in the crystal which would differ in the vibrational frequencies.

The infrared spectra of the two nitrate compounds contain strong absorptions in the 1040–1010 cm.$^{-1}$ and the 1320–1280 cm.$^{-1}$ range characteristic of coördinated nitrates. The $La(NO_3)_3 \cdot 4DMA$ material exhibits bands at 1027 and 1303 cm.$^{-1}$ as well as absorption bands characteristic of ionic nitrate.[16]

The magnetic moments for all the complexes studied are close to the expected values except for $Cu(ClO_4)_2 \cdot 4DMA \cdot H_2O$. The value of 1.57 for the magnetic moment of a Cu(II) complex is somewhat low if the compound is monomeric. Apparently there is some spin–spin coupling occurring which results in the antiferromagnetism.[14] The magnetic moments of the cobalt, nickel, and manganese complexes correspond to the spin-free values.

All of the perchlorate salts were found to be strong electrolytes in dimethylacetamide. The molar conductances of the halide-containing complexes vary from 0.77 for $HgCl_2 \cdot DMA$ to 52 for $NiBr_2 \cdot 2DMA \cdot 3H_2O$. These conductance data indicate that halide coördination persists even at the dilutions used for these measurements. It is apparent in the cobalt series and the zinc series that replacement of the halide from the coördination sphere is most pronounced with the iodide followed by bromide and then chloride. The omission of brackets in some of the compounds listed in Table IV indicates considerable doubt as to the correct formulation of several possible structures for these materials.

It is of interest to note the similarities in the composition of the complexes of DMA with those of dimethyl sulfoxide (DMSO). The compositions of the cadmium, mercury, and lead halide compounds of DMA and DMSO are analogous, both ligands forming compounds in which the mole ratio of ligand to metal halide is 1:1. Likewise, the $FeCl_3 \cdot 2DMA$ is analogous to $FeCl_3 \cdot 2DMSO$. Of the anhydrous DMA compounds isolated only the cobalt halides differ in their composition when compared to the corresponding DMSO compounds.

Acknowledgments.—The authors gratefully acknowledge the Special Projects in Science Education section of the National Science Foundation for the support of S. K. M. and J. E. W. The authors also thank Miss Beverly Corelle for her assistance in performing the conductance measurements.

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CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH 13, PENNSYLVANIA

Transition Metal Complexes of Secondary Phosphines. II. Complexes of Diethylphosphine and Ethylphenylphosphine with Palladium(II)[1]

BY R. G. HAYTER AND F. S. HUMIEC

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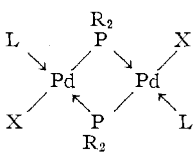
Diethylphosphine and ethylphenylphosphine react with palladium halides and with $[PdCl_2(PR_3')]_2$ ($R' = C_2H_5, C_6H_5$) to give complexes of the type $[PdX_2L'L'']$ (X = halogen; $L' = L'' = (C_2H_5)_2PH, C_2H_5C_6H_5PH$, and $L' = (C_2H_5)_2PH, L'' = PR_3'$, respectively). In the presence of a base, $[PdX_2L'L'']$ lose HX to give the phosphorus-bridged complexes *trans*-$[PdX(PR_2)L]_2$ ($R_2 = (C_2H_5)_2, C_2H_5C_6H_5$; $L = (C_2H_5)_2PH, C_2H_5C_6H_5PH$, or $R_3'P$), which react with chelate ligands to give $[Pd_2(PR_2)_2(chelate)_2]X_2$.

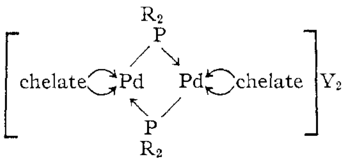
Introduction

A recent investigation of the reactions of diphenylphosphine with palladium halides under a variety of conditions yielded two series of binuclear complexes I (X = halogen, SCN; $R = C_6H_5$; $L = (C_6H_5)_2PH$ or a tertiary phosphine) and II (chelate = $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$, *o*-phenan; $Y = Cl^-, ClO_4^-, B(C_6H_5)_4^-$, etc.).[2,3] Since the stable Pd_2P_2 ring in these compounds was readily formed, we have investigated the conditions under which analogous compounds may be obtained with diethylphosphine and ethylphenylphosphine. No complexes of these ligands with palladium halides have been described previously although Issleib and Wenschuh[4] have reported that, unlike diphenylphosphine, dialkyl- and dicycloalkylphosphines do not displace acid in their reactions with palladium halides, *i.e.*, reactions such as (1) are not observed. We have con-

$$PdX_2 + 2R_2PH = [PdX(PR_2)(HPR_2)]_2 + HX \quad (1)$$



I



II

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[1] Presented in part at the Seventh International Conference on Coördination Chemistry in Stockholm, June 24–29, 1962.

[2] Part I. R. G. Hayter, *J. Am. Chem. Soc.*, **84**, 3046 (1962).

[3] R. G. Hayter, *Nature*, **193**, 872 (1962).

[4] K. Issleib and E. Wenschuh, *Z. anorg. allgem. Chem.*, **305**, 15 (1960).

firmed this observation for diethylphosphine and also find that acid elimination and formation of complexes of type I (R = C_2H_5) occur readily in the presence of a base.

Experimental

The microanalyses, molecular weights, and melting points were carried out as described in part I.[2]

Preparation of the Phosphine Ligands.—The liquid phosphines were handled exclusively under nitrogen. Triethylphosphine was prepared by the Grignard method[5] and 1,2-bis-(diphenylphosphino)-ethane by the method of Chatt and Hart.[6] Diethylphosphine was obtained in 30% yield as described by Wymore and Bailar,[7] and diphenylphosphine by hydrolysis of $(C_6H_5)_2PNa$, which was prepared by the reaction of triphenylphosphine with sodium (2 atoms) in liquid ammonia.[8] The yields were in the range 70–80% for the product boiling at 152–153° (14 mm.). Triphenylphosphine was purchased from Eastern Chemical Corporation and tri-*n*-butylphosphine from Chemical Procurement Laboratories, Inc.

Ethylphenylphosphine was prepared by a modification of Issleib and Volker's method[9] as outlined in eq. 2

$$(C_6H_5)_2PC_2H_5 + 2Li \xrightarrow{THF} C_6H_5Li + C_2H_5C_6H_5PLi \xrightarrow{H_2O} C_2H_5C_6H_5PH + C_6H_6 + 2LiOH \quad (2)$$

Ethyldiphenylphosphine (35.0 g.) in dry tetrahydrofuran (200 ml.) was stirred with lithium foil (2.3 g.) at room temperature until all the metal dissolved to give a red solution (3 hr.). After hydrolysis, the solution was dried over Na_2SO_4 and distilled. The phosphine distilled slowly at 40° (3 mm.) leaving a viscous residue; yield, 7.5 g. (33%).

Anal. Calcd. for $C_8H_{11}P$: C, 69.55; H, 8.0; P, 22.4. Found: C, 69.7; H, 8.3; P, 22.2.

Preparation of the Complexes.—The palladium complexes were prepared with exclusion of air, under a blanket of nitrogen. Once obtained, they were not appreciably dissociated or oxidized and thus could be purified by crystallization without any particular precautions being taken against oxidation. The absence of oxygen in the purified complexes was confirmed both by the absence of absorption bands attributable to P=O or to P–OH vibrations in their infrared spectra and by direct oxygen analysis on selected compounds (zero % oxygen was found in III, VII, VIII, X, XVI, and XX).

Complexes prepared by more than one route were identified by their thermal behavior on a heated Kofler block, X-ray powder pattern, and analysis. The solvents used for crystallizations, analytical figures, and other data are given for the neutral complexes in Table I and for the ionic complexes in Table II.

Dichlorobis-(diethylphosphine)-palladium.—Sodium tetrachloropalladate(II) (0.54 g.) in ethanol (20 ml.) was treated with diethylphosphine (0.33 g., 2 moles) to give a white precipitate. After standing overnight, the product was filtered, washed with water, and crystallized from acetone to give pure III as matted needles.

$$Na_2PdCl_4 + 2(C_2H_5)_2PH = [PdCl_2\{HP(C_2H_5)_2\}_2] + 2NaCl \quad (3)$$

The complexes IV–VII were similarly prepared, except that in the case of the bromides and iodide, the ethanolic solution of Na_2PdCl_4 was treated with lithium halide (10 moles) before addition of the phosphine.

III also was prepared in 69% yield from a solution of $PdCl_2$ in ethanolic hydrochloric acid and $(C_2H_5)_2PH$ (2 moles) and purified as above.

$PdCl_2$ also reacted with $(C_2H_5)_2PH$ (2 moles) in boiling benzene to give a greenish yellow solution which deposited colorless crystals on standing overnight. The crystals did not then redissolve in benzene and crystallization from acetone gave a 35% yield of pure III.

Dichloro-(diethylphosphine)-(triethylphosphine)-palladium (VIII).—$[PdCl_2\{P(C_2H_5)_3\}]_2$[10] (1.0 g.) in dichloromethane (40 ml.) was treated with diethylphosphine (0.31 g., 2 moles) to give a rapid change in color from orange to pale yellow. Evaporation to dryness left a pale yellow solid which gave colorless needles from acetone.

$$[PdCl_2\{P(C_2H_5)_3\}]_2 + 2(C_2H_5)_2PH = 2[PdCl_2\{HP(C_2H_5)_2\}\{P(C_2H_5)_3\}] \quad (4)$$

IX was similarly prepared.

trans-**Di-μ-diethylphosphido-dichlorobis-(diethylphosphine)-dipalladium (X).**—III (0.50 g.) was suspended in benzene (20 ml.) and treated with a solution of *p*-toluidine (0.15 g., 1 mole) in benzene (5 ml.). A yellow solution and a fine white precipitate immediately began to form and, after refluxing for 15 min., the solution was filtered. The residual white solid was identified as *p*-toluidine hydrochloride (97% yield) (eq. 9) by comparison of its X-ray powder pattern and m.p. (sealed tube) with that of an authentic specimen. The yellow filtrate was evaporated to dryness and the residue crystallized from benzene–hexane or acetone to give the pure complex as plates.

XI, XII, and XIII were similarly prepared and also by reaction between PdX_2 (X = Br, I), the secondary phosphine (2 moles), and *p*-toluidine (1 mole) in boiling benzene.

trans-**Di-μ-diethylphosphido-dichlorobis-(triethylphosphine)-dipalladium (XIV).**—$[PdCl_2\{P(C_2H_5)_3\}]_2$[10] (1.0 g.) was suspended in benzene (50 ml.) and treated with *p*-toluidine (0.37 g., 2 moles) to give a yellow-orange solution of *trans*-$[PdCl_2(p\text{-toluidine})\{P(C_2H_5)_3\}]$ (eq. 10a). Diethylphosphine (0.31 g., 2 moles) then was added and the solution refluxed for 30 min. After filtering from the precipitated *p*-toluidine hydrochloride, the solution was evaporated to dryness, leaving a yellow solid. Crystallization from benzene gave the pure complex as yellow needles.

The complexes XV–XVIII were similarly prepared. XIV also was prepared, in about 5% yield, by reaction between $[PdCl_2\{P(C_2H_5)_3\}]_2$[10] and $(C_2H_5)_2PNa$ in liquid ammonia. After hydrolysis, the product was extracted into benzene and crystallized by addition of hexane.

$$[PdCl_2\{P(C_2H_5)_3\}]_2 + 2(C_2H_5)_2PNa = [PdCl\{P(C_2H_5)_2\}\{P(C_2H_5)_3\}]_2 + 2NaCl \quad (5)$$

Di-μ-diethylphosphido-dibromobis-(tri-*n*-butylphosphine)-dipalladium (XIX).—$PdBr_2$ (0.925 g.), *p*-toluidine (0.37 g., 1 mole), tri-*n*-butylphosphine (0.70 g., 1 mole), and diethylphosphine (0.31 g., 1 mole) were refluxed together in benzene (50 ml.) for 40 hr. After filtering from amine hydrobromide and a small amount of unreacted $PdBr_2$, the solution was evaporated to dryness, leaving an orange oil, which crystallized in hexane. Repeated crystallization from benzene–hexane gave pure XIX in about 10% yield. The hexane washings yielded pale yellow needles (m.p. 138–180°) and orange rods (m.p. 68–74°), which were identified as impure XI and $[PdBr_2\{P(C_4H_9)_3\}_2]$, respectively.

$$2PdBr_2 + 2(C_4H_9)_3P + 2(C_2H_5)_2PH + 2p\text{-}CH_3C_6H_4NH_2 = [PdBr\{P(C_2H_5)_2\}\{P(C_4H_9)_3\}]_2 + 2p\text{-}CH_3C_6H_4NH_2\cdot HBr \quad (6)$$

Di-μ-diethylphosphido-dithiocyanatobis-(diethylphosphine)-dipalladium (XX).—X (0.50 g.) and potassium thiocyanate (0.50 g., excess) were refluxed together in acetone solution for 30 min. The solution then was filtered and evaporated to dry-

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[5] G. M. Kosolopoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, p. 16.

[6] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[7] C. E. Wymore and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **14**, 42 (1960).

[8] K. Issleib and H. O. Fröhlich, *Z. Naturforsch.*, **14b**, 349 (1959).

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[10] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 235 (1957).

TABLE I

CHARACTERIZATION OF THE MONONUCLEAR AND PHOSPHORUS-BRIDGED COMPLEXES[a]

	Compound	Crystn. solvent	Yield, %	M.p., °C. (dec.)	Color	Carbon, %		Hydrogen, %		Halogen, %		Molecular weight[f]		
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Solvent
III	$[PdCl_2\{HP(C_2H_5)_2\}_2]$	$(CH_3)_2CO$	83	170	Colorless	26.9	26.8	6.2	6.15	19.8	19.9[e]	357.5	415	$(CH_3)_2CO$[g]
IV	$[PdBr_2\{HP(C_2H_5)_2\}_2]$	$(CH_3)_2CO$	32	175	Pale yellow	21.5	21.5	5.0	5.3					
V	$[PdI_2\{HP(C_2H_5)_2\}_2]$	$(CH_3)_2CO–H_2O$	80	147–149	Yellow	17.8	17.9	4.1	4.0	47.0	46.9	540	570	C_6H_6[h]
VI	$[PdCl_2(HPC_2H_5C_6H_5)_2]$	C_6H_6	37	141–157	Pale yellow	42.4	42.8	4.9	5.2			454	539	CH_2Br_2
VII	$[PdBr_2(HPC_2H_5C_6H_5)_2]$	$CHCl_3$	58	201–204	Pale yellow	35.4	35.4	4.1	4.35					
VIII	$[PdCl_2\{HP(C_2H_5)_2\}\{P(C_2H_5)_3\}]$	$(CH_3)_2CO$	38	145–164	Colorless	31.15	31.3	6.8	6.9			386	405	CH_2Br_2
IX	$[PdCl_2\{HP(C_2H_5)_2\}\{P(C_6H_5)_3\}]$	$CHCl_3–n\text{-}C_6H_{14}$	42	185–200	Pale yellow	49.9	50.4	4.95	5.1	13.4	13.4	530	513	CH_2Br_2
X	$[PdCl\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$	$C_6H_6–n\text{-}C_6H_{14}$	77	157–162	Pale yellow	29.9	29.9	6.6	6.7	11.0	11.0	642	677	C_6H_6
XI	$[PdBr\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$	$C_6H_6–n\text{-}C_6H_{14}$	45	194–197	Yellow	26.3	26.5	5.8	5.65	21.9	21.8	731	703	CH_2Br_2
XII	$[PdI\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$	$C_6H_6–n\text{-}C_6H_{14}$	64	250	Yellow	23.3	23.4	5.1	5.55	30.8	31.2	825	734	C_6H_6
XIII	$[PdBr(PC_2H_5C_6H_5)(HPC_2H_5C_6H_5)]_2$	$C_6H_6–c\text{-}C_6H_{12}$	15	201–204	Yellow	41.6	41.3	4.6	4.8					
XIV	$[PdCl\{P(C_2H_5)_2\}\{P(C_2H_5)_3\}]_2$	$C_6H_6–n\text{-}C_6H_{14}$	72	183–186[b]	Pale yellow	34.4	34.45	7.2	7.3	10.2	10.0	698	680	C_6H_6
XV	$[PdCl\{P(C_2H_5)_2\}\{P(C_4H_9)_3\}]_2$	$C_6H_6–n\text{-}C_6H_{14}$	39	175–176[b]	Yellow	44.4	44.3	8.6	8.5	8.2	8.2	866	824	C_6H_6
XVI	$[PdCl\{P(C_2H_5)_2\}\{P(C_6H_5)_3\}]_2$	$CHCl_3–n\text{-}C_6H_{14}$	43	180	Yellow	53.6	54.2	5.1	5.4	7.2	7.0	986.5	890	CH_2Br_2
XVII	$[PdCl(PC_2H_5C_6H_5)\{P(C_4H_9)_3\}]_2$	$C_6H_6–n\text{-}C_6H_{14}$	42	161–170	Yellow	49.9	50.3	7.75	7.9			963	923	C_6H_6[h]
XVIII	$[PdCl\{P(C_6H_5)_2\}\{P(C_4H_9)_3\}]_2$	$c\text{-}C_6H_{12}$	22	157–158	Yellow-orange	54.45	54.6	7.05	7.5			1058	1089	C_6H_6
XIX	$[PdBr\{P(C_2H_5)_2\}\{P(C_4H_9)_3\}]_2$	$C_6H_6–n\text{-}C_6H_{14}$	10	184–186[b]	Pale yellow	40.2	40.6	7.8	7.8			955	925	C_6H_6
XX	$[Pd(SCN)\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$	$C_6H_6–n\text{-}C_6H_{14}$	37	135–137	Yellow	31.45	31.6	6.2	6.0[c]			687	733	C_6H_6
XXI	$[Pd(SCN)\{P(C_2H_5)_2\}\{P(C_4H_9)_3\}]_2$	$(CH_3)_2CO$	20	154–158[b]	Yellow	44.8	44.7	8.2	8.9			912	925	C_6H_6
XXII	$[Pd(SCN)\{P(C_6H_5)_2\}\{P(C_4H_9)_3\}]_2$	$(CH_3)_2CO–H_2O$	38	154–157	Yellow-orange	54.4	54.5	6.8	6.7[d]			1104	1117	C_6H_6[h]

[a] The complexes were all found to be non-electrolytes in nitromethane solution. [b] Without decomposition. [c] Calcd.: N, 4.1. Found: N, 4.7. [d] Calcd.: N, 2.5. Found: N, 2.6. [e] Calcd. P, 17.3; Pd, 29.8. Found: P, 17.7; Pd, 29.7. [f] Isopiestic measurements unless otherwise indicated. [g] Ebullioscopic measurement; value obtained by extrapolation to zero concentration. [h] Value obtained using a vapor pressure osmometer.

TABLE II

ANALYTICAL, CONDUCTANCE, AND IONIC WEIGHT DATA FOR THE COMPLEXES $[Pd(PR_2)_2(chelate)_2]X_2$

	Compound	Crystn. solvent	M.p., °C. (dec.)	Color	Carbon, %		Hydrogen %		Molar conductance in CH_3NO_2 (ohm^{-1})[e]	Ionic weight[g]		
					Calcd.	Found	Calcd.	Found		Calcd.[f]	Found	Solvent
XIII	$[Pd_2\{P(C_2H_5)_2\}_2\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}_2][ClO_4]_2$	CH_3OH	330–335	Yellow	52.0	52.3	4.9	5.2[a]	192.5	462	633, 656	$(CH_3)_2CO$
XXIV	$[Pd_2\{P(C_2H_5)_2\}_2\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}_2][picrate]_2$	CH_3OH	206–213	Yellow	52.6	53.3	4.4	4.8[b]	152.0	548	545, 549	$(CH_3)_2CO$
XXV	$[Pd_2\{P(C_6H_5)_2\}_2\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}_2][B(C_6H_5)_4]_2$	DMF–CH_3OH	165–172	Yellow	71.0	70.8	6.0	6.2	122.1		...	
XXVI	$[Pd_2\{P(C_2H_5)_2\}(o\text{-phenan})_2][B(C_6H_5)_4]_2$	DMF–CH_3OH	202–215	Colorless	69.1	69.5	5.5	5.6[c]	145.8		...	
XXVII	$[Pd_2\{P(C_6H_5)_2\}(NH_2C_2H_4NH_2)_2][B(C_6H_5)_4]_2$	$(CH_3)_2CO–C_6H_6$	155	Yellow	68.0	68.3	5.7	5.8[d]	162.1	447	547	$(CH_3)_2CO$

[a] Calcd.: Cl, 5.1. Found: Cl, 4.8. [b] Calcd.: N, 5.1; P, 11.3. Found: N, 5.5; P, 11.4. [c] Calcd.: N, 4.0. Found: N, 3.9. [d] Calcd.: N, 4.2. Found: N, 4.25. [e] Measurements made at a concentration in the range 6–8 × 10^{-4} *M*. [f] Calcd. for complete dissociation into ions. [g] Values obtained using a vapor pressure osmometer.

TABLE III

CONDUCTIVITY DATA FOR $[Pd_2\{P(C_2H_5)_2\}_2\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}_2]X_2$ ($X = ClO_4^-, OC_6H_2(NO_2)_3^-$) in methanol at 25°[a]

Compound	Λ_0 (ohm^{-1})	ω[b]	A	B	($A + \omega B\Lambda_0$) Calcd.	($A + \omega B\Lambda_0$) Found	Concn. range (equiv./l. × 10^4)
XXIII	119.3	1.016	278.8	1.801	497	560	2.8–14.1
XXIV	98.2	1.080	278.8	1.801	470	643	1.4– 5.4
$[Ni(1,10\text{-phen})_3]Cl_2$[c]	110.2	1.080	278.8	1.801	493	514	1.4–31.0

[a] $D^{25} = 32.63$; $\eta = 0.00547$ poise. [b] Calcd. using $l^0_{ClO_4^-} = 70.9$ ohm^{-1} (E. D. Copley and H. Hartley, *J. Chem. Soc.*, 2488 (1930); $l^0_{OC_6H_2(NO_2)_3^-} = 46.9$ ohm^{-1} (L. Fischer, G. Winkler, and G. Jander, *Z. Elektrochem.*, **62,** 1 (1958). [c] See ref. 2.

TABLE IV

CONDUCTIVITY DATA FOR SOME COMPLEXES OF TYPE II AND FOR SOME KNOWN ELECTROLYTES IN NITROMETHANE AT 25°[a]

Compound	Λ_0 (ohm^{-1})	ω	A	B	($A + \omega B\Lambda_0$) Calcd.	($A + \omega B\Lambda_0$) Found	Concn. range (equiv./l. × 10^4)
$[(n\text{-}C_4H_9)_4N]Br$	103.5	0.586	126	1.210	199	183	3.1–66.0
$NaB(C_6H_5)_4$	100.2	0.586	126	1.210	197	216	4.2–96.0
$[Ni(1,10\text{-phen})_3]Cl_2$	117.6	1.111[b]	232	1.482	425	420	3.0–21.3
XXV	76.0	1.038[c]	232	1.482	348	410	1.6–13.8
XXVI	88.0	1.080[c]	232	1.482	372	392	0.8–14.3
XXVII	86.4	1.075[c]	232	1.482	369	430	2.0–16.6
XXVIII[d]	80.0	1.053[c]	232	1.482	356	455	0.9–14.3
$[Co(dipy)_3][ClO_4]_3$[e]	144.0	1.462[f]	357	1.711	717	1020	1.7–16.1

[a] $D^{25} = 36.82$; $\eta^{25} = 0.00620$ poise. [b] Calculated using an estimated value of $l^0_{Cl^-} = 50$ ohm^{-1}. [c] $l^0_{B(C_6H_5)_4^-} = 42$ ohm^{-1} (obtained from $l^0_{Na^+} = 58$ ohm^{-1}[g] and Λ_0 $[NaB(C_6H_5)_4] = 100.2$ ohm^{-1}. [d] XXVIII = $[Pd_2\{P(C_6H_5)_2\}_2\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}_2][B(C_6H_5)_4]_2$ (see ref. 2). [e] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952). [f] $l^0_{ClO_4^-} = 64$ ohm^{-1}.[g] [g] C. P. Wright, D. M. Murray-Rust, and H. Hartley, *J. Chem. Soc.*, 199 (1931).

ness and the pale yellow residue was washed with water and crystallized from benzene–hexane to give pure XX.

$$[PdCl\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2 + KSCN = [Pd(SCN)\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2 + KCl \quad (7)$$

XXI and XXII were similarly prepared.

Di-μ-diethylphosphido-di-[1,2-bis-(diphenylphosphino)-ethane]-dipalladium Diperchlorate (XXIII).—XV (0.50 g.) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.46 g., 2 moles) were dissolved together in hot ethanol (50 ml.) to give a yellow–orange solution (eq. 11). Excess $NaClO_4$ (0.50 g.) in water (2 ml.) then was added and the solution refluxed for 30 min. Cooling gave yellow crystals, which were recrystallized from methanol to give pure XXIII in 20% yield.

XXIV, XXV, and XXVI were similarly prepared in 21, 70, and 26% yields, respectively.

Di-μ-diphenylphosphido-di-(ethylenediamine)-dipalladium Ditetraphenylborate (XXVII).—XVIII (0.50 g.) in benzene (20 ml.) was treated with ethylenediamine (0.20 ml., excess) to give a yellow crystalline precipitate from a red solution. After standing overnight, the yellow product was filtered, washed with benzene, and treated with $NaB(C_6H_5)_4$ (0.50 g.) in ethanolic solution to give a thick pale yellow precipitate. After filtration, this product yielded pure XXVII by crystallization from acetone–benzene mixtures as yellow needles (31% yield).

Conductance Measurements.—These measurements were made at 25° using a Model RC-16B2 conductivity bridge (Industrial Instruments, Inc.) and a cell with platinum electrodes coated with platinum black having a cell constant of about 0.1. Conductivity *vs.* concentration data were obtained over as wide a concentration range as possible (see Tables III and IV), the lower limit occurring when the conductivity due to the solute was of the same order of magnitude as that of the solvent and the upper limit when deviations from linearity of a plot of Λ_c *vs.* $c^{1/2}$ became noticeable. Λ_0 was obtained from this plot by linear extrapolation to zero concentration. A subsequent plot of $(\Lambda_0 - \Lambda_c)$ *vs.* $c^{1/2}$ (eq. 8) yields a line whose slope is $(A + \omega B\Lambda_0)$.[11]

$$\Lambda_0 - \Lambda_c = (A + \omega B\Lambda_0)c^{1/2} \quad (8)$$

(Λ_0, Λ_c = equivalent conductances at concentrations zero and c, respectively; A and B are constants depending on the dielectric constant and viscosity of the solvent, temperature, and the ionic charges ($Z_\pm$); $\omega = 0.586$ for uni-univalent electrolytes and is a function of the ionic charges and mobilities ($l^0_\pm$) for more highly charged electrolytes).

Semi-empirical values of $(A + \omega B\Lambda_0)$ thus can be calculated,[11] the only unknown quantity being the charge on the cation, Z_+ ($Z_- = 1$). It is noteworthy that the calculated gradient $(A + \omega B\Lambda_0)$ increases roughly in the same ratio as the chosen values of Z_+. Z_+ thus can be found by comparison of the experimental $(A + \omega B\Lambda_0)$ with both the calculated values for various charge sizes and with the experimental values for electrolytes of known types in the same solvent. The results are summarized in Tables III and IV.

The value of this method lies in the fact that the charge on an ion may be determined *without any assumption being made about molecular complexity,* since equivalent conductances only are required. It thus is possible to distinguish unequivocally between the monomeric structure $[\text{chelate}\curvearrowright\text{Pd}(PR_2)]Y$, the dimeric structure (II), and higher polymeric structures having six- or eight-membered or larger heterocyclic rings. All the possible structures of this type have the same equivalent weight and comparison of their molar conductances with those of electrolytes of known type does not distinguish between them.[2]

Titration Curves.—These were obtained by following the change in pH caused by the addition of 0.1 N NaOH to 10^{-3} M solutions of the complexes in ethanol using a Leeds and Northrup pH meter. Back titration was similarly and immediately carried out using 0.1 N HCl. The results for $[PdX_2\{HP(C_2H_5)_2\}_2]$ (X = I, Cl) are shown in Fig. 1. When X = I, a sharp end point was found at 1.1 equivalents of NaOH (pH 8.3), and there was no further evidence of reaction below pH 12. Back titration with acid confirmed the original end point at 1.03 equivalents (Fig. 1(a)). The bridged complex $[PdI\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$ was isolated from the neutral solution, although only in low yield.

The corresponding bromo and chloro complexes behave differently in that the titration curve does not have a well defined equivalence point. Back-titration with acid shows that in each case about 1.4 equivalents of base have reacted with the complexes (Fig. 1(b)).

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(11) L. Onsager, *Physik. Zeit.*, **28,** 277 (1927).

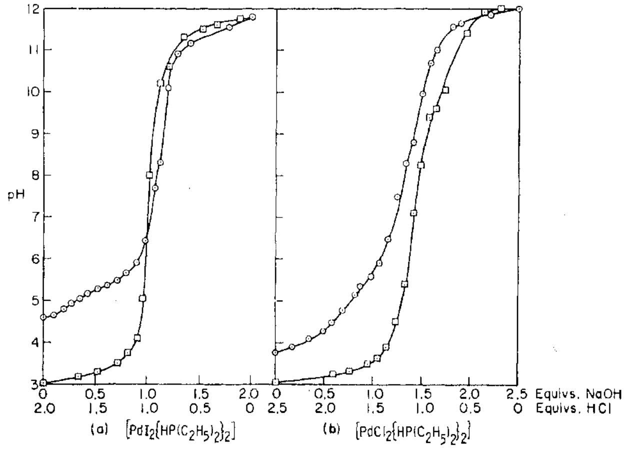

Fig. 1.—Titration of $[PdX_2\{HP(C_2H_5)\}_2]$ with 0.1 *N* NaOH (⊙) and back titration with 0.1 *N* HCl (⊡).

Dipole Moments.—These were obtained by Mr. J. V. Kennedy of the Physical Measurements Department of Mellon Institute, using the method of Everard, Hill, and Sutton[12] and a Wissenschaftlich—Technische Werkstätten Dipolemeter. The equations relating the dielectric constant, (ϵ_{12}), refractive index (n_{12}), and specific volume (V_{12}) of the dilute benzene solutions to the weight fraction of solute (ω_2) were obtained by a least squares procedure and are given in Table V. It was assumed that the sum of the electronic (P_E) and atomic (P_A) polarizations was approximately equal to the molar refraction for the sodium D line (R_D). Some authors prefer to assume $P_E = R_D$ and to make an allowance for P_A amounting to 10–15% R_D. If this is done for the dipole moments reported in Table V, it is found that the larger moments are lowered by 0.1 D. and the smaller by about 0.3 D. Changes of this magnitude do not substantially affect the conclusions reached in the Discussion.

TABLE V

DATA FOR THE EVALUATION OF DIPOLE MOMENTS

$[PdI_2\{HP(C_2H_5)_2\}_2]$		
$\epsilon_{12} = 2.260 + 5.686\omega_2$		$P_T = 658.6$ cc.
$n_{12} = 1.4978 + 0.1899\omega_2$	ω_2: $0\text{–}18 \times 10^{-4}$	$R_D = 134.4$ cc.
$V_{12} = 1.1461 - 0.6677\omega_2$		$P_0 = 524.2$ cc.
		$\mu = 5.1$ D.
$[PdI_2\{HP(C_6H_5)_2\}_2]$[2]		
$\epsilon_{12} = 2.266 + 6.768\omega_2$		$P_T = 1043$ cc.
$n_{12} = 1.4975 + 0.1492\omega_2$	ω_2: $0\text{–}29 \times 10^{-4}$	$R_D = 167.4$ cc.
$V_{12} = 1.1460 - 0.6573\omega_2$		$P_0 = 875.6$ cc.
		$\mu = 6.5$ D.
$[PdCl\{P(C_6H_5)_2\}\{P(C_2H_5)_3\}]_2$[2]		
$\epsilon_{12} = 2.265 + 1.838\omega_2$		$P_T = 485.8$ cc.
$n_{12} = 1.4976 + 0.1407\omega_2$	ω_2: $0\text{–}57 \times 10^{-4}$	$R_D = 246.0$ cc.
$V_{12} = 1.1460 - 0.4776\omega_2$		$P_0 = 239.8$ cc.
		$\mu = 3.4$ D.
$[PdCl\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$		
$\epsilon_{12} = 2.269 + 2.253\omega_2$		$P_T = 395.2$ cc.
$n_{12} = 1.4975 + 0.0959\omega_2$	ω_2: $0\text{–}31 \times 10^{-4}$	$R_D = 155.7$ cc
$V_{12} = 1.1460 - 0.5055\omega_2$		$P_0 = 239.5$ cc.
		$\mu = 3.4$ D.
$[PdCl\{P(C_2H_5)_2\}\{P(C_2H_5)_3\}]_2$		
$\epsilon_{12} = 2.267 + 1.907\omega_2$		$P_T = 389.6$ cc.
$n_{12} = 1.4977 + 0.0948\omega_2$	ω_2: $0\text{–}56 \times 10^{-4}$	$R_D = 174.2$ cc.
$V_{12} = 1.1460 - 0.4795\omega_2$		$P_0 = 215.4$ cc.
		$\mu = 3.25$ D.

Discussion

Mononuclear Complexes.—Complexes of the type $[PdX_2L'L'']$ (X = Cl, Br, I) were prepared by the reaction of diethylphosphine or ethylphenylphosphine either with palladium halides ($L' = L'' = (C_2H_5)_2PH$, $C_2H_5C_6H_5PH$) or with the chloro-bridged complexes $[PdCl_2(PR_3')]_2$[10] ($L' = PR_3'$, $L'' = (C_2H_5)_2PH$). $[PdX_2L'L'']$ are monomeric in acetone or benzene solutions and non-electrolytes in nitromethane, indicating a four-coördinate structure, probably containing square planar palladium(II), as has been found in all such complexes of this metal which have so far been subjected to X-ray structural analysis.[13] It is well known that compounds of this type may exist either as *cis* or *trans* isomers,[14] and although both isomers of platinum(II) complexes usually can be obtained, the more labile palladium(II) complexes have only been isolated in the solid state in one isomeric form, usually *trans*. Among the isomeric platinum complexes, it has been observed that *cis* and *trans* isomers can be distinguished by such properties as color, melting point, solubility, and dipole moments, the *cis* isomers being paler in color, higher melting, less soluble in benzene, and possessing a high dipole moment. Since $[PdCl_2\{HP(C_2H_5)_2\}_2]$ and $[PdCl_2\{HP(C_2H_5)_2\}\{P(C_2H_5)_3\}]$ are insufficiently soluble in benzene for their dipole moments to be measured, it has proved necessary to consider the remaining three of the four properties listed above and comparison is made with the triethylphosphine complexes of palladium(II) and platinum(II) in Table VI.

From Table VI, it seems likely that the diethylphosphine complexes have the *cis* rather than the *trans* configuration in the solid state, the contrast in properties with *trans*-$[PdCl_2\{P(C_2H_5)_3\}_2]$ being particularly noticeable. This deduction is supported by the observation that the more soluble $[PdI_2\{HP(C_2H_5)_2\}_2]$ has a dipole moment of 5.1 D., indicating that an appreciable proportion of the highly polar *cis* isomer is present in solution. Since replacement of iodine by chlorine in these complexes favors the *cis* isomer,[14] it is probable that $[PdCl_2\{HP(C_2H_5)_2\}_2]$, if soluble, would exist almost entirely in the *cis* form in benzene solution.

Although the above evidence for the *cis* structure is not definitive, it is felt to be sufficiently certain to allow some discussion as to why replacement of ethyl groups by hydrogen in $[PdX_2\{P(C_2H_5)_3\}_2]$ appears to favor the *cis* isomer at the expense of the *trans*. This effect may be partially steric, since it is to be expected that the lesser steric requirements of the secondary phosphine would tend to favor the more crowded *cis* isomer. Another important factor may be the greater electronegativity of hydrogen as compared with that of the ethyl group. This will increase the π-acceptor capacity of phosphorus and hence the strength of the π-band between phosphorus and the metal. There will also be an

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(12) K. B. Everard, R. A. W. Hill, and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

(13) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, 1962 (3rd edition), p. 920 *et seq.*

(14) R. G. Wilkins and M. J. G. Williams in J. Lewis and R. G. Wilkins, Ed., "Modern Coördination Chemistry," Interscience Publishers, Inc., New York, N. Y., p. 174.

TABLE VI

COMPARISON OF THE PROPERTIES OF *cis* AND *trans*-$[MCl_2L_2]$
(M = Pd, Pt; L = substituted phosphine)

Compound	Color	M.p., °C.	Solubility in benzene	Dipole moment
trans-$[PdCl_2\{P(C_2H_5)_3\}_2]$[a]	Yellow	139	High	0
trans-$[PtCl_2\{P(C_2H_5)_3\}_2]$[b]	Pale yellow	142–143	High	0
cis-$[PtCl_2\{P(C_2H_5)_3\}_2]$[b]	Colorless	192–193	Low	10.7 D.
$[PdCl_2\{HP(C_2H_5)_2\}_2]$	Colorless	170 dec.	Low	. . .
$[PdCl_2\{HP(C_2H_5)_2\}\{P(C_2H_5)_3\}]$	Colorless	145–164 dec.	Low	. . .

[a] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935), and ref. 17. [b] K. Jensen, *Z. anorg. allgem. Chem.*, **229**, 250 (1936).

associated weakening of the σ-bond, so that the resultant total bond strength will depend on two opposing effects and cannot be accurately predicted. However, in the *cis* isomer, the phosphorus atoms are able to form more effective π-bonds than in the *trans* isomer, where the phosphorus atoms are competing for the same metal d-orbital.[15] Hence, any effect which increases the extent of d_π–d_π bonding in complexes of this type will probably tend to increase the stability of the *cis* isomer *relative* to that of the *trans*.[16] A combination of the steric and electronic effects discussed above may be operating here.

The only other series of mononuclear monodentate-ligand complexes of palladium(II) which are thought to be of *cis* configuration is $[PdCl_2(SbR_3)_2]$.[17] These are yellow in the crystalline state, and slowly dissolve in benzene with partial isomerization to give red solutions containing 60–96% of the *trans* isomer.

Binuclear Complexes.—The above reactions show that, unlike diphenylphosphine,[2] diethylphosphine and ethylphenylphosphine do not yield phosphorus-bridged complexes directly from palladium halides. However, treatment of the mononuclear complexes III–VII with a weak base, such as an amine, causes rapid elimination of HX and the formation of the dimeric complexes X–XIII, for example

$$2[PdCl_2\{HP(C_2H_5)_2\}_2] + 2p\text{-toluidine} = [PdCl\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2 + 2p\text{-toluidine}\cdot HCl \quad (9)$$

These reactions usually are carried out in benzene, amine·HX being precipitated, leaving the bridged complex in solution. Compounds of the type $[PdCl(PR_2)(PR'_3)]_2$ (XIV–XVIII) were obtained by a similar method, using the chloro-bridged complexes, and two slightly different routes as outlined below

$$\begin{tikzcd}
 & 2[PdCl_2(PR_3')\text{amine}]^{18} \arrow[dr, "R_2PH"] & (10a) \\
{[PdCl_2(PR_3')]_2} \arrow[ur, "\text{amine}"] \arrow[dr, "R_2PH"'] & & {[PdCl(PR_2)(PR_3')]_2 + \text{amine}\cdot HCl} \\
 & 2[PdCl_2(HPR_2)(PR_3')] \arrow[ur, "\text{amine}"'] & (10b)
\end{tikzcd}$$

We have found eq. 10a to be the more convenient route since the intermediate amine complex, unlike $[PdCl_2(HPR_2)(PR_3')]$, is benzene-soluble and the second stage occurs rapidly and completely on addition of R_2PH. In neither (10a) nor (10b) is it necessary to isolate the intermediate complex. $[PdCl\{P(C_6H_5)_2\}\{P(C_2H_5)_3\}]_2$ was prepared in this way and was found to be identical with the complex previously obtained by reaction between triethylphosphine and $[PdCl\{P(C_6H_5)_2\}\{HP(C_6H_5)_2\}]_2$.[2] $[PdBr\{P(C_6H_5)_2\{P(C_4H_9)_3\}]_2$ was similarly prepared, although in low yield, by reaction between equimolar quantities of $PdBr_2$, diethylphosphine, tri-*n*-butylphosphine, and *p*-toluidine; $[PdBr\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$ and $[PdBr_2\{P(C_4H_9)_3\}_2]$ also were obtained.

The thiocyanate complexes XX–XXII were prepared by treating the corresponding chloro complexes with potassium thiocyanate in acetone.

Structure and Reactions of the Binuclear Complexes.—The dipole moments of $[PdCl\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$ and $[PdCl\{P(C_2H_5)_2\}\{P(C_2H_5)_3\}]_2$ are 3.4 and 3.25 D., respectively, while that of $[PdCl\{P(C_6H_5)_2\}\{P(C_2H_5)_3\}]_2$[2] was found to be 3.4 D. These complexes therefore exist mainly as *trans* isomers in benzene solution, although a small amount of a *cis* isomer (*ca.* 10%) also may be present due to partial isomerization. These results are consistent with the findings of Dr. G. S. Smith, who has made a preliminary X-ray investigation of single crystals of $[PdCl\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2$ and has found the dimer to have a center of symmetry and and hence the *trans* configuration. The crystallographic data were reported in an earlier communication.[3]

In general, the dimeric complexes X–XXII have reactions similar to those of the corresponding diphenylphosphido complexes previously shown to have structure I ($R = C_6H_5$). Thus, they do not undergo bridge-splitting reactions with amines or with tertiary phosphines, showing that they do not contain a halogen bridge. In addition, the thiocyanato complexes show absorption at 2080–2090 cm.$^{-1}$ due to terminal thiocyanate groups,[19] showing that diethylphosphido rather than SCN groups are in the bridge. The type I complexes react with chelate ligands such as $C_2H_4\{P(C_6H_5)_2\}_2$, *o*-phenanthroline, and ethylenediamine, thus

$$n[PdCl\{P(C_2H_5)_2\}\{P(C_4H_9)_3\}]_2 + 2n(C_6H_5)_2PC_2H_4P(C_6H_5)_2 = 2[Pd_n\{P(C_2H_5)_2\}_n\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}_n]Cl_n + 2n(C_4H_9)_3P \quad (11)$$

The ionic products were isolated as salts of large anions such as ClO_4^-, $B(C_6H_5)_4^-$, or $OC_6H_2(NO_2)_3^-$ (see Table II). The application of the Onsager equation[11] (8) to conductivity *vs.* concentration data leads to the conclusion that the salts have structure II ($n = 2$ in eq. 11).

It was shown previously that in methanol at 25°,

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(15) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 4300 (1952).
(16) J. Chatt and R. G. Wilkins, *ibid.*, 525 (1956).
(17) J. Chatt and R. G. Wilkins, *ibid.*, 70 (1953).
(18) J. Chatt and L. M. Venanzi, *ibid.*, 2445 (1957).
(19) J. Chatt and L. A. Duncanson, *Nature*, **178**, 997 (1956).

uni-bivalent electrolytes are expected to have $(A + \omega B \Lambda_0)$ values in the region 460–520, while the experimental values are usually 500–600. In contrast, uni-univalent electrolytes have $(A + \omega B \Lambda_0)$ values around 240 and the values for uni-trivalent electrolytes are expected to lie above 720.[2]

The conductance data obtained in methanol (Table III) show that the new complexes XXIII and XXIV behave as uni-bivalent electrolytes, although $(A + \omega B \Lambda_0)$ for XXIV is larger than calculated or expected by analogy with similar uni-bivalent electrolytes.[2]

Relatively large deviations in this direction from the calculated values are not uncommon, however, particularly in non-aqueous solvents, and usually are ascribed to ion-pair formation. In addition, the calculated $(A + \omega B \Lambda_0)$ for XXIV behaving as a uni-trivalent electrolyte is about 720, and this can be considered a *minimum* figure, since experimental values probably will lie considerably above this (For example, see $[Co(dipy)_3][ClO_4]_3$ in Table IV.) A more highly charged structure for XXIV is also not consistent with the observed ionic weight values in acetone, which agree well with that expected for a completely ionized uni-bivalent electrolyte.

We have now extended these conductivity measurements to nitromethane solutions, and find that the methanol-insoluble tetraphenylborates give a linear relationship between Λ_c and $\sqrt{c}$ over a wider concentration range than do similar chloride, perchlorate, and picrate salts in methanol. The results are summarized in Table IV, along with data obtained for some known 1:1, 2:1, and 3:1 electrolytes. These clearly show that the complexes XXV–XXVII behave as uni-bivalent electrolytes in nitromethane. Thus, in order for palladium(II) to retain four coördination in the binuclear cation, the diethylphosphido- and diphenylphosphido- groups must occupy bridging positions as shown in II.

Reaction of $[PdX_2\{HP(C_2H_5)_2\}_2]$ with Strong Base.—The reactions of $[PdX_2\{HP(C_2H_5)_2\}_2]$ with NaOH in aqueous alcoholic solution have been followed potentiometrically and evidence has been found for at least two consecutive reactions, the first of which is probably

$$[PdX_2\{HP(C_2H_5)_2\}_2] + NaOH = {}^1/_2[PdX\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2 + NaX + H_2O \quad (12)$$

When X = Cl or Br (but not I), a second reaction, possibly (13), closely follows (12), although under the titration conditions it does not occur quantitatively.

$${}^1/_2[PdX\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2 + NaOH = [Pd\{P(C_2H_5)_2\}_2] + NaX + H_2O \quad (13)$$

It is interesting to note that reaction 12 occurs at higher pH in the order Cl < Br < I and reaction 13 to a decreasing extent under the titration conditions in the order Cl > Br ≫ I. This behavior is similar to that qualitatively observed with $[PdX_2\{HP(C_6H_5)_2\}_2]$, which was found to become more stable with respect to loss of HX in the order Cl < Br < I. The factors which determine this order were discussed previously.[2] The diphenylphosphine complexes lose HX more readily than those of $(C_2H_5)_2PH$ and $C_2H_5C_6H_5PH$, $[PdCl_2\{HP(C_6H_5)_2\}_2]$, for example, being too unstable to be isolated, while the corresponding bromo complex, although stable in benzene, decomposes rapidly in ethanol, giving HBr and $[PdBr\{P(C_6H_5)_2\}\{HP(C_6H_5)_2\}]_2$.[2] The progressive substitution of the ethyl groups in diethylphosphine by the more electronegative phenyl probably causes an electron drift away from the ligand atom into the aromatic system. This will result in a decrease in the electron density in the P–H bond and hence in a more acidic proton.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA

The Donor Properties of Bis-(diisopropoxyphosphinyl)-methane and Bis-(di-N-butylphosphinyl)-methane

BY JUDITH A. WALMSLEY AND S. Y. TYREE

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Some new coördination compounds containing the ligands $(C_3H_7O)_2P(O)CH_2P(O)(OC_3H_7)_2$ (designated L_1) and $(C_4H_9)_2P(O)CH_2P(O)(C_4H_9)_2$ (designated L_2) have been prepared and have been characterized by means of their infrared spectra, visible spectra, conductance measurements, and magnetic susceptibility measurements. The compounds which have been prepared are $[FeCl_2(L_1)_2][FeCl_4]$, $CoCl_2 \cdot L_1 \cdot H_2O$, $[Co(L_1)_3](ClO_4)_2$, $[Ni(L_1)_3](ClO_4)_2$, $8CuCl_2 \cdot 5L_1$, $[Cu(L_1)_2](ClO_4)_2$, $ZnCl_2 \cdot L_1$, $[Zn(L_1)_2](ClO_4)_2$, $[SbCl_4(L_1)][SbCl_6]$, $[Fe(L_2)_3][FeCl_4]_3$, $[Fe(L_2)_3](ClO_4)_3$, $[Co(L_2)_3][CoCl_4]$, and $[Ni(L_2)_3][NiCl_4]$.

Introduction

Since substituted phosphine oxides have been found to be good coördinating agents and since many complexes of them have been prepared and studied[1–4] it was decided to investigate the donor properties of ligands containing two phosphoryl groups. Compounds containing one methylene group between the two phosphoryl groups were chosen so as to permit the

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[1] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 262 (1906).

[2] J. C. Sheldon and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1958).

[3] F. A. Cotton, E. Bannister, R. Barnes, and R. H. Holm, *Proc. Chem. Soc.*, 158 (1959).

[4] E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1873, 1878, 2276 (1960).