Acta Cryst. (1996). C**52**, 1105–1106

trans-Tetrakis(acetonitrile)dichloro-ruthenium(II), $[RuCl_2(MeCN)_4]$

MARK BOWN AND DAVID C. R. HOCKLESS

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, ACT 0200, Australia. E-mail: david@rschp1.anu.edu.au

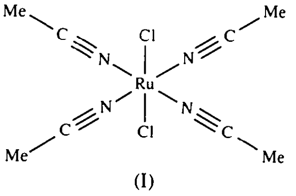
(*Received 21 June 1995; accepted 9 November 1995*)

Abstract

In accord with its optical and electrochemical properties, the title compound, $[RuCl_2(C_2H_3N)_4]$, displays tetragonal symmetry, with *trans* linear Cl coordination.

Comment

The title compound, (I), is a member of an extended substitutional series with the general formula $[Ru^{II}Cl_{6-n}(MeCN)_n]^{n-4}$ or $[Ru^{III}Cl_{6-n}(MeCN)_n]^{n-3}$ (n = 1–6), under examination in this laboratory. These redox-related families show orderly progressions in metal-centred electrode potentials and charge-transfer spectra as a function of stoichiometry and structure, and have provided a means of testing conflicting electronic theories of ligand additivity (Duff & Heath, 1991*a*,*b*). The title compound, (I), has been prepared by other routes (Gilbert, Rose & Wilkinson, 1970; Newton & Searles, 1973; Johnson, Lewis & Ryder, 1977), but it was obtained as a poorly soluble precipitate which was not suitable for X-ray structure determination. The synthesis of (I) by photolysis of $[RuCl_2(\eta^6\text{-}o\text{-}^n\text{Bu}_2C_6H_4)]_2$ in MeCN proceeds slowly and gives good quality crystals.



(I)

The pertinent bond lengths and angles in (I) are unexceptional and may be compared with those in $Et_4N[\textit{trans}\text{-}RuCl_4(MeCN)_2]$ (Gheller, Heath & Hockless, 1995). The linear arrangement of the *trans*-Cl—Ru—Cl, *trans*-N(1)—Ru—N(1) and *trans*-N(2)—Ru—N(2) fragments is crystallographically imposed as is the coplanarity of the four N atoms with the Ru-atom centre. The Ru—N(1)—C(1) and Ru—N(2)—C(3) angles are 172.7 (3) and 171.7 (3)°, respectively, and thus the bonding of the two crystallographically independent acetonitrile ligands is within the usual range for η^1-N-bonding (170–180°; Endres, 1987). The bonding within the acetonitrile ligands themselves is much closer to being linear [N(1)—C(1)—C(2) and N(2)—C(3)—C(4) being 178.7 (5) and 178.1 (4)°, respectively], as is the norm (Endres, 1987).

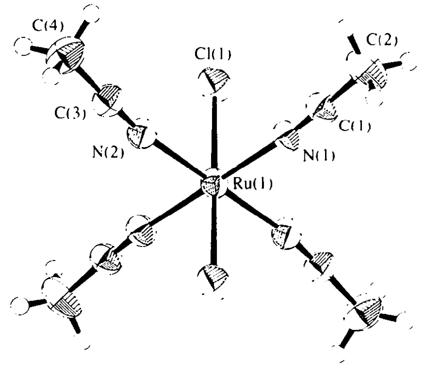


Fig. 1. Molecular structure of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as circles of arbitrary radii.

Experimental

The title compound was synthesized in 72% yield as a poorly soluble yellow solid by the photolytic displacement of *o*-di-*n*-butylbenzene from $[RuCl_2(\eta^6\text{-}o\text{-}^n\text{Bu}_2C_6H_4)]_2$ in acetonitrile. The latter was prepared similarly to its *p*-cymene analogue (Bennett, Huang, Matheson & Smith, 1982) as a poorly soluble solid in 66% yield by reaction of $RuCl_3.3H_2O$ with 1,2-di-*n*-butyl-1,4-cyclohexadiene in refluxing ethanol. A crystal suitable for X-ray analysis was grown from the reaction mixture by carrying the reaction out in sunlight in a 5 mm-o.d. Pyrex tube.

Crystal data

$[RuCl_2(C_2H_3N)_4]$
$M_r = 336.19$
Orthorhombic
Pbca
$a = 11.792\,(2)$ Å
$b = 8.563\,(2)$ Å
$c = 13.061\,(4)$ Å
$V = 1318.8\,(10)$ Å^3
$Z = 4$
$D_x = 1.693$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 11.5\text{–}17.0°$
$\mu = 1.569$ mm^{-1}
$T = 296\,(1)$ K
Block
0.20 × 0.20 × 0.12 mm
Orange

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical using azimuthal (ψ) scan data (North, Phillips & Mathews, 1968)
$T_{min} = 0.88$, $T_{max} = 1.00$
1377 measured reflections
1377 independent reflections

807 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 25.02°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = -15 \rightarrow 0$
3 standard reflections monitored every 150 reflections intensity decay: none

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

Refinement

Refinement on F
$R = 0.0208$
$wR = 0.0165$
$S = 1.577$
807 reflections
94 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.003F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru(1)	0	0	0	0.0320 (1)
Cl(1)	0.06866 (8)	0.1215 (1)	0.15448 (7)	0.0452 (3)
N(1)	0.0684 (2)	−0.2059 (3)	0.0436 (2)	0.0366 (9)
N(2)	−0.1402 (2)	−0.0682 (3)	0.0768 (2)	0.0363 (9)
C(1)	0.0955 (3)	−0.3246 (4)	0.0714 (3)	0.039 (1)
C(2)	0.1287 (4)	−0.4784 (6)	0.1094 (4)	0.057 (2)
C(3)	−0.2097 (3)	−0.1180 (4)	0.1256 (3)	0.038 (1)
C(4)	−0.2978 (4)	−0.1835 (6)	0.1922 (4)	0.053 (1)

Table 2. *Selected geometric parameters (Å, °)*

Ru(1)—Cl(1)	2.4101 (9)	N(2)—C(3)	1.123 (4)
Ru(1)—N(1)	2.021 (3)	C(1)—C(2)	1.461 (6)
Ru(1)—N(2)	2.020 (3)	C(3)—C(4)	1.466 (5)
N(1)—C(1)	1.125 (4)		
Cl(1)—Ru(1)—N(1)	90.39 (8)	Ru(1)—N(2)—C(3)	171.7 (3)
Cl(1)—Ru(1)—N(2)	90.92 (8)	N(1)—C(1)—C(2)	178.7 (5)
N(1)—Ru(1)—N(2)	93.7 (1)	N(2)—C(3)—C(4)	178.1 (4)
Ru(1)—N(1)—C(1)	172.7 (3)		

The θ-scan width was $(0.80 + 1.3\tan\theta)°$ at a speed of 4.0° min^{-1} (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak-to-background counting time. H atoms were refined isotropically. The structure was solved using heavy-atom Patterson methods (Beurskens *et al.*, 1992) and expanded using Fourier techniques (Beurskens *et al.*, 1992).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We wish to thank The Royal Society (UK) Australian Scheme for the award of a Postdoctoral Fellowship to MB, and Dr Graham Heath and Professor Martin Bennett for stimulating discussions and encouragement.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1049). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bennett, M. A., Huang, T. N., Matheson, T. W. & Smith, A. K. (1982). *Inorg. Synth.* **21**, 74–78.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Duff, C. M. & Heath, G. A. (1991*a*). *Inorg. Chem.* **30**, 2528–2535.

Duff, C. M. & Heath, G. A. (1991*b*). *J. Chem. Soc. Dalton Trans.* pp. 2401–2411.

Endres, H. (1987). *Comprehensive Coordination Chemistry*, Vol. 2, edited by G. Wilkinson, R. D. Gillard & J. A. McCleverty, pp. 261–267. Oxford: Pergamon Press.

Gheller, S. F., Heath, G. A. & Hockless, D. C. R. (1995). *Acta Cryst.* **C51**, 1805–1807.

Gilbert, J. D., Rose, D. & Wilkinson, G. (1970). *J. Chem. Soc. A*, pp. 2765–2769.

Johnson, B. F. G., Lewis, J. & Ryder, I. E. (1977). *J. Chem. Soc. Dalton Trans.* pp. 719–724.

Newton, W. E. & Searles, J. E. (1973). *Inorg. Chim. Acta*, **7**, 349–352.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Acta Cryst. (1996). **C52**, 1106–1110

Two Monomeric Ruthenium Complexes Containing Bidentate Bis(diphenylphosphino) Ligands

WAYNE H. PEARSON,[a] JOYCE E. SHADE,[a] JAMES E. BROWN[a] AND THOMAS E. BITTERWOLF[b]

[a]*Department of Chemistry, United States Naval Academy, Annapolis, Maryland 21402-5026, USA, and* [b]*Department of Chemistry, University of Idaho, Moscow, Idaho 83843, USA. E-mail: pearson@gold.nadn.navy.mil*

(*Received 6 January 1995; accepted 25 August 1995*)

Abstract

The crystal structures of chloro(η^5-cyclopentadienyl)[methylenebis(diphenylphosphine-*P*)]ruthenium–chloroform (1/1), [$RuCl(C_5H_5)(C_{25}H_{22}P_2)$].$CHCl_3$, (*A*), and chloro($\eta^5$-cyclopentadienyl)[1,2-ethanediylbis(diphenylphosphine-*P*)]ruthenium–chloroform (1/1), [$RuCl(C_5H_5)(C_{26}H_{24}P_2)$].$CHCl_3$, (*B*), are reported. Both complexes contain a central ring structure in which a pair of P atoms, linked by a —CH_2— [in (*A*)] or a —C_2H_4— [in (*B*)] group, are bonded to a central Ru atom. The P—Ru—P bond angle undergoes expansion from 72.07 (2)° in (*A*) to 83.48 (2)° in (*B*). The bond distances around the Ru center are compared with values reported for