272. *Di(tertiary Arsine) Iron Carbonyls and Oxidation Products.*

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When treated with the di(tertiary arsine), *o*-phenylenebisdimethylarsine, iron pentacarbonyl gives two new compounds, $Fe(CO)_3$Diarsine and FeCO(Diarsine)$_2$. These are both monomeric and are virtually non-electrolytes in nitrobenzene solution. On treatment with iodine, under carefully controlled conditions, the paramagnetic univalent iron complex [Fe(CO)$_2$DiarsineI]^0 is formed; this is monomeric in nitrobenzene and a non-electrolyte, showing that the iron atom is quinquecovalent. Further addition of iodine, or the use of bromine, yields [Fe(CO)$_2$Diarsine X$_2$]^0 ($X = Br,I$). The compound [Fe(CO)(Diarsine)$_2$]^0 yields only the known complex [Fe(Diarsine)$_2$I$_2$]^0(Br$_2$) on treatment with iodine or bromine. The reaction of the zerovalent iron compounds with nitric oxide has been investigated.

THE replacement of one or more CO groups from iron pentacarbonyl has been effected previously with a variety of ligands forming compounds of the type [Fe(CO)$_n$(Ligand)$_{5-n}$]^0. These include tertiary phosphines, arsines, and stibines, the *iso*nitriles and certain amines like dipyridyl and *o*-phenanthroline.[1] Practically all of the ligands which can replace the CO group to give mixed carbonyls are at least theoretically capable of forming, in addition to the usual σ bonds, dative π bonds using *d*-electron pairs of the metal fed into a vacant *d* (or *p* orbital made available) on the ligand atom. Exceptions include ammonia, ethylenediamine, and certain tertiary amines. However, there is now considerable doubt as to whether certain compounds formed by these ligands really are mixed iron amine carbonyls. Thus, recent work has shown that $Fe_3(CO)_8(NH_3)_6$,[2] formerly believed to have the composition $Fe(CO)_3(NH_3)_2$, is actually a salt of the type $[Fe(NH_3)_6][Fe_2(CO)_8]$. Even certain *o*-phenanthroline compounds [3] appear not to be direct substitution products; conductivity measurements and other studies show that the salt [Fe(*o*-phen)$_3$][Fe$_2$(CO)$_8$] is formed. Similarly the ethylenediamine compounds are apparently salts also.[4]

The use of chelate groups for the direct replacement of CO is of special interest because of the expected stability of the products owing to the entropy effect and also because they necessarily replace CO groups in *cis*-positions. In view of the powerful co-ordinating

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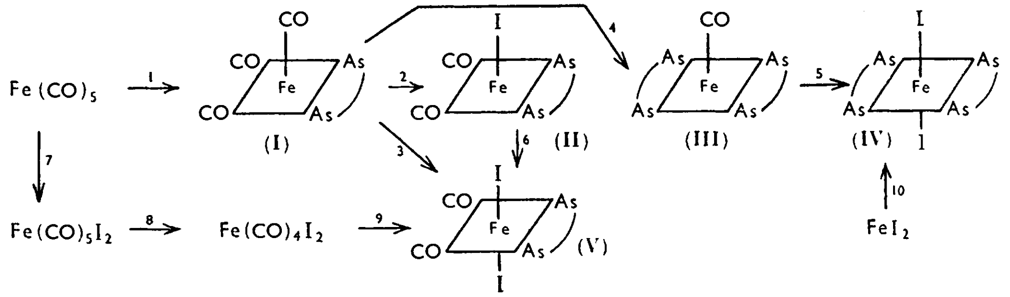
[1] See Review by Hieber, *Angew. Chem.*, 1952, **64**, 465.
[2] Hieber and Werner, *Chem. Ber.*, 1957, **90**, 1116.
[3] Hieber and Floss, *Chem. Ber.*, 1957, **90**, 1617.
Hieber, Sedlmeier, and Werner, *Chem. Ber.*, 1957, **90**, 278.

ability of the chelating di(tertiary arsine), *o*-phenylenebisdimethylarsine [5,6], its behaviour with iron pentacarbonyl has been investigated.

With nickel carbonyl, the compound $Ni(CO)_2$Diarsine is formed readily [7] by displacing two CO groups. Recently [8] we have found that the remaining CO groups can be displaced by heating this compound with diarsine *in vacuo* to yield $[Ni(Diarsine)_2]^0$ as a white crystalline compound similar to the corresponding bisdiphosphine compound prepared by Chatt and Hart.[9] Considerable interest attaches to the use of a diarsine chelate group in substitution reactions with $Fe(CO)_5$ as it was hoped that four CO groups might be replaced; previously a maximum of three only appears to have been substituted.

When iron pentacarbonyl and the diarsine are heated *in vacuo* at about 140° for about 4 hr., two CO groups are replaced readily to yield a golden-yellow crystalline compound having the formula $Fe(CO)_3$Diarsine. This is monomeric in organic solvents and is a non-electrolyte in nitrobenzene. Further heating of this compound with diarsine causes further substitution yielding $Fe(Diarsine)_2CO$. This is also monomeric and a non-electrolyte in nitrobenzene. Both compounds are more stable to light than is $Fe(CO)_5$; even so they gradually darken on standing. The bisdiarsine monocarbonyl is the less stable of the two as is reflected in the analysis and the conductivity. The properties of these compounds are shown in the diagram; for convenience, both substitution products are shown as square pyramidal; there is no experimental evidence for favouring this shape over trigonal bipyramidal which is generally accepted for $Fe(CO)_5$, although some doubt remains as to whether this is correct. Electron-diffraction work first led to the adoption of this structure; the small electric dipole moment 0·6—0·8D can scarcely be used with any confidence to differentiate between the two shapes in view of the uncertainty as to atom polarisation. To obtain best results from spectroscopy both infrared and Raman data are desirable. The infrared spectrum is well known but the determination of the Raman spectrum is difficult owing to the ease with which $Fe(CO)_5$ polymerises in ultraviolet light; there have recently been conflicting conclusions based on these data. Thus, Sheline and Pitzer [10] satisfactorily assigned all the infrared frequencies of gaseous $Fe(CO)_5$ on the basis of a trigonal bipyramid. In addition to the infrared, King and Lippincourt [11] also measured the Raman spectrum of a dilute solution in *n*-hexane using sodium light and agreed with Sheline and Pitzer's conclusions. Recently, however, O'Dwyer [12] re-assigned the infrared frequencies and concluded that the molecule is a square pyramid. Even if



1, Diarsine at 130°; 2, 1 equiv. of I_2 in benzene; 3, 2 equiv. of I_2 in ether; 4, Diarsine at 140—150°; 5, 2 equiv. of I_2 in ether; 6, I_2 in benzene; 7, I_2 below 0°; 8, above 0°; 9, Diarsine; 10, Diarsine in alcohol.

(I) Yellow, m. p. 131°; (II) brown-yellow, decomp. 195°; (III) brown-yellow, m. p. 150°; (IV) orange-yellow; (V) brown, m. p. 186°.

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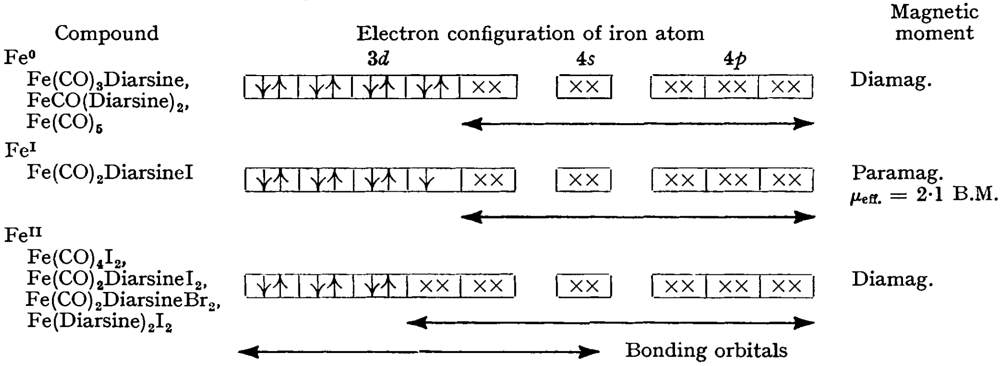
[5] Chatt and Mann, *J.*, 1939, 610.
[6] See Nyholm and Sutton, *J.*, 1958, 560 for references.
[7] Nyholm, *J.*, 1951, 2906.
[8] Nyholm and Rao, unpublished work.
[9] Chatt and Hart, *Chem. and Ind.*, 1958, 1474.
[10] Sheline and Pitzer, *J. Amer. Chem. Soc.*, 1950, **72**, 1107.
[11] King and Lippincourt, *J. Amer. Chem. Soc.*, 1956, **78**, 4192.
[12] O'Dwyer, *J. Mol. Spectroscopy*, 1958, **2**, 144.

$Fe(CO)_5$ is unambiguously shown to be a trigonal bipyramid, this will not necessarily mean that substituted iron carbonyls will have this shape. It may well be that the presence of different degrees of d_π–d_π bonding and steric effects generally could change the preferred stereochemistry. The crystal structures of $Fe(CO)_3$Diarsine and FeCO(Diarsine)$_2$ are being studied by *X*-rays by Mr. H. M. Powell, F.R.S., and his collaborators in the Inorganic Chemistry Laboratory at Oxford.

The behaviour of these substituted carbonyls with halogens leads to a series of very interesting new compounds. Treatment of $Fe(CO)_3$Diarsine with excess of iodine in absolute ether gives rise to a diamagnetic compound having the empirical formula [$Fe(CO)_2$DiarsineI_2], monomeric in organic solvents and a non-electrolyte in nitrobenzene. It is clearly an octahedral spin-paired complex as shown in the diagram; we show the two CO groups as *cis* for convenience only since no experimental evidence for these assignments is available. The corresponding dibromide [$Fe(CO)_2$DiarsineBr_2]^0 can be prepared by use of bromine as the oxidising agent. Unfortunately the corresponding chloro-complexes could not be isolated, presumably owing to high reactivity of the chloro-derivatives (cf. attempts[7] to prepare NiDiarsineCl_2). These complexes are clearly analogous with the iron compound $Fe(CO)_2$(Pyridine)$_2I_2$ described by Hieber and Bader[13] and the ruthenium compounds $Ru(CO)_2L_2I_2$ (L = CH_3AsPh_2, aniline, etc.) prepared by Irving.[14] These can be formed by treating $Ru(CO)_2I_2$, which is a red insoluble material, with a large excess of the ligand. The resulting compounds are monomeric and diamagnetic. The compound $Fe(CO)_2$DiarsineI_2 can be prepared also by treating $Fe(CO)_4I_2$ with diarsine. The product is identical with that obtained from the action of iodine on $Fe(CO)_3$Diarsine.

If $Fe(CO)_3$Diarsine is treated with only one equivalent of iodine under carefully controlled conditions it is possible to isolate a product having the empirical formula $Fe(CO)_2$DiarsineI. This is obtained by carefully avoiding local concentrations of iodine and by carrying out the reaction in the cold. The monoiodide is virtually a non-electrolyte in nitrobenzene and is monomeric in such solvents, suggesting that the iron atom is quinquecovalent, having an oxidation state of +1. This is confirmed by the magnetic moment (2·1 B.M.), indicating one unpaired electron. The relationship between the electronic configuration of this compound, the zerovalent iron compounds, and the bivalent derivatives is shown in the annexed scheme; the desire of the iron atom to use all nine orbitals of the 3*d*, 4*s*, and 4*p* orbitals is noteworthy.



The oxidation state of +1 for iron is very unusual; it has been reported previously in $Fe(CO)_2I$ and in some nitric oxide complexes of iron.[14a] According to Hieber and Lagally[15] the former is obtained by heating $Fe(CO)_4I_2$ in carbon dioxide. However, $Fe(CO)_2I$ was not obtained pure owing to its instability. It was reported that on further

[13] Hieber and Bader, *Ber.*, 1930, **63**, 1405.

[14] Irving, *J.*, 1956, 2879.

[14a] Griffith, Lewis, and Wilkinson, *J.*, 1958, 3993.

[15] Hieber and Lagally, *Z. anorg. Chem.*, 1940, **245**, 295; 1943, **251**, 96.

heating it yielded FeI as a very reactive red powder. Magnetic data are not available for these compounds. A second feature of interest is the fact that the compound contains quinquecovalent iron. This co-ordination number is relatively uncommon with the transition metals but it is relevant that an isoelectronic series of paramagnetic, quinquecovalent complexes exist having a d^7 non-bonding shell (*i.e.*, for Mn^0, Fe^I, Co^{II}, and Ni^{III}). Thus Mn^0 forms $Mn(CO)_4PPh_3$ which has one unpaired electron and is monomeric;[16] Co^{II} forms several paramagnetic, presumably quinquecovalent complexes, *e.g.*, $K_3Co(CN)_5$[17] and $[CoBr_2,Triarsine]^0$;[18] also, Ni^{III} gives derivatives such as $[NiBr_3,2Et_3P]^0$[19,20] which is monomeric in benzene and also contains one unpaired electron. $NiBr_3$,Diarsine[7] is undoubtedly similar. Since Jensen's studies on $NiBr_3,2Et_3P$ there has been much speculation as to the stereochemistry of this quinquecovalent compound. If the $d_{x^2-y^2}$ orbital hybridises with the *s* and *p*, then a square pyramid will result. However, use of the d_{z^2} orbital should give a trigonal bipyramid. Generally speaking the former seems the more likely. By adding one electron one gets another isoelectronic sequence of quinquecovalent compounds: Fe(O), *e.g.*, $Fe(CO)_5$; Co^I, *e.g.*, $[Co(RNC)_5]^+X^-$,[21] and Ni^{II}, *e.g.*, $NiBr_2$,Triarsine.[18] The earlier discussion on whether these are square pyramidal or trigonal bipyramidal resolves itself into the question of whether the lone pair is in the $d_{x^2-y^2}$ or d_{z^2} orbital and although the latter seems definite for the Ni^{II} compounds at least, conclusions based upon this compound will not necessarily have any relevance for $Fe(CO)_5$. Another interesting point about $Fe(CO)_2$DiarsineI is that it is one of the very few known paramagnetic substituted metal carbonyls. All non-substituted carbonyls are diamagnetic; apparently the strong tendency of CO to cause the metal to reach the inert gas configuration is outweighed if the number of remaining CO groups is sufficiently small (in this compound 2) and other influences become more important.

When FeCO(Diarsine)$_2$ is treated with two equivalents of iodine, the CO group is lost to yield the bivalent iron compound $[Fe(Diarsine)_2I_2]^0$ previously obtained[22] by treating ferrous iodide with the diarsine in alcohol. It is a typical diamagnetic octahedral Fe^{II} complex. Treatment with bromine gives the corresponding diamagnetic dibromide. In no case were we able to obtain any carbonyl diarsine complexes of tervalent iron. Ferric salts could be obtained by treating the zerovalent carbonyl diarsine compounds with chlorine but in these all carbon monoxide had been displaced.

The infrared frequencies of the various compounds which can be confidently assigned to CO stretching are given in the Table. FeCo(Diarsine)$_2$ gives only one CO stretching frequency, as expected if only one CO is present. The similarity of the $Fe(CO)_2$DiarsineBr$_2$ and $Fe(CO)_2$DiarsineI$_2$ spectra is apparent as is also the difference between these and that of $Fe(CO)_2$DiarsineI.

Compound	Infrared frequencies attributed to C–O stretching (In Nujol mull)	Compound	Infrared frequencies attributed to C–O stretching. (In Nujol mull)
$Fe^0(CO)_5$ *	2028, 1994	$Fe^{II}(CO)_2$DiarsineI$_2$	2062vs, 2008vs
$Fe^0(CO)_3$Diarsine	2009vs, 1916vs, 1880sh	$Fe^{II}(CO)_2$DiarsineBr$_2$	2083vs, 2008s
$Fe^0(CO)(Diarsine)_2$	1953s	$Fe^{II}(Diarsine)_2I_2$	Nil
$Fe^I(CO)_2$DiarsineI	2083s 2024s, 1976w		

* Sheline and Pitzer (ref. 10).

The behaviour of the monodiarsine complex with nitric oxide has also been investigated. Malatesta and Araneo[23] showed that complexes of the type $Fe(Ph_3P)_2(NO)_2$ can be obtained

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[16] Hieber and Wagner, *Z. Naturforsch.*, 1957, **12**b, 478.
[17] Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5710.
[18] Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.
[19] Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.
[20] Jensen and Nygaard, *Acta Chem. Scand.*, 1949, **3**, 474.
[21] Malatesta and Sacco, *Z. anorg. Chem.*, 1953, **273**, 247.
[22] Nyholm, *J.*, 1950, 851.
[23] Malatesta and Araneo, *J.*, 1957, 3803.

by treating $Fe(CO)_3(Ph_3P)_2$, which is equivalent to $Fe(CO)_3$Diarsine, with nitric oxide. This involves the usual behaviour in which the two NO groups replace three CO or one CO and the metal–metal link. When $Fe(CO)_3$Diarsine in benzene was treated with a stream of dry nitric oxide for some hours a clear solution was obtained from which an off-white material was precipitated on the addition of light petroleum. Unfortunately, since some decomposition products are formed in addition to what is probably $Fe(NO)_2$Diarsine, this could not be obtained pure.

The compounds prepared are shown in the diagram together with their interconversions. It is noteworthy that iron has now been stabilised with the di(tertiary arsine) in all the oxidation states from 0 to IV, the tervalent [24] complexes being of the general type $[Fe^{III}Cl_2(\text{Diarsine})_2]ClO_4$ and the quadrivalent $[Fe^{IV}Cl_2(\text{Diarsine})_2][ClO_4]_2$.

EXPERIMENTAL

*Mono-*o*-phenylenebisdimethylarsinetricarbonyliron*(0).—Iron pentacarbonyl (1·5 g.) and diarsine (2·5 g.) were mixed in a hard-glass tube (length 12 in., diam. 1 in.), the tube and the contents were cooled in liquid nitrogen, and the tube was evacuated and sealed, then heated at 130—140° for 3—4 hr. On cooling the tube was opened carefully owing to the CO pressure and the golden-yellow crystalline *product* was washed with dry light petroleum and recrystallised (ether). Dried *in vacuo* (3·5 g.), the compound melted at 131° (Found: C, 36·5; H, 3·9; As, 35·1; Fe, 13·4%; *M*, cryoscopic in 0·51% solution in benzene, 401. $C_{13}H_{16}O_3As_2Fe$ requires C, 36·64; H, 3·76; As, 35·2; Fe, 13·2%; *M*, 426). The compound is readily soluble in all common organic solvents and sparingly soluble in light petroleum. It is fairly stable in a dry, dark and inert atmosphere. In solution it is unstable in presence of air, a brown precipitate being formed gradually. It is a poor conductor in nitrobenzene ($\Lambda_m = 3$ mho in $1{\cdot}01 \times 10^{-3}$M-solution at 25°. This figure increases with time, indicating decomposition). The compound is diamagnetic ($\chi_g = -0{\cdot}15 \times 10^{-6}$ at 21°).

*Bis-*o*-phenylenebisdimethylarsinemonocarbonyliron*(0).—The monosubstituted diarsine complex FeDiarsine$(CO)_3$ (1·59 g.) and diarsine (1·0 g.) were mixed as before in a hard-glass tube and evacuated and sealed. The tube was then heated at 140—150° for 3—4 hr. The CO liberated was then pumped off and the process of heating repeated four times. The *compound* was recrystallised from the minimum volume of ether and dried *in vacuo* (1·5 g.), m. p. *ca.* 150° (decomp.) (Found: C, 37·1; H, 4·1; As, 45·6; Fe, 8·8%; *M*, cryoscopic in 0·47% solution in benzene, 600. $C_{21}H_{32}OAs_4Fe$ requires C, 38·4; H, 4·8; As, 45·7; Fe, 8·5%; *M*, 656). The compound is soluble in all common organic solvents. Both in the solid state and in solution it is less stable than the previous monodiarsine substituted complex and is difficult to obtain very pure (this is reflected in the analyses). It is a poor conductor in nitrobenzene ($\Lambda_m = 2{\cdot}4$ mho in $1{\cdot}24 \times 10^{-3}$M-solution at 25°) and diamagnetic in powder form.

*Monoiodomono-*o*-phenylenebisdimethylarsinedicarbonyliron*(I).—Fresh $Fe(CO)_3$Diarsine (0·6 g.) in a cold dry mixture of benzene (50 ml.) and dry nitrobenzene (5 ml.) was treated slowly with iodine (0·18 g.) in cold, dry benzene (75 ml.) with constant stirring in an atmosphere of dry nitrogen. Care is necessary; a very slow addition favours decomposition of $Fe^0(CO)_3$Diarsine whilst a quick addition gives rise to large local concentrations of iodine favouring the higher (bivalent) oxidation state. Both factors may vitiate results. Light petroleum was added to the resulting solution; the compound (0·65 g.) was precipitated as a brownish-yellow microcrystalline powder and dried *in vacuo* (Found: C, 26·8; H, 3·11; I, 23·3; Fe, 10·55%; *M*, cryoscopic in 0·46% nitrobenzene solution, 410. $C_{12}H_{16}O_2As_2IFe$ requires C, 27·4; H, 3·05; I, 24·2; Fe, 10·66%; *M*, 525). The *compound* is fairly soluble in benzene and readily soluble in nitromethane and nitrobenzene. It is a very poor conductor in the latter ($\Lambda_m = 3{\cdot}6$ mho in $1{\cdot}36 \times 10^{-3}$M-solution at 25°). Magnetic susceptibility of the powder at 22·5° is $\chi_g = 2{\cdot}9 \times 10^{-6}$, $\chi_m = 1523 \times 10^{-6}$; diamagnetic correction 245×10^{-6}, whence $\mu_{\text{eff.}} = 2{\cdot}1$ B.M. The molecular weight is low, presumably owing to slight decomposition, an effect reflected in the conductivity also. A chloroform solution shows a peak in the visible region at 4300 Å and a shoulder in the ultraviolet at 3100 Å. On being heated the compound decomposes at *ca.* 195°.

*Di-iodomono-*o*-phenylenebisdimethylarsinedicarbonyliron*(II).—The monodiarsinetricarbonyl complex of iron, $Fe(CO)_3$Diarsine (0·6 g.) dissolved in dry ethyl ether (60 ml.) was treated with

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[24] Nyholm and Parish, *Chem. and Ind.*, 1956, 470.

iodine (0·33 g.) in ether (40 ml.) in an inert and dry atmosphere with constant stirring. A dark brown shining microcrystalline precipitate was formed. The *compound* (0·8 g.) was filtered off under dry nitrogen and washed thoroughly with ether before being dried *in vacuo* (Found: C, 22·5; H, 2·65; I, 39·6; Fe, 8·8%; *M*, cryoscopic in 0·5% nitrobenzene solution, 624. $C_{12}H_{16}O_2As_2I_2Fe$ requires C, 22·0; H, 2·45; I, 39·0; Fe, 8·59%; *M*, 652). The substance, m. p. 186° (decomp.), dissolves readily in acetone or nitrobenzene, is moderately soluble in benzene, chloroform, and ethyl alcohol and sparingly soluble in absolute ether and insoluble in light petroleum or water. It is diamagnetic in powder form. In nitrobenzene the complex is virtually a non-electrolyte (Λ_m in 1·04 × 10^{-3}M-solution = 1·2 mho at 25°). A chloroform solution shows two peaks in the ultraviolet and visible spectrum at 3500 Å and 5000 Å respectively. Measurements could not be made further towards the ultraviolet region owing to heavy absorption by the diarsine.

*Dibromomono-*o*-phenylenebisdimethylarsinedicarbonyliron*(II).—$Fe(CO)_3$Diarsine (0·6 g.), in dry absolute ether (50 ml.), was treated with bromine (0·24 g.) in ether (35 ml.) in a dry nitrogen atmosphere with constant stirring. The orange-yellow crystals (0·79 g.), isolated as for the iodide, had m. p. 225° (decomp.) (Found: C, 25·5; H, 3·2; Br, 30·5; Fe, 10·1%; *M*, cryoscopic in 0·39% nitrobenzene solution, 508. $C_{12}H_{16}O_2As_2Br_2Fe$ requires C, 25·8; H, 2·9; Br, 28·7; Fe, 10·04%; *M*, 558). Solubilities are as for the iodide and it is diamagnetic. It is virtually a non-electrolyte in nitrobenzene, Λ_M = 1·9 mho in 1·24 × 10^{-3}M-solution at 25°. A chloroform solution shows peaks in the ultraviolet and visible spectrum at 3400 Å (shoulder) and 4800 Å.

*Di-iodobis-*o*-phenylenebisdimethylarsineiron*(II).—Bis-*o*-phenylenebisdimethylarsinemonocarbonyliron(0) (0·6 g.) in dry absolute ether (100 ml.) was treated with iodine (0·25 g.) in ether (50 ml.) with constant stirring. A brownish yellow precipitate was formed. This was filtered off, washed thoroughly with ether, and dried *in vacuo* (Found: C, 28·4; H, 4·2; I, 28·1; Fe, 6·3. $C_{20}H_{32}As_4I_2Fe$ requires C, 27·2; H, 3·7; I, 28·8; Fe, 6·33%). The *substance* is insoluble in all the common organic solvents and sparingly soluble in acetone or nitrobenzene. It could not be purified, although it is well characterised. An acetone solution of the compound gave no immediate precipitate of silver iodide on addition of silver nitrate solution, indicating that it is a non-electrolyte. The compound is diamagnetic in powder form. In Nujol, it shows no absorption peak in the C–O stretching-frequency range, indicating the absence of a carbonyl group.

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