The Synthesis and Structural Characterization of (2-Pyridyldiphenylphosphine oxide)platinum(IV)tetrabromide. A Chelating Phosphine Oxide with a Substantially Bent Pt–O–P Angle

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Abstract

The complex (pyPh$_2$PO)PtBr$_4$ (pyPh$_2$PO is 2-pyridyldiphenylphosphine oxide) has been synthesized by three different pathways, and its structure has been established by X-ray crystallography. C$_{17}$H$_{14}$Br$_4$NOPPt crystallizes in the space group $P2_1/c$ (no. 14) with cell dimensions (at 140 K) of a = 13.696(7), b = 16.653(5), c = 17.612(7) Å, β = 92.23(4)°, Z = 8 and V = 3993(3) Å^3. The structure was refined by block-cascade least-squares to a conventional R value of 0.048 using 3647 significant data. The structure involves a six-coordinate platinum(IV) ion with the chelated ligand bound through its nitrogen and oxygen atoms. The two crystallographically independent molecules in the asymmetric unit have very similar dimensions. To our knowledge this is the first reported structure of a chelating phosphine oxide. The Pt–O–P angles within the rings are 114.4(6)° and 117.4(6)°.

Introduction

The coordination chemistry of phosphine oxides has been studied extensively for transition metals of the first row [1], lanthanides [2] and actinides [3]. However, phosphine oxide complexes of the second and third transition series (particularly Group VIII) have been less studied. This is surprising since phosphine oxides have practical applications in selective extraction processes of platinum metals [4] and as additives in some catalytic reactions [5].

We report here the preparation and structural characterization of a phosphine oxide complex of platinum(IV). This compound, (pyPh$_2$PO)PtBr$_4$ (pyPh$_2$PO is 2-pyridyldiphenylphosphine oxide), contains the first structurally characterized example of a chelate ring containing a phosphine oxide unit. The M–O–P angle in monodentate phosphine oxide complexes is subject to considerable variation. Examples range from a strictly linear case, (Ph$_3$PO)$_4$Cu$_4$OCl$_6$ [6], to an extremely bent one, 133° in (Me$_3$PO)$_2$Co(NO$_3$)$_2$ [7], *vide infra*. However, incorporation of the M–O–P unit into a chelate ring requires even further contraction of that angle and consequently polydentate ligands containing phosphine oxide functionalities do not appear to have received much attention.

Experimental

Preparation of Compounds

2-(Diphenylphosphino)pyridine (Ph$_2$Ppy) [8], 2-pyridyldiphenylphosphine oxide [9], *cis*-(Ph$_2$Ppy)$_2$PtBr$_2$ [10], RhPt(Ph$_2$Ppy)$_2$(CO)Br$_3$ [10] and (1,5-COD)PtBr$_2$ [11] were prepared as described elsewhere.

(pyPh$_2$PO)PtBr$_4$. Method 1

A solution of 127 mg (0.117 mmol) of RhPt(Ph$_2$Ppy)$_2$(CO)Br$_3$ in 50 ml of dichloromethane was treated with a dichloromethane solution (20 ml) containing excess bromine (0.02 ml, 0.40 mmol). The solution was stirred upon mixing. The volume of the solution was reduced to 25 ml, and diethylether was slowly added. The orange-red product precipitated as an extremely fine microcrystalline substance. The material was filtered and washed with cold diethylether and dried under vacuum. A portion was dissolved in dichloromethane to give a saturated solution. This was filtered and placed in a long tube (8 mm diameter) and allowed to slowly evaporate in a freezer. The well-formed crystals that grew were identified as (pyPh$_2$PO)PtBr$_4$ from the X-ray diffraction study.

(pyPh$_2$PO)PtBr$_4$. Method 2

Potassium hexabromoplatinum(IV) (125 mg, 0.166 mmol) was dissolved in a water/acetone mixture (1/5, v/v) and 59.1 mg (0.211 mmol) of pyPh$_2$PO was added. The solution changed color from dark red to dark orange, over a period of two hours. Upon cooling, orange microcrystals began to

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TABLE I. Summary of Crystal Parameters, Data Collection and Refinement for $(pyPh_2PO)PtBr_4$.

Formula	$C_{17}H_{14}Br_4NOPPt$
FW	793.98
a, Å	13.696(7)
b, Å	16.653(5)
c, Å	17.612(7)
β, deg	92.23(4)
V, Å^3	3993(3)
Z	8
density, g/cm^3	2.64 (calcd., 140 K) 2.47 (exptl., 298 K)
space group	$P2_1/c$ (no. 14)
crystal dimens., mm	0.10 × 0.08 × 0.22
crystal color	red-orange
radiation	Mo Kα (λ = 0.71069 Å)
temperature, K	140
μ, cm^{-1}	151.2
absorp. corr. fac	7.49–14.2
2θ max, deg	48
scan type	ω
scan speed, deg/min	8
scan range, deg	1
background offset, deg	1
refl. betw. ck. refl.	198
no. ck. refl.	2
uniq. data meas.	6275
data used ($I > 2.5\sigma(I)$)	3647
final no. of var.	281
mean shift/esd. max	0.006
G.O.F.	1.231
R	0.048
R_w	0.045

drop out. These were collected by filtration, washed with acetone and ether, and dried under vacuum. Yield 84%. *Anal.* Calcd for $C_{17}H_{14}NOPPtBr_4$: C, 25.71; H, 1.78; N, 1.76. Found: C, 24.92; H, 1.74; N, 1.72%.

$(pyPh_2PO)PtBr_4$. Method 3

A solution of 135 mg (0.20 mmol) of (1,5-COD)-$PtBr_2$ in hot dichloromethane was added to a solution of 79 mg (0.28 mmol) of $pyPh_2PO$ in 25 ml of hot propanol. The solution was heated under reflux for two days. At this point, 0.30 mmol of bromine dissolved in 1.5 ml of dichloromethane was added to the light orange solution. After distilling off one-half of the solvent, the solution was allowed to cool for two days at 0 °C. The orange microcrystalline product was isolated by filtration, washed with ether, and vacuum dried. Yield, 41%. *Anal.* Calcd. for $C_{17}H_{14}NOPPtBr_4$: C, 25.71; H, 1.78; N, 1.76. Found: C, 24.56; H, 1.74; N, 1.76%.

X-ray Data Collection, Solution and Refinement of $(pyPh_2PO)PtBr_4$

An orange crystal of $(pyPh_2PO)PtBr_4$ was mounted on a Syntex $P2_1$ diffractometer equipped with a modified LT-1 low temperature apparatus. Reflections were initially located from a rotation photograph. With these centered reflections, and the Synthex $P2_1$ automatic indexing program, the lattice was assigned as monoclinic, P. Quick scans of the reflections for space group determination gave the conditions 0k0, $k = 2n$ and $h0l$, $l = 2n$ which are consistent with the space group $P2_1/c$ (no. 14). The experimental density measurements were done by the flotation method with $C_2H_4Br_2/CCl_4$ solutions. The results of these measurements as well as data collection parameters are summarized in Table I. No decay in the intensity of the check reflections was observed.

Solution of the structure was accomplished by the Patterson method. All non-hydrogen atoms of both molecules were found on successive difference Fourier maps and refined with the use of isotropic thermal parameters to an R of 0.105. Due to the large absorption coefficient ($\mu = 151.2$ cm^{-1}) an absorption correction was applied. In the final cycles of refinement all atoms heavier than carbon were assigned anisotropic thermal parameters. The R value then fell to 0.054. Complete refinement of 281 parameters using 3647 reflections gave an $R = 0.048$. Hydrogen atoms were not included. The final difference map was essentially featureless. Positional parameters and equivalent isotropic thermal motion parameters for both molecules are given in Table II.

Results and Discussion

Synthesis of $(pyPh_2PO)PtBr_4$

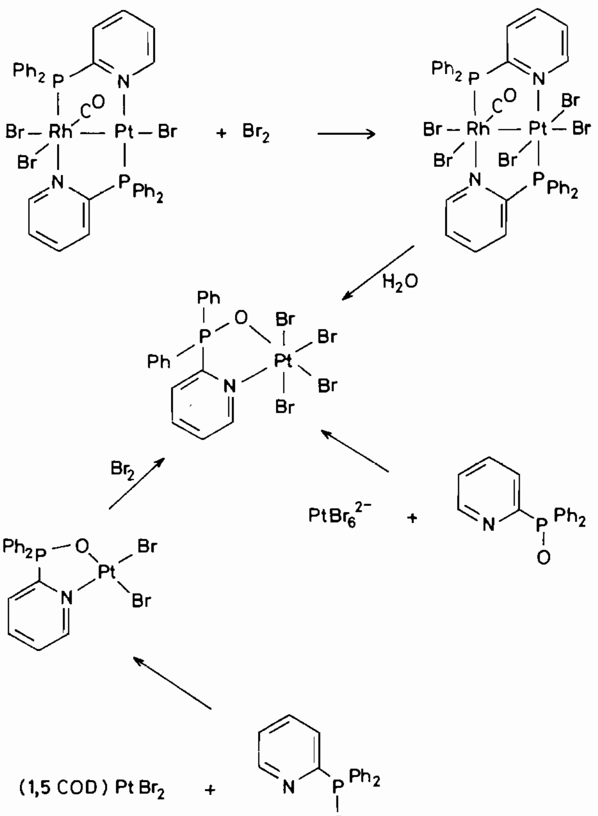
The original preparation of this substance occurred accidentally. In an attempt to obtain crystals of the heterobinuclear complex $PtRh(\mu\text{-}Ph_2Ppy)_2(CO)Br_5$ [10] (Ph_2Ppy is 2-(diphenylphosphino)pyridine, also known as 2-pyridyldiphenylphosphine) we oxidized a sample of $PtRh(\mu\text{-}Ph_2Ppy)_2(CO)Br_3$ [10] with bromine, isolated an orange red microcrystalline product and then subjected it to a slow recrystallization. This was done by dissolving the sample in dichloromethane and allowing it to evaporate in a freezer at −5 °C over a ten day period. This produced small but well formed crystals which were found by the X-ray diffraction study reported here to contain $(pyPh_2PO)PtBr_4$ rather than the desired heterobinuclear complex. During the crystallization process the sample was not protected from the humid atmo-

TABLE II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $(pyPh_2PO)PtBr_4$.

Atom^b	x	y	z	U
Pt	5144(1)	2933(1)	1588(1)	17(1)^a
Pt(A)	361(1)	3221(1)	2304(1)	13(1)^a
Br(1)	5443(2)	2676(1)	254(1)	23(1)^a
Br(2)	4826(2)	3131(1)	2929(1)	25(1)^a
Br(3)	4052(2)	4036(1)	1176(1)	24(1)^a
Br(4)	6495(2)	3862(1)	1737(1)	30(1)^a
Br(1A)	251(1)	1779(1)	2021(1)	21(1)^a
Br(2A)	504(1)	4652(1)	2644(1)	19(1)^a
Br(3A)	−729(2)	3536(1)	1163(1)	23(1)^a
Br(4A)	1752(1)	3363(1)	1590(1)	23(1)^a
P	4193(4)	1284(3)	1771(3)	14(2)^a
P(A)	−640(4)	2917(3)	3767(3)	15(2)^a
O	3953(8)	2126(7)	1462(7)	17(4)^a
O(A)	−844(8)	3109(7)	2928(7)	16(4)^a
N	6018(11)	1931(8)	1928(10)	20(6)^a
N(A)	1201(10)	2953(8)	3341(8)	7(4)^a
C(1)	6995(13)	1945(10)	2065(11)	16(4)
C(2)	7503(15)	1256(12)	2326(12)	27(5)
C(3)	7005(14)	515(11)	2433(12)	23(5)
C(4)	5986(14)	530(12)	2284(12)	24(5)
C(5)	5501(13)	1225(10)	2063(11)	14(4)
C(6)	3887(13)	572(11)	1063(11)	15(4)
C(7)	3909(14)	833(11)	294(12)	21(5)
C(8)	3767(15)	260(12)	−351(13)	30(5)
C(9)	3652(14)	−541(11)	−129(12)	21(5)
C(10)	3633(13)	−797(10)	592(11)	13(4)
C(11)	3760(13)	−253(11)	1202(11)	17(5)
C(12)	3596(13)	1029(11)	2607(12)	18(5)
C(13)	2641(13)	797(10)	2512(11)	16(4)
C(14)	2139(14)	610(11)	3141(12)	20(5)
C(15)	2644(15)	632(12)	3864(12)	27(5)
C(16)	3641(15)	859(12)	3972(13)	32(6)
C(17)	4109(14)	1057(11)	3333(12)	22(5)
C(1A)	2178(12)	2906(10)	3419(11)	12(4)
C(2A)	2716(15)	2724(11)	4144(12)	24(5)
C(3A)	2212(14)	2587(11)	4760(12)	19(5)
C(4A)	1151(13)	2622(11)	4683(11)	16(5)
C(5A)	694(13)	2822(10)	3957(11)	13(4)
C(6A)	−1149(13)	1981(11)	4057(11)	18(5)
C(7A)	−589(14)	1279(11)	3967(12)	19(5)
C(8A)	−1038(13)	522(11)	4122(11)	18(5)
C(9A)	−1965(14)	503(12)	4364(12)	25(5)
C(10A)	−2486(15)	1220(12)	4462(12)	27(5)
C(11A)	−2085(14)	1960(11)	4319(12)	22(5)
C(12A)	−993(13)	3717(11)	4345(11)	17(5)
C(13A)	−1020(14)	3605(11)	5151(11)	17(5)
C(14A)	−1191(13)	4271(11)	5604(11)	17(5)
C(15A)	−1318(14)	5048(11)	5240(11)	18(5)
C(16A)	−1295(13)	5132(10)	4456(11)	14(4)
C(17A)	−1155(12)	4481(10)	3985(11)	10(4)

^{a}Equivalent isotropic U defined as one third of the trace of the orghogonalised U_{ij} tensor. ^{b}Atoms of molecule II are designated by A.

sphere which provided the source of the oxygen atom in the product. The overall reaction probably involved degradation of the complex, oxidation of the Ph_2Ppy to $pyPh_2PBr_2$, hydrolysis to form $pyPh_2PO$, and then coordination to platinum. The formation of phosphine oxides by halogen oxidation followed by hydrolysis is well established [12].



Scheme 1

After discovering the nature of the product, rational routes to its preparation were devised. 2-Pyridyldiphenylphosphine oxide, obtained from hydrogen peroxide oxidation of Ph_2Ppy, reacts with $PtBr_6^{2-}$ to form $(pyPh_2PO)PtBr_4$. Despite the generally inert character of platinum(IV) complexes, this reaction occurs readily and is the preferred method of preparation. It is also possible to prepare $(pyPh_2PO)PtBr_4$ by the reaction of $(1,5\text{-COD})PtBr_2$ with $pyPh_2PO$ and subsequent oxidation with bromine, but the yield by this method is poor. These reactions are summarized in Scheme 1.

The infrared spectrum of the complex in dichloromethane shows a strong phosphorus–oxygen stretching vibration at 1115 cm^{-1}. This is in good agreement with other values [1]. It also shows the usual low energy shift relative to the ν(P–O) (1180 cm^{-1}) of the free ligand [13]. This low energy shift has been explained as being due to the reduced π character of the P–O bond because of the interaction of the 2p electrons of oxygen with the metal [14]. The ^{31}P NMR of the complex exhibits a singlet at δ = 25.4 ppm (free ligand, 21.4 ppm). Unfortunately, $^3J(Pt-P)$ is too small to be observed.

TABLE III. Selected Interatomic Distances (A) for (pyPh$_2$PO)PtBr$_4$.

Molecule *I*		Molecule *II*	
Pt–O	2.106(11)	Pt(A)–O(A)	2.087(12)
Pt–N	2.102(14)	Pt(A)–N(A)	2.098(13)
Pt–Br(1)	2.465(2)	Pt(A)–Br(1A)	2.454(2)
Pt–Br(2)	2.471(2)	Pt(A)–Br(2A)	2.459(2)
Pt–Br(3)	2.429(2)	Pt(A)–Br(3A)	2.428(2)
Pt–Br(4)	2.404(2)	Pt(A)–Br(4A)	2.406(2)
P–O	1.527(13)	P(A)–O(A)	1.508(14)
P–C(5)	1.812(18)	P(A)–C(5A)	1.828(18)
P–C(6)	1.738(19)	P(A)–C(6A)	1.804(19)
P–C(12)	1.812(21)	P(A)–C(12A)	1.777(20)
N–C(5)	1.406(23)	N(A)–C(5A)	1.368(24)
Ring C–C mean	1.399(28)		1.411(28)

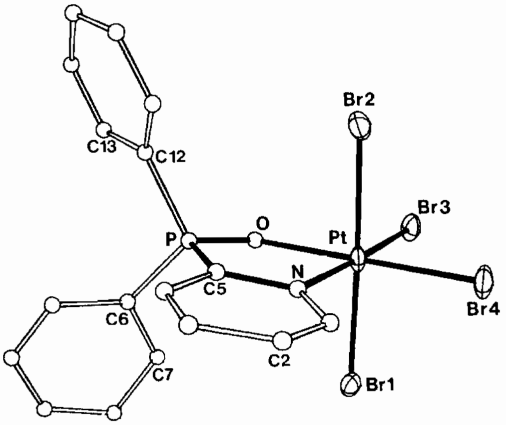


Fig. 1. A perspective drawing of (pyPh$_2$PO)PtBr$_4$, molecule I, showing the atomic labelling scheme.

The Molecular Structure of (pyPh$_2$PO)PtBr$_4$

The complex crystallizes with two independent molecules in the asymmetric unit and no unusual contacts between them. Atomic coordinates are given in Table II. Tables III and IV give a selection of pertinent interatomic distances and angles. A perspective drawing of molecule I is given in Fig.1. Figures 2 and 3 show stereoscopic views of molecule I and II respectively. The difference between the two molecules, as can be observed from the tables, is very slight. The major difference is exhibited by the relative planarity of the five-membered chelate rings. In molecule **II** the ring is much more planar than in molecule **I**. This can be quantified by calculating least squared planes through the platinum, oxygen and nitrogen and examining the out-of-plane deviations of the phosphorus and the carbon atoms. For molecule **I** the phosphorus deviates by 0.22(1) Å and C(5) by 0.23(2) Å. The deviations are less in the more planar molecule **II**, where P(A) is

TABLE IV. Selected Bond Angles (deg) for (pyPh$_2$PO)PtBr$_4$.

Molecule I		Molecule **II**	
Pt–O–P	114.4(6)	Pt(A)–O(A)–P(A)	117.4(6)
Br(1)–Pt–Br(2)	177.6(1)	Br(1A)–Pt(A)–Br(2A)	177.5(1)
Br(1)–Pt–Br(3)	90.4(1)	Br(1A)–Pt(A)–Br(3A)	91.4(1)
Br(2)–Pt–Br(3)	91.0(1)	Br(2A)–Pt(A)–Br(3A)	91.0(1)
Br(1)–Pt–Br(4)	90.6(1)	Br(1A)–Pt(A)–Br(4A)	91.4(1)
Br(2)–Pt–Br(4)	91.3(1)	Br(2A)–Pt(A)–Br(4A)	89.2(1)
Br(3)–Pt–Br(4)	89.3(1)	Br(3A)–Pt(A)–Br(4A)	89.8(1)
Br(1)–Pt–O	89.8(4)	Br(1A)–Pt(A)–O(A)	89.1(3)
Br(2)–Pt–O	88.3(4)	Br(2A)–Pt(A)–O(A)	90.3(3)
Br(3)–Pt–O	90.3(3)	Br(3A)–Pt(A)–O(A)	90.3(3)
Br(4)–Pt–O	179.5(3)	Br(4A)–Pt(A)–O(A)	179.5(3)
Br(1)–Pt–N	89.2(5)	Br(1A)–Pt(A)–N(A)	89.1(4)
Br(2)–Pt–N	89.3(5)	Br(2A)–Pt(A)–N(A)	88.5(4)
Br(3)–Pt–N	176.6(4)	Br(3A)–Pt(A)–N(A)	175.3(4)
Br(4)–Pt–N	94.2(4)	Br(4A)–Pt(A)–N(A)	94.9(4)
O–Pt–N	86.2(5)	O(A)–Pt(A)–N(A)	85.1(5)
O–P–C(5)	108.6(7)	O(A)–P(A)–C(5A)	105.9(8)
O–P–C(6)	110.2(8)	O(A)–P(A)–C(6A)	115.2(8)
O–P–C(12)	114.0(8)	O(A)–P(A)–C(12A)	111.6(8)
C(5)–P–C(6)	108.7(9)	C(5A)–P(A)–C(6A)	106.4(8)
C(5)–P–C(12)	106.0(9)	C(5A)–P(A)–C(12A)	106.8(8)
C(6)–P–C(12)	109.1(9)	C(6A)–P(A)–C(12A)	110.3(9)
Pt–N–C(5)	115.5(11)	Pt(A)–N(A)–C(5A)	116.5(10)
P–C(5)–N	114.0(12)	P(A)–C(5A)–N(A)	115.1(12)

TABLE V. Dimensions of Coordinated Phosphine Oxides.

Compound	M–O–P (deg)	P–O (A)	Ref.
Ph_3PO		1.46(1)	18
$(Ph_3PO)_4Cu_4OCl_6$	180	1.51(2)	6
$(Ph_3PO)_2CoCl_2$	176.0(8)		19
$(Ph_3PO)_3SmS_2P(OC_2H_5)_2^+$	175.5(1.6)	1.51(1)	20
	174.8(1.2)	1.51(1)	
	171.2(1.0)	1.50(3)	
$(Ph_3PO)La[N(SiCH_3)_2]_3$	174.6(9)	1.52	21
$(Ph_3PO)Fe[S_2C_2(CF_3)_2]_2^-$	169		22
$(Ph_3PO)_2MoCl_3O$	168.6(7)	1.515(12)	23
	145.6(7)	1.506(12)	
$(Ph_3PO)_2La[S_2P(OC_2H_5)_2]_3$	168.2(8)	1.487(13)	20
	165.7(7)	1.496(12)	
$[(Ph_3PO)Ti(C_6HF_4)Cl]_2$	168.0(6)	1.480(9)	24
$(Ph_3PO)_2MoBr_2O_2$	168.0(8)	1.49(1)	25
	160.8(6)	1.49(1)	
$[(Ph_2P(O)CH_2)_2SnCl(C_4H_9)_2]_n$	167.8(4)	1.483(6)	26
	163.9(4)	1.491(7)	
$(Ph_3PO)_2NpCl_2O_2$	167(1)	1.50(1)	27
	153(1)	1.55(2)	
$(Ph_3PO)_2MoCl_2O_2$	165.97(9)	1.507(1)	25
	159.20(8)	1.492(1)	
$(Ph_3PO)_2WCl_2O_2$	165.4(5)	1.500(7)	28
	159.0(4)	1.499(8)	
$(Ph_3PO)UCl_5$	163.7(1)	1.53(2)	29
$(Ph_3PO)_2U(NO_3)_2O_2$	160.0(4)	1.505(9)	27
$(Ph_3PO)_2Np(NO_3)_2O_2$	159.1(4)	1.502(9)	27
$(Ph_3PO)_2UCl_2O_2$	158.7(6)	1.518(8)	30
$(Ph_3PO)_2ZnBr_2$	157.0(7)	1.486(8)	31
	145.0(4)	1.523(12)	
$[(Ph_3PO)Te(C_6F_5)_2O_2C_7F_5]_2$	150.5(4)	1.488(7)	32
$(Ph_3PO)Sn(C_3H_5O_2)Cl_3$	148.8(6)	1.494(11)	33
$(Ph_3PO)SnBr(SC_4H_3)_3$	146.9(2)	1.510(4)	34
$(Ph_3PO)_2SbCl_3$	141.1(1)		35
$(Me_3PO)_2Co(NO_3)_2$	140(1)	1.55	7
	133(1)	1.53(3)	
$(Me_3PO)SbCl_5$	139(1)	1.61	36
$(Ph_3PCH(Ph)_2PO)W(CO)_5$	137.1(4)	1.523(8)	37
$(pyPh_2PO)PtBr_4$	114.4(6)	1.527(13)	this
	117.4(6)	1.508(14)	work

0.02(2) Å and C(5A) is 0.00(2) Å out of the plane. Although this difference is slight, it does cause the phenyl rings to be oriented quite differently in the two complexes. In the more planar molecule **II** the phenyl rings have dihedral angles of 74° and 78° relative to the five-membered chelate ring, whereas in molecule **I**, the dihedral angles are 103° and 67°.

In both molecules the angular disposition of ligands about the platinum is near the ideal with *cis* angles ranging from 88.3(4) to 94.9(4)° and the *trans* angles all greater than 175.3(4)°. The bond distances around the platinum are comparable with those found in other platinum(IV) complexes [15–17].

The P–O bond distances (1.527(13), 1.508(14) Å) are also within the range of distances found for phosphine oxides bound to transition metals as can be seen from the data in Table V. As would be expected, coordination to a metal causes this distance to be longer than found in free triphenylphosphine oxide whose P–O bond distance is 1.46(1) Å [18].

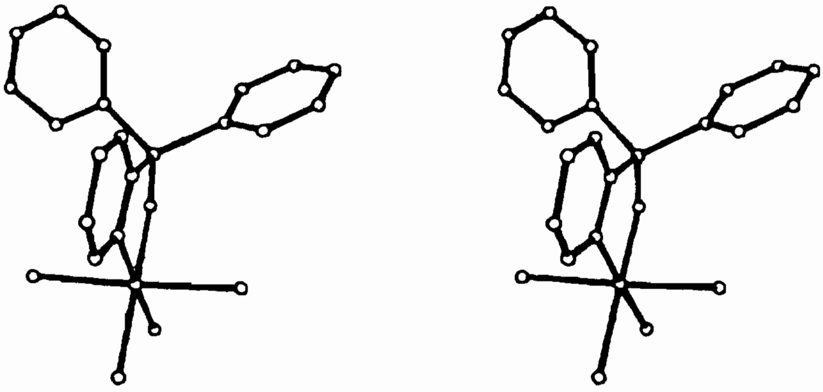


Fig. 2. A stereoscopic view of (pyPh$_2$PO)PtBr$_4$, molecule **I**.

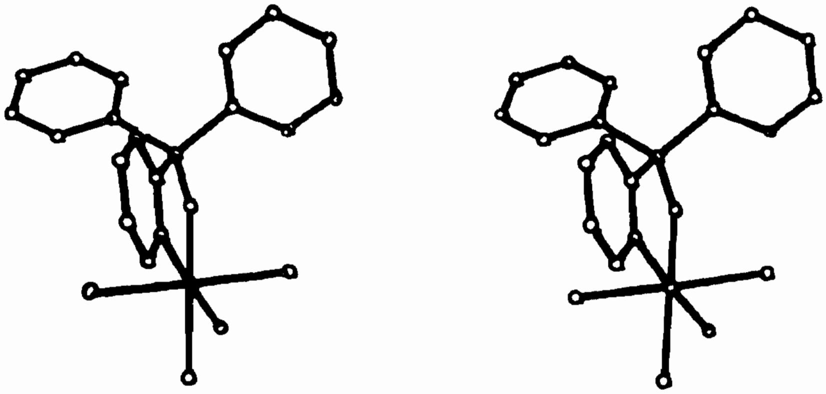


Fig. 3. A stereoscopic view of (pyPh$_2$PO)PtBr$_4$, molecule **II**.

The tetrahedral coordination around the phosphorus atoms is fairly close to ideal, with angles ranging from 105.9(8) to 114.0(8)°. The phenyl rings are nearly perfectly planar and there are no significant departures from the expected structural parameters.

The most striking feature of this structure is the degree of bending of the P–O–Pt unit which is necessary to form a chelate ring. The data in Table V show the degree of variability in the P–O–M angle in twenty-six monodentate phosphine oxide complexes. There is no correlation between the P–O–M angle and the P–O distance so that there is no electronic effect governing the angle. The variation of this angle in compounds containing two phosphine oxide ligands, particularly $(Ph_3PO)_2MoCl_3O$, is striking and leads to the suggestion that in solution there would be considerable freedom for bending of this group. Steric effects and packing effects contribute to the variability of this angle and it is noteworthy that complexes of the less bulky trimethylphosphine oxide fall at the most sharply bent end of the compilation. In the chelated metal complex the Pt–O–P angle is 16–19° less than found for any of the monodentate complexes. The other angles and distances within the chelate ring are normal and there is no expression of undue strain within the ring.

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