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## Key indicators

Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å  
 $R$  factor = 0.047  
 $wR$  factor = 0.106  
Data-to-parameter ratio = 19.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Dichloro(4,4'-di-*tert*-butyl-2,2'-bipyridine- $\kappa^2N,N$ )bis(triphenylphosphine- $\kappa P$ )ruthenium(II)  
dichloromethane solvate

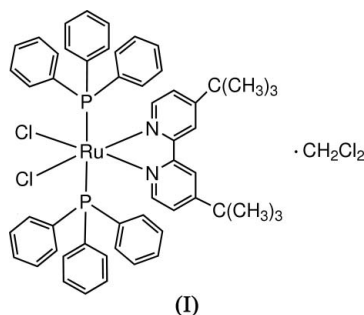
In the title ruthenium(II) mononuclear complex,  $[\text{RuCl}_2(\text{C}_{18}\text{H}_{24}\text{N}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})_2] \cdot \text{CH}_2\text{Cl}_2$ , the  $\text{Ru}^{\text{II}}$  ion exhibits an octahedral coordination environment consisting of the two *trans* P atoms of triphenylphosphine, the two chelating N atoms of 4,4'-di-*tert*-butyl-2,2'-bipyridine and the two *cis* Cl atoms. The average Ru–P, Ru–N and Ru–Cl bond lengths are 2.3736 (8), 2.043 (2) and 2.4518 (8) Å, respectively.

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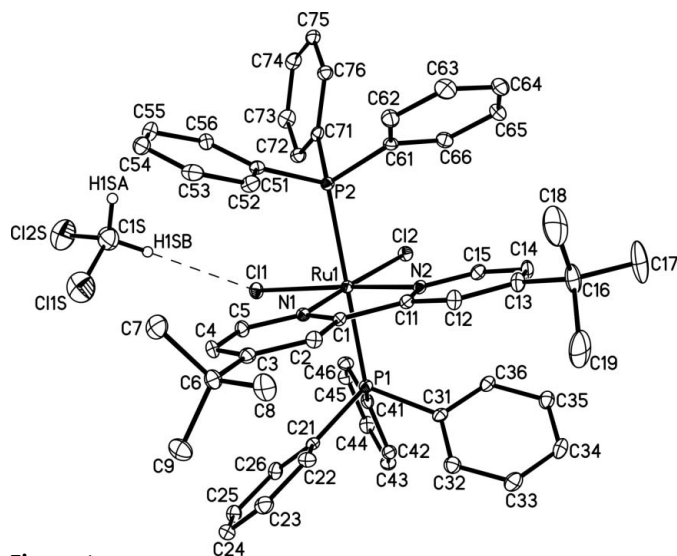
## Comment

Ruthenium(II) polypyridine complexes have been intensively investigated to date, not only to accumulate knowledge of the fundamental coordination chemistry (Juris *et al.*, 1988), electrochemistry (Lever, 1990), photochemistry, and photophysics of these complexes (Roundhill, 1994), but also to investigate the potential applicability of these complexes to energy conversion (Ward & Barigelletti, 2001), luminescent sensors (Dernas & DeGraff, 2001), electroluminescence displays (Gao & Bard, 2000), and biotechnology (Gray & Winkler, 1996). Ruthenium(II)–phosphine complexes have also been extensively studied from the viewpoint of their high catalytic properties (Noyori & Ohkuma, 1999) and potential uses as organometallic molecular wires and non-linear optical materials (Zhu *et al.*, 1999). It is therefore rather surprising that quite a few studies have been carried out for ruthenium(II) complexes with polypyridine and phosphine ligands (Rogers *et al.*, 2001; Batista *et al.*, 1995). Recently,  $[\text{Ru}(\text{PPh}_3)_2(\text{Me}_2\text{bipy})\text{Cl}_2]$  ( $\text{Me}_2\text{bipy} = 4,4'$ -dimethyl-2,2'-bipyridine) (Adams, 2002), which has *trans* phosphine ligands and *cis* terminal Cl atoms, has been found to be a good starting material to react with acetylide to give bipyridyl–ruthenium–acetylide and –vinylidene complexes with interesting photocatalytic properties (Adams & Pope, 2004). In this paper, we describe the structural characterization of the title complex as the ruthenium–bipyridyl–phosphine analogue,  $[\text{RuCl}_2(R_2\text{bipy})(\text{PPh}_3)_2]$  ( $R = \text{H}$  and  $\text{Me}$ ) (Batista *et al.*, 1995; Adams, 2002).



(I)

The asymmetric unit of the crystal structure of the title compound, (I), consists of one  $[\text{RuCl}_2(\text{Bu}_2\text{bipy})(\text{PPh}_3)_2]$



**Figure 1**  
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Non-solvent H atoms have been omitted. The dashed line indicates a hydrogen bond.

molecule and one dichloromethane solvent molecule. The coordination geometry around the ruthenium center is approximately octahedral; the deviation is caused by the small bite angle of the bipyridyl ligand [ $\text{N1—Ru1—N2} = 79.32(10)^\circ$ ]. The two axial triphenylphosphine ligands are slightly bent away from a linear *trans* geometry [ $\text{P1—Ru1—P2} = 177.47(3)^\circ$ ]. Two Ru—P bonds are bent toward the space between two *cis* Cl atoms as a result of the steric bulk of the triphenylphosphine and bipyridine ligands, indicated by the average P—Ru—Cl angle [ $89.15(3)^\circ$ ] being smaller than the average P—Ru—N angle [ $90.97(7)^\circ$ ]. The average Ru—P bond length of 2.3737(8) Å is in agreement with those in related ruthenium(II) complexes, such as  $[\text{Ru}(\text{PPh}_3)_2(\text{MeIm})\text{Cl}_2]$  (MeIm = *N*-methylimidazole) [2.3741(6) Å; Batista *et al.*, 1995], *trans*- $[\text{Ru}(\text{PPh}_3)_2(3,5\text{-Me}_2\text{pz})\text{Cl}_2]$  (pz = pyrazole) [2.4116(6) Å; Chantapromma *et al.*, 2001] and  $[\text{Ru}(\text{PPh}_3)_2(\text{Me}_2\text{bipy})\text{Cl}(\text{C}\equiv\text{C}^t\text{Bu})]$  [2.3697(13) Å; Adams & Pope, 2004]. The two Ru—N bond lengths in (I) are comparable with those in  $[\text{Ru}(\text{bipy})\text{Cl}_3(\text{CH}_3\text{CN})]$  [2.047(3) and 2.054(3) Å; Heseck *et al.*, 2000], *trans*-(*P*)- $[\text{Ru}(\text{bipy})(\text{Me}_2\text{Pqn})_2][\text{PF}_6]_2$  ( $\text{Me}_2\text{Pqn}$  = 8-(dimethylphosphino)quinoline) [2.063(5) and 2.078(5) Å; Suzuki *et al.*, 2003] and that in  $[\text{Ru}(\text{PPh}_3)_2(\text{Me}_2\text{bipy})\text{Cl}(\text{C}\equiv\text{C}^t\text{Bu})]$  opposite chlorine [2.051(3) Å; Adams & Pope, 2004]. The two Cl atoms bind to the ruthenium in a *cis* arrangement, opposite to two N atoms of *t*Bu<sub>2</sub>bipy. The Ru—Cl bond lengths in (I) are normal. There is one intermolecular hydrogen-bond  $\text{C—H}(\text{CH}_2\text{Cl}_2)\cdots\text{Cl}(\text{Ru})$  weak interaction,  $\text{C1S—H1SB—Cl1}$ , with an H—Cl distance of 2.66 Å.

## Experimental

The title complex was synthesized by a modification of a literature method (Adams, 2002). To a  $\text{CH}_2\text{Cl}_2$  solution (25 ml) of  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  (105 mg, 0.11 mmol) was added one equivalent of *t*Bu<sub>2</sub>bipy (56 mg, 0.11 mmol). The mixture was stirred at room

temperature for 2 h during which time an orange solution was obtained. The solvent was pumped off and the residue was washed with hexane. The orange solid was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (1:5) to give block-shaped crystals.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.43 (s, 18H, *t*Bu), 6.29 (*d*, 6.2 Hz, 2H, bipy), 7.04–7.21 (*m*, 18H, Ph), 7.34 (*d*, 2.1 Hz, 2H, bipy), 7.44–7.57 (*m*, 12H, Ph), 8.45 (*d*, 6.2 Hz, 2H, bipy).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  24.65. MS (FAB):  $m/z$  965 ( $M^+ + 1$ ). Analysis calculated for  $\text{C}_{54}\text{H}_{54}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}\cdot\text{CH}_2\text{Cl}_2$ : C 62.9, H 5.33, N 2.67%; found: C 62.7, H 5.31, N 2.65%.

## Crystal data

$[\text{RuCl}_2(\text{C}_{18}\text{H}_{24}\text{N}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})_2]\cdot\text{CH}_2\text{Cl}_2$   
 $M_r = 1049.83$   
 Monoclinic,  $P2_1/n$   
 $a = 11.9856(7)$  Å  
 $b = 28.2762(16)$  Å  
 $c = 15.1591(9)$  Å  
 $\beta = 103.034(1)^\circ$   
 $V = 5005.2(5)$  Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.393$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5428 reflections  
 $\theta = 2.3\text{--}26.4^\circ$   
 $\mu = 0.63$  mm<sup>-1</sup>  
 $T = 100(2)$  K  
 Block, orange  
 $0.30 \times 0.12 \times 0.10$  mm

## Data collection

Bruker SMART CCD area-detector  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS, Sheldrick, 1996)  
 $T_{\text{min}} = 0.822$ ,  $T_{\text{max}} = 0.941$   
 30208 measured reflections

11425 independent reflections  
 8142 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -15 \rightarrow 8$   
 $k = -36 \rightarrow 36$   
 $l = -18 \rightarrow 19$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.106$   
 $S = 1.00$   
 11425 reflections  
 580 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0473P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.88$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ru1—N1	2.040(2)	Ru1—P1	2.3744(9)
Ru1—N2	2.046(2)	Ru1—Cl2	2.4470(8)
Ru1—P2	2.3730(8)	Ru1—Cl1	2.4567(8)
N1—Ru1—N2	79.32(10)	P2—Ru1—Cl2	88.12(3)
N1—Ru1—P2	90.72(7)	P1—Ru1—Cl2	89.90(3)
N2—Ru1—P2	90.09(7)	N1—Ru1—Cl1	92.32(7)
N1—Ru1—P1	91.43(7)	N2—Ru1—Cl1	171.63(7)
N2—Ru1—P1	91.63(7)	P2—Ru1—Cl1	89.75(3)
P2—Ru1—P1	177.47(3)	P1—Ru1—Cl1	88.82(3)
N1—Ru1—Cl2	173.26(7)	Cl2—Ru1—Cl1	94.32(3)
N2—Ru1—Cl2	94.04(7)		

All H atoms were found in difference density maps, but were then placed in calculated positions ( $\text{C—H} = 0.99\text{--}1.00$  Å) and included in the refinement using the riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1998); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXTL.

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