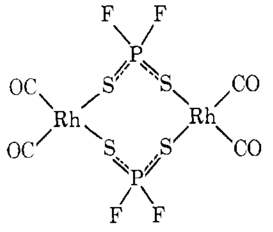
TABLE I

INFRARED DATA[a] (CM^{-1})

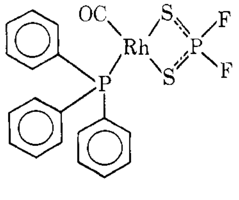
Complex	Metal–carbonyl str freq	P=S
$[Rh(CO)_2(S_2PF_2)]_2$	2088 s, 2075 ms, 2025 s, 1998 ms[b]	692 s, 670 sh
	2083 s, 2070 sh, 2020 s, 1992 mw	690 s, 670 sh
$[Rh(CO)_2(CH_3CO_2)]_2$	2083 vs, 2067 vs, 2027 vs, 1980 s	. . .
$Rh(CO)[P(C_6H_5)_3](S_2PF_2)$	1991 s	697 s, 689 s
$\{Rh(CO)[As(C_6H_5)_3](S_2PF_2)\}_n$[c]	2025 s, 2015 sh, 1996 s	702 s, 688 s
$\{Rh(CO)[Sb(C_6H_5)_3](S_2PF_2)\}_n$[c]	2027 s, 2010 s, 1995 sh	699 s, 685 s

[a] Nujol mulls unless noted otherwise. Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] Pentane solution. [c] Chloroform solution.

$(CO)_2(CH_3CO_2)]_2$[7] which contains bridged acetate groups. The composite data suggest structure I for the parent difluorodithiophosphato complex.



I



II

The reaction of I with triphenylphosphine proceeds with the evolution of carbon monoxide and yields air-stable, yellow crystals. The physical and chemical properties of this material indicate the rupture of the bridged dithiophosphates and the rearrangement to a four-atom chelate as depicted in structure II. When I was allowed to react with triphenylarsine or -stibine, CO was again evolved and air-stable solids were obtained. Analytical data are in close agreement with complexes containing one carbonyl group, one triphenylarsine or -stibine, and one $PS_2F_2^-$ ligand per rhodium atom. Molecular weight determinations indicate that these materials are polymeric. However, the unexpectedly complex patterns in the metal–carbonyl region of the infrared spectra preclude acceptable structural assignments at this time.

---

[7] D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NAVAL WEAPONS CENTER, CORONA, CALIFORNIA 91720

Derivatives of Dichlorohexaphenylphosphonitrile Tetramer

BY A. J. BILBO, C. M. GRIEVE, D. L. HERRING,
AND D. E. SALZBRUNN

Received August 9, 1968

During an investigation of the formation of polymers containing the phosphonitrile ring systems, dichlorohexaphenylphosphonitrile tetramer (Ia), mp 303–304°, was prepared by treating sodium azide with a mixture of diphenylchlorophosphine and phenyldichlorophosphine.[1] This communication describes the preparation of several amine derivatives and some interconversions among halogen, hydroxy, and amine ligands to give a series of tetrameric compounds with the general formula $(C_6H_5)_6X_2P_4N_4$ where X = Cl (Ia, Ib), OH (II), Br (III), $N(CH_3)_2$ (IV), and F (V).

Dihydroxyhexaphenylphosphonitrile tetramer (II) may be prepared by the hydrolysis of Ia in hot, aqueous pyridine.[1] Treatment of II with an excess of PCl_5 resulted in the regeneration of Ia in good yield

$$\text{Ia} \underset{\text{PCl}_5\text{-CHCl}_3}{\overset{\text{H}_2\text{O-py}}{\rightleftharpoons}} \text{II}$$

The reaction of II with $SOCl_2$, however, gave two isomeric forms of dichloro tetramer: Ia, mp 303–304°, in 67% yield, and a low-melting form (Ib), mp 194–195°, in 12% yield. This result is analogous to that found for diazidohexaphenyltetraphosphonitrile which has two isomers melting at 147.5–148 and 206–208°.[2] With the exception of the diazido and dichloro compounds, no other isomers of this cyclic tetramer have been isolated. Elucidation of the structure of these isomers awaits the attention of an X-ray crystallographer.

Hydrolysis of the low-melting isomer (Ib) in aqueous pyridine yielded the same product (II) that was obtained from hydrolysis of Ia, based upon comparison of infrared spectra.

The six amine derivatives shown in Table I were prepared by adding an excess of the appropriate amine to a chloroform suspension of Ia.

Dibromohexaphenylphosphonitrile tetramer (III) was prepared from II and phosphorus pentabromide; however, attempts to synthesize III by allowing thionyl bromide to react with II yielded no characterizable products.

The preparation of trimethyltrichlorophosphonitrile trimer, $(CH_3(Cl)PN)_3$, by treatment of trimethyltrisdimethylaminophosphonitrile trimer, $(CH_3((CH_3)_2N)PN)_3$, with anhydrous hydrogen chloride has been described.[3] In the present work, the cleavage of dimethylamino groups from phosphorus has been used to prepare Ia and III from hexaphenylbis(dimethylamino)phosphonitrile tetramer (IV) by reaction with an excess of the appropriate hydrogen halide

$$\text{IV} \xrightarrow[\text{CHCl}_3]{\text{excess HX}} \text{Ia or III} + (CH_3)_2NH\cdot HX$$

However, no identifiable products were isolated from the reaction of IV with hydrogen iodide, and none of the starting material was recovered.

Replacement of chlorine by fluorine in Ia was accomplished by use of cesium fluoride in refluxing acetonitrile. Other alkali metal fluorides in nitrobenzene as the solvent were employed in this substitution reaction, although the yield of the difluoro analog was considerably lower under these conditions.

---

[1] D. L. Herring and C. M. Douglas, *Inorg. Chem.*, **4**, 1012 (1965).

[2] C. M. Sharts, A. J. Bilbo, and D. R. Gentry, *ibid.*, **5**, 2140 (1966).

[3] G. Tesi and P. J. Slota, Jr., *Proc. Chem. Soc.*, 404 (1960).

TABLE I

AMINE DERIVATIVES OF $(C_6H_5)_6Cl_2P_4N_4$

			Analyses					
Compound	Mp, °C	Yield, %		% C	% H	% P	% N	Mol wt
$(C_6H_5)_6(NH_2)_2P_4N_4$	205–207	85	Calcd	64.1	5.0	18.4	12.5	674
			Found	64.0	5.0	18.1	12.6	668
$(C_6H_5)_6(NHCH_3)_2P_4N_4$	192–194	70	Calcd	65.0	5.4	17.7	12.0	702
			Found	65.3	5.7	17.5	11.9	710
$(C_6H_5)_6[N(CH_3)_2]_2P_4N_4$ (IV)	189–190	60	Calcd	65.8	5.8	17.0	11.5	730
			Found	66.0	6.0	16.7	11.6	723
$(C_6H_5)_6[N(C_2H_5)_2]_2P_4N_4$	260–265 (subl)	70	Calcd	67.2	6.4	15.8	10.7	786
			Found	67.2	6.6	15.5	10.9	774
$(C_6H_5)_6[N(CH_3)C_6H_5]_2P_4N_4$	183–184	60	Calcd	70.3	5.4	14.5	9.8	854
			Found	70.1	5.5	14.3	9.7	840
$(C_6H_5)_6(NC_5H_{10})_2P_4N_4$	290–292	60	Calcd	68.1	6.2	15.3	10.4	810
			Found	68.1	6.4	15.1	10.5	832

Experimental Section

Apparatus.—Molecular weight measurements were determined in benzene, using a Mechrolab Model 301A vapor pressure osmometer. All reactions were carried out either in an inert-atmosphere chamber or under nitrogen to exclude contamination by oxygen and moisture.

Reagents.—Phosphorus pentachloride, phosphorus pentabromide, thionyl chloride, piperidine, N-methylaniline, and diethylamine were supplied by Matheson Scientific Co. and used without further purification. Chloroform and acetonitrile were distilled from phosphorus pentoxide; bromoform was also distilled from phosphorus pentoxide under reduced pressure. The hydrogen halide gases, ammonia, methylamine, and dimethylamine were supplied by the Matheson Co., Inc. Hexaphenyldichlorophosphonitrile tetramer (Ia) was supplied on contract by Alfa Inorganics and was prepared by the method previously described.[1]

Preparation of Amine Derivatives of Ia.—Anhydrous ammonia was bubbled through a stirred slurry of Ia (0.028 mol, 20.0 g) in 500 ml of chloroform for 6 hr. The reaction mixture was then filtered to remove ammonium chloride (1.3 g) and the solvent was evaporated *in vacuo*. The crude product was crystallized from heptane to yield long white needles of hexaphenyldiaminophosphonitrile tetramer (16.0 g).

In the amine reactions, the chloroform was evaporated from the reaction mixture and the solid residue was extracted with benzene. The benzene was removed *in vacuo* and the crude product was recrystallized from hexane. The benzene-insoluble residue was the corresponding amine hydrochloride with no trace of phosphonitrile as determined by an infrared spectrum.

Reaction of II with Phosphorus Pentachloride.—Phosphorus pentachloride (16.6 g, 0.08 mol) was added over a 20-min period to a rapidly stirred slurry of II (27.0 g, 0.04 mol) contained in 250 ml of chloroform. The addition of the phosphorus pentachloride was accompanied by moderate foaming and the slightly yellow solution became clear but clouded again after 1 hr. The reaction was carried out for 48 hr at room temperature with continuous stirring. The reaction mixture was filtered and 9.0 g of hexaphenyldichlorophosphonitrile was isolated (mp 298–300°). The chloroform-soluble reaction product was recovered by evaporation of the solvent. The residue was washed with 200 ml of benzene and filtered to give 18.0 g of Ia (mp 296–298°). The conversion was 95% of the theoretical yield. The two crops of Ia were combined and recrystallized twice from toluene to give a product (mp 303–304°) with an infrared spectrum identical with that of an authentic sample.

Reaction of II with Phosphorus Pentabromide.—Compound II (27.0 g, 0.04 mol) was treated with phosphorus pentabromide (34.0 g, 0.08 mol) in 250 ml of bromoform. The solution was stirred at room temperature for 65 hr. The solvent was then distilled under reduced pressure and the crude brown product was washed with boiling benzene to give 21.0 g (66%) of white crystalline material. Recrystallization from toluene yielded hexaphenyldibromophosphonitrile tetramer (III), mp 245°. *Anal.* Calcd for $C_{36}H_{30}P_4N_4Br_2$: C, 53.9; H, 3.7; P, 15.5; N, 7.0; Br, 20.0; mol wt, 802. Found: C, 54.4; H, 3.6; P, 15.3; N, 6.8; Br, 20.0; mol wt, 822.

Reaction of II with Thionyl Chloride.—A slurry of II (15.0 g, 0.022 mol) in 250 ml of chloroform was treated with thionyl chloride (10.4 g, 0.09 mol). The mixture was refluxed for 20 hr. The precipitate formed during the heating cycle was removed by filtration and dried *in vacuo*. This white crystalline material was identified as Ia, mp 303–304; yield, 10.5 g (67%).

The chloroform solution was evaporated to dryness and the residue was recrystallized from a 1:1 mixture of benzene and heptane to yield 2.0 g of Ib, mp 194–195°. *Anal.* Calcd for $C_{36}H_{30}P_4N_4Cl_2$: C, 60.7; H, 4.2; P, 17.4; N, 7.8; Cl, 9.9; mol wt, 713. Found: C, 60.5; H, 4.5; P, 17.4; N, 8.0; Cl, 10.0; mol wt, 711.

Reaction of Hexaphenylbis(dimethylamino)phosphonitrile Tetramer (IV) with Hydrogen Chloride.—Compound IV (22.0 g, 0.03 mol) was dissolved in 250 ml of chloroform and anhydrous hydrogen chloride was slowly bubbled into the solution. After 3 hr a precipitate was formed in the initially clear solution; the reaction was continued for a total of 7 hr. The precipitate, Ia, was removed by filtration and extracted with boiling chloroform to remove dimethylamine hydrochloride. Compound Ia was then recrystallized from toluene and dried *in vacuo*, mp 303–304°; yield, 18.5 g (90%).

Reaction of IV with Hydrogen Bromide.—Compound IV (18.5 g, 0.025 mol) was dissolved in 400 ml of chloroform and anhydrous hydrogen bromide was bubbled into the stirred solution. The reaction was carried out at room temperature for 24 hr and then refluxed for 24 hr. The solvent was evaporated and the solid residue was extracted with boiling benzene. The benzene-insoluble residue (5.5 g) was identified by infrared spectral analysis as dimethylamine hydrobromide. Upon cooling the benzene solution, hexaphenyldibromophosphonitrile tetramer (III) was precipitated. Two additional recrystallizations from benzene were required to provide pure III, mp 254°; yield, 15.6 g (85%). The infrared spectrum was identical with that of the product from the reaction of II with phosphorus pentabromide.

Preparation of Hexaphenyldifluorophosphonitrile Tetramer (V).—A mixture of Ia (20.0 g, 0.028 mol) and CsF (21.3 g, 0.14 mol) in 500 ml of acetonitrile was stirred at room temperature for 1.5 hr and then refluxed for 24 hr. The hot reaction mixture was filtered. As the acetonitrile solution cooled, brown crystals were deposited. This material was collected and recrystallized twice from acetonitrile to yield white crystalline V, mp 176–177°; yield, 11.8 g (62%). *Anal.* Calcd for $C_{36}H_{30}P_4N_4F_2$: C, 63.53; H, 4.44; P, 18.21; N, 8.23; F, 5.58; mol wt, 681. Found: C, 63.70; H, 4.62; P, 18.02; N, 8.52; F, 5.36; mol wt, 690.

This experiment was repeated under similar conditions using nitrobenzene as the solvent with potassium fluoride or sodium fluoride as the fluorinating agent. In each case, V was isolated with difficulty in 2% yield.

Acknowledgments.—This investigation was supported by the Naval Air Systems Command, Department of the Navy. The elemental analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. It is a pleasure to acknowledge the helpful discussions with Drs. C. P. Haber and N. R. Fetter.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS 60637

The Addition of Diphenylacetylene and of Triphenyltin Chloride to Platinum(0) Complexes. Determination of the Dissociation Constant of Tris(triphenylphosphine)platinum(0)

BY J. P. BIRK, JACK HALPERN, AND A. L. PICKARD

Received August 14, 1968

We have previously described[1] the kinetics of various substitution and oxidative addition reactions of platinum(0) complexes including the reactions of $\mathrm{Pt(P(C_6H_5)_3)_2(C_2H_4)}$ with $\mathrm{CH_3I}$, $\mathrm{C_6H_5CH_2Br}$, $\mathrm{CH_2ICH_2I}$, and $\mathrm{C_6H_5C{\equiv}CH}$ to yield the adducts $\mathrm{Pt(P(C_6H_5)_3)_2(CH_3)I}$, $\mathrm{Pt(P(C_6H_5)_3)_2(CH_2C_6H_5)Br}$, $\mathrm{Pt(P(C_6H_5)_3)_2I_2}$, and $\mathrm{Pt(P(C_6H_5)_3)_2(C_6H_5C{\equiv}CH)}$, respectively. It was concluded that all of these reactions proceed by dissociative mechanisms involving the coordinately unsaturated intermediate $\mathrm{Pt(P(C_6H_5)_3)_2}$. The above investigation also led to the conclusion that the compound $\mathrm{Pt(P(C_6H_5)_3)_4}$ is completely dissociated in benzene solution to $\mathrm{Pt(P(C_6H_5)_3)_3}$, the further dissociation of which, to $\mathrm{Pt(P(C_6H_5)_3)_2}$, is slight.

In this paper we describe kinetic investigations of several further reactions of platinum(0) complexes, depicted by eq 1–4. The results of these investigations support our earlier mechanistic conclusions and, furthermore, lead to a determination of the equilibrium quotient, $K_{\mathrm{P(C_6H_5)_3}}$, for the dissociation of $\mathrm{Pt(P(C_6H_5)_3)_3}$ according to

$$\mathrm{Pt(P(C_6H_5)_3)_2(C_2H_4) + (C_6H_5)_3SnCl \longrightarrow Pt(P(C_6H_5)_3)_2(Sn(C_6H_5)_3)Cl + C_2H_4} \tag{1}$$

$$\mathrm{Pt(P(C_6H_5)_3)_2(C_2H_4) + C_6H_5C{\equiv}CC\ H_5 \longrightarrow Pt(P(C_6H_5)_3)_2(C_6H_5C{\equiv}CC_6H_5) + C_2H_4} \tag{2}$$

$$\mathrm{Pt(P(C_6H_5)_3)_3 + (C_6H_5)_3SnCl \longrightarrow Pt(P(C_6H_5)_3)_2(Sn(C_6H_5)_3)Cl + P(C_6H_5)_3} \tag{3}$$

$$\mathrm{Pt(P(C_6H_5)_3)_3 + C_6H_5C{\equiv}CC_6H_5 \longrightarrow Pt(P(C_6H_5)_3)_2(C_6H_5C{\equiv}CC_6H_5) + P(C_6H_5)_3} \tag{4}$$

$$\mathrm{Pt(P(C_6H_5)_3)_3} \xrightleftharpoons{K_{\mathrm{P(C_6H_5)_3}}} \mathrm{Pt(P(C_6H_5)_3)_2 + P(C_6H_5)_3} \tag{5}$$

Experimental Section

$\mathrm{Pt(P(C_6H_5)_3)_4}$ was prepared from $\mathrm{K_2PtCl_4}$, KOH, and excess $\mathrm{P(C_6H_5)_3}$ in aqueous ethanol according to the procedure of Malatesta and Cariello.[2] $\mathrm{Pt(P(C_6H_5)_3)_2(C_2H_4)}$ was prepared, through the oxide $\mathrm{Pt(P(C_6H_5)_3)_2O_2}$, according to the procedure of Cook and Jauhal.[3] $\mathrm{Pt(P(C_6H_5)_3)_3}$ was generated *in situ* by the addition of 1 equiv of $\mathrm{P(C_6H_5)_3}$ to a benzene solution of $\mathrm{Pt(P(C_6H_5)_3)_2(C_2H_4)}$, through which argon was passed to remove the displaced ethylene.[1] Diphenylacetylene (Eastman) was recrystallized from hot ethanol. Ethylene (Matheson), triphenylphosphine (Matheson, mp 80–81°), and triphenyltin chloride (M & T) were used without purification. Solutions were prepared from reagent grade benzene, deoxygenated with purified nitrogen. Diphenylacetylene and triphenyltin chloride, both as solids and in solution, were protected from light.

All of the kinetic measurements were made in benzene solution at 25°. The reactions were followed spectrophotometrically in a Cary 14 spectrophotometer with a cell compartment thermostated to ±0.3°. The rates of reactions 1, 3, and 4 were measured by following the disappearance of the reactant platinum(0) complexes (whose extinction coefficients at the indicated wavelength are given in parentheses) at 335 mμ ($4.0 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$), 437 mμ ($6.3 \times 10^2\ M^{-1}\ \mathrm{cm}^{-1}$), and 415 mμ ($1.5 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$), respectively. The rate of reaction 2 was measured by following the appearance of the product $\mathrm{Pt(P(C_6H_5)_3)_2(C_6H_5C{\equiv}CC_6H_5)}$ at 372 mμ ($\epsilon\ 3 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$), where the absorbance of the reactant, $\mathrm{Pt(P(C_6H_5)_3)_2(C_2H_4)}$ ($\epsilon\ 3 \times 10^2\ M^{-1}\ \mathrm{cm}^{-1}$), was small. The initial concentration of the platinum(0) complex was generally in the range 5×10^{-4} to $1 \times 10^{-3}\ M$. The initial concentration ranges of the other species were as follows (the number in parentheses refers to the equation describing the reaction): (1) 1.2×10^{-2} to $1.5 \times 10^{-1}\ M\ \mathrm{C_2H_4}$, 3.5×10^{-3} to $1 \times 10^{-1}\ M\ \mathrm{(C_6H_5)_3SnCl}$; (2) 2.5×10^{-2} to $1.4 \times 10^{-1}\ M\ \mathrm{C_2H_4}$, 1.0×10^{-2} to $2.7 \times 10^{-2}\ M\ \mathrm{C_6H_5C{\equiv}CC_6H_5}$; (3) 2.7×10^{-3} to $8.3 \times 10^{-2}\ M\ \mathrm{P(C_6H_5)_3}$, 7.6×10^{-3} to $3.5 \times 10^{-2}\ M\ \mathrm{(C_6H_5)_3SnCl}$; (4) 9.6×10^{-3} to $3.3 \times 10^{-2}\ M\ \mathrm{P(C_6H_5)_3}$, 1×10^{-2} to $8 \times 10^{-2}\ M\ \mathrm{C_6H_5C{\equiv}CC_6H_5}$.

Results and Discussion

The kinetic behavior of each of the reactions resembled that previously observed[1] for the reactions of $\mathrm{Pt(P(C_6H_5)_3)_2(C_2H_4)}$ with $\mathrm{CH_3I}$, $\mathrm{C_6H_5CH_2Br}$, and $\mathrm{CH_2ICH_2I}$. This behavior is accommodated by the mechanism depicted by eq 6 and 7, involving a preequilibrium dissociation of the platinum(0) complex $\mathrm{Pt(P(C_6H_5)_3)_2X}$ (where X = $\mathrm{P(C_6H_5)_3}$ or $\mathrm{C_2H_4}$) into $\mathrm{Pt(P(C_6H_5)_3)_2}$ and X, followed by addition of the substrate (YZ = $\mathrm{C_6H_5C{\equiv}CC_6H_5}$ or $\mathrm{(C_6H_5)_3SnCl}$) to $\mathrm{Pt(P(C_6H_5)_3)_2}$. Over the extensive concentration ranges of X and YZ cited earlier, each of the reactions obeyed the rate law deduced from the above mechanism, *i.e.*

$$\mathrm{Pt(P(C_6H_5)_3)_2X} \xrightleftharpoons{K_{\mathrm{X}}} \mathrm{Pt(P(C_6H_5)_3)_2 + X} \quad \text{(rapid equilibrium)} \tag{6}$$

$$\mathrm{Pt(P(C_6H_5)_3)_2 + YZ} \xrightarrow{k_{\mathrm{YZ}}} \mathrm{Pt(P(C_6H_5)_3)_2YZ} \tag{7}$$

$$-\mathrm{d[Pt(P(C_6H_5)_3)_2X]_{tot}}/\mathrm{d}t = k_{\mathrm{YZ}}K_{\mathrm{X}}\mathrm{[Pt(P(C_6H_5)_3)_2X][YZ][X]^{-1}} \tag{8}$$

where $\mathrm{[Pt(P(C_6H_5)_3)_2X]_{tot} = [Pt(P(C_6H_5)_3)_2X] + [Pt(P(C_6H_5)_3)_2]}$. Under the conditions of our measurements, *i.e.*, with [X] and [YZ] in sufficient excess over $\mathrm{[Pt(P(C_6H_5)_3)_2X]}$ so as to remain essentially constant during each reaction, and with [X] sufficiently high so that dissociation of $\mathrm{Pt(P(C_6H_5)_3)_2X}$ was neg-

---

[1] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Am. Chem. Soc.*, **90**, 4491 (1968). This paper cites pertinent earlier references.

[2] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

[3] C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, **90**, 1464 (1968).