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Trinuclear Complexes from the Reactions of $[Fe_3(CO)_{12}]$ with Group VA Ligands

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The reactions of various P^{III}, As^{III}, *and* Sb^{III} *ligands, L, with* $[Fe_3(CO)_{12}]$ *under mild conditions give* $[Fe_3(CO)_{11}(L)]$, $[Fe_3(CO)_{10}(L)_2]$, *and* $[Fe_3(CO)_9\{P(OR)_3\}_3]$ *derivatives as well as the mononuclear* $[Fe(CO)_4(L)]$ *and* $[Fe(CO)_3(L)_2]$ *complexes. Cluster breakdown is greatest with phosphines and least with phosphites. Of the compounds thus obtained, only* $[Fe_3(CO)_9\{P(OR)_3\}_3]$ *(R =* ^iPr*, cyclo-*C_6H_{11} *and, perhaps, Et, o-*MeC_6H_4 *and p-*MeC_6H_4*) exist solely as non-bridged isomers in the solid state as well as in solution. The remainder are found as CO-bridged species in the solid state with structures that are probably based on that of the CO-bridged form of* $[Fe_3(CO)_{12}]$*. In solution, they isomerise to a mixture of the CO-bridged isomers together with others which do not have bridging ligands. The latter predominate. The i.r. spectra of the non-bridged tautomers do not allow any conclusions to be drawn as to their structures.*

Introduction

Although the structure adopted by $[Fe_3(CO)_{12}]$ in the solid state has been elucidated unambiguously [1, 2], the same cannot be said for the structure in solution. It is quite clear that the principal isomer present does not possess bridging carbonyl groups (*e.g.* ref. 3), but equally its i.r. spectrum bears no resemblance to that of $[Ru_3(CO)_{12}]$ or of $[Os_3(CO)_{12}]$ [4]. As the i.r. spectra [5] of the isostructural $[Mn_2(CO)_{10}]$ [6], $[Tc_2(CO)_{10}]$ [7], and $[Re_2(CO)_{10}]$ [8] are similar, it seems reasonable to assume that this *nb*† species does not have the $Os_3(CO)_{12}$ -type of structure with D_{3h} symmetry [9]. A number of attempts have been made to resolve this anomaly, but few are convincing. The most reasonable suggestion has been that due to Johnson [10]. He has suggested that the spatial distribution of carbonyl groups in this *nb* isomer is the same as in the *b* form found as the minor isomer in solution and the sole species in the solid state. The two differ in the orientation of the Fe_3 triangle within the icosahedron defined by the twelve CO ligands.

We felt that some insight into the above problem may be provided by replacement of one or more CO groups of $[Fe_3(CO)_{12}]$ by Group Va ligands. Particularly, we hoped that CO substitution may allow the isolation of tri-iron complexes without bridging carbonyl ligands in the same way as one of the non-bridged forms of $[Co_2(CO)_8]$ [11] may be isolated as *nb*-$[Co_2(CO)_6(PBu^n_3)_2]$ and its structure determined [12].

Most workers have found that the reactions of Group Va ligands, L, with $[Fe_3(CO)_{12}]$ give the well-known mononuclear $[Fe(CO)_4(L)]$ and *trans*-$[Fe(CO)_3(L)_2]$ complexes [13]. However, there have been reports of *tris*-iron complexes: $[Fe_3(CO)_{11}(PPh_3)]$ [14a], $[Fe_3(CO)_{12-n}\{P(OMe)_3\}_n]$ (n = 1,2, 3) [15], $[Fe_3(CO)_9(PMe_2Ph)_3]$ [16], $[Fe_3(CO)_{10}\{\overline{Me_2AsC{=}C(AsMe_2)CF_2CF_2}\}]$ [17], and $[Fe_3(CO)_{12-n}\{P(C{\equiv}CCF_3)Ph_2\}_n]$ (n = 1 or 2) [18]. CO-bridged isomers appear to be important in all instances. X-ray diffraction studies (references 14b, 16 and 17b) have confirmed the *b*-$Fe_3(CO)_{12}$ type of structure for some of these in the solid state.

We have undertaken a systematic study of the reactions of $[Fe_3(CO)_{12}$ with tertiary phosphites, phosphines, arsines, and stibines, L, under mild conditions. A number of *tris*-iron complexes have been prepared. The i.r. spectra of these $[Fe_3(CO)_{12-n}(L)_n]$ (n = 1, 2 or 3) derivatives have been recorded both in the solid state and in solution.

Experimental

Literature methods were used to prepare $[Fe_3(CO)_{12}]$ [19] and certain of the Group V ligands [20, 21], whilst others were purchased. All reactions were carried out in purified solvents under an atmosphere of nitrogen at 50 °C.

The general procedure adopted during all of the reactions was as follows. A solution of the ligand, L, in benzene was added dropwise over a period of *ca.* 1–2 hr to a stirred solution of $[Fe_3(CO)_{12}]$ (*ca.* 1–2 g) in the same solvent (50 ml). The (L) : $[Fe_3(CO)_{12}]$ mol ratios used were 1:1, 2:1 and 5:1 to obtain as the principal products $[Fe_3(CO)_{11}(L)]$, $[Fe_3(CO)_{10}(L)_2]$,

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† *b* = CO-bridged, *nb* = non-bridged.

and $[Fe_3(CO)_9(L)_3]$ respectively. The reaction mixtures were stirred for a further 2–4 hr until most or all of the $[Fe_3(CO)_{12}]$ had been consumed. The solvents were then removed at reduced pressures, the residues extracted with benzene/hexane mixtures, and chromatographed on alumina or silica gel using the same solvent mixture as eluant. The various fractions were collected, their solvents removed at reduced pressures, and the residues recrystallized from mixtures of hexane with dichloromethane or toluene. The melting points, yields, and analyses of the products are summarised in Table I.

$[Fe_3(CO)_9\{P(OPh)_3\}_3]$ was also prepared using the above method, but by replacing $[Fe_3(CO)_{12}]$ with $[Fe_3(CO)_{10}\{P(OPh)_3\}_2]$. The yield of product was 48%.

Infrared spectra were obtained on a Perkin Elmer 337 i.r. spectrometer equipped with a Hitachi-Perkin Elmer 56 readout recorder; and calibrated using gaseous DCl and DBr [22]. They are summarised in Tables II and III.

Results and Discussion

The reactions of $[Fe_3(CO)_{12}]$ with Group Va ligands give a mixture of complexes of the general formula $[Fe_3(CO)_{12-n}(L)_n]$. All are green solids which, like dodecacarbonyltriiron, decompose more or less slowly in air at room temperature, and more rapidly in solution. The phosphite derivatives are more stable than those of the phosphines, arsines and stibines respectively. All are soluble in the usual organic solvents.

The reaction yields (Table I) are apparently rather low, due perhaps to the separation and isolation of the products requiring chromatography, which appears to result in much decomposition. Thus $[Fe_3(CO)_{11}P(OR)_3]$ derivatives may only be obtained using a silica gel column; on alumina their colour slowly fades and they may not be isolated. Furthermore, the formation of the $[Fe_3(CO)_{12-n}(L)_n]$ complexes is accompanied in most instances by cluster breakdown to give the well-known $[Fe(CO)_4(L)]$ and $[Fe(CO)_3(L)_2]$ compounds [13]. This process may be monitored by i.r. spectroscopy, and it can be seen that the degree of fragmentation increases along the series $L = R_3Sb \sim (RO)_3P < R_3As < R_3P$. It is promoted by higher reaction temperatures, or too rapid addition of the ligand. Also, we found that the presence of phosphine oxides in the tertiary phosphines caused the formation of mononuclear compounds and reduced the yields of $[Fe_3(CO)_{12-n}\{PR_3\}_n]$, sometimes to zero. Prior distillation of the phosphine alleviated this problem.

Mono-, di-, and tri-substituted complexes of the phosphite ligands may be prepared, but only the first two series could be obtained for $Ph(MeO)_2P$, tertiary phosphines, arsines or stibines, except for Ph_3P, Ph_3As and Ph_3Sb which gave only the first. These results were surprising in view of the preparation of $[Fe_3(CO)_9\{P(Me)_2Ph\}_3]$ from a reaction in refluxing tetrahydrofuran [16]. Attempts to form more highly substituted derivatives than those listed in Table I were never successful. Only products resulting from cluster breaddown could be detected.

The i.r. spectra of all compounds between 1700 and 2100 cm^{-1} (Tables II and III) are similar in many respects to that of $[Fe_3(CO)_{12}]$ but with the anticipated successive lowering of the frequencies of the absorption bands due to the C–O stretching $\nu(CO)$ vibrations on replacement of CO with weaker π-acceptor ligands. The spectra are often poorly resolved. In most instances absorption bands are broad and have numerous shoulders. Only the best defined of these are quoted in Tables II and III.

The i.r. spectra of the monosubstituted derivatives $[Fe_3(CO)_{11}(L)]$ in the solid state may be divided into four groups. The first, where L = $(MeO)_3P$, $(EtO)_3P$ and Et_3P, show only two principal absorption bands in the 1900–2100 cm^{-1} region which may be attributed to the C–O stretching vibrations of their terminal CO ligands, $\nu(CO_t)$ modes. The second group, where L = Et_3Sb or $^nPr_3Sb$, show three such bands. The remainder of the complexes, except for $[Fe_3(CO)_{11}(AsMe_2Ph)]$ which constitutes group four, make up the third group. Their spectra are far more complicated and show up to eight absorption bands or well-defined shoulders in this region. The i.r. spectra of these three groups show two principal bands with frequencies between 1700 and 1850 cm^{-1}. These are due to the C–O stretching vibrations of bridging carbonyl groups, $\nu(CO_\mu)$ modes. However, the compounds of the third group often show extra shoulders. The variations in spectral complexity may be due to solid state effects, or they may be due to the presence of isomers in the solid state. This last is a distinct possibility as $[Fe_3(CO)_{11}(PPh_3)]$, which has a complicated i.r. spectrum, has been shown to exist as a 1:1 mixture of two separate CO-bridged isomers in its crystals [14]. In all spectra, the ratios of the intensities of the absorption bands due to the $\nu(CO_t)$ vibrations to those due to the $\nu(CO_\mu)$ modes are comparable. This strongly suggests that, whith the exception of $[Fe_3(CO)_{11}\{AsMe_2Ph\}]$, all of the monosubstituted derivatives exist solely as CO bridged forms in the solid state (*cf.* $[Fe_3(CO)_{11}(PPh_3)]$).

The sole member of the fourth group is $[Fe_3(CO)_{11}(AsMe_2Ph)]$. The very low intensity of its absorption bands in the $\nu(CO_\mu)$ region suggests either that they are not due to the fundamental vibrations of this type or that the CO-bridged species are not very important. In either event, *nb* isomers (or isomer) must predominate in solid samples of this compound.

TABLE I. Melting Points, Yields, and Analyses of Some $[Fe_3(CO)_{12-n}(L)_n]$ Complexes.

L	M.p. (°C)[a]	Yield	Analyses[b]	
			%C	%H
n = 1				
$(MeO)_3P$	69–70	12	27.6(28.0)	1.4(1.5)
$(EtO)_3P$	58–59	17	31.8(31.8)	2.6(2.3)
$(PhO)_3P$	110–112	8	44.2(44.4)	1.8(1.9)
$(o\text{-}CH_3C_6H_4O)_3P$	116–118	16	46.3(46.5)	2.8(2.5)
$(o\text{-}ClC_6H_4O)_3P$[c]	115–116	4	38.1(38.9)	1.8(1.4)
$(p\text{-}ClC_6H_4O)_3P$[d]	134–136	12	38.2(38.9)	1.4(1.4)
$Ph(MeO)_2P \cdot \frac{1}{2}CH_2Cl_2$	84–85	3	34.9(34.5)	1.4(1.8)
Et_3P	65	12	34.1(34.4)	2.9(2.5)
$PhMe_2P$	115–116	8	36.7(37.2)	1.9(1.8)
$PhEt_2P$	105 (dec.)	14	38.4(39.2)	2.2(2.3)
Ph_2MeP	94–96	8	42.7(42.5)	2.3(1.9)
Ph_2EtP	120–122	3	42.9(43.5)	2.6(2.2)
$Ph_2{}^iBuP$	115 (dec.)	1	45.1(45.0)	2.5(2.6)
$PhCH_2(Me)_2As$	73–75	11	37.5(37.6)	2.0(2.4)
$PhMe_2As$	95–97 (dec.)	1	34.2(34.6)	1.8(1.7)
$(p\text{-}FC_6H_4)Et_2As$[e]	105 (dec.)	19	35.4(35.8)	2.0(2.0)
Et_3Sb	48–50	16	29.4(29.8)	2.2(2.2)
${}^nPr_3Sb$	93–94	13	32.6(33.0)	3.0(2.9)
Ph_3Sb	98 (dec.)	12	41.6(42.0)	2.1(1.8)
n = 2				
$(MeO)_3P$	110–111	20	27.2(27.6)	2.5(2.6)
$(EtO)_3P$	108–110	25	33.4(33.8)	3.7(3.8)
$({}^iPrO)_3P$	104	17	38.6(38.9)	5.2(4.9)
$({}^sBuO)_3P$	88–89	20	42.8(43.1)	6.0(5.7)
$(C_6H_{11}O)_3P$	125 (dec.)	5	48.8(49.1)	6.3(6.0)
$(PhO)_3P$	111 (dec.)	16	51.9(51.6)	2.7(2.8)
$(o\text{-}CH_3C_6H_4O)_3P$	106–107	8	54.4(54.1)	3.7(3.6)
$(p\text{-}CH_3C_6H_4O)_3P \cdot \frac{1}{2}CH_2Cl_2$	106–108	18	53.0(52.7)	4.0(3.6)
$(p\text{-}ClC_6H_4O)_3P \cdot \frac{1}{2}CH_2Cl_2$	117–118	22	42.1(42.3)	1.9(1.9)
$Ph(MeO)_2P$	101–102	1	39.6(39.6)	2.7(2.8)
Et_3P	83–85	1	38.4(38.6)	4.7(4.4)
$PhMe_2P$	120–122 (dec.)	10	42.8(43.0)	3.1(3.4)
$PhEt_2P$	113 (dec.)	1	44.8(46.2)	3.8(3.9)
Ph_2MeP	89–91	3	50.9(51.0)	3.3(3.1)
Ph_2EtP	105–107 (dec.)	7	50.1(52.1)	3.8(3.4)
$Ph_2({}^iBu)P$	102–103	3	53.9(54.0)	3.8(4.1)
${}^nPr_3As$	97	9	39.2(39.2)	5.3(4.9)
$(PhCH_2)Et_2As$	110 (dec.)	1	43.0(42.8)	4.0(3.8)
$PhMe_2As$	100–102 (dec.)	33	38.0(38.4)	2.7(2.7)
$(p\text{-}FC_6H_4)Et_2As$[f]	98–99	9	39.6(39.9)	3.0(3.1)
Et_3Sb	85–87	12	30.3(30.6)	3.3(3.5)
${}^nPr_3Sb$	93–95	5	35.0(35.4)	4.2(4.4)
n = 3				
$(MeO)_3P$	108–110	9	27.0(27.3)	3.2(3.4)
$(EtO)_3P$	94–95	12	35.0(35.4)	4.8(4.9)
$({}^iPrO)_3P$	102–104	2	41.2(41.4)	6.0(6.1)
$(C_6H_{11}O)_3P$	118–120	0.2	53.4(53.8)	7.4(7.1)
$(PhO)_3P$	117–118	5	56.3(56.1)	3.6(3.3)
$(o\text{-}CH_3C_6H_4O)_3P$	101–103	18	59.0(58.6)	4.3(4.3)
$(p\text{-}CH_3C_6H_4O)_3P$	127–128	13	58.7(58.6)	4.5(4.2)
$(p\text{-}ClC_6H_4O)_3P$	134	11	45.3(45.6)	2.4(2.2)

[a] Determined in sealed tubes. (dec.) signifies melting with decomposition. [b] Found values with the calculated ones in parentheses. [c] %Cl = 12.4(11.9). [d] %Cl = 12.1(11.9). [e] %F = 2.8(2.7). [f] %F = 4.1(4.2).

TABLE II. The I.r. Spectra (1700–2100 cm^{-1}) of the $[Fe_3(CO)_{12-n}(L)_n]$ Complexes in the Solid State (KBr Pressed Discs).

L	Absorption Bands[a]				
n = 1					
$(MeO)_3P$	1797(5.7)	1831(5.2)			
$(EtO)_3P$	1799(3.3)	1839(3.0)			
$(PhO)_3P$	1790(2.0)	1827(1.3)		1953(1.3, sh)	1978(2.0, sh)
$(o\text{-}MeC_6H_4O)_3P$	1811(4.2)	1825(2.0)		1957(6.5)	
$(p\text{-}ClC_6H_4O)_3P$	1808(1.1)	1842(0.8)		1968(0.8, sh)	1987(1.8, sh)
Et_3P	1784(6.0)	1817(4.1)			
$PhMe_2P$	1794(6.7)	1823(5.6)		1935(2.7)	1959(5.8, sh)
Ph_2MeP	1778(3.7)	1817(1.9)		1935(1.1)	
Ph_2EtP	1805(1.0)	1836(0.7)		1938(1.9)	1964(2.8, sh)
$Ph_2(^{i}Bu)P$	1786(3.0)	1826(2.0)		1933(1.8)	1958(4.8)
Ph_3P	1781(2.4)	1830(2.2)		1949(5.4)	1955(4.3, sh)
$PhCH_2(Et)_2As$	1804(4.3)	1837(2.5)		1939(8.3)	1955(1.3)
$PhMe_2As$	1782(0.3)	1802(0.5)		1923(1.7, sh)	1936(2.0, sh)
Et_3Sb	1796(5.7)	1832(4.9)			
$^{n}Pr_3Sb$	1801(4.2)	1832(2.6)			1943(7.8)
Ph_3Sb	1812(2.7)	1844(1.2)			
n = 2					
$(MeO)_3P$	1780(7.5)	1818(6.6)			
$(EtO)_3P$	1790(1.2)	1826(0.7)		1953(3.8, sh)	
$(^{i}PrO)_3P$	1783(3.0)	1818(2.0)		1940(4.3)	1972(7.3, sh)
$(^{s}BuO)_3P$	1789(1.4)	1824(0.7)		1940(2.9)	1959(4.0)
$(C_6H_{11}O)_3P$	1772(2.3, sh)	1786(3.3)	1823(2.4)		1967(10, br)
$(PhO)_3P$	1797(0.9)		1875(0.5)	1934(2.1)	
$(o\text{-}MeC_6H_4O)_3P$	1793(2.4)	1828(2.0)		1950(4.2)	1972(7.7)
$(p\text{-}MeC_6H_4O)_3P$	1791(1.6)	1830(1.3)		1957(2.8)	1972(4.9)
$(p\text{-}ClC_6H_4O)_3P$	1790(2.7)	1829(1.8)		1957(5.1, sh)	
Et_3P	1774(7.5)	1825(3.2)			1922(7.8, sh)
$PhMe_2P$	1768(2.4)	1812(2.2)			1933(5.1)
$PhEt_2P$	1767(2.6)	1802(2.4)			1921(4.0)
Ph_2MeP	1803(3.0)	1768(4.2)			1925(4.5)
Ph_2EtP	1771(1.8)	1809(1.0)			1934(5.4)
$Ph_2(^{i}Bu)P$	1774(1.7)	1806(1.2)			1929(3.9)
$^{n}Pr_3As$	1772(2.2)	1804(1.6)			1932(4.8, sh)
$PhCH_2(Et)_2As$	1782(1.7)	1812(1.1)		1926(3.1)	1941(5.2)
$PhMe_2As$	1764(1.9)	1805(1.3)			1932(5.5)
$(p\text{-}FC_6H_4)Et_2As$	1763(1.4)	1803(0.8)		1948(3.5)	1952(2.7, sh)
Et_3Sb	1766(4.6)	1804(2.9)		1921(8.1)	1924(8.1)
$^{n}Pr_3Sb$	1773(4.3)	1804(3.3)			1926(6.9, sh)
n = 3					
$(MeO)_3P$	1770(4.3)	1812(3.6)			1909(1.6, sh)
$(EtO)_3P$	1779(0.5)	1809(0.5)			
$(^{i}PrO)_3P$			1890(1.0, sh)		1912(1.3, sh)
$(C_6H_{11}O)_3P$					
$(PhO)_3P$	1780(1.3)	1830(1.5)			1925(1.0, sh)
$(o\text{-}MeC_6H_4O)_3P$	1786(0.5)	1812(0.4)			
$(p\text{-}MeC_6H_4O)_3P$	1787(0.4)	1832(0.4)			1933(1.7, sh)
$(p\text{-}ClC_6H_4O)_3P$	1783(1.8)	1826(1.4)			1931(1.8, sh)

[a] Peak positions with relative peak heights in parentheses. br = broad and sh = well-defined shoulder. Those absorption bands

When the $[Fe_3(CO)_{11}(L)]$ derivatives, except for L = $PhMe_2As$, are dissolved in organic solvents, there is a marked decline in the intensities of their $\nu(CO_\mu)$ absorption bands; in some instances more than two of these may be observed. In such cases, it points to the presence of more than one bridged isomer. However, these are always the minor components in the solutions. Non-bridged (*nb*) species predominate, but the

1986(10.0, br)					2085(7.9)
1995(10.0, br)					2082(7.0)
1993(7.0)	2003(10)	2021(7.6, sh)	2034(5.6)	2048(6.7)	2093(7.0)
	2009(10.0)			2061(1.4, sh)	2085(3.8)
2003(8.9)	2008(7.3, sh)	2019(4.8, sh)	2035(10, br)		2092(2.7)
	1986(10, br)				2072(8.9)
1973(9.8)	1987(9.8)		2012(10, br)	2032(9.9, sh)	2082(9.5)
1976(6.1)		2007(10, br)		2024(10)	2081(6.9)
1983(4.9, sh)		2001(10)	2013(7.6, sh)	2028(6.5)	2078(3.9)
1976(8.0)	1986(8.6)	2002(10, br)		2036(9.4)	2080(8.0)
1978(7.2)	1993(8.1)	2022(10)		2041(6.7, sh)	2083(7.6)
1978(7.0)	1997(10, sh)	2009(10)	2030(8.3, sh)	2039(7.5, sh)	2075(6.1)
1964(5.2, sh)	1973(6.9, sh)	1987(10)	2019(7.6)		2080(2.8)
1959(10)			2023(9.2)		2070(8.5)
		2003(10)			2075(8.4)
			2019(9.4, br)	2032(7.0, sh)	2080(7.0)
1981(10, br)					2061(3.9)
	1990(10, br)		2010(10)		2059(0.9)
	1996(10, br)				2059(1.5)
1984(9.1, br)			2011(10)		2056(0.8)
					2052(3.4)
	1992(7.1)	2002(7.6)	2017(10)	2022(10, sh)	2063(0.5)
1982(7.2)	1997(10)	2006(8.9, sh)	2022(10)		2065(1.8)
	1996(10)	2002(9.2, sh)	2021(8.8)		2065(1.0)
1986(9.7, sh)	1997(10)		2024(8.3, sh)	2050(1.8)	2070(2.2)
	1940(9.0, sh)	1960(10, br)	1993(10)	2008(10, sh)	2046(4.0)
1943(5.1)	1946(4.6, sh)	1966(4.9, sh)	1993(10)	2001(8.5, sh)	2047(0.5)
	1945(5.0)	1957(4.8)	1995(10)	2003(9.4, sh)	2049(1.5)
	1950(6.2, sh)	1963(8.2, sh)	1977(10)	2007(9.4, sh)	2048(2.0)
	1965(9.5)	1984(9.1)	2001(10)	2012(5.0, sh)	2048(1.8)
	1960(6.9, sh)	1974(10)		2004(9.2, sh)	2047(0.9)
	1958(10)		1999(9.1)		2039(0.7)
1952(5.1, sh)	1963(10)	1972(10, br)	1998(7.0)	2007(8.7)	2041(0.6)
	1941(5.5)	1967(8.2, sh)	1989(10, br)		2044(0.5)
1962(3.2, sh)	1974(5.6, sh)	1981(10)	1999(6.7)	2003(5.5, sh)	2044(0.5)
1938(8.4, sh)		1959(9.7)	1993(10, br)	2040(2.1)	2068(0.3)
	1958(10, br)	1999(10, br)	2025(3.9, sh)	2039(2.3, sh)	2081(0.7)
1931(3.3, sh)	1949(7.5, sh)	1969(10, br)	1984(9.8, sh)	2039(7.1)	2054(0.2)
1928(0.9)		1966(10, br)	1979(8.5, sh)	2034(1.0)	2052(0.1)
	1953(10, br)	1960(8.8, sh)	1974(6.3, sh)	2031(0.3)	
	1957(10, br)		2006(1.0)		2053(0.4)
1959(6.0)	1969(6.4)	1984(9.0)	1999(10)	2048(4.9)	2064(0.6)
1955(4.0, sh)	1969(6.3, sh)	1984(10, br)		2046(0.8)	2063(0.3)
	1965(7.8, sh)	1980(10, br)		2047(1.9)	2058(0.4)
	1965(7.2, sh)	1986(10, br)		2053(4.3)	2067(1.0)

having frequencies below 1900 cm^{-1} are due to $\nu(CO_{\mu})$ vibrations; the remainder are due to the $\nu(CO_{t})$ modes.

numbers and relative intensities of absorption bands due to their $\nu(CO_t)$ vibrations cannot be determined definitely, and provide no guide as to the numbers of such isomers which are present or to their structure.

Many of the comments made about the spectra of the monosubstituted compounds apply equally to those of the disubstituted derivatives, $[Fe_3(CO)_{10}(L)_2]$. For example, where L = $(MeO)_3P$ the spectrum

TABLE 111. The I.r. Spectra (1700–2100 cm^{-1}) of $[Fe_3(CO)_{12-n}(L)_n]$ Complexes in Carbon Disulphide Solution.

L	Absorption Bands[a]				
n = 1					
$(MeO)_3P$		1809(0.5)	1842(0.2)		
$(EtO)_3P$		1811(0.6)	1843(0.4)		
$(PhO)_3P$		1813(0.5)	1844(0.4)		1972(0.8, sh)
$(o\text{-}MeC_6H_4O)_3P$	1792(sh)	1804(0.2)	1838(0.1)		1966(1.2, sh)
$(o\text{-}ClC_6H_4O)_3P$	1803(sh)	1815(0.5)	1846(0.2)		1972(0.7, sh)
$(p\text{-}ClC_6H_4O)_3P$	1793(sh)	1805(0.3)	1840(0.2)	1963(0.7)	
$Ph(MeO)_2P$	1799(0.4)	1829(0.3)	1814(0.1, sh)		
Et_3P	1795(0.6)	1826(0.3)		1963(0.8, sh)	1972(2.2)
$PhMe_2P$	1792(0.5)	1827(0.4)			1981(1.9, sh)
$PhEt_2P$	1794(0.4)	1832(0.3)		1958(0.6, sh)	1985(1.8, sh)
Ph_2MeP	1789(0.5)	1822(0.4)			1985(1.7, sh)
Ph_2EtP	1783(0.3)	1825(0.2)		1963(0.7, sh)	1984(1.9, sh)
$Ph_2(^iBu)P$	1793(0.5)	1829(0.5)		1954(0.6, sh)	1983(1.8, sh)
Ph_3P	1792(0.3)	1825(0.2)			1982(2.0)
$PhCH_2(Et)_2As$	1791(0.4)	1821(0.3)		1968(1.0, sh)	1978(2.4)
$PhMe_2As$	1794(0.3)	1823(0.3)			1981(2.0, sh)
$(p\text{-}FC_6H_4)Et_2As$	1787(0.8)	1815(0.7)		1957(1.2, sh)	1983(2.7, sh)
Et_3Sb	1794(0.2)	1817(0.4)	1844(0.4)	1963(1.2, sh)	1977(3.0, sh)
$^nPr_3Sb$	1792(sh)	1813(0.2)	1842(sh)		1976(3.2)
Ph_3Sb	1795(0.2, sh)	1819(0.2)	1846(0.2)	1963(0.2)	
n = 2					
$(MeO)_3P$	1791(0.5)		1828(0.4)	1965(2.0, sh)	1978(3.5, sh)
$(EtO)_3P$	1791(1.0)		1828(0.6)	1958(2.0, sh)	1975(3.8, sh)
$(^iPrO)_3P$	1791(0.8)		1828(0.6)	1954(2.2, sh)	1973(3.8, sh)
$(^sBuO)_3P$	1792(1.0)		1829(0.7)	1949(3.6, sh)	1970(9.7, sh)
$(C_6H_{11}O)_3P$	1789(0.9)	1803(0.4, sh)	1828(0.6)	1949(1.5, sh)	1970(3.3, sh)
$(PhO)_3P$	1797(0.7)		1830(0.4)	1957(1.1, sh)	
$(o\text{-}MeC_6H_4O)_3P$	1794(0.6)		1831(0.5)	1953(1.2, sh)	1973(2.0, sh)
$(p\text{-}MeC_6H_4O)_3P$	1795(0.7)	1805(0.6, sh)	1831(0.5)	1957(1.3, sh)	1976(2.1, sh)
$(p\text{-}ClC_6H_4O)_3P$	1789(0.5)		1831(0.5)	1960(1.8, sh)	1982(4.0, sh)
$Ph(MeO)_2P$	1775(0.7)		1818(0.4)	1931(2.2, sh)	
Et_3P	1779(0.7)		1817(0.5)	1932(1.1, sh)	1955(2.5, sh)
$PhMe_2P$	1775(1.0)		1813(0.8)	1938(1.0, sh)	1958(3.4, sh)
$PhEt_2P$	1776(0.9)		1814(0.6)		1949(2.4, sh)
Ph_2MeP	1773(0.9)		1815(0.7)	1938(1.2, sh)	
Ph_2EtP	1778(0.8)		1818(0.5)	1935(1.0, sh)	
$Ph_2(^iBu)P$	1776(0.6)		1815(0.7)	1934(1.2, sh)	1946(1.8, sh)
$^nPr_3As$	1776(0.6)		1811(0.6)	1938(1.2, sh)	1952(4.8, sh)
$PhCH_2(Et)_2As$	1780(0.7)		1815(0.5)	1933(1.5, sh)	1954(2.8, sh)
$PhMe_2As$	1776(0.8)		1813(0.5)	1938(1.1, sh)	1956(3.0, sh)
$(p\text{-}FC_6H_4)Et_2As$	1776(0.8)		1811(0.7)	1936(1.2, sh)	1956(2.8, sh)
Et_3Sb	1777(0.7)		1811(0.5)	1934(1.7, sh)	1950(3.7, sh)
$^nPr_3Sb$	1772(0.7)		1809(0.5)	1927(1.6, sh)	1949(3.7, sh)
n = 3					
$(MeO)_3P$	1770(0.6)	1814(0.5)			
$(EtO)_3P$	1786(0.4)	1814(0.4)			
$(^iPrO)_3P$					1962(10, br)
$(C_6H_{11}O)_3P$					1962(10, br)
$(PhO)_3P$	1788(0.4)	1829(0.4)			
$(o\text{-}MeC_6H_4O)_3P$	1784(0.3)	1824(0.2)			1980(9.0, sh)
$(p\text{-}MeC_6H_4O)_3P$	1788(0.4)	1829(0.4)			
$(p\text{-}ClC_6H_4O)_3P$	1786(0.5)	1828(0.5)			

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses. br = broad and sh = shoulder. Absorption bands with frequen-

1993(3.2, sh)	2008(10)	2014(7.3, sh)	2030(10)	2083(1.4)	
1990(2.5, sh)	2007(10)	2016(5.7, sh)	2030(10)	2083(1.6)	
1998(2.5, sh)	2011(9.9)		2035(10)	2082(1.5)	
1998(2.1, sh)	2009(8.6)		2032(10)	2084(1.5)	
2001(2.7, sh)	2012(9.5)	2015(9.5, sh)	2035(10)	2084(1.3)	
1997(2.7, sh)	2014(9.5)	2018(9.3, sh)	2036(10)	2087(1.2)	
	2006(2.6, sh)	2010(10.5)	2029(10)	2082(0.2)	
	2002(10)	2008(7.8, sh)	2025(11.2)	2080(2.6)	
1988(2.0, sh)	2007(10)	2010(8.3, sh)	2027(10.5)	2079(3.3)	
	2003(10)	2010(8.9, sh)	2027(9.2)	2082(3.3)	
	2004(10)	2008(8.6, sh)	2029(8.8)	2082(2.9)	
	2002(10)	2006(10, sh)	2026(8.8)	2079(2.5)	
1998(3.6, sh)	2004(10)	2013(3.8, sh)	2027(9.6)	2079(3.8)	
	2005(10)	2008(8.2, sh)	2029(7.8)	2082(3.1)	
	2003(10)	2006(9.5, sh)	2025(11.0)	2078(3.3)	
	2003(10)	2009(3.8, sh)	2027(9.5)	2079(2.9)	
	2002(10)	2007(8.6, sh)	2026(9.3)	2078(2.1)	
1990(3.1, sh)	2001(10)	2006(9.3, sh)	2024(10.2)	2077(3.0)	
	2003(10)	2007(8.9, sh)	2023(10.4)	2078(3.4)	
1991(2.0, sh)	2004(10)	2007(8.0, sh)	2029(8.5)	2080(3.0)	
	1993(10)	1995(10.0, sh)		2013(9.1)	2062(1.3)
	1989(10)	1994(9.5, sh)		2011(10.6)	2060(1.5)
	1988(10)	1993(9.2, sh)		2010(12.9)	2060(1.4)
	1985(10)	1989(8.0, sh)		2009(12.5)	2058(1.2)
	1986(10)			2008(12.3)	2056(1.2)
1985(2.5, sh)	2000(10)	2003(8.9, sh)		2023(8.6)	2068(1.1)
	1997(10)			2019(9.4)	2065(0.9)
	1999(10)			2019(9.9)	2064(1.1)
1992(7.0, sh)	2001(10)			2023(7.0)	2072(0.9)
	1989(10)		1992(10, sh)	2011(8.8)	2058(1.5)
	1974(10.3)		1987(4.2, sh)	1999(10)	2053(1.5)
	1979(9.3)		1986(6.5, sh)	2002(10)	2053(2.3)
1965(3.3, sh)	1979(8.5)		1986(5.7, sh)	2002(10)	2051(1.0)
1962(2.7, sh)	1982(9.3)		1993(6.0, sh)	2003(10)	2054(1.9)
	1984(7.9, br)			2006(10)	2054(1.9)
	1982(7.5)		1990(6.6, sh)	2004(10)	2051(1.8)
	1972(9.3)		1987(4.3, sh)	1998(10)	2050(1.8)
	1975(9.5)		1990(4.7, sh)	1999(10)	2051(2.4)
	1979(9.0)	1987(6.7, sh)		2003(10)	2054(2.5)
	1979(8.5)	1985(5.0, sh)		2002(10)	2053(2.4)
1958(3.9, sh)	1973(9.8)	1977(5.7, sh)	1989(6.0, sh)	1997(10)	2049(3.4)
1958(3.7, sh)	1972(9.3)			1996(10)	2048(3.1)
1974(10, br)	1980(9.2, sh)	1983(8.0, sh)		2040(1.6)	
1970(10, br)	1975(9.0, sh)	1979(8.0, sh)		2034(0.9)	
			2027(0.3, br)		
1974(5.9, sh)			2005(0.9, sh)		
1988(10, br)				2049(2.2)	
1986(10, br)				2049(0.9)	
1986(10, br)				2047(1.7)	
1993(10, br)				2051(1.8)	

cies which are less than 1900 cm^{-1} are due to $\nu(CO_{\mu})$ vibrations; the remainder are due to $\nu(CO_{t})$ modes.

of the solid is much simpler than those of the other compounds. Also, all of the disubstituted compounds appear to exist solely as CO-bridged isomers in the solid state, but on dissolving them in organic solvents there is a marked decline of the intensities of absorption bands due to the $\nu(CO_\mu)$ modes. This is again attributed to the greatly increased importance of the *nb* tautomers in solution. However, there is an additional feature of importance in the spectrum of solid samples of $[Fe_3(CO)_{10}\{P(OPh)_3\}_2]$ which shows an absorption band with a frequency of 1875 cm^{-1}, midway between those of the stretching vibrations of terminal and bridging CO ligands.[≠] It is not observed in carbon disulphide solution.

The trisubstituted compounds, $[Fe_3(CO)_9\{P(OR)_3\}_3]$ may be divided into three groups on the basis of their i.r. spectra in the solid state. The first group, where R = cyclo-C_6H_{11} or ^{i}Pr, show no absorption bands due to the C–O stretching vibrations of bridging carbonyl groups. This indicates that only *nb*-forms of these compounds are found in the solid state. For the sole compound in the second group, R = Me, such absorption bands are strong and have intensities relative to those of the $\nu(CO_t)$ bands which suggest that only CO-bridged isomers are present. For the remaining compounds, the third group, an intermediate situation pertains. This suggests that either (a) the absorption bands in the 1770–1830 cm^{-1} region are not due to $\nu(CO_\mu)$ fundamentals, or (b) that a mixture of *b* and *nb* isomers are present in the solid state.

The i.r. spectra of $[Fe_3(CO)_9\{P(OR)_3\}_3]$ in solution show no evidence for the *b* species where R = C_6H_{11} or ^{i}Pr. When R = Me, the decline in intensity of the $\nu(CO_\mu)$ absorption bands suggest that the *b*-form (or forms) is in equilibrium with *nb* tautomers and the latter predominate. The $(PhO)_3P$ and $(p\text{-}ClC_6H_4O)_3P$ complexes also show a decline in the intensities of their $\nu(CO_\mu)$ bands indicating that (b) above was probably applicable, but for the $(EtO)_3P$, $(o\text{-}MeC_6H_4O)_3P$ and $(p\text{-}MeC_6H_4O)_3P$ derivatives dissolution has no such effect. Consequently, it appears that (a) above was probably the correct interpretation. There is further evidence for this in that for $[Fe_3(CO)_9\{P(OC_6H_4Me\text{-}o)_3\}_3]$, these absorption bands are found at 1785 and 1825 cm^{-1} in cyclohexane solution, and at 1779 and 1822 cm^{-1} in bromoform solutions. A similar variation in solvent for $[Fe_3(CO)_{10}\{P(Bu^{sec})_3\}_2]$ causes its $\nu(CO_\mu)$ absorption bands to shift from 1798 and 1833 cm^{-1} to 1781 and 1819 cm^{-1}; behaviour which is more typical of a CO-bridging system [23].

The relative intensities of the two absorption bands due to the $\nu(CO_\mu)$ vibrations of the various *b*-isomers are similar to those of the comparable vibrations of $[Fe_3(CO)_{12}]$ and $[Fe_3(CO)_{11}(PPh_3)]$. This suggests that the $Fe(CO_\mu)_2Fe$ bridging systems, and probably the whole molecules, have similar overall geometries.

Unfortunately, the i.r. spectra of the *nb* isomers do not allow any conclusions to be drawn as to their structure. It is often difficult to separate the various absorption bands due to the *nb* species from those which arise from other tautomers. Consequently it is not possible to estimate their numbers or relative intensities with any degree of confidence.

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[≠] It may be due to the appropriate C–O stretching vibration of a tautomer with a semi-bridging carbonyl group. This could arise from an orientation of the Fe_3 triangle which is intermediate between those of the *b* isomer of C_{2v} symmetry and Johnson's *nb* isomer of D_3 symmetry.