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dichlorobis(triphenylphosphine-*P*)-
ruthenium(II) 1.33-methanol
0.33-dichloromethane solvate**

diimine-*N,N'*)-

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**(*o*-Benzoquinone diimine-*N,N'*)-
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0.33-dichloromethane solvate**Diego Venegas-Yazigi,^{a*} Hameed Mirza,^b A. B. P. Lever,^b
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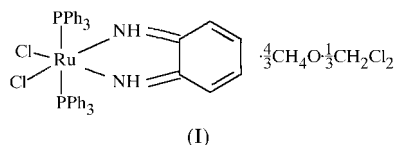
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The Ru atom in the title compound, $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\{\text{C}_6\text{H}_4(\text{NH})_2\}]\cdot 1.33\text{CH}_3\text{OH}\cdot 0.33\text{CH}_2\text{Cl}_2$, shows a six-coordinate octahedral geometry, with a *trans* arrangement of the triphenylphosphine groups. One and a half molecules of complex, two molecules of methanol and a half molecule of dichloromethane form the asymmetric unit, with crystallographic twofold rotation symmetry for the complex molecule in a special position.

Comment

In order to understand the bonding between ruthenium and redox-active (non-innocent) ligands (Auburn & Lever, 1990; Da Cunha *et al.*, 1996, 1999; Lever *et al.*, 1993; Masui, Auburn & Lever, 1993; Masui, Lever & Dodsworth, 1993; Masui *et al.*, 2000; Metcalfe *et al.*, 1993, 1996, 1999; Metcalfe & Lever, 1997), we have synthesized several complexes which contain the *o*-benzoquinone diimine (BQDI) ligand $\text{C}_6\text{H}_4(\text{NH})_2$ and ruthenium, forming $[\text{Ru}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\{\text{C}_6\text{H}_4(\text{NH})_2\}X_2]$, where *X* is chloride, acetonitrile, diethyldithiocarbamate *etc.* The title complex, (I), is the first member of this family to be crystallographically characterized.



Many crystal structures have been reported for ruthenium species containing the triphenylphosphine ligand and the chloride ligand (Anillo *et al.*, 1993; Batista *et al.*, 1994; Belser *et al.*, 1981; Del Zotto *et al.*, 1997; Jüstel *et al.*, 1998; La Placa & Ibers, 1965; Menon *et al.*, 1995; Syamala *et al.*, 1995) and there are several ruthenium species containing *o*-benzoquinone diimine in its quinoid or diamide form with reported crystal structures.

The asymmetric unit of (I) corresponds to one and a half $[\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\{\text{C}_6\text{H}_4(\text{NH})_2\}\text{RuCl}_2]$ molecules, two molecules of methanol and one half molecule of dichloromethane. The two non-equivalent ruthenium complex molecules are denoted 1A (Ru1A) and 1B (Ru1B). Both ruthenium centres present a distorted octahedral coordination geometry, with two diametrically opposed triphenylphosphine molecules at the axial positions and two *cis*-Cl⁻ ions and two *cis*-N atoms from the $\text{C}_6\text{H}_4(\text{NH})_2$ group in the four equatorial positions. The Ru atom in molecule 1B lies on a special position (type *a*) on a twofold axis, which bisects the Cl–Ru–Cl and N–Ru–N angles. There are no dramatic differences between molecules 1A and 1B. In the reference literature, it has been established that the non-innocent ligand $\text{C}_6\text{H}_4(\text{NH})_2$ may have two forms: the diamide form [with a formally single C–N bond and a delocalized bond (N)C=C(N)] and the quinoid form (with a formally double C=N bond and a single C–C bond) depending on several electronic and structural factors. The most important criteria used to distinguish between these two forms are Ru–N, N–C and (N)C–C(N) distances. A ‘short’ value of the Ru–N and N–C distances associated with a ‘long’ (N)C–C(N) distance is a clear sign of the quinoid form. The opposite case is related to the diamide form (Jüstel *et al.*, 1998). The values for the Ru–N distances are 1.979 (3) (Ru1A–N1A), 1.974 (3) (Ru1A–N2A) and 1.985 (3) Å (Ru1B–N1B); for the N–C distance are 1.322 (4) (N1A–C1A), 1.318 (4) (N2A–C2A) and 1.321 (3) Å (N1B–C1B); and for the (N)C–C(N) distance are 1.445 (5) (C1A–C2A) and 1.444 (7) Å [C1B–C1Bⁱ; symmetry code: (i) 2 – *x*, *y*, $\frac{1}{2}$ – *z*]. The average values are 1.979 (Ru–N), 1.320 (N–C) and 1.445 Å, which are well related to the described values for a ‘quinoid’ form, calculated from the structural data of four complexes [Ru–N 1.99 Å, N–C 1.32 Å and (N)C–C(N) 1.44 Å (Jüstel *et al.*, 1998)].

Experimental

Tris(triphenylphosphine)dichlororuthenium(II) and *o*-phenylenediamine were mixed (ratio 1:1.2) in ethanol under a nitrogen atmosphere and refluxed for 4 h. Once reflux was completed, the reaction mixture was cooled to room temperature and opened to air. A few drops of triethylamine were added and the mixture was stirred for 10 h under air. A red precipitate was isolated by filtration, washed with diethyl ether and dried under vacuum at 408 K over P_2O_5 for 5 h. To obtain crystals, a dichloromethane solution of the complex was placed in a tube 20 cm long. Methanol was carefully added to the tube to form two layers. The tube was sealed and left in the dark for 4 d. Deep-purple crystals were obtained as a result of the slow diffusion of the methanol into the dichloromethane layer.

Crystal data

[RuCl₂(C₁₈H₁₅P)₂(C₆H₆N₂)]·
1.33CH₄O·0.33CH₂Cl₂
M_r = 873.67
Monoclinic, C2/c
a = 47.7172 (11) Å
b = 10.3463 (2) Å
c = 33.7261 (8) Å
β = 133.694 (8)°
V = 12038.9 (5) Å³
Z = 12

D_x = 1.446 Mg m⁻³
Mo Kα radiation
Cell parameters from 39381
reflections
θ = 4.09–26.35°
μ = 0.686 mm⁻¹
T = 150 (2) K
Prism, purple
0.35 × 0.26 × 0.24 mm

Data collection

KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan
(DENZO-SMN; Otwinowski &
Minor, 1997)
T_{min} = 0.807, T_{max} = 0.862
39 381 measured reflections
12 170 independent reflections

8058 reflections with I > 2σ(I)
R_{int} = 0.067
θ_{max} = 26.35°
h = 0 → 59
k = 0 → 12
l = -42 → 30
Intensity decay: none

Refinement

Refinement on F²
R(F) = 0.041
wR(F²) = 0.106
S = 0.991
12170 reflections
701 parameters

H-atom parameters constrained
w = 1/[σ²(F_o²) + (0.0516P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.84 e Å⁻³
Δρ_{min} = -0.50 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ru1A–N2A	1.974 (3)	C2A–C3A	1.424 (5)
Ru1A–N1A	1.979 (3)	C3A–C4A	1.356 (5)
Ru1A–P2A	2.3976 (9)	C4A–C5A	1.422 (6)
Ru1A–P1A	2.4042 (9)	C5A–C6A	1.358 (5)
Ru1A–Cl2A	2.4372 (9)	Ru1B–N1B	1.985 (3)
Ru1A–Cl1A	2.4389 (9)	Ru1B–P1B	2.3996 (9)
N1A–C1A	1.322 (4)	Ru1B–Cl1B	2.4440 (9)
N2A–C2A	1.318 (4)	N1B–C1B	1.321 (4)
ClA–C6A	1.431 (5)	C1B–C6B	1.422 (4)
ClA–C2A	1.445 (5)	C5B–C6B	1.354 (5)
N2A–Ru1A–N1A	77.78 (12)	P2A–Ru1A–Cl2A	90.90 (3)
N2A–Ru1A–P2A	92.42 (8)	P1A–Ru1A–Cl2A	90.67 (3)
N1A–Ru1A–P2A	89.83 (8)	N2A–Ru1A–Cl1A	170.83 (8)
N2A–Ru1A–P1A	90.88 (8)	N1A–Ru1A–Cl1A	93.16 (9)
N1A–Ru1A–P1A	89.23 (8)	P2A–Ru1A–Cl1A	88.95 (3)
P2A–Ru1A–P1A	176.30 (3)	P1A–Ru1A–Cl1A	87.54 (3)
N2A–Ru1A–Cl2A	91.74 (8)	Cl2A–Ru1A–Cl1A	97.31 (3)
N1A–Ru1A–Cl2A	169.51 (9)		

By examination of difference Fourier maps, it became obvious there was a partial-occupancy disordered solvent molecule in the crystal structure. The crystals prepared for the analysis were grown from CH₂Cl₂ and methanol; therefore, either of these molecules was a possible choice. The pattern of the peaks in the difference Fourier did correspond with a severely disordered orientation of 0.5 of a dichloromethane molecule. Many attempts to model the disordered solvent molecule did not give reasonable values in the refinement. Accordingly, the contribution of the density of the disordered solvent molecule was subtracted from the measured structure factors using the SQUEEZE (van der Sluis & Spek, 1990) option in PLATON (Spek, 1999). Subsequent refinement converged with a lower R factor

than when attempts were made to model the disordered solvent. There were no significant changes to the geometry of the ruthenium-containing cations. It was possible to locate and refine two methanol solvent molecules in the lattice.

Data collection: KappaCCD Server Software (Nonius, 1997); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1997); program(s) used to refine structure: SHELXTL/PC; molecular graphics: SHELXTL/PC; software used to prepare material for publication: SHELXTL/PC.

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