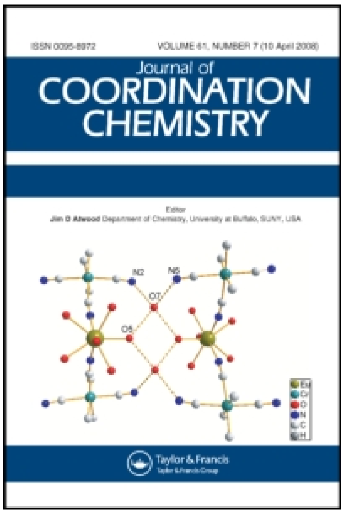

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Ru(II) COMPLEXES CONTAINING CHELATING PHOSPHINE LIGANDS. SYNTHESIS, CHARACTERIZATION, AND X-RAY CRYSTAL STRUCTURES OF DICHLOROBIS(1,2-BIS(DIPHENYLPHOSPHINO)ETHANE)Ru(II) AND THE COORDINATIVELY UNSATURATED TRIGONAL-BIPYRAMIDAL CATION, CHLOROBIS-(1,2-BIS(DIPHENYLPHOSPHINO)ETHANE)Ru(II)

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Ru(II) COMPLEXES CONTAINING CHELATING PHOSPHINE LIGANDS. SYNTHESIS, CHARACTERIZATION, AND X-RAY CRYSTAL STRUCTURES OF DICHLOROBIS(1,2-BIS(DIPHENYLPHOSPHINO)ETHANE)Ru(II) AND THE COORDINATIVELY UNSATURATED TRIGONAL-BIPYRAMIDAL CATION, CHLOROBIS-(1,2-BIS(DIPHENYLPHOSPHINO)ETHANE)Ru(II)

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The reaction of *trans*-$RuCl_2(dppe)_2$ (**1**), with $AgBF_4$ in tetrahydrofuran leads to abstraction of one of the halide ligands to produce the trigonal-bipyrimidal complex, $[RuCl(dppe)_2]BF_4$ (**2**). Both products are characterized by ^{31}P NMR spectroscopy and their crystal structures determined. For the coordinatively unsaturated trigonal-bipyramidal complex (**2**), we found no evidence for the presence of more than one species or fluxional behaviour at room temperature in the ^{31}P NMR spectrum. This complex was found to possess a trigonal-bipyramidal geometry in the solid state. Crystals of **1** are monoclinic, space group $P2_1/c$ with $a=23.713(4)$Å, $b=11.156(1)$Å, $c=17.595(2)$Å, $\beta=103.23(1)°$ and $V=4531(1)$Å^3. Convergence to conventional R values of $R=0.043$ and $R_w=0.042$ was obtained for 416 variable parameters and 2746 reflections with $I>3\sigma(I)$. Compound **2** in triclinic, $P\bar{1}$, $a=12.482(3)$Å, $b=12.543(3)$Å, $c=17.582(3)$Å, $\alpha=87.52(2)°$, $\beta=72.70(2)°$, $\gamma=74.35(2)°$ and $V=2529(1)$Å^3. Values of $R=0.072$ and $R_w=0.097$ were obtained for 487 variable parameters and 3242 reflections with $I>3\sigma(I)$.

KEY WORDS: Ruthenium, phosphines, X-ray structure, NMR.

INTRODUCTION

Ruthenium(II) complexes containing tertiary phosphines have been extensively studied, particularly in connection with their ability to function as homogeneous catalysts in a variety of reactions.[1] A number of Ru(II) complexes containing chelating phosphines have also been prepared. However, considerably less is known concerning the chemistry of these systems.[2] In these complexes, reaction rates and selectivity appear to be highly dependent on a number of factors; quite frequently steric considerations play a major role, although electronic effects, as well as factors such as chelate ring size, are also important.[3–5]

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Ruthenium(II), with its d^6 electron configuration, tends to favour octahedral coordination geometries. As a result, relatively few examples of five-coordinate complexes of Ru(II) containing chelating phosphine ligands have been described.[6-8] Specific examples include a series of cationic complexes having the formula $[RuX(dcpe)_2]^+$ ($X = Cl^-, Br^-, I^-$) where dcpe is 1,2-bis(dicyclohexylphosphino)ethane, and the hydrido complex, $[RuH(dcpe)_2]^+$.[8] The crystal structure of one of these, $[RuCl(dcpe)_2]^+$, has been determined and shown to possess a trigonal-bipyramidal geometry.[8] The syntheses of a series of five-coordinate Ru(II)-halide complexes containing bidentate phosphines of the type $R_2P(CH_2)_nPR_2$ n = 1–4, R = phenyl or methyl) has also been described, although, interestingly, it was reported that no product could be obtained with n = 2 and R = phenyl.[6]

Recently we succeeded in preparing the missing member of this series, $[RuCl(dppe)_2][BF_4]$, where dppe is the chelating phosphine, 1,2-bis(diphenylphosphino)ethane. Although the ^{31}P NMR data indicated the presence of only one species in solution, the stereochemistry of the complex could not be unambiguously determined. Owing to the paucity of structural data on five-coordinate Ru(II) complexes, we undertook an X-ray crytal structure determination of this cation in order to establish its configuration. In this paper we also report for the first time the crystal structure of the parent compound, *trans*-$RuCl_2(dppe)_2$.

EXPERIMENTAL

Materials and Methods

All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or argon. Triphenylphosphine, 1,2-bis(dicyclohexylphosphino)-ethane, and $AgBF_4$ were purchased from the Aldrich Chemical Company, Inc., and used as received. Ruthenium trichloride was provided by the Engelhard Corporation. All solvents were freshly distilled prior to use using appropriate drying agents. ^{31}P NMR spectra were recorded in $CDCl_3$ using a Bruker AC 200 spectrometer and referenced to an 85% solution of H_3PO_4 in D_2O.

Preparation of dichlorobis(1,2-bis(diphenylphosphino)ethane)Ru(II), (**1**)

$RuCl(dppe)_2$ was prepared either from $RuCl_2(PPH_3)_3$ according to the literature[9] procedure, or from the anionic Ru(III) complex, $[RuCl_4(PPh_3)_2]^-$, by procedures that have also been described.[10] Recrystallization from a dichloromethane-diethyl ether solution led to the formation of numerous well-formed yellow crystals. ^{31}P: 39.85 ppm(s).

Preparation of [chlorobis(1,2-bis(diphenylphosphino)ethane)Ru(II)][BF₄], (**2**)

Preparation of the cationic Ru(II) complex was carried out by halide abstraction using $AgBF_4$. To 100 mg of $RuCl_2(dppe)_2$ in THF was added a two-fold excess (40 mg) of $AgBF_4$. The reaction was stirred for one hour whereupon it developed a purple colour. The solution was filtered to remove AgCl and the solvent was removed under reduced pressure. Crystals suitable for X-ray analysis were obtained by slow evaporation from a $CHCl_3$-diethyl ether solution. ^{31}P NMR: 79.02(s) ppm, 50.79(t) ppm; J_{P-P} 11.5 Hz.

X-ray Crystallography

X-ray data collection for both compounds carried out using a Siemens R3m/V diffractometer equipped with graphite-monochromated MoKα p0.71073Å) radiation. Refined cell parameters were obtained from the setting of 25 high angle reflections. Data collection was carried out at ambient temperature using the ω-scanning technique in bisecting geometry. For both structures, three standards measured every 97 data showed no significant variation over the period of data collection. The data were corrected for Lorentz and polarization effects, as well as absorption. Absorption coorrections for both data sets were applied semi-empirically on the basis of azimuthal scans of several reflections spanning a range of 2Θ values. The structures of both were solved using standard Patterson and difference Fourier techniques and refined using scattering factors that included terms for anomalous dispersion.[11,12] Crystal data and details of the crystallographic experimental procedure for both complexes are summarized in Table 1.

Dichlorobis(1,2bis(diphenylphosphino)ethane)Ru(II), (**1**)

A small, regularly shaped crystal displaying a prismatic habit was mounted on the end of a glass fibre in a random orientation. Monoclinic symmetry was suggested on the basis of the interaxial angles and confirmed by axial rotation photographs. Assignment to the $P2_1/c$ space group was based on an inspection of the systematically absent reflections. Phenyl rings were refined as rigid idealized polygons (C-C = 1.395Å)

Table 1 Crystal data, and details of intensity data collection and refinement

	1	2
Molecular Formula	$C_{52}H_{48}Cl_2P_4Ru$	$C_{52}H_{48}BClF_4P_4Ru$
Molecular Weight	968.8	1020.1
a (Å)	23.713(4)	12.482(3)
b (Å)	11.156(1)	12.543(3)
c (Å)	17.595(2)	17.582(3)
α (°)		87.52(2)
β (°)	103.23(1)	72.70(2)
γ (°)		74.35(2)
V(Å^3)	4531(1)	2529(1)
Space group	$P2_1/c$	$P\bar{1}$
z	4	2
$D_{(calc)}$Mg/m^3	1.420	1.340
μ (cm^{-1})	6.32	5.28
F(000)	1992	1044
h, k, l range	$-25<h<25$, $-12<k<2$, $-18<l<2$	$0<h<13$, $-13<k<13$ $-18<l<18$
Total number of reflections	8821	7036
Number of unique reflections	5920	6669
Number of reflections used	2746	3242
Number of Parameters	416	487
Scan type	ω	ω
Scan range (°)	1.5	1.5
2Θ range	3.0, 45.0	3.0, 45.0
Weighting scheme (w^{-1})	$[\sigma^2(F)+0.0003(F^2)]$	$[\sigma^2(F)+0.0025(F^2)]$
Final R, R_w	0.043, 0.042	0.072, 0.097

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **1**

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)*
Ru(1)	2427(1)	557(1)	2065(1)	31(1)
Cl(1)	1992(1)	2317(2)	2530(1)	44(1)
Cl(2)	2813(1)	−1317(2)	1715(1)	47(1)
P(1)	1790(1)	−498(2)	2666(1)	36(1)
P(2)	3014(1)	500(3)	3343(1)	41(1)
P(3)	3094(1)	1576(2)	1452(1)	38(1)
P(4)	1878(1)	433(2)	744(1)	37(1)
C(1)	2010(3)	−259(8)	3744(5)	46(3)
C(2)	2514(3)	603(9)	4002(5)	48(3)
C(3)	2835(3)	1395(8)	368(5)	45(3)
C(4)	2427(3)	330(8)	155(5)	47(3)
C(11)	786(3)	806(5)	1984(3)	49(4)
C(12)	196	1069	1840	58(4)
C(13)	−168	386	2190	76(5)
C(14)	60	−560	2685	68(5)
C(15)	650	−822	2829	54(4)
C(16)	1013	−139	2478	37(4)
C(21)	1306(3)	−2655(7)	2005(3)	58(5)
C(22)	1269	−3899	1932	81(6)
C(23)	1677	−4624	2418	88(7)
C(24)	2123	−4106	2977	81(6)
C(25)	2161	−2861	3050	72(5)
C(26)	1752	−2136	2564	42(4)
C(31)	3397(3)	−1494(8)	4328(4)	71(5)
C(32)	3740	−2506	4556	95(6)
C(33)	4129	−2883	4119	103(7)
C(34)	4176	−2247	3454	86(6)
C(35)	3834	−1234	3226	60(5)
C(36)	3445	−858	3663	50(4)
C(41)	4056(3)	1431(6)	4268(4)	70(5)
C(42)	4430	2365	4575	81(5)
C(43)	4280	3546	4361	67(5)
C(44)	3755	3794	3839	67(5)
C(45)	3381	2861	3531	61(5)
C(46)	3531	1679	3745	44(4)
C(51)	3739(2)	3609(5)	1221(4)	57(5)
C(52)	3839	4836	1169	75(5)
C(53)	3448	5661	1350	71(5)
C(54)	2957	5260	1584	75(6)
C(55)	2857	4034	1636	62(5)
C(56)	3248	3209	1454	39(4)
C(61)	3958(3)	−21(6)	1250(3)	55(4)
C(62)	4508	−538	1449	71(5)
C(63)	4927	−74	2067	70(5)
C(64)	4796	909	2487	66(5)
C(65)	4247	1426	2288	52(4)
C(66)	3828	962	1669	41(4)
C(71)	1635(2)	−1947(6)	249(3)	55(4)
C(72)	1270	−2929	27	63(5)
C(73)	676	−2817	−30	65(5)
C(74)	446	−1722	135	56(4)
C(75)	811	−740	357	51(4)
C(76)	1405	−852	415	35(4)
C(81)	1354(3)	2720(6)	601(3)	50(4)
C(82)	1030	3655	190	66(5)
C(83)	787	3534	−607	68(5)
C(84)	868	2478	−993	69(5)
C(85)	1191	1543	−582	61(5)
C(86)	1435	1664	215	45(4)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

with hydrogen atoms included in idealized positions with fixed isotropic $U = 0.08\text{Å}^2$. For the final cycle, maximum shift/$\sigma = 0.001$ with minimum and maximum residual electron densities of -0.33eÅ^{-3} and 0.35eÅ^{-3}. Atomic coordinates, bond lengths and angles are listed in Tables 2 and 3.

[Chlorobis(1,2-bis(diphenylphosphino)ethane)Ru(II)][BF_4], (**2**)

The crystal of this compound consisted of a very thin plate which was mounted on the end of a glass fibre. Triclinic symmetry was suggested on the basis of the interaxial angles and confirmed by a Delaunay reduction. Intensity statistics favoured a

Table 3 Geometrical data for **1**

Bond lengths (Å)			
Ru(1)-Cl(1)	2.445(3)	Ru(1)-Cl(2)	2.417(3)
Ru(1)-P(1)	2.349(3)	Ru(1)-P(2)	2.359(2)
Ru(1)-P(3)	2.394(3)	Ru(1)-P(4)	2.394(2)
P(1)-C(1)	1.869(8)	P(1)-C(16)	1.840(7)
P(1)-C(26)	1.837(8)	P(2)-C(2)	1.841(10)
P(2)-C(36)	1.842(8)	P(2)-C(46)	1.827(7)
P(3)-C(3)	1.876(8)	P(3)-C(56)	1.857(7)
P(3)-C(66)	1.827(7)	P(4)-C(4)	1.843(10)
P(4)-C(76)	1.831(7)	P(4)-C(86)	1.847(7)
C(1)-C(2)	1.521(12)	C(3)-C(4)	1.523(12)
Bond angles (°)			
Cl(1)-Ru(1)-Cl(2)	173.3(1)	Cl(1)-Ru(1)-P(1)	83.5(1)
Cl(2)-Ru(1)-P(1)	90.1(1)	Cl(1)-Ru(1)-P(2)	84.5(1)
Cl(2)-Ru(1)-P(2)	92.6(1)	P(1)-Ru(1)-P(2)	81.8(1)
Cl(1)-Ru(1)-P(3)	98.1(1)	Cl(2)-Ru(1)-P(3)	88.2(1)
P(1)-Ru(1)-P(3)	178.2(1)	P(2)-Ru(1)-P(3)	97.8(1)
Cl(1)-Ru(1)-P(4)	101.2(1)	Cl(2)-Ru(1)-P(4)	81.7(1)
P(1)-Ru(1)-P(4)	98.3(1)	P(2)-Ru(1)-P(4)	174.3(1)
P(3)-Ru(1)-P(4)	81.9(1)	Ru(1)-P(1)-C(1)	109.1(3)
Ru(1)-P(1)-C(16)	122.1(2)	C(1)-P(1)-C(16)	100.7(3)
Ru(1)-P(1)-C(26)	118.5(3)	C(1)-P(1)-C(26)	103.7(4)
C(16)-P(1)-C(26)	100.0(3)	Ru(1)-P(2)-C(2)	105.9(3)
Ru(1)-P(2)-C(36)	118.6(3)	C(2)-P(2)-C(36)	104.5(4)
Ru(1)-P(2)-C(46)	123.2(3)	C(2)-P(2)-C(46)	100.5(4)
C(36)-P(2)-C(46)	101.4(3)	Ru(1)-P(3)-C(3)	108.1(3)
Ru(1)-P(3)-C(56)	127.9(2)	C(3)-P(3)-C(56)	97.3(3)
Ru(1)-P(3)-C(66)	115.0(2)	C(3)-P(3)-C(66)	104.3(3)
C(56)-P(3)-C(66)	101.0(3)	Ru(1)-P(4)-C(4)	104.5(4)
Ru(1)-P(4)-C(76)	120.7(2)	C(4)-P(4)-C(76)	103.5(4)
Ru(1)-P(4)-C(86)	124.5(2)	C(4)-P(4)-C(86)	99.0(3)
C(76)-P(4)-C(86)	100.7(3)	P(1)-C(1)-C(2)	114.2(6)
P(2)-C(2)-C(1)	110.4(6)	P(3)-C(3)-C(4)	112.1(6)
P(4)-C(4)-C(3)	107.7(6)	P(1)-C(16)-C(1))	120.2(2)
P(1)-C(16)-C(15)	119.8(2)	P(1)-C(26)-C(21)	119.6(2)
P(1)-C(26)-C(25)	120.4(2)	P(2)-C(36)-C(31)	122.0(3)
P(2)-C(36)-C(35)	118.0(3)	P(2)-C(46)-C(41)	122.1(2)
P(2)-C(46)-C(45)	117.9(2)	P(3)-C(56)-C(51)	119.4(2)
P(3)-C(56)-C(55)	120.5(2)	P(3)-C(66)-C(61)	120.0(2)
P(3)-C(66)-C(65)	119.9(2)	P(4)-C(76)-C(71)	120.7(2)
P(4)-C(76)-C(75)	119.2(2)	P(4)-C(86)-C(81)	120.6(2)
P(4)-C(86)-C(85)	119.4(2)		

centrosymmetric cell which was assigned to the $P\bar{1}$ space group. Phenyl rings were refined as rigid idealized polygons (C-C = 1.395Å) including hydrogen atoms placed in idealized positions with fixed isotropic $U = 0.08Å^2$. Two reflections (1,0,0) and −1,0,1) suffered from extinction, and were therefore omitted during the refinement process. For the final cycle, maximum shift/$\sigma = 0.002$ with minimum and maximum residual electron densities of −0.68eÅ^{-3} and 0.95eÅ^{-3}. Atomic coordinates, bond lengths and angles are listed in Tables 4 and 5.

RESULTS AND DISCUSSION

Dichlorobis(1,2-bis(diphenylphosphino)ethane)Ru(II), (**1**)

This complex (Figure 1) possesses a *trans* octahedral stereochemistry with two chloride ligands coordinating axially and the chelating dppe ligands occupying equatorial sites. Bonds to the Cl$^-$ ligands measure 2.445(3) and 2.417(3)Å for Ru-Cl(1) and Ru(1)-Cl(2), respectively, and bonds to the P atoms range from a minimum of 2.349(3) to a maximum of 2.394(3)Å. (Ru-P average 2.374(3)Å). The Ru atom is displaced just slightly (0.077Å) from the least-squares plane defined by the four P atoms to which it is attached. Small deviations from ideal octahedral geometry are most noticeably evident within the interaxial angles associated with the coordination sphere of the Ru atom. The Cl(1)-Ru(1)-Cl(2) atoms define an angle of 173.3(1)°, and within the five-membered rings formed by the chelating dppe ligands the interaxial angles are

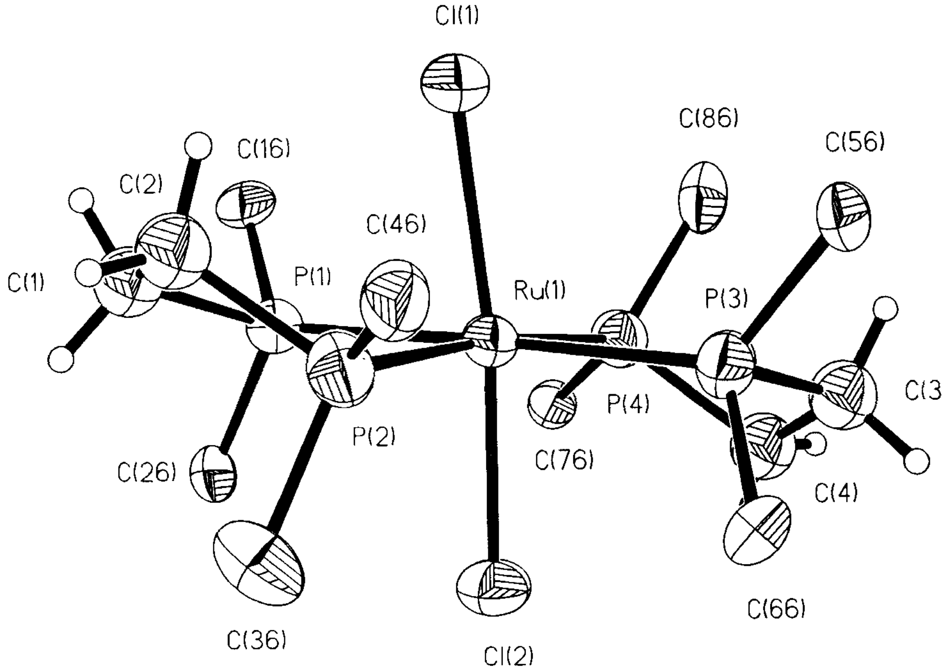

Figure 1 A perspective view of **1** illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level and phenyl rings have been omitted for clarity.

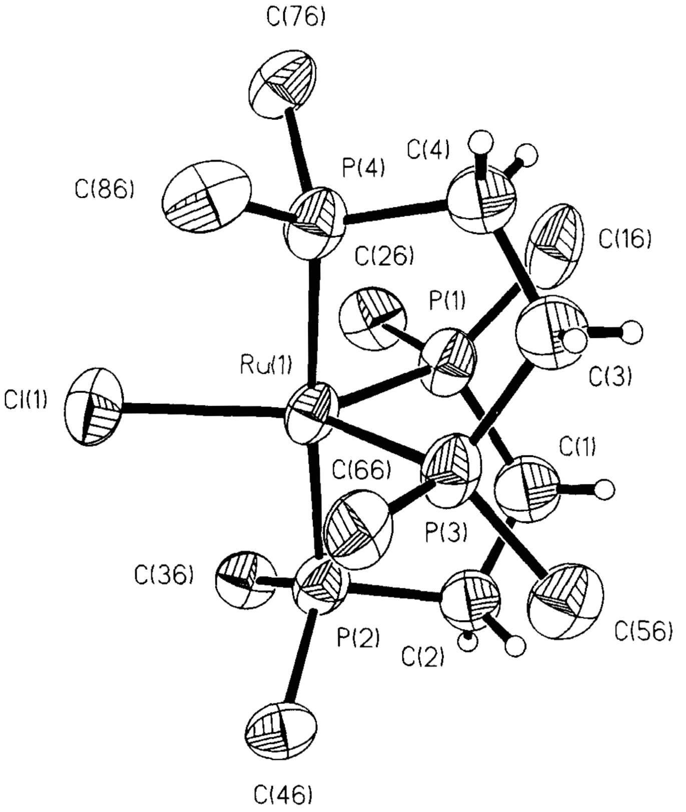

Figure 2 A perspective view of **2** illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. Phenyl rings are not shown in order to highlight the coordination geometry. Not shown also is the BF_4^- counterion.

acute (81.8(1) and 81.9(1)° for P(1)-Ru(1)-P(2) and P(3)-Ru(1)-P(4), respectively). Many of the structural features of this complex are similar to those observed in the structure of *trans*-$RuCl_2(PPhMe(CH_2)_2PPhMe)$, particularly the chelate bite angle which, in that complex, displayed a value of 82.7°.[13]

The ^{31}P NMR spectrum of this complex shows a sharp singlet at 39.85 ppm, consistent with the *trans* stereochemistry observed in the solid state. These values are shifted significantly downfield relative to free dppe, and while we found small peak at −10.39 ppm indicative of a small amount of free triphenylphosphine, we found no evidence for the presence of any of the *cis* isomer.

[*Chlorobis(1,2-bis(diphenylphosphino)ethane)Ru(II)*][BF_4], (**2**)

Square-pyramidal coordination geometry has been predicted to be favoured for low-spin d^6 transition metal complexes.[14,15] We find, however, that our complex possesses a trigonal-bipyramidal structure in the solid state with the P atoms of the dppe ligands occupying both equatorial and axial sites. Bonds to the axial P atoms are longer, on the average, by 0.040Å compared with those occupying equatorial

Table 4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **2**

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)*
Ru(1)	313(1)	3564(1)	2922(1)	41(1)
Cl(1)	−152(3)	3616(3)	4349(2)	63(2)
P(1)	975(4)	2141(3)	2023(2)	52(2)
P(2)	2337(4)	3164(3)	2757(2)	49(2)
P(3)	211(4)	4875(3)	2017(2)	51(2)
P(4)	−1685(4)	3964(3)	3000(2)	50(2)
F(1)	6530(21)	−1335(19)	1891(13)	126(13)
F(2)	5805(20)	−2564(23)	1831(12)	132(15)
F(3)	5829(18)	−1353(15)	880(13)	95(11)
F(4)	7448(15)	−2635(14)	994(10)	76(8)
F(5)	6019(15)	2059(18)	805(13)	95(10)
F(6)	5327(20)	738(15)	663(14)	121(12)
F(7)	5245(24)	2104(22)	−97(14)	128(16)
F(8)	6920(19)	836(33)	−184(16)	218(22)
B(1)	6470(44)	−2082(39)	1425(28)	72(12)
B(2)	5969(47)	1479(43)	248(32)	82(12)
C(1)	2474(14)	2101(13)	1362(9)	66(5)
C(2)	3076(12)	2756(12)	1705(8)	52(4)
C(3)	−866(13)	4857(12)	1502(8)	58(4)
C(4)	−1803(13)	4282(12)	1997(8)	53(4)
C(11)	467(11)	2127(10)	574(7)	85(10)
C(12)	−172	1914	96	119(15)
C(13)	−1054	1391	410	117(15)
C(14)	−1299	1081	1201	89(11)
C(15)	−660	1294	1679	70(9)
C(16)	223	1818	1366	67(8)
C(21)	1705(11)	−161(9)	2115(6)	93(11)
C(22)	1909	−1156	2504	115(13)
C(23)	1613	−1148	3334	119(14)
C(24)	1114	−146	3776	94(10)
C(25)	909	849	3387	61(7)
C(26)	1205	841	2557	58(7)
C(31)	2806(9)	2160(7)	4120(6)	63(8)
C(32)	3262	1293	4555	74(9)
C(33)	3921	271	4174	76(9)
C(34)	4124	117	3357	69(8)
C(35)	3668	984	2921	66(8)
C(36)	3009	2005	3303	49(7)
C(41)	2290(8)	5007(8)	3585(6)	58(8)
C(42)	2701	5889	3721	72(9)
C(43)	3750	6021	3215	88(11)
C(44)	4389	5270	2573	96(11)
C(45)	3978	4388	2438	69(9)
C(46)	2929	4256	2944	52(7)
C(51)	2059(12)	5783(9)	1435(6)	73(9)
C(52)	3018	5994	864	85(10)
C(53)	3349	5556	86	103(12)
C(54)	2720	4908	−119	91(10)
C(55)	1761	4697	453	70(8)
C(56)	1430	5135	1230	62(8)
C(61)	−356(10)	6289(7)	3361(6)	68(8)
C(62)	−704	7325	3751	87(10)
C(63)	−1041	8283	3351	100(11)
C(64)	−1031	8204	2560	113(12)
C(65)	−683	7167	2169	92(10)

Table 4 *Continued*

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)*
C(66)	−345	6210	2569	55(7)
C(71)	−2065(8)	2144(8)	3867(6)	57(7)
C(72)	−2552	1256	4088	74(9)
C(73)	−3375	1095	3746	87(10)
C(74)	−3711	1821	3184	83(10)
C(75)	−3224	2709	2963	81(10)
C(76)	−2401	2870	3304	54(7)
C(81)	−3190(9)	4978(7)	4451(6)	68(8)
C(82)	−4006	5846	4950	80(9)
C(83)	−4389	6869	4636	84(9)
C(84)	−3955	7025	3824	80(9)
C(85)	−3139	6157	3325	71(8)
C(86)	−2756	5133	3639	55(7)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5 Geometrical data for **2**

Bond lengths (Å)

Ru(1)-Cl(1)	2.400(4)	Ru(1)-P(1)	2.245(4)
Ru(1)-P(2)	2.368(5)	Ru(1)-P(3)	2.243(4)
Ru(1)-P(4)	2.371(5)	P(1)-C(1)	1.875(16)
P(1)-C(16)	1.810(16)	P(1)-C(26)	1.844(12)
P(2)-C(2)	1.829(13)	P(2)-C(36)	1.854(10)
P(2)-C(46)	1.806(13)	P(3)-C(3)	1.836(19)
P(3)-C(56)	1.820(12)	P(3)-C(66)	1.828(9)
P(4)-C(4)	1.832(15)	P(4)-C(76)	1.812(12)
P(4)-C(86)	1.841(9)	F(1)-B(1)	1.302(62)
F(2)-B(1)	1.202(57)	F(3)-B(1)	1.544(56)
F(4)-B(1)	1.258(44)	F(5)-B(2)	1.271(68)
F(6)-B(2)	1.426(61)	F(7)-B(2)	1.304(64)
F(8)-B(2)	1.279(51)	C(1)-C(2)	1.499(26)
C(3)-C(4)	1.561(22)		

Bond angles (°)

Cl(1)-Ru(1)-P(1)	131.6(1)	Cl(1)-Ru(1)-P(2)	92.3(1)
P(1)-Ru(1)-P(2)	80.1(2)	Cl(1)-Ru(1)-P(3)	133.7(1)
P(1)-Ru(1)-P(3)	94.7(1)	P(2)-Ru(1)-P(3)	97.8(2)
Cl(1)-Ru(1)-P(4)	91.3(1)	P(1)-Ru(1)-P(4)	97.6(2)
P(2)-Ru(1)-P(4)	176.5(1)	P(3)-Ru(1)-P(4)	79.7(2)
Ru(1)-P(1)-C(1)	110.7(6)	Ru(1)-P(1)-C(16)	126.4(4)
C(1)-P(1)-C(16)	105.0(7)	Ru(1)-P(1)-C(26)	108.3(4)
C(1)-P(1)-C(26)	103.3(6)	C(16)-P(1)-C(26)	100.5(6)
Ru(1)-P(2)-C(2)	106.5(6)	Ru(1)-P(2)-C(36)	118.8(4)
C(2)-P(2)-C(36)	104.3(5)	Ru(1)-P(2)-C(46)	119.0(3)
C(2)-P(2)-C(46)	104.4(6)	C(36)-P(2)-C(46)	102.2(5)
Ru(1)-P(3)-C(3)	112.7(5)	Ru(1)-P(3)-C(56)	126.4(4)
C(3)-P(3)-C(56)	103.7(6)	Ru(1)-P(3)-C(66)	106.7(3)
C(3)-P(3)-C(66)	104.7(6)	C(56)-P(3)-C(66)	100.2(5)
Ru(1)-P(4)-C(4)	107.5(5)	Ru(1)-P(4)-C(76)	117.6(4)
C(4)-P(4)-C(76)	104.7(7)	Ru(1)-P(4)-C(86)	120.3(5)
C(4)-P(4)-C(86)	104.5(5)	C(76)-P(4)-C(86)	100.7(5)
F(1)-B(1)-F(2)	106.5(36)	F(1)-B(1)-F(3)	101.3(31)

Table 5 *Continued*

Bond angles (°), *continued*

F(2)-B(1)-F(3)	106.4(42)	F(1)-B(1)-F(4)	113.8(46)
F(2)-B(1)-F(4)	119.0(41)	F(3)-B(1)-F(4)	108.0(34)
F(5)-B(2)-F(6)	103.4(37)	F(5)-B(2)-F(7)	107.7(38)
F(6)-B(2)-F(7)	102.2(45)	F(5)-B(2)-F(8)	118.1(52)
F(6)-B(2)-F(8)	103.8(41)	F(7)-B(2)-F(8)	119.1(46)
P(1)-C(1)-C(2)	113.0(10)	P(2)-C(2)-C(1)	113.0(10)
P(3)-C(3)-C(4)	111.8(10)	P(4)-C(4)-C(3)	112.7(12)
P(1)-C(16)-C(11)	121.6(4)	P(1)-C(16)-C(15)	118.3(4)
P(1)-C(26)-C(21)	118.8(3)	P(1)-C(26)-C(25)	121.2(3)
P(2)-C(36)-C(31)	118.5(3)	P(2)-C(36)-C(35)	121.5(3)
P(2)-C(46)-C(41)	118.8(3)	P(2)-C(46)-C(45)	121.1(3)
P(3)-C(56)-C(51)	117.1(4)	P(3)-C(56)-C(55)	122.8(4)
P(3)-C(66)-C(61)	121.1(3)	P(3)-C(66)-C(65)	118.8(3)
P(4)-C(76)-C(71)	118.1(4)	P(4)-C(76)-C(75)	121.8(4)
P(4)-C(86)-C(81)	118.6(3)	P(4)-C(86)-C(85)	121.4(3)

sites. The length of the bond to Cl(1) in this structure is shorter than either of the Ru-Cl bonds observed in the structure of **1** (Ru(1)-Cl(1) = 2.400(4)Å) but compares favourably with that observed in the X-ray crystal structure of the trigonal-bipyramidal [RuCl(dcpe)$_2$]$^+$ cation (Ru-Cl = 2.386(3)Å), as well as two square-pyramidal Ru(II) complexes where an average Ru-Cl bond length of 2.390(4)Å was found.[16,17]

The P(2)-Ru(1)-P(4) atoms in this structure are essentially collinear (176.5(1)°). However, substantial deviations from ideal trigonal bipyramidal geometry are evident in the interaxial angles associated with atoms located at equatorial sites. Thus we find in this complex that the Cl-Ru-P angles are obtuse (Cl(1)-Ru(1)-P(1) = 131.6(1)°; Cl(1)-Ru(1)-P(3) = 133.7(1)°), whereas the angle defined by the P(1)-Ru(1)-P(3) atoms is nearly orthogonal (94.7(1)°). Similar patterns of bond lengths and angles have been observed in the structure of Ir(dppe)$_2$CO and have been attributed to steric interactions involving the *ortho* H atoms of the phenyl rings.[18]

Although fluxional behaviour is frequently the norm for five coordinate complexes, the presence of chelating ligands might be expected to increase the stereochemical rigidity of the complex. ^{31}P NMR data for the complex described here shows a pair resonance with quite different chemical shifts centred at 79.02 ppm and 50.79 ppm. The peak at 79.02 ppm was present as a sharp singlet, whereas that at 50.79 ppm was observed as a triplet ($J\text{-}J_{P\text{-}P} = 11.5$ Hz). Fluxional behaviour has been documented in other five-coordinate complexes of Ru(II) containing bidentate phosphines, however, the sharp resonances observed in this complex suggest we are observing only one species in solution.[8]

Although these data are consistent with the trigonal-bipyramidal geometry observed in the solid state, it could be argued that a similar spectrum would be obtained for a complex possessing a square-pyramidal structure with some degree of distortion in the basal plane as, for example, in the structure of RuCl$_2$(PPh$_3$)$_3$. In the latter case, however, the differences in the ^{31}P NMR chemical shifts would not be expected to be very great. Since rather large chemical shifts are observed in the ^{31}P NMR spectrum of the complex described here, it suggests that the trigonal-bipyramidal geometry observed in the solid state also persists in solution, at least when non-coordinating solvents are involved.

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Supplementary Data

Lists of structure factors, anisotropic thermal parameters, and hydrogen atoms coordinates are available from the authors upon request.

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