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Complexes of Trivalent Phosphorus Derivatives. XIII. 1,4-Bis(Diphenylphosphino)Butyne-2 and its Complexes[1]

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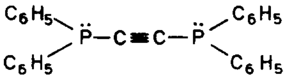
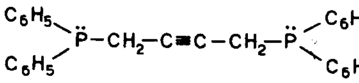
Reaction of 1,4-dichlorobutyne-2 with lithium diphenylphosphide gives the new acetylenic ditertiary phosphine $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2(PfC{\equiv}CPf)$ which could be converted to its dioxide and disulfide by conventional methods. This ditertiary phosphine forms bridging complexes of various types. Thus the following monobridged complexes can be prepared: (a) $(PfC{\equiv}CPf)[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ by reaction of $PfC{\equiv}CPf$ with $CH_3Mo(CO)_3C_5H_5$; (b) $(PfC{\equiv}CPf)[FeBr(CO)C_5H_5]_2$ and the cation $(PfC \equiv CPf)[Fe(CO)_2C_5H_5]_2^{2+}$ by reaction of $PfC{\equiv}CPf$ with $C_5H_5Fe(CO)_2Br$; (c) $(PfC{\equiv}CPf)[CoI_2C_5H_5]_2$ by reaction of $PfC{\equiv}CPf$ with $C_5H_5Co(CO)I_2$; and (d) $(PfC{\equiv}CPf)(AuCl)_2$ by reaction of $PfC{\equiv}CPf$ with chloroauric acid. It was also possible to prepare the dibridged complexes $(PfC{\equiv}CPf)_2(PtCl_2)_2$ and $(PfC{\equiv}CPf)_2[Ni(CO)_2]_2$ by reactions of $PfC{\equiv}CPf$ with chloroplatinic acid and $[C_5H_5NiCO]_2$, respectively. However, all attempts to prepare tribridged complexes of $PfC{\equiv}CPf$ were unsuccessful.

Introduction

Numerous metal complexes of the acetylenic ditertiary phosphine $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ (I) (abbreviated as $Pf{\equiv}Pf$) have been prepared.[4-9] This ditertiary phosphine was shown to behave almost exclusively as a bidentate bimetallic[9] (bridging) ligand. Moreover, complexes with one (*e.g.* $[C_5H_5Mn(CO)(NO)]_2(Pf{\equiv}Pf)[PF_6]_2)$, two (*e.g.* $[Pf{\equiv}PfNi(CO)_2]_2)$, or three (*e.g.* $(Pf{\equiv}Pf)_3[NiCO]_2$ or $(Pf{\equiv}Pf)_3[Mo(CO)_3]_2)$ bridging $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ (I) ligands could be prepared. The complexing properties of I can be attributed to the rigidity of the linear $-C{\equiv}C-$ bridge between the two phosphorus atoms which forces the two phosphorus atoms to remain too far apart to form chelate (bidentate monometallic[9]) derivatives but which holds the two phosphorus atoms rigidly in positions suitable for forming multiple bridges between metal atoms.

This paper examines the complexing properties of the acetylenic ditertiary phosphine $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(_6H_5)_2$ (II) (abbreviated as $PfC{\equiv}CPf$) which has a four carbon bridge between the two phosphorus atoms. The methylene groups in this four carbon bridge give it considerable additional flexibility. This flexibility is not nearly sufficient to give II chelating properties but can affect the types of bridging complexes formed by II. In order to investigate the complexes formed by II a sample of this ligand was prepared from lithium diphenylphosphide and 1,4-dichlorobutyne-2 and reacted with a variety of metal complexes known to form bridging compounds of various types with the more rigid ligand I.


I


II

Experimental Section

Triphenylphosphine and diphenylchlorophosphine were purchased from Eastern Chemical Corporation, Pequannock, New Jersey. 1,4-Dichlorobutyne-2 was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin. Tetrahydrofuran was freshly redistilled over lithium aluminum hydride. Melting and decomposition points were determined in capillaries and are uncorrected. Reactions with organometallic compounds were performed in a nitrogen atmosphere.

Preparation of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ *(II).* A mixture of 150 g (0.573 moles) of triphenylphosphine, 8.0 g (1.15 g atom) of lithium wire, and 1000 ml of tetrahydrofuran was stirred for 7 hr at room temperature. The red solution of lithium diphenylphosphide was treated dropwise with a solution of 52.5 g (0.566 moles) of *tert*-butyl chloride in 50 ml of tetrahydrofuran in order to destroy the phenyllithium byproduct.[10] During the addition of the *tert*-butyl chloride the reaction mixture was kept at room tempe-

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[1] For Part XII of this series see R. B. King and P. N. Kapoor, *J. Organometal. Chem.*, *18*, 357 (1969).
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[4] A. J. Carty and A. Efraty, *Canad. J. Chem.*, *46*, 1598 (1968).
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[7] A. J. Carty and A. Efraty, *Inorg. Chem.*, *8*, 543 (1969).
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[9] R. B. King and A. Efraty, *Inorg. Chem.*, *8*, 2374 (1969).
[10] A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, *27*, 1001 (1962).

rature by cooling with an ice bath. After the addition of *tert*-butyl chloride was complete, the reaction mixture was cooled in a –78° bath and then treated dropwise with 35 g (0.285 moles) of 1,4-dichlorobutyne-2 over a period of one hour. The reaction mixture was then allowed to warm slowly to room temperature, stirred at room temperature for 12 hr, and finally boiled under reflux for 30 minutes. The volume of the reaction mixture was then reduced to ~300 ml by evaporation at 25°/40 mm. A large excess (~600 ml) of water was then added. This precipitated an oily product which was separated by decantation. The oil was dissolved in benzene (~200 ml) and the filtered solution concentrated to ~100 ml at 25°/15 mm. Addition of 50 ml of ethanol followed by storage at –10° in a freezer for several days gave 27 g (24% yield) of white crystalline $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$, (II) m.p. 79-80°, after filtration and drying.

Slightly better results (32% yield and a more readily purified product) could be obtained by substituting diphenylchlorophosphine for the triphenylphosphine in the above preparation and omitting the *tert*-butyl chloride treatment.

Conversion of II to its Dioxide $(C_6H_5)_2P(O)CH_2C{\equiv}CCH_2P(O)(C_6H_5)_2$. A mixture of 0.20 g (0.5 mmole) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (II), 5 ml (8.8 mmoles) of 6% aqueous hydrogen peroxide, and 40 ml of acetone was boiled under reflux with stirring for 2 hr. Solvent was removed at 25°/15 mm and the residue recrystallized from a mixture of dichloromethane and hexane to give 0.21 g (97% yield) of white $(C_6H_5)_2P(O)CH_2C{\equiv}CCH_2P(O)(C_6H_5)_2$ m.p. 214-216°.

Conversion of II to its Disulfide $(C_6H_5)_2P(S)CH_2C{\equiv}CCH_2P(S)(C_6H_5)_2$. A mixture of 0.15 g (0.37 mmole) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (II), 0.15 g (4.7 mg atom) of sulfur, and 25 ml of carbon disulfide was boiled under reflux with stirring for 5 hr. Solvent was removed at ~25°/15 mm and the residue crystallized twice from a mixture of dichloromethane and hexane to give 0.050 g (29% yield) of white $(C_6H_5)_2P(S)CH_2C{\equiv}CCH_2P(S)(C_6H_5)_2$, m.p. 139-141°.

Reaction of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ *with* $CH_3Mo(CO)_3C_5H_5$. A mixture of 1.0 g (2.48 mmoles) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (II), 2.0 g (7.7 mmoles) of $CH_3Mo(CO)_3C_5H_5$,[11] and 100 ml of acetonitrile was stirred at room temperature for 72 hr. The yellow precipitate which formed was filtered and recrystallized twice from mixtures of dichloromethane and hexane to give 1.44 g (62% yield) of yellow $(PfC{\equiv}CPf)[Mo(CO)_2(COCH_3)(C_5H_5)]_2$, m.p. 172-174°.

Reaction of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ *with* $C_5H_5Fe(CO)_2Br$. A mixture of 1.0 g (2.48 mmoles) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (II), 0.75 g (2.92 mmoles) of $C_5H_5Fe(CO)_2Br$,[12] and 50 ml of dichloromethane was boiled under reflux for 1 hr. The dichloromethane was removed at ~25°/15 mm and 50 ml of toluene then added to the residue. This mixture was then boiled under reflux for 45 minutes. After cooling to room temperature the brown precipitate was filtered and washed with benzene. It was dissolved in a mixture of acetone and absolute ethanol and treated with 1.5 g (9.2 mmoles) of ammonium hexafluorophosphate. After ~ 36 hours the solvents were removed at 25°/15 mm. Excess ammonium hexafluorophosphate was washed from the residue with water. The water-insoluble portion was then recrystallized from a mixture of acetone and absolute ethanol to give 0.065 g (2.5% yield) of $[C_5H_5Fe(CO)_2]_2(PfC{\equiv}CPf)[PF_6]_2$, m.p. 244-246°.

The toluene solution from the original reaction was treated with 75 ml of hexane and then chromatographed on a 2×25 cm alumina column prepared in hexane. A green band was eluted with dichloromethane, but no crystalline product could be obtained from this eluate. Further elution of the column with acetone gave a green solution from which 0.035 g (1.6% yield) of green $(PfC{\equiv}CPf)[FeBr(CO)(C_5H_5)_2]_2$, m.p. 147-149°, could be obtained by evaporation at 25°/15 mm.

Reaction of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ *with* $C_5H_5CoCOI_2$. A mixture of 1.0 g (2.48 mmoles) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (II), 2.2 g (5.42 mmoles) of $C_5H_5CoCOI_2$,[13] and 100 ml of benzene was stirred at room temperature for 50 hr. The dark precipitate which formed was removed by filtration and washed with dichloromethane, acetone, and methanol to give 1.6 g (55% yield) of $(PfC{\equiv}CPf)[CoI_2C_5H_5]_2$. The solubility of this compound in the usual organic solvents was too low to permit recrystallization. Upon heating it decomposed without melting, but the decomposition point could not be determined owing to the dark color of the compound.

Reaction of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ *with* $[C_5H_5NiCO]_2$. A mixture of 2.0 g (5.0 mmoles) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (II), 0.50 g (1.65 mmoles) of $[C_5H_5NiCO]_2$,[14] and 100 ml of benzene was stirred for 57 hours at room temperature. After addition of 75 ml of hexane, solvent was removed from the filtered green solution at ~25°/15 mm. The residue was recrystallized from a mixture of dichloromethane and hexane to give 0.35 g (20% yield) of very pale green $(PfC{\equiv}CPf)_2[Ni(CO)_2]_2$, m.p. 80-81°.

Reaction of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ *with Chloroplatinic Acid.* A mixture of 0.75 g (1.85 mmoles) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (II), 0.5 g (1.22 mmoles) of commercial chloroplatinic acid (37.5% platinum), and 100 ml of 95% ethanol was stirred for 26 hr at room temperature. The reaction mixture turned from deep yellow to colorless almost immediately. The white precipitate which separated was removed by filtration and washed with boiling hexane to remove any excess ligand II. The product was recrystallized from a mixture of dichloromethane and absolute ethanol to give 0.7 g (85% yield) of white crystalline $(PfC{\equiv}CPf)_2(PtCl_2)_2$, m.p. 207-210°.

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Reaction of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ with Chloroauric Acid. A mixture of 1.0 g (2.48 mmoles) of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ (II), 1.30 g (3.83 mmoles) of commercial chloroauric acid (49% gold), and 40 ml of absolute ethanol was boiled under reflux for 10 minutes. After cooling to room temperature, the product was removed by filtration and purified by recrystallization from a mixture of dichloromethane and ethanol to give 0.15 g (9% yield) of pale yellow crystalline $(PfC{\equiv}CPf)(AuCl)_2$, m.p. 214-215°.

Infrared Spectra. The following spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 257 infrared spectrometer with grating optics:

A. $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ *(II)*. ν(CH) frequencies at 3072 (w), 3055 (vw, sh), 3025 (vw), 3010 (sh), 2928 (vw, sh), 2918 (vw), and 2898 (vw) cm^{-1}; other bands at 1480 (w), 1460 (vw), 1433 (m), 1407 (w), 1326 (vvw), 1306 (vw), 1199 (m), 1157 (vw), 1132 (vvw), 1117 (w), 1102 (vw, sh), 1095 (w), 1065 (w), 1024 (w), 1010 (vvw), 995 (w), 901 (vw), 841 (vvw), 806 (m), 731 (m), 723 (m, sh), 704 (w), and 682 (m) cm^{-1}.

B. $(C_6H_5)_2P(O)CH_2C{\equiv}CCH_2P(O)(C_6H_5)_2$. ν(CH) frequencies at 3080 (vvw), 3060 (vw), 2915 (w), 2885 (w), and 2785 (vvw) cm^{-1}; ν(PO) frequency at 1182 (s) cm^{-1}; other bands at 1480 (vw), 1437 (m), 1400 (m), 1368 (m), 1253 (w, sh), 1245 (w), 1156 (m), 1117 (m), 1103 (m), 1067 (vw), 1024 (vw), 995 (vw), 916 (vw), 810 (m), 724 (m), 708 (m), and 681 (m) cm^{-1}.

C. $(C_6H_5)_2P(S)CH_2C{\equiv}CCH_2P(S)(C_6H_5)_2$. ν(CH) frequencies at 3060 (vvw), 2925 (vw), and 2880 (vw) cm^{-1}; other bands at 1478 (w), 1433 (m), 1379 (w), 1308 (vw), 1180 (vw, br), 1152 (vvw), 1145 (vvw), 1135 (vvw), 1097 (s), 1068 (vw), 1022 (vw), 993 (vw), 813 (m), 735 (m, sh), 723 (m), and 679 (s) cm^{-1}.

D. $(PfC{\equiv}CPf)[Mo(CO)_2(COCH_3)(C_5H_5)]_2$. ν(CH) frequencies at 3135 (vvw), 3110 (vvw), 3075 (vvw, sh), 3055 (vw), 3005 (vvw), 2935 (w), 2905 (w), and 2815 (vvw) cm^{-1}; ν(CO) frequencies at 1945 (vs), 1855 (vvs), and 1610 (vs) cm^{-1}; other bands at 1490 (m), 1440 (s), 1420 (m), 1340 (m), 1318 (w), 1285 (vvw, sh), 1280 (vw), 1269 (vw), 1196 (w), 1169 (w), 1165 (w), 1120 (vw), 1102 (m), 1072 (s), 1035 (w), 1020 (m), 1010 (w), 998 (vw), 920 (m), 855 (w), 840 (s), 825 (s), 816 (s), 762 (s), 756 (s), 722 (s), and 702 (s) cm^{-1}.

E. $[C_5H_5Fe(CO)_2]_2(PfC{\equiv}CPf)[PF_6]_2$. ν(CH) frequencies at 3128 (w), 3075 (vw), 2960 (vvw), 2920 (vvw), and 2910 (vvw) cm^{-1}; ν(CO) frequencies at 2050 (s) and 2008 (s) cm^{-1}; ν(PF) frequency at 830 (vvs) cm^{-1}; other bands at 1480 (w), 1435 (m), 1420 (vw), 1403 (m), 1363 (vvw), 1309 (vw), 1273 (vvw), 1259 (vvw), 1220 (vvw), 1188 (vw), 1161 (vvw), 1153 (vvw), 1144 (vvw), 1092 (m), 1070 (vw, sh), 1025 (vvw), 1015 (vw), 1005 (vvw), 995 (w), 748 (m), and 684 (m) cm^{-1}.

F. $(PfC{\equiv}CPf)[FeBr(CO)(C_5H_5)]_2$. ν(CH) frequencies at 3068 (vvw), 3040 (vvw), 2920 (vvw), and 2850 (vvw) cm^{-1}; ν(CO) frequency at 1940 (s) cm^{-1}; other bands at 1485 (vw), 1435 (m), 1405 (w), 1365 (vw), 1338 (vvw), 1311 (vvw), 1265 (vvw), 1225 (vw), 1177 (vvw), 1160 (vvw), 1100 (w), 1079 (vvw), 1031 (vvw, sh), 1020 (vw), 1008 (vw), 825 (m), 751 (m), 722 (w), and 698 (m) cm^{-1}.

G. $(PfC{\equiv}CPf)(AuCl)_2$. ν(CH) frequencies at 3050 (vvw), 2922 (vw), and 2893 (vw) cm^{-1}; other bands at 1482 (w), 1434 (m), 1395 (vw, br), 1327 (vw), 1305 (vw), 1183 (vw), 1156 (vw), 1138 (vw), 1100 (m), 1066 (vw, sh), 1021 (vw), 992 (w), 825 (m), 727 (m), and 675 (m) cm^{-1}.

H. $(PfC{\equiv}CPf)_2[Ni(CO)_2]_2$. ν(CH) frequencies at 3050 (vw), 2985 (vvw), and 2920 (vw) cm^{-1}; ν(CO) frequencies at 2000 (s) and 1940 (s) cm^{-1}; other bands at 1480 (w), 1433 (m), 1395 (w, br), 1328 (vvw), 1305 (vvw), 1260 (vvw), 1178 (m), 1116 (m), 1093 (m), 1066 (w), 1022 (w), 992 (w), 963 (vw), 805 (w), 732 (m), 705 (w), and 682 (m) cm^{-1}.

Raman Spectra. The following $\nu(C{\equiv}C)$ frequencies were determined from Raman spectra taken in the solid state on the Spex Raman Spectrometer with Spectraphysics 6328 Å helium-neon laser excitation located at McMaster University, Hamilton, Ontario, Canada:

A.	$(C_6H_5)_2P(O)CH_2C{\equiv}CCH_2P(O)(C_6H_5)_2$	2239±2 cm^{-1}
B.	$(C_6H_5)_2P(S)CH_2C{\equiv}CCH_2P(S)(C_6H_5)_2$	2241±2 cm^{-1}
C.	$(PfC{\equiv}CPf)[Mo(CO)_2(COCH_3)(C_5H_5)]_2$	2240±2 cm^{-1}

The following compounds were too fluorescent under the excitation conditions for the Raman spectra to be obtained: $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$, $(PfC{\equiv}CPf)(AuCl)_2$ and $(PfC{\equiv}CPf)_2(PtCl_2)_2$.

Mass Spectra. The following mass spectra were obtained at 70 e.v. electron energies and the indicated sample temperatures using a Perkin-Elmer Hitachi RMU-6 mass spectrometer. Relative intensities are given in parentheses.

A. $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_7$ *(200°)*. $(C_6H_5)_4P_2C_4H_1^+$ (54), $(C_6H_5)_3P_2C_4H_4^+$ (6), $(C_6H_5)_3PC_4H_3^+$ (6), $(C_6H_5)_3PC_3H_2^+$ (6), $(C_6H_5)_3P^+$ (6), $(C_6H_5)_2PC_4H_4^+$ (9), $(C_6H_5)_2P^+$ (59), $C_{12}H_8P^+$ (100), $C_{10}H_8P^+$ (6), $C_{10}H_6P^+$ (5), $C_{12}H_8^+$ (14), $C_8H_6P^+$ (7), $C_7H_6P^+$ (6), $C_6H_5P^+$ (12), $C_6H_4P^+$ (13), $C_7H_7^+$ (9), and $C_6H_5^+$ (7).

B. $(C_5H_5)_2P(O)CH_2C{\equiv}CCH_2P(O)(C_6H_5)_2$ *(360°)*. $(C_5H_5)_4P_2O_2C_4H_4^+$ (2.2), $(C_6H_5)_4P_2O_2C_4H_3^+$ (1.7), $(C_6H_5)_3P(O)C_4H_3^+$ (3.5), $(C_6H_5)_3P(O)C_4H_2^+$ (1.7), $(C_6H_5)_3PC_4H_3^+$ (1.9), $(C_6H_5)_3P^+$ (2.3), $(C_6H_5)_2P(O)C_4H_4^+$ (100), $(C_6H_5)_2PC_4H_3^+$ (7.6), $C_{15}H_{10}P^+$? (1.7), $(C_6H_5)_2PO^+$ (18), $(C_6H_5)_2P^+$(16), $C_{12}H_8P^+$ (24), $C_{10}H_8PO^+$ (4.5), $C_{11}H_{10}P^+$ (2.3), $C_{11}H_8P^+$ (1.5), $C_{11}H_7O^+$ (3.4), $C_{12}H_{10}^+$ (2.2), $C_{12}H_9^+$ (2.9), $C_{12}H_8^+$ (4.5), $C_8H_6P^+$ (3.0), $C_{10}H_8^+$ (15), $C_6H_6PO^+$ (4.8), $C_6H_5PO^+$ (3.0), $C_6H_6P^+$ (2.2), $C_6H_5P^+$ (3.0), $C_6H_4P^+$ (3.1), $C_7H_7^+$ (5.4), $C_6H_6^+$ (7.5), $C_6H_5^+$ (16), and PO^+ (17).

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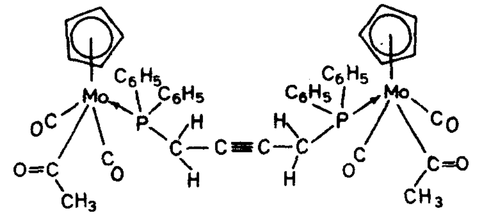
C. *$(C_6H_5)_2P(S)CH_2C{\equiv}CCH_2P(S)(C_6H_5)_2$ (340°).* $(C_6H_5)_4P_2S_2C_4H_4^+$ (5.8), $(C_6H_5)_4P_2S_2C_4H_3^+$ (2.5), $(C_6H_5)_4P_2SC_4H_4^+$ (3.2), $(C_6H_5)_3P_2SC_4H_4^+$ (2.4), $(C_6H_5)_3P_2C_4H_4^+$ (15), $(C_6H_5)_2PSC_4H_4^+$ (91), $(C_6H_5)_2PSC_4H_4^+$ (100), $(C_6H_5)_3P^+$ (2.4), $(C_6H_5)_2POC_4H_4^+$? (3.1), $(C_6H_5)_2PC_4H_4^+$ (5.2), $(C_6H_5)_2PS^+$ (91), $(C_6H_5)_2P^+$ (25), $C_{12}H_8P^+$ (40), $C_{10}H_8P^+$ (3.0), $C_{10}H_6P^+$ (2.7), $C_{12}H_8^+$ (6.1), $C_6H_4PS^+$ (57), $C_8H_6P^+$ (4.1), $C_{10}H_8^+$ (4.5), $C_6H_6P^+$ (2.9), $C_6H_5P^+$ (7.5), $C_6H_4P^+$ (9.3), $C_7H_7^+$ (2.6), $C_6H_6^+$ (2.5), $C_6H_5^+$ (11), and PS^+ (11).

Discussion

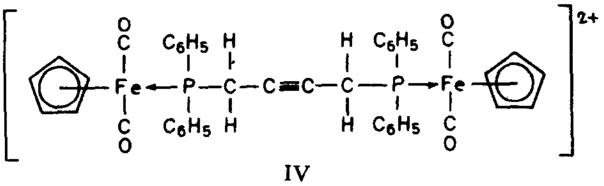
The 1,4-bis(diphenylphosphino)butyne-2, a new compound, was characterized by its elemental analysis and mass spectrum (see below). The proton n.m.r. spectrum supports structure II and excludes the possibility of rearrangement of the propargylic halide $ClCH_2C{\equiv}CCH_2Cl$ to an allenic derivative such as $(C_6H_5)_2PCH{=}C{=}CHCH_2P(C_6H_5)_2$ upon reaction with the lithium diphenylphosphide. Furthermore, the 1,4-bis(diphenylphosphino)butyne-2 can be converted to a dioxide and a disulfide by standard methods. Laser Raman spectra of both the dioxide and disulfide show a $\nu(C{\equiv}C)$ frequency around 2240 cm^{-1} indicating further the retention of the carbon-carbon triple bond in II.

Reactions of 1,4-bis(diphenylphosphino)butyne-2 (II) with several transition metal derivatives give bidentate bimetallic derivatives where a single PfC≡CPf ligand bridges two metal atoms. Thus the reaction of PfC≡CPf (II) with $CH_3Mo(CO)_3C_5H_5$ in acetonitrile solution readily gives a yellow precipitate of $(PfC{\equiv}CPf)[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ which exhibits the expected infrared metal ν(CO) frequencies at 1945 and 1855 cm^{-1}; the expected infrared acyl ν(CO) frequency at 1610 cm^{-1}; and the expected Raman $\nu(C{\equiv}C)$ frequency at 2240 cm^{-1}. The formation of $(PfC{\equiv}CPf)[Mo(CO)_2(COCH_3)(C_5H_5]_2$ (III) from $CH_3Mo(CO)_3C_5H_5$ and PfC≡CPf (II) in acetonitrile solution corresponds completely to the reported[17] formation of analogous $(diphos)[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ compounds from $CH_3Mo(CO)_3C_5H_5$ and all other ditertiary phosphines tried except the unusually good chelating agent *cis*–$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$.

The cyclopentadienyliron dicarbonyl halides $C_5H_5Fe(CO)_2X$ (X = Cl, Br, or I) are reported to react with tertiary phosphines to give both yellowish ionic derivatives of the type $[C_5H_5Fe(CO)_2PR_3]^+$ and green non-ionic derivatives of the type $C_5H_5Fe(CO)(PR_3)X$.[18] The reaction between $C_5H_5Fe(CO)_2Br$ and PfC≡CPf (II) likewise gives both the tan ionic $(PfC{\equiv}CPf)[Fe(CO)_2C_5H_5]_2^{2+}$ (IV) and the green non-ionic $(PfC{\equiv}CPf)[FeBr(CO)C_5H_5]_2$ (V). Only low yields of the pure products could be isolated from the reaction mixture.

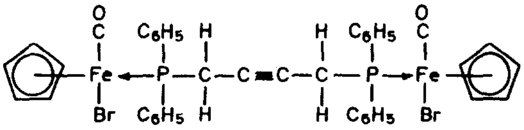


III

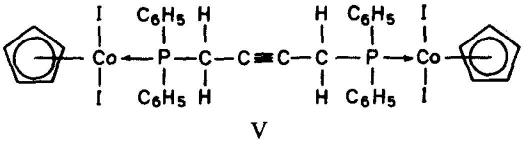


IV

Both IV and V have a single PfC≡CPf bridge between the two iron atoms and exhibit the expected number of ν(CO) frequencies (two for IV and one for V) for the proposed structures. Another similar compound is the cobalt derivative $(PfC{\equiv}CPf)[CoI_2C_5H_5]_2$ (VI) obtained from PfC≡CPf and $C_5H_5CoCOI_2$ analogous to the preparation of other $C_5H_2CoI_2PR_3$ derivatives from $C_5H_5CoCOI_2$ and the appropriate tertiary phosphine under mild conditions.[13] The insolubility of the black cobalt derivative VI in all non-reactive organic solvents tried prevented purification by recrystallization or study of its n.m.r. spectrum. Another binuclear (PfC≡CPf) derivative of a cyclopentadienylmetal system with one bridge between two metal atoms is the previously reported[9] $(PfC{\equiv}CPf)[Mn(CO)(NO)(C_5H_5)]_2[PF_6]_2$.



VI



V

Two PfC≡CPf (II) derivatives with two bridges between a pair of metal atoms were prepared, but the preparation and purification of such compounds appear to be considerably more difficult than similar compounds of the ligand $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ (I) without the CH_2 groups. Reaction of $[C_5H_5NiCO]_2$ with PfC≡CPf (II) gives the dicarbonyl derivative $(PfC{\equiv}CPf)_2[Ni(CO)_2]_2$ (VII) with two PfC≡CPf bridges between the nickel atoms. The infrared spectrum of VII exhibits the expected two ν(CO) frequencies of a $(R_3P)_2Ni(CO)_2$ derivative.[19] Furthermore, molecular weight determinations on VII in solution support the binuclear formulation rather than formulation as either a mononuclear derivative with a sterically impossible chelating PfC≡CPf (II) ligand

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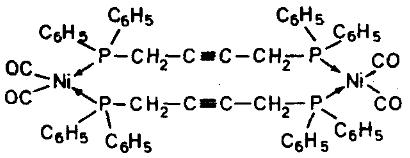
[17] R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, *8*, 1792 (1969).

[18] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, *5*, 1177 (1966).

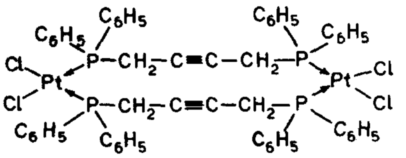
[19] G. R. Van Hecke and W. De W. Horrocks, Jr., *Inorg. Chem.*, *5*, 1960 (1966).

or a trinuclear or higher molecular weight derivative. The other PfC$\equiv$CPf derivative prepared in this work which has two bridges between a pair of metal atoms is the platinum derivative (PfC$\equiv$CPf)$_2$(PtCl$_2$)$_2$ (VIII), a typical square planar platinum(II) phosphine complex.

Several derivatives of Pf$\equiv$Pf (*e.g.* (Pf$\equiv$Pf)$_3$[Mo(CO)$_3$]$_2$ [20] and (Pf$\equiv$Pf)$_3$(MCl)$_2$ (M = Cu or Au),[7] have been prepared which have three Pf$\equiv$Pf (I) bridges between a pair of metal atoms. All attempts to prepare similar derivatives of PfC$\equiv$CPf (II) with three bridges between a pair of metal atoms were unsuccessful. Thus reaction of chloroauric acid with PfC$\equiv$CPf (II) (even in excess) gave only the derivative (PfC$\equiv$CPf)(AuCl)$_2$ with a single PfC$\equiv$CPf bridge. Attempts to prepare a derivative with three PfC$\equiv$CPf bridges analogous to the reported (Pf$\equiv$Pf)$_3$[NiCO]$_2$ gave only the compound VII discussed above. Other attempts to prepare complexes with three PfC$\equiv$CPf bridges by reaction of PfC$\equiv$CPf with the cycloheptatriene derivative C$_7$H$_8$Mo(CO)$_3$ or with solutions of copper(II) salts give ill-defined products of uncertain composition.



VII



VIII

These studies on the preparation of complexes of 1,4-bis(diphenylphosphino) butyne-2 (II) indicate that this ligand forms very easily a single bridge between a pair of metal atoms and can form two bridges between a pair of metal atoms, but apparently cannot form three bridges between a pair of metal atoms. The reluctance for PfC$\equiv$CPf to form multiple bridges can be attributed to the flexibility of the four carbon chain between the two phosphorus atoms because of the presence of the two CH$_2$ groups. Once one bridge is formed this flexibility of the PfC$\equiv$CPf ligand (II) makes it increasingly difficult for the phosphorus atoms of this ligand to be in proper relative positions to form additional bridges between the same pair of metal atoms. On the other hand, the Pf$\equiv$Pf ligand (I) without CH$_2$ groups in the bridge is rigid. Its phosphorus atoms can remain in proper relative positions to form additional bridges between a pair of metal atoms even after the first bridge is formed. For this reason the Pf$\equiv$Pf (I) ligand unlike the PfC$\equiv$CPf (II) ligand readily forms complexes with three ligand bridges between two metal atoms. Neither Pf$\equiv$Pf (I) nor PfC$\equiv$CPf (II) can form chelate (bidentate monometallic) derivatives, since the linearity of the carbon-carbon triple bond in both cases forces the phosphorus atoms to remain too far apart to bond to a single metal atom.

The proton n.m.r. spectra of all of the PfC$\equiv$CPf (II) derivatives studied in this work exhibit the expected resonances from the ten equivalent phenyl protons and the four equivalent methylene protons. The fine structure of the methylene protons in the n.m.r. spectra of the various PfC$\equiv$CPf derivatives is of some interest. If the methylene protons are coupled only to the phosphorus atom (spin 1/2) to which the methylene group is directly bonded, a doublet with a separation of about 6 c.p.s. is expected. The platinum complex (PfC$\equiv$CPf)$_2$(PtCl$_2$)$_2$ (VIII) exhibits a pattern of this type. However, if the methylene protons are coupled not only to the phosphorus atom to which the methylene group is directly bonded but also to the other phosphorus atom by interaction through the carbon-carbon triple bond and the other methylene group, a triplet is expected. The parent ligand (C$_6$H$_5$)$_2$PCH$_2$C$\equiv$CCH$_2$P(C$_6$H$_5$) (II) exhibits a triplet pattern of this type. It thus appears that complex formation by PfC$\equiv$CPf (II) decreases markedly the coupling from the phosphorus atoms to the methylene protons through the carbon-carbon triple bond. In case where the coupling from the phosphorus atoms to the methylene protons through the carbon-carbon triple bond is intermediate between the large coupling in PfC$\equiv$CPf (II) and the negligible coupling in the platinum complex (PfC$\equiv$CPf)$_2$(PtCl$_2$)$_2$ (VIII), a doublet superimposed on a broad resonance is observed (d* in Table I). Examples of complexes exhibiting this intermediate pattern are (PfC$\equiv$CPf)(AuCl)$_2$ and (PfC$\equiv$CPf)[Mo(CO)$_2$(COCH$_3$)(C$_5$H$_5$)]$_2$ (III) as well as the disulfide. The number of complexes of PfC$\equiv$CPf on which n.m.r. data of suitable quality to observe this effect are available is still too small for more detailed conclusions on the factors affecting the amount of coupling through the carbon-carbon triple bond and the other methylene group of the protons of one methylene group to the far phosphorus atom to be elucidated. The qualitative effects on the n.m.r. spectra caused by this variation of coupling of the methylene protons to the far phosphorus atom are similar to the effects on the n.m.r. spectra of the methyl protons of tris(dimethylamino)phosphine complexes[21] caused by variations in the couplig through the metal atom of the methyl protons in one tris(dimethylamino)phosphine ligand to the phosphorus atoms of other tris(dimethylamino)phosphine ligands despite the different origins of the two effects.

In connection with the characterization of (C$_6$H$_5$)$_2$PCH$_2\equiv$CCH$_2$P(C$_6$H$_5$)$_2$ (II) its mass spectrum was obtained. The fragmentation pattern exhibits features similar to those reported[22] for the mass spectra of other ditertiary phosphines such as bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane. The molecular ion undergoes cleavage of phosphorus-carbon bonds giving fragment ions such as

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(20) R. B. King and A. Efraty, unpublished results (1968).

(21) R. B. King, *Inorg. Chem.*, 2, 936 (1963).

(22) R. Colton and Q. N. Porter, *Austral. J. Chem.*, *21*, 2215 (1968).

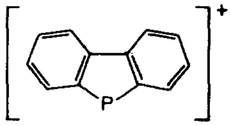
Table I. New Compounds prepared in this work

Compound [a]	Color	m.p.		Analyses, % [b]				Proton N.M.R., τ [c]		
				C	H	P	Other	C_6H_5	CH_2	C_5H_5
$Ph_2PCH_2C{\equiv}CCH_2PPh_2$	white	79-80°	Calcd.	78.5	6.0	15.4	—	2.63d (4)	7.21t (3)	—
			Found	78.5	6.1	15.6	—			
$Ph_2P(O)CH_2C{\equiv}CCH_2P(O)Ph_2$	white	214-216°	Calcd.	72.8	5.6	14.3	7.4 (O)	~2.3 m	6.85d (11)	—
			Found	73.1	5.4	14.1	7.3 (O)	2.55		
$Ph_2P(S)CH_2C{\equiv}CCH_2P(S)Ph_2$	white	139-141°	Calcd.	67.9	5.0	13.3	13.7 (S)	~2.25 m	6.67d* (9)	—
			Found	68.8	5.0	13.7	13.2 (S)	~2.26		
$(PfC{\equiv}CPf)[Mo(CO)_2(COCH_3)(C_5H_5)]_2$	yellow	172-174°	Calcd.	58.6	4.3	6.6	10.2 (O)	2.42, 2.50	6.63d* (6)	4.92 s
			Found	58.3	4.4	6.3	10.1 (O)			
$(PfC{\equiv}CPf)[FeBr(CO)C_5H_5]_2$ [d]	green	147-149°	Calcd.	54.5	3.9			Solubility in $CDCl_3$		
			Found	54.4	4.0			and $(CD_3)_2CO$ too low		
$(PfC{\equiv}CPf)[Fe(CO)_2C_5H_5]_2[PF_6]_2$	tan	244-246°	Calcd.	47.3	3.2	11.6	21.4 (F)	2.37, 2.42	5.97d* (6)	4.38
			Found	48.1	3.4	11.7	21.4 (F)			
$(PfC{\equiv}CPf)[CoI_2C_5H_5]_2$	black	[e]	Calcd.	38.7	2.9	5.3	43.2 (I)	Solubility too low		
			Found	40.2	2.9	4.9	41.5 (I)			
$(PfC{\equiv}CPf)(AuCl)_2$	pale yellow	214-215°	Calcd.	38.0	2.7		8.0 (Cl)	2.53	6.71d* (6)	—
			Found	37.7	2.9		8.1 (Cl)			
$(PfC{\equiv}CPf)_2(PtCl_2)_2$	white	207-210°	Calcd.	48.9	3.5		10.3 (Cl)	~2.7 vbr	6.26d (6)	
			Found	50.1	3.7		10.3 (Cl)	2.74		
$(PfC{\equiv}CPf)_2[Ni(CO)_2]_2$ [g]	pale yellow	80-81°	Calcd.	67.0	4.5	11.5	6.0 (O)	2.42, 2.66	~7.0 vbr	
			Found	67.0	5.0	11.6	6.3 (O)		~7.4 vbr	
$(PfC{\equiv}CPf)[Mn(CO)(NO)(C_5H_5)]_2[PF_6]_2$ [d, f]								2.36, 2.43	6.01d (3)	4.26 s

[a] The following abbreviations were used: Ph = phenyl; $PfC{\equiv}CPf$ = 1,4-bis(diphenylphosphino)-butyne-2. [b] Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. [c] These proton n.m.r. spectra were taken either on the Varian HA-100 spectrometer at 100 Mc. or on the Perkin-Elmer Hitachi R-20 spectrometer at 60 Mc. Unless otherwise indicated $CDCl_3$ was used as the solvent. Coupling constants in c.p.s. are given in parentheses. The following abbreviations are used to indicate the fine structure: s = singlet, d = doublet, d* = doublet superimposed on a broad peak, t = triplet, m = multiplet, vbr = very broad. [d] The n.m.r. spectra of these compounds were obtained in $(CD_3)_2CO$ solution. [e] This compound did not liquefy upon heating up to 300°. Instead decomposition appeared to take place, but the decomposition temperature could not be identified because of the black color of the compound. [f] Data from R. B. King and A. Efraty, *Inorg. Chem.*, *8*, 2374 (1969). [g] Molecular weight: Calcd: 1074, Found: 1011, 1100 (Mechrolab vapor pressure osmometer in benzene). These determinations were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

$(C_6H_5)_3P_2C_4H_4^+$ from cleavage of the phosphorus-phenyl bond and $(C_6H_5)_2PC_4H_4^+$ from cleavage of the phosphorus-propargylic bond. The ion $(C_6H_5)_3P^+$ is observed in the mass spectra of II as in the reported[22] mass spectra of ditertiary phosphines. A phenyl shift has been postulated[22] to account for the presence of the $(C_6H_5)_3P^+$ ion; however, the triphenylphosphine could be produced from the pyrolysis of the ditertiary phosphines at the necessarily elevated temperatures in the mass spectrometer inlet system. The observation of $(C_6H_5)_3P^+$ in th mass spectrum of II suggests a pyrolytic origin for this ion since in order to form $(C_6H_5)_3P^+$ in the case of II a phenyl group would have to shift from a phosphorus atom at one end of a four carbon chain to a phosphorus atom at the other end, a relatively unlikely process. Further fragmentation gives $(C_6H_5)_2P^+$ which can undergo dehydrogenation to give $C_{12}H_8P^+$, probably a 9-phosphafluorene ion IX. Further fragmentation occurs by acetylene (C_2H_2) elimination to give ions such as $C_{10}H_8P^+$, and $C_8H_6P^+$.

The mass spectra of the dioxide $(C_6H_5)_2P(O)CH_2C{\equiv}CCH_2P(O)(C_6H_5)_2$ and the disulfide $(C_6H_5)_2P(S)CH_2C{\equiv}CCH_2P(S)(C_6H_5)_2$ were also obtained. The molecular ions are observed. However, the relatively high inlet temperatures (~350°) necessary to obtain mass spectra of the only slightly volatile dioxide and disulfide make pyrolytic processes likely. It is therefore uncertain which of the observed ions arise from fragmentation of the molecular ion and which of the observed ions arise from pryolysis products. The general fragmentation patterns of the mass spectra of the dioxide and disulfide resemble those of the parent ditertiary phosphine $PfC{\equiv}CPf$ (II) with some, but not all, of the fragment ions containing oxygen or sulfur from the dioxide or disulfide, respectively. The mass spectra of the dioxide and disulfide of II exhibit the ion $(C_6H_5)_3P^+$ but not the corresponding chalcogenides $(C_6H_5)_3PE^+$ (E = O or S) suggesting further that triphenylphosphine is a pyrolysis rather than a fragmentation product in these mass spectra.



IX

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