type may exist in five isomeric forms, depending on the relative positions of the halogen atoms and carbonyl groups. However, only in the two isomers in which the halogen atoms occupy mutually *trans* apical or equatorial positions on the respective iron atoms can all the methyl groups have equivalent environments, as indicated by the single methyl resonances observed in the n.m.r. spectra. The infrared spectra of the complexes show three carbonyl stretching vibrations and do not help in distinguishing between the two isomers.

It was recently reported that $Fe(CO)_5$ reacts with $(CF_3)_2PI$ to give a dark red crystalline complex $[FeI\{P(CF_3)_2\}(CO)_3]_2$.[22] It is possible that this complex has a structure analogous to $[FeX\{E(CH_3)_2\}(CO)_3]_2$.

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[22] H. J. Emeléus and J. Grobe, *Angew. Chem.*, **74**, 467 (1962).

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Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. VII.[1] Complexes Derived from Iron Dicarbonyl Dinitrosyl

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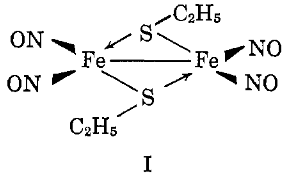
The reactions of R_4E_2 (E = P, R = CH_3, C_6H_5; E = As, R = CH_3) with $[Fe(CO)_2(NO)_2]$ yield the dark red E-bridged complexes, $[Fe(ER_2)(NO)_2]_2$. The tetramethylbiphosphine complexes, $[Fe_2(CO)_2\{P_2(CH_3)_4\}(NO)_4]$ and $[Fe_2\{P_2(CH_3)_4\}_2(NO)_4]$, can also be prepared. $Hg[Fe(CO)_3NO]_2$ reacts with R_4E_2 to give mixtures of complexes, most of which are better prepared by other routes.

Our previous investigations in this series[1] have yielded a number of phosphorus- and arsenic-bridged dimeric complexes of metals of the first transition series. The ligands, other than those forming the bridge, have usually been carbon monoxide and/or cyclopentadienyl. In this paper we report bridged complexes of iron which contain nitric oxide as a terminal ligand.

Sulfur-bridged nitrosyl complexes of iron have been known for some time[2] and the structure of Roussin's red ethyl ester $[Fe(SC_2H_5)(NO)_2]_2$ (I) has been determined.[3] The iron atoms were found to have approximately tetrahedral coordination and the ring to be a planar rhombus. The ethyl groups are *trans* with respect to each other. The only analogous previously known complex containing a bridging group V element is $[Fe(NH)(NO)_2]_2$.[4] This compound has been shown to contain bridging imino groups, but the geometry of the molecule has not been established with certainty and the ring may be folded, as suggested for the corresponding carbonyl complex, $[Fe(NH)(CO)_3]_2$, which has a relatively high dipole moment (3.3 D.).



I

Attempts to prepare phosphorus- and arsenic-bridged nitrosyl complexes by displacement of carbon monoxide from a suitable carbonyl complex (for example, $[Fe\{P(CH_3)_2\}(CO)_3]_2$[1]) by nitric oxide were not successful. We have therefore investigated the reactions of P_2R_4 (R = CH_3, C_6H_5) and of $As_2(CH_3)_4$ with iron dicarbonyl dinitrosyl and find that the formation of bridged complexes occurs under conditions similar to those found in analogous metal carbonyl reactions.[1]

Experimental

Microanalyses and molecular weight determinations were by Schwarzkopf Microanalytical Laboratories. Infrared spectra were measured on a Beckman IR-9 spectrophotometer using Nujol (400–1300 cm.$^{-1}$) and halocarbon (1300–4000 cm.$^{-1}$) mulls. Proton n.m.r. spectra were obtained with a Varian Associates A-60 spectrometer, using tetramethylsilane as an internal standard. Unless otherwise stated, the compounds gave sharp spectra, methyl resonances being observed in the range τ 7.7–8.4. Melting points were determined in evacuated capillaries and are uncorrected.

The biphosphine and biarsine ligands,[5] $[Fe(CO)_2(NO)_2]$, and $Hg[Fe(CO)_3NO]_2$[6] were prepared by previously described methods. All operations except the manipulation of the solid complexes were carried out under nitrogen. Merck acid-washed alumina was used for chromatographic purifications.

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[1] Part VI: R. G. Hayter, *Inorg. Chem.*, **3**, 711 (1964).

[2] N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. II, Oxford University Press, 1950, p. 1373.

[3] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, **11**, 599 (1958).

[4] W. Hieber and H. Beutner, *Z. anorg. allgem. Chem.*, **317**, 63 (1962).

[5] R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

[6] W. Hieber and H. Beutner, *Z. anorg. allgem. Chem.*, **320**, 101 (1963).

Preparation of the Complexes. Di-μ-(dimethylphosphido)-bis(dinitrosyliron).—[Fe(CO)$_2$(NO)$_2$] (3.78 g., 22.0 mmoles), tetramethylbiphosphine (1.34 g., 11.0 mmoles), and methylcyclohexane (70 ml.) were refluxed together for 16 hr. to give an intense purple-brown solution. The solution was filtered to remove an insoluble brown solid and the filtrate evaporated at 15 mm. to give a purple solid. Crystallization from methylcyclohexane gave dark red crystals (m.p. 201–203°, darkening above 150°; yield 23%).

Anal. Calcd. for $C_4H_{12}Fe_2N_4O_4P_2$: C, 13.6; H, 3.4; Fe, 31.6; N, 15.8; mol. wt., 354. Found: C, 13.7; H, 3.7; Fe, 31.35; N, 15.7; mol. wt. (C_6H_6), 335.

N.m.r. Spectrum (CS_2 Solution).—A doublet (with a weak central absorption) at τ 7.78 (splitting 11.7 c.p.s.).

Infrared Spectrum.—Nitrosyl bands at 1753 (s) and 1733 (s) cm.$^{-1}$; other absorption bands at 1402 (w), 1284 (w), 1278 (m), 948 (s), 881 (s), 842 (m), 742 (m), 716 (m), 667 (m), 600 (s), and 483 (w) cm.$^{-1}$.

Di-μ-(diphenylphosphido)bis(dinitrosyliron).—[Fe(CO)$_2$(NO)$_2$] (1.07 g., 6.22 mmoles), tetraphenylbiphosphine (3.11 mmoles), and toluene (60 ml.) were refluxed together for 5 hr. On cooling to 0°, red and white solids separated and were filtered off. Washing with warm toluene removed most of the white material, and the residue was crystallized from a large volume of boiling toluene to give dark red plates (m.p. 313–314°, darkening above 150°; yield 25%).

Anal. Calcd. for $C_{24}H_{20}Fe_2N_4O_4P_2$: C, 47.9; H, 3.35; Fe, 18.55; N, 9.3. Found: C, 48.0; H, 3.5; Fe, 18.7; N, 9.3.

N.m.r. Spectrum.—This was not obtained owing to insufficient solubility.

Infrared Spectrum.—Nitrosyl bands at 1756, 1740, and 1728 (all vs) cm.$^{-1}$; other absorption bands at 1478 (w), 1432 (m), 1273 (w), 1182 (w), 1159 (w), 1100 (m), 1088 (m), 1070 (w), 1027 (w), 1000 (w), 970 (w), 920 (w), 849 (m), 748 (s), 742 (s), 730 (sh), 711 (m), 692 (s), 676 (m), 600 (vs), 517 (s), 480 (s), 472 (m), 446 (w), and 440 (w) cm.$^{-1}$.

Di-μ-(dimethylarsenido)bis(dinitrosyliron).—Tetramethylbiarsine (1.65 g., 7.85 mmoles) was added to a suspension of Hg[Fe(CO)$_3$NO]$_2$ (4.25 g., 7.85 mmoles) in toluene (75 ml.) to give vigorous gas evolution. The resulting mixture was refluxed for 16 hr. to give a dark orange solution, which was then filtered from elemental mercury and a small amount of yellow solid. Evaporation of solvent from the filtrate left a brown solid which was sublimed at 100° and 0.2 mm. to give orange crystals (0.995 g.). The sublimate was shown by n.m.r. to be a mixture of [Fe{As(CH$_3$)$_2$}(CO)$_3$]$_2$[1] and [Fe{As(CH$_3$)$_2$}(NO)$_2$]$_2$. The dark brown residue from the sublimation was crystallized from a large volume of boiling hexane to give dark red crystals (m.p. 227–230°, with darkening above 150°; yield 26%).

Anal. Calcd. for $C_4H_{12}As_2Fe_2N_4O_4$: C, 10.9; H, 2.7; Fe, 25.3; N, 12.7; mol. wt., 442. Found: C, 11.6, 11.9; H, 2.7, 2.8; Fe, 25.1; N, 12.9; mol. wt. (C_6H_6), 316.

N.m.r. Spectrum ($CHCl_3$ Solution).—A singlet at τ 7.73.

Infrared Spectrum.—Nitrosyl bands at 1757 (sh) and 1727 (vs) cm.$^{-1}$; other absorption bands at 1404 (m), 1256 (m), 1248 (m), 976 (w), 909 (s), 848 (s), 735 (sh), 726 (m), 666 (m), 613 (m), 598 (s), and 582 (m) cm.$^{-1}$.

This complex can also be prepared in 55% yield from [Fe(CO)$_2$(NO)$_2$], as described for [Fe{P(CH$_3$)$_2$}(NO)$_2$]$_2$ above.

μ-(Tetramethylbiphosphine)bis(carbonyldinitrosyliron).—[Fe(CO)$_2$(NO)$_2$] (2.50 g., 14.6 mmoles), tetramethylbiphosphine (0.89 g., 7.28 mmoles), and toluene (50 ml.) were refluxed together for 5 hr. to give a dark red solution. After filtration to remove a small amount of black solid, the solution was evaporated at 15 mm. leaving a red oil which solidified at 0°. Crystallization from a small volume of hexane gave dark red crystals (m.p. 70–72° dec.; yield 34%).

Anal. Calcd. for $C_6H_{12}Fe_2N_4O_6P_2$: C, 17.6; H, 2.95; Fe, 27.25; N, 13.7; P, 15.1; mol. wt., 410. Found: C, 17.4; H, 3.2; Fe, 26.9; N, 14.2, 13.1; P, 14.5; mol. wt. (C_6H_6), 419.

N.m.r. Spectrum (CS_2 Solution).—A doublet at τ 8.37 (J_{HP} = 3.3 c.p.s.).

Infrared Spectrum.—Carbonyl bands at 2012 (vs) and 1987 (sh) cm.$^{-1}$; nitrosyl bands at 1765 (vs), 1730 (vs), and 1690 (sh) cm.$^{-1}$; other absorption bands at 1413 (m), 1294 (w), 1287 (w), 948 (m), 879 (s), 856 (m), 822 (w), 742 (m), 722 (m), 690 (m), 662 (s), 616 (vs), 562 (sh), 469 (m), and 448 (m) cm.$^{-1}$.

Di-μ-(tetramethylbiphosphine)bis(dinitrosyliron).—[Fe(CO)$_2$(NO)$_2$] (1.27 g., 7.36 mmoles), tetramethylbiphosphine (0.92 g., 7.52 mmoles), and methylcyclohexane (75 ml.) were refluxed together for 5 hr. to give a dark red solution and precipitate. The solid was filtered off and crystallized from dichloromethane–hexane to give dark purple crystals (decomposition at 285°, with darkening above 150°; yield 27%).

Anal. Calcd. for $C_8H_{24}Fe_2N_4O_4P_4$: C, 20.2; H, 5.1; Fe, 23.5; N, 11.8; P, 26.0; mol. wt., 476. Found: C, 20.5, 20.2; H, 5.2, 5.0; Fe, 23.5; N, 11.9; P, 27.1; mol. wt. (CH_2Br_2), 446.

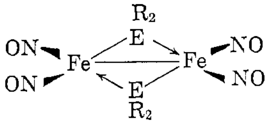
N.m.r. Spectrum ($CHCl_3$ Solution).—A doublet (with a central absorption about the same height as each of the outer two peaks) at τ 7.85 (splitting 4.5 c.p.s.).

Infrared Spectrum.—Nitrosyl bands at 1705, 1684, 1650 (all vs) cm.$^{-1}$; other absorption bands at 2994 (w), 2981 (w), 2968 (w), 2908 (w), 1424 (m), 1406 (s), 1290 (s), 1282 (m), 1274 (w), 938 (s), 897 (vs), 860 (m), 852 (m), 823 (m), 732 (m), 725 (m), 690 (m), 679 (m), 656 (m), 584 (m), and 480 (m) cm.$^{-1}$.

The Reaction between Hg[Fe(CO)$_3$NO]$_2$ and P$_2$(CH$_3$)$_4$.—Tetramethylbiphosphine (1.42 g., 11.7 mmoles) was added to a suspension of Hg[Fe(CO)$_3$NO]$_2$ (6.30 g., 11.7 mmoles) in toluene (125 ml.) to give vigorous gas evolution and precipitation of an orange solid. The mixture was refluxed for 16 hr. and then filtered to remove elemental mercury and a yellow-orange insoluble solid (total weight 1.62 g.), subsequently shown to be HgFe(CO)$_4$ by comparison of its infrared spectrum with that of an authentic specimen.[7] The filtrate was evaporated to give a brown solid which was extracted into hexane and chromatographed. Elution with hexane gave yellow and red-brown bands. The yellow band yielded red-brown crystals (0.23 g.) which were shown by n.m.r. to be a mixture consisting mainly of [Fe{P(CH$_3$)$_2$}(CO)$_3$]$_2$[1] and [Fe{P(CH$_3$)$_2$}(NO)$_2$]$_2$. The red-brown band yielded a dark red oil which crystallized on cooling. Recrystallization from hexane gave red-orange crystals (m.p. 50–52°; 0.28 g.) which were shown by n.m.r. and infrared spectra to be mainly [Fe$_2$(CO)$_2${P$_2$(CH$_3$)$_4$}(NO)$_4$]. Another unidentified compound was also present and showed n.m.r. absorptions at τ 8.16 and 8.24 and infrared bands in the carbonyl region at 2084 (vs), 2042 (vs), and 1940 (vs) cm.$^{-1}$.

Discussion

In general, the biphosphines and biarsine react with [Fe(CO)$_2$(NO)$_2$] to give binuclear complexes (II) which appear to be analogous to Roussin's red ethyl ester.[3] The compounds are dark red and their infrared spectra show strong bands in the range 1728–1757 cm.$^{-1}$ due to the nitrosyl groups and no absorption in the usual carbonyl region. Metal–metal bonding is assumed in order to achieve diamagnetism and the complexes may be considered to be derived from [Fe(ER$_2$)(CO)$_3$]$_2$[1] by replacement of the six carbonyl groups by four nitrosyl groups. However, unlike the carbonyl complexes, the



E = P, R = CH$_3$, C$_6$H$_5$
E = As, R = CH$_3$
II

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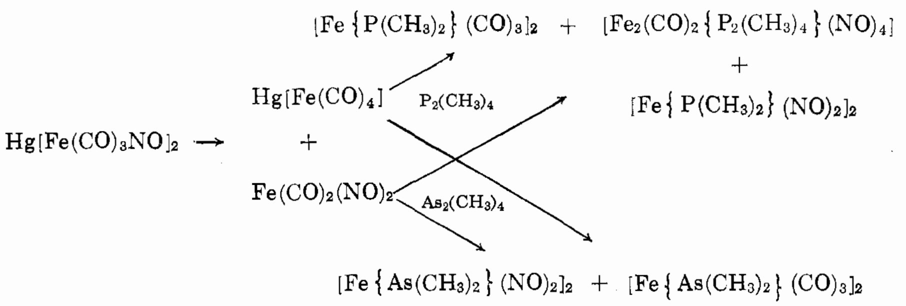
[7] G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Vol. II, Ferdinand Enke Verlag, Stuttgart, 1960, p. 1519.

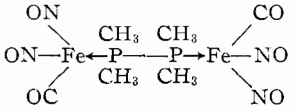
SCHEME I



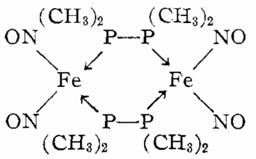
n.m.r. spectra show only a single methyl resonance, indicating a planar rather than a folded ring. Indeed, folding is not expected here, since each iron atom is attached to four ligands, probably in an approximately tetrahedral arrangement, and folding will introduce strain, rather than relieve it.

The methyl resonance in $[Fe\{P(CH_3)_2\}(NO)_2]_2$ consists of a doublet with a weak central peak, a pattern indicative of phosphorus–phosphorus coupling in the molecule. Complexes containing this type of ring have usually been found to give methyl resonances in the form of a 1:2:1 triplet.[1] However, in all such compounds which previously were known, for example $[Fe\{P(CH_3)_2\}(CO)_3]_2$,[1] or *cis* and *trans*-$[C_5H_5Fe\{P(CH_3)_2\}(CO)]_2$,[5] the metal atoms are octahedrally coordinated, or essentially so. If a comparison were to be made with a strictly analogous carbonyl complex, it would have to be with the nickel complex $[Ni\{P(CH_3)_2\}(CO)_2]_2$, which is at present unknown, in spite of various attempts at synthesis.[1] One interpretation of the presently available data is that the strength of phosphorus–phosphorus coupling depends on the coordination of the metal atom, being greater for octahedral than tetrahedral coordination in the compounds under consideration. It is interesting that a similar deduction has been made from a study of the n.m.r. spectra of some disubstituted metal carbonyl complexes of tris(dimethylamino)phosphine (Tdp).[8] In the octahedral Tdp complexes, however, the phosphorus ligands were mutually *trans*, whereas in the bridged complexes, they are *cis*. Strong transmission of coupling effects between ligand atoms in these octahedral complexes therefore appears to be independent (as far as can be detected by this method) of their relative positions.

Under conditions different from those which gave the cyclic complex, $P_2(CH_3)_4$ reacts with $[Fe(CO)_2(NO)_2]$ to give complexes of the uncleaved biphosphine, III and IV. These compounds are the binuclear analogs of the mono- and disubstituted complexes $[Fe(CO)L(NO)_2]$ and $[FeL_2(NO)_2]$ (L = $(C_6H_5)_3P$, $(C_6H_5)_3As$).[9]



III



IV

III was obtained by reaction for a relatively short time in boiling toluene and is a low-melting, very soluble, dark red complex. The infrared spectrum shows both carbonyl and nitrosyl absorption bands. The methyl resonance in the n.m.r. spectrum consists of a doublet, indicating that all the methyl groups are equivalent and that phosphorus–phosphorus coupling is zero or very small.

IV is prepared by using an excess of the biphosphine and represents the first example of double bridging by this type of ligand. Molecular models[10] show that $P_2(CH_3)_4$ can form complexes analogous to IV with little if any strain when the metal is tetrahedral. Attempts to make models of analogous compounds of an octahedral metal, however, were unsuccessful owing to strain in forming the ring. This may account, at least in part, for our earlier observation[1] that complexes of the type $[M(CO)_4\{As_2(CH_3)_4\}]_n$[11] (M = Cr, Mo) formed polymers (n = 13–20) rather than dimers similar to IV.

The reactions of $Hg[Fe(CO)_3NO]_2$ with $P_2(CH_3)_4$ and $As_2(CH_3)_4$ were also investigated with the aim of preparing substitution complexes of the mercury salt. As indicated in the Experimental section, the reactions are complex and only $[Fe\{As(CH_3)_2\}(NO)_2]_2$ of the complexes described above was readily isolated in a pure state by this method. It has previously been reported that $Hg[Fe(CO)_3NO]_2$ disproportionates into $HgFe(CO)_4$ and $Fe(CO)_2(NO)_2$,[6] and this disproportionation accounts for the identified reaction products, as summarized in Scheme I.

[8] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

[9] D. W. McBride, S. L. Stafford, and F. G. A. Stone, *ibid.*, **1**, 386 (1962), and references therein.

[10] Fisher–Hirschfelder–Taylor metal coordination models.

[11] Similar polymers containing $P_2(CH_3)_4$ were also obtained although these were less readily purified.