cis and *trans* Palladium(II) and Platinum(II) Complexes with 1,8-Bis(diphenylphosphino)-3,6-dioxaoctane and their Structural Characterization.† The First Example of an Eleven-membered Diphosphine Chelate involving *cis* Geometry

W. Eugene Hill* and John G. Taylor
Chemistry Department, Auburn University, Auburn, AL 36849, U.S.A.
Christopher P. Falshaw and (the late) Trevor J. King
Chemistry Department, University of Nottingham, Nottingham NG7 2RD
Brian Beagley, David M. Tonge, Robin G. Pritchard, and Charles A. McAuliffe*
Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M13 9PL

Monomeric *cis* and *trans* complexes of Pt^{II} and Pd^{II} with 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (dpdo) of general formulae $[M(dpdo)X_2]$ (M = Pd, X = Cl, Br, I, or NCS; M = Pt, X = Cl or I), in which the ligand binds only by the two phosphine donor atoms, have been synthesized and characterized by i.r., electronic, and ^{31}P n.m.r. spectroscopy and molecular weight measurements. The isolation of these complexes illustrates that both *cis* and *trans* 11-membered chelate rings are obtainable under appropriate conditions; for example, both *cis*- and *trans*-monomeric $[Pt(dpdo)Cl_2]$ are reported. Syntheses of *cis*-palladium(II) complexes were carried out in polar solvents while *trans* isomers were prepared in less polar solvents. *cis*-Platinum complexes were prepared from $[PtCl_4]^{2-}$ while the *trans* isomers were prepared from Zeise's salt. Crystal structures of *cis*-$[Pd(dpdo)Cl_2]$ and *trans*-$[Pd(dpdo)I_2]$ are reported and discussed.

A number of recent studies[1-7] have shown that bidentate tertiary phosphine and arsine ligands with suitably long carbon backbones connecting the donor atoms can form *trans* chelate square-planar complexes with rhodium(I), iridium(I), palladium(II), and platinum(II). Although it does appear that the presence of bulky substituents at the donor atoms, notably t-butyl groups, seems to aid the isolation of *trans* chelates,[1,3] we[5-7] and others[4] have shown that ligands with methyl or phenyl substituents can form this kind of *trans* species provided that a suitable backbone connecting the two donor atoms exists and a kinetically labile precursor complex is used. Moreover, phosphorus or arsenic donor atoms are not necessary since we have recently isolated and characterized *trans* chelate complexes of the type $[MLCl_2]$ (M = Pd or Pt) and $[PdLBr_2]$, where L = 1,12-bis(phenylthio)dodecane.[8]

In addition, it has now become obvious that certain facultative potentially quadridentate ligands can act as quadridentate chelating or *trans*-bidentate chelating agents. Thus, for example, 1,3-bis(3′-dimethylarsinopropylthio)propane (L′) forms complexes with MCl_2 (M = Pd or Pt) which initially exist as the As_2S_2-bonded five-co-ordinate $[ML'Cl]Cl$ complexes in dichloromethane, but rapidly cleave two M–S bonds to form the As_2-bonded *trans*-bidentate chelates $[M(L')Cl_2]$.[6] We have extended our interest in this type of ligand to include 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$ (dpdo), which was previously investigated by Dapporto and Sacconi.[9] These workers prepared diamagnetic $[Ni(dpdo)I_2]$, the *X*-ray crystal structure of which showed it to be a distorted planar complex (P–Ni–P 162.1°) with a bidentate P_2 ligand; the Ni–O distances are large, 3.20 and 3.16 Å. A further crystal structure of *trans*-$[Rh(dpdo)(EtOH)(CO)]PF_6$ by Alcock *et al.*[4,10] similarly showed that the ligand can act as a *trans*-bidentate diphosphine. We have prepared a series of nickel(II) complexes of dpdo of varied stereochemistry and reported the *X*-ray crystal structure of planar *trans*-$[Ni(dpdo)(NCS)_2]$.[11] We here wish to report our studies of palladium(II) and platinum(II) complexes of dpdo, which include the *X*-ray crystal structures of the monomeric complexes *cis*-$[Pd(dpdo)Cl_2]$ and *trans*-$[Pd(dpdo)I_2]$. The former is the first example of an 11-membered chelating bidentate ligand co-ordinating *cis* to a metal.

Experimental

Materials.—Palladium(II) chloride, potassium tetrachloroplatinate(II), lithium salts, sodium iodide, and ammonium thiocyanate were reagent grade and were used without further purification. Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, was prepared by a standard literature method;[12] lithium tetrachloropalladate(II) was prepared by stirring a 2:1 molar ratio of LiCl and $PdCl_2$ in methanol; the ligand dpdo was prepared as previously described.[11]

Physical Measurements.—Phosphorus-31 n.m.r. spectra were recorded on a Varian CFT-20 Fourier-transform n.m.r. spectrometer at 32.1 MHz. Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer. Molecular weight measurements were determined in chloroform solution by vapour phase osmometry.

Preparation of the Complexes.—*cis*-$[Pd(dpdo)Cl_2]$. The ligand dpdo (1.00 g, 2.0 mmol), dissolved in absolute ethanol (20 cm^3), was mixed with a solution of lithium tetrachloropalladate(II) (0.52 g, 2.0 mmol) in dry methanol (20 cm^3) and stirred for 20 min. The resulting mixture was filtered and anhydrous diethyl ether (200 cm^3) added to the filtrate. Upon standing for *ca.* 24 h the resulting pale yellow crystals were collected by filtration and washed successively (10 cm^3 portions) with water (in order to remove any possible lithium chloride remaining), cold methanol and, finally, diethyl ether.

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† *Supplementary data available* (No. SUP 56553, 8 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Summary of crystal data

(*a*) Crystal parameters		
Complex	*trans*-[Pd(dpdo)I_2]	*cis*-[Pd(dpdo)Cl_2]
Molecular formula	$C_{30}H_{32}I_2O_2P_2Pd$	$C_{30}H_{32}Cl_2O_2P_2Pd$
M	846.74	663.84
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	15.219(3)	11.097(6)
b/Å	18.371(3)	12.380(4)
c/Å	11.756(3)	21.456(18)
β/°	113.92(3)	103.96(7)
U/Å^3	3 004.5	2 860.6
D_c/g cm^{-3}	1.87 ($Z = 4$)	1.54 ($Z = 4$)
F(000)	1 640	1 352
(*b*) Measurement of intensities[a]		
Laboratory	Nottingham	UMIST
Diffractometer	Y290	CAD4
Reflections measured	$hkl, hk\bar{l}$	$hkl, hk\bar{l}$
No. measured	5 507	3 441
Reflections used	$I > 3\sigma(I)$	$I > 3\sigma(I)$
No. used	4 000	3 081
$\theta_{max.}$/°	25	23
Crystal dimensions/mm	0.3 × 0.3 × 0.2	0.3 × 0.3 × 0.2
μ/mm^{-1}	2.81	0.96
(*c*) Solution of the structures		
Method	Heavy atom	Heavy atom
Minimized function[b]	$w\Delta^2$	$w\Delta^2$
Weighting function	Chebyshev scheme	$w = 1.8646/[\sigma^2(F) + 0.000\,49F^2]$
Anomalous dispersion		Pd, Cl, P
Refined scale factor	0.322 4(1)	1.376(2)
Residual, $R = \Sigma\|\Delta\|/\Sigma\|F_o\|$	0.0559	0.0322

[a] Mo-K_α radiation, $\lambda = 0.710\,69$ Å. [b] $\Delta = F_o - F_c$.

trans-[Pd(dpdo)X_2] (X = Br, I, *or* NCS). A ten-molar excess of the appropriate halide or pseudohalide salt was added to a solution of Li_2[PdCl_4] (0.52 g, 2.0 mmol) in methanol (20 cm^3) and to this, dpdo (1.00 g, 2.0 mmol), dissolved in toluene (20 cm^3), was added. The mixture was stirred for 30 min, filtered, and n-pentane (200 cm^3) added to the filtrate. Upon standing overnight, crystals of the complexes formed. These were collected by filtration and washed successively with 10-cm^3 portions of water, cold methanol, and n-pentane.

cis-[Pt(dpdo)I_2]·NaCl. Potassium tetrachloroplatinate(II) (0.83 g, 2.0 mmol), the dpdo (1.00 g, 2.0 mmol), and a ten-molar excess of NaI were stirred in acetone (50 cm^3) for 12 h. The solution was filtered and n-pentane (250 cm^3) added to the filtrate. After standing overnight, the pale orange-yellow complex was collected by filtration and washed successively with 10-cm^3 portions of water, ethanol, and n-pentane.

cis-[Pt(dpdo)Cl_2]. The ligand (1.00 g, 2.0 mmol) and K_2[PtCl_4] (0.83 g, 2.0 mmol) were refluxed with stirring in absolute ethanol (30 cm^3) for 12 h. The solvent was then removed *in vacuo* and the residue treated with CH_2Cl_2 (10 cm^3) and filtered to remove KCl. n-Pentane (50 cm^3) was added to the filtrate followed by refrigeration overnight. The white complex was collected by filtration, washed successively with 10-cm^3 portions of water, ethanol, and n-pentane and dried *in vacuo*.

trans-[Pt(dpdo)Cl_2]. A solution of dpdo (0.50 g, 1.0 mmol) in acetone (30 cm^3) was added dropwise to a stirred solution of K[Pt(C_2H_4)Cl_3] (0.30 g, 1.0 mmol) in acetone (100 cm^3) and filtered. n-Pentane (300 cm^3) was added to the filtrate resulting in the precipitation of a pale yellow complex. The precipitate was collected and washed successively with 10-cm^3 portions of water, ethanol and, finally, n-pentane.

trans-[Pt(dpdo)I_2]·KCl. A ten-fold excess of NaI was added to a solution of K[Pt(C_2H_4)Cl_3] (0.18 g, 0.5 mmol) in acetone (100 cm^3). The mixture was stirred at room temperature for 0.5 h. The ligand (0.24 g, 0.50 mmol), dissolved in acetone (30 cm^3), was added dropwise over 0.5 h. After stirring for a further 0.5 h, the solution was filtered and the volume reduced to *ca.* 20 cm^3 *in vacuo*. Approximately 100 cm^3 of n-pentane was added and the resulting mixture was left standing overnight in a refrigerator. Orange crystals were collected by filtration, washed successively with 10-cm^3 portions of water, ethanol, and n-pentane and dried in a vacuum desiccator.

trans-[Pt(dpdo)$(NCS)_2$] was prepared similarly using ammonium thiocyanate instead of NaI for the metathesis reaction.

Collection and Reduction of X-*Ray Data*.—Light brown crystals of *trans*-[Pd(dpdo)I_2] were obtained by dissolving the complex in methanol–toluene (1:1), diluting with a five-fold excess of n-pentane, and cooling. Single-crystal *X*-ray diffraction data were collected on a Hilger and Watts four-circle diffractometer. The positions of the palladium, iodine, and phosphorus atoms were obtained by using the direct methods SHELX[13] program. The remaining portion of the structure was solved using Fourier methods and the CRYSTALS[14] program at the University of Nottingham. The trial structure was refined using first isotropic and then anisotropic thermal parameters. After several cycles of such refinement the majority of the hydrogen atoms were located in a Fourier difference map. Hydrogen atoms were then included in their calculated positions, then further refinement, excluding the hydrogen atoms, gave a final R value of 0.0559.

Pale yellow crystals of *cis*-[Pd(dpdo)Cl_2] were obtained by recrystallization from methanol–chloroform (1:1) diluted with a five-fold excess of n-pentane. Approximate unit-cell parameters obtained photographically were refined after measurement of selected reflections by computer control on the CAD 4 diffractometer. Consideration of systematic absences established the space group, and, after collection of the intensity data, subsequent calculations were carried out on the joint CDC7600/ICL 1906 computer system at the University of Manchester Regional Computing Centre. The phase problem was solved by the heavy-atom method and the structure was refined using SHELX.[13]

Other details of the collection and reduction of the data for both complexes appear in Table 1.

Results and Discussion

Preparation of the Complexes.—The complexes isolated are listed in Table 2, and full preparative details are given in the Experimental section. Here we give brief details and items of special interest.

The complex *cis*-[Pt(dpdo)Cl_2] was prepared by treating K_2[PtCl_4] with dpdo in absolute ethanol or K_2[PtCl_4] with dpdo in acetone. The corresponding iodides and thiocyanates were prepared by addition of a ten-fold excess of sodium iodide or sodium thiocyanate respectively.

The *trans*-[Pt(dpdo)X_2] (X = Cl or I) species were isolated from the reaction of Zeise's salt, K[Pt(C_2H_4)Cl_3], with dpdo (X = Cl or I) in the presence of a large excess of sodium iodide (X = I). An acetone solution of the ligand was added to Zeise's salt dissolved in a large volume of acetone in order to minimize the formation of oligomeric species. Isomerization to the *cis* isomer was avoided by keeping Zeise's salt in excess of the

Table 2. Elemental analyses and molecular weight data for the complexes

Complex	Colour	Analysis[a] (%) C	H	X	M[b,c]
cis-$[Pd(dpdo)Cl_2]$	Yellow	53.0 (54.2)	4.8 (4.9)	10.5 (10.7)	680 (663)
trans-$[Pd(dpdo)Br_2]$	Yellow	48.1 (47.9)	4.5 (4.3)	20.9 (21.3)	734 (752)
trans-$[Pd(dpdo)I_2]$	Brown	42.3 (42.5)	3.7 (3.8)	29.0 (30.0)	
trans-$[Pd(dpdo)(NCS)_2]$[d]	Orange	54.3 (54.2)	4.7 (4.5)	3.7 (4.0)[e]	715 (708)
cis-$[Pt(dpdo)Cl_2]$	White	47.8 (47.9)	4.3 (4.3)	9.7 (9.4)	743 (752)
trans-$[Pt(dpdo)Cl_2]$	Pale yellow	47.6 (47.9)	4.2 (4.3)	9.4 (9.4)	770 (752)
cis-$[Pt(dpdo)I_2]\cdot NaCl$	Orange-yellow	36.7 (36.2)	3.4 (3.2)		342 (935[f])
trans-$[Pt(dpdo)I_2]\cdot KCl$	Orange	35.6 (35.6)	3.1 (3.2)		

[a] Calculated values in parentheses. [b] Determined in $CHCl_3$ solution. [c] Calculated molecular weight for monomers in parentheses. [d] Contains one *N*-bonded and one *S*-bonded thiocyanato group. [e] X = N. [f] For *cis*-$[Pt(dpdo)I_2]$ the calculated value of M would be 935.

Table 3. ^{31}P N.m.r. and electronic spectra of dpdo and the palladium(II) complexes

Compound	^{31}P/p.p.m.[a]	Δ_c/p.p.m.[b]	Approximate %[c]	Solid reflectance $10^{-3}\nu_{max}/cm^{-1}$	Solution[d] electronic $10^{-3}\nu_{max}/cm^{-1}$	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$
dpdo	+21.8					
cis-$[Pd(dpdo)Cl_2]$	−32.0	−53.8	100	25.5	29.4	Shoulder
trans-$[Pd(dpdo)Br_2]$	−14.5	−36.3	100			
trans-$[Pd(dpdo)I_2]$	−6.5	−28.3	100	20.9	30.6	9 515
trans-$[Pd(dpdo)(NCS)_2]$	−13.8	−35.6	44[e]		21.1	1 940
	−14.8	36.6	34			
	−11.7	−33.5	15			
	−16.2	−38.0	6			

[a] Relative to 85% H_3PO_4 (downfield negative). [b] Co-ordination chemical shift (Δ_c) = chemical shift of ligand − chemical shift of complex. [c] Based on ^{31}P-{^1H} n.m.r. spectra. [d] Chloroform solvent. [e] Mixture of *N,N*-, *N,S*-, and *S,S*-bonded isomers.

Table 4. ^{31}P N.m.r. and electronic spectra of the platinum(II) complexes

Complex	^{31}P/p.p.m.[a]	$^1J(Pt-P)$/Hz	Approximate %[b]	Solid reflectance $10^{-3}\nu_{max.}/cm^{-1}$	Solution[c] electronic $10^{-3}\nu_{max.}/cm^{-1}$	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$
cis-$[Pt(dpdo)Cl_2]$	−10.4	3 719	100	29.3		
trans-$[Pt(dpdo)Cl_2]$	−14.8	2 660	59	31.4	36.9	8 460
	−8.6	2 560	31	23.0		
	−9.2	2 567	6			
	−4.1	3 632	4			
cis-$[Pt(dpdo)I_2]\cdot NaCl$	−7.3	3 481	86	23.6	27.7	3 120
	+0.2	2 420	8			
	−5.5	2 506	6			
trans-$[Pt(dpdo)I_2]\cdot KCl$	+0.9	2 411	41	20.0	30.2	Shoulder
	−5.4	2 506	14			
	+0.3	2 420	12			
	−7.3	3 482	12			
	−3.1	3 632	5			

[a] Relative to 85% H_3PO_4 (downfield negative). [b] Based on ^{31}P-{^1H} n.m.r. spectra. [c] Chloroform solvent.

phosphine during the reaction, which was carried out at room temperature. Excess phosphine or elevated temperatures have been shown to cause *trans–cis* isomerization in complexes of the type *trans*-$[Pt(PR_3)_2X_2]$ (R = alkyl or aryl, X = anionic ligand).[15] Our method is a modified version of that used to prepare complexes of the type *trans*-$[Pt(PR_3)_2Cl_2]$ (R = Ph or Bu^t).[16] Elemental analyses of the *cis* and *trans* iodo complexes indicate that, in the solid state, one molecule of salt (NaCl or KCl) is associated with the complex. Molecular weight data for *cis*-$[Pt(dpdo)I_2]\cdot NaCl$ are in agreement with the presence of Na^+, Cl^-, and $[Pt(dpdo)I_2]$ in solution, the observed value (342) being extremely close to that calculated from an equimolar mixture of these species (333).

The complex *cis*-$[Pd(dpdo)Cl_2]$ was prepared from the reaction of $Li_2[PdCl_4]$ in methanol with dpdo in ethanol; and the other palladium(II) derivatives from $[PdX_4]^{2-}$ dissolved in methanol and dpdo dissolved in toluene.

For the majority of complexes it was possible to obtain molecular weight data in chloroform; all those examined were monomeric (Table 2).

^{31}P *N.M.R. of the Complexes*.—The ^{31}P n.m.r. spectra of all the palladium complexes (Table 3) consist of a single peak, except the spectrum of the thiocyanate derivative which consists of two strong, equally intense lines at −13.8 and −14.8 p.p.m. as well as two relatively weak lines at −16.2 and −11.7 p.p.m. The major lines are assigned to the *N,S*-bonded isomer. The two minor components are assigned to the linkage isomers, *N,N* at −16.2 p.p.m. and *S,S* at −11.7 p.p.m. It is expected that the *N,N*-bonded isomer would be shifted to lower field relative to the *N,S*-isomer, due to the higher electronegativity of the nitrogen. It should be noted that, upon standing in $CDCl_3$ solution, the resonance at −16.2 p.p.m. ascribed to the *N,N*-bonded isomer grew at the expense of the −13.8 p.p.m. and

Table 5. Infrared data (cm $^{-1}$) for the complexes

Complex	ν(COC)	ν(M–X)[a]	ν(M–P)	ν(CN)
dpdo	1 110 (sh) 1 063s			
cis-[Pd(dpdo)Cl_2]	1 093s	292 315	348 374	
trans-[Pd(dpdo)I_2]	1 098 (sh) 1 070w	*b*	*b*	
trans-[Pd(dpdo)-(NCS)(SCN)]	*c* 1 070w	280w	*b*	2 090s 2 104 (sh)
cis-[Pt(dpdo)Cl_2]	1 096s 1 060w	299m 325m	350w 375w	
trans-[Pt(dpdo)Cl_2]	1 095 (sh)	338s	362w	

[a] X = Cl, I, or S. [b] Not observed. [c] Obscured by other bands.

Table 6. Fractional co-ordinates for *trans*-[Pd(dpdo)I_2], with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	0.328 64(5)	0.319 72(3)	0.162 70(6)
P(2)	0.434 7(2)	0.251 5(1)	0.108 2(2)
C(3)	0.527 4(7)	0.208 8(5)	0.245 7(9)
C(4)	0.573(1)	0.258 8(7)	0.354(1)
O(5)	0.560 1(9)	0.326 9(5)	0.328(1)
C(6)	0.604 0(9)	0.379 8(8)	0.423(1)
C(7)	0.562 1(9)	0.450 3(8)	0.372(1)
O(8)	0.464 7(7)	0.448 9(6)	0.358(1)
C(9)	0.407 4(9)	0.500 1(6)	0.292(1)
C(10)	0.305 0(8)	0.491 1(5)	0.268 1(8)
P(11)	0.260 2(2)	0.397 5(1)	0.259 6(2)
I(12)	0.296 03(6)	0.201 93(3)	0.265 02(7)
I(13)	0.768 10(5)	0.093 04(3)	0.468 34(6)
C(14)	0.291 4(7)	0.376 2(5)	0.424 9(8)
C(15)	0.380 0(8)	0.348 5(6)	0.493 8(9)
C(16)	0.409(1)	0.336 6(7)	0.620(1)
C(17)	0.349(1)	0.355 0(7)	0.678(1)
C(18)	0.259(1)	0.381 2(8)	0.606(1)
C(19)	0.229(1)	0.392 4(8)	0.479(1)
C(20)	0.131 2(7)	0.407 9(5)	0.192 3(9)
C(21)	0.088 1(9)	0.475 6(7)	0.190(1)
C(22)	−0.013 0(9)	0.480 3(8)	0.143(2)
C(23)	−0.067 6(8)	0.420 2(8)	0.099(1)
C(24)	−0.026(1)	0.356 1(8)	0.101(2)
C(25)	0.073 1(9)	0.349 6(6)	0.149(1)
C(26)	0.384 4(7)	0.177 9(5)	−0.002(1)
C(27)	0.321(1)	0.196 7(7)	−0.120(1)
C(28)	0.285(1)	0.145 5(8)	−0.214(1)
C(29)	0.309(1)	0.074 1(8)	−0.187(2)
C(30)	0.373(1)	0.055 9(8)	−0.072(2)
C(31)	0.410(1)	0.105 4(6)	0.024(1)
C(32)	0.507 0(7)	0.298 7(5)	0.039 8(9)
C(33)	0.554 7(9)	0.259 6(6)	−0.020(1)
C(34)	0.615 7(9)	0.293 2(7)	−0.062(1)
C(35)	0.629 2(8)	0.368 2(7)	−0.050(1)
C(36)	0.579 9(8)	0.407 6(6)	0.003(1)
C(37)	0.519 2(7)	0.372 9(5)	0.051(1)

Table 7. Distances (Å), angles (°), and torsion angles (°) in *trans*-[Pd(dpdo)I_2], with estimated standard deviations in parentheses

(*i*) Around Pd(1) atom

Pd(1)–P(2)	2.330(2)	P(2)–Pd(1)–P(11)	164.9(1)
Pd(1)–P(11)	2.321(2)	I(12)–Pd(1)–I(13)	146.8(1)
Pd(1)–I(12)	2.620(1)	P(2)–Pd(1)–I(12)	87.9(1)
Pd(1)–I(13)	2.636(1)	P(11)–Pd(1)–I(13)	89.1(1)
		P(2)–Pd(1)–I(13)	97.2(1)
		P(11)–Pd(1)–I(12)	94.4(1)
		Sum of last four	368.6

(*ii*) Around P(2) atom

P(2)–Pd(1)	2.330(2)	Pd(1)–P(2)–C(3)	110.9(3)
P(2)–C(3)	1.84(1)	Pd(1)–P(2)–C(26)	117.3(3)
P(2)–C(26)	1.81(1)	Pd(1)–P(2)–C(32)	118.4(3)
P(2)–C(32)	1.83(1)	C(3)–P(2)–C(26)	105.3(5)
		C(3)–P(2)–C(32)	101.9(4)
		C(26)–P(2)–C(32)	101.2(4)

(*iii*) Phenyl groups

	Av. C–C		Av. C–C
C(26—31)	1.375(8)	C(32—37)	1.388(7)
C(14—19)	1.380(7)	C(20—25)	1.370(8)

(*iv*) 11-Membered ring

		Ring torsion angle		
Pd(1)–P(2)	2.330(2)	43(1)	Pd(1)–P(2)–C(3)	110.9(3)
P(2)–C(3)	1.84(1)	−47(1)	P(2)–C(3)–C(4)	114.7(7)
C(3)–C(4)	1.50(2)	−16(1)	C(3)–C(4)–O(5)	115.0(11)
C(4)–O(5)	1.29(2)	−177(1)	C(4)–O(5)–C(6)	120.0(11)
O(5)–C(6)	1.42(2)	−170(1)	O(5)–C(6)–C(7)	107.1(10)
C(6)–C(7)	1.46(2)	69(1)	C(6)–C(7)–O(8)	107.0(12)
C(7)–O(8)	1.42(2)	−167(1)	C(7)–O(8)–C(9)	118.2(13)
O(8)–C(9)	1.30(2)	173(1)	O(8)–C(9)–C(10)	115.9(11)
C(9)–C(10)	1.48(2)	−30(1)	C(9)–C(10)–P(11)	117.0(7)
C(10)–P(11)	1.84(1)	−38(1)	C(10)–P(11)–Pd(1)	111.9(3)
P(11)–Pd(1)	2.321(2)	59(1)	P(11)–Pd(1)–P(2)	164.9(1)

−14.8 p.p.m. resonances of the *N*,*S*-isomer, suggesting isomerization of the mixed complex to the *N*,*N*-bonded species. Such isomerization has been previously noted,[17] and is consistent with our observations of the i.r. spectrum of a chloroform solution of this complex (see below).

The ^{31}P n.m.r. spectra of *cis*-[Pt(dpdo)X_2] (X = Cl or I) (Table 4) exhibit the expected 1:4:1 pattern centred at −10.4 p.p.m. [^1J(Pt–P) = 3 719] and −7.3 p.p.m. [^1J(Pt–P) = 3 481 Hz], respectively. The coupling constants are typical of *cis*-[Pt(PR_3)$_2$$X_2$] complexes.[18] The co-ordination chemical shifts of −32.2 p.p.m. for the chloride and −29.1 p.p.m. for the iodide are in accordance with the lower electronegativity of the iodide ligands. The chemical shift difference between the two complexes (+3.1 p.p.m.) compares favourably with that observed for *cis*-[Pt(PBu^n_3)$_2$$X_2$] of +2.6 p.p.m. from X = Cl to X = I. Two minor components are observed in the spectrum of the *cis*-iodide complex at −5.5 p.p.m. [^1J(Pt–P) = 2 506] and +0.2 p.p.m. [^1J(Pt–P) = 2 420 Hz]. These components have coupling constants typical of *trans*-Pt(PR_3)$_2$ complexes.

The spectra of *trans*-[Pt(dpdo)X_2] (X = Cl or Br) are much more complex even though molecular weight measurements are consistent with a monomeric formulation in chloroform. In $CDCl_3$ *trans*-[Pt(dpdo)Cl_2] exhibits three resonances suggestive of *trans* species, *viz*. at −14.8 [^1J(Pt–P) = 2 660], −8.6 [^1J(Pt–P) = 2 560], and −9.2 p.p.m. [^1J(Pt–P) = 2 567 Hz]; in addition, a very small amount of *cis* species is present, as evidenced by a resonance at −4.1 p.p.m. [^1J(Pt–P) = 3 632 Hz]. The existence of more than one species in solutions of *trans*-bonded phosphine chelates has been previously observed and it was suggested by Shaw and co-workers[1] that this arises from the presence of different stable conformers. In view of our molecular weight data, it seems that the n.m.r. data also point to the presence of different stable conformers in these complexes. However, the minor *cis* component is not a *cis* monomer, since its chemical shift and coupling constants differ from that of the monomeric *cis* complex detailed above.

The spectrum of *trans*-[Pt(dpdo)I_2] also consists of three

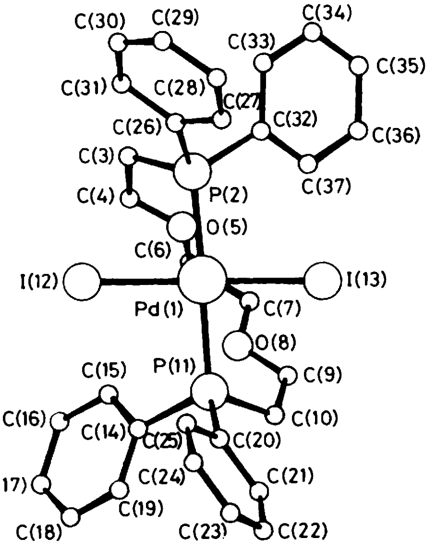

Figure 1. Molecular structure of *trans*-[Pd(dpdo)I_2] showing the atom-numbering scheme

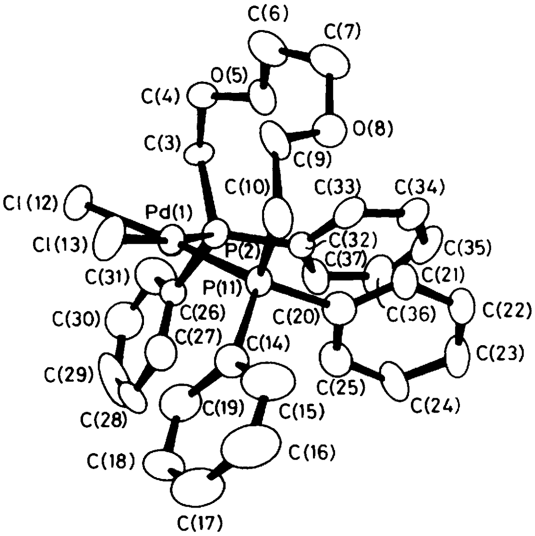

Figure 2. Molecular structure of *cis*-[Pd(dpdo)Cl_2] showing the atom-numbering scheme

Table 8. Final fractional co-ordinates for *cis*-[Pd(dpdo)Cl_2], with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	0.132 34(3)	0.330 37(3)	0.318 43(2)
P(2)	0.209 4(1)	0.373 8(1)	0.233 2(1)
C(3)	0.149 1(4)	0.504 3(4)	0.198 8(2)
C(4)	0.134 4(5)	0.587 8(4)	0.246 5(2)
O(5)	0.244 9(3)	0.592 7(3)	0.295 1(2)
C(6)	0.235 1(6)	0.657 1(5)	0.347 4(3)
C(7)	0.348 4(6)	0.639 6(5)	0.400 1(3)
O(8)	0.369 1(3)	0.530 4(3)	0.420 9(2)
C(9)	0.276 0(5)	0.487 2(4)	0.448 2(3)
C(10)	0.308 2(5)	0.371 4(4)	0.465 8(2)
P(11)	0.299 6(1)	0.282 7(1)	0.397 3(1)
Cl(12)	−0.056 1(1)	0.371 7(1)	0.247 0(1)
Cl(13)	0.022 5(1)	0.298 3(1)	0.396 2(1)
C(14)	0.281 7(4)	0.148 0(4)	0.428 2(2)
C(15)	0.347 8(6)	0.120 5(5)	0.488 7(3)
C(16)	0.338 3(7)	0.017 1(6)	0.511 4(3)
C(17)	0.262 8(7)	−0.056 2(5)	0.474 4(3)
C(18)	0.197 8(6)	−0.031 1(5)	0.414 9(3)
C(19)	0.206 8(5)	0.072 0(5)	0.391 0(3)
C(20)	0.455 9(4)	0.270 4(4)	0.385 5(2)
C(21)	0.556 3(4)	0.327 6(4)	0.419 3(2)
C(22)	0.671 5(5)	0.311 1(5)	0.408 0(3)
C(23)	0.689 1(5)	0.238 5(5)	0.363 1(3)
C(24)	0.588 9(5)	0.181 7(5)	0.328 2(5)
C(25)	0.472 1(5)	0.197 3(4)	0.339 3(3)
C(26)	0.152 4(4)	0.274 8(4)	0.171 0(2)
C(27)	0.152 6(5)	0.167 5(4)	0.187 0(3)
C(28)	0.112 6(5)	0.090 3(5)	0.140 8(3)
C(29)	0.069 7(6)	0.120 9(6)	0.078 5(3)
C(30)	0.067 2(6)	0.226 7(6)	0.062 3(3)
C(31)	0.109 7(6)	0.304 0(5)	0.107 5(2)
C(32)	0.373 1(4)	0.386 8(4)	0.234 0(2)
C(33)	0.450 0(4)	0.446 1(4)	0.281 2(3)
C(34)	0.571 8(5)	0.466 9(4)	0.278 4(3)
C(35)	0.614 6(5)	0.431 2(5)	0.228 1(3)
C(36)	0.538 3(6)	0.373 7(6)	0.179 4(3)
C(37)	0.417 7(5)	0.349 9(5)	0.182 7(3)

trans components, presumably different conformers, centred at $+0.9$ [^1J(Pt–P) = 2 411], -5.4 [^1J(Pt–P) = 2 506], and $+0.3$ p.p.m. [^1J(Pt–P) = 2 420 Hz]. Interestingly, the *trans* conformers at $+0.3$ and -5.4 p.p.m. are the minor components observed in the spectrum *cis*-[Pt(dpdo)I_2]. Two minor *cis* species at -7.3 [^1J(Pt–P) = 3 482], and -3.1 p.p.m. [^1J(Pt–P) = 3 632 Hz] are observed in the spectrum of *trans*-[Pt(dpdo)I_2], one of which is readily assignable to the *cis* monomer, since its coupling constant and chemical shift are identical to that observed for the monomer.

I.r. Spectra of the Complexes. The i.r. spectra of the complexes, Table 5, support the conclusions drawn from the ^{31}P n.m.r. studies. The spectrum of *cis*-[Pd(dpdo)Cl_2] in the solid state shows two bands at 292 and 315 cm^{-1}, assignable to ν(Pd–Cl) of *cis* geometry.[19] Similarly, two bands at 299 and 325 cm^{-1} are observed for *cis*-[Pt(dpdo)Cl_2]. We are also able to assign ν(M–P) bands for these two complexes at 348 and 374 cm^{-1} (M = Pd) and 350 and 375 cm^{-1} (M = Pt) in agreement with other reported values.[19] As expected, we observe only one ν(Pt–Cl) band at 338 cm^{-1} for *trans*-[Pt(dpdo)Cl_2], in close agreement with other complexes of the type *trans*-[Pt(PR_3)$_2$$Cl_2$].[18]

The i.r. spectrum of *trans*-[Pd(dpdo)(NCS)(SCN)] exhibits a strong ν(CN) stretch at 2 090 cm^{-1} with a pronounced shoulder at 2 104 cm^{-1}. Ligand absorptions obscured the ν(CS) and δ(NCS) regions, making these assignments impossible. The observed ν(CN) values are in the generally accepted range for a complex which contains Pd–NCS (2 090 cm^{-1}) and Pd–SCN (2 104 cm^{-1}) linkages,[20] and we also detected the *N*,*S*-bonded species links in solution *via* ^{31}P n.m.r. (see above). Palladium(II) complexes containing both *N*- and *S*-bonded thiocyanate groups are well known.[21] Additional evidence for a mixed-linkage complex comes from the presence of a weak band at 280 cm^{-1}, assignable to ν(Pd–S).[22]

The ν(COC) absorptions for the free ligand occur at 1 110 and 1 063 cm^{-1}. It is well established that co-ordination of the ether function affects these absorptions a great deal, shifting them to significantly lower energy.[23] However, these ligand absorptions occur at essentially the same energies in the complexes (Table 5) and are strong evidence for the absence of M–O bonds.

Electronic Spectra of the Complexes.—The solid reflectance and solution electronic spectra of the complexes are listed in Tables 3 and 4. In general, a high-energy visible band is

Table 9. Distances (Å), angles (°), and torsion angles (°) in *cis*-[Pd(dpdo)Cl$_2$], with estimated standard deviations in parentheses

(*i*) Around Pd(1) atom

Pd(1)–P(2)	2.263(1)	P(2)–Pd(1)–P(11)	105.4(1)
Pd(1)–P(11)	2.268(1)	Cl(12)–Pd(1)–C(13)	88.1(1)
Pd(1)–Cl(12)	2.332(1)	P(2)–Pd(1)–Cl(12)	82.5(1)
Pd(1)–Cl(13)	2.326(1)	P(11)–Pd(1)–Cl(13)	84.0(1)
		Sum	360.0

(*ii*) Around P(2) atom

P(2)–Pd(1)	2.263(1)	Pd(1)–P(2)–C(3)	111.2(2)
P(2)–C(3)	1.834(5)	Pd(1)–P(2)–C(26)	107.6(2)
P(2)–C(26)	1.809(5)	Pd(1)–P(2)–C(32)	125.7(2)
P(2)–C(32)	1.820(5)	C(3)–P(2)–C(26)	105.8(2)
		C(3)–P(2)–C(32)	101.1(2)
		C(26)–P(2)–C(32)	103.8(2)

(*iii*) Around P(11) atom

P(11)–Pd(1)	2.268(1)	Pd(1)–P(11)–C(10)	108.6(2)
P(11)–C(10)	1.819(5)	Pd(1)–P(11)–C(14)	111.6(2)
P(11)–C(14)	1.822(5)	Pd(1)–P(11)–C(20)	123.6(2)
P(11)–C(20)	1.819(5)	C(10)–P(11)–C(14)	104.4(2)
		C(10)–P(11)–C(20)	107.3(2)
		C(14)–P(11)–C(20)	99.5(2)

(*iv*) Phenyl groups

	av. C–C		av. C–C
C(26—31)	1.367(3)	C(32—37)	1.378(3)
C(14—19)	1.369(3)	C(20—25)	1.376(3)

(*v*) 11-Membered ring

		Ring torsion angle		
Pd(1)–P(2)	2.263(1)	−131(1)	Pd(1)–P(2)–C(3)	111.2(2)
P(2)–C(3)	1.834(5)	37(1)	P(2)–C(3)–C(4)	115.1(3)
C(3)–C(4)	1.491(7)	50(1)	C(3)–C(4)–O(5)	108.6(4)
C(4)–O(5)	1.406(6)	−171(1)	C(4)–O(5)–C(6)	113.3(4)
O(5)–C(6)	1.403(7)	169(1)	O(5)–C(6)–C(7)	108.1(5)
C(6)–C(7)	1.490(8)	−58(1)	C(6)–C(7)–O(8)	114.8(5)
C(7)–O(8)	1.425(7)	−63(1)	C(7)–O(8)–C(9)	114.2(4)
O(8)–C(9)	1.409(6)	179(1)	O(8)–C(9)–C(10)	108.2(4)
C(9)–C(10)	1.504(8)	−68(1)	C(9)–C(10)–P(11)	114.2(4)
C(10)–P(11)	1.819(5)	−39(1)	C(10)–P(11)–Pd(1)	108.6(2)
P(11)–Pd(1)	2.268(1)	121(1)	P(11)–Pd(1)–P(2)	105.4(1)

(*vi*) Phenyl–phenyl interaction*

C(32) · · · C(20)	3.47	C(35) · · · C(23)	3.70
C(33) · · · C(21)	3.26	C(36) · · · C(24)	3.90
C(34) · · · C(22)	3.35	C(37) · · · C(25)	3.78

(*vii*) Interplanar angles

C(32—37)–C(20—25)	17(1)	C(20—25)–C(14—19)	88(1)
C(32—37)–C(26—31)	101(1)	C(26—31)–C(14—19)	19(1)

* C(32), distance above PPdP plane = 0.22; C(25), distance below PPdP plane = 0.17 Å.

observed and, in addition, a weakly defined shoulder is seen in some cases in the solid state. These spectra are consistent with planar d^8 species,[24] although it is not possible to distinguish *cis*- and *trans*-isomers.[25]

Molecular Structures of trans-[Pd(dpdo)I$_2$] *and cis*-[Pd(dpdo)Cl$_2$].—Tables 6 and 7 present the atomic co-ordinates, bond distances, bond angles, and ring torsion angles for *trans*-[Pd(dpdo)I$_2$]. Tables 8 and 9 contain the corresponding information for *cis*-[Pd(dpdo)Cl$_2$]. The molecular structure of the iodide is shown in Figure 1 and that of the chloride in Figure 2.

The co-ordination at palladium is *trans* for [Pd(dpdo)I$_2$] but there is a small deviation from square-planar geometry (see Table 7). The 11-membered ring and, indeed, the whole molecule has an approximate two-fold axis passing through the Pd atom and the midpoint of C(6)–C(7). The bond angles I–Pd–I and P–Pd–P are slightly larger than those of the analogous complex [Ni(dpdo)I$_2$],[9] as expected due to the larger metal-ion radius of Pd. The Pd–P bond lengths are not unusual for *trans* palladium(II) phosphine complexes.[26] However, in contrast to [Ni(dpdo)I$_2$], where more than one conformer of the chelate backbone was observed, only one conformation exists for [Pd(dpdo)I$_2$] and the O–CH$_2$–CH$_2$–O torsion angle of 69° supports the earlier prediction for [Ni(dpdo)I$_2$] that staggered conformations would be the most stable.

In *cis*-[Pd(dpdo)Cl$_2$] the P–Pd–P and Cl–Pd–Cl bond angles and bond lengths are very similar to those observed for *cis*-[Pd(PPr$_3$)$_2$Cl$_2$].[27] In the latter complex the deviation of the P–Pd–P angle from 90° was ascribed to steric effects, which may also be present in the chelate. A highlight of the intramolecular packing for the chelate is the juxtapositioning of the two phenyl rings C(32—37) and C(20—25) (see Figure 2). These rings are not exactly superimposed and are inclined 17° from being parallel, but corresponding C · · · C distances between the rings are all less than 4 Å, Table 9. Interaction between the π systems is suggested, and this is supported by the longer C–C distances within these two phenyl rings (1.376, 1.378 Å), compared with 1.367 and 1.369 Å for the other two phenyl rings, which are distant from each other. The 11-membered chelate ring is asymmetrical, as its ring torsion angles show (Table 9); pseudo-mirror symmetry is destroyed in the C(6)–C(7) region, although elsewhere a pseudo-mirror plane containing the Pd atom and bisecting C(6)–C(7) approximately relates the remaining ring atoms.

A unique feature of this study is the isolation of square-planar palladium(II) complexes which contain either a *cis* or *trans* 11-membered chelate ring. Such a phenomenon has not been previously observed.

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