

PLATE II

nation of a metal ion with the substrate in two different ways, as indicated above, to produce an unreactive species competing with the reactive coordination intermediate.

Effect of Metal Ion.—One would not expect direct correlation between the half times listed in Table IV and the stabilities of analogous chelates of a series of metal ions, since the interactions with the ligand as shown in formulas VI and VII would depend on a balance between various factors such

as the residual coordinating tendency of the metal ion in the catalytic metal chelate, the tendencies of the metal ion and the metal chelate to hydrolyze and the relative tendencies of metal ions and metal chelates to form coordination compounds having linkages to the substrate of the type illustrated in V.

Detailed studies of these various factors are now being undertaken and will be reported in a subsequent communication.

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Transition Metal Complexes of Secondary Phosphines. I. Palladium(II) and Diphenylphosphine

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The reactions of diphenylphosphine with palladium(II) halides have yielded four types of complexes, whose structures and reactions have been investigated. The binuclear complexes $[PdX(PPh_2)(HPPH_2)]_2$ ($X = Cl, Br, I, SCN$) are shown to have a phosphorus-bridged structure and the factors affecting the formation and stability of the bridge are discussed. The Debye-Hückel-Onsager equation has been used to show that $[Pd_2(PPh_2)_2(chelate)_2]X_2$ (chelate = $C_2H_4(PPh_2)_2$, 1,10-phenanthroline; $X = Cl, ClO_4, picrate$) behave as uni-bivalent electrolytes in methanol.

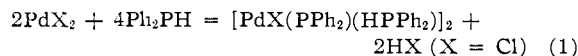
Introduction

This study is part of a general investigation of the transition metal complexes formed by secondary phosphines. Previous work in this field by Issleib and his co-workers¹ has shown that R_2PH ($R = C_2H_5, C_6H_{11}, C_6H_5$) forms stable complexes, in some cases of unusual types, with the halides of iron, cobalt, nickel, chromium and palladium. However, the properties, reactions and structures of these complexes were not investigated in detail.

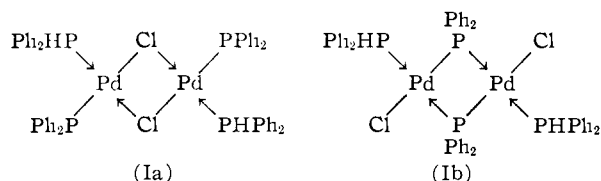
(1) (a) K. Issleib and G. Doll, *Z. anorg. u. allgem. Chem.*, **305**, 1 (1960); (b) K. Issleib and E. Wenschuh, *ibid.*, **305**, 15 (1960).

Our aim has been to study the effect of the P-H hydrogen on complex formation, using the corresponding tertiary phosphine complexes for comparison. The lower steric requirements of the secondary phosphine might be expected to lead to changes in stoichiometry or structure. Also, in complexes of the type $[MX_n(HPR_2)_n]$ (where $M = metal$ and $X = acid radical$) there exists the interesting possibility of inter- or intramolecular elimination of acid to give complexes derived from the anionic ligand PR_2^- . Thiols readily undergo reactions of this type to give either mer-

captides, $M(SR)_n$,² or sulfur-bridged complexes³; indeed no complexes containing the unchanged thiol appear to be known. Secondary phosphines are less reactive in this respect, although Issleib and Wenschuh have shown that $PdCl_2$ reacts with diphenylphosphine (2–4 moles) in benzene or methanol to give the yellow dimeric complex $[PdCl(PPh_2)(HPPH_2)]_2$,^{1b} according to equation (1)



Six isomeric structures, of which two are shown below, are feasible for this compound.

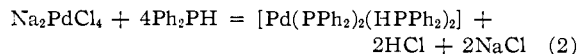


Issleib and Wenschuh proposed the chloro-bridged structure (Ia), although no supporting chemical or structural evidence was given.^{1b} Our results, however, show that the complex must contain a phosphorus bridge and probably exists as the *trans*-symmetrical isomer (Ib).

Results

Diphenylphosphine has yielded four types of complex (II–V) from its reactions with palladium halides. The compounds were obtained under the

excess acid only when $X = Cl$. Further, (V) is only obtained pure by the reaction^{1b}

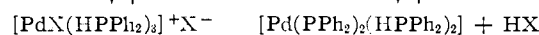
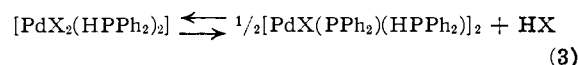


(ii) Halogen acid opposes the formation of (II) or (V) and favors the dihalide complexes, (III).

(iii) Excess diphenylphosphine favors the formation of (II) or (V) in alcohol and $[PdBr(HPPh_2)_3]Br$ in benzene.

(iv) The use of alcohols as solvents favors the acid displacement reactions, and thus (II) or (V), while benzene favors the formation of the dihalide complexes (III or IV).

These observations indicate that the reaction products are determined by a series of reversible reactions



The bromo complexes, being of intermediate character, best show this reversible behavior. Thus, $[PdBr_2(HPPH_2)_2]$ is reasonably stable in cold benzene, but elimination of HBr occurs slowly in boiling benzene (accounting for the observed high molecular weight values) and rapidly in ethanol or aqueous acetone or on addition of a weak base such as *p*-toluidine to its cold benzene solution.

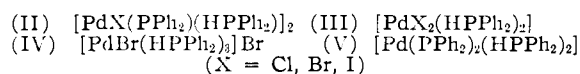
TABLE I

COMPLEXES OBTAINED BY REACTIONS BETWEEN DIPHENYLPHOSPHINE AND PdX_2 OR $[PdX_4]^{2-}$ ($X = Cl, Br, I$)^a

Method ^b	Reagents	Solvent	Products and yields		
			$X = Cl$	$X = Br$	$X = I$
1(a)	$Na_2PdX_4 + 2Ph_2PH$	EtOH	II (96%) [†]	II (93%) [†]	II + III (20%) [†]
1(b)	$Na_2PdX_4 + 4Ph_2PH$	EtOH	V	II + V (40%) [‡]	II + III (56%) [†]
2(a)	$H_2PdX_4 + 2Ph_2PH$	EtOH-HX	II (85%) [‡]	II + III (30%) [‡]	II + III (2%) [‡]
2(b)	$H_2PdX_4 + 4Ph_2PH$	EtOH-HX	(III?) [°] → V	II	II + III
3(a)	$PdX_2 + 2Ph_2PH$	C_6H_6	II	II + III	III
3(b)	$PdX_2 + 4Ph_2PH$	C_6H_6	II	IV	III
4	$PdX_2 + 2Ph_2PH$	MeOH	II	II	...

^a Percentage yields refer to the bridged complexes (II) obtained according to equation 1; yields marked (†) are based on the liberated acid and (‡) refers to yields of (II) isolated by crystallization. ^b See Experimental Section; [°] not isolated owing to instability.

conditions summarized in Table I and their properties and analytical data are given in Table II.



Some general conclusions can be drawn from the data outlined in Table I.

(i) The tendency to form the complexes containing the anionic ligand, PPh_2^- , (II and V) decreases in the order $Cl > Br > I$. This can be seen both from the precipitation reactions (methods 1 and 2) in which equilibrium is probably not attained and from the reactions in benzene (method 3) where a homogeneous solution and probably also equilibrium is reached. The bridged complex (II) is formed quantitatively in the presence of

(2) F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

(3) J. Chatt and F. A. Hart, *ibid.*, 2363 (1953), and references therein.

The reverse reaction takes place slowly when dry HBr is passed into a suspension of $[PdBr(PPh_2)(HPPH_2)]_2$ in benzene. Inspection of Table I shows that reactions (3') and (3'') occur under suitable conditions when $X = Br$ and these are also reversible (see below).

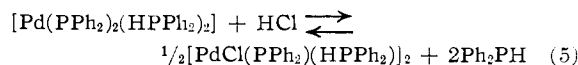
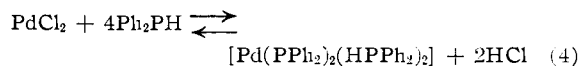
In method 2b ($X = Cl$), the initial precipitate of $[PdCl(PPh_2)(HPPH_2)]_2$ dissolves to give a transient red solution, rapidly fading to pale yellow and depositing yellow crystals on cooling. These crystals are stable only when moistened by acid and drying leads to decomposition to a brown solid, which, on crystallization gives only $[PdCl(PPh_2)(HPPh_2)]_2$. Further reaction occurs on allowing the crystals to stand in the mother liquor, a dark red solution and pink needles of $[Pd(PPh_2)_2(HPPH_2)]_2$ being formed. The color and behavior of the unstable intermediate complex indicate that it is probably $[PdCl_2(HPPH_2)]_2$.

TABLE II
PROPERTIES AND ANALYTICAL DATA FOR THE COMPLEXES OF TYPES (II)-(VI)

(N)	Compound	Method of prepn.	Yield, %	M.p., °C. (decompn.)	Color	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Molar conductance in MeNO ₂ (ohm ⁻¹) ⁿ	Molecular weight Found	Solvent
(X)	[PdCl(PPh ₂)(HPPH ₂) ₂] ₂	1(a)	80 ^e	215 ^f	Yellow-orange	56.2 56.5	4.1 4.5 ^g	1.17	1026	C ₆ H ₆ ^f
(XI)	[PdBr(PPh ₂)(HPPH ₂) ₂] ₂	1(a)	94 ^e	205 ^e	Orange	51.7 51.7	4.1 3.8	2.43	1115	CHCl ₃ ^f
(XII)	[PdI(PPh ₂)(HPPH ₂) ₂] ₂	5	70 ^e	200-220	Orange-red	47.7 48.25	3.5 3.6 ^h	1.09	..	CHCl ₃ ^f
(XIII)	[Pd(SCN)(PPh ₂)(HPPH ₂) ₂] ₂	1(a)	82 ^b	185 ^f	Orange	56.0 56.6	3.95 4.1 ⁱ	1.52 ^o
(XIV)	[PdBr ₂ (HPPH ₂) ₂]-C ₆ H ₆	3(a)	22 ^a	98-105	Yellow	50.3 50.3	3.9 4.2 ^j	8.83 ^o	860 ^q	C ₆ H ₆ ^f
(XV)	[PdI ₂ (HPPH ₂) ₂]	3(a)	70 ^e	224-229 ^f	Red-orange	39.35 39.6	3.0 3.1 ^k	8.90 ^o	763	C ₆ H ₆ ^f
(IV)	[PdBr(HPPH ₂) ₂] ₂ Br ^{-1/2} C ₆ H ₆	3(b)	78 ^b	140-160	Bronze	54.2 54.3	4.2 4.3 ^l	41.4 ^p	864	C ₆ H ₆ ^f
(V)	[Pd(PPh ₂)(HPPH ₂) ₂]	1(b)	81 ^b	110-120	Salmon-pink	67.9 68.0	5.0 5.0	7.35	849	C ₆ H ₆ ^f
(XVI)	[PdCl(PPh ₂)(PEt ₃) ₂] ₂	5	44 ^c	215-219 ^f	Yellow	48.6 48.6	5.7 5.85 ^m	0.20	890	Me ₂ CO ^r
(XVII)	[PdCl(PPh ₂)(PMe ₃ Ph)] ₂	5	34 ^d	227-228	Yellow	51.6 51.3	4.55 4.35	0.31 ^o

^a Cryst. from benzene. ^b Cryst. pure from reaction mixture. ^c Cryst. from aqueous acetone. ^d Cryst. from chloroform-hexane. ^e Decompl. without melting. ^f Melts without decompn. ^g Calcd.: P, 12.1. Found: P, 12.2. ^h Calcd.: I, 21.0. Found: I, 21.2. ⁱ Calcd.: N, 2.6; P, 11.6. Found: N, 2.55; P, 11.8. ^j Calcd.: Br, 23.3; P, 8.6. Found: Br, 23.0, 22.3; P, 8.7. ^k Calcd.: I, 34.65. Found: I, 34.55. ^l Calcd.: Br, 18.5; P, 10.8. Found: Br, 18.5; P, 10.8. ^m Calcd.: Cl, 8.45. Found: Cl, 8.0. ⁿ Concn. range 5-15 × 10⁻⁴ M. ^o Measured in nitrobenzene. ^p See text. ^q Extrapolated value at zero concn. ^r Isopiestic measurement. ^s Ebulioscopic measurement.

PdCl₂ dissolves in a methanolic solution of Ph₂PH (2 moles) (method 4) to give an intense red solution, from which slowly deposit yellow crystals of [PdCl(PPh₂)(HPPH₂)₂]₂. The precipitation of the complex may be accelerated by adding ether and refluxing.^{1b} The intermediate red solution was found to absorb at 516, 393 and 250-(sh) mμ and probably contains [Pd(PPh₂)₂(HPPH₂)₂], which also absorbs at these wave lengths. In methanol, therefore, even when the Ph₂PH/PdCl₂ ratio is only two, reaction occurs in two stages



PdBr₂ gives a similar sequence of reactions.

Although [PdI(PPh₂)(HPPH₂)₂]₂ frequently was found as one of the products of the iodo reactions (Table I), it was not easily obtained pure and a better preparation was by the reaction of [PdCl(PPh₂)(HPPH₂)₂]₂ with lithium iodide in tetrahydrofuran (method 5). [Pd(SCN)(PPh₂)(HPPH₂)₂]₂ was similarly prepared or by method 1a in the presence of excess potassium thiocyanate.

Structure of the Complexes [PdX(PPh₂)(HPPH₂)₂]₂ (X = Cl, Br, I, SCN).—The type (II) complexes are dimeric in benzene or chloroform and non-electrolytes in nitromethane or nitrobenzene solution. These measurements confirm those of Issleib and Wenschuh for (II, X = Cl).^{1b}

The limited solubility in benzene of [PdX(PPh₂)(HPPH₂)₂]₂ has precluded measurement of dipole moments so that it has not been possible to distinguish between polar and non-polar structures. However, the soluble derivative, [PdCl(PPh₂)(PEt₃)₂]₂, has a low dipole moment and the *trans*-symmetrical structures (Ia) and (Ib) are thus indicated. [PdCl(PEt₃)(HPET₂)₂]₂ has been shown to have a *trans*-symmetrical structure in the solid state by X-ray analysis.⁴ In any case, unsymmetrical structures probably can be discounted since none of the numerous previously known chloro- or thio-bridged complexes of palladium have been found to exist in these forms.³

Chloro-bridged complexes, e.g. [PdCl₂(PR₃)₂]₂, are known to react rapidly with amines such as *p*-toluidine or piperidine to give mononuclear complexes of the type *trans*-[PdCl₂(amine)(PR₃)].⁵ However, *p*-toluidine does not react with (II) even in boiling benzene, so that if there is a halobridge in (II) it is an exceptionally stable one. It seems more likely that (II) contains a phosphorus-bridge, as in (Ib), and that this, like the sulfur-bridge in palladium(II) complexes, is stable to *p*-toluidine.³ Slightly stronger bases such as diethylamine or piperidine react slowly with (II, X = Cl) to give intense red solutions, the amine hydrochlorides being precipitated. In this case, a different type of reaction, acid elimination, is occurring. The products which may be of type [Pd(PPh₂)₂(amine)]₂ or [Pd(PPh₂)₂(amine)₂] are very soluble, rather unstable materials which could not be isolated in a pure state.

(1) R. G. Hayter, *Nature* **193**, 872 (1962).

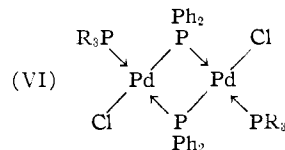
(5) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2415 (1957).

TABLE III
 PROPERTIES AND ANALYTICAL DATA FOR $[\text{Pd}_2(\text{PPh}_2)_2(\text{CHELATE})_2]\text{X}_2$

No.	Chelate	X	Yield, %	M.p., °C. (decompn.)	Color	Carbon, %		Hydrogen, %		Molar conductance in MeNO ₂ (ohm ⁻¹)	Ionic weight		Solvent
						Calcd.	Found	Calcd.	Found		Calcd. ^a	Found	
(XVIII)	C ₂ H ₄ (PPh ₂) ₂	Cl	88 ^a	173-175	Pale orange	62.9	62.4	4.7	4.9 ^c	157	484	498	MeOH ^o
(XIX)	C ₂ H ₄ (PPh ₂) ₂	I	55 ^b	181-184	Red-orange	55.9	55.65	4.2	4.6 ^f	191	..	858, 894	EtOH ^o
(XX)	C ₂ H ₄ (PPh ₂) ₂	NO ₂	20 ^b	202-204	Orange	59.3	59.5	4.7	4.9 ^g	195	..	876, 865	..
(XXI)	C ₂ H ₄ (PPh ₂) ₂	ClO ₄	41 ^b	280-282	Orange	57.8	58.1	4.3	4.7 ^h	214	526	757, 721	Me ₂ CO ^o
(XXII)	C ₂ H ₄ (PPh ₂) ₂	BPh ₄	55 ^c	166-169	Orange-red	73.8	74.2	5.4	5.5 ⁱ	134	673	781	MeNO ₂
(XXIII)	C ₂ H ₄ (PPh ₂) ₂	Picrate	54 ^d	223-225	Orange	57.6	57.1	3.95	4.2 ^j	157	606	1046	EtMeCO ^o
(XXIV)	C ₂ H ₄ (PPh ₂) ₂	HgCl ₃	15 ^e	Decompn. 185	Orange	45.8	45.9	3.4	3.4	196 ^m	..	821, 751, 815	Me ₂ CO ^o
(XXV)	1,10-phenan	ClO ₄	15 ^d	>350	Levon-yellow	50.5	49.95	3.2	3.3 ^k	209.5

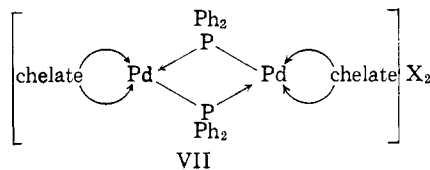
^a Cryst. pure from reaction mixture. ^b Cryst. from aqueous ethanol. ^c Cryst. from methanol. ^d Cryst. from aqueous acetone. ^e Cryst. from aqueous acetone. ^f Cryst. from methanol. ^g Calcd.: Cl, 4.9; P, 12.8. Found: Cl, 4.7; P, 12.8. ^h Calcd.: I, 15.1. ⁱ Calcd.: Cl, 4.5. ^j Calcd.: P, 9.2. Found: P, 9.5. ^k Calcd.: N, 4.6. Found: N, 4.5. ^l Calcd.: N, 4.9; P, 5.4. Found: N, 5.6; P, 5.3. ^m Concentration range 3.5-5.5 × 10⁻⁴ M. ⁿ Extrapolated value at zero concn. ^o Calcd. for complete ionic dissociation. ^p Isopiestic measurement. ^q Ebullioscopic measurement.

$[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$ reacts with tertiary phosphines, which may also split chloro-bridges, to give dimeric complexes of the type $[\text{PdCl}(\text{PPh}_2)(\text{PR}_3)]_2$ ($\text{PR}_3 = \text{PEt}_3, \text{PMe}_2\text{Ph}$). It is probable that these compounds have the *trans* phosphorus-bridged structure (VI) since they do not react with *p*-toluidine or piperidine and (VI, R = Et) has a dipole moment of 3.4D. The finite dipole moment indicates that about 10% *cis* isomer is also present in solution. Triphenylphosphine does not displace



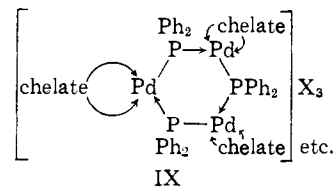
diphenylphosphine from $[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$, showing that it is not a markedly stronger donor than the secondary phosphine to palladium(II).

In further attempts to split the phosphorus-bridge, the reactions of (II, X = Cl) with the chelate ligands C₂H₄(PPh₂)₂ and *ortho*-phenanthroline were investigated and found to give stable ionic complexes of the type (VII, X = Cl), by displacement of the terminal ligands, Ph₂PH and Cl⁻. Derivatives were also prepared in which



X = I⁻, NO₃⁻, ClO₄⁻, BPh₄⁻, OC₆H₂(NO₂)₃⁻ and HgCl₃⁻ (see Table III).

It was necessary to distinguish between (VII) (dimer) and the alternative structures (VIII) (monomer), (IX) (trimer), etc.



Conductivity measurements, as usually carried out at one concentration in the region of 10⁻⁴ M, do not help in this respect since (VII), (VIII), (IX) etc. are all expected to have the same molar conductance. This situation is typical of a series of possible polymeric structures having identical equivalent weights. However, application of a form of the Debye-Hückel-Onsager equation⁶ shows that (VII) is the correct structure. ($\Lambda_0 =$

$$\Lambda_0 - \Lambda_c = (A + \omega B \Lambda_0) \sqrt{c} \quad (6)$$

equivalent conductance at zero concentration; Λ_c = equivalent conductance at concentration c ; A and B are constants depending on the solvent, temperature and type of electrolyte; $\omega = 1$ for uni-univalent electrolytes and is a function of the

(6) L. Onsager, *Physik. Zitt.*, **28**, 277 (1927).

TABLE IV
CALCULATED AND EXPERIMENTAL VALUES OF $(A + \omega B\Lambda_0)$ FOR ELECTROLYTES OF KNOWN TYPE IN METHANOL AT 25°^a

Electrolyte	Λ_0 (ohm. ⁻¹)	Calculated values			$(A + \omega B\Lambda_0)$	Exptl. $(A + \omega B\Lambda_0)$	Concn. range (equiv./l. $\times 10^4$)
		ω	A	B			
KCl ^b	105.1	1	152	0.862	242	252	1.0-20.4
NaCNS ^c	107.0	1	152	.862	244	255	1.4-17.0
[<i>n</i> -Bu ₄ N]Br	102.8	1	152	.862	240	256	11.0-110
CaCl ₂	105.4	1.07 ^e	279	1.80	482	530	4.9-51.0
[Ni(1,10-phenan)] ₂ Cl ₂	110.2	1.08 ^e	279	1.80	493	514	1.4-31.0
MCl ₃ ^d	(110)	1.42 ^e	429	2.08	755

^a $D^{25} = 32.63$, $\eta^{25} = 0.00547$ poise. ^b Experimental data from ref. 7. ^c Experimental data from ref. 8. ^d No methanol-soluble uni-trivalent electrolyte was found; the value of Λ_0 was assumed. ^e Calculated using $l_{Cl}^0 = 52.4$ ohm.⁻¹ (ref. 9).

ionic charges and mobilities (l_{\pm}^0) for more highly charged electrolytes.) For measurements carried out on dilute solutions in a given solvent at constant temperature, the term $(A + \omega B\Lambda_0)$ depends, within relatively narrow limits, only on the type of electrolyte. The agreement between theory and experiment is very good for aqueous solutions and is reasonably good for methanolic solutions (see Table IV). The values of $(A + \omega B\Lambda_0)$ for 1:1, 2:1 and 3:1 electrolytes increase roughly in the ratio 1:2:3 for both water and methanol.

Measurements of electrical conductivity over a concentration range were also carried out for the new complexes and the calculated values of $(A + \omega B\Lambda_0)$ for the structures (VII-IX) are compared with the experimental values in Table V.

a not unusual observation, particularly in non-aqueous solvents.

Ionic weight measurements in a number of suitable organic solvents are also consistent with (VII). However, the experimental values are higher than those calculated for completely ionized (VII), owing to ion-pair formation in the relatively concentrated solutions in which the measurements were made. These results therefore do not clearly distinguish between (VII) and higher polymers such as (IX).

Further evidence in favor of a phosphorus-bridged structure for (II) comes from the absorption of $\nu_{C=N}$ at 2080 cm.⁻¹ in [Pd(SCN)(PPh₂)(H-PPh₂)₂]. This absorption is in the range expected

TABLE V
CALCULATED AND EXPERIMENTAL VALUES OF $(A + \omega B\Lambda_0)$ FOR THE COMPLEXES [Pd(PPh₂)(CHELATE)]_nX_n [*n* = 1, 2, 3] IN METHANOL AT 25°^a

Compound	Λ_0 (ohm. ⁻¹)	Calcd. values of $(A + \omega B\Lambda_0)$			Exptl. $(A + \omega B\Lambda_0)$	Concn. range (equiv./l. $\times 10^4$)
		<i>n</i> = 1 (VII)	<i>n</i> = 2 (VIII)	<i>n</i> = 3 (IX)		
[Pd(PPh ₂) ₂ {C ₂ H ₄ (PPh ₂) ₂ }] _n Cl _n	98.1	236	464	706	510	0.7-9.0
[Pd(PPh ₂) ₂ {C ₂ H ₄ (PPh ₂) ₂ }] _n [ClO ₄] _n	120.9	256	501	757	552	1.0-6.1
[Pd(PPh ₂) ₂ {C ₂ H ₄ (PPh ₂) ₂ }] _n [picrate] _n	101.8	239	480	734	540	0.8-4.2
[Pd(PPh ₂) ₂ {1,10-phenan}] _n [ClO ₄] _n	126.8	261	515	781	654	3.0-25.0

^a $l_{ClO_4}^0 = 70.9$ ohm.⁻¹; $l_{picrate}^0 = 46.9$ ohm.⁻¹ (ref. 9).

The concentration range, over which a linear relationship between $(\Lambda_0 - \Lambda_c)$ and \sqrt{c} was obtained, was limited owing to ion association at higher concentrations and to experimental errors due to the low conductivity of dilute solutions at the lower concentrations. A sufficient concentration range was usually available, however, to make an accurate extrapolation to zero concentration.

Inspection of Table V and comparison with the results in Table IV clearly show that the complexes behave as uni-bivalent electrolytes in methanol and thus have the dimeric structure (VII). Only the phenanthroline complex shows a large deviation from the theoretical value and this may be due either to incomplete dissociation or to the presence of some higher polymeric species. The semi-empirical calculated values of $(A + \omega B\Lambda_0)$ are consistently lower than the experimental values, the deviations increasing with the charge on the

for terminal rather than bridging thiocyanate groups.¹⁰

Finally, the bridged complexes do not show any reactions attributable to terminal diphenylphosphido groups, although such reactions are expected on the basis of chloro-bridged structures. Thus, (II) does not react with alkyl halides, is stable to oxidation in solution and reacts only slowly, if at all, with halogen acids. This behavior is in contrast to that observed with [Pd(PPh₂)₂(HPPH₂)₂].

The chemical and physical evidence discussed above strongly indicates that [PdX(PPh₂)(HPPh₂)₂] (X = Cl, Br, I, SCN) have a phosphorus-bridged structure and that the Pd₂P₂ ring is preserved unchanged in the complexes of types (VI) and (VII). The phosphorus-bridge can be split by HBr to give [PdBr₂(HPPH₂)₂] and by diphenylphosphine to give [Pd(PPh₂)₂(HPPH₂)₂].

[PdX₂(HPPH₂)₂], (X = Br, I).—[PdX₂(HPPH₂)₂] (X = Br, I) are monomeric in boiling benzene and have a slight conductivity in nitromethane, due possibly to liberation of acid. They undoubtedly have a square planar structure, as is well estab-

(7) J. E. Frazer and H. Hartley, *Proc. Roy. Soc. (London)*, **109A**, 351 (1925).

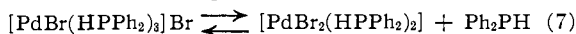
(8) A. Unmack, D. M. Murray-Rust and H. Hartley, *ibid.*, **127A**, 228 (1930).

(9) L. Fischer, G. Winkler and G. Jander, *Z. Elektrochem.*, **62**, 1 (1958); E. D. Copley and H. Hartley, *J. Chem. Soc.*, 2488 (1930); J. W. Williams, *Chem. Rev.*, **8**, 303 (1931); A. G. Ogston, *Trans. Faraday Soc.*, **32**, 1679 (1936).

(10) J. Chatt and L. A. Duncanson, *Nature*, **178**, 997 (1956).

lished for four-coördinate palladium(II).¹¹ The dipole moment of the iodo complex is 6.5D., indicating that about equal amounts of *cis* and *trans* isomers are present in solution. However, only one crystalline complex was isolated.

[PdBr(HPPH₂)₃]Br (IV).—(IV) crystallizes in bronze needles from the dark red benzene reaction mixture. On redissolving in benzene, a yellow solution was obtained to which the red color was restored by the addition of excess diphenylphosphine. The molecular weight and conductivity data also indicate partial dissociation in solution



The molar conductance of (IV) in nitromethane is 41.4 ohm⁻¹ but is raised to a value (75.2 ohm⁻¹) in the normal range for an uni-univalent electrolyte in the presence of excess ligand (20 moles). This behavior resembles that of [PdBr(AsMePh₂)₃]Br¹² and [PdBr(PMePh₂)₃]Br¹³ which are also extensively dissociated in solution. The dark red color of benzene solutions containing (IV) and excess Ph₂PH may indicate the presence of a non-ionic five-covalent complex [PdBr₂(HPPH₂)₃], analogous to [NiX₂(HPPH₂)₃] (X = Cl, Br, I),¹³ although ion-pair formation is also possible in a solvent of such low dielectric constant. Attempts to prepare the corresponding iodo complex gave only [PdI₂(HPPH₂)₂] (see Table I). However, the conductivity of [PdI₂(HPPH₂)₂] in nitromethane was raised from 8.9 to 86.0 ohm⁻¹, by the addition of an excess of diphenylphosphine (20 moles), which indicates the presence of [PdI(HPPH₂)₃]I in solution.

[Pd(PPh₂)₂(HPPH₂)₂] (V).—[Pd(PPh₂)₂(HPPH₂)₂] is monomeric in benzene, a non-electrolyte in nitromethane, diamagnetic in the solid state and has a dipole moment of 9.8D. These data indicate a *cis* square planar structure. Its X-ray powder pattern is very similar to that of [Ni(PPh₂)₂(HPPH₂)₂], which previously has been shown to be square planar.^{1b}

(V) is not oxidized in air in the solid state, but oxidation occurs quite rapidly in solution, owing to the presence of terminal diphenylphosphido groups in the molecule. Some of the reactions of this complex resemble those of a tertiary phosphine.

Reactions of [Pd(PPh₂)₂(HPPH₂)₂].—[Pd(PPh₂)₂(HPPH₂)₂] reacts with acids, halogens or alkyl halides with loss of one or both of the diphenylphosphido groups. Thus, [Pd(PPh₂)₂(HPPH₂)₂] in benzene reacts with dry hydrogen chloride according to equation 5. This reaction goes to completion only with three or more equivalents of acid. The excess acid probably removes the displaced Ph₂PH as a phosphonium salt. The reverse reaction occurs in the presence of excess diphenylphosphine.

Under similar conditions, excess dry hydrogen bromide gives [PdBr(HPPH₂)₃]Br. In alcohol or acetone, however, the bridged complex [PdBr(PPh₂)(HPPH₂)₂] is obtained owing to the instability of [PdBr(HPPH₂)₃]Br in these solvents.

(11) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, 1945, p. 523.

(12) R. S. Nyholm, *J. Chem. Soc.*, 848 (1950).

(13) R. G. Hayter, unpublished results.

The formation of the ionic complex implies that HBr reacts by coördination of the proton to the free electron pair of a diphenylphosphido group. This may be followed by nucleophilic attack on the metal atom by Br⁻, with simultaneous expulsion of diphenylphosphine. Repetition of the first step gives [PdBr(HPPH₂)₃]Br. The corresponding reaction with HCl proceeds rapidly to [PdCl(PPh₂)(HPPH₂)₂], owing to the instability of the intermediate chloro complexes.

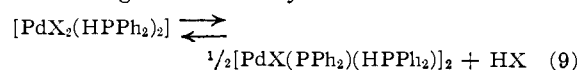
The reactions of alkyl halides with [Pd(PPh₂)₂(HPPH₂)₂] in benzene occur more slowly than the reactions with acid to give [PdX(PPh₂)(HPPH₂)₂] 2[Pd(PPh₂)₂(HPPH₂)₂] + 6MeI = [PdI(PPh₂)(HPPH₂)₂]₂ + 4[Ph₂Me₂P]I + 2HI (8)

Ethyl bromide or benzyl chloride give the corresponding bromo or chloro complexes. There was no indication that mononuclear complexes were formed as intermediates, even in the iodo case. It was not possible to detect the mixed tertiary phosphines, Ph₂RP (R = Me, Et, benzyl) as separate reaction products since both Ph₂RP and Ph₂PH give the same quaternary salt, [Ph₂R₂P]X, with excess alkyl halide.

Halogens also cleave diphenylphosphido groups from [Pd(PPh₂)₂(HPPH₂)₂], chlorine (2 moles) giving [PdCl(PPh₂)(HPPH₂)₂] and iodine [PdI₂(HPPH₂)₂].

Discussion

Factors Affecting the Formation of Phosphorus-bridged Complexes.—It has been shown that the formation of the phosphorus-bridged complexes (equation 9) is affected greatly by the nature of the anionic ligand X and by the solvent. The effect



of X is consistent with the implication of equation 9 that Pd-X bonds are being broken, since the ease with which [PdX₂(HPPH₂)₂] loses HX is observed to decrease Cl > Br > I, whereas the affinity of a class (b) metal such as palladium(II) for halide ion is known to increase Cl < Br < I.¹⁴ Other factors, particularly the heats of formation of HX, may also be important, but the qualitative nature of the observations does not allow them to be evaluated reliably.

When alcohol rather than benzene is used as solvent the formation of HX is favored owing to the larger heats of solution in the former solvent (HCl, 14.8 kcal./mole in 2-propanol,¹⁵ 4.3 kcal./mole in benzene¹⁶). This deduction, although consistent with experiment, assumes that the difference between the heats of solution of the two complexes in equation 9 does not change appreciably with the solvent and this may not be justified.

Changing the secondary phosphine ligand also affects the elimination of HX, by altering the P-H bond strength. For example, diethylphosphine in its complexes behaves as a weaker acid

(14) S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, **12**, 265 (1958).

(15) C. H. Campbell, D. H. Chadwick and S. Kaufmann, *Ind. Eng. Chem.*, **49**, 1871 (1957).

(16) S. J. O'Brien, *J. Am. Chem. Soc.*, **63**, 2709 (1941).

than diphenylphosphine and forms stable mononuclear complexes, $[\text{PdX}_2(\text{HPEt}_2)_2]$, even when $\text{X} = \text{Cl}$. Elimination of acid does occur, however, on treatment with a base such as *p*-toluidine and good yields of $[\text{PdX}(\text{PEt}_2)(\text{HPEt}_2)]_2$ are thus obtained.⁴

Structure and Reactivity in Phosphorus-bridged Complexes.—The most extensive previously known series of phosphorus bridged complexes are those of boron and aluminum, $[\text{R}_2\text{P}\cdot\text{MR}'_2]_n$, ($\text{M} = \text{B}, \text{Al}$; $\text{R} = \text{alkyl, aryl}$; $\text{R}' = \text{H, alkyl, aryl}$; $n = 1, 3, 4, \dots$).¹⁷ The only dimers so far reported of this type are $[\text{Ph}_2\text{P}\cdot\text{BX}_2]_2$ ($\text{X} = \text{halogen}$)¹⁸ but, in this case, no evidence was given for the nature of the bridging atom, which may be either phosphorus or halogen. Experiments with molecular models show that it is not possible to make a four-membered ring containing the tetrahedral atoms phosphorus and boron but that six-membered rings show little strain except with large substituent groups such as phenyl. Thus, it seems probable that in compounds of this type, steric effects play a large part in determining the degree of polymerization. Recently it has been shown that electronic factors are also important in preventing the polymerization of $\text{Ph}_2\text{B}\cdot\text{PR}_2$.¹⁹

With palladium(II), however, we have found evidence for four-membered rings only. (The related complex $[\text{Mn}(\text{AsPh}_2)(\text{CO})_4]_2$ is also thought to contain a four-membered Mn_2As_2 ring.²⁰) Models indicate that, although there is considerable strain in forming a ring containing two tetrahedral phosphorus atoms and two square planar palladium atoms, there is little or no steric hindrance between the substituents of such a ring, provided they are not unusually bulky. The corresponding six- and eight-membered rings, on the other hand, can be made without strain but show considerable steric hindrance between their substituent groups. The balance between these two effects probably is important in determining the observed ring size.

The strain in the ring will have an effect upon the reactivity of the complex, and it is interesting to consider how this strain might vary with the bridging group Y in the compounds $[\text{PdXY}(\text{PR}_3)]_2$ ($\text{X} = \text{halogen, Y} = \text{Cl, SR', PR}'_2$; $\text{R, R}' = \text{alkyl or aryl}$). If a single Y group were to bridge two palladium atoms, the four electron pairs of the ligand atoms would be approximately tetrahedrally arranged so as to minimize electrostatic repulsions. Since such repulsions are thought to decrease in the order lone pair-lone pair > lone pair-bond pair > bond pair-bond pair,²¹ the arrangement would not be perfectly tetrahedral. Instead, the angle PdYPd is expected to decrease in the order $\text{P} > \text{S} > \text{Cl}$, as the number of Y lone pairs increases. It would therefore be expected that the energy required to compress this angle to about 90° , in order to form the four-membered

ring, and hence the strain in such a ring, would decrease in the same order. On the other hand, the coordinating affinity of Y for palladium(II) is also expected to decrease in the order $\text{P} > \text{S} > \text{Cl}$,¹⁴ as will therefore the strength of binding in the bridge.

These two opposing effects may explain the observed irregular order of reactivity of the bridged complexes, which appears to be $\text{S} < \text{P} < \text{Cl}$. Thus, whereas chloro-bridged complexes are easily cleaved and we have seen that under certain conditions phosphorus-bridged complexes can also be cleaved, there are no reported analogous reactions of the sulfur-bridged complexes of palladium(II) or platinum(II).³

Experimental

Microanalyses are by Schwarzkopf Microanalytical Laboratory, who also measured some of the molecular weights by an isopiestic method. The ebullioscopic molecular weights and the dipole moments (by the method of Everard, Hill and Sutton)²² were done in the Physical Measurements Department of Mellon Institute. Melting points were determined on a Kofler hot stage and are corrected. Conductivity measurements were made at 25° on a Model RC-16B2 bridge (Industrial Instruments, Ltd.).

Reactions using phosphines were carried out under nitrogen. The complexes, once formed, were usually sufficiently stable to handle in air. Some of them were obtained under a variety of conditions and were then identified by thermal behavior on the Kofler hot stage, X-ray powder pattern and, in some cases, analysis. The yields of acid obtained in methods 1a and 1b (Table I) were estimated by diluting the filtrate obtained after removal of the precipitated complex to a known volume with water and titrating aliquots with 0.1 *N* NaOH.

Typical examples of the reactions outlined in Table I are given below. The (a) and (b) methods differ only in the amount of phosphine and are not described separately.

Method 1. Di- μ -diphenylphosphido-dichlorobis-(diphenylphosphine)-dipalladium (X).—Diphenylphosphine (0.63 g., 2 moles) was added to sodium tetrachloropalladium(II) (0.50 g.) in ethanol (20 ml.) to give an orange precipitate, which partially dissolved toward the end of the addition to give a dark red solution. After standing overnight, the precipitate was filtered and washed with water and ethanol. Crystallization from benzene gave the pure complex as prisms.

(X) also was obtained by methods 2(a), 3(a) and 4 (see below) and was identical with the compound prepared as described by Issleib and Wenschuh.^{1b}

The bromo complex (XI) was similarly prepared except that the solution of Na_2PdCl_4 was treated with LiBr (ca. 12 moles) before addition of the phosphine. (XI) was also obtained in 13 and 60% yields by methods 4 and 5, respectively, and, mixed with $[\text{PdBr}_2(\text{HPPH}_2)_2]\cdot\text{C}_6\text{H}_6$, by methods 2(a) and 3(a). In the presence of an acid-acceptor such as *p*-toluidine method 3(a) gives an almost quantitative yield of $[\text{PdBr}(\text{PPh}_2)(\text{HPPH}_2)]_2$.

Di- μ -diphenylphosphido-dithiocyanatobis-(diphenylphosphine)-dipalladium (XIII).— Na_2PdCl_4 (0.50 g.) in ethanol (100 ml.) was treated with KSCN (1.32 g., 8 moles), the solution refluxed for 10 minutes and filtered. Diphenylphosphine (0.64 g., 2 moles) was added to the red filtrate, giving a yellow-orange precipitate which redissolved on shaking. On standing overnight, the red solution deposited a mixture of orange crystals and white solid. Washing with water and ethanol gave pure (XIII).

cis-Bis-(diphenylphosphido)-bis-(diphenylphosphine)-palladium (V).—A filtered solution of Na_2PdCl_4 (0.30 g.) in ethanol (20 ml.) was added to diphenylphosphine (0.76 g., 4 moles) in ethanol (20 ml.) with stirring to give an intense red solution, which, on cooling overnight, deposited salmon-pink needles. Washing with water and ethanol gave pure (V).

On storage in the air, (V) changes color to pale orange, without change in m.p. The complex was also prepared by

(17) G. E. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 109, 140.

(18) W. Gee, R. A. Shaw, B. C. Smith and G. J. Bullen, *Proc. Chem. Soc.*, 432 (1961).

(19) G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 1000 (1961).

(20) R. F. Lambert, *Chem. & Ind. (London)*, 830 (1961).

(21) R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 11, 339 (1957).

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

treating $[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$ with Ph_2PH (4 moles) in ethanol. After refluxing for 15 minutes, the dark red solution was filtered, and on cooling (V) crystallized in 33% yield.

Anal. Calcd. for $\text{C}_{48}\text{H}_{42}\text{P}_4\text{Pd}$: C, 67.9; H, 5.0; P, 14.6. Found: C, 67.5; H, 5.35; P, 14.1.

Method 2.—A solution of PdCl_2 (0.50 g.) in concd. hydrochloric acid (9 ml.) was diluted with ethanol (20 ml.) and treated with diphenylphosphine (1.05 g., 2 moles). The thick yellow precipitate was filtered and washed with water and ethanol to give the crude product (1.40 g., 97%). Crystallization from benzene gave pure (X), identical with that prepared by method 1(a).

Anal. Found: C, 56.4; H, 4.3.

Method 3.—**Dibromobis-(diphenylphosphine)-palladium (XIV).**—Palladium bromide (1.0 g.) and diphenylphosphine (1.40 g., 2 moles) were refluxed together in benzene (75 ml.) until all the PdBr_2 dissolved to give a yellow-orange solution (3 hr.). After concentrating the solution to about 60 ml., a mixture of yellow and orange crystals (1.87 g.) separated on cooling. Two rapid crystallizations from benzene gave pure (XIV) as plates (m.p. 98–105° with recrystallization and subsequent decomp. above 215°). The compound crystallizes as a mono-benzene solvate. After drying in vacuum at 100° for 6 hr., about 50% of the solvated benzene is lost. The less soluble orange crystalline product obtained in this preparation is $[\text{PdBr}(\text{PPh}_2)(\text{HPPH}_2)]_2$ (15% yield).

(XV) was similarly prepared from PdI_2 ; there was no evidence for the formation of (XII).

Bromotris-(diphenylphosphine)-palladium Bromide (IV).—Palladium bromide (0.25 g.) and diphenylphosphine (0.70 g., 4 moles) were refluxed together in benzene (20 ml.) for 30 minutes to give a clear red solution, which was filtered under nitrogen. On standing, the filtrate deposited bronze rods, which were filtered and washed with benzene and hexane to give pure (IV). The complex crystallizes with a half-molecule of benzene.

Method 4.—Palladium chloride (0.20 g.) and diphenylphosphine (0.42 g., 2 moles) were refluxed together in methanol (50 ml.) for 2 hr. The solution was filtered from some residual black solid and the dark red filtrate slowly deposited yellow needles of $[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$ (40% yield) on standing for several days.

Ligand Displacement Reactions (Method 5). **Di- μ -diphenylphosphido-diiodobis-(diphenylphosphine)-dipalladium (XII).**— $[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$ (0.50 g.) was suspended in tetrahydrofuran (75 ml.) and treated with lithium iodide (1.05 g., 16 moles) to give an orange-red solution. After refluxing for 8 hr., the solvent was evaporated and the residue, after washing with water and ethanol, and crystallizing from benzene afforded pure (XII).

trans-Di- μ -diphenylphosphido-dichlorobis-(triethylphosphine)-dipalladium (XVI).— $[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$ (1.0 g.) was suspended in acetone (50 ml.) and treated with triethylphosphine (0.40 g., 3.5 moles) to give an orange-red solution. After refluxing for 10 minutes, the solution was evaporated to dryness leaving oily red crystals which were treated with a little ethanol and cooled overnight. The resulting yellow-orange crystals were filtered and crystallized from aqueous acetone to give pure (XVI) as plates.

(XVII) was prepared similarly in benzene solution.

Di- μ -diphenylphosphido-dl-[1,2-bis-(diphenylphosphino)ethane]-dipalladium Dichloride (XVIII).—Filtered benzene solutions of (X) (0.20 g.) and 1,2-bis-(diphenylphosphino)ethane (0.155 g., 2 mole) were mixed and the resulting orange solution allowed to stand. Crystals slowly separated during 24 hr. and were filtered and washed with hot benzene to give the pure complex as plates.

Di- μ -diphenylphosphido-dl-[1,2-bis-(diphenylphosphino)ethane]-dipalladium Diiodide (XIX).—(XVIII) (0.10 g.)

in ethanol (5 ml.) was treated with lithium iodide (0.19 g., 20 moles) in ethanol (5 ml.). The resulting orange solution was diluted with water (10 ml.), filtered and cooled to give thick reddish-orange rods. Recrystallization from aqueous ethanol gave pure (XIX).

(XIX) was also prepared in 74% yield by reaction between $\text{C}_2\text{H}_4(\text{PPh}_2)_2$ and $[\text{PdI}(\text{PPh}_2)(\text{HPPH}_2)]_2$ in benzene.

The type (VII) complexes (chelate = $\text{C}_2\text{H}_4(\text{PPh}_2)_2$) were similarly prepared from (XVIII) and an appropriate metal salt in ethanol or water. The properties and analytical data of these compounds are given in Table III.

Di- μ -diphenylphosphido-dl-(1,10-phenanthroline)-dipalladium Diperchlorate (XXV).—(X) (0.50 g.) slowly dissolved in a refluxing ethanolic solution of 1,10-phenanthroline (0.36 g., 4 moles in 50 ml.) to give an intense red solution. After 15 minutes, the solution was filtered and NaClO_4 (0.5 g.) in water (2 ml.) added. Evaporation gave a brown solid residue which afforded a mixture of white and yellow crystals from ethanol. Washing with water and recrystallization from methanol gave pure (XXV) as needles.

Reactions of cis- $[\text{Pd}(\text{PPh}_2)_2(\text{HPPH}_2)]$ (V). **Hydrogen Chloride.**—(V) (0.10 g.) in benzene (5 ml.) was treated with a 0.123 N solution of HCl in ether (3 equiv., 2.9 ml.). The dark red solution faded rapidly to orange and after 1 hr., yellow prisms (28 mg., 46%) of $[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$ (decomp. 215°) had formed.

Hydrogen Bromide.—(V) (0.20 g.) in benzene (10 ml.) was treated with 6 equiv. of HBr in ether. The solution changed to a cloudy orange and an orange-red oil precipitated, which crystallized to red needles (0.21 g.) on standing. Crystallization from benzene gave bronze needles (0.10 g., 50%), which were identical with $[\text{PdBr}(\text{HPPH}_2)]_2\text{Br}$ by m.p. and X-ray powder pattern.

Methyl Iodide.—(V) (0.30 g.) in benzene (10 ml.) was treated with excess methyl iodide (2 ml.), the solution slowly fading to orange and precipitating white and orange crystals during two days. Crystallization from benzene gave red-orange rods of $[\text{PdI}(\text{PPh}_2)(\text{HPPH}_2)]_2$ (85 mg., 40%) and an insoluble white solid, which gave colorless needles of $[\text{Ph}_2\text{Me}_2\text{P}]\text{I}$ (m.p. 254.5–6.5°, lit. 241°) in 34% yield from acetone.

Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{IP}$: C, 49.1; H, 4.7. Found: C, 49.3; H, 4.7.

Benzyl Chloride.—(V) dissolves in benzyl chloride on warming to give a dark red solution, which slowly fades to yellow-orange. After dilution with ethanol, yellow needles separated and were found to be identical with $[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$ by X-ray powder pattern.

Chlorine.—(V) (0.30 ml.) in benzene (10 ml.) was treated with a 0.398 N solution of chlorine in CCl_4 (4 equivs., 3.5 ml.), to precipitate an orange-red oil. After taking to dryness the oil crystallized to a yellow solid in ethanol and crystallization from benzene gave $[\text{PdCl}(\text{PPh}_2)(\text{HPPH}_2)]_2$ as yellow needles (60%).

Anal. Found: C, 56.0; H, 4.3.

Iodine.—(V) (0.30 g.) in benzene was treated with I_2 (4 equiv., 0.18 g.), precipitating an orange solid and a red oil, which solidified on standing. Crystallization from benzene-hexane gave orange-red needles of $[\text{PdI}_2(\text{HPPH}_2)]_2$ (45%), which were identified by m.p. and X-ray powder pattern.

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