a) group IV-halides (M'—X) or (b) with oxy-derivatives M'—OR (R = H, $COCR_3$). 3. Reactions of carbonyl hydrides with (a) group IV-hydrides or (b) with oxy- or amido-derivatives M'—Y (Y = O_2CR, OH, NR_2). 4. Exchange types of reaction (see text for examples). [b] ea = Elemental analysis, ir = infra-red, R = Raman, pmi = parent molecular ion, *m/s* = details of mass spectra reported, nmr = nuclear magnetic resonance, XD = single crystal X-ray diffraction study, ME = Mössbauer study. [c] $R_3M'(H)M(CO)_4$ complexes have also been reported (see section (iii)b for further examples). [d] Synthesized from $R_3M'M(CO)_4^-$ anions. [e] Halogen derivatives of these complexes have been studied [56]. [f] $R_3M'(X)M(CO)_4$ complexes, X = halogen, were isolated (see section (iii)b for further examples).
[g] Prepared from HX cleavage of phenyl groups from precursors.

$Na_2Fe(CO)_4$ has also been produced from Na/Hg reductions in THF of $Fe(CO)_5$ [14] or $Fe_3(CO)_{12}$ [15] (where red colours were again attributed to polynuclear derivatives), or from direct reaction of $Fe(CO)_5$ with Na in dioxane with $C_6H_5COC_6H_5$ at 100°C (producing $Na_2Fe(CO)_4 \cdot 1,5\text{-dioxane}$) [14].

Although most reactions with these iron triad carbonyl anions proceed without complication, it should be recognized that an anion system can be a mixture with the complexity dependent in part upon the method of synthesis.

(iii) Derivatives with one iron triad metal

(a) $(R_3M')_2M(CO)_4$ complexes. Table 1 lists almost ninety complexes of this type reported to date. Silicon and tin derivatives are most numerous (30 and 35 examples respectively), with about half this number of germanium examples (17) and only 5 lead compounds. Iron and ruthenium are represented about equally (33 and 30 examples) and osmium compounds number 24. Thus, although most of the earlier work was concerned with iron derivatives, the more ready availability of the higher congener carbonyls has accelerated work with the heavier analogues. As indicated in Table 1, most complexes have been well characterized.

Preparative route 1a (reaction of a group IV hydride with a metal carbonyl, $Fe(CO)_5$ or $M_3(CO)_{12}$) is the most widely used method of synthesis for these complexes. Together with route 1b (analogous reactions using group IV halides), method 1 has produced over one half of the compounds.

The syntheses are carried out under a variety of conditions depending on the complex desired and route employed. Route 2 requires only a few minutes reaction at ambient temperatures between the metal anion and group IV precursor, e.g. $H_3SiI + Na_2Fe(CO)_4 \xrightarrow[\text{10 min RT}]{\text{butane}} (H_3Si)_2Fe(CO)_4$ (70% based on H_3SiI consumed) + 1% $H_3Si(H)Fe(CO)_4$, 2% $H_2Fe(CO)_4$ and 7% SiH_4 [17]. This type of more volatile derivative, together with by-products, is conveniently handled in vacuum apparatus and separated by vacuum fractionation. Less volatile complexes are generally extracted, chromatographed and recrystallized (or sublimed), e.g. [54]

$$Ph_3SnCl + Na_2Os(CO)_4 \xrightarrow[\text{10 min RT}]{\text{THF}}$$

(i) solvent removed
(ii) extraction with C_6H_6 followed by column chromatography (silica gel)
(iii) evaporation of solvent left 91% $(Ph_3Sn)_2Os(CO)_4$, recrystallized from dichloromethane—hexane.

More forcing conditions or longer reaction times are required with route 1, e.g. [33]

$$GeCl_4 + Fe(CO)_5 \xrightarrow[\text{3 weeks RT}]{\text{benzene}}$$

(i) removal of volatiles
(ii) cold hexane extraction of residues yielded an orange-red oil
(iii) petroleum ether extraction of the oil and subsequent cooling yielded 2% *cis* $(Cl_3Ge)_2Fe(CO)_4$ (sublimed with considerable decomposition at 40—50°C)
(iv) warm pentane extraction of the reaction residues yielded 8% *trans* $(Cl_3Ge)_2Fe(CO)_4$ after cooling (purified by sublimation at 45°C).
$Fe_3(CO)_{12}$ could also be used in the above reaction [34]. Other examples of syntheses using route 1 are, e.g. [47]

$Me_3GeH + Ru_3(CO)_{12} \xrightarrow[96\,h\ 100^\circ C]{hexane}$ red solution

(i) With chromatography, hexane elution gave a yellow solution from which 2% $[Me_3GeRu(CO)_3Me_2Ge]_2$ was crystallized.
(ii) Evaporation of solvent left 80% $(Me_3Ge)_2Ru(CO)_4$; a yellow liquid purified by distillation at 70—80°C.
Higher reaction temperatures are required for analogous reactions involving $Os_3(CO)_{12}$, e.g. [47]

$Me_3GeH + Os_3(CO)_{12} \xrightarrow[260\,h\ 150^\circ C]{hexane}$ pale yellow solution

(i) Concentration of solution and cooling crystallized 12% $[Me_3GeOs(CO)_3\text{-}Me_2Ge]_2$
(ii) Evaporation of solvent left a yellow oil from which 16% $Me_3Ge(H)Os(CO)_4$ was sublimed at 20—40°C, and finally 15% $(Me_3Ge)_2Os(CO)_4$ at 60—80°C.
The last three examples indicate that route 1 may produce other higher molecular weight species with the longer reaction periods and higher temperatures employed. An example of a synthesis using another type of group IV precursor is [36]

$Me_6Sn_2 + Fe(CO)_5 \rightarrow (Me_3Sn)_2Fe(CO)_4 + CO$

($[Me_2SnFe(CO)_4]_2$ was found as a by-product)

The less widely used route 3 involves reaction of a transition metal hydride, e.g. [54]

$PhN(SnBu_3)CHO + H_2Os(CO)_4 \xrightarrow[1\,h\ RT]{acetonitrile}$

(i) treatment of mixture with CCl_4
(ii) chromatography through silica gel
(iii) removal of solvent left 71% $(Bu_3Sn)_2Os(CO)_4$.

Route 2 did not produce the complex $(Me_3Si)_2Fe(CO)_4$ (i.e. from $Me_3SiX + Na_2Fe(CO)_4$) and resort was thus made to an exchange type of reaction (listed as route 4 in Table 1) [19].

$Hg(SiMe_3)_2 + Fe(CO)_5 \xrightarrow[sunlight\ 4-5h]{hexane, intense}$ 28% $Hg[Fe(CO)_4SiMe_3]_2$ (crystallized from hexane) and 36% $(Me_3Si)_2Fe(CO)_4$ (sublimed from residues). It is worth noting that $(Me_3Si)_2Fe(CO)_4$ reacts rapidly with THF, since this ether had been used in the reactions of Me_3SiX with $Na_2Fe(CO)_4$. Conceivably then, route 2 may produce the complex if say a hydrocarbon solvent were used.

Preparations of the $(R_3M')_2M(CO)_4$ complexes may result in either 100% *cis* or 100% *trans* forms, or in a mixture of the two. Reference is made in the left hand column of Table 1 to the geometric configurations adopted by complexes (established largely from vibrational and nmr data, see later spectroscopic discussions in Parts C—E). In some cases the isomers are separable but in other cases interconversion is too rapid at room temperature. The delicate balance between the two isomers is best illustrated through a few examples.

(i) Both $(Me_3Si)_2Ru(CO)_4$ and $(Me_3Sn)_2Ru(CO)_4$ have purely *cis* configurations, but the mixed derivative $(Me_3Si)(Me_3Sn)Ru(CO)_4$ exists as a mixture of *cis* and *trans* forms [45].

(ii) A 40% : 60% inseparable mixture of isomers was found for the complex $(Me_{3-x}SiCl_x)_2Os(CO)_4$ when $x = 1$ (303 K), but in the case when $x = 2$ the *cis* and *trans* isomers were separated, and when $x = 3$ only the *trans* form was found [20]. For the ruthenium analogues $(Me_{3-x}SiCl_x)_2Ru(CO)_4$, when $x = 1$ the complex is 100% *cis*, when $x = 2$ an inseparable (88% : 12%) mixture of *cis* and *trans* forms are found, and when $x = 3$ both isomers can be isolated [20].

(iii) $(Ph_3Sn)_2Fe(CO)_4$ exists only as the *cis* isomer [37], but both $(Ph_3Sn)_2M(CO)_4$, M = Ru and Os, are found only as *trans* isomers [40,54]. These cases serve to indicate the delicate interplay of electronic and steric effects as the nature of the group IV ligands, the group IV metal, or the iron triad metal is changed. Early qualitative rationalizations of electronic factors are now being given a more rigorous footing [57].

The air stabilities of the $(R_3M')_2M(CO)_4$ complexes vary from extremely air-sensitive in the case of $(Me_3Ge)_2Fe(CO)_4$ (where an exothermic reaction occurred in a glove-box during handling [32]), to air stable compounds as in the case of $(Ph_3Sn)_2Os(CO)_4$ [11].

The chemical relationships between $(R_3M')_2M(CO)_4$ compounds and higher molecular weight clusters have been examined in a few cases

$$2(R_2GeH)_2Fe(CO)_4 \xrightarrow{RT} [R_2GeFe(CO)_4]_2 + 2R_2GeH_2 \ (R_2 = Me_2 \text{ and } MeH)$$

There was 97% conversion after 15 days in the case when $R_2 = Me_2$, but the reaction of the complex when $R_2 = MeH$ was slower in the dark and produced other clusters with light [30, 31].

$$2(Me_3Sn)_2Fe(CO)_4 \xrightarrow{140^\circ C} [Me_2SnFe(CO)_4]_2 + ?\ 2\ Me_4Sn \ [35]$$

The stoichiometry was not well established in the last case, but this reaction has also been noted during more recent work [37]. Earlier on, reactions of R_3PbX compounds with $Na_2Fe(CO)_4$ which produced $[R_2PbFe(CO)_4]_2$ complexes were suggested to proceed via the tri-alkyl lead derivatives [38,39,44]. The complex $(Me_3Sn)_2Ru(CO)_4$ has been found to convert partially to the complex $Me_{10}Sn_4Ru_2(CO)_6$ [40], and the complexes $[Me_2GeM(CO)_3]_3$, M = Ru, Os, have only been produced from the pyrolyses of the mononuclear derivatives [47] (see Table 4 and later discussion in section (v)).

(b) Other complexes. As noted in footnote (e) of Table 1, a number of $R_3M'(H)M(CO)_4$ species have been reported, usually as by-products with $(R_3M')_2M(CO)_4$ complexes. Separate reports have referred to the hydrides $R_3Si(H)Fe(CO)_4$ when $R_3 = Cl_3$ [24,58,59], Ph_3 [24,59], Me_3, Me_2Cl, $MeCl_2$, $PhCl_2$, $PhMe_2$, PhMeCl [59 and references therein]. These silicon hydrides are best prepared through photochemical reactions, e.g. [59]

$$R_3SiH + Fe(CO)_5 \xrightarrow{h\nu} R_3Si(H)Fe(CO)_4 + CO$$

$Ph_3Ge(H)Fe(CO)_4$ has been prepared from its conjugate base $Ph_3GeFe(CO)_4^-$ [59]. As with the osmium hydrides mentioned in Table 1, the compounds $X_3Sn(H)Os(CO)_4$; X = Cl, Br; were isolated from systems which would also produce the $(X_3M')_2Os(CO)_4$ complexes, depending on the reaction conditions employed [60]. Another report has referred to several other hydride complexes [55]. On the basis of their infra-red spectra (see Part E) the $R_3M'(H)M(CO)_4$ complexes are believed to adopt cisoid configurations, and in one case, for $Ph_3Si(H)Fe(CO)_4$, this has been confirmed by a single crystal x-ray diffraction study [61].

Halogen species of the type *cis* $X_3M'(X)Fe(CO)_4$ have been reported as intermediates from reactions of group IV tetrahalides (see footnote (f) in Table 1) [33], and the complexes *trans* $Me_3M'M(CO)_4X$ have been isolated from the direct cleavage by Br_2 or I_2 of the compounds $[Me_3M'M(CO)_4]_2$ when M' = Si and Ge for M = Ru; and when M' = Si, M = Os [62].

One methyl-substituted complex, $Me_3Si(Me)Os(CO)_4$ has been reported [51].

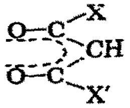
Anions of the type $R_3M'M(CO)_4^-$ (i.e. the conjugate bases of the hydrides) are known in the following cases; $Ph_3SiFe(CO)_4^-$ [26,59,63], $Cl_3SiFe(CO)_4^-$ [26], $H_3GeFe(CO)_4^-$ [64], $Cl_3GeFe(CO)_4^-$ [65,66], $Ph_3GeFe(CO)_4^-$ [59], $Ph_3SnFe(CO)_4^-$ [59,67], $Cl_3SnFe(CO)_4^-$ [65,66], $Br_3SnFe(CO)_4^-$ [66], $Me_3SiRu(CO)_4^-$ [45] and $Me_3SiOs(CO)_4^-$ [51]. In several cases these anions have been used to synthesize asymmetrically substituted complexes listed in Table 1 (see footnote (d)).

Monomeric compounds of the formulae $B \rightarrow R_2M'Fe(CO)_4$ have been proposed as products from cleavage by the Lewis base B of the $[R_2M'Fe(CO)_4]_2$ compounds. These complexes are further discussed in Parts E and G since these studies have mainly involved comparison of infra-red and Mössbauer data for the adducts and their precursors.

(iv) Derivatives with two iron triad metals

These compounds occur in a wide variety of structural types with group IV metals in bridging and/or terminal positions. Table 2 lists 36 complexes of the type $[R_2M'M(CO)_4]_2$ and the other 56 derivatives are found in Table 3,

$[R_2M'M(CO)_4]_2$ complexes

Complex	Preparative routes[a]	Characterization	Refs.
$[Cl_2SiFe(CO)_4]_2$	1a	ea, ir, pmi (XD ref. 68)	23
$[RGeHFe(CO)_4]_2$			
R = H	*b,c*	ir, *m/s*, ^1H nmr	56
Me	*c,d*	ir, *m/s*, ^1H nmr	30
$[Me_2GeFe(CO)_4]_2$	2a,	ea, ir, *m/s*, ^1H nmr	31, 69, 70
$[Et_2GeFe(CO)_4]_2$	2a	ea, ir (XD ref. 71)	22, 69
$[Cl_2GeFe(CO)_4]_2$	1b	ea, ir (pmi for Cl complex)	33
$[Br_2GeFe(CO)_4]_2$			
$[I_2GeFe(CO)_4]_2$			
$[Ph_2GeFe(CO)_4]_2$	2a	ea, ir $(P{-}CO)^+$ in m/s	70, 92
$[Me_2SnFe(CO)_4]_2$	1a & d, 2a,[d]	ea, ir, ^1H nmr (ME ref. 75; XD ref. 76; PE ref. 91)	35, 36, 41, 70, 72—74
$[Et_2SnFe(CO)_4]_2$	1a? & d, 2a	ea, ir, mw	22, 35, 41, 73, 74, 77—79
$[(vinyl)_2SnFe(CO)_4]_2$	1d & e, 2b	ea, ir, mw, *m/s*	41, 80, 81
$[Pr_2SnFe(CO)_4]_2$	1d & e	ir, mw	41, 78, 79
$[Bu_2SnFe(CO)_4]_2$ (both Bu^t and Bu^n)	1a, d, e & f; 2a	ea, ir, ^{13}C & ^1H nmr, mw (ME refs. 75 & 84; PE ref. 91)	35, 41, 42, 70 72—74, 82, 83
$[(C_5H_4R)_2SnFe(CO)_4]_2$ R = H, Me	1c	ea, ir, mw, ^1H nmr, ME (XD for R = H, ref. 88)	85—87
$[Ph_2SnFe(CO)_4]_2$	1e, 2a	ea, ir (PE ref. 91)	35, 39, 41, 70
$[MeSnPhFe(CO)_4]_2$	2a	ea, ir, pmi, ^{13}C & ^1H nmr	82, 83
$[(C_8H_{17})_2SnFe(CO)_4]_2$	1e	ea, ir	41
$[X_2SnFe(CO)_4]_2$ X = Cl, Br	1c	ea, ir, ME	85, 89
$[R_2SnFe(CO)_4]_2$ R =  where X = X' = Me X = X' = CF_3 X = X' = Ph X = Me, X' = CF_3 & Ph	1c	ea, ir, mw, ^1H nmr, ME (^{19}F nmr for CF_3-containing complexes)	85, 89
$[Me_2PbFe(CO)_4]_2$	2b	ea, ir	35, 44, 90
$[Et_2PbFe(CO)_4]_2$	2a & b[d]	ea, ir	8, 22, 35, 44, 74, 77
$[Pr_2PbFe(CO)_4]_2$	2b	ea	44, 90
$[Bu_2PbFe(CO)_4]_2$	2a & b	ea, ir, ^1H nmr	44, 70, 90
$[(i\text{-}amyl)_2PbFe(CO)_4]_2$	2b	—	44
$[Ph_2PbFe(CO)_4]_2$	2a & b	ea, ir	38, 39, 70
$[Me_2SnRu(CO)_4]_2$	*e*	ea, ir, *m/s*, ^1H nmr	45
$[Me_2SnOs(CO)_4]_2$	2a	ea, ir, pmi, ^1H nmr	11
$[Bu_2SnOs(CO)_4]_2$	3b	ea, ir, R, mw	54
$[Ph_2SnOs(CO)_4]_2$	3b	ea, ir, R	54

[a] See Table 1 footnote (a). [b] Prepared from $H_3GeFe(CO)_4^-$ + Me_3GeCl. [c] Halogen derivatives of these complexes have also been characterized [56]. [d] Prepared from the rearrangements of $(R_3M')_2M(CO)_4$ complexes. [e] Prepared from $Me_3SiRu(CO)_4^-$ + Me_2SnCl_2.

grouped according to the type of structure believed adopted. As noted in the general introduction to this Part (B), a general approach to preparative routes is continued for the $[R_2M'M(CO)_4]_2$ complexes, but more details regarding syntheses are given in Table 3 for the other complexes where there are fewer examples in each of the groups.

(a) *$[R_2M'M(CO)_4]_2$ complexes.* In contrast to the $(R_3M')_2M(CO)_4$ compounds, we find here that most examples of this type involve derivatives of iron (32 complexes) and only four involve ruthenium and osmium. The dimeric nature of these complexes was recognized soon after the first report [44], and several of the compounds have been extensively studied with most spectroscopic techniques available to chemists.

The most widely used routes to these compounds are reactions of metal carbonyls and of the anions $M(CO)_4^{2-}$. A variety of group IV precursors have been used in the reactions involving the neutral carbonyls, e.g. [33]

$GeCl_4 + Fe(CO)_5 \xrightarrow[90^\circ C\ 4\ days]{xylene}$ large orange crystals and a dark material

(i) Extraction of orange crystals with $CHCl_3$.
(ii) Concentration of solution, addition of pentane, and cooling produced 14% yellow $[Cl_2GeFe(CO)_4]_2$, recrystallized from CH_2Cl_2/pentane.
Initial hexane washings from this reaction had contained some $(Cl_3Ge)_2Fe(CO)_4$. This latter complex was produced from the same system in 10% yield at room temperature (see section (iii)). The iodo-analogue $[I_2GeFe(CO)_4]_2$ could be prepared in 90% yield from heated reactions of $Fe(CO)_5$ with $I_3Ge(I)Fe(CO)_4$. $(I_3Ge)_2Fe(CO)_4$ was identified as an intermediate [33]. For the metal carbonyl reactions the largest number of examples involve insertion of bivalent tin derivatives into $Fe_2(CO)_9$ [89].

$SnI_2 + Fe_2(CO)_9 \xrightarrow[48\,h\ RT]{benzene} [I_2SnFe(CO)_4]_2$ (obtained in 92% yield as a vermilion orange solid, which crystallized as a powder during removal of solvent).
From the reactions of tin(II) precursors with $Fe(CO)_5$, however, no characterizable products were afforded [85]. Other group IV precursors used in the syntheses of $[R_2M'Fe(CO)_4]_2$ compounds include alkynyl derivatives, e.g. [78,79]

$R_2Sn(C \vdots CBu^n)_2 + Fe_3(CO)_{12} \xrightarrow[ca.\ 11\,h\ 100^\circ C]{light\ petroleum}$ orange-brown oils, which after chromatography yielded 28—30% $[R_2SnFe(CO)_4]_2$, for R = Et, Pr^n, Bu^n.

Reactions employing route 2 proceed largely as expected, e.g. [70]

$Bu_2^tSnCl_2 + Na_2Fe(CO)_4 \xrightarrow[7\,h\ from\ -60^\circ C\ to\ RT]{THF,\ stirred\ for}$ red-orange mixture

(i) Removal of solvent left an orange oil.
(ii) Extraction with hexane (and filtration of the first extract through diato-

maceous earth) followed by evaporation of some solvent and cooling left yellow $[Bu_2{}^tSnFe(CO)_4]_2$ (50% after recrystallization from hexane).
The osmium anion reacted in an analogous fashion with Me_2SnCl_2 to produce $[Me_2SnOs(CO)_4]_2$ [11], but the compound $[Me_2SnRu(CO)_4]_2$ could not be obtained from reaction with the ruthenium anion. As noted in Table 2 (footnote (c)), the binuclear ruthenium complex was eventually obtained from the reaction of Me_2SnCl_2 with $Me_3SiRu(CO)_4^-$ [45].

As commented upon in the preceeding section (iii), some $[R_2M'M(CO)_4]_2$ derivatives can be prepared from the rearrangements of $(R_3M')_2M(CO)_4$ complexes. This type of rearrangement is thought to occur in several other systems involving initial reaction of R_3PbX ($X = OH, Br$) compounds with the iron carbonyl anion [8,37—39,44,90].

The rearrangements of $[R_2M'M(CO)_4]_2$ complexes to other clusters have been examined for two types of reaction. With irradiation several of these complexes have been found to evolve CO and form $(R_2M'M)_2(CO)_7$ complexes (see below). Another study has reported that the complex $[(C_5H_5)_2SnFe(CO)_4]_2$ converts to a pentairon cluster $[(C_5H_5)Fe(CO)_2Sn]_2[Fe(CO)_3]_3$ in which the cyclopentadienyl moieties are reattached to two iron atoms [94].

(b) Other dinuclear complexes. The $(R_2M'M)_2(CO)_7$ complexes have been prepared from type 1a reaction systems (cf. footnote (a), Table 1), e.g. [92]

$Ph_2GeH_2 + Fe_3(CO)_{12} \xrightarrow[90^\circ C]{\text{hexane}} (Ph_2GeFe)_2(CO)_7$ as the predominant product

together with some $[Ph_2GeFe(CO)_4]_2$
The heptacarbonyl complex could be prepared more cleanly from reaction of Ph_2GeH_2 with $Fe_2(CO)_9$ [92]. Alternatively, irradiation or heating of octacarbonyl derivatives will produce these heptacarbonyls in significant yields. More recently analogous tin derivatives have been reported from photolytic reactions, e.g. [83]

$[MeSnPhFe(CO)_4]_2 \xrightarrow[10\,h\;0^\circ C]{\text{MCH}\;h\nu}$ dark orange solution and solids

(i) Solvent removed.
(ii) Dark orange residues rinsed with pentane, then a solution in CH_2Cl_2 was layered with pentane.
(iii) During cooling to −35°C for ca. 2 days, dark orange crystals of $(MeSnPhFe)_2(CO)_7$ separated. After further cooling, separation, washing and recrystallization, a 20% yield was obtained.

The complexes $(Me_2Ge)_3M_2(CO)_6$, $M = Ru$ and Os, were isolated in very small yields from the pyrolyses of the related mononuclear derivatives (see notes in Table 3). However, the other examples of this type of cluster have been prepared in larger yields, e.g. [97].

$Me_2SiH_2 + Fe_2(CO)_9 \xrightarrow{140^\circ C}$ 28% $(Me_2Si)_3Fe_2(CO)_6$

TABLE 3

Other derivatives with two iron triad metals

Complex	Preparative systems[a]	Characterization	Refs.
(i) Compounds analogous to $Fe_2(CO)_9$ with bridging $M'R_2$ replacing CO			
$(Me_2SiFe)_2(CO)_7$	1a (using $Me_4Si_2H_2$)	ea, ir, *m/s*, ^1H nmr	95
$(Me_2GeFe)_2(CO)_7$	1a, [b]	ir	31, 92
$(MeGeHFe)_2(CO)_7$	[b]	ir	30
$(Ph_2GeFe)_2(CO)_7$	1a, [b]	pmi (XD ref. 96)	92
$(Bu^n_2SnFe)_2(CO)_7$	[b]	ea, ir, pmi, ^{13}C nmr	83
$(MeSnPhFe)_2(CO)_7$	[b]	ea, ir, pmi, ^1H & ^{13}C nmr	83
$(Me_2Si)_3Fe_2(CO)_6$	1a	ea, ir, ^1H nmr	97
$(Me_2Si)_3Ru_2(CO)_6$	$[Me_3M'Ru(CO)_4]_2$ + $(HMe_2Si)_2$ (M' = Si, Ge)	ea, ir, pmi, ^1H nmr	98
$(Me_2Ge)_3Fe_2(CO)_6$	1a	ea, ir, pmi, ^1H nmr (XD ref. 100)	92, 99
$(Me_2Ge)_3Ru_2(CO)_6$	[c] (<1%)	ir, *m/s*, ^1H nmr	47, 101, 102
$(Me_2Ge)_3Os_2(CO)_6$	[c] (traces)	ir	47, 101, 102
(ii) Compounds related to the $[R_2M'M(CO)_4]_2$ complexes, but with: (a) digermanyl bridging linkages			
$(Me_2GeGeMe_2)_2Fe_2(CO)_8$	2a (using $(Me_2GeCl)_2$)	ea, ir, pmi, ^1H nmr	103
$(Me_2Ge)(Me_2GeGeMe_2)Fe_2(CO)_8$	2a (using $(Me_2GeCl)_2$)	ea, ir, pmi, ^1H nmr	14, 103
(b) two R_3M' terminal groups as as well as the two R_2M' bridging groups			
$[Me_3SiM(CO)_3Me_2Si]_2$ M = Ru, Os	Me_5Si_2H + $M_3(CO)_{12}$, $(Me_3Si)_2M(CO)_4$ or $[Me_3M'M(CO)_4]_2$	ea, ir, pmi, ^1H nmr (XD for M = Ru, ref. 104)	98
$[Me_3GeM(CO)_3Me_2Ge]_2$ M = Ru, Os	1a	ea, ir, pmi, ^1H nmr	47
$[Me_3SnRu(CO)_3Me_2Sn]_2$	1a & f, ([c] <3%)	ea, ir, $(P-2Me)^+$ seen in *m/s*, ^1H nmr (XD ref. 105)	40, 49
$[Bu_3SnRu(CO)_3Bu_2Sn]_2$	1a (traces)	ir	40
(iii) Compounds with an unbridged M—M bond			
$[Cl_3SiFe(CO)_4]_2$	$Cl_3Si(H)Fe(CO)_4$ + C_2F_4	ea, ir, pmi	24, 59
$[R_3SiRu(CO)_4]_2$ R_3 = Me_3, Et_3, Pr_3, $(EtO)_3$, Ph_3, Cl_3, $MeCl_2$	1a	ea, ir, pmi, ^1H nmr (ir only for R_3 = Ph_3, $(OEt)_3$)	45, 49
$[Me_3GeRu(CO)_4]_2$	1a	ea, ir, pmi, ^1H nmr	47
$[Me_3SnRu(CO)_4]_2$	2a (very low yield)	ir, pmi, ^1H nmr, XD	13
$[R_3SiOs(CO)_4]_2$ R = Me, Et	1a	ea, ir, pmi (R & *m/s* for R = Me)	51, 106
$Me_3SiOs(CO)_4Ru(CO)_4SiMe_3$	$Me_3SiRu(CO)_4I$ + $Me_3SiOs(CO)_4^-$	ir, pmi, ^1H nmr	51

Table 3 (continued)

Complex	Preparative systems [a]	Characterization	Refs.
(iv) Compounds with bridging halogen atoms			
$[Me_3SiRu(CO)_3X]_2$ X = Br		ir	
X = I		ea, ir $(P—Me)^+$ in *m/s* ^{1}H nmr	
$[Me_3SiOs(CO)_3X]_2$ X = Br, I	$R_3M'M(CO)_4X/\Delta$	ea, ir, pmi, ^{1}H nmr $((P—Me—CO)^+$ observed for X = Br)	62
$[Me_3M'Ru(CO)_3I]_2$ M' = Ge, Sn		ea, ir, ^{1}H nmr	
$[Me_3GeOs(CO)_3Br]_2$		ea, ir, pmi, ^{1}H nmr	
$Cl_6SiRu_2(CO)_5$			
$X_6GeRu_2(CO)_5$ X = Br, I			
$Cl_6GeOs_2(CO)_5$	1b	ea, ir, pmi $((P—I)^+$ observed for I complexes; mw for $Br_6GeRu_2(CO)_5$; R for $Cl_6SnRu_2(CO)_5$) (XD for $Cl_6SnRu_2(CO)_5$ refs. 93, 107)	34
$X_6SnRu_2(CO)_5$ X = Br, I			
$Cl_6SnOs_2(CO)_5$			
(v) Other complexes			
$Cl_3Sn(X)Os_2(CO)_8$ X = H	$H_2Os_2(CO)_8$ + $SnCl_4$	ea, ir, ^{1}H nmr	58
X = Cl, Br	$Cl_3Sn(H)Os_2(CO)_8$ + CX_4	ea, ir	
$I_4SiFe_2(CO)_6$	1b	ir, mw	108
$Ph_2Ge[Fe(CO)_4]_2$	1b	ea, ir, pmi	92, 99
$R_2Sn[Fe(CO)_4]_2$ [d] R = 4-phenylbutane-2,4-dionate	1c (minor product)	ea, ir	85, 89
$(Ph_2Ge)_2OFe_2(CO)_8$	$(Ph_2GeFe)_2(CO)_7$(RT)	XD	109
$(Ph_2Ge)(PhGeH)Fe_2(CO)_6$	1a		92
$Cl_2Sn[Fe(CO)_4SiCl_3]_2$	$SnCl_4$ + $Cl_3SiFe(CO)_4^-$ [e]	ea, ir	26
$Cl_6SiRu_2(CO)_6$	1b (a very air-sensitive by-product with $Cl_6SiRu_2(CO)_5$)	ir	34

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[a] See footnote (a) in Table 1 for details of routes 1—3. Where complexes arise as minor by-products (< 5% yields), this is noted in parentheses. Specific reagents are mentioned in some cases to shorten footnotes. [b] Prepared from photolyses (or pyrolyses) of $(R_2M'Fe)_2(CO)_7$ complexes. [c] Prepared from pyrclyses of $(Me_3M')_2M(CO)_4$ complexes. [d] Since this complex exhibits an ir absorption in the bridging CO region, it may belong to the class (i) above or as suggested [85,89] may possess a terminal R_2Sn group. [e] An anion whose analysis was consistent with the the formula $Cl_6SiSnFe_2(CO)_7^-$ was also isolated.

The germanium analogue has been prepared in a similar manner (Me_2GeH_2 + $Fe_3(CO)_{12}$ (65°C)) and in this case unstable crystals of $(Me_2GeFe)_2(CO)_7$ were also formed [92,99]. The complex $(Me_2Si)_3Ru_2(CO)_6$ was prepared from a disilane precursor

$(Me_2SiH)_2 + [Me_3M'Ru(CO)_4]_2 \xrightarrow{RT} (Me_2M')_3Ru_2(CO)_6 \quad (M' = Si, Ge)$

Yields of 35 and 10% were obtained after 12 and 19 day reactions for the silicon and germanium derivatives respectively. However, the silylosmium analogue could not be prepared from this route [98].

Reaction of digermanyl dichloride with the iron carbonyl anion produced the two digermanyl-bridged complexes $(Me_2Ge)(Me_2GeGeMe_2)Fe_2(CO)_8$ and $(Me_2GeGeMe_2)_2Fe_2(CO)_8$ [14,103]. Both of these compounds rapidly convert to $(Me_2Ge)_3Fe_2(CO)_6$ even under weak irradiation [103].

The silicon derivatives with group IV metals in both bridging and terminal positions have been produced from the reactions of a disilane, e.g. [98].

$Me_5Si_2H + Ru_3(CO)_{12} \xrightarrow[40\,h\,h\nu]{hexane}$ red solution

(i) Removal of solvent and cooling produced yellow crystals of $[Me_3SiRu(CO)_3Me_2Si]_2$ (97 mg).
(ii) Chromatography of the remaining oil (silica gel) produced a further 51 mg $[Me_3SiRu(CO)_3Me_2Si]_2$. Total yield was 20%.
This complex was also produced in 44% yield from the reaction of Me_5Si_2H with $[Me_3SiRu(CO)_4]_2$. The osmium analogue was prepared in 9% yield from a reaction at 160°C for 44 h between Me_5Si_2H and $Os_3(CO)_{12}$ [98]. In the case of germanium and tin this type of complex has been produced as a by-product from systems used to synthesize $(R_3M')_2M(CO)_4$ compounds, e.g. [47]

$Me_3GeH + Os_3(CO)_{12} \xrightarrow[150^\circ C\ 260\,h]{hexane}$ pale yellow solution

(i) Concentration and cooling to −78°C yielded 12% $[Me_3GeOs(CO)_3Me_2Ge]_2$.
(ii) Removal of hexane from the supernatant left $(Me_3Ge)_2Os(CO)_4$ (68% after sublimation).
The tin—ruthenium analogue has been referred to in section (iii) (the reaction of Me_3SnH with $Ru_3(CO)_{12}$). In this case $[Me_3SnRu(CO)_3Me_2Sn]_2$ was shown to arise from pyrolysis of the mononuclear precursor $(Me_3Sn)_2Ru(CO)_4$ (1% conversion after 44 h at 80°C) [40].

Complexes of the type $[R_3SiRu(CO)_4]_2$ have been produced in good yields from reactions of silanes with $Ru_3(CO)_{12}$, e.g. [45]

$Cl_3SiH + Ru_3(CO)_{12} \xrightarrow[60\,h\ 80^\circ C]{hexane}$ 61% yellow $[Cl_3SiRu(CO)_4]_2$ as crystals (purified

by recrystallization from dichloromethane-hexane)
The methyl analogue $[Me_3SiRu(CO)_4]_2$ produces the anion $Me_3SiRu(CO)_4^-$ from reaction with sodium amalgam, and this anion has been used to synthesize a variety of new types of complex as noted earlier in section (iii). With $Ru_3(CO)_{12}$ and Me_3GeH, uv irradiation was required to produce the complex

$[Me_3GeRu(CO)_4]_2$ (47). The osmium compounds $[R_3SiOs(CO)_4]_2$, R = Me, Et, have been produced from reactions of the silanes with $Os_3(CO)_{12}$ either at elevated temperatures or under uv irradiation, together with the species $R_3Si(H)Os(CO)_4$ and $(R_3Si)_2Os(CO)_4$. All three products are interrelated both thermally and upon further reaction with the silanes R_3SiH [51,106]

$$\begin{tikzcd}
Me_3Si(H)Os(CO)_4 \arrow[r, "Me_3SiH", "\text{(ca. 50\% conversion after 98 h at 80°C)}"'] \arrow[dr, bend right, "\text{80°C/—}[H_2\ \&\ (Me_3Si)_2O]"] & (Me_3Si)_2Os(CO)_4 \\
& {[Me_3SiOs(CO)_4]_2} \arrow[u, "\text{Me}_3\text{SiH, 6 days, 100°C [67\% yield, plus a trace of } Me_3Si(H)Os(CO)_4]"'] \arrow[ul, bend left, "Me_3SiH"]
\end{tikzcd}$$

A series of derivatives of Ru and Os with bridging Br or I atoms has been prepared from pyrolyses of the mononuclear halogen complexes referred to briefly in section (iii), e.g. [62]

$$Me_3SiRu(CO)_4I \xrightarrow[\text{15 min —CO}]{\text{refluxing hexane}} 74\%\ \text{red}\ [Me_3SiRu(CO)_3I]_2$$

Another series of complexes, shown in one case to have three bridging halogen atoms and X_3M' terminal groups, has been reported from reactions of the halides $M'X_4$ with the dodecacarbonyls of ruthenium and osmium, e.g. [93]

$$SnCl_4 + Ru_3(CO)_{12} \xrightarrow[135^\circ C]{\text{xylene}} 90\%\ Ru_2(CO)_5SnCl_6$$

Several other types of complex believed to contain two iron triad metals are referred to in Table 3.

(v) Higher molecular weight complexes

(a) Complexes with three iron triad metals. The few complexes of this type reported so far are included in Table 4. An interesting silicon complex with the stoichiometry $[Cl_2SiFe(CO)_4]_3$ but an unknown structure has been reported [110]

$$3[Et_4N][Cl_3SiFe(CO)_4] + 3\ AlCl_3 \xrightarrow{\text{pentane}} [Cl_2SiFe(CO)_4]_3 + 3[Et_4N][AlCl_4]$$

The complex $(PhGe)_2[Fe(CO)_3]_3$ has been briefly mentioned [111] and is proposed with a *closo* arrangement of metal atoms as found for the compound $[C_5H_5Fe(CO)_2Sn]_2[Fe(CO)_3]_3$ (see structure in Part C). As mentioned earlier (section (iii)) the complexes $[Me_2GeM(CO)_3]_3$ are produced from the pyrolyses of the mononuclear derivatives. However, the silyl—osmium analogue was synthesized from reaction of Me_5Si_2H with $H_2Os(CO)_4$ [98].

Whereas the higher temperature reactions of tin tetrachloride with $M_3(CO)_{12}$, M = Ru, Os, produce dinuclear derivatives (see discussion in section (iv)), the room temperature reactions produce the trinuclear derivatives $M_3(CO)_{12} \cdot SnCl_4$, for which linear M—M—M frameworks have been suggested on the basis of infra-red data.

TABLE 4
Higher complexes

Complex	Preparative route [a]	Characterization	Refs.
(i) Complexes with three iron triad metals			
$[Cl_2SiFe(CO)_4]_3$	$Cl_3SiFe(CO)_4^- + AlCl_3$	ea, ir, *m/s*, mw, ME	110
$(PhGe)_2[Fe(CO)_3]_3$	1a	ir	111
$[Me_2SiOs(CO)_3]_3$	3 (using Me_5Si_2H, 2% yield)	ea, ir, pmi, ^1H nmr	98
$[Me_2GeM(CO)_3]_3$ M = Ru, Os	[b]	ea, ir, pmi, ^1H nmr (XD for M = Ru, ref. 112)	47, 101
$Cl_3Sn[M(CO)_4]_3Cl$			
M = Ru	1b	ea, ir, R	34, 93
M = Os	1b	ea, ir, R, *m/s*	34, 58
(ii) Complexes with four or more iron triad metals			
$Ge[Fe(CO)_4]_4$	2a (traces), 1b (using $GeCl_3^-$; 5%)	ea, ir, mw	35, 113
$Sn[Fe(CO)_4]_4$	1a (<2%), c (2%) & f, 2a	ea, ir, mw (XD ref. 114)	35, 41, 42
$Pb[Fe(CO)_4]_4$	?	ir	35
$(vinyl)_2Sn[Fe(CO)_4]_2Sn[Fe(CO)_4]_2$	2b (<1%)	ea, ir, *m/s* XD	80
$Me_2Sn[Fe(CO)_4]_2Sn[Fe(CO)_4]_2SnMe_2$	2a (<4%)	ea, ir, mw, ^1H nmr XD (ME ref. 75)	115
$R_2Sn[Fe(CO)_4]_2Sn[Fe(CO)_4]_2SnR_2$ R = Et, Bu	1b (<6%)	ir (ea and mw for R = Bu)	35
$Me_2Pb[Fe(CO)_4]_2Pb[Fe(CO)_4]_2$	?	ir	35
$[C_5H_5Fe(CO)_2Sn]_2[Fe(CO)_3]_3$	[c]	ea, ^1H nmr, XD	94
$Sn_2Fe_5(CO)_{20}$	2a (using $SnCl_6^{2-}$)	ea, mw	116
$[PbFe_3(CO)_{12}]_n$	2b	ea	116

[a] See footnote (a) of Table 1. Where complexes were isolated as minor by-products, the yields are noted in parentheses. [b] Major products from the pyrolyses of the $(Me_3Ge)_2M(CO)_4$ complexes. [c] Produced from pyrolysis of $[(C_5H_5)_2SnFe(CO)_4]_2$.

(b) Complexes with four or more iron metals. The majority of higher complexes have been isolated in low yields, as noted in Table 4, e.g. [115]

$$MeSnCl_3 + Na_2Fe(CO)_4 \xrightarrow[0^\circ C,\ 0.5\,h;\ reflux\ 4\,h]{THF} \text{deep red mixture}$$

(i) Filtration and removal of solvent.
(ii) Extraction with benzene, removal of benzene; extraction with petroleum ether.

(iii) A series of chromatography steps (on alumina) separated yellow $[Me_2SnFe(CO)_4]_2$ (yield not determined) from red $Me_4Sn_3[Fe(CO)_4]_4$ (3.9% yield after recrystallization from benzene).

As mentioned earlier (section iv)), $[(C_5H_5)_2SnFe(CO)_4]_2$ thermally rearranges to $[C_5H_5Fe(CO)_2Sn]_2[Fe(CO)_3]_3$ in 33% yield [94]. The complexes $Sn_2Fe_5(CO)_{20}$ and $PbFe_3(CO)_{12}$ (the molecular weight was not established for the latter) were isolated from the reactions of $(NH_4)_2SnCl_6$ and $Pb(CH_3COO)_n$, $n = 2$ or 4, with the iron anion obtained from the reaction of KOH with $Fe(CO)_5$ in methanol [116].

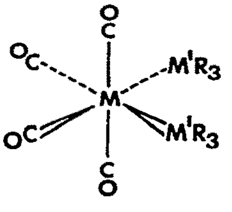
(vi) Other derivatives

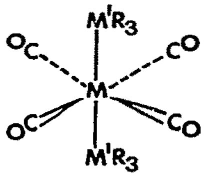
Brief mention ought to be made in this review of examples which include other transition metals in their structures; $(OC)_5M^{\star}Ru(CO)_4M'Me_3$; $M^{\star}$ = Mn, M' = Si [45]; $M^{\star}$ = Re, M' = Si [62] and Ge [47]; $[(OC)_5M^{\star}GePh_2]_2Fe(CO)_4$, $M^{\star}$ = Mn, Re [117]; $[(OC)_5ReSnBu_2]_2Os(CO)_4$ [54], $(OC)_7Co_2(GeCl_2)_2Fe(CO)_4$ [118] and $(OC)_7Co_2[SiClMn(CO)_5]_2Fe(CO)_4$ [119]. The incentive in the more complex transition metal area has been the hope of eventually being able to synthesize linear polymers having covalently bonded metal atom backbones. Other derivatives worth mentioning at this point include $Me_3GeRu(CO)_4AuPPh_3$ [47], $Hg[M(CO)_4SiMe_3]_2$, M = Fe [19] and Ru [47], and the polymer derivatives Ⓟ—(C_6H_4)—$SnBu_2(H)Os(CO)_4$ and Ⓟ—(C_6H_4)—$SnBu_2Os(CO)_4Bu_2SnCl$ [55].

C. X-RAY CRYSTAL STRUCTURES

(i) Mononuclear derivatives

X-ray structural analyses have been performed on both *cis* and *trans* examples with one iron triad metal, and key data are included in Table 5. The studies with *trans* $(Cl_3Si)_2Fe(CO)_4$ [25] and the hydrido derivative *cis*$Ph_3Si(H)Fe(CO)_4$ [61] have only been referred to briefly.

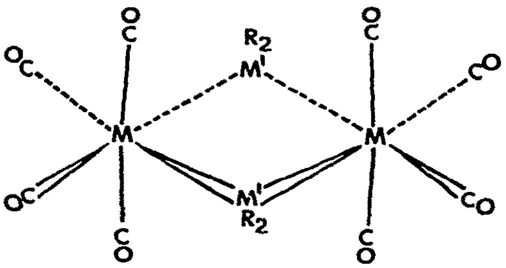




The *cis* and *trans* isomers of $(Cl_3Ge)_2Ru(CO)_4$ have structures close to regular octahedral geometry, but in both *cis*$(Ph_3Sn)_2Fe(CO)_4$ and to a greater extent in *cis*$(Me_3Si)_2Fe(CO)_4$ there is distortion towards bicapped tetrahedral geometry. Thus $C_{ax}FeC_{ax}$ for *cis*$(R_3M')_2Fe(CO)_4$ is 141.2 (1)° when R_3M' = Me_3Si [21] and 159.6 (4)° when R_3M' = Ph_3Sn [37] whereas the values determined for *cis*$(Cl_3Ge)_2Ru(CO)_4$ were 173 (1) and 174 (2)° [48]. A relationship between distortion from regular octahedral geometry and the ease of carbonyl scrambling (see section (ii), Part D) has been suggested [37].

(ii) Dinuclear derivatives

Four complexes of the type $[R_2M'Fe(CO)_4]_2$ have been studied by x-ray diffraction. A preliminary report has appeared for $[Et_2GeFe(CO)_4]_2$ [71], for $[Me_2SnFe(CO)_4]_2$ the reliability of data is low due to severe crystal disorder problems [76], and the complex $[Cl_2SiFe(CO)_4]_2$ has so far only been referred to briefly [68]. Thus, the recent report of Harrison et al. [88] for $[(C_5H_5)_2SnFe(CO)_4]_2$ is the first complete and uncomplicated study to appear for this type of complex. Data from the various studies show that in the solid state the molecules possess near planar $M_2'Fe_2$ rings which are lozenge in shape. The axial CO groups are bent away from the ring and there is a concomitant opening of the $C_{eq}FeC_{eq}$ angles from 90° (see values listed in Table 5). The study of $[(C_5H_5)_2SnFe(CO)_4]_2$ showed that the mode of attachment of the tin atoms to cyclopentadienyl groups was monohapto, characteristic of a Sn(IV) complex [88].



Studies of the two complexes $(Ph_2GeFe)_2(CO)_7$ [96] and $(Me_2Ge)_3Fe_2(CO)_6$ [100] establish that these are structurally related to $Fe_2(CO)_9$ with bridging carbon monoxide replaced by two and three bridging R_2Ge units respectively. The FeGeFe angles are very small in both derivatives (see Table 5) with iron—iron bonds envisaged to complete 18 electron configurations at iron. (The Fe—Fe distances of 2.67 and 2.75 Å for the phenyl and methyl derivatives are, however, far greater than the 2.52 Å found in $Fe_2(CO)_9$ [120].) The apparent strain in these acute FeGeFe angles is not manifest in the bonding of the R_2Ge groups themselves, i.e. near tetrahedral values were found for the CGeC angles. This observation for related compounds with bridging group IV groups has prompted the suggestion that the major electron density in these bridging group IV—metal bonds does not lie along the lines connecting the metal

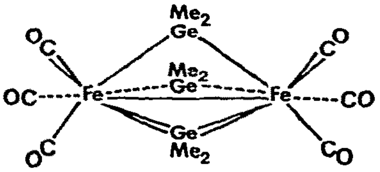


TABLE 5

Selected intramolecular bond-lengths (Å) and angles (°)

Complex	M′M	MM′M	M′MM′
cis$(Me_3Si)_2Fe(CO)_4$ [a]	2.456	—	111.8
cis$(Ph_3Sn)_2Fe)CO)_4$	2.666	—	95.94
cis$(Cl_3Ge)_2Ru(CO)_4$ [b]	2.466	—	91.5
	2.488		90.5
trans$(Cl_3Ge)_2Ru(CO)_4$	2.481	—	ca. 180
trans$(Ph_3Sn)_2Os(CO)_4$	2.712	—	ca. 180
	2.711		
$[Et_2GeFe(CO)_4]_2$	2.49	104.5	75.5
$[Me_2SnFe(CO)_4]_2$ [b]	2.647	102.6	77.4
$[(C_5H_5)_2SnFe(CO)_4]_2$	2.670	102.04	77.96
	2.651		
$(Ph_2GeFe)_2(CO)_7$	2.402—2.440	66.7	98.3
		66.8	96.9
$(Me_2Ge)_3Fe_2(CO)_6$	2.398	70.0	90.3
$[Me_3SiRu(CO)_3Me_2Si]_2$	2.507 ($RuSi_t$)		105.4 (Si_bRuSi_b)
	2.491 (*trans* to Si_t)		162.6 (to Si_t)
	2.391		
$[Me_3SnRu(CO)_3Me_2Sn]_2$	2.686 ($RuSn_t$)	71.50	108.50 (Sn_bRuSn_b)
	2.694 (*trans* to Sn_t)		165.69 (to Sn_t)
	2.638		
$[Me_3SnRu(CO)_4]_2$	2.691	{Ru′RuSn = 176.8°, C_{ax}RuRu′	
$Cl_6SnRu_2(CO)_5$	2.565	{$RuCl_bRu$ = 80.4—81.2}	
$(Ph_2Ge)_2OFe_2(CO)_8$	2.475	{GeO = 1.78}	
$[Me_2GeRu(CO)_3]_3$	2.482—2.500	71.9	168.1
$Sn[Fe(CO)_4]_4$	2.53—2.55	68.9 and ca. 133	
$Me_2Sn[Fe(CO)_4]_2Sn$-$[Fe(CO)_4]_2SnMe_2$	2.731—2.766	98.1 [c]	104.4
	($FeSn_{central}$)	99.5 [c]	106.0
	2.606—2.640	113.8—115.8	
	($FeSn_{outer}$)	($FeSn_{outer}Fe'$)	
$[C_5H_5Fe(CO)_2Sn]_2[Fe(CO)_3]_3$	2.537 ($SnFe_{eq}$)	64.5 ($Fe_{eq}SnFe_{eq,average}$)	
	2.471 ($SnFe_t$)	140.5 ($Fe_{eq}SnFe_{t,average}$)	

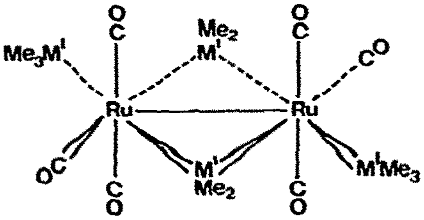
[a] Fe—Si bond lengths for two other silicon derivatives have been reported: 2.326 Å for *trans*$(Cl_3Si)_2Fe(CO)_4$ [25] and 2.415 Å for *cis* $Ph_3Si(H)Fe(CO)_4$ [61]. [b] Two independent molecules were contained in the asymmetric unit cell. [c] $FeSn_{central}Fe'$.

nuclei [121]. A bonding scheme was then proposed [122] with bridging R_2M' groups considered as bridging carbenoid ligands, and in which four-centre, two electron bonding orbitals completed the $M_2'M_2$ sections.

The two complexes $[Me_3M'Ru(CO)_3Me_2M']_2$, M′ = Si [104] and Sn [105] consist of planar $Ru_2(M'Me_2)_2$ units. The ruthenium—ruthenium bond, proposed to complete the electron counting, was found to decrease from 3.12 Å to 2.96 Å as the bridging tin atoms were replaced by the smaller silicon atoms. In both cases the two mutually *trans* RuM′ bonds (involving terminal and

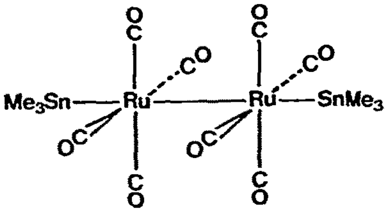
$C_{ax}MC_{ax}$	$C_{eq}MC_{eq}$	CM′C	MM	Refs.
141.2	89.5			21
159.6	92.0			37
173	95			48
174				
(CRuGe = 89.8—90.0)				48
				54
				71
165.4	119	109	4.131	76
163.6	99.4	101.0	ca. 4.14	88
		109.3	2.666	96
		105.3	2.750	100
ca. 172		105.5 (Si_b)	2.958	104
168.6		109 (Sn_b)	3.116	105
= 89.6—89.9°}			2.943	13
			3.157	107
			2.876	109
176 (bent inwards)		96	2.926	112
169.3—176.6	106.3—107.1		2.87 (4.61—4.69 for Fe···Fe)	114
158—164	91—96			115
			2.792	94

bridging M′ atoms) are of about equal lengths. However, the third bond

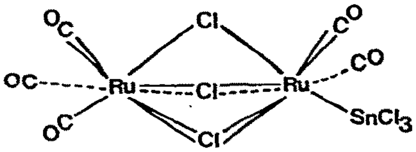


between ruthenium and M′ which is *trans* to a carbonyl is significantly shorter in both cases, and this has suggested that both R_2M' and R_3M' (M' = Si, Sn) ligands have a greater *trans* influence than CO [104].

Crystals of the silicon and germanium derivatives $[Me_3M'Ru(CO)_4]_2$ proved unsuitable for x-ray crystallographic studies, but a study with the tin analogue established the structure in which the carbonyl groups on adjacent ruthenium atoms are eclipsed. The Ru—Ru bond length of 2.943 Å is long compared with the 2.85 Å found for $Ru_3(CO)_{12}$ [123], whereas the Sn—Ru bond lengths of 2.691 Å were considered rather short.



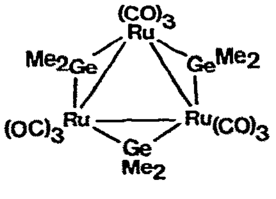
The study with $Cl_6SnRu_2(CO)_5$ established a triply chlorine-bridged structure [107]. The Sn—Ru distance of 2.565 Å is shorter than that found in $[Me_3SnRu(CO)_3Me_2Sn]_2$ (see Table 5) and was rationalized in terms of a greater π acceptor character of the $SnCl_3$ ligand [107].



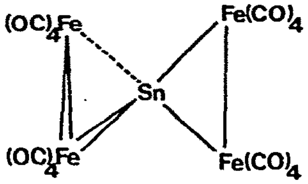
The structure of the oxide derivative $O[GePh_2Fe(CO)_4]_2$ has been determined as a five-membered OGeFeFeGe ring containing a digermyl—oxide linkage [109].

(iii) Higher derivatives

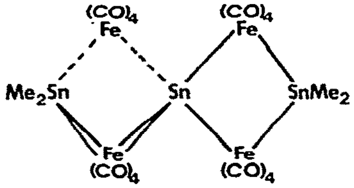
The complex $[Me_2GeRu(CO)_3]_3$ contains an equilateral triangle of ruthenium atoms with three symmetrically disposed and coplanar Me_2Ge bridging groups. The Ru—Ru distances of 2.93 Å are only 0.08 Å longer than in $Ru_3(CO)_{12}$ [123] where bridging groups are absent. The mean bridging angle at the Ge atoms is 71.9°, and this prompted the suggestion that here also maximum overlap to complete the framework bonding was not along the lines joining the metal atoms [112] (see discussion in section (ii)).



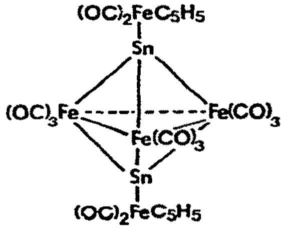
For the complex $Sn[Fe(CO)_4]_4$ [114], x-ray analysis showed that the overall symmetry was close to D_{2d}, so that there was tetragonal distortion at tin to bring the iron atoms closer together in pairs. A model with a tetrahedral tin atom and trigonal bipyramidal geometry at the iron atoms would make all O· · · O intramolecular contacts about 3 Å, and hence steric factors alone are not thought to produce the distortion at tin in $Sn[Fe(CO)_4]_4$. An electronic rationalization involving interaction between the iron atoms through the tin 5*d* orbitals was then proposed [114].



The complex $Me_2Sn[Fe(CO)_4]_2Sn[Fe(CO)_4]_2SnMe_2$ [115] also possesses a spiro structure with idealized D_{2d} symmetry. The three tin atoms are almost linear. The observed deviations from a model in which each half of the framework possessed D_{2h} symmetry, were rationalized as resulting from a balance between the maintenance of regular tetrahedral and octahedral angles and normal bond lengths, and a tendency for non-bonded atoms to achieve normal Van der Waals contacts [115].



Because the cyclopentadienyl groups in $[C_5H_5Fe(CO)_2Sn]_2[Fe(CO)_3]_3$ are not bonded to atoms involved in the cluster formation, the complex is included in this review. This is the first case where a *closo* arrangement of iron and group IV metal atoms has been established [94]. The iron—iron bonds (2.792 Å) are considerably longer than the two unbridged bonds in $Fe_3(CO)_{12}$ (2.677, 2.683 Å) [124].



D. NMR STUDIES

(i) ^1H nmr spectroscopy

^1H nmr data have been widely reported for alkyl- and hydride-group IV derivatives. Table 6 includes data for a series of germanium—ruthenium com-

TABLE 6

Selected nmr data

(i) ^1H nmr

Complex	τCH_3	$\tau M'H_x$	Solvent	Refs.
$(Me_3Ge)_2Ru(CO)_4$	9.46		C_6H_6	47
$[Me_3GeRu(CO)_4]_2$	9.28			
$[Me_3GeRu(CO)_3Me_2Ge]_2$	9.35 [a], 8.85 [a]			
$(Me_2Ge)_3Ru_2(CO)_6$	8.71			
$[Me_2GeRu(CO)_3]_3$	8.76			
$(MeGeH_2)_2Fe(CO)_4$	9.27	6.22 $\{^3J = 3.8$ Hz$\}$	CS_2	30
$[MeGeHFe(CO)_4]_2$ [b]	8.84, 8.81	6.33, 6.23 $\{^3J = 3.4$ Hz$\}$	12% C_6H_6 in CS_2	30

(ii) ^{13}C nmr

Complex	$\delta^{13}CO$	$\delta^{13}CH_x$	Temp. (K)	Solvent	Refs.
cis$(Cl_3Si)_2Fe(CO)_4$	199.71 197.88		308	CD_2Cl_2	
trans$(Cl_3Si)_2Fe(CO)_4$	199.49		308	CD_2Cl_2	
cis$(Me_2SiCl)_2Fe(CO)_4$	204.53	12.30	303	Toluene-d_8	20
	205.70 203.27	12.09	253	Toluene-d_8	
cis$(Me_3Pb)_2Ru(CO)_4$ [c]	196.96 (axial) 192.21 (equatorial)	−0.86	303	Toluene-d_8	
$(Bu^n_2SnFe)_2(CO)_7$ [d]	252.1 (bridging) 206.0 (2C) (terminal) 208.9 (4C) (terminal)	12.1, 22.3, 23.8 26.3, 28.0	229	CH_2Cl_2	83
	ca. 214	12.1, ca. 23.1 26.3, 28.3	279	CH_2Cl_2	83

[a] These resonances were in the ratio 3 : 2 respectively. [b] The two sets of methyl and germyl resonances were consistent with about equal proportions of the two isomers. [c] $^{1 and 3}J(^{207}Pb—^{13}CH_3)$ = 108 and 12 Hz respectively; $^2J(^{207}Pb—^{13}CO_{ax})$ = 94 Hz; $^2J(^{207}Pb_{trans}—^{13}CO_{eq})$ = 252 Hz; $^2J(^{207}Pb_{cis}—CO_{eq})$ = 66 Hz. [d] $^2J(^{117,119}Sn—^{13}CO_{terminal})$ = 66.3 (2C peak) and 56.6, 29.2 Hz (4C peak); $^2J(^{117,119}Sn—CO_{bridge})$ = 61.6 Hz.

plexes which indicate the clear difference in resonance positions for terminal and bridging Me_xM' groups. The data for two germyl—iron compounds further indicate a reduction in the ^3J(HCGeH) value as germanium adopts a bridging position. Mixtures of *cis* and *trans* isomers of $(R_3M')_2M(CO)_4$ complexes may in some cases be distinguished by ^{1}H nmr, e.g. $(Me_3Ge)_2Os(CO)_4$ exhibits two resonances at 9.37 and 9.27 τ [47]. However, the resonances cannot generally be assigned to the individual isomers without other evidence.

In two instances variable temperature ^{1}H nmr has been used to study stereochemical non-rigidity in iron systems. The complex $(Me_2SiFe)_2(CO)_7$ exhibited two methyl resonances at 8.77 and 8.97 τ at $-80°$C [95]. These resonances broadened on warming, coalesced at $-46.5°$C and produced one sharp resonance at 8.89 τ at room temperature. This averaging of the *syn* and *anti* methyl resonances was attributed [95] to intramolecular rearrangement involving the opening of at least one bridging ligand, for which $\Delta G^{\neq}$ has been calculated at 11.5 ± 0.5 kcal mol^{-1} [83]. Another more recent study has been concerned with an analogous tin system, $(MeSnPhFe)_2(CO)_7$, for which two isomers are found. Variations in ^{1}H nmr spectra at lower temperatures were consistent with bridge deformation (or 'flapping') of the less symmetric isomer, so that only one methyl resonance was observed for this isomer at 272 K. $\Delta G^{\neq}_{298}$ was calculated at 11.8 ± 0.6 kcal mol^{-1} for this process. With further warming (up to 406 K) the resonance then coalesced with the single methyl resonance attributed to the symmetrically-substituted isomer, and this was rationalized in terms of a bridge-scission process for which $\Delta G^{\neq}_{298}$ was calculated at 19.2 ± 0.9 kcal mol^{-1}. A stannylene intermediate of the type $PhMeSn:\rightarrow Fe_2(CO)_7$-(MeSnPh) was proposed for this latter process [83]. An alternative view would be to consider the bonding in this cluster with the MeSnPh group as a bridging carbenoid-type ligand (see Part C, section (ii)), in which case 180° rotation of the bridging tin—dialkyl ligand may possibly disrupt only more minor overlaps in the M'_2M_2 bonding (compare delta bond breaking in $Re_2Cl_8^{2-}$ [125]).

Brief mention should be made in this section of the value of ^{1}H nmr in studies of reactions of compounds containing M'—H linkages [56], and in the identification of hydrides such as $R_3M'(H)M(CO)_4$ (which are thermally unstable when M is iron or ruthenium, and thus may be studied conveniently at lower temperatures in the nmr). An example of the second type of hydride is $H_3Ge(H)Fe(CO)_4$ [29], for which two resonances were found at 6.65 and 19.87 τ in the ratio 3 : 1.

(ii) ^{13}C nmr spectroscopy

This technique is now becoming more widely used with the introduction of instruments operating on the Fourier principle. Early problems with slow relaxation of the ^{13}C nucleus in the metal carbonyl environment have been solved by either using slow pulsing rates, or through the addition of small quantities of paramagnetic ions such as $Cr(acac)_3$ to the sample to accelerate relaxation.

Table 6 includes ^{13}C nmr data for several $(R_3M')_2M(CO)_4$ complexes and for $(Bu^n_2SnFe)_2(CO)_7$. The ^{13}C resonance for terminally bonded carbonyl groups is shifted about 200 ppm to higher frequency from TMS. There is an increase in carbonyl carbon shielding as the atomic weight of the transition metal is increased. The data for the dinuclear complex indicate that bridging carbonyl resonances are to be expected about a further 50 ppm to higher frequency.

For the $(R_3M')_2M(CO)_4$ complexes, ^{13}C nmr will identify *cis* or *trans* isomers, or mixtures of the two which may or may not be in rapid equilibrium at a given temperature. As indicated by the coupling data given in footnote (c) of Table 6, assignment of axial and equatorial ^{13}CO resonances of the cisoid complexes is firm for tin and lead derivatives from inspection of $^{117,119}Sn$ or ^{207}Pb satellites. For the osmium and ruthenium complexes the $^{13}CO_{eq}$ is 100—200 Hz to lower frequency and in one case, for *cis*$(Cl_3Si)_2Ru(CO)_4$, stereospecific ^{13}CO exchange of the two equatorial groups has further confirmed this assignment [46]. In the iron complexes there are smaller separations between the ^{13}CO resonances and thus assignments cannot be made without spin satellite evidence.

Table 6 also includes data for two complexes which exhibit temperature dependent ^{13}C nmr spectra. For a variety of *cis*$(R_3M')_2M(CO)_4$ complexes the two ^{13}CO resonances were found to coalesce at higher temperatures consistent with a scrambling process which becomes rapid relative to the nmr time scale at higher temperatures. The process is intramolecular since coupling between $^{13}CO—^{57}Fe$ and $^{13}CO—M—M'$ ($M' = {}^{117,119}Sn$, ^{207}Pb) is preserved for the various compounds, in agreement with the relatively small $\Delta S^{\neq}$ values determined (e.g. 2.3 ± 2.6 e.u. for *cis*$(Me_3Si)_2Fe(CO)_4$). There is evidence to suggest that the *trans* derivatives may be involved as intermediates in these processes since (i) the chelate complex $(Me_2SiCH_2CH_2SiMe_2)Fe(CO)_4$ does not exhibit temperature dependent spectra whereas $(Me_3Si)_2Fe(CO)_4$ does [20], and (ii) the three ^{13}CO resonances observed for a mixture of *cis* and *trans*$(Me_3Si)_2Os(CO)_4$ appeared to coalesce to a single resonance at the same rate [20] with analysis producing about the same activation parameters as those derived from a ^1H nmr study of the *cis—trans* isomerization [53]. Free energies of activation for the averaging process were 6—8 kcal mol^{-1} higher for ruthenium and osmium derivatives, e.g. the $\Delta G^{\neq}$ values (kcal mol^{-1}) for the following compounds were: $(Me_3Si)_2Fe(CO)_4$ 10.7, $(Me_3Si)_2Os(CO)_4$ 16.8, $(Me_3Sn)_2Fe(CO)_4$ 10.2, $(Me_3Sn)_2Ru(CO)_4$ 17.4. The values calculated for $\Delta G^{\neq}$ also increase through the series $(Me_xSiCl_{3-x})_2M(CO)_4$, M = Ru or Fe; e.g. for M = Fe values of 13.2, 16.5 and 17.5 were found for the derivatives when $x = 2$, 1 and 0 respectively. As noted in Part C, Section (i), a relationship between distortion from regular octahedral geometry in $(R_3M')_2M(CO)_4$ complexes, and the barriers to this type of stereochemical non-rigidity has been suggested [37].

In one report [59] reference has been made to fluxionality in the $R_3Si(H)Fe(CO)_4$ complexes.

As noted in Table 6 $(Bu^n_2SnFe)_2(CO)_7$ also exhibits temperature dependent

^{13}C nmr spectra. Analyses of the changes in the α and β ^{13}C resonances for the butyl groups, and of the carbonyl resonances produced about the same $\Delta G^{\neq}$ values (12.5 ± 0.5 and 12.4 ± 0.3 kcal mol^{-1} respectively). It is worth noting that the three ^{13}CO resonances observed at lower temperatures did not collapse symmetrically. The bridging CO resonance and the other resonance of intensity 2 (see Table 6) were found to broaden more rapidly, indicating a non-random process which was proposed as bridge-opening with concurrent or subsequent Fe_2Sn_2 ring flattening, followed by the entering of an 'intensity 2' type CO ligand into the bridging position and a $2\pi/6$ rotation of the uninvolved $Fe(CO)_3$ group.

(iii) Nmr studies with other nuclei

^{19}F nmr chemical shifts have been measured for the complexes $(F_3Si)_2M(CO)_4$, M = Ru and Os [34]. The resonances of the *cis* and *trans* isomers when M = Os were measured 82.87 and 82.30 ppm upfield from $CFCl_3$, and for the *cis* ruthenium complex the resonance was found at 82.30 ppm. Thus there are very large shifts in these complexes from the values of the silyl-fluorides (cf. SiF_4 and Si_2F_6 at 171.4 and 126.0 ppm respectively [125]).

^{19}F nmr data have also been reported recently for two fluorine-substituted bis(β-ketoenolate)tin derivatives, e.g. for $[(tbd)_2SnFe(CO)_4]_2$ (tbd = 4-trifluoromethylbutane-2,4-dionate) the ^{19}F nmr shift was measured at 77.45 ppm [89].

A number of phosphine-substituted derivatives of the complexes discussed in this review have been reported, and thus nmr studies in the area will no doubt be extended to work with the ^{31}P nucleus.

E. VIBRATIONAL DATA

Infra-red data have been widely reported for the carbonyl stretching region of group IV—iron triad derivatives. Data from the lower and far regions of infra-red spectra and Raman data are, however, less common. Discussion of vibrational data for the complexes is conveniently divided into two main parts, data for complexes with one iron triad metal (sections (i) and (ii)) and data for polynuclear derivatives (section (iii)).

(i) $(R_3M')_2M(CO)_4$ derivatives

The two characteristic regions for $(R_3M')_2M(CO)_4$ complexes are the carbonyl stretching and metal—metal stretching regions. The irreducible representations for these vibrations are listed below for three configurations.

Configuration	$\Gamma_{\nu CO}$	$\Gamma_{\nu M'M}$
cis C_{2v}*	$2a_1 + b_1 + b_2$	$a_1 + b_1$
trans C_{2h}	$2a_g + a_u + b_u$	$a_g + b_u$
trans D_{4h}	$a_{1g} + b_{1g} + e_u$	$a_{1g} + a_{2u}$

* The more common convention [17, 22, 127 and references therein] for the labelling of axes in this type of molecule has the *y*-axis as the axis containing the Fe atom and the axial CO groups.

For a C_{2v} molecule the a_1, b_1 and b_2 modes are all active in both the Raman and infra-red. In the Raman the a_1 modes are polarized. In the C_{2h} and D_{4h} groups the u modes are ir active and the g modes are Raman active (with the a_g and a_{1g} modes polarized).

(a) The carbonyl stretching region. Before discussing the general features a brief note should be made of factors which may cause complications. (i) The effective symmetry of the $(R_3M')_2M(CO)_4$ molecule may be lowered by unsymmetrical ligands on the group IV atoms. For example, extra carbonyl bands have been reported in the infra-red spectra of the complexes $(Cl_nMe_{3-n}Si)_2M(CO)_4$, $n = 1, 2$ [20], and in several *trans* derivatives (see below). (ii) A mixture of *cis* and *trans* isomers will not be reliably detected by carbonyl region infra-red spectroscopy alone, because the single e_u mode of the *trans* isomer is often coincident with one of the four infra-red active modes of the *cis* isomer (see Table 7). Another problem in the carbonyl region is that the Raman modes are relatively weak.

Table 7 includes data from the νCO region for several *cis* and *trans* $(R_3M')_2M(CO)_4$ complexes. The *cis* complexes exhibit three or four carbonyl absorptions in the infra-red, with one clearly separated to higher energy. This last absorption is firmly assigned to the νCO_{axial} (a_1) mode [127—129] (see polarization data in Table 7). 'Force constant' calculations for several *cis*-$(R_3M')_2M(CO)_4$ complexes (see below) have indicated that $k_{axial} > k_{equatorial}$ in these complexes, and thus the mode at lowest energy is assigned $\nu CO_{equatorial}$ (b_1). The order of the two remaining modes νCO_{axial} (b_2) and $\nu CO_{equatorial}$ (a_1) is sensitive to compound type and even to solvent [127, and references therein]. It is generally thought that the strongest band in the infra-red νCO region will be due to the νCO (b_2) vibration [22,127]. However, inconsistencies can arise. Thus, for example, in both of the complexes *cis*$(Cl_3Si)_2Fe(CO)_4$ [22] and *cis*$(Br_3Sn)_2Fe(CO)_4$ [33] the second to lowest in energy of the four infra-red νCO absorptions were clearly the most intense and thus attributed to the b_2 vibrations, whereas another report for *cis*$(Cl_3Si)_2Ru(CO)_4$ shows clearly that the lowest energy fundamental in the infra-red carbonyl region is in fact the strongest although attributable to the b_1 (equatorial) vibration on the basis of force constant analysis [46].

For the *trans*$(R_3M')_2M(CO)_4$ derivatives only one strong (e_u) absorption is found in the infra-red spectrum. Often one or two weak bands are observed at higher frequencies and these are consistent with the a_{1g} and b_{1g} fundamentals gaining intensity because the three-fold symmetry of the R_3M' groups reduces the true molecular symmetry. This situation is also found for other *trans* $L_2M(CO)_4$ complexes, e.g. *trans*-$(Ph_3P)_2Cr(CO)_4$ [129]. It is worth noting that for *trans*$(Ph_3Sn)_2Os(CO)_4$ the weak ir absorption at 2110 cm^{-1} is matched by one of the Raman modes (see Table 7).

In a vibration where several CO groups are involved, $\nu^{13}CO$ satellite bands may be observed arising from in-phase or out-of-phase coupling [127]. Well-defined satellite bands are expected at about 35—40 cm^{-1} lower than an out-of-

TABLE 7

Selected vibrational data (cm^{-1})[a]

		νCO frequencies				νMM′ frequencies	Refs.
cis$(H_3Ge)_2Fe(CO)_4$[b]	ir	2091.5s (2084.5w, sh)	2033m, br, sh	2024.3vs	2008.5ws (1987.6w, 1974.2w)	229vw[c] 216vw[c]	56
	R	2099s		2042vs	2023s, sh	229vs(p)[d] 216m(dp)[d]	29
cis$(Cl_3Ge)_2Fe(CO)_4$	ir	2135m	2095m	2089vs	2082s		33
trans$(Cl_3Ge)_2Fe(CO)_4$	ir			2088vs	(2052vw)	{R 205 vs}	33,34
cis$(Cl_3Ge)_2Ru(CO)_4$	ir	2161		2103			34
trans$(Cl_3Ge)_2Ru(CO)_4$	ir			[e]		248vw {R 220vs[f]}	34
trans$(Ph_3Sn)_2Os(CO)_4$	ir	2017s[g]		2017s[g]	2110w[g]		54
	R		2055		2111	112	54
$[Ph_2SnOs(CO)_4]_2$	ir		2080[h]	2025[h]	2010[h]		54
	R	2106		2031	2013	77 145	

[a] Ir data were for C_6H_{12} solutions unless otherwise noted. ν^{13}CO modes are listed in parentheses. Raman data were recorded for solid samples unless noted. [b] νGeH was observed at 2072—2042 (w, br). [c] Gaseous sampling. [d] C_6H_{12} solution. [e] One νCO band was observed at ca. 2110 cm^{-1}. [f] Polarized in solution. [g] CH_2Cl_2 solution. [h] Hexane solution.

phase mode. There is also expected to be a much weaker satellite band a few wavenumbers to the low frequency side of the in-phase vibrations (seen in the infra-red for the in-phase vibration of the two axial groups in the *cis* complexes). In Table 7 the ν^{13}CO vibrations are listed in parentheses.

'Approximate' carbonyl force constant analyses have been performed for the cisoid complexes $(Et_2SnCl)_2Fe(CO)_4$, $(Bu_2SnCl)_2Fe(CO)_4$, $(Me_3Sn)_2Fe(CO)_4$ [130,131]; $(Cl_3Si)_2Fe(CO)_4$ [132]; and for both isomers of the complexes $(Cl_3Si)_2Ru(CO)_4$ [34,46] and $(Cl_3Ge)_2Ru(CO)_4$ [34,133]. These calculations have used the Cotton—Kraihanzel field or modifications thereof (see discussion in ref. 127). None of the studies has used corrections for anharmonicity. Although the neglect of all force constants in metal carbonyl complexes other than the primary CO stretching force constants and the CO,CO interaction constants has led to some concern (particularly that the 'approximate' force constants may not be interpreted with respect to the bonding [134]), the approximate treatment has proven useful for the assignment of vibrational frequencies and thus data from the vibrational analyses will be discussed briefly here.

In the iron compounds the primary axial force constant varies from 17.76 to 16.42 mdyn Å^{-1} for the complexes *cis*$(Cl_3Si)_2Fe(CO)_4$ and *cis*$(Me_3Sn)_2Fe(CO)_4$ respectively and is from 0.45 to 0.76 mdyn Å^{-1} larger than the respective equatorial values. In the ruthenium complexes the values of k_{axial} were higher (18.25 and 17.96 mdyn Å^{-1} for the germanium and silicon derivatives) and were separated by only 0.18 and 0.05 mdyn Å^{-1} from the $k_{\text{equatorial}}$ values. Thus for the *cis*$(R_3M')_2M(CO)_4$ complexes there is the same ordering of k_{axial} and $k_{\text{equatorial}}$ as found for $X_2Fe(CO)_4$ [135] and $Fe(CO)_5$ [136]. The values of k_c and k_c' which have been found to reproduce the observed frequencies vary from 0.17 to 0.28 mdyn Å and are generally of about the same value, with k_t about 1.5 to 2 times these values (0.32—0.42 mdyn Å^{-1}). For the two *trans* isomers $k_{\text{equatorial}}$ was calculated at about the same values as the k_{axial} values for the *cis* complexes.

(b) The metal—metal stretching region. Factors which may complicate spectra from this region include: (i) The νM'M modes are rather weak in the infra-red (although of good intensity in the Raman with laser excitation), and thus rigorous flushing of the spectrometer is required to provide good quality spectra. (ii) With laser spectrometers very strong plasma lines can arise in the νM'M region (e.g. at 220 cm^{-1} when using a 488 nm exciting line), and care must be made to filter these out. (iii) Laser excitation may decompose coloured complexes. Use of longer wavelength exciting lines does alleviate this problem. (iv) Again for a mixture of isomers the mode due to the *trans* isomer may be obscured by one of the modes of the *cis* isomer, especially when the proportion of *trans* is low.

Table 7 includes Raman data from the metal—metal stretching region for both *cis* and *trans* $(R_3M')_2M(CO)_4$ complexes. Complementary far infra-red data are listed for examples of both isomers. For *cis*$(H_3Ge)_2Fe(CO)_4$ the Raman and infra-red νGeFe modes are coincident as expected (a_1 + b_1) although polarization data in the Raman demonstrate that the higher frequency mode is the a_1 fundamental which represents an unusual ordering of vibrations. A strong interaction between the germyl hydrogen atoms has been proposed to account for this ordering [137], which has also been observed for $(MeGeH_2)_2Fe(CO)_4$ [30]. For *cis*$(Me_3Ge)_2Fe(CO)_4$ the Raman data from the νGeFe region required careful examination; although a single mode was observed at 200 cm^{-1}, the contour of this band changed during polarization studies, consistent with the superimposition of the a_1 and b_1 modes [32].

A series of *trans*$(X_3M')_2M(CO)_4$ (X = halogen) complexes has been examined by far infra-red and Raman spectroscopy [34]. There is evidence here for mixing with the νM'X vibrations, but as shown in Table 7 for *trans*-$(Cl_3Ge)_2Ru(CO)_4$, two non-coincident modes are found in the two types of spectra. A strong and polarized (a_{1g}) mode is found in the Raman at 220 cm^{-1}, and a weak (a_{2u}) absorption is found in the infra-red at 248 cm^{-1}. Single νOsSn Raman modes have been reported elsewhere for the *trans* complexes $(R_3Sn)_2Os(CO)_4$ [54].

(c) Other regions. In relatively few instances have vibrational data from other regions of $(R_3M')_2M(CO)_4$ spectra been reported. For the iron carbonyl derivatives $(Me_xGeH_{3-x})_2Fe(CO)_4$, $x = 0$ [29] and 1—3 [30—32], a strong δFeCO (a_1) absorption is observed in the infra-red between about 600 and 640 cm^{-1} (weak in the Raman) and νFeC modes are observed at about 430—450 cm^{-1} (weak in the infra-red and stronger in the Raman, e.g. the a_1 mode is at 436 cm^{-1} for $(H_3Ge)_2Fe(CO)_4$ [29]). In other cases modes involving the group IV substituents may complicate this lower region, e.g. for *cis*$(Cl_3Si)_2Fe(CO)_4$ a total of twelve infra-red absorptions were found from 486 to 645 cm^{-1} [22]. For the hydride derivatives *cis*$(H_3M')_2M(CO)_4$ two characteristic absorptions are observed in the MH_3 deformation region of the infra-red spectra, e.g. for $(H_3Si)_2Fe(CO)_4$ these are at 924 (vs) and 898 (vs) cm^{-1} and these data were interpreted in terms of the *cis* isomer since for disilyl derivatives where the SiYSi angle is large (e.g. 144° for $(H_3Si)_2O$) only one δSiH_3 absorption is found in the infra-red spectrum [17].

(ii) Other derivatives with one iron triad metal

Complexes of the type *cis* $R_3M'(X)M(CO)_4$, X = H or halogen, also exhibit four νCO fundamentals in their infra-red spectra as expected for C_s isomers, e.g. (cm^{-1}) 2125s, 2088s, 2078vs and 2064s for $I_3Ge(I)Fe(CO)_4$ [33]; 2107s, 2050vs, 2044vvs, 2036vvs for $H_3Si(H)Fe(CO)_4$ [17]. The vibrations are assigned in an analogous manner to the *cis* $(R_3M')_2M(CO)_4$ complexes, e.g. the absorption at highest energy is attributed to νCO_{axial} (a'). For the hydride derivatives νMH is weak in the infra-red (expected to be strong in the Raman) although in the lower infra-red region a stronger characteristic δFeH band has been found for iron derivatives, e.g. at 728 and 719 cm^{-1} for $H_3M'(H)Fe(CO)_4$, M' = Ge [29] and Si [17]. Only in the case of halogen derivatives of ruthenium and osmium have *trans* configurations for the $R_3M'(X)M(CO)_4$ complexes been inferred. Again, this was from infra-red data in the νCO region e.g. $Me_3Ge(I)Os(CO)_4$ exhibits a single strong absorption at 2043 cm^{-1} (with a weak out-of-phase ν^{13}CO mode at 2011 cm^{-1}) [62].

Infra-red spectroscopy in the carbonyl stretching region has also proved very valuable in studies of the interaction of Lewis bases with molecules of the type $[R_2M'M(CO)_4]_2$, where species of the form base · $R_2M'M(CO)_4$ are postulated [41,70,85,87,89]. In some cases these adducts can be isolated, e.g. $Me_2GeFe(CO)_4 \cdot C_5H_5N$ [70], but with weaker bases the best evidence for such adducts comes from molecular weight and infra-red measurements. The base adducts are thought to contain trigonal bipyramidal iron, exhibiting spectra similar to ions of the type $R_3M'Fe(CO)_4^-$. As an example of the change in infra-red spectra with adduct formation, the complex $[Me_2GeFe(CO)_4]_2$ exhibits the following infrared absorptions in n-hexadecane 2053.0, 2000.4, 1987.0 cm^{-1}, [69]; whereas the dark-orange pyridine adduct has 2021s, 2040m, 1908vs cm^{-1}, [70].

(iii) Polynuclear derivatives

A more general approach will be made to vibrational studies of higher derivatives since data are less complete and tend to be less definitive. The $[R_2M'M(CO)_4]_2$ complexes will be treated separately since more vibrational work has been carried out with these molecules.

(a) $[R_2M'M(CO)_4]_2$ complexes. With the group IV substituents in optimized positions (and where both R substituents are the same) this type of molecule has D_{2h} overall symmetry for which $\Gamma\nu CO = 2a_g + b_{2g} + b_{3g} + 2b_{1u} + b_{2u} + b_{3u}$, with the four u modes infra-red active and the g modes Raman active. In two early reports [130,131] (see also ref. 89) it was assumed that there was no coupling between the $M(CO)_4$ units in these molecules and thus the three or four infra-red u absorptions were assigned to the four modes expected for the local C_{2v} $M(CO)_4$ groups. (Indeed the infra-red spectra of the νCO regions for the complexes *cis*$(R_3M')_2M(CO)_4$ and $[R_2M'M(CO)_4]_2$ are very similar; for instance compare the spectra shown in ref. 33 for *cis*$(Br_3Sn)_2Fe(CO)_4$ and $[I_2GeFe(CO)_4]_2$). However, this approximation is both unnecessary and incorrect, and the overall symmetry of these complexes must be considered (see e.g. refs. 69, 74, 127). More generally [127, 138 and references therein] it has been recognised that long-range CO···C'O' interactions are important in polynuclear derivatives.

The νCO modes observed for the $[R_2M'M(CO)_4]_2$ molecules are assigned to in- and out-of-phase combinations of the vibrations found for the *cis*$(R_3M')_2M(CO)_4$ complexes. Thus the highest energy infra-red absorption is attributed to νCO_{axial} (b_{2u}) and the lowest to $\nu CO_{equatorial}$ (b_{2u}) (assuming $k_{axial} > k_{equatorial}$), and the order of the two other infra-red vibrations is not certain although it is thought [69] that the b_{1u} mode will be the more intense. Similarly the symmetric in-phase νCO_{axial} vibration is the highest energy Raman mode (a_g) and the b_{1g} mode involving the four equatorial CO groups is expected to be at lowest energy. Thus, (as shown for $[Ph_2SnOs(CO)_4]_2$ in Table 7), the Raman and infra-red νCO frequencies in this type of molecule are non-coincident. In several cases [31,130] extra, weak infra-red absorptions have been found in the νCO region for more concentrated solutions, consistent with some deviation of the molecules from D_{2h} symmetry, resulting in intensity of the in-phase (g) modes. Such deviation could be due to unfavourable alignment of the bridging groups or to non-planar $M_2'M_2$ units (short range disorder was found in the x-ray study of $[Me_2SnFe(CO)_4]_2$ [76]).

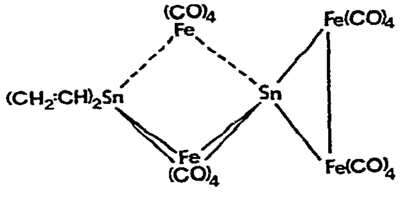
As for the $(R_3M')_2M(CO)_4$ complexes (section (i)) in relatively few cases have data from the lower energy regions of vibrational spectra been reported. The δFeCO and νFeC modes are found in the expected regions, e.g. $[Et_2GeFe(CO)_4]_2$ has δFeCO at 624vs, 615vs, 585w, 558m, 524m and νFeC at 476m, 435m in the infra-red spectrum of a n-hexadecane solution [22].

By analogy with the D_{2h} complex $[Me_2GeMn(CO)_4]_2$ [139], three Raman active metal—metal vibrations might be expected for the $[R_2M'M(CO)_4]_2$ complexes. Two modes were found for $[Ph_2SnOs(CO)_4]_2$ (see Table 7) attributable to symmetric and asymmetric ring deformations. Two extra modes were found, however, for $[Bu_2SnOs(CO)_4]_2$ in this lower region [54].

(b) Other complexes. Infra-red data from the carbonyl stretching region have been reported for most of the complexes listed in Tables 3 and 4. These data serve not only as a 'fingerprint', but in a general manner help also to decide the geometric configuration adopted at the iron triad metal. For example, a linear SiOsOsSi framework was deduced for $[Me_3SiOs(CO)_4]_2$ on the basis of three strong Raman modes (2121, 2043, 2024 cm^{-1}) and three non-coincident infra-red bands at 2052w, 2012s, 2003w,sh, cm^{-1}, consistent with overall D_{4h} or D_{2d} symmetry [51]. As another example, infra-red spectroscopy will identify isomers of $[Me_3M'M(CO)_3X]_2$ complexes; five absorptions were observed in the carbonyl stretching region, three of which have the pattern and intensities typical for structures with *mer*$M(CO)_3$ groups (this pattern is similar to that found for the structurally related $[Me_3M'M(CO)_3Me_2M']_2$ complexes [47,98]). The two remaining carbonyl absorptions were then attributed to isomers with *fac*$M(CO)_3$ groups [62].

As with other metal carbonyl compounds, the CO stretching vibration for a bridging carbonyl group is shifted about 150 cm^{-1} to lower energy from the highest $\nu CO_{terminal}$ absorptions providing a valuable criterion when trying to assign structures to certain polynuclear compounds. For example, the complex $(pbd)_2Sn[Fe(CO)_4]_2$ (pbd = 4-phenylbutane-2,4-dionate) exhibits νCO absorptions at 2030s, 1995s, 1925s, 1800m cm^{-1} [89], indicating a structure with bridging carbonyl groups. A structure was proposed with one terminal CO group of $Fe_2(CO)_9$ replaced with the $(pbd)_2Sn$: group [89] (although an equally probable structure would be with the $(pbd)_2Sn$ group in a bridging position replacing one μCO group of $Fe_2(CO)_9$, i.e. belonging to class (i) of Table 3). On the other hand, the complex $Ph_2Ge[Fe(CO)_4]_2$ does not exhibit an absorption in the bridging carbonyl region, and the seven terminal carbonyl absorptions were interpreted in terms of a structure with two $Fe(CO)_4$ groups bound by an iron—iron bond and bridged by the Ph_2Ge group [99].

Conclusions may in some cases be drawn from the pattern of νCO bands for higher molecular weight clusters when compared with the band patterns found for established species. For example, the structure for a new complex of the formula $(vinyl)_2Sn_2Fe_4(CO)_{16}$ was proposed as [80]



because the νCO infra-red spectrum appeared to be the gross superimposition of the νCO patterns for the established $Sn[Fe(CO)_4]_4$ [35] and $[vinyl)_2SnFe(CO)_4]_2$ [81] complexes.

F. MASS SPECTRAL DATA

As indicated in Tables 1—4, mass spectrometry has been widely used to determine the molecular weights of these types of derivatives especially of the more simple complexes. However, in relatively few cases have fragmentation data been reported. This may reflect in part the complexity of spectra for complexes which contain polyisotopic elements, e.g. ruthenium has seven naturally occurring isotopes, and germanium and tin have five and ten respectively. However, the patterns obtained in these mass spectra can provide valuable support for the assignments of fragment and parent molecular ions. Programmes to calculate envelope shapes for polyisotopic ions have been referred to in the literature [e.g. 140, 141]. A review volume has appeared which includes some discussion of the complexes under study in this article [142].

The common fragmentation routes followed by the complexes are; (i) CO loss (often metastable supported for stronger ions); (ii) R loss where the group IV substituent R = alkyl, halogen, H, etc. and (iii) M′—M scission (or M—M scission for polynuclear derivatives). Specific mention will now be made of the data which have been reported for these complexes in their respective structural types.

(i) Mononuclear derivatives

(a) $(R_3M')_2M(CO)_4$ *complexes.* Generally these complexes exhibit relatively weak molecular ions, with fragments arising from loss of CO or of a group IV substituent producing the highest strong envelope. For example, the first envelopes of strong intensity in the spectra of the *cis* derivatives $(H_3Ge)_2Fe(CO)_4$ [29] and $(MeGeH_2)_2Fe(CO)_4$ [30] were due to the ions $(P\text{—}CO\text{—}xH)^+$. The

highest (weak) envelopes carried 0.4 and 0.7% of the ion current respectively and in both cases these were due mainly to the ions $(P{-}H)^+$ (5 times the intensity of P^+ for the methyl compound). The bulk of the ion current in both these spectra was carried by Ge_2Fe-containing ions (57 and 64% respectively) and to a lesser extent by GeFe families (26 and 25%), with the base peaks due to the ions $Ge_2H_xFe^+$ (25.2%) and $C_2H_xGe_2Fe(CO)_3^+$ (16.8%) respectively. In both spectra the only rearrangement ions observed were very weak $HFe(CO)_n^+$ species. For the methyl derivative methyl loss is minor until most of the CO groups have been removed. In comparison, in the spectrum of *cis*$(Me_3Ge)_2Fe(CO)_4$, a substantial portion (15%) of the ion current is carried by the even-electron fragments $Me_5Ge_2Fe(CO)_n^+$ $n = 0{-}4$, with the parent molecular ion again weak (ca. 1.3%). (The fragmentation behaviour of most alkyl germanes themselves is dominated by the low abundance of odd-electron ions [143].) The ions $Me_2GeFe(CO)_n^+$, $n = 0{-}4$, form the strongest series in the mass spectrum of $(Me_3Ge)_2Fe(CO)_4$ (ca. 27%) and these are metastable supported to arise from the elimination of Me_4Ge. Overall, the proportions of Ge_2Fe- and GeFe-containing ions are about the same (32 and 37% respectively) [32].

For the tin—ruthenium analogue, *cis*$(Me_3Sn)_2Ru(CO)_4$, the main ions observed were $[P{-}Me{-}n(CO)]^+$, $n = 0{-}4$; Me_nSn^+, $n = 0{-}3$; and Sn_2Ru^+ [40] and the parent ion was weak [49]. A similar pattern was reported for the complex *cis*$(Et_3Sn)_2Ru(CO)_4$ [40] where the loss of four CO groups and the organic groups was observed leaving the Sn_2Ru^+ ion. For the mixed complex $Me_3SiRu(CO)_4GeBu_3$ a weak molecular ion was reported together with ions down to $SiRuGe^+$ resulting from the removal of alkyl and CO groups. Other ions observed included Me_3Si^+ and Bu_3Ge^+ [45].

The mass spectra of the two isomers of $(Cl_3Si)_2Ru(CO)_4$ were found to differ markedly. Thus, the percentages of ion current carried by the molecular ions were 0.3% for the *cis* isomer compared with 4.5% for *trans*, and the percentages carried by Si_2Ru- and SiRu-containing fragments were 33 and 45% respectively for *cis*, compared with 15 and 73% for the *trans* isomer [34]. Another difference between the two spectra is that fragments arising from both CO and Cl loss were far more predominant for the *trans* case (accounting for more than half the current carried by the Si_2Ru family). The differences between the two spectra are underlined by comparison of the respective base peaks; $(Cl_3Si)_2Ru(CO)_2^+$ for the *cis* isomer (16.6%) and $Cl_3SiRu(CO)_3^+$ for the *trans* complex (25.2%).

The above complexes are the only cases for which mass spectra fragmentation patterns have been detailed. In other cases, for *trans*$(Cl_3Ge)_2Fe(CO)_4$ [33] and for various halogen derivatives of the complexes $(RGeH_2)_2Fe(CO)_4$ (R = Me, H) [56], weak parent molecular ions have been found, but for $(Cl_3Ge)_2Ru(CO)_4$ the highest ion found in the mass spectrum was due to $(P{-}Cl)^+$ [47].

Rearrangements of $(R_3M')_2M(CO)_4$ complexes under mass spectral handling conditions have been reported in several instances. Thus, both of the complexes $R_3SiRu(CO)_4Me_3Sn$, R = Me, Et, gave ions due to the complex

$(Me_3Sn)_2Ru(CO)_4$ when the mass spectrometer was operated at 150—200°C [45]. More recently the mass spectra of some $(R_3Sn)_2Fe(CO)_4$ complexes have been reported with weak peaks due to the respective $[R_2M'Fe(CO)_4]_2$ complexes [37], and when the complexes $(Me_xGeH_{3-x})_2Fe(CO)_4$, $x = 1$ and 2 were introduced as liquid samples spectra were complicated by the dinuclear ions $(Me_xGeH_{2-x}Fe)_2(CO)_n^+$ [30,31].

(b) Other complexes. Mass spectral data have been reported for two other mono-iron complexes. For $Ph_3Ge(H)Fe(CO)_4$ the ions $Ph_3Ge(H)Fe(CO)_n^+$, $n = 1$—4, were observed (the pmi was extremely weak), and fragments due to phenyl loss were in relatively low abundance [59]. In the spectrum of $H_3Ge(H)Fe(CO)_4$, the GeFe-containing ions were also in high abundance (38%) after a weak molecular ion (1.1%). The base peak for this complex was GeH_x^+ (27.8%) [29].

(ii) Dinuclear derivatives

(a) $[R_2M'M(CO)_4]_2$ complexes. These complexes also exhibit weak molecular ions in their mass spectra. Thus, for $[Me_2GeFe(CO)_4]_2$ the molecular ion represented less than 1% of the ion current, with the major portion carried by the ions $(Me_2GeFe)_2(CO)_n^+$, $n = 0$—7; and $C_yH_xFe_2Ge_2^+$, $y = 0$—3 (>85%) [31]. The ions observed are compatible with a scheme in which stepwise loss of CO is the favoured process (supported by metastables for the ions when $n = 7 \rightarrow 6$, $4 \rightarrow 3$ and $3 \rightarrow 2$), and with minor loss of H_2 or CH_x ($x = 2$—4) from the $Me_2Ge_2Fe_2(CO)_n^+$ ions. All four methyl carbons are lost after all the CO groups have been removed, but processes involving scission of the Ge_2Fe_2 unit are minimal. Similar patterns have been found for the complexes $[RGeHFe(CO)_4]_2$, R = Me [30] and H [56], although for the latter complex the parent molecular ion is significantly stronger relative to the $(P—CO)^+$ ion.

No molecular ion was found for $[Ph_2GeFe(CO)_4]_2$ and the spectrum observed was reported identical with that found for $(Ph_2GeFe)_2(CO)_7$ [92]. These mass spectral observations were rationalized by other studies which established that $[Ph_2GeFe(CO)_4]_2$ partially converted to $(Ph_2GeFe)_2(CO)_7$ during heating. In view of the general nature of this type of reaction (see Part B, section (iv)b), the mass spectra obtained for other $[R_2M'M(CO)_4]_2$ complexes may be of mixtures containing also the respective $(R_2M'M)_2(CO)_7$ derivatives.

Similarly, for $[Me_2SnRu(CO)_4]_2$ the molecular ion was observed as a weak envelope of peaks. The fragmentation pattern here differed significantly from $[Me_2GeFe(CO)_4]_2$, so that there was stepwise loss of four CO groups before a methyl group was lost, followed by competitive Me/CO loss to leave the $Sn_2Ru_2^+$ ion [45].

More recently in the mass spectrum of $[(vinyl)_2SnFe(CO)_4]_2$ the ions $(CH_2:CH)_4Sn_2Fe_2(CO)_n^+$, $n = 0$—8, and $Sn_2Fe_2^+$ (strong) were observed, together with other ions 'due to further subdivision of these units' [81].

(b) Other dinuclear complexes. The complex $(Me_2SiFe)_2(CO)_7$ was reported to exhibit the ions $[P—n(CO)]^+$, $n = 0—7$, in the mass spectrum [95], and for the structurally related compound $(Me_2Ge)_3Ru_2(CO)_6$ a parent ion with successive loss of six CO groups was observed, in addition to the $Ge_3Ru_2^+$ and $Ge_2Ru_2^+$ ions [47].

The dinuclear complexes of the type $[R_3M'M(CO)_4]_2$ exhibit strong parent molecular ions. For $[Me_3SiRu(CO)_4]_2$ the ion $Me_3SiRu(CO)_4^+$ was also mentioned [45], together with ions resulting from competitive loss of methyl and carbonyl groups although interpretation was complicated by the wide spread of the Ru_2-containing envelopes. In the mass spectrum of $[Cl_3SiRu(CO)_4]_2$, ions consistent with stepwise loss of eight carbonyl groups were observed after a strong parent ion [45]. The $Cl_3SiRu(CO)_4^+$ ion was also observed together with related ions resulting from CO loss. For $[Me_3SiOs(CO)_4]_2$ an intense molecular ion was reported together with the ions $(P—Me)^+$; $[P—Me—n(CO)]^+$, $n = 1, 2$; $[P—n(CO)]^+$, $n = 2, 3$; $Si_2Os_2^+$ and $Me_3SiOs(CO)_4^+$ [51]. The high abundances of the $R_3M'M(CO)_4^+$ fragments in these spectra are to a degree paralleled in the chemistry of the $[R_3M'M(CO)_4]_2$ complexes where there is also cleavage of the M—M linkages (by sodium amalgam) producing the respective $R_3M'M(CO)_4^-$ anions [45,51].

In the mass spectrum of the chlorine bridged complex $Cl_6SnRu_2(CO)_5$ a molecular ion was observed, although the first strong ion was due to $(P—SnCl_2)^+$ [93].

As noted in Table 3 parent molecular ions were not observed for the following complexes (the highest ions found are listed in parentheses); $Me_{10}Sn_4Ru_2(CO)_6$[$(P—2Me)^+$] [40]; $[Me_3SiRu(CO)_3I]_2$, [$(P—Me)^+$] and $[Me_3SiOs(CO)_3Br]_2$, [$(P—Me—CO)^+$] [62]; $I_6M'Ru_2(CO)_5$, M' = Ge, Sn [$(P—I)^+$] [34].

(iii) Higher molecular weight derivatives

The relatively high volatilities of these carbonyl-containing clusters mean that in many cases good spectra may be obtained without reaching probe temperatures at which rapid decomposition occurs. Apart from the cases in which parent molecular ions only have been reported (see Table 4), fragmentation data have been listed for the following complexes.

For the complex $[Cl_2SiFe(CO)_4]_3$ three series of ions, with three, two (the strongest series) and one silicon—iron units are found, with predominantly loss of CO within these groups. The base peak in the spectrum was $Fe_2(SiCl_2)_2(CO)_3^+$ [110]. The ions P^+, $(P—CO)^+$ and $(P—2CO—2Me)^+$ have been reported from the spectrum of $[Me_2SiOs(CO)_3]_3$ [98]. A minor by-product from the reaction of $(vinyl)_2SnO_2CCF_3$ with $Fe(CO)_5$ exhibited a series of envelopes attributable to the ions $(CH_2 : CH)_2Sn_2Fe_4(CO)_n^+$, $n = 16—0$ in the mass spectrum, and the highest ion was preposed as a molecular ion [80]. For the complex $Cl_4SnOs_3(CO)_{12}$ the only ions containing both tin and osmium were $Os_3(CO)_nSnCl_x$, $n = 12—1$, $x = 4$ or 3, and these accounted for 6.6% of the ion current. The strongest peaks in this spectrum were due to $Os_3(CO)_nCl^+$,

$n = 8$—6, $SnCl_3^+$ and $SnCl^+$ [34]. With an 80 eV ionization potential and an inlet temperature of 60°C, the highest ion observed for a complex formulated as $(OC)_7Co_2[ClSiMn(CO)_5]_2Fe(CO)_4$ was attributed to the fragment $Fe(SiCl)_2Co_2CO^+$ [119].

G. OTHER SPECTROSCOPIC DATA

Two other types of spectroscopic data reported for group IV—iron triad carbonyl derivatives will be mentioned briefly here: Mössbauer spectra (section (i)) and photoelectron spectra (section (ii)).

(i) Mössbauer studies

Table 8 lists Mössbauer data for a variety of tin and iron complexes. Early work was prompted in this area to improve understanding of the bonding in these clusters. Later work with $[R_2M'Fe(CO)_4]_2$ complexes has been concerned with investigating the nature of Lewis base adducts.

The major difference between the *cis* and *trans* isomers of $(Cl_3Sn)_2Fe(CO)_4$ is in the quadrupole splitting of the ^{57}Fe resonance, which is about halved for the *cis* isomer as expected from point charge model [43]. The ^{119}Sn data were interpreted as clearly showing that there is no intramolecular bridging in this type of *cis* complex (such bridging had been proposed at one stage to explain the higher solubility of *cis* isomers [33]).

For the $[(RC_5H_4)_2SnFe(CO)_4]_2$ derivatives (R = H, Me) the nearly octahedral and tetrahedral geometries at iron and tin are reflected by single resonances in both the iron and tin spectra, the electronegativities of the groups bonded to each metal being apparently very similar [87]. Replacement of the electron-withdrawing C_5H_4R groups by relatively electron-donating butyl (or methyl)

TABLE 8

Selected Mössbauer data

Complex	^{119m}Sn		^{57}Fe		Refs.
	δ	Δ	δ	Δ	
cis$(Cl_3Sn)_2Fe(CO)_4$	1.53	1.25	0.28	0.20	43
trans$(Cl_3Sn)_2Fe(CO)_4$	1.53	1.26	0.26	0.46	43
$[Bu^n_2SnFe(CO)_4]_2$	1.70	1.26	0.24	~0.2	75
$[(MeC_5H_4)_2SnFe(CO)_4]_2$	1.81	—	0.01	—	86
$(MeC_5H_4)_2SnFe(CO)_4 \cdot C_5H_5N$	1.45	1.89	−0.08	2.36	86
$Me_4Sn_3[Fe(CO)_4]_4$	2.20	—	0.16	0.30	75
	1.45	1.24			
$[Cl_2SiFe(CO)_4]_3$			0.11	1.33	110
			0.14	0.64	

groups results in an electric field gradient and small quadrupole splittings (see Table 8). Earlier it was stated that the quadrupole splitting observed for the ^{119}Sn resonance in this type of molecule, meant that the bonding was not adequately described in terms of sp^3 hybridization [84]. It has been stated elsewhere that resolvable quadrupole splittings in asymmetric organo-tin(IV) compounds arises only when population of empty tin 5*d* orbitals by electron pairs from adjacent atoms can take place; thus the resolved splitting in these compounds was proposed as prima facie evidence for $(d-d)\pi$ bonding [144].

When $[R_2M'Fe(CO)_4]_2$ complexes are dissolved in pyridine there are marked changes in the ME parameters. The induction of a large QS in the iron spectrum is consistent with trigonal bipyramidal geometry at iron as expected for $R_2M'Fe(CO)_4 \cdot C_5H_5N$ species (cf. 1.84 mm s^{-1} reported for $[Cl_3SiFe(CO)_4]$-$[NEt_4]$ [110]). The isomer shifts found for these adducts are consistent with tin(IV) complexes.

For the complex $[Cl_2SiFe(CO)_4]_3$ two iron resonances both exhibiting quadrupole splittings were observed, indicating a possible mixture of isomeric forms [110].

(ii) Photoelectron spectra

Although photoelectron spectroscopy has been used as a probe in investigations of the bonding of group IV derivatives of other transition metals [e.g. 145] only one report dealing with iron derivatives has appeared to date. Marks and co-workers [91] have reported the tin $3d_{5/2}$ electron binding energies of several $[R_2SnFe(CO)_4]_2$ complexes and their Lewis base adducts. All the compounds had the same binding energies within experimental error (ca. 487 eV) and thus the base adducts are best considered tin(IV) complexes.

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