

**Three ruthenocene derivatives:
(η^5 -4,7-dimethylindenyl)(η^5 -penta-
methylcyclopentadienyl)ruthenium(II),
[η^5 -[2](4,7)indeno[2]paracyclophanyl]-
(η^5 -pentamethylcyclopentadienyl)-
ruthenium(II) and bis[η^5 -[2](4,7)-
indeno[2]paracyclophanyl]-
ruthenium(II)**

Peter G. Jones,^{a*} Thorsten Hartig^b and Henning Hopf^b

^aInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and ^bInstitut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Correspondence e-mail: jones@xray36.anchem.nat.tu-bs.de

Received 9 April 2002

Accepted 2 May 2002

Online 31 May 2002

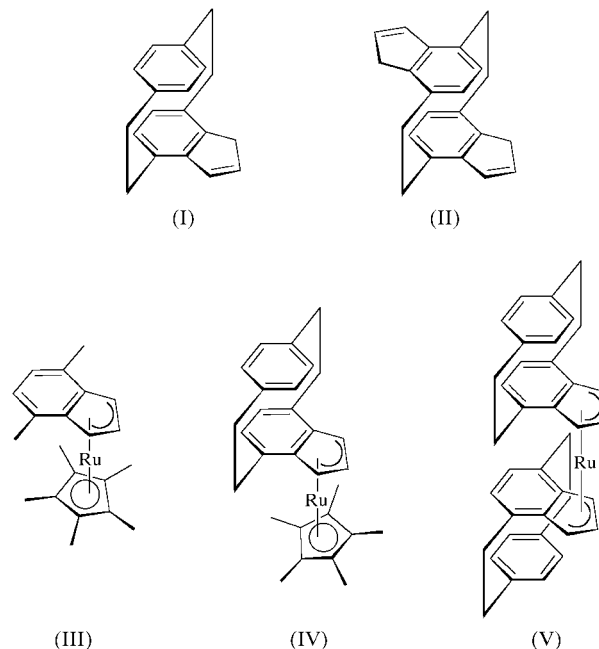
In the title compounds, [Ru(C₁₀H₁₅)(C₁₁H₁₁)], (III), [Ru(C₁₀H₁₅)(C₁₉H₁₇)], (IV), and [Ru(C₁₉H₁₇)₂], (V), respectively, the coordinating ring systems are planar and parallel, with the Ru atoms lying at perpendicular distances of Ru–Cp* 1.790 (1) Å and Ru–indenyl 1.836 (1) Å in (III), Ru–Cp* 1.791 (1) Å and Ru–indenyl 1.837 (1) Å in (IV), and Ru–indenyl 1.812 (1) Å and 1.809 (1) Å in (V) (Cp* is pentamethylcyclopentadienyl). The ring conformations are eclipsed for (III), staggered for (IV) and intermediate for (V). All three compounds show short intermolecular contacts from C–H groups to some ring centroids; these could be regarded as C–H··· π hydrogen bonds. The molecules of each compound are thus connected *via* the 2₁ screw axis to form layers parallel to the *xy* plane.

Comment

We have previously shown that indenophanes, such as (I) and (II), can be used for the preparation of novel multi-metal ferrocenophanes (Hopf & Dannheim, 1988). In an extension of these studies, we needed the title Ru complexes, (III)–(V), for comparison. Whereas complex (III) can be considered as a 'half' metallocenophane, the derivatives (IV) and (V) both contain cyclophane units. Here, we present the structures of compounds (III)–(V).

The molecules are shown in Figs. 1–3. Compound (III) is isostructural with its Fe analogue (Jones *et al.*, 2002). The coordinating ring systems are planar (details of the planes are given in the deposited material), except for the cyclophane

bridgehead atoms, which are, as usual, displaced from the plane of the remaining four atoms of the respective rings [atoms C3 and C7 in (IV) by 0.150 (3) and 0.147 (3) Å, respectively, and atoms C12, C15, C12' and C15' in (V) by 0.150 (4), 0.144 (5), 0.149 (4) and 0.139 (4) Å, respectively]. These atoms were omitted from calculations of the best planes.



The distances of the Ru atoms from the best planes of the ligands (in Å) are, in (III), Ru–Cp* 1.790 (1) and Ru–indenyl (nine-atom plane) 1.836 (1), in (IV), Ru–Cp* 1.791 (1) and Ru–indenyl (seven-atom plane) 1.837 (1), and in (V), Ru–indenyl (seven-atom plane) 1.812 (1) and 1.809 (1). The absence of a Cp* ligand thus leads to shorter Ru–indenyl distances in (V). It is tempting to attribute this to the reduction of steric pressure from the methyl groups, but this supposition is difficult to prove. The planes are essentially parallel, with interplanar angles of 1.7 (1), 0.2 (1) and 4.5 (2)°, respectively. The individual Ru–C distances (Tables 1–3) indicate a slight distortion towards an η^3 coordination of the indenyl ligands in (III) [Ru–C3a 2.220 (2) Å and Ru–C7a

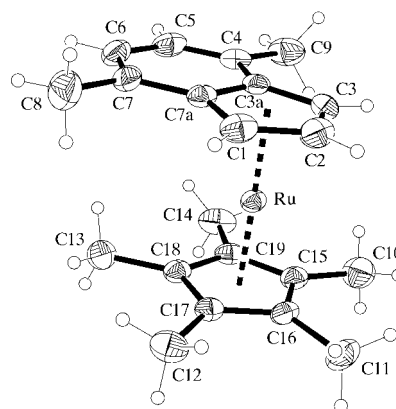


Figure 1

The molecule of (III) in the crystal. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

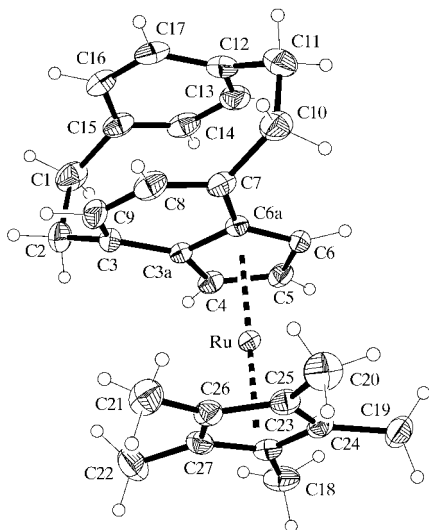


Figure 2
The molecule of (IV) in the crystal. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

2.226 (2) Å are somewhat longer than the other Ru–C distances] and in (IV) [Ru–C3a 2.224 (2) Å and Ru–C6a 2.221 (2) Å], but not in (V). The values may be compared with the range of 2.181–2.188 (2) Å in ruthenocene itself (Seiler & Dunitz, 1980).

The mutual ring conformation differs in the three structures. In (III), the rings are eclipsed, with a typical torsion angle of 1.3° for C1–Cg1–Cg2–C17 (Cg indicates a ring centroid), in (IV), they are staggered (C4–Cg1–Cg2–C27

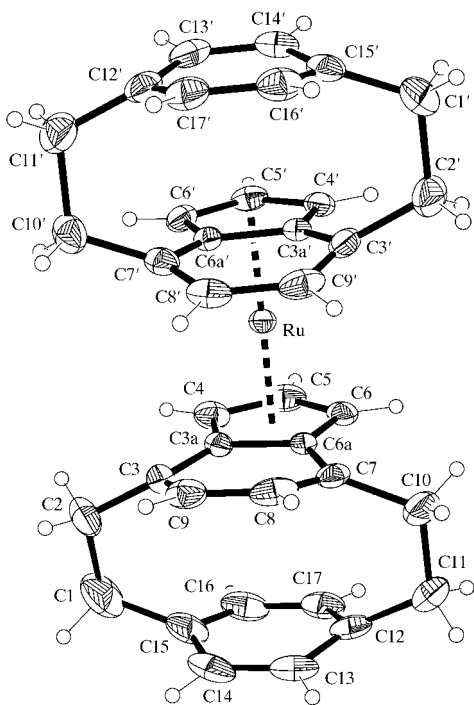


Figure 3
The molecule of (V) in the crystal. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

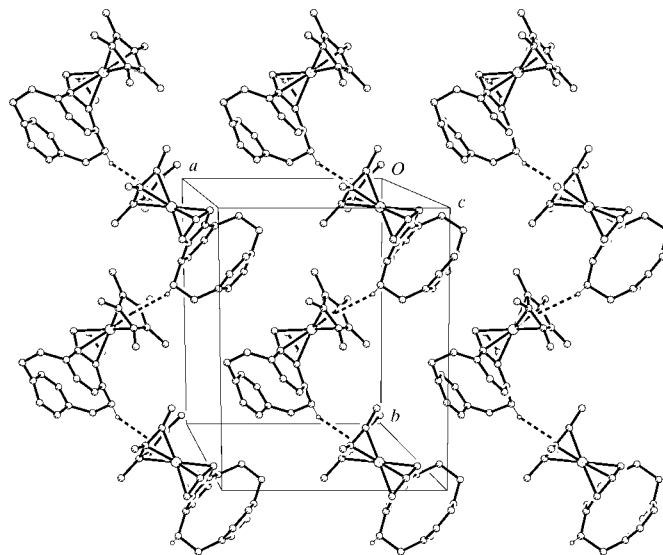


Figure 4
The packing diagram for (III) viewed along the *z* axis. Weak hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

–29.8°), and in (V), the conformation is intermediate (C5–Cg1–Cg2–C5' 12.6°). Ruthenocene itself is almost ideally eclipsed (Hardgrove & Templeton, 1959; Seiler & Dunitz, 1980).

The molecular packing (Figs. 4–6) shows considerable qualitative similarity in all three compounds; all crystallize in the same space group ($P2_1/n$), all form layers of molecules parallel to the *xy* plane (two layers per *z*-axis repeat) and all involve short H···Cg contacts that could be classified as C–H··· π hydrogen bonds. In (III), this contact is C6–

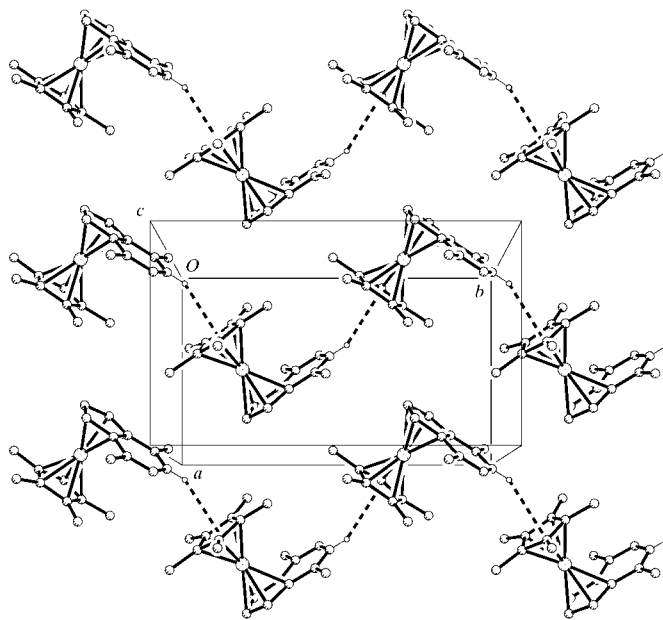
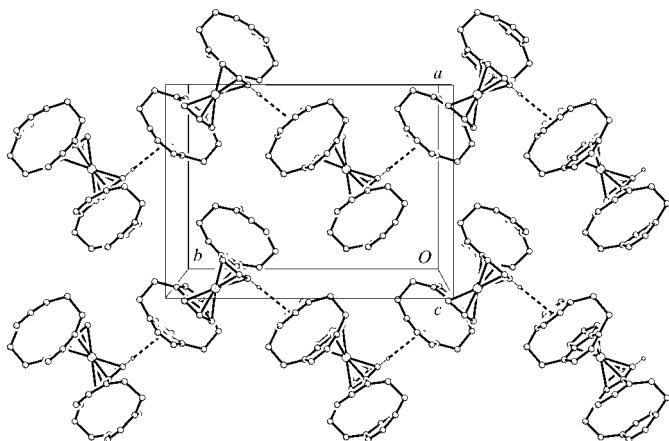


Figure 5
The packing diagram for (IV) viewed along the *z* axis. Weak hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.


Figure 6

The packing diagram for (V) viewed along the z axis. Weak hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

$H6 \cdots Cg(C15-C19)$ (symmetry code: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), with a contact distance of 2.80 Å and an angle at H6 of 154°. For (IV), the contact is $C2-H2A \cdots Cg(C23-C27)$ (symmetry code: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), with $H \cdots Cg$ 2.63 Å and an angle of 150°. For (V), the contact is $C6'-H6' \cdots Cg(C13/C14/C16/C17)$ (symmetry code: $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$), with $H \cdots Cg$ 2.75 Å and an angle at H6' of 169°.

Experimental

All three compounds were prepared by conventional methods, namely the metallation of the respective indene with methyl lithium in anhydrous tetrahydrofuran, followed by treatment of the anions thus formed with the pentamethylcyclopentadienylruthenium chloride tetramer (Fagan *et al.*, 1989) for (III) (83% yield) and (IV) (86%), and with commercial (cyclooctadiene)ruthenium dichloride for (V) (38%); for the original preparation, see Bennett & Wilkinson (1959). All compounds were fully characterized by their spectroscopic and analytical data (Hartig, 1991). Single crystals were obtained by slow cooling of warm saturated solutions in hexane.

Compound (III)

Crystal data

$[Ru(C_{10}H_{15})(C_{11}H_{11})]$	$D_x = 1.407 \text{ Mg m}^{-3}$
$M_r = 379.49$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 46 reflections
$a = 8.609 (2) \text{ \AA}$	$\theta = 10.0\text{--}11.5^\circ$
$b = 14.232 (3) \text{ \AA}$	$\mu = 0.87 \text{ mm}^{-1}$
$c = 14.752 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 97.50 (2)^\circ$	Prism, orange-yellow
$V = 1792.1 (7) \text{ \AA}^3$	$0.70 \times 0.50 \times 0.35 \text{ mm}$
$Z = 4$	

Data collection

Nicolet R3 diffractometer	$R_{\text{int}} = 0.011$
ω/θ scans	$\theta_{\text{max}} = 25.1^\circ$
Absorption correction: ψ scan (XEMP; Nicolet, 1987)	$h = -10 \rightarrow 2$
$T_{\text{min}} = 0.608, T_{\text{max}} = 0.737$	$k = 0 \rightarrow 16$
4248 measured reflections	$l = -17 \rightarrow 17$
3172 independent reflections	3 standard reflections
2605 reflections with $I > 2\sigma(I)$	every 147 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 0.4415P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.056$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
3172 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
207 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0025 (4)

Table 1

Selected bond lengths (Å) for (III).

Ru—C1	2.190 (3)	Ru—C15	2.163 (2)
Ru—C2	2.188 (3)	Ru—C16	2.165 (2)
Ru—C3	2.185 (3)	Ru—C17	2.169 (2)
Ru—C3a	2.220 (2)	Ru—C18	2.161 (3)
Ru—C7a	2.227 (2)	Ru—C19	2.160 (2)

Compound (IV)

Crystal data

$[Ru(C_{10}H_{15})(C_{19}H_{17})]$	$D_x = 1.385 \text{ Mg m}^{-3}$
$M_r = 481.62$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 46 reflections
$a = 11.648 (2) \text{ \AA}$	$\theta = 10.0\text{--}11.5^\circ$
$b = 14.757 (3) \text{ \AA}$	$\mu = 0.69 \text{ mm}^{-1}$
$c = 13.798 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 103.134 (15)^\circ$	Prism, orange-yellow
$V = 2309.7 (7) \text{ \AA}^3$	$0.7 \times 0.4 \times 0.3 \text{ mm}$
$Z = 4$	

Data collection

Nicolet R3 diffractometer	$R_{\text{int}} = 0.014$
ω/θ scans	$\theta_{\text{max}} = 25.1^\circ$
Absorption correction: ψ scan (XEMP; Nicolet, 1987)	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.643, T_{\text{max}} = 0.819$	$k = 0 \rightarrow 17$
8161 measured reflections	$l = -16 \rightarrow 16$
4086 independent reflections	3 standard reflections
3547 reflections with $I > 2\sigma(I)$	every 147 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 0.5968P]$
$R[F^2 > 2\sigma(F^2)] = 0.021$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
4086 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
276 parameters	
H-atom parameters constrained	

Table 2

Selected bond lengths (Å) for (IV).

Ru—C3a	2.2238 (19)	Ru—C23	2.154 (2)
Ru—C4	2.197 (2)	Ru—C24	2.165 (2)
Ru—C5	2.188 (2)	Ru—C25	2.166 (2)
Ru—C6	2.192 (2)	Ru—C26	2.168 (2)
Ru—C6a	2.2209 (19)	Ru—C27	2.164 (2)

Compound (V)

Crystal data

$[Ru(C_{19}H_{17})_2]$	$D_x = 1.414 \text{ Mg m}^{-3}$
$M_r = 591.72$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 50 reflections
$a = 12.620 (3) \text{ \AA}$	$\theta = 10.0\text{--}11.5^\circ$
$b = 17.026 (4) \text{ \AA}$	$\mu = 0.59 \text{ mm}^{-1}$
$c = 13.005 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 95.92 (2)^\circ$	Parallelepiped, orange-yellow
$V = 2779.5 (11) \text{ \AA}^3$	$0.5 \times 0.5 \times 0.4 \text{ mm}$
$Z = 4$	

Table 3
Selected bond lengths (Å) for (V).

Ru—C4	2.172 (3)	Ru—C3a'	2.195 (3)
Ru—C5'	2.174 (3)	Ru—C6a'	2.198 (2)
Ru—C5	2.175 (3)	Ru—C3a	2.198 (2)
Ru—C4'	2.178 (3)	Ru—C6a	2.201 (2)
Ru—C6	2.181 (3)	C1—C15	1.534 (6)
Ru—C6'	2.192 (3)	C1—C2	1.560 (6)

Data collection

Nicolet R3 diffractometer	$R_{\text{int}} = 0.015$
ω scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scan (<i>XEMP</i> ; Nicolet, 1987)	$h = -15 \rightarrow 5$
$T_{\text{min}} = 0.716$, $T_{\text{max}} = 0.775$	$k = 0 \rightarrow 20$
7056 measured reflections	$l = -15 \rightarrow 15$
4889 independent reflections	3 standard reflections
4008 reflections with $I > 2\sigma(I)$	every 147 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.9725P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.079$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.56 \text{ e } \text{Å}^{-3}$
4889 reflections	$\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{Å}^{-3}$
353 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0015 (3)

Methyl H atoms were identified in difference syntheses, idealized and then refined using rigid methyl groups allowed to rotate but not tip. Other H atoms were included using a riding model with fixed C—H bond lengths (aromatic 0.93, methyl 0.96 and methylene

0.97 Å); $U_{\text{iso}}(\text{H})$ values were fixed at 1.2 times the U_{eq} value of the parent atom.

For all compounds, data collection: *P3 Software* (Nicolet, 1987); cell refinement: *P3 Software*; data reduction: *XDISK* (Nicolet, 1987); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Mr A. Weinkauff for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1496). Services for accessing these data are described at the back of the journal.

References

- Bennett, M. A. & Wilkinson, G. (1959). *Chem. Ind. (London)*, p. 1516.
 Fagan, P. J., Ward, M. D. & Calabrese, J. C. (1989). *J. Am. Chem. Soc.* **111**, 1698–1719.
 Hardgrove, G. L. & Templeton, D. H. (1959). *Acta Cryst.* **12**, 28–32.
 Hartig, T. (1991). PhD dissertation, Technical University of Braunschweig, Germany.
 Hopf, H. & Dannheim, J. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 701–702.
 Jones, P. G., Hopf, H. & Hartig, T. (2002). *Acta Cryst.* **E58**, m139–m140.
 Nicolet (1987). *P3 Software*, *XDISK* and *XEMP*. Nicolet Analytical X-ray Instruments, Madison, Wisconsin, USA.
 Seiler, P. & Dunitz, J. D. (1980). *Acta Cryst.* **B36**, 2946–2950.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.