

Complexes of Trivalent Phosphorus Derivatives. XIII.
1,4-Bis(Diphenylphosphino)Butyne-2 and its Complexes¹R. B. King² and A. Efraty³

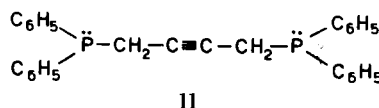
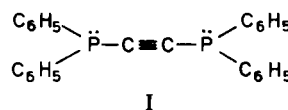
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Reaction of 1,4-dichlorobutyne-2 with lithium diphenylphosphide gives the new acetylenic ditertiary phosphine $(C_6H_5)_2PCH_2C\equiv CCH_2P(C_6H_5)_2(PfC\equiv CPf)$ which could be converted to its dioxide and disulfide by conventional methods. This 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 bimetallic⁹ (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 monometallic⁹) 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 $(C_6H_5)_2PCH_2C\equiv CCH_2P(C_6H_5)_2$ (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.



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 by-product.¹⁰ During the addition of the *tert*-butyl chloride the reaction mixture was kept at room temperature.

(10) A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, **27**, 1001 (1962).

(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).
 (5) A. J. Carty and A. Efraty, *Inorg. Nucl. Chem. Letters*, **4**, 427 (1968).
 (6) A. J. Carty and A. Efraty, *Chem. Comm.*, 1559 (1968).
 (7) A. J. Carty and A. Efraty, *Inorg. Chem.*, **8**, 543 (1969).
 (8) A. J. Carty, A. Efraty, and T. W. Ng, *Canad. J. Chem.*, **47**, 1429 (1969).
 (9) R. B. King and A. Efraty, *Inorg. Chem.*, **8**, 2374 (1969).

perature 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-dichlorobutylene-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 $25^{\circ}/40$ 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 $25^{\circ}/15$ 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. $79-80^{\circ}$, 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 $25^{\circ}/15$ 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. $214-216^{\circ}$.

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 $\sim 25^{\circ}/15$ 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. $139-141^{\circ}$.

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. $172-174^{\circ}$.

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 $\sim 25^{\circ}/15$ 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 $25^{\circ}/15$ 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. $244-246^{\circ}$.

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. $147-149^{\circ}$, could be obtained by evaporation at $25^{\circ}/15$ 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 $\sim 25^{\circ}/15$ 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. $80-81^{\circ}$.

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. $207-210^{\circ}$.

(13) R. B. King, *Inorg. Chem.*, **5**, 82 (1966).

(11) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); R. B. King, *Organometal. Syn.*, **1**, 145 (1965).

(14) J. F. Tilney-Bassett, *J. Chem. Soc.*, 577 (1961); R. B. King, *Organometal. Syn.*, **1**, 119 (1965).

(15) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

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). $\nu(CH)$ 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 (vww), 1306 (vw), 1199 (m), 1157 (vw), 1132 (vww), 1117 (w), 1102 (vw, sh), 1095 (w), 1065 (w), 1024 (w), 1010 (vww), 995 (w), 901 (vw), 841 (vww), 806 (m), 731 (m), 723 (m, sh), 704 (w), and 682 (m) cm^{-1} .

B. $(C_6H_5)_2P(O)CH_2C\equiv CCH_2P(O)(C_6H_5)_2$. $\nu(CH)$ frequencies at 3080 (vww), 3060 (vw), 2915 (w), 2885 (w), and 2785 (vww) cm^{-1} ; $\nu(PO)$ 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. $(C_6H_5)_2P(S)CH_2C\equiv CCH_2P(S)(C_6H_5)_2$. $\nu(CH)$ frequencies at 3060 (vww), 2925 (vw), and 2880 (vw) cm^{-1} ; other bands at 1478 (w), 1433 (m), 1379 (w), 1308 (vw), 1180 (vw, br), 1152 (vww), 1145 (vww), 1135 (vww), 1097 (s), 1068 (vw), 1022 (vw), 993 (vw), 813 (m), 735 (m, sh), 723 (m), and 679 (s) cm^{-1} .

D. $(Pfc\equiv CPf)[Mo(CO)_2(COCH_3)(C_6H_5)]_2$. $\nu(CH)$ frequencies at 3135 (vww), 3110 (vww), 3075 (vww, sh), 3055 (vw), 3005 (vww), 2935 (w), 2905 (w), and 2815 (vww) cm^{-1} ; $\nu(CO)$ 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 (vww, 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. $[C_5H_5Fe(CO)_2]_2(Pfc\equiv CPf)[PF_6]_2$. $\nu(CH)$ frequencies at 3128 (w), 3075 (vw), 2960 (vww), 2920 (vww), and 2910 (vww) cm^{-1} ; $\nu(CO)$ frequencies at 2050 (s) and 2008 (s) cm^{-1} ; $\nu(PF)$ frequency at 830 (vvs) cm^{-1} ; other bands at 1480 (w), 1435 (m), 1420 (vw), 1403 (m), 1363 (vww), 1309 (vw), 1273 (vww), 1259 (vww), 1220 (vww), 1188 (vw), 1161 (vww), 1153 (vww), 1144 (vww), 1092 (m), 1070 (vw, sh), 1025 (vww), 1015 (vw), 1005 (vww), 995 (w), 748 (m), and 684 (m) cm^{-1} .

F. $(Pfc\equiv CPf)[FeBr(CO)(C_6H_5)]_2$. $\nu(CH)$ fre-

quencies at 3068 (vww), 3040 (vww), 2920 (vww), and 2850 (vww) cm^{-1} ; $\nu(CO)$ frequency at 1940 (s) cm^{-1} ; other bands at 1485 (vw), 1435 (m), 1405 (w), 1365 (vw), 1338 (vww), 1311 (vww), 1265 (vww), 1225 (vw), 1177 (vww), 1160 (vww), 1100 (w), 1079 (vww), 1031 (vww, sh), 1020 (vw), 1008 (vw), 825 (m), 751 (m), 722 (w), and 698 (m) cm^{-1} .

G. $(Pfc\equiv CPf)(AuCl)_2$. $\nu(CH)$ frequencies at 3050 (vww), 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. $(Pfc\equiv CPf)_2[Ni(CO)_2]_2$. $\nu(CH)$ frequencies at 3050 (vw), 2985 (vww), and 2920 (vw) cm^{-1} ; $\nu(CO)$ frequencies at 2000 (s) and 1940 (s) cm^{-1} ; other bands at 1480 (w), 1433 (m), 1395 (w, br), 1328 (vww), 1305 (vww), 1260 (vww), 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:

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|--|--------------------|
| 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. $(Pfc\equiv CPf)[Mo(CO)_2(COCH_3)(C_6H_5)]_2$ | 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. $(C_6H_5)_2PCH_2C\equiv CCH_2P(C_6H_5)_2$ (200°). $(C_6H_5)_4P_2C_4H_4^+$ (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. $(C_6H_5)_2P(O)CH_2C\equiv CCH_2P(O)(C_6H_5)_2$ (360°). $(C_6H_5)_4P_2O_2C_4H_4^+$ (2.2), $(C_6H_5)_3P_2O_2C_4H_3^+$ (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), $(C_6H_5)_2PC_3H_3^+$ (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), $C_6H_5PO^+$ (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).

(16) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, 86, 2299 (1964).

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), $(C_6H_5)_2PSC_4H_3^+$ (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

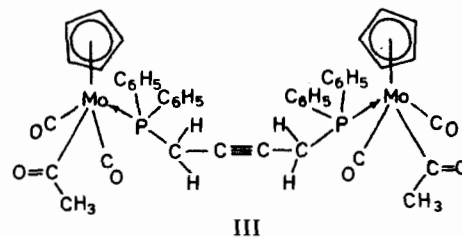
The 1,4-bis(diphenylphosphino)butyne-2, a new compound, was characterized by its elemental analysis and mass spectrum (see below). The proton n.m.r. spectrum supports structure II and excludes the possibility of rearrangement of the propargylic halide $ClCH_2C \equiv CCH_2Cl$ to an allenic derivative 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 $PfC \equiv CPf$ ligand bridges two metal atoms. Thus the reaction of $PfC \equiv CPf$ (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 $\nu(CO)$ frequencies at 1945 and 1855 cm^{-1} ; the expected infrared acyl $\nu(CO)$ 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 $PfC \equiv CPf$ (II) in acetonitrile solution corresponds completely to the reported¹⁷ 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*- $(C_6H_5)_2PCH=CHP(C_6H_5)_2$.

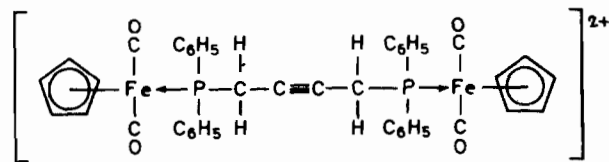
The cyclopentadienyliron dicarbonyl halides $C_5H_5Fe(CO)_2X$ ($X = Cl, Br, \text{ or } I$) are reported to react with tertiary phosphines to give both yellowish ionic derivatives of the type $[C_5H_5Fe(CO)_2PR_3]^+$ and green non-ionic derivatives of the type $C_5H_5Fe(CO)(PR_3)X$.¹⁸ The reaction between $C_5H_5Fe(CO)_2Br$ and $PfC \equiv CPf$ (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.

(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).

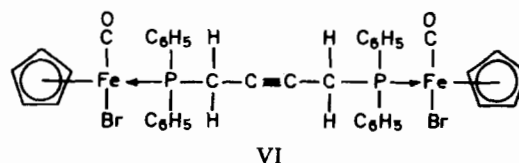


III

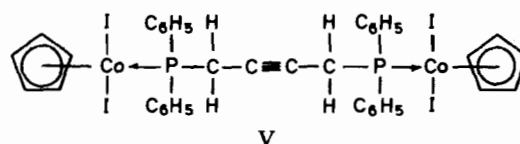


IV

Both IV and V have a single $PfC \equiv CPf$ bridge between the two iron atoms and exhibit the expected number of $\nu(CO)$ 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 $PfC \equiv CPf$ and $C_5H_5CoCOI_2$ analogous to the preparation of other $C_5H_5CoI_2PR_3$ 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 $(PfC \equiv CPf)$ derivative of a cyclopentadienylmetal system with one bridge between two metal atoms is the previously reported⁹ $(PfC \equiv CPf)[Mn(CO)(NO)(C_5H_5)]_2[PF_6]_2$.



VI



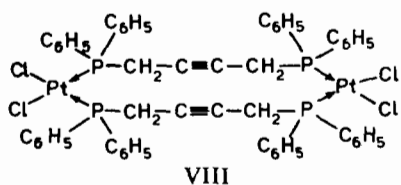
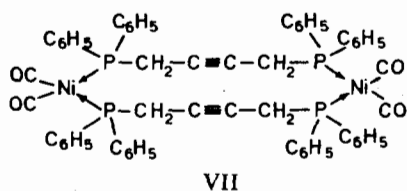
V

Two $PfC \equiv CPf$ (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 $PfC \equiv CPf$ (II) gives the dicarbonyl derivative $(PfC \equiv CPf)_2[Ni(CO)_2]_2$ (VII) with two $PfC \equiv CPf$ bridges between the nickel atoms. The infrared spectrum of VII exhibits the expected two $\nu(CO)$ 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 $PfC \equiv CPf$ (II) ligand

(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 $\text{Pfc}\equiv\text{CPf}$ derivative prepared in this work which has two bridges between a pair of metal atoms is the platinum derivative $(\text{Pfc}\equiv\text{CPf})_2(\text{PtCl}_2)_2$ (VIII), a typical square planar platinum(II) phosphine complex.

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



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 $\text{Pfc}\equiv\text{CPf}$ 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 $\text{Pfc}\equiv\text{CPf}$ 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 $\text{Pfc}\equiv\text{Pfc}$ 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 $\text{Pfc}\equiv\text{Pfc}$ (I) ligand unlike the $\text{Pfc}\equiv\text{CPf}$ (II) ligand readily forms complexes with three ligand bridges between two metal atoms. Neither $\text{Pfc}\equiv\text{Pfc}$ (I) nor $\text{Pfc}\equiv\text{CPf}$ (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 $\text{Pfc}\equiv\text{CPf}$ (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 $\text{Pfc}\equiv\text{CPf}$ 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 $(\text{Pfc}\equiv\text{CPf})_2(\text{PtCl}_2)_2$ (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 $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{C}\equiv\text{CCH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (II) exhibits a triplet pattern of this type. It thus appears that complex formation by $\text{Pfc}\equiv\text{CPf}$ (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 $\text{Pfc}\equiv\text{CPf}$ (II) and the negligible coupling in the platinum complex $(\text{Pfc}\equiv\text{CPf})_2(\text{PtCl}_2)_2$ (VIII), a doublet superimposed on a broad resonance is observed (d^* in Table I). Examples of complexes exhibiting this intermediate pattern are $(\text{Pfc}\equiv\text{CPf})(\text{AuCl})_2$ and $(\text{Pfc}\equiv\text{CPf})[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_2$ (III) as well as the disulfide. The number of complexes of $\text{Pfc}\equiv\text{CPf}$ 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 complexes²¹ caused by variations in the coupling 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 $(\text{C}_6\text{H}_5)_2\text{PCH}_2\equiv\text{CCH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (II) its mass spectrum was obtained. The fragmentation pattern exhibits features similar to those reported²² 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

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

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

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

Table I. New Compounds prepared in this work

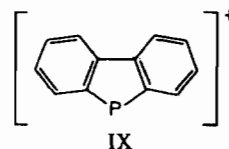
Compound ^a	Color	m.p.	C	Analyses, % ^b				C ₆ H ₅	Proton N.M.R., τ ^c		
				H	P	Other	CH ₂		CH ₃	C ₆ H ₅	
Ph ₂ PCH ₂ C≡CCH ₂ PPh ₂	white	79-80°	Calcd. 78.5 Found 78.5	6.0 6.1	15.4 15.6	—	2.65d (4)	7.21t (3)	—		
Ph ₂ P(O)CH ₂ C≡CCH ₂ P(O)Ph ₂	white	214-216°	Calcd. 72.8 Found 73.1	5.6 5.4	14.3 14.1	7.4 (O) 7.3 (O)	~2.3 m 2.35	6.85d (11)	—		
Ph ₂ P(S)CH ₂ C≡CCH ₂ P(S)Ph ₂	white	139-141°	Calcd. 67.9 Found 68.8	5.0 5.0	13.3 13.7	13.7 (S) 13.2 (S)	~2.25 m ~2.26	6.67d* (9)	—		
(Pfc≡Cpf)[Mo(CO) ₂ (COCH ₃)(C ₆ H ₅) ₂]	yellow	172-174°	Calcd. 58.6 Found 58.3	4.3 4.4	6.6 6.3	10.2 (O) 10.1 (O)	2.42, 2.50	6.65d* (6)	4.92 s		
(Pfc≡Cpf)[FeBr(CO)C ₆ H ₅] ₂ ^d	green	147-149°	Calcd. 54.5 Found 54.4	3.9 4.0	—	—	Solubility in CDCl ₃ and (CD ₃) ₂ CO too low				
(Pfc≡Cpf)[Fe(CO) ₂ C ₆ H ₅] ₂ [PF ₆] ₂	tan	244-246°	Calcd. 47.3 Found 48.1	3.2 3.4	11.6 11.7	21.4 (F) 21.4 (F)	2.37, 2.42	5.97d* (6)	4.38		
(Pfc≡Cpf)[CoI ₂ C ₆ H ₅] ₂	black	°	Calcd. 38.7 Found 40.2	2.9 2.9	5.3 4.9	43.2 (I) 41.5 (I)	Solubility too low				
(Pfc≡Cpf)(AuCl) ₂	pale yellow	214-215°	Calcd. 38.0 Found 37.7	2.7 2.9	—	8.0 (Cl) 8.1 (Cl)	2.55	6.71d* (6)	—		
(Pfc≡Cpf) ₂ (PtCl ₂) ₂	white	207-210°	Calcd. 48.9 Found 50.1	3.5 3.7	—	10.3 (Cl) 10.3 (Cl)	~2.7 vbr 2.74	6.26d (6)	—		
(Pfc≡Cpf) ₂ [Ni(CO) ₂] ₂ ^e	pale yellow	80-81°	Calcd. 67.0 Found 67.0	4.5 5.0	11.5 11.6	6.0 (O) 6.3 (O)	2.42, 2.66	~7.0 vbr ~7.4 vbr	—		
(Pfc≡Cpf)[Mn(CO)(NO)(C ₆ H 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≡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 CDCl₃ 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 (CD₃)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.

(C₆H₅)₃P₂C₄H₄⁺ from cleavage of the phosphorus-phenyl bond and (C₆H₅)₂PC₄H₄⁺ from cleavage of the phosphorus-propargylic bond. The ion (C₆H₅)₃P⁺ is observed in the mass spectra of II as in the reported²² mass spectra of ditertiary phosphines. A phenyl shift has been postulated²² to account for the presence of the (C₆H₅)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 (C₆H₅)₃P⁺ in the mass spectrum of II suggests a pyrolytic origin for this ion since in order to form (C₆H₅)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 (C₆H₅)₂P⁺ which can undergo dehydrogenation to give C₁₂H₈P⁺, probably a 9-phosphafluorene ion IX. Further fragmentation occurs by acetylene (C₂H₂) elimination to give ions such as C₁₀H₈P⁺, and C₈H₆P⁺.

The mass spectra of the dioxide (C₆H₅)₂P(O)CH₂C≡CCH₂P(O)(C₆H₅)₂ and the disulfide (C₆H₅)₂P(S)CH₂C≡CCH₂P(S)(C₆H₅)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 un-

certain which of the observed ions arise from fragmentation of the molecular ion and which of the observed ions arise from pyrolysis products. The general fragmentation patterns of the mass spectra of the dioxide and disulfide resemble those of the parent ditertiary phosphine Pfc≡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 (C₆H₅)₃P⁺ but not the corresponding chalcogenides (C₆H₅)₃PE⁺ (E = O or S) suggesting further that triphenylphosphine is a pyrolysis rather than a fragmentation product in these mass spectra.



Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grants AF-AF-AFOSR-68-1435 and AF-AFOSR-68-1435A. We also thank Prof. R. J. Gillespie and his assistant Mrs. Beryl Spear for running the Raman spectra on the McMaster University laser Raman Spectrometer.