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Hexacarbonyl-1κ^4C,2κ^2C-[μ-1κC^6:2(η^5)-6-methylfulvene]diruthenium(*Ru*—*Ru*), [$Ru_2(C_5H_4CHCH_3)(CO)_6$]

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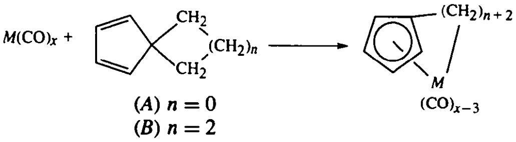
Abstract

The reaction of spiro[2.4]hepta-4,6-diene with [$Ru_3(CO)_{12}$] leads to the title compound, a diruthenium–fulvene complex which contains a μ-1κC:2(η^5)- (or, simplistically, μ-η^1:η^5-) $C_5H_4CHCH_3$ bridging ligand. The Ru—Ru distance is 2.7954 (8) Å, while Ru–ligand distances are: Ru—C(η^1) 2.232 (8) Å, average Ru—C(Cp) (Cp = cyclopentadienyl) 2.237 Å, average Ru—C(CO) 1.945/1.879 Å with/without *trans* influence. Excepting the methyl group, the molecule has approximate *m* point symmetry.

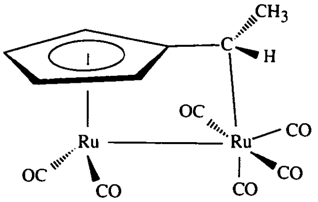
Comment

Reaction (1) below has been shown to be quite general for spiro[2.4]heptadiene (*A*) and spiro[4.4]nonadiene (*B*) with a variety of metal carbonyls (Eilbracht & Dahler, 1977; Braun, Dahler & Eilbracht, 1978). In an attempt to establish a new synthetic route for the insertion of Cp rings into Ru—Ru bonds, a reaction analogous to (1) between *A* and [$Ru_3(CO)_{12}$] was studied. We found that the insertion does take place, but with C—C bond cleavage resulting in the formation of a diruthenium fulvene complex and elimination of a $Ru(CO)_4$ unit.



(1)

The structure analysis of the reaction product showed that the crystal contains discrete molecules of [$Ru_2(C_5H_4CHCH_3)(CO)_6$], (I), which contain a μ-1κC:2(η^5)- (or, simplistically, μ-η^1:η^5-) C_5H_4CH moiety (Fig. 1). Excepting the methyl group, the molecule has approximate *m* point symmetry; the plane of symmetry defined by the Ru(1)—Ru(2)—C(1)—C(6) metallacycle makes a dihedral angle of 89.8° with the plane of the Cp ring.



The Ru(2)—C(1) distance is slightly, but not significantly, longer than the other four Ru—C(Cp) bond lengths. This elongation may be due to the strain imposed on the η^5 interaction by the Ru(2)—Ru(1)—C(6) bridge. A similar structural feature, with larger differences, has been observed in other Ru complexes containing a μ-η^1:η^5-C_5H_4 moiety, such as [Ru_2(6,6-diphenylfulvene)$(CO)_5(SbPh_3)$], (II) (Töfke, Haupt & Beherens, 1986), the only other Ru μ-η^1:η^5-fulvene complex structurally characterized so far, and in isolobal trinuclear analogues, such as [$Ru_3(C_5H_4)(CO)_9(PPh_3)$], (III) (Heineke & Vahrenkamp, 1993), and [$Ru_3(C_5H_4)(CO)_{10}$], (IV) (Arce, De Sanctis, Manzur & Capparelli, 1994). The Ru(1)—C(6) distance is intermediate between the equivalent bond length in (II) [2.29 (1) Å] and the Ru—C bond lengths observed for ligands with secondary alkyl substituents (*ca* 2.14–2.18 Å; Orpen *et al.*, 1989).

In the Cp ring the C(3)—C(4) distance is the shortest of the five C—C bonds. Although in the present study this shortening is not significant, it probably corresponds to a structural feature of the ring, since in (III), (IV) and binuclear complexes with a μ-η^1:η^5-C_5H_4 unit (Hoxmeier, Knobler & Kaesz, 1979, and references therein; Herrmann, Kriechbaum, Bauer, Guggolz & Ziegler, 1981) it was also observed that the C—C bond opposite to the σ-bonded C atom was the shortest of the ring. The C(1)—C(6) distance is consistent with partial double-bond character, when compared with the value

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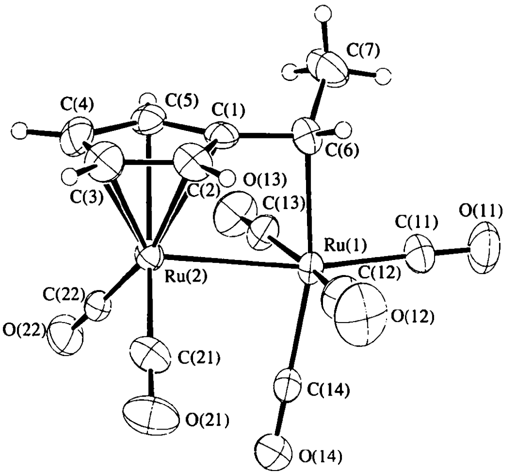

Fig. 1. Molecular structure of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at 30% probability.

of 1.513 (14) Å tabulated by Allen *et al.* (1987) for a similar single bond.

There are two distinctly different groups of Ru—C(CO) bond lengths: those involving C(12), C(13) and C(14) (average 1.945 Å), and the other three, which are significantly shorter (average 1.879 Å). The latter values are similar to the mean of 1.896 Å reported by Orpen *et al.* (1989), whereas the longer values are affected by the *trans* influence of the alkyl and carbonyl ligands (Appleton, Clark & Manzer, 1973; Shustorovich, Porai-Koshits & Buslaev, 1975). Similar distances were observed in (II) and (IV).

The carbonyl ligands show little variability in their geometry: all six C—O distances (average 1.134 Å) are within 0.037 Å of one another (*i.e. ca* four e.s.d.'s), while the corresponding Ru—C—O angles are within 3.7° (*i.e. ca* five e.s.d.'s) of 180°.

The ranges of *cis* [78.0 (2)–102.1 (3)°] and *trans* [166.2 (3)–170.4 (3)°] angles about Ru(1) reveal that the μ-Ru(2)—Cp—C(6) bridge produces a moderate distortion of the octahedral geometry.

Experimental

Spiro[2.4]hepta-4,6-diene was prepared by the method of Wilcox & Craig (1961). To a solution of $[Ru_3(CO)_{12}]$ (0.14 g, 0.22 mmol) in cyclohexane (30 ml), was added a tenfold excess of the prepared spiro[2.4]hepta-4,6-diene; this was heated under reflux under nitrogen for 16 h. Removal of the solvent *in vacuo* and TLC separation (SiO_2) yielded the title compound (I) (0.02 g, 20%) as a yellow solid. Crystals suitable for X-ray analysis were obtained by slow evaporation of a cyclohexane solution.

Crystal data

$[Ru_2(C_7H_8)(CO)_6]$
$M_r = 462.34$
Monoclinic
$P2_1/c$
$a = 13.256 (2)$ Å
$b = 8.644 (3)$ Å
$c = 13.484 (2)$ Å
$\beta = 103.23 (1)°$
$V = 1504.0 (7)$ Å^3
$Z = 4$
$D_x = 2.042$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 16.2–19.2°$
$\mu = 2.030$ mm^{-1}
$T = 295 (1)$ K
Prism
0.38 × 0.22 × 0.10 mm
Yellow

Data collection

AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan
$T_{min} = 0.771$, $T_{max} = 1.000$
3848 measured reflections
3696 independent reflections
2061 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0549$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 150 reflections
intensity decay: 8.25%

Refinement

Refinement on *F*
$R = 0.0368$
$wR = 0.0367$
$S = 1.962$
2061 reflections
198 parameters
Only H-atom *U*'s refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{max} = 0.0005$
$\Delta\rho_{max} = 1.67$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ 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 equivalent isotropic displacement parameters* (Å^2)

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

	x	*y*	*z*	U_{eq}
Ru(1)	0.18259 (5)	0.01135 (7)	−0.11478 (4)	0.0426 (2)
Ru(2)	0.32005 (5)	−0.11145 (7)	−0.22340 (4)	0.0413 (2)
O(11)	0.0543 (5)	0.1981 (8)	0.0019 (5)	0.101 (3)
O(12)	0.0133 (6)	−0.0323 (10)	−0.3099 (6)	0.126 (3)
O(13)	0.3751 (5)	0.0444 (7)	0.0590 (4)	0.080 (2)
O(14)	0.1528 (5)	−0.3192 (7)	−0.0403 (5)	0.074 (2)
O(21)	0.1845 (6)	−0.3778 (7)	−0.3179 (5)	0.093 (3)
O(22)	0.4429 (4)	−0.3056 (6)	−0.0524 (4)	0.068 (2)
C(1)	0.2999 (6)	0.1464 (8)	−0.2432 (5)	0.046 (2)
C(2)	0.2731 (7)	0.0726 (9)	−0.3396 (6)	0.058 (3)
C(3)	0.3623 (8)	−0.003 (1)	−0.3585 (6)	0.068 (3)
C(4)	0.4449 (7)	0.020 (1)	−0.2742 (7)	0.070 (3)
C(5)	0.4082 (6)	0.1116 (9)	−0.2013 (5)	0.050 (2)
C(6)	0.2287 (6)	0.2216 (9)	−0.1899 (6)	0.053 (3)
C(7)	0.2752 (8)	0.3528 (9)	−0.1197 (7)	0.078 (3)
C(11)	0.1010 (7)	0.1309 (10)	−0.0448 (7)	0.066 (3)
C(12)	0.0758 (7)	−0.018 (1)	−0.2389 (7)	0.072 (3)
C(13)	0.3044 (6)	0.0346 (9)	−0.0061 (6)	0.052 (3)
C(14)	0.1619 (6)	−0.1992 (9)	−0.0686 (6)	0.051 (3)
C(21)	0.2368 (7)	−0.2774 (9)	−0.2796 (6)	0.060 (3)
C(22)	0.3953 (6)	−0.2336 (8)	−0.1166 (6)	0.045 (2)

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

Ru(1)—Ru(2)	2.7954 (8)	C(1)—C(2)	1.417 (9)
Ru(1)—C(6)	2.232 (8)	C(1)—C(5)	1.449 (9)
Ru(2)—C(1)	2.253 (7)	C(1)—C(6)	1.464 (9)
Ru(2)—C(2)	2.219 (7)	C(2)—C(3)	1.42 (1)
Ru(2)—C(3)	2.231 (7)	C(3)—C(4)	1.40 (1)
Ru(2)—C(4)	2.241 (8)	C(4)—C(5)	1.43 (1)
Ru(2)—C(5)	2.239 (7)		

Ru(2)—Ru(1)—C(6)	78.0 (2)	C(11)—Ru(1)—C(14)	102.1 (3)
Ru(2)—Ru(1)—C(11)	169.2 (3)	C(12)—Ru(1)—C(13)	170.4 (3)
Ru(2)—Ru(1)—C(12)	86.2 (3)	C(12)—Ru(1)—C(14)	91.5 (4)
Ru(2)—Ru(1)—C(13)	84.5 (2)	C(13)—Ru(1)—C(14)	90.5 (3)
Ru(2)—Ru(1)—C(14)	88.2 (2)	Ru(1)—Ru(2)—C(1)	67.2 (2)
C(6)—Ru(1)—C(11)	91.7 (3)	Ru(1)—Ru(2)—C(21)	96.3 (3)
C(6)—Ru(1)—C(12)	86.3 (3)	Ru(1)—Ru(2)—C(22)	96.2 (2)
C(6)—Ru(1)—C(13)	89.5 (3)	C(21)—Ru(2)—C(22)	92.3 (3)
C(6)—Ru(1)—C(14)	166.2 (3)	Ru(2)—C(1)—C(6)	116.9 (5)
C(11)—Ru(1)—C(12)	96.5 (4)	Ru(1)—C(6)—C(1)	97.8 (4)
C(11)—Ru(1)—C(13)	92.2 (3)		

The absorption correction was based on ψ-scan measurements for five representative strong reflections. The structure was solved by Patterson methods (*DIRDIF*92; Beurskens *et al.*, 1992). H atoms were placed in calculated positions (C—H 0.96 Å) and assigned fixed coordinates and refined isotropic displacement parameters.

MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1993*a*) was used for data collection and cell refinement. The *TEXSAN* software package (Molecular Structure Corporation, 1993*b*) was used for all other calculations, molecular graphics and preparation of the material for publication.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Die Chloroindate $[PPh_4]_2[In_2Cl_6]$ und $[PPh_4]_2[InCl_5].CH_3CN$

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Abstract

Tetraphenylphosphonium hexachlorodiindate contains centrosymmetric $[In_2Cl_6]^{2-}$ ions having an In—In bond length of 2.727 (1) Å. In tetraphenylphosphonium pentachloroindate acetonitrile solvate, the $[InCl_5]^{2-}$ ions have trigonal bipyramidal configurations and thus differ from the square pyramidal arrangement seen in $[NEt_4]_2[InCl_5]$.

Kommentar

Bei der Reaktion von Indiummonochlorid mit Tetraphenylphosphoniumchlorid entsteht in Acetonitril das Hexachlorodiindat(II) neben metallischem Indium (Bubenheim & Müller, 1994; dort sind auch die experimentellen Details angegeben):

$$4InCl + 2Cl^- \rightarrow [In_2Cl_6]^{2-} + 2In$$

Diese Reaktion ist insofern überraschend, als Indium(I)-Verbindungen normalerweise zu In und In^{III} disproportionieren (Tuck, 1993). Andererseits ist die Bildung von In^{II}-Verbindungen aus In^I und In^{III} bekannt. So wurden die Verbindungen $[NBu_4]_2[In_2X_6]$ (X = Cl, Br, I) durch Reaktion von NBu_4X mit den Halogeniden $In^+[InX_4]^-$ hergestellt und spektroskopisch charakterisiert (Freeland, Hencher, Tuck & Contreras, 1976). Ähnlich wurden auch Addukte $In_2X_4(tmen)_2$ durch Umsetzung von Tetramethyl-ethandiamin (tmen) mit $In[InX_4]$ erhalten; in diesen Verbindungen liegen In—In-Bindungen vor (Peppe & Tuck, 1984; Khan, Peppe & Tuck, 1984). Ein Ion $[In_2Br_6]^{2-}$ mit In—In-Bindung liegt auch im $In_2[In_2Br_6]$ vor (Staffel & Meyer, 1987). Entsprechende Verbindungen, die $[Ga_2X_6]^{2-}$-Ionen ent-

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