

Carbonyl[1-(2-pyridylmethyl)-1,4,7-triazacyclononane- κ^4N](triphenylphosphine)ruthenium(II) dichloride dichloromethane sesquisolvate

Andrew L. Gott,
Patrick C. McGowan* and
Mark Thornton-Pett

Department of Chemistry, University of Leeds,
Woodhouse Lane, Leeds LS2 9JT, England

Correspondence e-mail:
patrickm@chem.leeds.ac.uk

Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(C-C)$ = 0.006 Å
Disorder in solvent or counterion
R factor = 0.045
wR factor = 0.105
Data-to-parameter ratio = 17.1

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

The title ruthenium–carbonyl complex, $[Ru(C_{12}H_{20}N_4)(C_{18}H_{15}P)(CO)]Cl_2 \cdot 1.5CH_2Cl_2$, crystallizes in the triclinic space group $P\bar{1}$ as a monomeric complex.

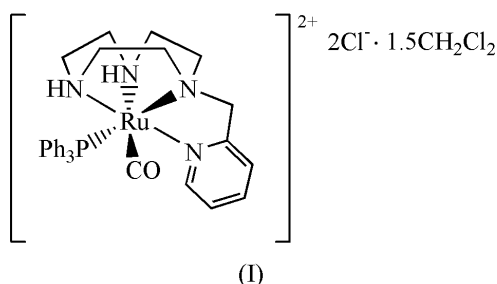
Received 18 September 2003

Accepted 8 October 2003

Online 15 October 2003

Comment

We have recently published the first studies of *N*-mono-functionalized 1,4,7-triazacyclononane complexes of ruthenium (Gott *et al.*, 2002, 2003). We have also investigated the reaction of such ligands with compounds of the general type $RuHClL_4$ (Gott & McGowan, 2003). Here we report the crystal structure of the product of a reaction between 1-(2-methylpyridyl)-1,4,7-triazacyclononane (McGowan *et al.*, 2001) and the ruthenium hydride $RuH_2(CO)(PPh_3)_3$. Ruthenium–carbonyl compounds supported by a 1,4,7-triazacyclononane ligand system are known in the literature (Yang, Cheng, Peng *et al.*, 1995; Ng *et al.*, 1998), and indeed ruthenium organometallics in general (Schröder, 1988; Yang, Cheng, Cheung *et al.*, 1995; Yang, Cheng, Peng *et al.*, 1995; Yang *et al.*, 1997, 1998; Lee *et al.*, 2000). However, this is the first reported example of a complex supported by a pendant-arm ligand system. The product is formed by the reaction of 1-(2-methylpyridyl)-1,4,7-triazacyclononane with $RuH_2(CO)(PPh_3)_3$ in toluene, followed by extraction with dichloromethane.



The title compound, (I), crystallized in the triclinic space group $P\bar{1}$. In addition to the dicationic complex, the asymmetric unit of the structure contains two chloride anions and one-and-a-half dichloromethane molecules of crystallization. The half molecule is disordered over a centre of inversion. The C and H atoms of this half molecule were set at 50% occupancy. The structure of the cation is that of a slightly distorted octahedron, as expected for a central d^6 ruthenium ion. The N–Ru–N bond angles are distorted from the ideal octahedral angle of 90° due to the somewhat constrained nature of the macrocyclic ligand, in which the *N*-donor atoms are ‘tied back’ with ethylene spacer units. The average Ru–N–Ru

bite angle in this case is 80.6°. The angle between the N atom of the macrocyclic ring and the N atom of the pendant pyridine arm donor [N1—Ru1—N12 = 79.20 (12)°] is slightly smaller due to the more strained nature of the interaction of the pendant arm with the ruthenium centre. The three Ru—N bond distances [Ru1—N1 = 2.136 (3) Å, Ru1—N4 = 2.167 (3) Å and Ru1—N7 = 2.113 (3) Å] are in agreement with expected values for general complexes of this type (Gott *et al.*, 2002, 2003); however, in the quoted reference, the values are more similar than in this instance. The fourth Ru—N bond, Ru1—N12 in this particular structure, is 2.120 (3) Å. This is in contrast with the first reported structure of this type, in which the pyridyl Ru—N bond of the pendant arm ligand is shorter than the Ru—N bonds involving the macrocycle (Gott *et al.*, 2002). As expected, the longest Ru—N bond (Ru1—N4) lies *trans* to the carbonyl ligand. The bond distance to the carbonyl C atom in this case (Ru1—C17) is 1.855 (4) Å, and the C17—O17 bond length is 1.146 (5) Å. Again, this bond length is in general agreement with other complexes published in the literature (Yang, Cheng, Peng *et al.*, 1995). The final coordination site is occupied by a triphenylphosphine ligand, where the Ru1—P1 bond distance is 2.3743 (10) Å.

Experimental

To a suspension of RuH₂(CO)(PPh₃)₃ in toluene was added 1-(2-methylpyridyl)-1,4,7-triazacyclononane. The grey suspension was refluxed for 18 h. After this time, the resulting pale-beige solid was isolated by filtration and extracted with dichloromethane. The resulting extracts were filtered, concentrated, and left to stand at room temperature, whereupon thin colourless plates formed after 1 week.

Crystal data

[Ru(C ₁₂ H ₂₀ N ₄)(C ₁₈ H ₁₅ P)- (CO)]Cl ₂ ·1.5CH ₂ Cl ₂	Z = 2
<i>M_r</i> = 809.96	<i>D_x</i> = 1.509 Mg m ⁻³
Triclinic, P1̄	Mo Kα radiation
<i>a</i> = 9.8492 (2) Å	Cell parameters from 34198 reflections
<i>b</i> = 12.7740 (3) Å	<i>θ</i> = 3.2–26.0°
<i>c</i> = 16.0631 (3) Å	<i>μ</i> = 0.89 mm ⁻¹
<i>α</i> = 74.5472 (14)°	<i>T</i> = 150 (2) K
<i>β</i> = 75.3838 (14)°	Plate, colourless
<i>γ</i> = 68.2566 (9)°	0.10 × 0.10 × 0.04 mm
<i>V</i> = 1782.47 (7) Å ³	

Data collection

Nonius KappaCCD area-detector diffractometer	6960 independent reflections
<i>φ</i> and <i>ω</i> scans	5492 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	<i>R</i> _{int} = 0.088
<i>T</i> _{min} = 0.916, <i>T</i> _{max} = 0.965	<i>θ</i> _{max} = 26.0°
34198 measured reflections	<i>h</i> = -12 → 12
	<i>k</i> = -15 → 15
	<i>l</i> = -19 → 19

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 2.9279P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.105$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.08	$\Delta\rho_{max} = 0.65 \text{ e } \text{Å}^{-3}$
6960 reflections	$\Delta\rho_{min} = -0.75 \text{ e } \text{Å}^{-3}$
406 parameters	
H-atom parameters constrained	

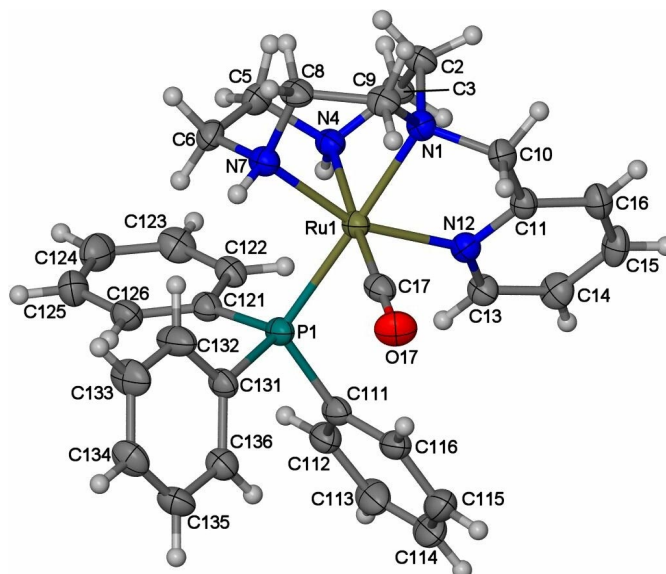


Figure 1

The molecular structure of complex (I). Chloride counter-anions and solvent of crystallization have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have arbitrary radii.

Table 1

Selected geometric parameters (Å, °).

Ru1—C17	1.855 (4)	Ru1—N4	2.167 (3)
Ru1—N7	2.113 (3)	Ru1—P1	2.3743 (10)
Ru1—N12	2.120 (3)	O17—C17	1.146 (5)
Ru1—N1	2.136 (3)		
N7—Ru1—N1	81.26 (12)	N7—Ru1—P1	97.28 (9)
N7—Ru1—N4	80.64 (12)	N12—Ru1—P1	102.10 (9)
N1—Ru1—N4	79.84 (12)	O17—C17—Ru1	178.1 (4)
C17—Ru1—P1	85.55 (12)		

One dichloromethane solvent molecule is disordered over a centre of inversion. The C atom was fixed at 50% occupancy and refined anisotropically. All H atoms were placed in calculated positions and refined using a riding model. The fixed distances were: N—H = 0.93 Å, alkyl C—H = 0.99 Å and aryl C—H = 0.95 Å. For all H atoms, *U*_{iso}(H) values were set at 1.2*U*_{eq}(C).

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XSeed (Barbour, 1999); software used to prepare material for publication: local program.

We thank the EPSRC for financial support

References

- Barbour, L. J. (1999). *XSeed*. University of Missouri, USA.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Gott, A. L. & McGowan, P. C. (2003). Unpublished results.
 Gott, A. L., McGowan, P. C., Podesta, T. J. & Tate, C. W. (2003). *Inorg. Chim. Acta*. In the press.
 Gott, A. L., McGowan, P. C., Podesta, T. J. & Thornton-Pett, M. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3619–3623.
 Lee, F. W., Choi, M. Y., Cheung, K. K. & Che, C. M. (2000). *J. Organomet. Chem.* **595**, 114–125.

- McGowan, P. C., Podesta, T. J. & Thornton-Pett, M. (2001). *Inorg. Chem.* **40**, 1445–1453.
- Ng, S. M., Fang, Y. Q., Lau, C. P., Wong, W. T. & Jia, G. (1998). *Organometallics*, **17**, 2052–2059.
- Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Schröder, M. (1988). *Pure Appl. Chem.* **60**, 517–524.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Yang, S. M., Chan, M. C. W., Cheung, K. K., Che, C. M. & Peng, S. M. (1997). *Organometallics*, **16**, 2819–2826.
- Yang, S. M., Chan, M. C. W., Peng, S. M. & Che, C. M. (1998). *Organometallics*, **17**, 151–155.
- Yang, S. M., Cheng, W. C., Cheung, K. K., Che, C. M. & Peng, S. M. (1995). *J. Chem. Soc. Dalton Trans.* pp. 227–230.
- Yang, S. M., Cheng, W. C., Peng, S. M., Cheung, K. K. & Che, C. M. (1995). *J. Chem. Soc. Dalton Trans.* pp. 2955–2959.