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Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. V.[1] Single-Bridged Ionic Complexes Derived from π-Cyclopentadienyliron Dicarbonyl Bromide

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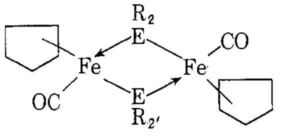
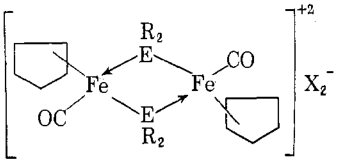
It was previously found that $[C_5H_5Fe(CO)_2]_2$ reacts with tetrasubstituted biphosphines and tetramethylbiarsine to give the dimeric complexes (I), which may exist in *cis* or *trans* isomeric forms.[3] In (I), the iron atoms are formally bivalent, and we considered it to be of interest to attempt the preparation of analogous cationic complexes of trivalent iron (II, X = uninegative anion) in which an iron–iron bond may also be present. For this reason, we investigated the reactions of the $E_2(CH_3)_4$ ligands with $[C_5H_5Fe(CO)_2Br]$ and isolated ionic complexes, not of type II, but of type III, in which iron is still bivalent. The reactions presumably occur according to the equation given below, although no attempt was made to detect the dimethylbromophosphine or -arsine.



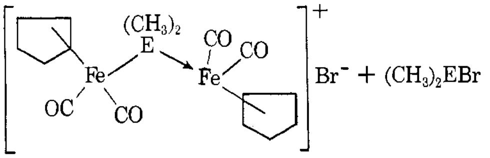
I



II

E = P, R = R′ = CH_3, C_6H_5
E = As, R = CH_3

$$2C_5H_5Fe(CO)_2Br + E_2(CH_3)_4 \longrightarrow$$



III

The complexes were isolated in the form of perchlorate or tetraphenylborate salts as air-stable yellow or orange crystals. The formulation III is supported by analysis, the presence of terminal metal carbonyl vibrations only in the infrared spectra, and molar conductance values in nitromethane solution which are in the range expected for 1 : 1 electrolytes. The n.m.r. spectra are also consistent with III. When E = P, both the methyl and cyclopentadienyl resonances are doublets due to spin–spin coupling with the single phosphorus nucleus ($I = {}^1/_2$).

Attempts to prepare a neutral complex of type I with different substituents on each side of the ring ($R \neq R'$) by reaction between III (E = P) and $P_2(C_6H_5)_4$ were unsuccessful. Reactions between $[C_5H_5Mo(CO)_3X]$ (X = Br, I) and E_2R_4 did not yield any tractable products analogous to III.

Experimental

Microanalyses were by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were measured on a Beckmann IR-9 spectrophotometer using Nujol (400–1300 cm.$^{-1}$) and halocarbon (1300–4000 cm.$^{-1}$) mulls. Melting points were determined in evacuated capillaries and are uncorrected. Conductivity measurements were made using an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with a constant of 0.110.

The biphosphines and biarsine were prepared as previously described[3] and $[C_5H_5Fe(CO)_2Br]$ was prepared by the reaction of bromine with $[C_5H_5Fe(CO)_2]_2$.[4] The reactions and manipulations involving the ligands were carried out in an atmosphere of nitrogen.

Preparation of the Complexes. μ-(Dimethylarsenido)di-π-cyclopentadienyltetracarbonyldiiron Perchlorate.—Tetramethylbiarsine (1.58 g., 7.52 mmoles), $[C_5H_5Fe(CO)_2Br]$ (3.88 g., 15.04 mmoles), and toluene (70 ml.) were refluxed together for 16 hr. with stirring. The initial dark red solution turned pale yellow and precipitated a dark brown solid, which was filtered off and dried. This solid was dissolved in water and filtered from insoluble impurities, and the filtrate was treated with excess concentrated aqueous $NaClO_4$. The yellow-orange precipitate was filtered off, dried, and crystallized from acetone–hexane to give orange crystals (dec. above 150°; yield 31%).

Anal. Calcd. for $C_{16}H_{16}AsClFe_2O_8$: C, 34.4; H, 2.9; Fe, 20.0; O, 22.9. Found: C, 34.2; H, 3.3; Fe, 20.15, 20.30; O, 21.3.

Infrared Spectrum.—Metal carbonyl bands at 2028 (sh), 2015 (vs), 1975 (vs), 1966 (vs), 1943 (m); other absorption bands at 3124 (w), 3108 (w), 1432 (m), 1423 (m), 1260 (w), 1104 (vs), 1066 (m), 1052 (m), 1018 (m), 1002 (m), 958 (w), 911 (w), 898 (w), 860 (s), 840 (w), 836 (w), 814 (w), 826 (w), 622 (s), 602 (m), 590 (m), 578 (s), 569 (s), 511 (m), 506 (m), and 451 (w) cm.$^{-1}$.

N.m.r. Spectrum (Dimethyl Sulfoxide Solution).—Singlets at 4.52 and 8.18 τ due to the cyclopentadienyl and methyl protons, respectively.

Conductivity in Nitromethane.—Molar conductance values were 105.8 and 102.8 ohm^{-1} at concentrations 2.1 and 1.4×10^{-3} *M*, respectively.

The tetraphenylborate salt was similarly prepared and crystallized from aqueous acetone as orange crystals (m.p. 211–213° dec.; yield 27%).

Anal. Calcd. for $C_{40}H_{36}AsBFe_2O_4$: C, 61.7; H, 4.7; Fe, 14.35. Found: C, 61.6; H, 5.1; Fe, 15.1.

Infrared Spectrum.—Metal carbonyl bands at 2028 (s), 2018 (vs), 1975 (sh), 1973 (vs), 1969 (vs), 1943 (m); other absorption bands at 3112 (w), 3102 (w), 3088 (w), 3054 (m), 3000 (w), 2985 (w), 1580 (m), 1480 (s), 1428 (s), 1418 (s), 1362 (w), 1265 (w), 1257 (w), 1182 (w), 1146 (m), 1066 (m), 1030 (m), 1015 (m), 1000 (m), 918 (w), 908 (w), 896 (m), 860 (s), 838 (sh), 833 (sh), 802 (w), 764 (w), 742 (vs), 735 (vs), 708 (vs), 620 (s), 615 (sh), 606 (s), 594 (m), 587 (s), 579 (vs), 565 (vs), 510 (m), 500 (sh), 484 (w), 465 (w), and 452 (w) cm.$^{-1}$.

Conductivity in Nitromethane.—Molar conductance values were 66.6 and 68.3 ohm^{-1} at concentrations 2.3 and 1.5×10^{-3} *M*, respectively.

μ-(Dimethylphosphido)di-π-cyclopentadienyltetracarbonyldiiron tetraphenylborate was similarly prepared from $P_2(CH_3)_4$ and $[C_5H_5Fe(CO)_2Br]$. Crystallization of the salt from aqueous acetone gave yellow needles (m.p. 191–194° dec.; yield 16%).

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(1) Part IV: R. G. Hayter and W. R. Cullen, *J. Am. Chem. Soc.*, **86**, 1030 (1964).

(2) Shell Development Company, Emeryville, Calif.

(3) R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

(4) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

Anal. Calcd. for $C_{40}H_{36}BFe_2O_4P$: C, 65.4; H, 4.9; Fe, 15.2; O, 8.7. Found: C, 67.05; H, 4.5; Fe, 14.2; O, 8.3.

Infrared Spectrum.—Metal carbonyl bands at 2038 (m), 2026 (s), 2015 (vs), 1992 (s), 1970 (vs), 1942 (m); other absorption bands at 3108 (w), 3102 (w), 3090 (w), 3050 (m), 3028 (w), 2998 (w), 2980 (w), 1578 (m), 1478 (m), 1426 (s), 1360 (w), 1288 (m), 1268 (w), 1247 (m), 1066 (m), 1061 (sh), 1030 (m), 1017 (w), 1000 (m), 947 (sh), 935 (m), 902 (m), 888 (w), 853 (w), 835 (sh), 742 (s), 734 (s), 709 (s), 620 (m), 614 (m), 606 (m), 581 (s), 568 (m), 505 (w), 482 (w), 466 (w), and 453 (w) cm.$^{-1}$.

N.m.r. Spectrum (Dimethyl Sulfoxide Solution).—Doublet at 4.54 τ (J_{HP} = 1.7 c.p.s.) and doublet at 8.11 τ (J_{HP} = 9.0 c.p.s.) due to the cyclopentadienyl and methyl protons, respectively.

Conductivity in Nitromethane.—Molar conductance values were 64.5 and 68.4 ohm.$^{-1}$ at concentrations 2.2 and 1.0 × 10^{-3} *M*, respectively.

Correspondence

The Structures of Bis-(4-amino-3-penten-2-ono)copper(II), -nickel(II), and -palladium(II) and Bis-(3-amino-1-phenyl-2-buten-1-ono)-copper(II) and -nickel(II)

Sir:

X-Ray examination of single crystals of the inner complex chelates of divalent Cu,[1] Ni,[2] and Pd[3] with 4-amino-3-penten-2-one has shown them to be isomorphous.

It has been suggested from measurements of the optical activity of the resolved *d* and *l* components of both the Cu(II) and Ni(II) compounds[4] that the arrangement of ligands around the central metal atom may be tetrahedral or distorted tetrahedral.

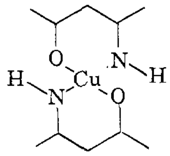
This possibility now becomes an unlikely one, Pd(II) compounds being square-planar as a rule, thus all three of the isomorphous compounds must be square-planar, or slightly distorted from it.

The unit cell is orthorhombic, space group Ccca, the following dimensions being measured: Ni, 16.7 × 15.1 × 13.5 Å., Cu, 16.9 × 15.2 × 13.8 Å., Pd, 17.2 × 15.2 × 13.4 Å.

There are twelve molecules per unit cell, the calculated density of the Ni compound being 1.49 as compared with the measured density of 1.484.

Preliminary calculations have located the heavy atoms in the unit cell. Eight of the twelve molecules in the cell have their metal atoms located at the special positions (e)—*i.e.*, (x, $^1/_4$, $^1/_4$), etc.—of the space group,[5] with x = $^1/_3$. These positions have point symmetry 2, which means that the molecules must have a twofold axis of rotation about the central metal atom. This implies that the molecules have the *trans* configuration. The presence of the twofold axis does not allow us to distinguish between a planar or tetrahedral arrangement, however.

The remaining four molecules in the cell are located at the special positions (a), which have 222-point symmetry. A single molecule of this compound, no matter what configuration it takes, cannot have 222-point symmetry. This indicates that the molecules at these sites are disordered, having at random either one of two possible orientations. Thus, the average of



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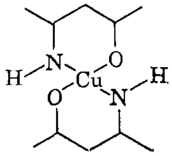
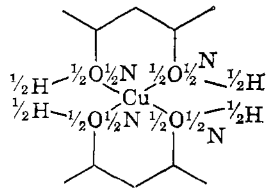


which can be written as



has 222-point symmetry about the metal atom.

It seems very plausible that disorder of this type should occur, as the two differently oriented molecules would be very similar from the viewpoint of molecular packing in the crystal.

The molecules are packed in the crystal in layers separated by approximately 2.9 Å., which also shows that if the molecules are not completely planar, they can be at most only slightly distorted from it.

The related chelates of divalent Cu and Ni with 3-amino-1-phenyl-2-buten-1-one have been prepared by Mr. N. P. Sweeny of these laboratories, and single crystals of these have been examined by X-ray diffraction methods. It has not been possible to prepare the Pd compound thus far.

The crystal structure of these compounds is much simpler than that of the chelates with 4-amino-3-penten-2-one. Crystals of the Cu and Ni chelates with 3-amino-1-phenyl-2-buten-1-one are isomorphous, belonging to the monoclinic space group $P2_1/c$. The Cu compound has the unit cell dimensions 6.52 × 13.13 × 12.50 Å., β = 123.8°.

There are two molecules in the unit cell. Thus the metal atoms can be placed at special positions (a) of the space group, with point symmetry $\bar{1}$. This implies that the molecules have the *trans* configuration and that the coordination of the metal atom with its four near neighbors is perfectly planar.

A more complete study of the two sets of isomorphous compounds described herein is in progress, with

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(1) H. F. Holtzclaw, Jr., J. P. Coleman, and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).

(2) R. D. Archer, *Inorg. Chem.*, **2**, 292 (1063).

(3) N. P. Sweeny, private communication, to be published.

(4) T.-M. Hseu, D. F. Martin, and T. Moeller, *Inorg. Chem.*, **2**, 587 (1963).

(5) International Tables for X-Ray Crystallography, Vol. 1, 1952.