# (Acetonitrile)(4′-phenyl-2,2′:6′,2″-terpyridine)-bis(tri-*n*-butylphosphine)ruthenium(II) bis(hexafluorophosphate) dichloromethane solvate

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.005 Å
H-atom completeness 98%
Disorder in main residue
$R$ factor = 0.050
$wR$ factor = 0.146
Data-to-parameter ratio = 11.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[Ru(C_2H_3N)(C_{21}H_{15}N_3)(C_{12}H_{27}P)_2](PF_6)_2 \cdot CH_2Cl_2$, the Ru atom is located in a distorted octahedral environment. The cation lies on a crystallographic twofold rotation axis. The terpyridine Ru—N distances are in the range 1.951 (3)–2.082 (2) Å and the acetonitrile Ru—N distance is 2.053 (4) Å.

## Comment

The chemistry of $[Ru(terpy)(PPh_3)_2]^{2+}$ (terpy is 2,2′:6′,2″-terpyridine) and its derivatives has recently received considerable attention due to their reversible redox properties. They are excellent building blocks for the preparation of binuclear ruthenium compounds, as models for molecular wires and other nanoscale devices (Al-Noaimi *et al.*, 2004; Gao *et al.*, 2005). Aiming at fine-tuning metal–metal communication in binuclear ruthenium compounds, one of the feasible approaches is to modify the ancillary ligands by changing their electronic and/or steric effects. With this in mind, we attempted to replace $PPh_3$ with $PBu^n_3$. Thus, the title compound, (I), was synthesized and isolated.



(I)
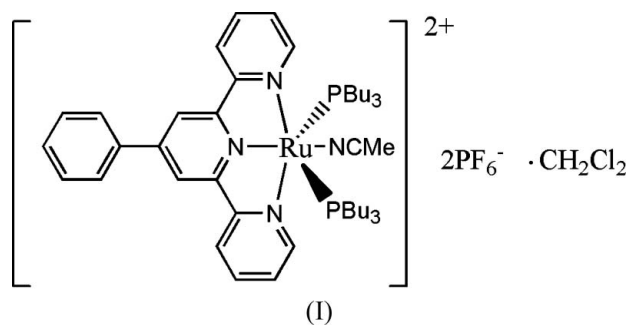
The coordination environment around the Ru atom in (I) (Fig. 1) is distorted octahedral. The 4′-phenyl-2,2′:6′,2″-terpyridine (Ph-terpy) ligand is coordinated to the ruthenium center in a meridional fashion. A crystallographic twofold rotation axis passes through Ru, N2, N3, C01, C02, C8, C9 and C12. The three pyridyl rings in the Ph-terpy are almost coplanar, but the phenyl ring makes a dihedral angle of 29.2 (3)° with the least-squares plane of terpyridine. The two $PBu^n_3$ ligands are coordinated in a *trans* fashion. The acetonitrile is linear. The distortion of the octahedral geometry around the Ru centre is due to the small bite angle of the Ph-terpy ligand [N1—Ru—N2 = 79.16 (7)° *cf.* N1—Ru—N3 = 100.84 (7)°]. This also results in different Ru—N distances among the central and outer pyridyl rings [Ru—N2 = 1.951 (3) Å, which is much shorter than that of Ru—N1 = 2.084 (3) Å]. The acetonitrile Ru—N distance is 2.053 (4) Å,

which is slightly longer than those reported previously (Yoshikawa *et al.*, 2005; Venegas-Yazigi *et al.*, 2000).

## Experimental

[Ru(Ph-terpy)(PBu$^n_3$)$_2$Cl]ClO$_4$ was synthesized by a similar procedure to those described in the literature (Sullivan *et al.*, 1980; Lomprey & Selegue, 1992). The title complex, (I), was prepared as follows: [Ru(Ph-terpy)(PBu$^n_3$)$_2$]Cl (0.05 mmol) was dissolved in MeCN (50 ml), then AgClO$_4$ (0.05 mmol) was added. The mixture was refluxed with stirring for 1 h. The solution was cooled to room temperature and filtered. To the filtrate, a saturated aqueous solution of KPF$_6$ (20 ml) was added. A red product precipitated which was collected by vacuum filtration. Red single crystals were grown by layering acetonitrile on to a dichloromethane solution.

### Crystal data

[Ru(C$_2$H$_3$N)(C$_{21}$H$_{15}$N$_3$)-  
(C$_{12}$H$_{27}$P)$_2$](PF$_6$)$_2$·CH$_2$Cl$_2$  
$M_r = 1230.96$  
Monoclinic, $C2/c$  
$a = 18.9433 (13)$ Å  
$b = 20.9992 (13)$ Å  
$c = 15.4852 (10)$ Å  
$\beta = 95.120 (3)°$

$V = 6135.3 (7)$ Å$^3$  
$Z = 4$  
$D_x = 1.333$ Mg m$^{-3}$  
Mo $K\alpha$ radiation  
$\mu = 0.52$ mm$^{-1}$  
$T = 293 (2)$ K  
Prism, red  
$0.70 \times 0.40 \times 0.20$ mm

### Data collection

Rigaku Mercury CCD diffractometer  
$\varphi$ and $\omega$ scans  
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2000)  
$T_{min} = 0.714$, $T_{max} = 0.904$

19100 measured reflections  
5404 independent reflections  
4961 reflections with $I > 2\sigma(I)$  
$R_{int} = 0.025$  
$\theta_{max} = 25.0°$

### Refinement

Refinement on $F^2$  
$R[F^2 > 2\sigma(F^2)] = 0.050$  
$wR(F^2) = 0.146$  
$S = 1.13$  
5404 reflections  
487 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0866P)^2 + 6.6163P]$  
where $P = (F_o^2 + 2F_c^2)/3$  
$(\Delta/\sigma)_{max} = 0.001$  
$\Delta\rho_{max} = 0.79$ e Å$^{-3}$  
$\Delta\rho_{min} = -0.71$ e Å$^{-3}$

## Table 1
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ru—N2 | 1.952 (4) | F2—P2 | 1.574 (6) |
| Ru—N3 | 2.052 (4) | F4—P2 | 1.549 (6) |
| Ru—N1$^i$ | 2.084 (3) | N3—C01 | 1.106 (6) |
| Ru—P1$^i$ | 2.4035 (9) | C1—C2 | 1.372 (5) |
| F1—P2 | 1.527 (5) | | |
| N2—Ru—N3 | 180.0 | C22—C21—P1 | 124 (2) |
| N2—Ru—N1 | 79.15 (7) | C21—C22—C23 | 111 (2) |
| N1—Ru—N1$^i$ | 158.29 (15) | C24—C23—C22 | 112 (2) |
| N2—Ru—P1 | 92.41 (2) | F1—P2—F4 | 89.9 (5) |
| P1$^i$—Ru—P1 | 175.19 (4) | F4—P2—F6 | 177.1 (6) |
| C29—P1—C21 | 105.1 (18) | F1—P2—F2 | 90.0 (4) |
| C29—P1—C25 | 105 (3) | N3—C01—C02 | 180.000 (1) |

Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.

H atoms attached to C were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.96 (CH$_3$), 0.97 (CH$_2$) or 0.93 Å (CH), and with $U_{iso}(H) = 1.5U_{eq}(CH_3)$ or $1.2U_{eq}(CH_2, CH)$. H atoms of the CH$_2$Cl$_2$ solvate were not located.
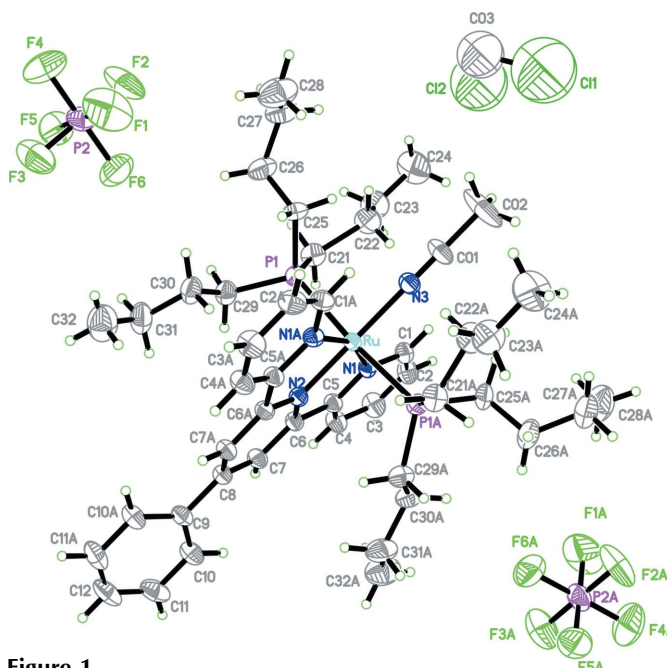


**Figure 1**  
A view of the structure of (I), showing 30% probability displacement ellipsoids and a partial atomic numbering scheme. H atoms of the CH$_2$Cl$_2$ solvate were not located. Only the major disorder components are shown. The suffix A indicates the symmetry position $-x, y, \frac{1}{2} - z$.

The disorder in the PF$_6^-$ anion and PBu$^n_3$ ligands was resolved into two partial-occupancy orientations. For one PF$_6^-$, the occupancy factors for two sets of F atoms were refined to 0.755 (8) and 0.245 (8). For the three Bu$^n$ groups in PBu$^n_3$, the occupancy factors were refined to 0.80 (2) and 0.20 (2), 0.646 (13) and 0.354 (13), and 0.52 (5) and 0.48 (5).

Data collection: *CrystalClear* (Rigaku/MSC, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

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