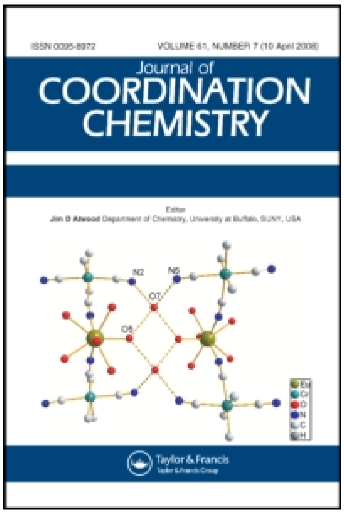

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NOTE: THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS[1,3-BIS(DIPHENYLPHOSPHINO) PROPANE] DICHLORORUTHENIUM (II)

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NOTE

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS[1,3-BIS(DIPHENYLPHOSPHINO) PROPANE] DICHLORORUTHENIUM (II)

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The title compound, *trans*-[Ru(dppp)$_2$Cl$_2$], crystallizes in the triclinic space group $P\bar{1}$, with a = 9.529(1), b = 11.071(1), c = 11.936(1)Å, α = 71.967(9), β = 72.879(6), γ = 88.703(9)°, V = 1141.1(2)Å^3 and Z = 1. The structure was solved and refined to a final R = 0.039, for 3126 independently observed reflections with $I > 3\sigma(I)$. The ruthenium(II) ion is located on a crystallographic centre of symmetry and shows a distorted octahedral coordination with the chloride atoms in an exactly *trans* configuration.

KEYWORDS: Ruthenium(II), diphosphine, X-ray structure

INTRODUCTION

Several ruthenium (II) complexes with diphosphine ligands have been previously reported.[1-8] Interest in their study arises from their potential use as catalysts.[9,10] In this paper we present the structure of the complex *trans*-[Ru(dppp)$_2$Cl$_2$], obtained in the course of our study of the electrochemical oxidation pathway in the synthesis of five coordinated di(tertiary phosphine) ruthenium compounds.[11]

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EXPERIMENTAL

trans-[Ru(dppp)$_2$Cl$_2$] was synthesized according to the previously described method[2] and recrystallized from a CH$_2$Cl$_2$/ether solution by slow evaporation. A single crystal of approximate dimensions 0.15 × 0.15 × 0.05 mm was used for data collection and cell parameter determination on an Enraf-Nonius CAD-4 diffractometer, with graphite-monochromatized CuKα radiation at room temperature (T = 25°C). Unit cell parameters were obtained by least-squares calculations from the setting angles of 19 reflections. Intensity data were collected in the ω-2θ scan mode up to θ_{max} = 60° ($0 \leq h \leq 10$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$), with scan rates between 1.41 and 5.5° min^{-1}. The intensity of one standard reflection was essentially constant throughout the experiment. Of the 3514 independent reflections measured, 3126 had $I > 3\sigma$ (I) and these were employed in the refinement procedure, which included 278 parameters. Data were corrected for Lp and absorption effects, with maximum and minimum correction factors $\bar{1}$.26 and 0.85, respectively, using the method of Walker and Stuart.[12]

The structure was solved using the heavy atom method and difference Fourier techniques. In the final cycles of least-squares refinement, all non-H atoms were

Table 1 Crystallographic and refinement data.

Crystal data	
Space group	$P\bar{1}$
a (Å)	9.529 (1)
b (Å)	11.071 (1)
c (Å)	11.936 (1)
α (°)	71.967 (9)
β (°)	72.879 (6)
γ (°)	88.703 (9)
V (Å^3)	1141.1 (2)
Mr	996.89
Z	1
D_x(g.cm^{-3})	1.451
λ (Cukα) (Å)	1.54056
μ (cm^{-1})	55.8
Crystal dimensions approx. (mm)	0.15 × 0.15 × 0.05
Data collection	
Mode	$\omega - 2\theta$
Scan rate (° min^{-1})	1.4, 5.5
θ range (°)	0-60
Range of *hkl*	$0 \leq h \leq 10$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$
Total reflections measured	3648
Unique reflections	3514
F(000)	513.0
Structure determination and refinement	
Reflections used $(I > 3\sigma(I))$]	3126
No. of variables	278
R, *Rw*	0.039, 0.043
Max. shift/e.s.d.	0.001
Max., min. density in final difference map (e Å^3)	0.92, −0.58
S	1.28
Max., min. absorption corr.	1.26, 0.85

treated anisotropically; all H-atoms were then included as fixed contributors with one refined common isotropic temperature factor [4.6(2)Å^2]. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$, where $w^{-1} = \sigma^2(Fo) + 0.0003Fo^2$, and the refinement converged to final $R = 0.039$, $Rw = 0.043$ and $S = 1.28$ [$S = (\Sigma w(|Fo| - |Fc|)^2/(M - N))^{1/2}$, where M = number of observations, N = number of refined parameters]. In the final refinement cycle, the maximum shift-to-e.s.d. ratio was 0.001 and the maximum and minimum electron densities in the difference map were 0.92 and − 0.58 e,A^3, respectively. Scattering factors for non-H atoms were taken from Cromer and Mann[13] with corrections for anomalous dispersion from Cromer and Liberman[14] for H atoms Stewart, Davidson and Simpson[15]. All calculations were performed with the program SHELX76.[16] Data collection and refinement parameters are summarized in Table 1. The atomic coordinates for non-H atoms are given in Table 2, and the relevant interatomic distances and angles are listed in Table 3. Figure 1 is a projection of the molecule showing the atom numbering scheme (drawn with ORTEP[17].) Listings of thermal parameters,

Table 2 Final atomic coordinates and isotropic temperature factors (Å^2).

Atom	*X/A*	Y*B*	*Z/C*	B_{iso}*
Ru	0	0	0	1.55 (2)
Cl	0.2130 (1)	− 0.0084 (1)	0.0747 (1)	2.48 (5)
P (1)	− 0.1078 (1)	0.1053 (1)	0.1514 (1)	2.21 (5)
P (2)	0.1237 (1)	0.2069 (1)	− 0.1354 (1)	2.36 (5)
C (1)	0.0171 (5)	0.2254 (4)	0.1588 (4)	2.6 (2)
C (2)	0.0776 (5)	0.3385 (4)	0.0418 (4)	2.7 (2)
C (3)	0.1930 (5)	0.3024 (4)	− 0.0562 (4)	2.8 (2)
C (111)	− 0.1516 (5)	0.0117 (4)	0.3163 (4)	2.7 (2)
C (112)	− 0.0474 (5)	− 0.0671 (4)	0.3540 (4)	3.1 (2)
C (113)	− 0.0694 (6)	− 0.1283 (5)	0.4797 (5)	4.1 (3)
C (114)	− 0.1938 (6)	− 0.1143 (5)	0.5663 (4)	4.1 (3)
C (115)	− 0.2984 (6)	− 0.0366 (5)	0.5303 (4)	4.3 (3)
C (116)	− 0.2778 (6)	0.0275 (5)	0.4050 (4)	3.5 (3)
C (121)	− 0.2749 (5)	0.1916 (4)	0.1468 (4)	2.6 (2)
C (122)	− 0.3926 (5)	0.1328 (4)	0.1334 (4)	2.8 (2)
C (123)	− 0.5208 (5)	0.1934 (5)	0.1283 (5)	3.5 (3)
C (124)	− 0.5320 (6)	0.3152 (5)	0.1347 (5)	3.9 (3)
C (125)	− 0.4186 (6)	0.3734 (4)	0.1502 (6)	4.5 (3)
C (126)	− 0.2902 (5)	0.3141 (4)	0.1565 (5)	3.6 (3)
C (211)	0.3022 (5)	0.2201 (4)	− 0.2569 (4)	2.9 (2)
C (212)	0.3154 (6)	0.2641 (5)	− 0.3831 (5)	4.0 (3)
C (213)	0.4534 (8)	0.2815 (6)	− 0.4691 (5)	5.6 (4)
C (214)	0.5778 (8)	0.2565 (6)	− 0.4353 (7)	6.2 (4)
C (215)	0.5659 (6)	0.2103 (6)	− 0.3115 (7)	5.6 (4)
C (216)	0.4298 (6)	0.1927 (5)	− 0.2225 (5)	4.0 (3)
C (221)	0.0217 (5)	0.3317 (4)	− 0.2133 (4)	2.9 (2)
C (222)	− 0.1310 (5)	0.3194 (4)	− 0.1778 (4)	3.3 (3)
C (223)	− 0.2095(6)	0.4174(5)	− 0.2298(5)	4.4(3)
C (224)	− 0.1370 (7)	0.5276 (5)	− 0.3175 (6)	5.1 (4)
C (225)	0.0149 (7)	0.5422 (5)	− 0.3521 (5)	5.2 (3)
C (226)	0.0950 (6)	0.4471 (5)	− 0.3009 (5)	4.3 (3)

$B_{iso} = \frac{4}{3}\sum_i \sum_j \beta_{ij} a_i \cdot a_j.$

Table 3 Selected interatomic distances (Å) and angles (°).

Ru	–	Cl	2.435 (1)	P (1)	–	C (111)	1.842 (4)
Ru	–	P (1)	2.416 (1)	P (1)	–	C (121)	1.844 (5)
Ru	–	P (2)	2.441 (1)	P (2)	–	C (3)	1.862 (5)
P (1)	–	C (1)	1.845(5)	P (2)	–	C (211)	1.857(5)
P (2)	–	C (3)	1.862 (5)	P (2)	–	C (221)	1.844 (5)
C (1)	–	C (2)	1.523 (6)	C (1)	–	C (2)	1.523 (6)
C (2)	–	C (3)	1.499 (6)	C (2)	–	C (3)	1.499 (6)
P (1)	–	C (1)	1.845 (5)				

Cl	–	Ru	–	P (1)	84.60 (4)	C (1)	–	C (2)	–	C (3)	112.3 (4)
Cl	–	Ru	–	P (2)	81.64 (4)	C (1)	–	P (1)	–	C (111)	94.8 (2)
P (1)	–	Ru	–	P (2)	86.79 (4)	C (1)	–	P (1)	–	C (121)	102.0 (2)
Ru	–	P (1)	–	C (1)	114.9 (1)	C (111)	–	P (1)	–	C (121)	102.3 (2)
Ru	–	P (2)	–	C (3)	114.6 (1)	C (3)	–	P (2)	–	C (211)	94.8 (2)
P (1)	–	C (1)	–	C (2)	116.7 (3)	C (3)	–	P (2)	–	C (221)	96.9 (2)
P (2)	–	C (3)	–	C (2)	115.5 (3)	C (211)	–	P (2)	–	C (221)	103.0 (2)

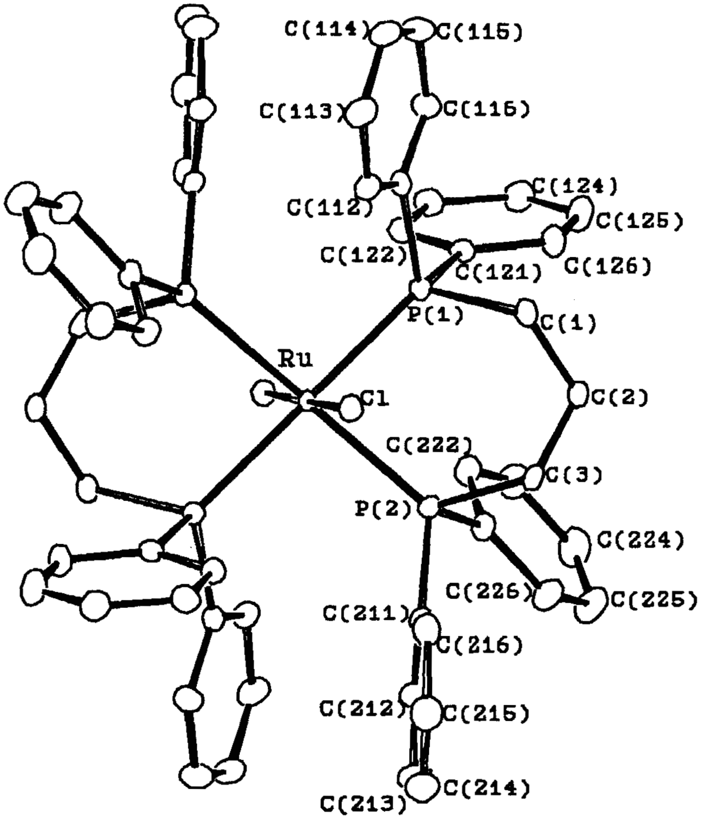

Figure 1 Perspective view of the molecule showing the atom labelling (except hydrogen atoms).

hydrogen atoms parameters, all bond distances and angles and the observed and calculated structure factors are available from the authors upon request.

RESULTS AND DISCUSSION

The ruthenium atom is sited on a crystallographic centre of inversion; therefore only half of the molecule is independently located in the asymmetric unit. The Ru(II) ion is bonded to two dppp groups through their phosphorous atoms, and to two chloride anions in a *trans* configuration, with a distorted octahedral coordination geometry.

Related structures have been described by Chakravarty *et al,*[18] *trans*-[Ru(dppm)$_2$Cl$_2$](1), and Lobana *et al.,*[19] *trans*-[Ru(dppe)$_2$Cl$_2$] (**2**), where dppm and dppe are bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane respectively. In both structures the ruthenium atom is also in a centrosymmetric position, with analogous coordination geometry. In all structures the Ru-Cl distances are very similar: 2.426(1) in (**1**), 2.436(1) in (**2**) and 2.435(1)Å in the present complex. It is noticeable that in each of the three structures, although the diphosphine ligands are symmetric, the Ru-P bond distances are slightly different: 2.340(1) and 2.367(1)Å in the dppm structure(**1**), 2.369(1) and 2.389(1)Å in the dppe structure (**2**) and 2.416(1) and 2.441(1)Å in the present dppp structure. As expected, the Ru-P bond distances increase proportionally to the length of the hydrocarbon chain between the diphosphines, due to the steric constraints imposed by the linkage on the conformation of the bidentate ligand.

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