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The Donor Properties of some α,ω-Bis(diphenylphosphino)alkanes towards Palladium(II). Polymeric, Dimeric and Monomeric *Trans*-Chelated Complexes

W. E. HILL
Department of Chemistry, Auburn University, Auburn, Ala. 36830, U.S.A.

CHARLES A. McAULIFFE, IAN E. NIVEN and R. V. (DICK) PARISH
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

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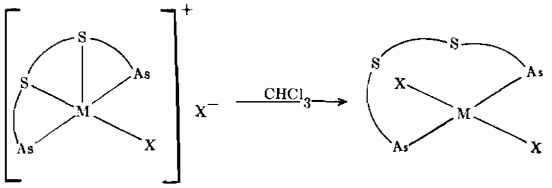
Palladium(II) complexes of 1,6-bis(diphenylphosphino)hexane (dph), 1,8-bis(diphenylphosphino)octane (dpo), 1,10-bis(diphenylphosphino)decane (dpd), and 1,12-bis(diphenylphosphino)dodecane (dpdod) have been isolated. The structures of the complexes seem to be a function of the length of the alkane chain between the donor atoms; generally dph bridges two palladium atoms and forms polymeric complexes, dpo and dpd bridge two palladium atoms and form dimeric 22- or 26-membered rings, and dpod acts as a trans*-chelating ligand and forms a monomeric complex containing a 15-membered ring.*

Introduction

It has been established that when short-chain bidentate phosphines (*i.e.*, ligands in which the carbon backbone linking the donor atoms consists of 2, 3 or 4 carbon atoms) behave as chelates, they necessarily coordinate *cis* to the metal atom [1]. Until recently it was thought unlikely that longer-chain bidentate ligands would be capable of coordinating *trans* to a metal atom. It was considered more probable that such ligands would bridge between metal atoms, producing polymeric species.

Fifteen years ago Isslieb [2] prepared the planar complexes [Ni(cy$_2$P(CH$_2$)$_n$Pcy$_2$)X$_2$] (cy = cyclohexy, X = Cl, Br) and concluded that for n = 3 and 4 the complexes are of *cis*-geometry whereas for n = 5 the complexes have a *trans*-configuration. These conclusions are based solely on dipole moment measurements and so the geometries deduced apply to the species present in solution rather than the solid complexes. Using diphosphines of the type Bu$^t_2$P(CH$_2$)$_n$PBu$^t_2$ (n = 9, 10) Shaw [3–5] and co-workers have prepared the complexes *trans*-[MLCl$_2$] (M = Pd, Pt) and *trans*-[Ir(CO)LCl]. Generally, in the preparations of the palladium and platinum complexes, mixtures of monomeric (I) and dimeric (II) products were formed and were separated using column chromatography. It was argued that the bulky t-butyl groups give favourable conformational effects and internal entropy changes which promote the formation of such complexes [6]. Indeed Shaw was unable to isolate complexes of palladium or platinum with the ligands Ph$_2$P(CH$_2$)$_{10}$PPh$_2$ and Me$_2$As(CH$_2$)$_{12}$AsMe$_2$ [5], apparent evidence for the necessity for bulky terminal groups. However, the complexes *trans*-[Pd(Me$_2$As(CH$_2$)$_{12}$AsMe$_2$)Cl$_2$] has recently been reported [7], and this appears to suggest that bulky terminal groups are not a necessary criterion for *trans*-chelation. It has also been observed that in halogenated solvents palladium and platinum complexes of the ligand 1,3-bis(dimethylarsinopropylthio)propane, Me$_2$As(CH$_2$)$_3$S(CH$_2$)$_3$S(CH$_2$)$_3$As, have planar structures [8] in which the ligand acts as a *trans*-chelating diarsine species. Although tetradentate chelation exists in the solid state:



Further evidence that bulky terminal groups are not a prerequisite for *trans*-chelation comes from the recent observation that the dithioether 1,12-bis(phenylthio)dodecane (dtd) forms *trans*-[M(dtd)Cl$_2$] (M = Pd, Pt) and *trans*-[Pd(dtd)Br$_2$] [9].

It has also been shown that with a rigid ligand with the correct steric properties, *e.g.* (III), complexes of *trans*-geometry with nickel(II), palladium(II) and platinum(II) can be isolated [10]. As with the ligand Bu$^t_2$P(CH$_2$)$_n$PBu$^t_2$, it is argued [10] that *trans*-coordination occurs primarily due to steric constraints inherent in the ligand used, in which case ligands without the constraints of a rigid backbone or bulky terminal groups should not produce similar behaviour. In view of the existence of com-

TABLE I. Analytical Data for the Palladium Complexes.

Compound	Colour	$\%C^a$	$\%H^a$	$\%X^{a,b}$
$Pd(dph)Cl_2$	Yellow	56.1(57.0)	4.8(5.1)	10.9(11.2)
$Pd(dph)Br_2$	Yellow	50.0(50.0)	4.4(4.5)	21.5(22.2)
$Pd(dph)I_2$	Orange	44.5(44.2)	3.8(4.0)	30.8(31.2)
$Pd(dph)(NCS)_2$	Yellow	57.0(56.8)	4.8(4.8)	3.9(4.1)
$Pd(dpo)Cl_2$	Yellow	58.5(58.2)	5.6(5.5)	10.8(10.7)
$Pd(dpo)Br_2$	Yellow	51.9(51.3)	4.8(4.8)	20.9(21.3)
$Pd(dpo)I_2$	Orange	45.8(45.6)	4.3(4.3)	29.8(30.1)
$Pd(dpo)(NCS)_2$	Yellow	57.4(57.9)	5.2(5.1)	3.7(4.0)
$Pd(dpd)Cl_2$	Yellow	59.4(59.4)	6.1(5.9)	9.6(10.3)
$Pd(dpd)Br_2$	Yellow	52.1(52.6)	5.3(5.2)	19.6(20.6)
$Pd(dpd)I_2$	Orange	46.6(46.9)	4.8(4.6)	28.8(29.1)
$Pd(dpd)(NCS)_2$	Yellow	59.1(59.0)	5.5(5.5)	3.8(3.8)
$Pd(dpdod)Cl_2$	Yellow	60.1(60.4)	6.5(6.2)	9.7(9.9)
$Pd(dpdod)Br_2$	Yellow	53.4(53.7)	5.6(5.5)	19.6(19.9)
$Pd(dpdod)I_2$	Orange	48.3(48.1)	4.8(4.9)	27.8(28.2)
$Pd(dpdod)(NCS)_2 \cdot \frac{1}{2}CHCl_3{}^c$	Yellow	56.4(56.3)	5.6(5.5)	3.5(3.4)

^{a}Found (calculated). ^{b}Halogen or nitrogen. ^{c}Cl = 6.0.

plexes of the type *trans*-$[MLX_2]$ in which the ligand does not have either a rigid backbone or bulky terminal groups [7, 8], it was decided to investigate the ligands $Ph_2P(CH_2)_nPPh_2$ (n = 6, dph; n = 8, dpo; n = 10, dpd; n = 12, dpdod). Their palladium complexes were studied to see whether these ligands were capable of acting as *trans*-chelating agents. It was expected that the shorter-chain C_6- and C_8- ligands might behave differently to the longer backbone C_{10}- and C_{12}-ligands since they might not be sufficiently flexible to bond *trans* to the same metal.

The ligands $Me_2Sb(CH_2)_nSbMe_2$ (n = 6, 10) were also prepared in order to observe the effect of the donor atom on the ability of this type of ligand to function as a *trans*-chelating ligand. However, these ligands were so readily oxidised that no pure complexes could be obtained.

Results and Discussion

On stirring the complex $[Pd(PhCN)_2Cl_2]$ with $Ph_2P(CH_2)_nPPh_2$ in a 1:1 ratio in $CHCl_3/EtOH$ yellow complexes are formed. In the case of the ligand $Ph_2P(CH_2)_6PPh_2$, this complex is insoluble and can be isolated. However, the ligands $Ph_2P(CH_2)_nPPh_2$ (n = 9, 10, 12) produce soluble complexes and the evaporation of these solutions leads to oils which contain benzonitrile. These oils crystallize very slowly from ethanol and appear to contain benzonitrile of crystallization, *e.g.* a complex of composition $(PhCN)_2Pd(Ph_2P(CH_2)_{10}PPh_2)Cl_2$ was isolated. Clearly this method of preparation is only suitable for complexes of the ligand $Ph_2P(CH_2)_6PPh_2$.

The addition of the ligands $Ph_2P(CH_2)_nPPh_2$ dissolved in a small volume of chloroform to palladium(II) chloride dissolved in ethanol in 1:1 ratio also yields yellow complexes, which are insoluble in ethanol, and can thus be isolated. However, most of the complexes prepared in this way contain some solvents of crystallization, quarter or ½ mol, *e.g.* $[Pd(Ph_2P(CH_2)_{12}PPh_2)(NCS)_2]0.5\ CHCl_3$ (Table I).

In order to obtain unsolvated complexes, it is necessary to use toluene as solvent for the ligands rather than chloroform. With this choice of solvent pure complexes of the type $PdLCl_2$ are precipitated, although the chloride complexes of the ligands $Ph_2P(CH_2)_nPPh_2$ (n = 10, 12) are formed as oils which solidify on standing under ether. If the palladium(II) chloride is stirred with excess LiX (X = Br, I) or NH_4SCN the analogous bromo- iodo-, or thiocyanato-complexes are produced. Analytical data for these complexes are listed in Table I.

The palladium(II) complexes of the ligand $Ph_2P(CH_2)_6PPh_2$ are insoluble in chloroform and thus no molecular weight measurements could be carried out. The chloro-complex $[Pd(dph)Cl_2]$ exhibits a single ν(Pd–Cl) absorption at 357 cm^{-1} (Table II), a value typical of a *trans*-arrangement of the chlorine atoms about the palladium atom [11]. The solid state reflectance spectrum of this complex shows a broad absorption band with peak maximum at 24.5 kK (Table II), characteristic of planar coordination about the palladium atom. It seems probable that this

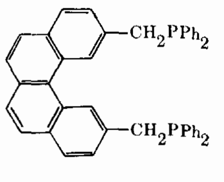
TABLE II. Electronic and Infrared Spectral Data for the Palladium(II) Complexes of α,ω-Bis(diphenylphosphino)alkanes.

Compound	E_{max} (ϵ_{mol})[a] $\times 10^{-3}$ cm^{-1}	E_{max}[b] $\times 10^{-3}$ cm^{-1}	I.R.[c] cm^{-1}
Pd{$Ph_2P(CH_2)_6PPh_2$}Cl_2		24.5	257 ν (Pd–Cl)
Pd{$Ph_2P(CH_2)_6PPh_2$}Br_2		23.4	
Pd{$Ph_2P(CH_2)_6PPh_2$}I_2		22.2	
		18.7(sh)	
Pd{$Ph_2P(CH_2)_6PPh_2$}$(NCS)_2$		22.0	2081 ν(C–N)
Pd{$Ph_2P(CH_2)_8PPh_2$}Cl_2	29.5(16,040)	24.0	349 ν(Pd–Cl)
Pd{$Ph_2P(CH_2)_8PPh_2$}Br_2	34.0(8,980)		
	27.8(3,960)	23.7	
Pd{$Ph_2P(CH_2)_8PPh_2$}I_2	31.0(12,660)		
	24.0(3,960)	22.6	
		16.6(sh)	
Pd{$Ph_2P(CH_2)_8PPh_2$}$(NCS)_2$	32.9(11,460)		2082 ν(C–N)
	29.4(10,960)	23.4	
Pd{$Ph_2P(CH_2)_{10}PPh_2$}Cl_2	29.4(14,000)	23.3	350 ν(Pd–Cl)
Pd{$Ph_2P(CH_2)_{10}PPh_2$}Br_2	33.7(9,180)		
	27.8(11,800)	22.4	
Pd{$Ph_2P(CH_2)_{10}PPh_2$}I_2	31.0(13,420)		
	23.9(4,050)	22.3	
		18.7(sh)	
Pd{$Ph_2P(CH_2)_{10}PPh_2$}$(NCS)_2$	32.8(12,970)		2079 ν(C–N)
	29.4(11,980)	24.6	
Pd{$Ph_2P(CH_2)_{12}PPh_2$}Cl_2	29.4(13,180)	22.8	342 ν(Pd–Cl)
Pd{$Ph_2P(CH_2)_{12}PPh_2$}Br_2	33.9(9,230)		
	27.6(11,070)	22.1	
Pd{$Ph_2P(CH_2)_{12}PPh_2$}I_2	31.0(15,200)		
	23.8(4,410)	22.1	
		18.7(sh)	
Pd{$Ph_2P(CH_2)_{12}PPh_2$}$(NCS)_2\cdot 0.5CHCl_3$	33.0(13,760)		2076 ν(C–N)
	29.4(12,900)	22.1	

[a] Chloroform solution, intensities in dm^3 cm^{-1} mol^{-1}. [b] Solid reflectance using MgO as dilutant. [c] Nujol and h.c.b.

complex is polymeric, since dimeric complexes, *e.g.* [Pd(Bu$^t_2$P(CH$_2$)PBu$^t_2$)Cl$_2$]$_2$ [5], have been found to be soluble in chloroform. This chloro-complex presumably has structure (IV).

Although no ν(Pd–Br) or ν(Pd–I) bands were observed in the infrared spectra of the corresponding



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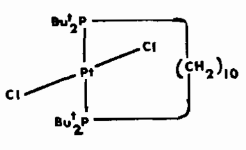

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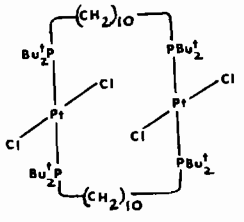

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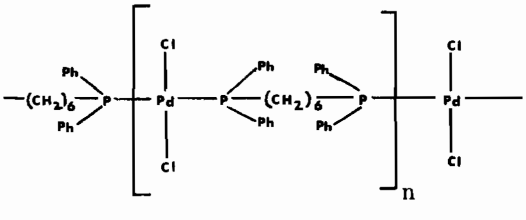

IV

TABLE III. Molecular Weight Data for the Palladium(II) Complexes of α,ω-Bis(diphenylphosphino)alkanes in Chloroform.

Compound	M[a]	N.M.R. Estimate[b]
$Pd(dpo)Cl_2$	1287(660)	1287(1267)
$Pd(dpo)Br_2$	1296(749)	1296(1423)
$Pd(dpo)I_2$	1571(843)	1571(1618)
$Pd(dpo)(NCS)_2$	1185(705)	
$Pd(dpd)Cl_2$	1334(688)	1334(1334)
$Pd(dpd)Br_2$	1023(777)	
$Pd(dpd)I_2$	1033(871)	
$Pd(dpd)(NCS)_2$	760(733)	
$Pd(dpdod)Cl_2$	812(716)	
$Pd(dpdod)Br_2$	909(805)	
$Pd(dpdod)I_2$	897(899)	
$Pd(dpdod)(NCS)_2\cdot ½CHCl_3$[c]	646(702)	

[a] Found calculated for monomer. [b] Found (calculated) assuming percentages of different species indicated by n.m.r. results, Table IV. [c] Calculated value does not include solvent of crystallization.

TABLE IV. ^{31}P N.M.R. Spectra of the Palladium Complexes.[a,b]

Complex	δ, ppm[c]	Coordination Chemical Shift[d]
$Pd(dpo)Cl_2$	−15.00	30.25
	−26.30 (8%)	
	−30.0 (2%)	
$Pd(dpo)Br_2$	−13.95	29.2
	−15.2 (10%)	
$Pd(dpo)I_2$	−6.73	21.98
	−31.73 (8%)	
$Pd(dpd)Cl_2$	−16.62	31.79
	−26.90 (6%)	
$Pd(dpd)(NCS)_2\cdot ½CHCl_3$	−19.24	34.41
$Pd(dpdod)Cl_2$	−16.58	32.13
$Pd(dpdod)I_2$	−7.00	22.55

[a] In $CDCl_3$ relative to 85% H_3PO_4. [b] Ligands: dph +15.20, dpo +15.25, dpd +15.17, dpdod +15.55. [c] Percent estimated. [d] $\delta_{complex} - \delta_{ligand}$ for most intense peak.

bromo- and iodo-complexes, it is likely that they too contain *trans*-(X–Pd–X) units. The reflectance spectra indicate the bromo-complex to have planar coordination about the palladium atom, but the iodo-complex exhibits a low-energy absorption at 18.7 kK indicative of association of planar $Pd(dph)I_2$ units through bridging iodine atoms to give pentacoordination about the palladium atoms (*cf.* $[Pd(SbR_3)_2I_2]$ [12, 13]). Thus whilst the bromo-complex is likely to be of a similar structure to the chloro-complex, the iodo-complex probably contains planar units linked to similar units above and below by means of iodine bridges.

The thiocyanato-complex $[Pd(dph)(NCS)_2]$ undoubtedly contains *N*-bonded thiocyanate groups as the C–N stretching frequency occurs at 2081 cm^{-1} [14, 15]. This is similar to the complex $[Pd(PPh_3)_2(NCS)_2]$, and presumably reflects the effect of the reduction in steric interactions between the phenyl groups and thiocyanate groups achieved by the use of linear Pd–NCS bonding rather than the angular Pd–SCN bonding [16]. It is probable that this complex also has structure (III).

The palladium(II) complexes of the ligands $Ph_2P(CH_2)_nPPh_2$ (n = 8, 10, 12) are soluble in chloroform, although those of the ligands dpo and dpd are only slightly soluble. All these complexes form oils on contact with chloroform and these oils slowly dissolve on warming or on vigorous shaking. All these

TABLE V. Solution Infrared Spectra of [$PdPh_2(CH_2)_nPPh_2(NCS)_2$].

n	ν (CN) (cm^{-1})[a]	ν (CN) (cm^{-1})[b]	$\Delta\nu_{1/2}$ (cm^{-1})	Λ (M^{-1} cm^{-2})[c]
8	2082	2085	34.8	10.9×10^4
10	2079	2084	35.8	11.4×10^4
12	2076	2084	35.6	10.2×10^4

[a] Nujol mull. [b] Chloroform solution. [c] 10^{-3} *M* $MeNO_2$.

complexes are nonconductors in 10^{-3} *M* nitromethane solution.

The electronic solution spectra of all these complexes indicate planar coordination about the palladium atoms (Table II). As with the complexes of dph, the chloro-, bromo-, and thiocyanato-compounds appear to also be planar, in the solid state. The iodo-complexes, however, again exhibit low-energy absorptions in the reflectance spectra, characteristic of pentacoordination about the palladium atoms [12, 13].

All three chloro-complexes show a single Pd–Cl stretching frequency at *ca.* 350 cm^{-1}, and must therefore contain *trans*-(Cl–Pd–Cl) units [11]. Although no ν(Pd–Br) or ν(Pd–I) absorptions can be assigned it seems likely that the bromo- and iodo-complexes also contain *trans*- (X–Pd–X) units. As with the complex [Pd(dph)$(NCS)_2$], the thiocyanates all contain N-bonded thiocyanate groups, all showing a broad absorption at *ca.* 2080 cm^{-1} (Table II).

The molecular weight measurements (Table III) indicate that the dpo complexes are essentially dimeric with slight dissociation of the dimers into monomeric units. Presumably in the solid state these complexes have structure(II), with the iodo-complexes being associated via bridging iodine atoms. We have obtained confirmation that the Pd(dpo)X_2 (X = Cl, Br, I) are essentially dimeric in chloroform from the ^{31}P n.m.r. spectra in this solvent, Table IV, (see later). These show in all cases another species to be present in small amounts (2–10%). We have calculated the expected molecular weight of, for example, Pd(dpo)Cl_2, assuming that 8% of it exists as a monomer. This gives excellent agreement with observed molecular weights in almost all cases looked at.

The ^{31}P n.m.r. chemical shifts of some of the complexes and the ligands are listed in Table IV, as well as the coordination chemical shifts. In all cases a downfield shift is observed upon coordination; thus, the phosphorus nucleus becomes less shielded upon coordination to the palladium. The coordination chemical shifts for the series Pd(dpo)X_2 (X = Cl, Br, I) follows the order Cl > Br > I implying stronger P–Pd–P σ-bonding in the chloride compound. Comparison of the Pd(dpd)X_2 (X = Cl, NCS) suggests greater Pd–P σ-bond strength for the thiocyanate. In all of these complexes one very intense ^{31}P resonance was observed, and in some cases small peaks corresponding to other ^{31}P-containing species were present, but can be accounted for if the n.m.r. data are taken in conjunction with molecular weight data. The amounts of these other species are estimated from the n.m.r. spectra and these estimates appear in parentheses in Table IV. Small variations in chemical shifts are observed as the backbone is lengthened although no regular trend is observed. Moreover, we suggest on the basis of n.m.r. and molecular weight data that the dpo and dpd complexes essentially are present with structure (II) whereas the dpod compounds have structure (I). Thus, minor differences in chemical shift may be due to monomer/dimer differences as well as to chelate chain length.

The dpd complexes, except for the thiocyanate, all appear to be somewhat associated (Tables III and IV). Attempts to separate monomeric and dimeric species by column chromatography [5] were unsuccessful, once more suggesting that these complexes are in fact dimeric in the solid state but dissociate somewhat into their monomeric units in solution. Possibly the 26-atom ring involved in such dimeric complexes is more prone to rupture than the 22-atom ring of the dpo complexes. The complex [Pd(dpd)$(NCS)_2$] and the dpdod complexes are all monomeric in solution, and also may well be of structure (I) in the solid state.

The solution infrared spectra of the thiocyanates are listed in Table V, together with the mull spectra. Little change occurs on dissolving the thiocyanates in chloroform. The band-widths and integrated absorption intensities are consistent with N-coordination [17, 18]. Since the thiocyanates are essentially unchanged in solution, the spectrochemical series for these complexes should also be of use in confirming the mode of attachment of the thiocyanate groups. In each case, the lowest energy band in the solution spectra of these complexes moves to lower energy in the order.

$$Cl^- \sim NCS^- > Br^- > I^-$$

This indeed is consistent with previous conclusions [19].

Conclusions

The backbone length in ligands of the type $Ph_2P(CH_2)_nPPh_2$ seems to be of paramount importance in determining the way such a ligand binds to palladium. For small values of n (n = 1–3), these ligands act as chelates forming *cis*-$[PdLX_2]$ complexes [1]. As the backbone length increases to *ca.* 6, polymeric species of structure (IV) are produced on coordination to palladium. Backbones containing 8 and 10 carbon atoms produce large-ring dimeric palladium complexes of structure (II). As the backbone is lengthened still further to 12 carbon atoms, the ligand then acts as a *trans*-chelating ligand, (I).

TABLE VI. Proton N.M.R. Spectra of $Ph_2P(CH_2)_nPPh_2$ in $CDCl_3$.

n	δ(Ph)[a]	$\delta(CH_2)$[a]	
6	7.49 (20.1)	2.35 (3.7)	1.65 (8.2)
8	7.40 (19.7)	2.20 (4.1)	1.51 (12.2)
10	7.41 (19.9)	2.20 (4.3)	1.43 (15.8)
12	7.47 (20.4)	2.31 (4.4)	1.65 (18.2)

[a] Relative to TMS internal standard; relative intensities in parentheses.

Experimental

Physical measurements were obtained as previously described [20].

Preparation of the Ligands

To a solution of lithium diphenylphosphide, prepared from triphenylphosphine (52.4 g, 0.2 mol) and lithium metal (5.25 g, 0.75 mol), was added dropwise a solution of the appropriate α,ω-dichloroalkane (0.06 mol) in dry THF (20 cm^3). The mixture was stirred for 30 minutes and deoxygenated water (250 cm^3) was added. The organic layer was separated and dried over anhydrous sodium sulphate. After removal of the THF, the residual oil was crystallised from toluene/methanol. Yields 50–60%. M.Pts: dph, 113–115 °C; dpo 101–102 °C; dpd, 87–88 °C; dpdod, 89–90 °C.

The ligands were characterised by their mass spectra [21] and proton n.m.r. spectra (Table VI). It can be seen that the methylene groups attached directly to the phosphorus atoms absorb at lower field than the other methylene groups.

Preparation of the Complexes

Pd(dph)Cl₂

Palladium(II) chloride (0.18 g, 1 mmol) was dissolved in ethanol (50 cm^3) and a solution of 1,6-bis(diphenylphosphino) hexane (0.45 g, 1 mmol) in toluene (15 cm^3) was added slowly with stirring. The mixture was stirred for 3 hours, and the resulting yellow complex was filtered, washed well with ethanol and ether, and dried *in vacuo*. Yield 83%.

$PdLX_2$ (L = dph, dpo, dpd, dpod, X = Cl, Br, I SCN)

These complexes were prepared as above. The bromo-, iodo-, and thiocyanato-complexes were prepared in the presence of excess LiX (Br, I) or NH_4SCN. Attempts to separate monomeric and dimeric products of dpd complexes by chromatography on columns of neutral alumina were unsuccessful.

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References

1 W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, *14*, 173 (1972).
2 K. Isslieb and G. Hohfeld, *Z. Anorg. Allg. Chem.*, *312*, 169 (1961).
3 A. J. Pryde, B. L. Shaw and B. Weeks, *J. Chem. Soc. Chem. Comm.*, 947 (1973).
4 F. C. March, R. Mason, K. M. Thomas and B. L. Shaw, *J. Chem. Soc. Chem. Comm.*, 584 (1975).
5 A. J. Pryde, B. L. Shaw and B. Weeks, *J. Chem. Soc. Dalton Trans.*, 322 (1976).
6 B. L. Shaw, *J. Am. Chem. Soc.*, *97*, 3856 (1975).
7 W. Levason, C. A. McAuliffe and S. G. Murray, *J. Organomet. Chem.*, *110*, C25 (1975).
8 W. Levason, C. A. McAuliffe and S. G. Murray, *J. Organomet. Chem.*, *101*, C29 (1976).
9 C. A. McAuliffe, H. E. Soutter, W. Levason, F. R. Hartley and S. G. Murray, *Inorg. Chim. Acta*, *35*, 265 (1979).
10 N. J. DeStefano, D. K. Johnson and L. M. Venanzi, *Angew. Chem. Int. Ed.*, *13*, 133 (1974).
11 G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).
12 J. G. Harley, L. M. Venanzi and D. C. Goodall, *J. Chem. Soc.*, 3930 (1963).
13 G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 2771 (1965).
14 A. Sabatini and I. Bertini, *Inorg. Chem.*, *4*, 1665 (1965).
15 I. Bertini and A. Sabatini, *Inorg. Chem.*, *5*, 1025 (1966).
16 J. L. Burmeister, *Coord. Chem. Rev.*, *1*, 205 (1966).
17 R. A. Bailey, S. K. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, *6*, 407 (1971).
18 C. Pecile, *Inorg. Chem.*, *5*, 210 (1966).
19 D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc.*, *92*, 5351 (1970).
20 C. A. McAuliffe, I. E. Niven and R. V. Parish, *Inorg. Chem. Acta*, *15*, 67 (1975).
21 W. Levason, C. A. McAuliffe, I. E. Niven, R. V. Parish and P. D. Randall, *J. Organomet. Chem.*, *125*, 209 (1979).