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A Redetermination of the Crystal Structure of Bis(cyclopentadienyldicarbonylruthenium)

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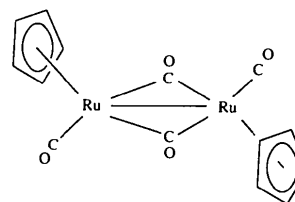
Abstract

The structure of *trans*-di- μ -carbonyl-bis[carbonyl-(η^5 -cyclopentadienyl)ruthenium], $[\{\text{Ru}(\text{C}_5\text{H}_5)\text{CO}\}_2(\mu\text{-CO})_2]$, has been redetermined from diffractometer data leading to considerably more accurate geometric parameters than those obtained in the original determination from film data.

Comment

Recently we have been investigating the use of the 'metalloligand' (η^5 -C₅H₅)RuCl{ η^1 -MeN(PF₂)₂}₂ (Mague & Lin, 1994) for the directed synthesis of ligand-bridged heterobimetallic complexes. On reacting this species [prepared from CpRuCl(CO)₂ (Eisenstadt, Tannenbaum & Efrati, 1981)] with RhCl(CO)(PMe₂Ph)₂, a small quantity of orange crystals was obtained, although little of the desired heterobimetallic complex appeared to have formed according to ³¹P NMR data for the crude reaction mixture. Presuming this to be the product, a structural study was initiated. From the unit cell obtained it was clear that this was not the case and a search of the Cambridge Structural Database showed that the crystals were in fact [Cp₂Ru₂(CO)₄], (1), which is a possible side product in the synthesis of CpRuCl(CO)₂, and was evidently present as a contaminant in the sample of the dicarbonyl used to prepare the 'metalloligand'. Noting that the original structure determination for (1) (Mills & Nice, 1967) was of low

quality (film data, $R = 0.097$), it was decided to continue with the structure determination in order to obtain more accurate structural parameters.



(1)

The quality of the present data set allowed for the refinement of anisotropic displacement parameters for all non-H atoms, as well as the location and refinement of all H atoms. While no substantial differences in the geometric parameters between the two structure determinations were found, an improvement in the e.s.d.'s by a factor of about four was realized, as was a greater uniformity in bond distances between comparable atoms. As a result of the improved accuracy, the apparent differences in the Ru—C(cyclopentadienyl) distances seen in the original determination now appear real, with Ru—C(5) and Ru—C(6) significantly shorter ($\Delta/\sigma = 11$ and 6, respectively) than the average of the other three Ru—C(cyclopentadienyl) bonds. At first sight, this could be taken to indicate a distortion of the bonding of the cyclopentadienyl group towards the 'allyl-ene' mode, but this is not supported by the C—C distances in the ring, which are equal within experimental error. Presumably it reflects more subtle electronic factors resulting from the low symmetry of the remainder of the coordination sphere. The Ru—Ru distance compares well with those found in a variety of related species, e.g.

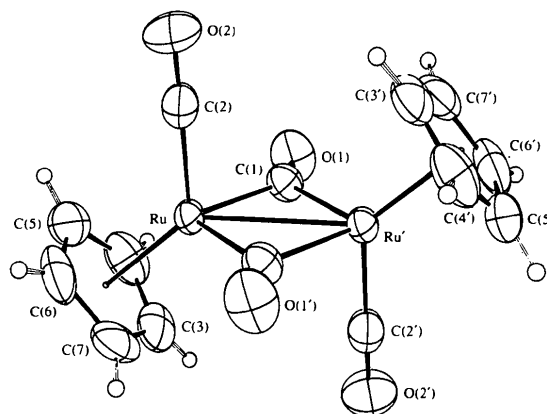


Fig. 1. A perspective view of *trans*-[Cp₂Ru₂(CO)₄], (1). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms while H atoms are represented by circles of arbitrary size. The primed atoms are related to the unprimed atoms by the crystallographic center of symmetry.

2.735 (1) Å in CpRu(CO)(μ-CH=CH₂)Ru(Me)Cp (Bruce, Gangnus, Garner, Know, Orpen & Phillips, 1990), 2.701 (1) Å in Cp₂Ru₂(μ-CMe₂)(μ-CHMe) (Colborn, Davies, Dyke, Knox, Mead, Orpen, Guerchais & Roué, 1989) and 2.703 (1) Å in CpRu(CO){μ-C(CF₃)=C(CF₃)H}(μ-CH=CH₂)Ru(Cp) (Brady, Dyke, Garner, Guerchais, Knox, Maher, Nicholls & Orpen, 1992). Both the {Ru₂(μ-CO)₂} core and the cyclopentadienyl ring are planar within experimental error and the dihedral angle between these weighted least-squares planes is 130.5 (2)°.

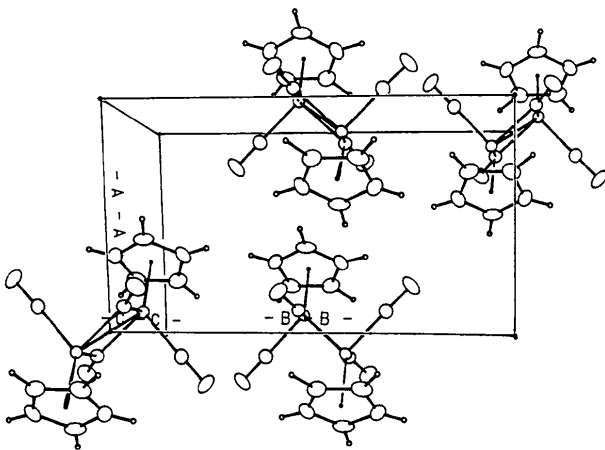


Fig. 2. Unit cell contents for *trans*-[Cp₂Ru₂(CO)₄] (1).

Experimental

The title complex was recrystallized from concentrated dichloromethane solution at 253 K

Crystal data

[Ru₂(C₅H₅)₂(CO)₄]

M_r = 444.37

Monoclinic

*P*2₁/*c*

a = 7.0888 (5) Å

b = 12.4846 (8) Å

c = 8.035 (1) Å

β = 104.208 (8)°

V = 689.3 (2) Å³

Z = 2

D_x = 2.14 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 12.13–17.94°

μ = 2.2 mm⁻¹

T = 293 K

Rectangular fragment

0.30 × 0.20 × 0.13 mm

Orange

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

ψ scans

T_{min} = 0.912, *T_{max}* = 0.999

1391 measured reflections

1215 independent reflections

1026 observed reflections

[*I* ≥ 2.0σ(*I*)]

R_{int} = 0.023

θ_{max} = 25.0°

h = 0 → 8

k = 0 → 14

l = -9 → 9

3 standard reflections

frequency: 120 min

intensity decay: 1.0%

Refinement

Refinement on *F*

R = 0.021

wR = 0.029

S = 1.07

1026 reflections

111 parameters

All H-atom parameters refined

w = 4*F*²/[σ²(*I*) + (0.04*F*²)²]

(Δ/σ)_{max} = 0.02

Δρ_{max} = 0.30 e Å⁻³

Δρ_{min} = -0.44 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

*B*_{iso} for H atoms; *B*_{eq} = (8π²/3)Σ_{*i*}Σ_{*j*}*U_{ij}a_i^{*}a_j^{*}* for all others.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} / <i>B</i> _{eq}
Ru	0.08938 (3)	0.06479 (2)	0.13357 (3)	2.418 (5)
C(1)	-0.1065 (5)	-0.0565 (2)	0.1151 (4)	3.01 (7)
O(1)	-0.1887 (4)	-0.1011 (2)	0.2039 (3)	4.89 (6)
C(2)	-0.1057 (5)	0.1667 (3)	0.0813 (5)	3.86 (7)
O(2)	-0.2251 (4)	0.2312 (2)	0.0503 (5)	6.68 (8)
C(3)	0.3502 (6)	-0.0261 (3)	0.2907 (6)	5.05 (9)
C(4)	0.2441 (6)	0.0102 (4)	0.4026 (5)	5.02 (9)
C(5)	0.2420 (6)	0.1213 (4)	0.3947 (5)	5.17 (9)
C(6)	0.3533 (6)	0.1535 (3)	0.2811 (5)	4.88 (9)
C(7)	0.4202 (5)	0.0613 (3)	0.2173 (5)	4.8 (1)
H(3)	0.380 (5)	-0.093 (3)	0.275 (5)	5.2 (9)
H(4)	0.179 (7)	-0.046 (3)	0.482 (6)	7 (1)
H(5)	0.174 (7)	0.163 (4)	0.454 (6)	9 (1)
H(6)	0.385 (6)	0.218 (3)	0.258 (5)	6 (1)
H(7)	0.502 (8)	0.070 (3)	0.140 (6)	7 (1)

Table 2. Selected geometric parameters (Å, °)

Primed atoms are related to unprimed atoms by the center of symmetry. C* represents the centroid of the cyclopentadienyl ring.

Ru—Ru	2.7377 (5)	Ru—C(4)	2.275 (4)
Ru—C(1)	2.036 (3)	Ru—C(5)	2.226 (4)
Ru—C(1')	2.034 (4)	Ru—C(6)	2.245 (4)
Ru—C(2)	1.850 (4)	Ru—C(7)	2.276 (4)
Ru—C(3)	2.270 (4)		
C(1)—Ru—C(2)	92.1 (2)	Ru—C(1)—Ru'	84.6 (3)
C(1)—Ru—C*	119.5 (1)	Ru'—C(1)—O(1)	137.4 (3)
C(2)—Ru—C*	129.0 (1)	Ru—C(1)—O(1)	138.1 (3)
Ru'—Ru—C(2)	93.0 (2)	Ru—C(2)—O(2)	178.9 (3)
Ru'—Ru—C*	138.0 (1)		

An empirical absorption correction based on ψ scans for three reflections with χ near 90° was applied to the data. Initial coordinates for the non-H atoms were those obtained in the previous determination (Mills & Nice, 1967). These were refined to near convergence with anisotropic displacement parameters for all non-H atoms by a full-matrix least-squares method and all H atoms were located from the resulting Δρ map. Refinement was completed on all atoms with the H atoms having isotropic displacement parameters. The average C—H distance is 0.95 (5) Å with the extreme values being 0.87 (5) [C(6)—H(6)] and 1.12 (5) Å [C(4)—H(4)].

Crystal orientation, unit-cell determination and refinement, and data collection: *CAD-4 Software* (Schagen, Staver, van Meurs & Williams, 1989). Data reduction, structure solution and refinement: *MolEN* (Fair, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976). All calculations were performed on a VAXstation 3100.

The support of the Tulane University Chemistry Department is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: BK1033). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trichlorotin(II)-(meso-Tetraphenylporphyrinato)rhodium(III), a Porphyrin Derivative with an Rh—Sn Bond

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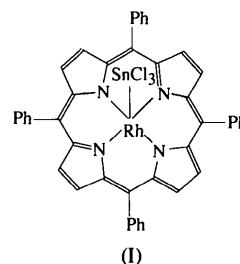
Abstract

The structure of the title compound, trichloro- $2\kappa^3Cl-(5,10,15,20\text{-tetraphenylporphyrinato-}1\kappa^4N^{21,22,23,24})\text{-rhodium(III)tin(II)(Rh—Sn)}$, $[\text{RhSnCl}_3(\text{C}_{44}\text{H}_{28}\text{N}_4)]$, consists of well separated units in which the Rh atom is five-coordinate at the center of a square-pyramidal polyhedron with the Sn atom at the top. The macrocyclic

unit is planar with the Rh atom displaced by only 0.02 Å from the ring plane. The Rh—Sn bond length is 2.450 (1) Å.

Comment

Metal–porphyrin derivatives containing metal–metal bonds have attracted interest because of their biological implications and their possible applications as unidirectional electron-conducting materials (Onaka *et al.*, 1985). We have reported the synthesis and spectroscopic characterization of $[(\text{TPP})\text{RhX}]$ derivatives, where X represents axial ligands containing different metal groups and TPP is tetraphenylporphyrinato (Boschi, Licocchia, Paolesse & Tagliatesta, 1988); while detailed structures of such complexes are not known, the true nature of the metal–metal bond may be a matter of debate. We report here the single-crystal X-ray characterization of the complex $[(\text{TPP})\text{RhSnCl}_3]$ (I).



Rh resides at the center of the TPP macrocyclic ligand; the environment of Rh is five-coordinate and is described as square-pyramidal with the —SnCl₃ ligand at the apex. The Rh atom is displaced by only 0.02 Å from the mean plane of the 16-atom core of the porphyrin, towards Sn; the largest deviations from this plane are –0.16 Å for C(16) and 0.18 Å for C(1). The Rh—Sn bond length [2.450 (1) Å] is outside the wide range (2.53–2.72 Å) of previously determined Rh—Sn distances (Hawkins, Hitchcock & Lappert, 1985; Balch, Hope & Wood, 1985; Chan & Marder, 1988; Veith, Stahl & Huch, 1989; Bott, Machell, Mingos & Watson, 1991) and this shorter distance could reflect a greater degree of Rh—Sn π bonding. The coordination geometry about the Sn atom is distorted from ideal tetrahedral, the Rh—Sn—Cl angles being 116.9 (1), 116.0 (2) and 114.8 (1)° and the Cl—Sn—Cl angles averaging 102.3 (1)°. The same feature is seen for other —SnCl₃ ligands coordinated to transition metals (Holt, Wilson & Nelson, 1989). The Rh—N mean distance of 2.02 Å is similar to those reported for other rhodium porphyrinates, such as $[(\text{EPI})\text{Rh}(\text{Me}_2\text{NH})_2]^+$ (Hanson, Gouterman & Hanson, 1973), $[(\text{OEP})\text{RhMe}]$ (Takenaka *et al.*, 1976) and $[(\text{EPD})\text{Rh}(\text{PHCO})]$ (Grigg, Trocha-Grimshaw & Henrick, 1982); furthermore, the bond lengths and angles in the porphyrinato core are in good agreement with those reported for several other metallo-