Polytertiary phosphines and arsines. VII. Zerovalent platinum complexes of arylated polytertiary phosphines and arsines

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The reaction of $[Pd(SPh)_2]_n$ with ethylenediamine reveals an unexpectedly high reactivity for the polymer. The isolation of IX shows that the ethylenediamine is not merely acting as a solvent (*cf.* Hunter and Krause).[34] Its high reactivity in this reaction contrasts with its behavior toward organic halides and suggests that steric effects of the phenyl groups may not be very important. The reactions with ethylenediamine are nucleophilic substitutions and have no electrophilic component as in the reactions with RX. We are unable to estimate at present the relative reactivities of the palladium polymers toward ethylenediamine, but work on this type of reaction is continuing.

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(34) G. E. Hunter and R. A. Krause, *Inorg. Chem.*, **9**, 537 (1970).

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Polytertiary Phosphines and Arsines. VII. Zerovalent Platinum Complexes of Arylated Polytertiary Phosphines and Arsines[1]

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Zerovalent platinum complexes of polytertiary phosphines and phosphine–arsines can be prepared by reaction of a mixture of K_2PtCl_4 and the ligand with sodium borohydride in aqueous ethanol. The chelating bidentate ligands $(m\text{-}CH_3C_6H_4)_2PCH_2CH_2P(C_6H_5)_2$, $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$, and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ form yellow to orange derivatives of the type (bidentate)$_2$Pt. The nonchelating ditertiary phosphines *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ and $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ form three-coordinate yellow [*trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]_3Pt$ and two-coordinate yellow $[(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2]_2Pt$, respectively. The potentially tridentate ligands $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ and $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ form the polymetallic derivatives $\{[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5\}_4Pt_3$ and $\{[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5\}_3Pt_2$, respectively. The tetratertiary phosphines $[(C_6H_5)_2PCH_2CH_2]_3P$ and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ form the yellow derivatives $[(C_6H_5)_2PCH_2CH_2]_3PPt$ and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2]_2Pt_2$, respectively. The new platinum(II) derivatives [*cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]PtCl_2$ and $\{$[*trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]_4Pt_2\}[PF_6]_4$ are also described.

Introduction

Zerovalent platinum derivatives of the type $(R_3P)_4Pt$,[3] particularly the triphenylphosphine derivative, form novel derivatives with small molecules of interest such as oxygen,[4] carbon monoxide,[5] carbon disulfide,[6] hexafluoroacetone,[7] and various alkynes.[8] This paper describes the preparation and properties of related zerovalent platinum derivatives of polytertiary phosphines and phosphine–arsines, particularly of the ligands made available by preparative techniques recently developed in this laboratory.[9,10]

Experimental Section

Potassium tetrachloroplatinate(II) (46.6% platinum), K_2PtCl_4, was purchased from Engelhard Industries, Newark, N. J. The ligands *cis*-bis(1,2-diphenylphosphino)ethylene, *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (abbreviated as cPf=Pf),[11] *trans*-bis(1,2-diphenylphosphino)ethylene, *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (abbreviated as tPf=Pf),[10] bis(1,2-diphenylphosphino)acetylene, $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ (abbreviated as Pf≡Pf),[12] 1-diphenylphosphino-2-diphenylarsinoethane, $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ (abbreviated as Asf-Pf),[10] bis(2-diphenylphosphinoethyl)phenylphosphine, $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (abbreviated as Pf-Pf-Pf),[10] bis(2-diphenylarsinoethyl)phenylphosphine, $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ (abbreviated as Asf-Pf-Asf),[10] tris(2-diphenylphosphinoethyl)phosphine, $[(C_6H_5)_2PCH_2CH_2]_3P$ [abbreviated as P(-Pf)$_3$],[13] and 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf-Pf-Pf),[10] were prepared by the cited published procedures.

Preparation of 1-Diphenylphosphino-2-di-*m*-tolylphosphinoethane.—The preparation of the ligand 1-diphenylphosphino-2-di-*m*-tolylphosphinoethane (abbreviated as Pmt-Pf) is given in detail here since it has not been previously described.

A mixture of 4.0 g (18.9 mmol) of diphenylvinylphosphine, 4.0 g (18.7 mmol) of di-*m*-tolylphosphine (from Pressure Chemical Corp., Pittsburgh, Pa.), 0.4 g (3.57 mmol) of potassium *tert*-butoxide, and 100 ml of redistilled tetrahydrofuran was boiled under reflux for 16 hr in a nitrogen atmosphere. Solvent was then removed at 25° (25 mm). The resulting brown oil was triturated with 100 ml of methanol, whereupon it solidified to give a white solid. This solid was filtered and crystallized from a mixture of benzene and methanol to give 7.6 g (95% yield) of white $(m\text{-}CH_3C_6H_4)_2PCH_2CH_2P(C_6H_5)_2$, mp 95°. *Anal.* Calcd for $C_{28}H_{28}P_2$: C, 78.8; H, 6.6; P, 14.5; mol wt, 426. Found: C, 78.6; H, 6.8; P, 14.5; mol wt, 422 (osmometer in benzene).

Preparations of the Zerovalent Platinum Derivatives (Table I).—The indicated quantity (Table I) of potassium tetrachloroplatinate(II), water (about 20 ml for each gram of K_2PtCl_4), the indicated quantity (Table I) of the polytertiary phosphine or

(1) For part VI of this series, see R. B. King and P. N. Kapoor, *Inorg. Chim. Acta*, in press.

(2) Postdoctoral research associate, 1968–1969 and 1970–1971.

(3) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(4) C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 561 (1968).

(5) (a) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958); (b) F. Cariati and R. Ugo, *Chim. Ind.* (*Milan*), **48**, 1288 (1961).

(6) M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 865 (1967).

(7) M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *Chem. Commun.*, 502 (1966); B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc. A*, 167 (1968).

(8) (a) J. Chatt, L. A. Duncanson, and R. G. Guy, *J. Chem. Soc.*, 827 (1961); (b) J. Chatt, R. G. Guy, L. A. Duncanson, and D. T. Thompson, *ibid.*, 5170 (1963); (c) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(9) R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, **91**, 5191 (1969).

(10) R. B. King and P. N. Kapoor, *ibid.*, **93**, 4158 (1971).

(11) A. M. Aguiar and D. Daigle, *ibid.*, **86**, 2299 (1964).

(12) H. Hartmann, C. Beerman, and H. Czempik, *Z. Anorg. Allg. Chem.*, **287**, 261 (1956).

(13) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).

TABLE I
PREPARATIONS AND PROPERTIES OF ZEROVALENT PLATINUM DERIVATIVES OF POLYTERTIARY PHOSPHINES AND PHOSPHINE-ARSINES

Compd[a]	Preparation,[b] mmol: Ligand[a,c]	K_2PtCl_4	Yield, %	Color	Mp,[d] °C	Analyses,[e] %: C	H	P	Mol wt[f]
$(Pmt\text{-}Pf)_2Pt$	Pmt-Pf (3.0)	1.2	72	Yellow	197	64.3 (64.2)	5.4 (5.4)	11.8 (11.8)	
$(Asf\text{-}Pf)_2Pt$	Asf-Pf (2.9)	1.2	46	Yellow	170–173	58.2 (57.8)	4.7 (4.7)	5.8[g] (5.7)[g]	1187 (1048)
$(cPf{=}Pf)_2Pt$	cPf=Pf (15)	6.0	91	Orange	249–253	62.7 (63.2)	4.5 (4.5)	12.1 (12.6)	863 (988)
$(tPf{=}Pf)_3Pt$	tPf=Pf (3.8)	1.2	60	Yellow	188–189	67.2 (67.7)	4.9 (4.8)	12.3 (13.4)	1363 (1383)
$(Pf{\equiv}Pf)_2Pt$	Pf≡Pf (7.6)	2.4	82	Yellow	183–187	62.9 (63.4)	4.5 (4.1)	11.3 (12.6)	890 (984)
$(Pf\text{-}Pf\text{-}Pf)_4Pt_3$	Pf-Pf-Pf (1.5)	0.72	77	Yellow-orange	181–184	59.8 (59.8)	5.2 (4.9)	12.3[h] (13.6)[h]	2719 (2723)
$(Asf\text{-}Pf\text{-}Asf)_3Pt_2$	Asf-Pf-Asf (1.3)	0.72	62	Orange	134–137	52.2 (54.3)	4.2 (4.4)	4.1[i] (4.1)[i]	2070 (2256)
$P(\text{-}Pf)_3Pt$	$P(\text{-}Pf)_3$ (2.2)	1.0	100	Yellow	105–107	57.2 (58.3)	5.5 (4.9)	14.0 (14.3)	900 (866)
$(Pf\text{-}Pf\text{-}Pf\text{-}Pf)_2Pt_2$	Pf-Pf-Pf-Pf (2.2)	1.45	72	Yellow	180–185	57.2 (58.3)	5.5 (4.9)	14.5 (14.3)	1631 (1732)

[a] The ligand abbreviations are given in the Experimental Section. [b] The preparations of these zerovalent platinum complexes were all carried out by the general procedure given in the Experimental Section. [c] The numbers of millimoles of ligand used in these reactions are indicated in parentheses. [d] Melting points were taken in open capillaries and are uncorrected. [e] Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Meade Microanalytical Laboratory, Amherst, Mass. All samples were dried at 80° (1 mm) for at least 12 hr before analysis. Calculated values are given in parentheses. [f] Molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., using a vapor pressure osmometer in benzene solution. Calculated values are given in parentheses. [g] Calcd: As, 13.8. Found: As, 15.8. [h] Calcd: Pt, 19.6. Found: Pt, 17.9. [i] Calcd: As, 19.9. Found: As, 20.5.

phosphine–arsine ligand, and about 100 ml of ethanol was stirred and heated until a clear yellow solution was obtained. Excess aqueous sodium borohydride was then added (3–6 g of $NaBH_4$). The yellow to orange precipitate of the zerovalent platinum derivative was removed by filtration and purified by crystallization from either a benzene–methanol or a benzene–hexane mixture.

Preparations of the Platinum(II) Derivatives of the Unsaturated Ditertiary Phosphines cPf=Pf and tPf=Pf.—The preparations of platinum(II) derivatives of cPf=Pf and tPf=Pf do not appear to have been described previously and thus are given here.

(a) **$(cPf{=}Pf)PtCl_2$.**—A mixture of 0.5 g (1.2 mmol) of potassium tetrachloroplatinate(II), 0.7 g (1.8 mmol) of cPf=Pf, 50 ml of water, and 50 ml of ethanol was stirred at room temperature for 6 hr. The resulting gray precipitate was removed by filtration and purified by crystallization from a mixture of dimethylformamide and diethyl ether to give 0.4 g (50% yield) of white crystalline $(cPf{=}Pf)PtCl_2$, mp >340°, ν(Pt–Cl) 318 (m) and 298 (m) cm^{-1}. *Anal.* Calcd for $C_{26}H_{22}Cl_2P_2Pt$: C, 47.1; H, 3.3; Cl, 10.7; P, 9.4. Found: C, 47.2; H, 3.4; Cl, 10.4; P, 9.1.

(b) **$[(tPf{=}Pf)_4Pt_2][PF_6]_4$.**—A mixture of 0.5 g (1.2 mmol) of potassium tetrachloroplatinate(II), 0.7 g (1.8 mmol) of tPf=Pf, 50 ml of water, and 50 ml of ethanol was stirred at room temperature for 6 hr. Solvent was removed from the resulting clear yellow solution at 40° (15 mm). The yellow solid residue was washed with water. The water-insoluble product was dissolved in acetone and treated with aqueous ammonium hexafluorophosphate. Evaporation of the acetone at 25° (25 mm) gave a precipitate which was filtered, washed with water, and crystallized from a mixture of acetone and ethanol to give 1.1 g (65% yield) of yellow crystalline $[(tPf{=}Pf)_4Pt_2][PF_6]_4$, mp 260–263° dec, molar conductance (0.001–0.003 *M* in acetone) 505 ± 25 ohm^{-1} cm^1 mol^{-1}. *Anal.* Calcd for $C_{52}H_{44}F_{12}P_6Pt$: C, 48.9; H, 3.4; F, 17.9; P, 14.5. Found: C, 48.3; H, 3.4; F, 17.8; P, 14.5.

Infrared Spectra.—The following infrared spectra (3500–600 cm^{-1}) were obtained in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics.

A. **$(Pmt\text{-}Pf)_2Pt$.**—3040 (w), 2932 (vw), 2897 (vw), 1594 (w), 1475 (m), 1430 (m), 1404 (m), 1301 (w), 1268 (w), 1170 (w), 1100 (m), 1080 (w), 1063 (vw), 1024 (w), 995 (w), 875 (m), 845 (w), 818 (m), 809 (m), 770 (m), 750 (m), 741 (m), 696 (s), and 663 (s) cm^{-1}.

B. **$(Asf\text{-}Pf)_2Pt$.**—3045 (w), 1473 (m), 1426 (m), 1396 (w), 1296 (vs), 1263 (vw), 1173 (vw), 1084 (w), 1065 (w), 1017 (w), 993 (w), 850 (w), 783 (w), 730 (s), 687 (s), and 633 (w) cm^{-1}.

C. **$(cPf{=}Pf)_2Pt$.**—3050 (vw, br), 1480 (w), 1433 (m), 1400 (vw), 1091 (w), 1028 (vw), 772 (vw), 730 (m), 690 (s), and 674 (m) cm^{-1}.

D. **$(tPf{=}Pf)_3Pt$.**—3050 (w), 1583 (w), 1570 (w), 1478 (m), 1433 (s), 1403 (w), 1306 (w), 1272 (w), 1191 (m), 1158 (w, sh), 1113 (m, sh), 1086 (m), 1070 (w, sh), 1026 (w), 1000 (w), 978 (vw), 915 (vw), 848 (vw), 833 (vw), 788 (w), 739 (s), 718 (vw), 695 (s), and 644 (w) cm^{-1}.

E. **$(Pf{\equiv}Pf)_2Pt$.**—3050 (w), 2002 (vw), 1583 (w), 1478 (m), 1433 (s), 1400 (vw, sh), 1328 (vw), 1306 (w), 1277 (vw), 1181 (w), 1158 (vw), 1089 (m), 1069 (vw), 1027 (w), 999 (w), 807 (m), 738 (s), and 690 (s) cm^{-1}.

F. **$(Pf\text{-}Pf\text{-}Pf)_4Pr_3$.**—3050 (w), 2900 (vw, br), 1480 (w), 1433 (m), 1403 (w), 1193 (m), 1175 (m), 1115 (w), 1100 (w), 1065 (vw), 1024 (w), 994 (vw), 735 (m), and 693 (s) cm^{-1}.

G. **$(Asf\text{-}Pf\text{-}Asf)_3Pt_2$.**—3050 (w), 1575 (vw), 1478 (w), 1433 (m), 1413 (w), 1402 (w), 1303 (vw), 1264 (vw), 1180 (w), 1153 (vw), 1103 (vw), 1083 (w), 1075 (w), 1021 (w), 995 (w), 881 (w), 841 (w), 733 (m), and 693 (s).

H. **$P(\text{-}Pf)_3Pt$.**—3075 (vw, sh), 3058 (w), 2940 (vw, br, sh), 2910 (vw), 1590 (w), 1484 (w), 1439 (m), 1412 (w), 1317 (vw), 1312 (w), 1185 (s), 1122 (m), 1105 (m, sh), 1071 (m), 1029 (w), 1000 (w), 744 (s), 725 (m), and 700 (s) cm^{-1}.

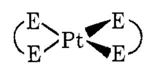
I. **$(Pf\text{-}Pf\text{-}Pf\text{-}Pf)_2Pt_2$.**—3055 (w), 2905 (vw), 1633 (w), 1589 (w), 1570 (w), 1482 (m), 1436 (s), 1415 (m), 1331 (vw), 1312 (w), 1279 (w), 1200 (s), 1178 (s), 1122 (s), 1108 (s), 1072 (m), 1029 (m), 1001 (m), 878 (w), 815 (w), 740 (s), and 700 (s) cm^{-1}.

J. **$(cPf{=}Pf)PtCl_2$.**—3060 (vw), 3043 (vw), 3007 (vw), 1665 (m), 1655 (m), 1572 (vw), 1557 (vw), 1483 (m), 1433 (m), 1387 (w), 1331 (w), 1308 (w), 1278 (w), 1186 (m), 1159 (w), 1103 (s), 1068 (vw), 1027 (w), 997 (w), 969 (w), 915 (vw), 848 (vw), 827 (w), 797 (w), 766 (s), 754 (s), 730 (s), 703 (s), and 688 (s) cm^{-1}.

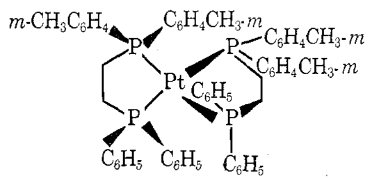
K. **$[(tPf{=}Pf)_4Pt_2][PF_6]_4$.**—3059 (w), 1583 (w), 1573 (w), 1480 (m), 1437 (s), 1402 (w), 1311 (w), 1279 (w), 1181 (m), 1164 (w), 1099 (s), 1024 (w), 1000 (m), 970 (w), 919 (vw), 836 (vs), 740 (s), and 687 (s) cm^{-1}.

Discussion

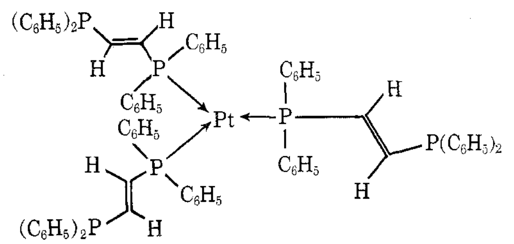
The chelating bidentate ligands Pmt-Pf, Asf-Pf, and cPf=Pf each react with K_2PtCl_4 in the presence of $NaBH_4$ to give zerovalent platinum derivatives of the type (bidentate)$_2$Pt analogous to the reported[14] derivative (Pf-Pf)$_2$Pt similarly obtained from 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf). These (bidentate)$_2$Pt derivatives contain tetrahedral platinum(0) as indicated schematically in structure I (E = donor atom). The proton nmr spectrum of the compound (Pmt-Pf)$_2$Pt ($CDCl_3$ solution) exhibits two methyl resonances of equal intensity at τ 8.03 and 8.06 in contrast with the single methyl resonance at τ 7.77 found in the free ligand Pmt-Pf. This is consistent with structure II for (Pmt-Pf)$_2$Pt in



I



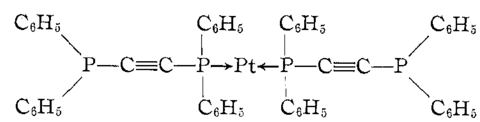
II



III

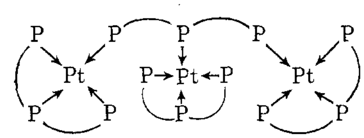
which half of the *m*-tolyl groups are located on the side of the chelate ring corresponding to the phosphorus atom bearing the two phenyl groups in the other chelate ring and the other half of the *m*-tolyl groups are located on the side of the chelate ring corresponding to the phosphorus atom bearing the two *m*-tolyl groups in the other chelate ring.

Zerovalent platinum derivatives of the two ligands tPf=Pf and Pf≡Pf were also investigated. In both of these ditertiary phosphines the rigidity of the unsaturated carbon backbone forces the two phosphorus atoms to remain too far apart for them both to bond to a single metal atom.[15,16] The ligand tPf=Pf forms a monometallic zerovalent platinum derivative of the formula (tPf=Pf)$_3$Pt, apparently a tricoordinate platinum(0) derivative of structure III similar to the reported[5a,17] triphenylphosphine derivative $[(C_6H_5)_3P]_3Pt$. The ligand Pf≡Pf forms a monometallic zerovalent platinum derivative of the formula (Pf≡Pf)$_2$Pt. We first thought that this derivative might be the oxygen complex (Pf≡Pf)$_2$PtO$_2$ but rejected this latter formula for the following reasons: (1) the absence of a strong infrared band in the 800–900-cm^{-1} ν(O–O) region other than bands attributed to the Pf≡Pf ligand; and (2) the stability of this complex to methanolic sodium borohydride. The compound (Pf≡Pf)$_2$Pt thus appears to be a linear two-coordinate platinum(0) derivative IV similar to the much more reactive triphenylphosphine derivative[18] $[(C_6H_5)_3P]_2Pt$ and isoelectronic with well-known linear two-coordinate gold(I) and mercury(II) derivatives. The apparent ability of the acetylenic ligand Pf≡Pf to stabilize linear two-coordinate platinum(0) over trigonal three-coordinate and tetrahedral four-coordinate platinum(0) may arise from the ability of the two carbon–carbon triple bonds, the empty d orbitals of the two coordinating phosphorus atoms in the Pf≡Pf ligands, and a single d orbital of the platinum atom to form a conjugated delocalized system. However, for maximum delocalization of this type, the two Pf≡Pf ligands must form a phosphorus–platinum–phosphorus angle of 180°. This is possible for linear coordination of the platinum atom but not for trigonal or tetrahedral coordination of the platinum atom. A very weak but sharp infrared band at 2002 cm^{-1} may arise from the weakly infrared-active ν(C≡C) frequency of the monoligate monometallic[19] Pf≡Pf which is lowered by removal of electrons from the bonding orbitals of the carbon–carbon triple bonds and/or addition of electrons to the antibonding orbitals of the carbon–carbon triple bonds through the conjugated delocalized system involving the phosphorus and platinum d orbitals.[20] A previously reported[21] example of a zerovalent platinum complex of Pf≡Pf is the bimetallic zerovalent platinum derivative $[(Ph_3P)_2Pt(Pf{\equiv}Pf)]_2$ also containing a triphenylphosphine ligand.

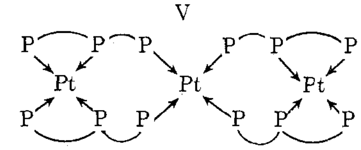


IV

The potentially tridentate ligands Pf-Pf-Pf and Asf-Pf-Asf give polymetallic platinum(0) derivatives. The tritertiary phosphine Pf-Pf-Pf forms a trimetallic derivative of stoichiometry (Pf-Pf-Pf)$_4$Pt$_3$. This stoichiometry is explicable on the basis of structures V and VI with all zerovalent platinum atoms tetrahedral and with all 12 phosphorus atoms of the 4 tritertiary phosphine ligands bonded to some platinum atom. The mixed phosphine–diarsine Asf-Pf-Asf gives a bimetallic derivative of stoichiometry (Asf-Pf-Asf)$_3$Pt$_2$. In this case the number of possible structures is much larger. However, even if both zerovalent platinum atoms are tetrahedral, only eight of the nine available donor atoms in the three Asf-Pf-Asf ligands can be used. The different stoichiometries of the zerovalent platinum derivatives of the closely related potentially tridentate ligands Pf-Pf-Pf and Asf-Pf-Asf can be attributed to the lower tendency of arsenic relative to phosphorus to bond to transition metals.



V



VI

(14) J. Chatt and G. A. Rowe, *Nature (London)*, **191**, 1191 (1961); G. Booth and J. Chatt, *J. Chem. Soc. A*, 2131 (1969).

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

(16) R. B. King and A. Efraty, *ibid.*, **8**, 2374 (1969).

(17) H. C. Clark and K. Itoh, *ibid.*, **10**, 1707 (1971).

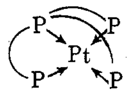
(18) R. Ugo, G. LaMonica, F. Cariati, S. Cenini, and F. Conti, *Inorg. Chim. Acta*, **4**, 390 (1970).

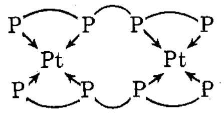
(19) R. B. King, *J. Coord. Chem.*, **1**, 67 (1971).

(20) A. J. Carty and A. Efraty, *Chem. Commun.*, 1559 (1968).

(21) K. S. Wheelock, J. H. Nelson, and H. B. Jonassen, *Inorg. Chim. Acta*, **4**, 399 (1970).

Chelating tetradentate ligands potentially can form tetrahedral platinum(0) derivatives of the type (tetraphos)Pt with all four donor atoms of the ligand bonded to the platinum atom. Such a compound is P(-Pf)$_3$Pt (VII) obtained from the chelating tripod tetratertiary phosphine P(-Pf)$_3$. The linear tetratertiary phosphine Pf-Pf-Pf-Pf also forms a zerovalent platinum complex of stoichiometry (tetraphos)Pt, but a solution molecular weight determination indicated it to be the dimeric derivative (Pf-Pf-Pf-Pf)$_2$Pt$_2$. This dimeric derivative can be formulated as VIII.


VII


VIII

The zerovalent platinum complexes discussed in this paper were originally prepared for use in oxidative addition reactions. However, up to the present time our attempts to obtain tractable oxidative addition products from these new platinum(0) complexes have given unpromising results. In this connection, (cPf=Pf)$_2$Pt was found to be unreactive toward alkynes such as 3-hexyne and phenylacetylene in boiling benzene. Similarly, (tPf=Pf)$_2$Pt was unreactive toward air, carbon monoxide (1 atm), carbon disulfide, and 3-hexyne when the reactions were carried out in boiling benzene. Even when reactions took place (as was the case when some of the zerovalent platinum complexes were treated with dimethyl acetylenedicarboxylate or diethyl azodicarboxylate in boiling benzene), the resulting products did not correspond to obvious stoichiometries and could not be unambiguously characterized by the techniques currently available in our laboratory.

Platinum(II) complexes of the ligands Pf-Pf-Pf,[22] P(-Pf)$_3$,[13] and Pf-Pf-Pf-Pf[13] have been reported in the cited papers. However, platinum(II) complexes of the unsaturated ditertiary phosphines cPf=Pf and tPf=Pf have not previously been described. The Experimental Section of this paper describes for the first time the preparation and characterization of the platinum(II) complexes (cPf=Pf)PtCl$_2$ and [(tPf=Pf)$_4$Pt$_2$][PF$_6$]$_4$. The formulations and properties of these platinum(II) complexes of the cis and trans isomers of $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ correspond completely to the reported[23] platinum(II) complexes of the cis and trans isomers of the closely related olefinic ditertiary arsine $(CH_3)_2As\text{-}CH{=}CHAs(CH_3)_2$.

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(22) R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971).
(23) M. A. Bennett, G. J. Erskine, and J. D. Wild, *Inorg. Chim. Acta*, **2**, 379 (1968).

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Reactions of Halides, Amines, and Organometallic Lewis Bases with Bis(tetracarbonylcobalt)mercury(II)

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Bis(tetracarbonylcobalt)mercury(II) reacts with bidentate nitrogen ligands giving the complexes (L-L)Hg[Co(CO)$_4$] where L-L = 1,10-phenanthroline or 2,2′-bipyridyl. With Co(CO)$_4^-$ or halide, Hg[Co(CO)$_4$] forms the three-coordinate species XHg[Co(CO)$_4$]$_2^-$ where X$^-$ = halide or Co(CO)$_4^-$. No reaction is observed between Hg[Co(CO)$_4$]$_2$ and the neutral organometallic Lewis bases (mesitylene)Mo(CO)$_3$, Fe(CO)$_5$, Fe(CO)$_3$[PPh$_3$]$_2$, and Fe(CO)$_4$AsPh$_3$. Neither amines, halides, Co(CO)$_4^-$, nor the neutral organometallic bases react with Hg[Mn(CO)$_5$]$_2$, Hg[(π-C$_5$H$_5$)Mo(CO)$_3$]$_2$, or Hg[(π-C$_5$H$_5$)Fe(CO)$_2$]$_2$. The Lewis acidity of mercury in HgR$_2$ depends greatly on the nature of the metal carbonyl groups, R, bonded to it. With strongly basic carbonyl groups mercury is a weak Lewis acid while with less basic metal carbonyl substituents its Lewis acidity is increased.

Introduction

Of the group IIb–transition metal carbonyl derivatives, the zinc and cadmium compounds readily add additional ligands giving three- or four-coordinate complexes. M[Mn(CO)$_5$]$_2$[1] (M = Zn, Cd), Cd[(π-C$_5$H$_5$)-Mo(CO)$_3$]$_2$,[2] and Cd[(π-C$_5$H$_5$)W(CO)$_3$]$_2$,[2] for example, add two monodentate nitrogen ligands or a bidentate nitrogen ligand such as 2,2′-bipyridyl. ICd[(π-C$_5$H$_5$)-Mo(CO)$_3$] and Cd[(π-C$_5$H$_5$)Mo(CO)$_3$]$_2$ react[2] with iodide giving anions which may be analogous to Br$_2$Cd-[Co(CO)$_4$]$^-$ which forms[3] from the reaction of Co(CO)$_4^-$ with CdBr$_2$.

The corresponding mercury compounds in general appear to be less reactive with no reaction of Hg[Mn-(CO)$_5$]$_2$,[1] Hg[(π-C$_5$H$_5$)M(CO)$_3$]$_2$[2] (M = Mo, W), or Hg[(π-C$_5$H$_5$)Fe(CO)$_2$]$_2$[2] observed with nitrogen ligands. IHg[(π-C$_5$H$_5$)Mo(CO)$_3$] and Hg[(π-C$_5$H$_5$)Mo(CO)$_3$]$_2$ did not react[2] with iodide. However, a few indications that the mercury in mercury–transition metal carbonyl derivatives may be active as a Lewis acid have been reported. An expanded coordination number about mercury has been observed in the crystal structure[4] of Fe(CO)$_4$(HgCl)$_2$·2py. The addition of halide to Fe(CO)$_4$(HgX)$_2$[5] may result from coordination of the

(1) A. T. T. Hsieh and M. J. Mays, *J. Chem. Soc. A*, 729 (1971).
(2) M. J. Mays and J. D. Robb, *ibid.*, 561 (1969).
(3) J. K. Ruff, *Inorg. Chem.*, **7**, 1499 (1968).
(4) R. W. Baker and P. Pauling, *Chem. Commun.*, 573 (1970).
(5) A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc. A*, 1013 (1968).