X-ray crystal structure of di-μ-carbonyldicarbonylbis(η^5-pentamethylcyclopentadienyl)diruthenium

A. S. Batsanov and Yu. T. Struchkov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

An X-ray diffraction study of $[(\eta^5\text{-}C_5Me_5)Ru(CO)(\mu\text{-}CO)]_2$ was performed, revealing its dimeric structure and centrosymmetric *trans* conformation. The Ru—Ru bond length (2.758(1) Å) and the separation between the Ru atom and the plane of the η^5-C_5Me_5 ligand (1.923 Å) are greater than those in the Cp analog and in the isostructural Cp and C_5Me_5 complexes of iron; this effect is due to the s inductive effect of the Me groups.

Key words: X-ray diffraction study; ruthenium(II) η-complexes; the metal—metal bond; the inductive effect.

It is known that the pentamethylcyclopentadienyl η^5-ligand Cp* differs essentially from the nonsubstituted cyclopentadienyl ligand (Cp) in its chemical behavior; in particular, the complexes with Cp* are substantially more stable.[1] Of interest is the manifestation of this difference in the geometry of the complexes of analogous structures, which differ only by the ligands Cp* and Cp. An X-ray diffraction study of $[CpFe(CO)(\mu\text{-}CO)]_2$ (**1a**)[2] and $[Cp^*Fe(CO)(\mu\text{-}CO)]_2$ (**1b**)[1] with regard to neutron diffraction study of **1a**[2] demonstrated that these compounds have nearly the same geometry. In this work, the crystal structure of $[Cp^*Ru(CO)(\mu\text{-}CO)]_2$ (**2b**) was studied in order to compare it with the known structure of $[CpRu(CO)(\mu\text{-}CO)]_2$ (**2a**).[3]

Results and Discussion

The molecular structure of **2b** is shown in Fig. 1; its geometric parameters are given in Table 1. The molecule occupies a special position in the inversion center of the unit cell, and, therefore, the Cp* and the terminal CO ligands have *trans* orientation with respect to the Ru—Ru' bond; the molecule has approximate (noncrystallographic) symmetry C_{2h}. The Ru atom is at the distance of 1.923 Å from the plane of the cyclopentadienyl ring (Cp*); the C(Cp)—C(Me) bonds are bent out of the ring plane in the opposite direction with respect to the metal atom by 2.8—6.0°.

A comparison of structures **1a** and **1b** indicates that when Cp is replaced by Cp*, the Fe—Fe bond and the Fe—Cp* distance are slightly lengthened (by 0.021 and 0.013 Å, respectively), whereas the Fe—CO bonds are virtually unchanged. Similarly, as one goes from **2a** to **2b**, the Ru—Ru and Ru—Cp* distances are lengthened (from 2.735(2) to 2.758(1) Å and from 1.910 to 1.923 Å, respectively), whereas the terminal Ru—CO bonds retain their lengths within experimental error (1.855(14) and 1.863(8) Å). Because the CH_3 groups in **1b** and **2b** induce no significant steric hindrance, the observed differences are completely attributable to the inductive σ effect of these groups, which is also confirmed by the fact that the geometric characteristics of **2b** and $[(C_5Me_4Et)Ru(CO)(\mu\text{-}CO)]_2$ (**3**)[4] are actually the same. Note, however, that the Ru—μ-CO bond lengths in **2a** and **2b** are significantly different (average values are 1.988(13) and 2.052(7) Å, respectively), though the poor accuracy of the structural study of **2a** by the photographic method casts some doubt on this difference.

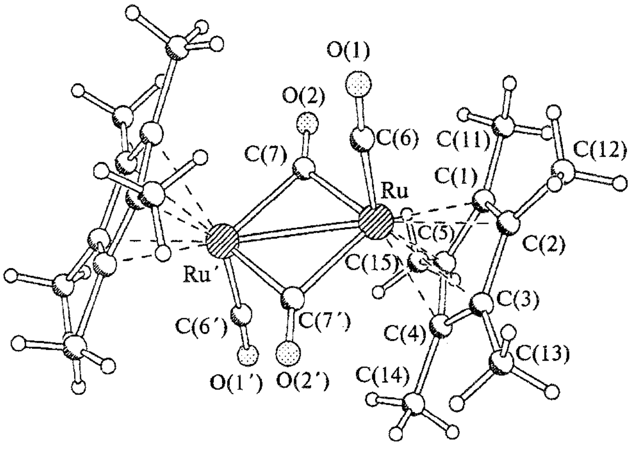

Fig. 1. The molecular structure of **2b**. Primed atoms are related to the basic atoms by an inversion center.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 543—544, March, 1994.

Table 1. Bond lengths and bond angles

Bond	d/Å	Bond	d/Å
Ru—C(1)	2.263(7)	O(2)—C(7)	1.162(8)
Ru—C(2)	2.240(7)	C(1)—C(2)	1.44(1)
Ru—C(3)	2.271(7)	C(1)—C(5)	1.42(1)
Ru—C(4)	2.303(7)	C(1)—C(11)	1.52(1)
Ru—C(5)	2.310(8)	C(2)—C(3)	1.429(9)
Ru—C(6)	1.863(8)	C(2)—C(12)	1.50(1)
Ru—C(7)	2.048(7)	C(3)—C(4)	1.45(1)
Ru—Ru′	2.758(1)	C(3)—C(13)	1.48(1)
Ru—C(7′)	2.055(7)	C(4)—C(5)	1.42(1)
Ru—Cp[a]	1.924	C(4)—C(14)	1.49(1)
O(1)—C(6)	1.14(1)	C(5)—C(15)	1.49(1)

Angle	ω/deg	Angle	ω/deg
C(6)—Ru—C(7)	91.6(3)	C(3)—C(2)—C(12)	126.7(6)
C(6)—Ru—Ru′	94.2(2)	C(2)—C(3)—C(4)	107.5(6)
C(7)—Ru—Ru′	47.8(2)	C(2)—C(3)—C(13)	126.9(6)
C(6)—Ru—C(7′)	94.0(3)	C(4)—C(3)—C(13)	125.3(6)
C(7)—Ru—C(7′)	95.5(2)	C(3)—C(4)—C(5)	107.8(6)
Ru′—Ru—C(7′)	47.6(2)	C(3)—C(4)—C(14)	125.5(7)
Cp—Ru—Ru′	138.4(2)	C(5)—C(4)—C(14)	126.2(7)
Cp—Ru—C(6)	127.4(3)	C(1)—C(5)—C(4)	108.7(6)
Cp—Ru—C(7)	120.6(3)	C(1)—C(5)—C(15)	124.5(7)
Cp—Ru—C(7′)	119.8(3)	C(4)—C(5)—C(15)	126.8(7)
C(2)—C(1)—C(5)	108.0(6)	Ru—C(6)—O(1)	175.5(8)
C(2)—C(1)—C(11)	125.4(7)	Ru—C(7)—O(2)	137.9(6)
C(5)—C(1)—C(11)	126.4(7)	Ru—C(7)—Ru′	84.5(2)
C(1)—C(2)—C(3)	108.1(6)	O(2)—C(7)—Ru′	137.5(6)
C(1)—C(2)—C(12)	124.9(6)		

[a] Cp is the center of the cyclopentadienyl ring.

The coordination of the Cp* ligand in **2b** deviates significantly from symmetric η^5 coordination, approaching pseudo-η^3 coordination. The shortest distance between Ru and C(Cp*) (2.240(7) Å) is observed for the C(2) atom, which is in the pseudo-*trans* position with respect to the Ru—Ru' bond; the atoms C(1) and C(3), which are opposite Ru—CO (bridging) bonds, are far removed from the Ru atom (on the average, by 2.267 Å); whereas the average distance from Ru to C(4) and C(5), which are opposite the Ru—CO (terminal) bond, is 2.307 Å. Hence, the Ru—C(Cp*) distances increase in parallel with the π accepting ability of the pseudo-*trans* ligands.[5] A similar effect is observed for complexes **1a**, **2a**, and **3**.

Table 2. Fractional atomic coordinates ($\times 10^4$ for O and C atoms and $\times 10^5$ for Ru atoms) and temperature factors (Å^2, $\times 10^3$ for O and C atoms and $\times 10^4$ for Ru atoms)

Atom	x	y	z	U[a]
Ru	570(5)	10748(6)	7302(3)	225(2)
O(1)	2950(6)	2166(8)	693(5)	57(2)
O(2)	995(6)	−2284(7)	1231(4)	44(2)
C(1)	−360(8)	1175(9)	2226(5)	32(2)
C(2)	−207(7)	2766(8)	1889(5)	28(2)
C(3)	−1309(7)	3059(8)	1124(5)	28(2)
C(4)	−2141(7)	1624(10)	987(5)	33(2)
C(5)	−1554(8)	492(9)	1674(5)	33(2)
C(6)	1862(8)	1699(10)	686(5)	35(2)
C(7)	576(7)	−1287(8)	698(5)	26(2)
C(11)	537(10)	419(13)	3078(6)	56(3)
C(12)	838(10)	3952(11)	2344(6)	48(3)
C(13)	−1645(9)	4585(10)	627(6)	43(3)
C(14)	−3479(8)	1465(12)	338(7)	51(3)
C(15)	−2107(12)	−1121(10)	1836(8)	59(4)

[a] 1/3 of the trace of the orthogonalized U_{ij} tensor.

Experimental

The X-ray diffraction study was performed on an automated four-circle Siemens P3/PC diffractometer (graphite-monochromated Mo-Kα radiation) at room temperature. Red crystals of **2b** (from THF) are monoclinic, a = 9.842(1), b = 8.384(1), c = 14.411(2) Å, β = 99.80(1)°, V = 1171.7(2) Å^3, Z = 4 ($C_{24}H_{30}O_4Ru_2$), mol. weight 584.6, d_{calc} = 1.66 g cm^{-3}, μ(Mo-Kα) = 13.2 cm^{-1}, F(000) = 588, space group $P2_1/n$. The intensities of 2411 independent reflections were measured using the $\theta/2\theta$ scanning technique ($2\theta \le 54°$), 2224 reflections with $I > 2\sigma(I)$ were used in calculations. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method using the SHELXTL PLUS program package.[6] Coordinates of all of the non-hydrogen atoms were refined anisotropically; all H atoms were refined using a riding model. The weighting scheme $w = \sigma^{-2}(F)$ was used. The final reliability factors are R = 0.045, R_w = 0.051, S = 3.27. Atomic coordinates are given in Table 2.

The authors wish to thank A. Z. Rubezhov and N. N. Zaitseva for providing the single crystals for the investigations.

References

1. R. G. Teller and J. M. Williams, *Inorg. Chem.*, 1980, **19**, 2770.
2. A. Mitschler, B. Rees, and M. S. Lehmann, *J. Am. Chem. Soc.*, 1978, **100**, 3390.
3. O. S. Mills and J. P. Nice, *J. Organomet. Chem.*, 1967, **9**, 339.
4. N. A. Baily, S. L. Radford, J. A. Sanderson, K. Tabatabian, C. White, and J. M. Worthington, *J. Organomet. Chem.*, 1978, **154**, 343.
5. A. S. Batsanov and Yu. T. Struchkov, *Metalloorg. Khim.*, 1992, **5**, 53 [*Organomet. Chem. USSR*, 1992, **5**, 26 (Engl. Transl.)].
6. G. M. Scheldrick, *SHELXTL PLUS, PC version*, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, 1989.

Received June 15, 1993