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CARBENE COMPLEXES

XX *. ELECTRON-RICH CARBENEIRON(0) TRIGONAL BIPYRAMIDAL CARBONYLS AND THEIR GERMANIUM(II) AND TIN(II) ANALOGUES $[Fe(CO)_3(L)(L')]$ ($L = \overline{CN(Me)(CH_2)_2N}Me$, $L' = PEt_3$, 3 CO's EQUATORIAL; OR $L = M(OAr)_2$ (EQUATORIAL: M = Ge OR Sn, $Ar = C_6H_2Bu^t{}_2$-2,6-Me-4), L′ = CO)

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Summary

The first bis(aryloxo)-main Group 14 metal(II)-transition-metal complexes *eq*-$[Fe(CO)_4\{M(OAr)_2\}]$ (*eq*- denotes equatorial, $Ar = C_6H_2Bu^t{}_2$-2,6-Me-4, and M = Ge (II) or Sn (III)) have been prepared, from $[Fe_2(CO)_9]$ and the appropriate aryloxide $M(OAr)_2$. X-ray structures of the complexes II and III show them to have the unusual (for a trigonal bipyramidal (tbp) $[Fe(CO)_4L]$ complex) *eq*-distorted tbp configuration. The related carbene complex $[Fe(CO)_3(L^{Me})(PEt_3)]$ (I) [$L^{Me} = \overline{CN(Me)(CH_2)_2N}Me$] has the tbp-*trans*-configuration in the crystal. The stereochemical integrity of each of I–III is maintained in solution. The exceptionally short Fe–Ge and Fe–Sn distances, and the relatively small deviation from coplanarity of the MO_2 plane and the $Fe(CO)_{ax}M$ planes are consistent with the ligands $M(OAr)_2$ being good π-acceptors but poor σ-donors in complexes II or III. By contrast, the X-ray data for complex I support the view that L^{Me} is a strong σ-donor but weak π-acceptor. For a series of tbp-*trans*-$[Fe(CO)_3(L)(L')]$ complexes, a comparison of $Fe–C_{carb}$ and Fe–P distances shows that the *trans*-influence of a ligand L falls in the sequence $L = CO > PR_3 > L^{Me}$.

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* For Part XIX. see ref. 1. No reprints available.

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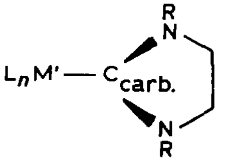
Introduction

This paper presents data on two related series of transition-metal complexes, which have been of interest to us for some time. The first has the formula **A** [1], where M′ is a transition metal and L_n represents the sum of all ligands other than



{abbreviated as $[M'(L_n)L^R]$}

(A)

$L_nM'\text{-}MX_2$

(B)

an electron-rich carbene ligand L^R, e.g., **A** = $[Fe(CO)_4(L^{Me})]$. The second has the formula **B** [2], where M = Ge, Sn, or Pb and X^- is a bulky *C*-, *N*-, or *S*-centred monohapto ligand, e.g., **B** = $[Cr(CO)_5(SnR_2)]$ [R = $CH(SiMe_3)_2$]. The present results relate to mononuclear iron(0) carbonyls.

The structures of many compounds of type **A** have been determined; for a review, including data for a wider range of electron-rich carbene-metal complexes, see ref. [3]. Bivalent monomeric group 14 metal(II) compounds MX_2 also have an extensive transition-metal chemistry [2]; however, only a relatively small number of compounds of type **B**, in which MX_2 behaves as a neutral terminal ligand, is known [2], and of these only five have been structurally characterised: $[Cr(CO)_5(MX_2)]$ (MX_2 = GeR_2 [4], SnR_2 [5], or $Ge(SC_6H_2Me_3\text{-}2,4,6)_2$) [6], and $[M'\{Sn(NR'_2)_2\}_3]$ (R′ = $SiMe_3$ and M′ = Pt [7] or M = Pd [8]).

It has become evident that both the electron-rich carbene ligand L^{Me}, and its heavy Group 14 metal near-congeners MX_2, can be regarded as neutral ligands, rather like a tertiary phosphine. However, unlike the latter, they are six-, rather than eight-, electron moieties (L^{Me}) or molecules (MX_2) and hence might be expected to be effective π-acceptors, similar to CO. Earlier spectroscopic and structural studies on complexes $[Cr(CO)_5(L)]$ (L = GeR_2 [4] or EPh_3 (E = P, As, Sb, or Bi) [9]) or *cis*-$[Mo(CO)_4(L^{Me})_2]$ [10] have led to the conclusions that for these octahedral d^6 M'^0 complexes (i) the *trans*-influence decreases in the order $GeR_2 \approx CO > L^{Me} \approx PPh_3$, and (ii) π-acceptor capacity follows the same sequence. With regard to their geometry, the Group 14 ligating atom C or M is in a trigonal planar environment; it appears that in **A** the coordination plane of the ligand L^{Me} or MX_2 is generally approximately orthogonal to the square plane of a d^8 metal complex.

Whereas the electron-rich carbenes, such as L^{Me}, are transients, their heavy atom near-congeners MR_2, $M(NR'_2)_2$, and $M(OAr)_2$ are stable molecules; structural data are available on the monomers, see Table 6 [11–14] (the alkyls exist as alkene-like dimers in the solid state, which readily dissociate in solution [15]). Transition-metal complexes of type **A** are generally accessible from the electron-rich olefins $L^R{}_2$, while those of type **B** are obtained from MX_2. For example *trans*-[Fe-

$(CO)_3(L^{Me})(PEt_3)]$ (I) was obtained from $[Fe(CO)_5]$ and successively $L^{Me}{}_2$ and PEt_3, via *ax*-$[Fe(CO)_4(L^{Me})]$ [16]; the *trans*-trigonal bipyramidal (tbp) geometry for complex I, and the *ax*-conformation for its precursor, were deduced from IR and NMR spectra; the prefix *ax*- or *eq*- denotes that L occupies an axial or equatorial site, respectively.

Five-coordinate d^8 iron(0) complexes generally have the tbp configuration. For complexes $[Fe(CO)_4(L)]$, the *ax*-configuration is by far the more common [17]. However, *eq*-$[Fe(CO)_4(L)]$ complexes are exemplified by L = alkene [18], L = $PPh(PPh_2)_2$ [19], L = $P(CR'_2)NR'_2$ (R' = $SiMe_3$) [20], or L = *trans*-Ar'P = PAr' (Ar' = $C_6H_2Bu^t{}_3$-2,4,6) [21], or for $[\{$*eq*-$Fe(CO)_4\}_2(\mu$-*trans*-RP=PR)] [22]. The *eq*-preference has been attributed to L having either good π-acceptor character [23] or exceptional bulk [19]; nevertheless for L = $PBu^t{}_3$, with a remarkably high cone angle of 179°, the Fe^0 carbonyl has the *ax*- geometry [24]. The disubstituted complexes $[Fe(CO)_3(L)(L')]$ are designated as *trans* if both L and L' occupy *ax*- sites. As far as we are aware, there has been no previous study of the relative *trans*-influence of various ligands L in such complexes.

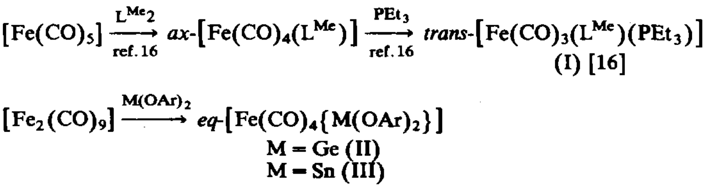
The present work had two further objectives. Firstly, conclusively to establish for d^8 iron(0) carbonyl complexes $[Fe(CO)_3(L)(L')]$ (L' = a neutral ligand, such as CO or PEt_3) the *ax/eq* preference in the crystal (X-ray) for (i) L = an electron-rich carbene such as L^{Me}, and (ii) L = a heavy Group 14 metal(II) near-congener MX_2 (M = Ge or Sn). Secondly, we sought to extend the range of MX_2 terminal ligands to X^- = an *O*-centred anion; the compounds $M(OAr)_2$ (Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4) [14] were selected. As for (i), it was already established that the carbene complex $[Fe(CO)_4\{\overline{CN(Me)CH{=}CHN}Me\}]$ has the *ax* configuration [25].

Results and discussions

1. *Preparation of germylene- or stannylene-iron(0) complexes: trans-$[Fe(CO)_4\{M(OAr)_2\}]$ (M = Ge (II), or Sn (III), Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4)*

Syntheses are illustrated in Scheme 1; for complex I, see ref. [16].

Nonacarbonyldi-iron(0) and SnR_2 [R = $CH(SiMe_3)_2$] were reported to react readily in benzene to give an iron(0) complex formulated as $[\{Fe(CO)_4\}_2(\mu\text{-}SnR_2)]$ [5]. A similar approach was used in this work: an excess of the soluble metal(II) aryloxide $M(OAr)_2$ (M = Ge or Sn) and $[Fe_2(CO)_9]$ under ambient conditions afforded complexes II or III (Table 1) in low yields (ca. 20%). The filtrate, upon further crystallisation, afforded unreacted $M(OAr)_2$. It is evident that $[Fe(CO)_5]$ (a coproduct of the reaction) and $M(OAr)_2$ do not readily react under the mild conditions of this synthesis.



$$[Fe(CO)_5] \xrightarrow[\text{ref. 16}]{L^{Me}{}_2} ax\text{-}[Fe(CO)_4(L^{Me})] \xrightarrow[\text{ref. 16}]{PEt_3} trans\text{-}[Fe(CO)_3(L^{Me})(PEt_3)]\ \text{(I) [16]}$$

$$[Fe_2(CO)_9] \xrightarrow{M(OAr)_2} eq\text{-}[Fe(CO)_4\{M(OAr)_2\}] \quad \begin{matrix} M = Ge\ (II) \\ M = Sn\ (III) \end{matrix}$$

SCHEME 1. Synthesis of the iron(0) carbonyl complexes I–III. Abbreviations: L^{Me} = $:\overline{CN(Me)(CH_2)_2N}Me$ and Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4.

2. *Spectroscopic data for trans-*$[Fe(CO)_3(L^{Me})(PEt_3)]$ *(I) and eq-*$[Fe(CO)_4\{M(OAr)_2\}]$ *(M = Ge (II) or Sn (III))*

Complexes I [16] and II are air-stable, while III is somewhat air- (and possibly light-) sensitive. Selected physical and IR spectroscopic data are collected in Table 1, and ^1H NMR data are shown in Table 2.

The solution IR spectra of complexes II and III show three carbonyl stretching bands in solution (Table 1). Axial tbp complexes $[Fe(CO)_4(L)]$ should have four IR-active carbonyl stretching modes, assuming that the ligand L lowers the symmetry from C_{3v} (which would require 3 IR bands: $2A + E$). However, in practice only three bands have often been reported, e.g., (i) in n-C_6H_{14} for L = PMe_3 or EPh_3 (E = As or Sb) [26]; (ii) for L = PPh_3 in CCl_4: at 2055, 1978, and 1943 cm^{-1}; or (iii) for L = L^{Me} in n-C_6H_{14}: at 2040, 1959, and 1938 cm^{-1} [16]. In several other *ax*-$[Fe(CO)_4(L)]$ complexes, four ν(CO) bands have been observed, e.g., in $[Fe(CO)_4(PPh_2CH_2CH_2PPh_2)]$ [28]. The complexes *eq*-$[Fe(CO)_4L]$ should likewise show four IR-active ν(CO)'s (C_{2v} symmetry, or lower), and hence IR spectra are not diagnostic for *ax-/eq*-differentiation. However, for a series of isoleptic complexes $[M'(CO)_4(L)]$ (M' = Ru or Os), equatorial–axial interconversion has been observed by solution IR spectroscopy [26]; e.g., complexes $[M'(CO)_4(AsPh_3)]$ (M' = Ru or Os) showed six ν(CO)'s, three assigned to each of *ax*- and *eq*-isomers. We conclude that complexes II and III are not mixtures of *ax*- and *eq*-isomers, and are presumed to retain their *eq*-integrity in solution (cf., X-ray data).

TABLE 1

SELECTED PHYSICAL AND IR SPECTROSCOPIC PROPERTIES FOR COMPLEXES *trans*-$[Fe(CO)_3(L^{Me})(PEt_3)]$ (I) AND *eq*-$[Fe(CO)_4\{M(OAr^{Me})_2\}]$ (M = Ge (II) or Sn (III)) [a]

Compound	Colour	M.p. (θ_c/°C) [c]	IR (cm^{-1}) [b]			
			ν(CO)			$\nu_{asym}(CN_2)$
trans-$[Fe(CO)_3(L^{Me})(PEt_3)]$ (I) [d]	cream	94	1969vw	1867vs		1500m
eq-$[Fe(CO)_4\{Ge(OAr)_2\}]$ (II)	bright-yellow	212–214d [e]	2076m	2007s	1984s	–
eq-$[Fe(CO)_4\{Sn(OAr)_2\}]$ (III)	orange-brown	120–125d [e]	2070m	2000s	1981s	–

[a] L^{Me} = $:\overline{CN(Me)(CH_2)_2N}Me$, Ar = $C_6H_2Bu^t_2$-2,6-Me-4. [b] Solution in n-C_6H_{14}. [c] Sealed capillaries. [d] Taken from ref. [16]. [e] With decomposition.

TABLE 2

^1H NMR CHEMICAL SHIFT DATA FOR COMPLEXES I–III [a]

	$(NCH_2)_2$	NMe	*o*-Bu^t	*p*-Me	3,5-Ar
I [b]	2.6	3.24			
II			1.79	2.37	6.97
III			1.84	2.42	[c]

[a] Chemical shifts (all singlets) are in ppm relative to the solvent peak (C_6D_6) at 7.27 ppm (C_6D_5H), recorded at 60 MHz. [b] Data from ref. [16] (PEt_3 signals were not reported). [c] Signals obscured by solvent resonances.

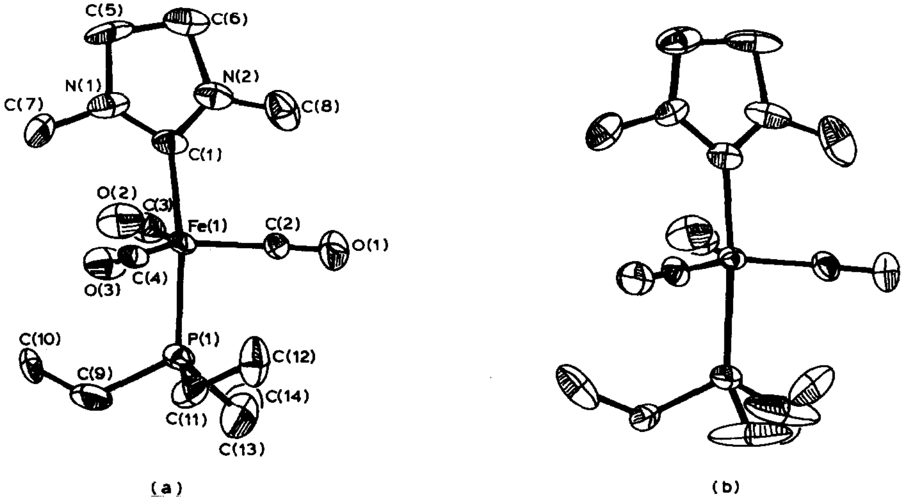
3. X-Ray structure of trans-[Fe(CO)$_3$(L^{Me})(PEt$_3$)] (I)

The conformations and atom numbering scheme for the two independent molecules *trans*-[Fe(CO)$_3$(L^{Me})(PEt$_3$)] (Ia) and (Ib) are shown in Fig. 1; bond lengths (Å) and angles (°), as well as torsion angles and mean planes, are listed in Table 3. The two molecules in the asymmetric unit for complex I are similar but not identical. Both iron atoms have a distorted tbp coordination about the metal centre with the carbene and phosphine occupying the axial sites. The iron atom is displaced slightly out of the equatorial co-ordination plane by 0.01 Å in Ia and 0.02 Å in Ib towards the carbene ligand.

The triethylphosphine ligands are in a nearly staggered arrangement about the Fe–P bond with respect to the three equatorial carbonyl groups, as shown by the torsion angle C(9)–P(1)–Fe–C(2) which is −166° in Ia and 172° in Ib. The ethyl carbon atoms in Ib have large anisotropic temperature factors which are probably a reflection of some slight disorder in these groups. For this reason the derived C–C bond lengths in the ethyl groups are not reliable. The angles subtended at the iron atoms by the phosphorus atom and the equatorial carbonyl groups are all close to 89°.

The planar carbene ligand is arranged at a small angle to the C(2) carbonyl group, the torsion angle C(2)–Fe–C(1)–N(2) being 23° in Ia and 34° in Ib. This causes short contacts between the methyl groups of the carbene ligand and the equatorial carbonyl groups, and the distortions from regular tbp symmetry may be correlated with this effect. Repulsion between the C(8) methyl group of L^{Me} and the C(2) carbonyl group causes a bending of the Fe–C(1) bond away from C(2), opening up the C(2)–Fe–C(1) angle to 99.4(4)° in Ia and 97.7(5)° in Ib. The observed contact distance C(2)...C(8) is 2.98 Å in Ia and 2.96 Å in Ib. The orientation of the carbene groups relative to the equatorial plane of the complex is shown schematically below. The methyl groups C(7) and C(8) have pushed apart the

(Continued on p. 34)



(a) (b)

Fig. 1. The molecular structure, and atom numbering scheme, for identical views of the two molecules Ia and Ib in the asymmetric unit for *trans*-[Fe(CO)$_3$(L^{Me})(PEt$_3$)] (I) [L^{Me} = $\overline{\mathrm{CN(Me)(CH_2)_2N}}$Me].

TABLE 3

INTRAMOLECULAR BOND LENGTHS (Å) AND ANGLES (°), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR *trans*-$[Fe(CO)_3(L^{Me})(PEt_3)]$ (I)

	Molecule a	Molecule b
Fe–P	2.202(3)	2.214(3)
Fe–C(1)	1.951(10)	1.949(10)
Fe–C(2)	1.800(10)	1.761(11)
Fe–C(3)	1.753(12)	1.804(12)
Fe–C(4)	1.766(10)	1.757(9)
P–C(9)	1.85(2)	1.76(3)
P–C(11)	1.86(2)	1.75(3)
P–C(13)	1.85(2)	1.71(2)
C(1)–N(1)	1.36(2)	1.37(1)
C(5)–N(1)	1.45(2)	1.43(2)
C(7)–N(1)	1.45(2)	1.45(2)
C(1)–N(2)	1.32(2)	1.36(1)
C(6)–N(2)	1.52(2)	1.38(2)
C(8)–N(2)	1.44(2)	1.51(2)
C(2)–O(1)	1.12(2)	1.15(2)
C(3)–O(2)	1.18(2)	1.10(2)
C(4)–O(3)	1.15(2)	1.15(1)
C(5)–C(6)	1.53(3)	1.52(3)
C(9)–C(10)	1.42(3)	1.36(3)
C(11)–C(12)	1.52(3)	1.19(3)
C(13)–C(14)	1.47(3)	1.32(3)
C(1)–Fe–P	171.5(3)	172.8(3)
C(2)–Fe–P	88.8(3)	88.5(4)
C(3)–Fe–P	89.4(4)	89.6(4)
C(4)–Fe–P	89.8(3)	88.1(3)
C(2)–Fe–C(1)	99.4(4)	97.7(5)
C(3)–Fe–C(1)	89.7(5)	92.0(4)
C(3)–Fe–C(2)	112.1(6)	107.9(5)
C(4)–Fe–C(1)	84.0(4)	85.3(4)
C(4)–Fe–C(2)	121.4(5)	126.1(5)
C(4)–Fe–C(3)	126.4(6)	125.8(5)
C(9)–P–Fe	113.9(6)	120.4(9)
C(11)–P–Fe	120.5(5)	116.4(9)
C(11)–P–C(9)	95.1(8)	102.2(15)
C(13)–P–Fe	118.8(8)	119.0(9)
C(13)–P–C(9)	104.6(10)	96.3(14)
C(13)–P–C(11)	100.3(8)	98.4(17)
C(5)–N(1)–C(1)	115(1)	112(1)
C(7)–N(1)–C(1)	130(1)	126(1)
C(7)–N(1)–C(5)	113(1)	120(1)
C(6)–N(2)–C(1)	114(1)	117(1)
C(8)–N(2)–C(1)	128(1)	123(1)
C(8)–N(2)–C(6)	117(1)	119(1)
N(1)–C(1)–Fe	124(1)	125(1)
N(2)–C(1)–Fe	130(1)	131(1)
N(2)–C(1)–N(1)	106(1)	104(1)
O(1)–C(2)–Fe	176(1)	178(1)
O(2)–C(3)–Fe	175(1)	175(1)
O(3)–C(4)–Fe	177(1)	176(1)
C(6)–C(5)–N(1)	103(1)	104(1)
C(5)–C(6)–N(2)	100(1)	101(1)

TABLE 3 (continued)

C(10)–C(9)–P	120(2)	130(2)
C(12)–C(11)–P	112(1)	136(2)
C(14)–C(13)–P	114(1)	134(2)

Torsion angles (°)

Molecule a

C(1)–Fe(1)–P(1)–C(9)	−1.7	C(4)–Fe(1)–C(3)–O(2)	33.2
C(1)–Fe(1)–P(1)–C(11)	−113.7	P(1)–Fe(1)–C(4)–O(3)	−101.1
C(1)–Fe(1)–P(1)–C(13)	122.2	C(1)–Fe(1)–C(4)–O(3)	84.7
C(2)–Fe(1)–P(1)–C(9)	−166.1	C(2)–Fe(1)–C(4)–O(3)	−12.6
C(2)–Fe(1)–P(1)–C(11)	82.0	C(3)–Fe(1)–C(4)–O(3)	169.9
C(2)–Fe(1)–P(1)–C(13)	−42.1	Fe(1)–P(1)–C(9)–C(10)	−48.8
C(3)–Fe(1)–P(1)–C(9)	81.8	C(11)–P(1)–C(9)–C(10)	77.9
C(3)–Fe(1)–P(1)–C(11)	−30.1	C(13)–P(1)–C(9)–C(10)	179.9
C(3)–Fe(1)–P(1)–C(13)	−154.2	Fe(1)–P(1)–C(11)–C(12)	−51.5
C(4)–Fe(1)–P(1)–C(9)	−44.6	C(9)–P(1)–C(11)–C(12)	−173.2
C(4)–Fe(1)–P(1)–C(11)	−156.6	C(13)–P(1)–C(11)–C(12)	81.0
C(4)–Fe(1)–P(1)–C(13)	79.3	Fe(1)–P(1)–C(13)–C(14)	−47.4
P(1)–Fe(1)–C(1)–N(1)	35.1	C(9)–P(1)–C(13)–C(14)	81.0
P(1)–Fe(1)–C(1)–N(2)	−141.5	C(11)–P(1)–C(13)–C(14)	179.1
C(2)–Fe(1)–C(1)–N(1)	−160.8	C(5)–N(1)–C(1)–Fe(1)	−175.7
C(2)–Fe(1)–C(1)–N(2)	22.6	C(5)–N(1)–C(1)–N(2)	1.6
C(3)–Fe(1)–C(1)–N(1)	−48.4	C(7)–N(1)–C(1)–Fe(1)	−12.1
C(3)–Fe(1)–C(1)–N(2)	134.9	C(7)–N(1)–C(1)–N(2)	165.3
C(4)–Fe(1)–C(1)–N(1)	78.3	C(1)–N(1)–C(5)–C(6)	−9.3
C(4)–Fe(1)–C(1)–N(2)	−98.3	C(7)–N(1)–C(5)–C(6)	−175.8
P(1)–Fe(1)–C(2)–O(1)	−53.2	C(6)–N(2)–C(1)–Fe(1)	−175.5
C(1)–Fe(1)–C(2)–O(1)	129.1	C(6)–N(2)–C(1)–N(1)	7.4
C(3)–Fe(1)–C(2)–O(1)	35.6	C(8)–N(2)–C(1)–Fe(1)	−0.5
C(4)–Fe(1)–C(2)–O(1)	−142.2	C(8)–N(2)–C(1)–N(1)	−177.6
P(1)–Fe(1)–C(3)–O(2)	−56.0	C(1)–N(2)–C(6)–C(5)	−12.6
C(1)–Fe(1)–C(3)–O(2)	115.6	C(8)–N(2)–C(6)–C(5)	171.9
C(2)–Fe(1)–C(3)–O(2)	−144.5	N(1)–C(5)–C(6)–N(2)	11.8

Molecule b

C(1)A–Fe(1)A–P(1)A–C(9)A	−39.4	C(4)A–Fe(1)A–C(3)A–O(2)A	153.9
C(1)A–Fe(1)A–P(1)A–C(11)A	−163.9	P(1)A–Fe(1)A–C(4)A–O(3)A	116.2
C(1)A–Fe(1)A–P(1)A–C(13)A	78.6	C(1)A–Fe(1)A–C(4)A–O(3)A	−61.0
C(2)A–Fe(1)A–P(1)A–C(9)A	171.6	C(2)A–Fe(1)A–C(4)A–O(3)A	−157.1
C(2)A–Fe(1)A–P(1)A–C(11)A	47.1	C(3)A–Fe(1)A–C(4)A–O(3)A	28.1
C(2)A–Fe(1)A–P(1)A–C(13)A	−70.4	Fe(1)A–P(1)A–C(9)A–C(10)A	0.2
C(3)A–Fe(1)A–P(1)A—C(9)A	63.7	C(11)A–P(1)A–C(9)A–C(10)A	131.1
C(3)A–Fe(1)A–P(1)A–C(11)A	−60.8	C(13)A–P(1)A–C(9)A–C(10)A	−128.8
C(3)A–Fe(1)A–P(1)A–C(13)A	−178.3	Fe(1)A–P(1)A–C(11)A–C(12)A	20.7
C(4)A–Fe(1)A–P(1)A–C(9)A	−62.2	C(9)A–P(1)A–C(11)A–C(12)A	−112.6
C(4)A–Fe(1)A–P(1)A–C(11)A	173.4	C(13)A–P(1)A–C(11)A–C(12)A	149.0
C(4)A–Fe(1)A–P(1)A–C(13)A	55.9	Fe(1)A–P(1)A–C(13)A–C(14)A	9.7
P(1)A–Fe(1)A–C(1)A–N(1)A	60.5	C(9)A–P(1)A–C(13)A–C(14)A	139.8
P(1)A–Fe(1)A–C(1)A–N(2)A	−114.6	C(11)A–P(1)A–C(13)A–C(14)A	−116.9
C(2)A–Fe(1)A–C(1)A–N(1)A	−150.9	C(5)A–N(1)A–C(1)A–Fe(1)A	−175.9
C(2)A–Fe(1)A–C(1)A–N(2)A	34.1	C(5)A–N(1)A–C(1)A–N(2)A	0.2
C(3)A–Fe(1)A–C(1)A–N(1)A	−42.5	C(7)A–N(1)A–C(1)A–Fe(1)A	−9.0
C(3)A–Fe(1)A–C(1)A–N(2)A	142.5	C(7)A–N(1)A–C(1)A–N(2)A	167.1
C(4)A–Fe(1)A–C(1)A–N(1)A	83.3	C(1)A–N(1)A–C(5)A–C(6)A	−9.5
C(4)A–Fe(1)A–C(1)A–N(2)A	−91.8	C(7)A–N(1)A–C(5)A–C(6)A	−177.3
P(1)A–Fe(1)A–C(2)A–O(1)A	1.6	C(6)A–N(2)A–C(1)A–Fe(1)A	−173.2

(continued)

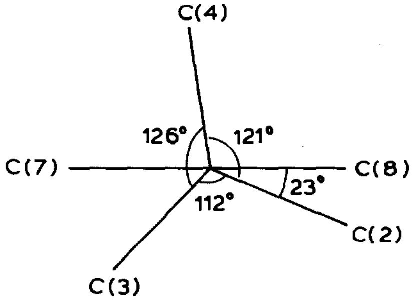
TABLE 3 (continued)

C(1)A–Fe(1)A–C(2)A–O(1)A	−175.7	C(6)A–N(2)A–C(1)A–N(1)A	11.0
C(3)A–Fe(1)A–C(2)A–O(1)A	89.4	C(8)A–N(2)A–C(1)A–Fe(1)A	−8.0
C(4)A–Fe(1)A–C(2)A–O(1)A	−86.2	C(8)A–N(2)A–C(1)A–N(1)A	176.2
P(1)A–Fe(1)A–C(3)A–O(2)A	66.6	C(1)A–N(2)A–C(6)A–C(5)A	−16.3
C(1)A–Fe(1)A–C(3)A–O(2)A	−120.4	C(8)A–N(2)A–C(6)A–C(5)A	177.8
C(2)A–Fe(1)A–C(3)A–O(2)A	−21.6	N(1)A–C(5)A–C(6)A–N(2)A	14.4

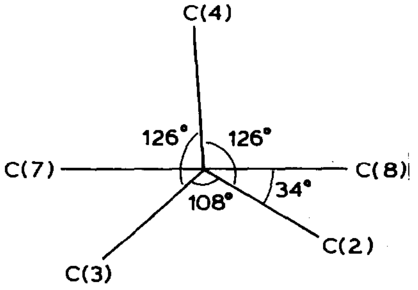
Mean planes [a]

Plane 1	Molecule a	Molecule b	Plane 2	Molecule a	Molecule b
Fe(1)	0.012	−0.024	C(1)	0.016	−0.024
C(2)	−0.004	0.008	N(1)	0.028	−0.025
C(3)	−0.004	0.007	N(2)	−0.043	0.054
C(4)	−0.004	0.008	C(5)	−0.052	0.056
O(1) [b]	−0.049	0.061	C(6)	0.052	−0.061
O(2) [b]	−0.057	0.053	C(7) [b]	−0.121	0.093
O(3) [b]	−0.006	0.002	C(8) [b]	−0.114	0.024
C(1) [b]	1.460	−1.493	Fe(1) [b]	0.025	−0.040
P(1) [b]	−1.644	1.659	P(1) [b]	−0.100	0.111

[a] Distances (Å) of atoms from some mean planes. [b] Atoms not included in the calculation of the plane.



(Ia)



(Ib)

C(3) and C(4) carbonyl groups, and also the C(2) and C(4) carbonyl groups, and thus closed up the C(2)–Fe–C(3) angle. A similar effect of the bending of the Fe–C_{carb} bond and variation in the angles between the equatorial carbonyl groups has been reported for *ax*-[Fe(CO)$_4${$\overline{\text{CN(Me)(CH)}_2\text{N}}$Me}] (IV) [25].

The carbene ligands in Ia and Ib have average bond lengths of 1.35(2) for N–C_{carb}, 1.45(5) for N–C(ring), 1.46(3) for N–C(methyl), and 1.52(3) Å for C–C(ring), in good agreement with similar ligands [3]. The average Fe–C_{carb} bond length in I, 1.95(1) Å, is slightly shorter than the value of 2.007(5) Å for Fe–C_{carb} in IV [25].

4. X-Ray structure of eq-[Fe(CO)$_4${M(OAr)$_2$}] (M = Ge (II) or Sn (III))

The conformation and atom numbering scheme for the isomorphous molecules II and III are shown in Fig. 2; bond lengths and angles are listed in Table 4. The iron atoms have a distorted tbp coordination about the metal centre, with the planar, 3-co-ordinate germylene or stannylene ligand in the unusual equatorial position.

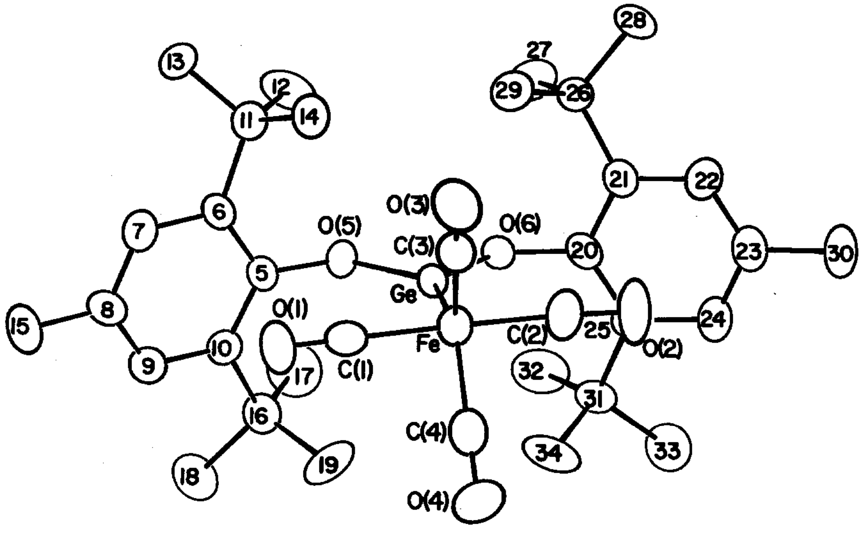


Fig. 2. The molecular structures, and atom numbering schemes, for *eq*-[Fe(CO)$_4${Ge(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_2$} (II). The corresponding tin compound is isostructural.

It is noted upon comparing complexes II and III with their appropriate free ligands M(OAr)$_2$ that there is a significantly smaller ⟨M–O⟩ bond length in II or III, but only a very slight opening of the OMO angle. However, as evident from Table 5, such trends, as between other MX$_2$ molecules and their transition-metal complexes of type **B**, cannot yet be regarded as general. Complexes II and III, like the others of type **B**, have an approximately trigonal planar geometry about M, the sum of the angles at Ge in II or at Sn in III being in each case 360°. This arrangement maximises the possibility of [d(Fe)–p(M)]π overlap, as is consistent with the Fe–M distances being by far the shortest yet recorded, 2.240(2) for II and 2.408(1) Å for III; cf. the range (i) 2.35–2.44 Å for eight Fe–Ge complexes and 2.28 Å for [Fe(η-C$_4$H$_6$)(η-C$_5$H$_5$)(GeCl$_2$Me)], and (ii) 2.46–2.67 for nineteen Fe–Sn complexes cited in a recent review [29]. The large ⟨OMFe⟩ angles of ca. 133° for each of M = Ge or Sn minimise non-bonding contacts between the M(OAr)$_2$ ligands and the axial carbonyl groups.

The MO$_2$ plane of M(OAr)$_2$ is tilted from the Fe(CO)$_{ax}$M planes by only 4.9° for M = Ge in II and 5.2° for M = Sn in III, presumably for steric reasons; thus, the formally (in absence of π-bonding) vacant p orbital on M is unable completely to achieve its electronically favoured equatorial position for π-bonding. The ion [Fe(CO)$_4${P(NEt$_2$)$_2$}]$^+$ (V) has the same *eq*-geometry [30]; we note that P(NEt$_2$)$_2$$^+$ is isoelectronic with the silylene ligand Si(NEt$_2$)$_2$, a near analogue of M(OAr)$_2$. The equatorial placement of the P(NEt$_2$)$_2$ moiety in V was attributed to the good π-acceptor character of the phosphenium ligand, consistent also with a very short Fe–P bond length and a planar geometry at P, but the PN$_2$ plane was also tilted between 31 and 38° from the two Fe(CO)$_{ax}$M planes.

5. The relative trans-influence of L^{Me} and some related ligands in tbp iron(0) carbonyl complexes and rationalisation of the ax-/eq problem

The shorter Fe–C$_{carb}$ bond length in *trans*-[Fe(CO)$_3$(L^{Me})(PEt$_3$)] (I) than in

(Continued on p. 38)

TABLE 4

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR *eq*-$[Fe(CO)_4\{M(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2\}]$ (M = Ge (II) or M = Sn (III))

	M = Ge	M = Sn		M = Ge	M = Sn
M–Fe	2.240(2)	2.408(1)	M–O(5)	1.778(6)	1.964(5)
M–O(6)	1.776(6)	1.983(5)	Fe–C(1)	1.827(11)	1.809(9)
Fe–C(2)	1.795(11)	1.808(10)	Fe–C(3)	1.771(11)	1.810(11)
Fe–C(4)	1.766(13)	1.807(12)	C(1)–O(1)	1.126(13)	1.137(11)
C(2)–O(2)	1.133(13)	1.141(12)	C(3)–O(3)	1.444(14)	1.127(13)
C(4)–O(4)	1.144(14)	1.113(15)	O(5)–C(5)	1.379(12)	1.390(11)
O(6)–C(20)	1.398(10)	1.403(9)	C(20)–C(21)	1.397(13)	1.412(11)
C(5)–C(6)	1.397(13)	1.420(12)	C(21)–C(22)	1.420(14)	1.386(12)
C(6)–C(7)	1.406(14)	1.386(13)	C(22)–C(23)	1.403(15)	1.409(14)
C(7)–C(8)	1.398(15)	1.389(13)	C(23)–C(24)	1.391(16)	1.405(14)
C(8)–C(9)	1.398(15)	1.403(14)	C(24)–C(25)	1.412(13)	1.406(12)
C(9)–C(10)	1.380(14)	1.398(14)	C(25)–C(20)	1.404(13)	1.400(11)
C(10)–C(5)	1.404(13)	1.400(12)	C(21)–C(26)	1.555(13)	1.536(12)
C(6)–C(11)	1.571(13)	1.548(12)	C(23)–C(30)	1.545(15)	1.522(14)
C(8)–C(15)	1.535(15)	1.522(15)	C(25)–C(31)	1.538(13)	1.537(12)
C(10)–C(16)	1.566(15)	1.580(14)	C(26)–C(27)	1.554(16)	1.536(15)
C(11)–C(12)	1.560(18)	1.550(17)	C(26)–C(28)	1.566(16)	1.589(15)
C(11)–C(13)	1.585(16)	1.559(16)	C(26)–C(29)	1.566(15)	1.533(14)
C(11)–C(14)	1.550(14)	1.562(13)	C(31)–C(32)	1.541(16)	1.532(16)
C(16)–C(17)	1.545(18)	1.526(19)	C(31)–C(33)	1.564(18)	1.568(17)
C(16)–C(18)	1.588(18)	1.551(17)	C(31)–C(34)	1.542(17)	1.530(16)
C(16)–C(19)	1.568(16)	1.552(16)			
Fe–M–O(5)	132.9(2)	132.9(1)	Fe–M–O(6)	133.6(2)	134.9(1)
O(5)–M–O(6)	93.5(2)	92.2(2)	M–Fe–C(1)	89.1(3)	87.6(2)
M–Fe–C(2)	93.6(3)	93.0(3)	M–Fe–C(3)	117.4(3)	116.0(3)
M–Fe–C(4)	120.5(3)	120.8(3)	C(1)–Fe–C(2)	177.3(4)	179.0(4)
C(1)–Fe–C(3)	90.0(4)	90.2(4)	C(1)–Fe–C(4)	89.5(5)	89.8(4)
C(2)–Fe–C(3)	89.1(5)	90.2(4)	C(2)–Fe–C(4)	88.9(5)	89.2(4)
C(3)–Fe–C(4)	122.0(5)	123.2(4)	Fe–C(1)–O(1)	177.5(4)	178.7(3)
Fe–C(2)–O(2)	173.8(4)	178.0(4)	Fe–C(3)–O(3)	178.8(4)	176.3(4)
Fe–C(4)–O(4)	179.3(5)	177.8(5)	M–O(5)–C(5)	126.1(3)	124.8(3)
M–O(6)–C(20)	121.3(3)	118.1(3)	O(6)–C(20)–C(21)	118.0(4)	116.7(4)
O(5)–C(5)–C(6)	121.1(4)	119.8(4)	O(6)–C(20)–C(25)	120.4(4)	119.2(4)
O(5)–C(5)–C(10)	119.5(4)	119.7(4)	C(25)–C(20)–C(21)	121.4(5)	124.1(4)
C(10)–C(5)–C(6)	119.1(5)	120.4(4)	C(20)–C(21)–C(22)	119.0(5)	116.3(4)
C(5)–C(6)–C(7)	119.8(5)	117.7(5)	C(20)–C(21)–C(26)	124.4(5)	124.4(4)
C(5)–C(6)–C(11)	122.7(5)	122.8(4)	C(22)–C(21)–C(26)	116.5(5)	119.1(4)
C(7)–C(6)–C(11)	117.5(5)	119.4(5)	C(21)–C(22)–C(23)	118.8(5)	122.7(5)
C(6)–C(7)–C(8)	119.7(5)	122.8(5)	C(22)–C(23)–C(24)	121.1(5)	117.5(5)
C(7)–C(8)–C(9)	119.2(5)	117.9(5)	C(22)–C(23)–C(30)	119.9(6)	121.5(5)
C(7)–C(8)–C(15)	119.5(6)	122.0(5)	C(24)–C(23)–C(30)	118.9(6)	120.8(5)
C(9)–C(8)–C(15)	121.2(6)	120.0(5)	C(23)–C(24)–C(25)	120.4(5)	122.8(5)
C(8)–C(9)–C(10)	121.0(5)	121.4(5)	C(24)–C(25)–C(20)	118.0(5)	115.7(4)
C(9)–C(10)–C(5)	119.7(5)	118.6(5).	C(24)–C(25)–C(31)	118.2(5)	119.7(5)
C(9)–C(10)–C(16)	117.3(5)	118.5(5)	C(20)–C(25)–C(31)	123.8(5)	124.4(4)
C(5)–C(10)–C(16)	123.0(5)	122.9(5)	C(21)–C(26)–C(27)	109.0(5)	109.0(5)
C(6)–C(11)–C(12)	111.9(5)	112.4(5)	C(21)–C(26)–C(28)	111.9(6)	110.6(5)
C(6)–C(11)–C(13)	110.7(5)	111.5(5)	C(21)–C(26)–C(29)	111.4(5)	111.5(5)
C(6)–C(11)–C(14)	109.5(5)	108.4(4)	C(27)–C(26)–C(28)	108.0(6)	107.7(6)
C(12)–C(11)–C(13)	107.4(6)	107.5(6)	C(27)–C(26)–C(29)	109.9(6)	111.6(5)

TABLE 4 (continued)

	M = Ge	M = Sn		M = Ge	M = Sn
C(12)–C(11)–C(14)	111.5(6)	112.3(5)	C(28)–C(26)–C(29)	106.6(6)	106.3(6)
C(13)–C(11)–C(14)	105.6(6)	104.5(5)	C(25)–C(31)–C(32)	111.1(6)	110.1(5)
C(10)–C(16)–C(17)	110.6(6)	109.8(6)	C(25)–C(31)–C(33)	110.8(6)	110.6(6)
C(10)–C(16)–C(18)	110.5(6)	110.2(6)	C(25)–C(31)–C(34)	110.1(6)	109.1(5)
C(10)–C(16)–C(19)	109.6(6)	108.5(6)	C(32)–C(31)–C(33)	108.1(7)	109.3(7)
C(17)–C(16)–C(18)	106.9(7)	109.0(7)	C(32)–C(31)–C(34)	111.7(7)	113.0(7)
C(17)–C(16)–C(19)	113.5(7)	113.3(7)	C(33)–C(31)–C(34)	104.8(7)	104.6(7)
C(18)–C(16)–C(19)	105.6(7)	106.0(7)			

Mean planes

M = Ge

Plane 1 Fe–Ge–C(1)–C(2) $0.9989x + 0.0349y + 0.0308z - 1.3675 = 0$

Plane 2 Fe–Ge–C(3)–C(4) $-0.0437x + 0.7901y + 0.6114z - 10.33067 = 0$

Plane 3 Ge–O(5)–O(6) $0.9992x - 0.0292y - 0.0269z - 0.4119 = 0$

Deviations (Å): Plane 1			*Plane 2*		
	Fe	−0.004		Fe	0.012
	Ge	0.000		Ge	−0.003
	C(1)	0.002		C(3)	−0.004
	C(2)	0.002		C(4)	−0.004

Dihedral Angles (°): Plane 1/Plane 3 = 4.9; Plane 2/Plane 3 = 85.2

M = Sn

Plane 1 Fe–Sn–C(1)–C(2) $0.9994x + 0.0268y + 0.0242z - 1.2138 = 0$

Plane 2 Fe–Sn–C(3)–C(4) $-0.0374x + 0.7852y + 0.6181z - 10.5599 = 0$

Plane 3 Sn–O(5)–O(6) $0.9986x - 0.0378y - 0.0383z - 0.1709 = 0$

Deviations (Å): Plane 1			*Plane 2*		
	Fe	−0.009		Fe	0.020
	Sn	0.000		Sn	−0.005
	C(1)	0.004		C(3)	−0.007
	C(2)	0.004		C(4)	−0.007

Dihedral angles (°): Plane 1/Plane 3 = 5.2; Plane 2/Plane 3 = 84.8

TABLE 5

COMPARATIVE STRUCTURAL DATA FOR GROUP 14 METAL(II) COMPLEXES MX_2 AND THEIR TRANSITION-METAL COMPLEXES OF TYPE **B** [a]

Compound MX_2 or **B**	$X\hat{M}X$ (°)	⟨M–X⟩ (Å)	Ref.
GeR_2	107(2) [b]	2.04(2) [b]	11
SnR_2	96(1) [b]	2.24(1) [b]	12
$[Cr(CO)_5(GeR_2)]$	102.8(2)	1.98(2)	4
$[Cr(CO)_5(SnR_2)]$	98	2.18(1)	5
$Ge(NR'_2)_2$	101(1.5) [b]	1.89(1) [b]	13
$Sn(NR'_2)_2$	96 [b], 104.7(2)	2.09(1) [b], 2.09(1)	13
$[Pd\{Sn(NR'_2)_2\}_3]$	107(1)	2.08(2)	8
$[Pt\{Sn(NR'_2)_2\}_3]$	104(1)	2.1(2)	7
$Ge(OAr)_2$	92.0(4)	1.80(2)	14
$Sn(OAr)_2$	88.4(2)	2.01(2)	14
eq-$[Fe(CO)_4\{Ge(OAr)_2\}]$ (II)	93.5(2)	1.777(8)	This work
eq-$[Fe(CO)_4\{Sn(OAr)_2\}]$ (III)	92.2(2)	1.974(15)	This work

[a] Abbreviations: $R = CH(SiMe_3)_2$, $R' = SiMe_3$, $Ar = C_6H_2Bu^t_2$-2,6-Me-4. [b] In the vapour (gas-phase electron diffraction); other data are for the crystal (X-ray).

TABLE 6

COMPARATIVE X-RAY DATA FOR SOME TRIGONAL BIPYRAMIDAL COMPLEXES *trans-ax-*[Fe(CO)$_3$(L)(PX$_2$X′)]

L	PX$_2$X′	Fe–P (Å)	Ref.
CO	$PHPh_2$	2.237(2)	25
CO	PPh_3	2.244(1)	32
CO	$PPh_2(CH_2)_2PPh_2$	2.246(2)	28
CO	$P(NMe_2)_3$	2.245(1)	33
CO	PBu^t_3	2.364(1)	24
CO	$\mathrm{P}\overline{\mathrm{F\{N(Me)(CH_2)_2N}}\mathrm{Me\}}$	2.174(1)	34
L^{Me}	PEt_3	2.208(6)	This work

ax-[Fe(CO)$_4${$\overline{\mathrm{CN(Me)(CH)_2N}}$Me}] (IV) [25] suggests that for axial ligands in such tbp complexes the *trans*-influence decreases in the sequence of CO > PEt$_3$; this is based on the assumption that the nature of the carbene ligand L^{Me} or :$\overline{\mathrm{CN(Me)(CH)_2N}}$Me has a negligible effect on the Fe–C_{carb} bond length. Other comparisons are based on Fe–P bond lengths in a series of complexes *ax*-[Fe(CO)$_3$(L)(PX$_2$X′)], Table 6; the longer the Fe–P bond, the greater is the *trans*-influence of L. Hence, the above order can be extended to CO > PX$_2$X′ > L^{Me} (except for the strong π-accepting F-containing-phosphine ligand, when the P/C_{carb} order is reversed). These conclusions are consistent with the proposition that electron-rich carbene ligands such as L^{Me} are good σ-donors but poor π-acceptors. The *ax*-form of [Fe(CO)$_4${C(H)OH}] was calculated (ab initio MO) to be more stable than the *eq*-isomer [31].

The *ax*/*eq* problem for tbp d^8 metal carbonyls has most recently been analysed for the series [M′(CO)$_4$(EPh$_3$)] [26]. In the crystal, the *ax* conformation was general for M′ = Fe and Ru and E = P, As, or Sb, except for *eq*-[M′(CO)$_4$(SbPh$_3$)] (M′ = Ru or Os); for M′ = Os and E = As the conformation was *ax*. Thus, for the Group 15 element (*E*)-centred ligands *eq*-preference appears to increase with increasing atomic number of E. The complex [Ru(CO)$_4$(SbMe$_3$)] also was the *ax*-conformer. A careful analysis of steric and electronic factors in influencing the *ax*/*eq* preference in the series [M′(CO)$_4$(EPh$_3$)] (M′ = Fe, Ru, or Os; E = P, As, or Sb) led to the conclusion that the dominant factor was the σ-donor character of the EPh$_3$ ligand, with its π-acceptor capacity or steric effect having a less significant role [26]. Thus, poor σ-donors and good π-acceptors were believed to favour the equatorial site, consistent with theoretical studies [23,35].

Evidently, the similar trend (i.e., that the *eq*-preference is found for a heavier ligating element) now revealed for Group 14 elements has some precedent. The overwhelming cause appears to be the better π-acceptor character of M(OAr)$_2$ (M = Ge or Sn) than of the carbene ligand such as L^{Me}. That the Group 14 metal(II) aryloxides are effective ligands in transition metal chemistry is consistent with the suggestion that they are effective π-acceptors; the electronegative oxygens in their α-positions, make it likely that they are poor σ-donors and certainly weaker in this respect than MR$_2$, M(NR′$_2$)$_2$, or M(SAr″)$_2$ (R = CHR′$_2$, R′ = SiMe$_3$, Ar″ = $C_6H_2Me_3$-2,4,6). However, the ligands M(OAr)$_2$ are very bulky, and this may well be a contributory factor.

TABLE 7

COMPARATIVE Fe–C BOND LENGTH DATA FOR SOME TRIGONAL BIPYRAMIDAL COMPLEXES *eq*-[Fe(CO)$_4$L]

L	Fe–C$_{ax}$ (Å)		Fe–C$_{eq}$ (Å)		Ref.
$C_{12}H_8$ [a]	1.812(3)	1.815(3)	1.804(4)	1.783(4)	38
PPh(PPh$_2$)$_2$	1.785(6)	1.791(6)	1.775(6)	1.785(6)	19
P(CR'$_2$)NR'$_2$ [b]	1.795(4)	1.787(4)	1.794(4)	1.768(7)	20
Ge(OAr)$_2$ [c]	1.827(11)	1.795(11)	1.771(11)	1.766(13)	This work
Sn(OAr)$_2$ [c]	1.809(9)	1.808(10)	1.807(12)	1.810(11)	This work
P(NEt$_2$)$_2$$^+$	1.80(2)	1.76(4)	1.81(1)	1.83(4)	30

[a] Acenaphthylene. [b] R' = SiMe$_3$. [c] Ar = $C_6H_2Bu^t_2$-2,6-Me-4.

Some comparative Fe–CO bond length data for a series of complexes *eq*-[Fe(CO)$_4$L], including those for complexes II and III, are listed in Table 7; but no significant trends are evident. Molecular orbital calculations in [Fe(CO)$_4$(SnH$_2$)]$^{2-}$ suggest an *ax* = tbp conformation [39]; the SnMe$_2$ analogue has been prepared [40].

Experimental

General procedures

All experiments were performed under argon using freshly distilled, dry, degassed solvents. ^{1}H NMR spectra were recorded on a Varian T60 (60 MHz) spectrometer,

TABLE 8

CRYSTAL DATA AND REFINEMENT PARAMETERS FOR *trans*-[Fe(CO)$_3$(L^{Me})(PEt$_3$)] (I) and *eq*-[Fe(CO)$_4${M(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_2$}] (M = Ge (II) or M = Sn (III))

	I	II	III
Crystal dimensions (mm^3)	0.65×0.25×0.10	0.23×0.25×0.41	ca. spherical, diameter 0.25
Diffractometer	Hilger and Watts Y290	Syntex P2$_1$	Syntex P2$_1$
M	356.2	679.18	725.28
Crystal system	Orthorhombic	Monoclinic	Monoclinic
a (Å)	15.952(12)	19.535(5)	19.342(3)
b (Å)	7.982(7)	9.426(1)	9.600(1)
c (Å)	28.444(8)	37.766(7)	38.176(1)
β (°)		94.27(2)	94.33(1)
U (Å)	3621.7	6935(2)	7068(2)
D_c (g cm^{-3})	1.306	1.301	1.363
F(000)	1504	2848	2992
Space group	$P_{ca}2_1$	$I2/c$	$I2/c$
μ(Mo-K_α) (cm^{-1})	9.5	13.89	11.73
2θ limits (°)	50	48	50
Reflections used in refinements [$I \geqslant 3\sigma(I)$](measured)	2896	2411 (5477)	3184 (6275)
Z	8	8	8
R	0.070	0.053	0.047
R'	0.087	0.065	0.049
Max residuals (eÅ^{-3})	0.7	0.5	0.52

TABLE 9

FINAL ATOM COORDINATES ($\times 10^4$), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR *trans*-[Fe(CO)$_3$(L^{Me})(PEt$_3$)] (I)

Atom	x	y	z	
Molecule a				
Fe(1)	−2370.1(7)	2892.5(13)	3444.9(6)	
P(1)	−1768(1)	4845(3)	3015(1)	
N(1)	−3695(8)	378(13)	3573(5)	
N(2)	−3044(7)	790(13)	4221(4)	
O(1)	−898(7)	2972(20)	4051(5)	
O(2)	−2169(9)	581(14)	2653(5)	
O(3)	−3796(7)	5098(14)	3604(5)	
C(1)	−3055(6)	1248(11)	3776(4)	
C(2)	−1479(6)	2951(12)	3833(4)	
C(3)	−2231(9)	1464(17)	2984(4)	
C(4)	−3242(6)	4222(11)	3531(4)	
C(5)	−4160(9)	−693(17)	3892(8)	
C(6)	−3634(12)	−640(20)	4340(7)	
C(7)	−4109(8)	628(21)	3126(5)	
C(8)	−2507(10)	1389(29)	4590(5)	
C(9)	−2480(11)	5849(28)	2585(8)	
C(10)	−2986(8)	4840(23)	2291(5)	
C(11)	−954(10)	4281(20)	2573(7)	
C(12)	−267(7)	3201(28)	2785(5)	
C(13)	−1241(11)	6615(24)	3314(9)	
C(14)	−1743(13)	7383(17)	3690(8)	
Molecule b				
Fe(1)A	−111.7(7)	−1817.7(14)	5770.5(6)	
P(1)A	−727(1)	207(3)	6176(1)	
N(1)A	1195(5)	−4392(13)	5620(4)	
N(2)A	571(8)	−3862(13)	4966(4)	
O(1)A	−1650(6)	−2088(14)	5224(4)	
O(2)A	−320(8)	−4016(14)	6574(4)	
O(3)A	1295(4)	414(13)	5605(3)	
C(1)A	561(6)	−3453(11)	5429(3)	
C(2)A	−1035(7)	−2005(14)	5435(4)	
C(3)A	−206(7)	−3187(12)	6273(5)	
C(4)A	720(5)	−429(12)	5661(3)	
C(5)A	1610(8)	−5396(13)	5274(7)	
C(6)A	1061(3)	−5214(21)	4840(7)	
C(7)A	1557(10)	−4187(21)	6086(7)	
C(8)A	−62(14)	−3200(30)	4616(5)	
C(9)A	−247(16)	1029(40)	6682(11)	
C(10)A	493(13)	614(24)	6884(5)	
C(11)A	−1747(16)	−192(31)	6372(14)	
C(12)A	−2168(10)	−1399(26)	6441(9)	
C(13)A	−906(28)	2093(27)	5907(8)	
C(14)A	−848(11)	2621(17)	5468(6)	
Molecule a				
H(1)	−4781	−199	3954	C(5)
H(2)	−4208	−1953	3757	C(5)
H(3)	−3298	−1799	4394	C(6)
H(4)	−4010	−366	4646	C(6)
H(5)	−3730	1429	2906	C(7)

(continued)

TABLE 9 (continued)

H(6)	−4713	1206	3183	C(7)
H(7)	−4194	−569	2955	C(7)
H(8)	−2662	759	4914	C(8)
H(9)	−2593	2722	4632	C(8)
H(10)	−1861	1134	4500	C(8)
H(11)	−2093	6603	2357	C(9)
H(12)	−2897	6652	2782	C(9)
H(13)	−3356	5635	2065	C(10)
H(14)	−3398	4083	2505	C(10)
H(15)	−2594	4034	2080	C(10)
H(16)	−676	5417	2438	C(11)
H(17)	−1247	3602	2289	C(11)
H(18)	191	2903	2519	C(12)
H(19)	−539	2057	2919	C(12)
H(20)	32	3872	3068	C(12)
H(21)	−1099	7563	3056	C(13)
H(22)	−665	6157	3468	C(13)
H(23)	−1394	8398	3847	C(14)
H(24)	−1886	6456	3955	C(14)
H(25)	−2320	7863	3543	C(14)
Molecule b				
H(1)A	2235	−4936	5206	C(5)A
H(2)A	1642	−6687	5386	C(5)A
H(3)A	685	−6320	4787	C(6)A
H(4)A	1429	−4955	4530	C(6)A
H(5)A	1157	−3388	6295	C(7)A
H(6)A	2170	−3625	6056	C(7)A
H(7)A	1611	−5397	6253	C(7)A
H(8)A	−389	−2145	4768	C(8)A
H(9)A	−506	−4177	4533	C(8)A
H(10)A	256	−2808	4300	C(8)A
H(11)A	−704	833	6956	C(9)A
H(12)A	−191	2353	6610	C(9)A
H(13)A	592	1375	7193	C(10)A
H(14)A	996	827	6637	C(10)A
H(15)A	483	−692	6983	C(10)A
H(16)A	−2114	440	6107	C(11)A
H(17)A	−1785	495	6698	C(11)A
H(18)A	−2792	−1036	6548	C(12)A
H(19)A	−1875	−2107	6720	C(12)A
H(20)A	−2204	−2162	6128	C(12)A
H(21)A	−491	2932	6093	C(13)A
H(22)A	−1548	2371	6001	C(13)A
H(23)A	−1017	3929	5450	C(14)A
H(24)A	−1270	1899	5251	C(14)A
H(25)A	14	2460	5343	C(14)A

IR spectra were obtained as dilute solutions between NaCl plates, using a Perkin–Elmer 597 spectrophotometer. Melting points were determined using an electrothermal melting point apparatus and are uncorrected. The complex *trans*-[$Fe(CO)_3(L^{Me})(PEt_3)$] [16], and $M(OAr)_2$ ($M = Ge$ or Sn) [14], were prepared by literature methods. A representative preparative procedure for one of the tetracarbonyl[Group 14 metal(II) aryloxide]iron(0) complexes II or III is given below.

Preparation of eq-$[Fe(CO)_4\{Ge(OAr)_2\}]$ *(Ar =* $C_6H_2Bu^t{}_2$*-2,6-Me-4) (II)*

The germylene $Ge(OAr)_2$ (0.51 g, 1.1 mmol) was added in portions during 0.5 h to a stirred suspension of $[Fe_2(CO)_9]$ (0.18 g, 0.5 mmol) in benzene (15.0 cm³). The solution became "muddy" in colour. The reaction mixture was warmed (ca. 70°C)

TABLE 10

FINAL ATOMIC COORDINATES ($\times 10^4$), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR *eq*-$[Fe(CO)_4\{M(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2\}]$ (M = Ge (II) or M = Sn (III))

Atom	M = Ge			M = Sn		
	x	*y*	*z*	*x*	*y*	*z*
M	991.6(5)	2015.7(12)	3839.1(3)	991.4(3)	2015.1(6)	3853.2(2)
Fe	1053.9(7)	573.4(16)	4311.8(4)	1058.0(7)	483.2(13)	4354.3(3)
O(1)	1068(4)	−1912(8)	3837(2)	1064(4)	−1864(6)	3858(2)
O(2)	1063(5)	2827(9)	4844(2)	1088(5)	2787(8)	4866(2)
O(3)	−230(4)	−428(10)	4571(2)	−257(4)	−520(9)	4599(2)
O(4)	2379(5)	−316(12)	4641(3)	2388(5)	−456(11)	4684(3)
O(5)	896(3)	1698(7)	3374(1)	871(3)	1680(6)	3345(1)
O(6)	1008(3)	3888(6)	3788(2)	1015(3)	4063(6)	3787(1)
C(1)	1057(5)	−946(12)	4012(2)	1053(5)	−960(9)	4049(2)
C(2)	1059(6)	2010(13)	4624(3)	1077(6)	1912(11)	4663(2)
C(3)	271(6)	−23(12)	4468(3)	238(6)	−94(10)	4502(3)
C(4)	1858(7)	28(13)	4510(3)	1887(6)	−93(12)	4552(3)
C(5)	895(4)	389(11)	3211(2)	882(4)	376(10)	3187(2)
C(6)	280(4)	−315(10)	3134(2)	251(4)	−345(10)	3102(2)
C(7)	295(5)	−1708(11)	2982(2)	292(5)	−1702(10)	2981(2)
C(8)	925(5)	−2353(11)	2931(2)	917(5)	−2355(10)	2931(2)
C(9)	1528(5)	−1554(11)	2982(2)	1526(5)	−1564(11)	2981(2)
C(10)	1515(5)	−185(11)	3111(2)	1512(4)	−180(10)	3094(2)
C(11)	−443(5)	374(13)	3152(2)	−469(4)	323(12)	3136(2)
C(12)	−474(6)	1937(15)	3017(3)	−524(6)	1805(13)	2976(3)
C(13)	−1024(5)	−484(17)	2929(3)	−1060(5)	−573(16)	2949(3)
C(14)	−626(5)	268(13)	3544(3)	−623(5)	307(12)	3532(2)
C(15)	941(6)	−3899(12)	2805(3)	954(7)	−3871(12)	2818(3)
C(16)	2199(5)	683(14)	3120(3)	2207(5)	691(14)	3108(3)
C(17)	2069(7)	2175(14)	2960(4)	2063(7)	2140(14)	2955(4)
C(18)	2737(7)	−78(17)	2889(4)	2747(6)	−50(18)	2893(4)
C(19)	2542(6)	711(20)	3509(3)	2525(6)	717(20)	3493(3)
C(20)	1027(5)	4793(9)	4082(2)	1030(4)	4910(8)	4087(2)
C(21)	403(5)	5268(10)	4197(2)	383(4)	5318(9)	4202(2)
C(22)	404(5)	6028(10)	4521(3)	400(5)	6022(9)	4519(2)
C(23)	1035(6)	6367(11)	4703(3)	1023(5)	6346(10)	4718(2)
C(24)	1652(6)	6054(11)	4559(3)	1647(5)	6046(9)	4567(2)
C(25)	1657(5)	5282(9)	4239(2)	1671(4)	5329(8)	4247(2)
C(26)	−304(5)	5083(11)	3984(3)	−314(4)	5135(10)	3986(3)
C(27)	−244(6)	5593(15)	3596(3)	−258(6)	5751(14)	3618(3)
C(28)	−879(6)	5977(15)	4146(4)	−911(6)	5951(14)	4164(4)
C(29)	−547(5)	3500(12)	3984(3)	−538(5)	3604(11)	3968(3)
C(30)	1051(7)	7175(14)	5059(3)	1025(7)	7107(14)	5068(2)
C(31)	2349(5)	5058(11)	4077(3)	2370(4)	5135(10)	4086(3)
C(32)	2285(6)	5322(17)	3674(3)	2301(6)	5537(16)	3696(3)
C(33)	2906(7)	6091(17)	4248(5)	2945(6)	6055(16)	4283(4)
C(34)	2628(6)	3561(14)	4168(4)	2618(6)	3636(13)	4148(4)

and stirred for a further 0.5 h. Volatiles were removed in vacuo to give a golden solid; this was extracted into toluene, and the extract was filtered through celite, and concentrated in vacuo. Cooling (−30°C) afforded bright-yellow crystals of tetracarbonyl{bis(2,6-di-t-butyl-4-methylphenoxy)germanium(II)}iron(0) (II) [0.124 g, 18% based on $Ge(OAr)_2$]. The orange-brown *eq*-$[Fe(CO)_4\{Sn(OAr)_2\}]$ (III) [19% based on $Sn(OAr)_2$] was similarly obtained.

X-Ray structure determinations

In each case the data were measured by an $\omega/2\theta$ step scan using monochromated Mo-K_α radiation (λ 0.71069 Å) and a crystal sealed in a Lindemann glass capillary under argon. Structures were solved by heavy-atom methods and refined by full matrix least squares with non-hydrogen atoms anisotropic unless otherwise stated. Scattering factors and dispersion corrections were taken from ref. 36. The structure solutions and refinements for I were performed with the SHELX program of G.M. Sheldrick. For II and III a package of programs described elsewhere [37] was utilised.

Crystal data, instrumentation, and refinement parameters for each of *trans*-$[Fe(CO)_3(L^{Me})(PEt_3)]$ (I) and *eq*-$[Fe(CO)_4\{M(OAr)_2\}]$ [M = Ge (II) or M = Sn (III)] are summarised in Table 8. Final atom coordinates for the three complexes are in Tables 9 (I) and 10 ((II) and (III)). Tables of temperature factors, hydrogen atom positions (for (I) only), and final structure factors are available from A.J.C. (for (II) and (III)) or P.B.H. (I).

Hydrogen atoms for complex I were inclined at fixed calculated positions with isotropic temperature factors equivalent to those atoms they are bonded to. A trial refinement as the opposite enantiomorph showed no significant difference in residuals from those shown in Table 8.

For complexes II or III, some hydrogen atoms were apparent in the final difference Fourier; many were unclear and, in view of the data limitations, were not included in the refinement.

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