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Structure of 1,3-(1,1′-Ruthenocenediyl)propane, $C_{13}H_{14}Ru$, and 1,4-(1,1′-Ruthenocenediyl)butane, $C_{14}H_{16}Ru$

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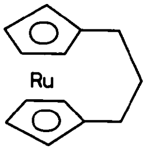
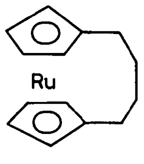
Abstract. $C_{13}H_{14}Ru$ (I): $M_r = 271{\cdot}3$, monoclinic, Pa, $a = 11{\cdot}448$ (1), $b = 7{\cdot}499$ (1), $c = 6{\cdot}273$ (1) Å, $\beta = 111{\cdot}30$ (1)°, $V = 501{\cdot}7$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}80$, $D_m = 1{\cdot}80$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, μ(Mo $K\alpha$) = 1·49 mm^{-1}, $F(000) = 272$, $T = 295$ (2) K, $R = 0{\cdot}016$ for 1389 unique reflections. $C_{14}H_{16}Ru$ (II): $M_r = 285{\cdot}4$, monoclinic, $P2_1/c$, $a = 11{\cdot}997$ (3), $b = 12{\cdot}718$ (2), $c = 7{\cdot}725$ (2) Å, $\beta = 107{\cdot}03$ (2)°, $V = 1126{\cdot}9$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}68$, $D_m = 1{\cdot}66$ (2) Mg m^{-3}, μ(Mo $K\alpha$) = 1·33 mm^{-1}, $F(000) = 576$, $T = 295$ (2) K, $R = 0{\cdot}033$ for 2025 unique reflections. The cyclopentadienyl (Cp) rings take the eclipsed conformation and the dihedral angles between them are 14·8 (2) and 1·7 (2)° for (I) and (II), respectively. The C—C—C angles in the carbon chain connecting the two Cp rings are in the range 114·5 (3) to 116·7 (3)°, showing slight strain in this bridge.

Introduction. The structures of several ferrocenophanes have been investigated by the X-ray diffraction method (Jones, Marsh & Richards, 1965; Laing & Trueblood, 1965; Cameron & Cordes, 1979). However, no ruthenocenophanes were reported. Recently, the [3](1,1′)- and [4](1,1′)ruthenocenophanes [(I) and (II), respectively] were synthesized (Kamiyama, Suzuki, Kimura & Kasahara, 1978). The crystal structure determination of these compounds has been undertaken to reveal the change in the molecular structure caused by introducing a heteroannularly bridged carbon chain into a ruthenocene molecule.



(I)



(II)

Experimental. Experimental conditions are shown in Table 1. D_m measured by flotation in aqueous solution of zinc iodide; X-ray intensity measurements performed on a Rigaku AFC-5 four-circle diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite plate, θ–2θ scan with a scan speed of 2° min^{-1} in θ. Space group Pa is derived from Pc by permutation of the standard abc to the $c\bar{b}a$ orientation, general equivalent positions x,y,z; $\frac{1}{2}+x,\bar{y},z$; the cell edges were labelled so that $c < a$ following the recommendations of the Commission on Crystallographic Data (Kennard, Speakman & Donnay, 1967). Corrections for Lorentz and polarization applied but not for absorption. Structure of (I) solved by the heavy-atom method, that

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of (II) by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), non-H atoms refined with anisotropic thermal parameters, some H-atom positions found from difference density maps and others calculated, positional and isotropic thermal parameters of H atoms also refined, $\sum w||F_o|-|F_c||^2$ minimized; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); *Universal Crystallographic Computation Program System UNICS* III (Sakurai & Kobayashi, 1979).

(II) is dimorphous; the crystals of (II) recrystallized from *n*-hexane are orthorhombic, space group *Pbca* with $a = 22·730$ (10), $b = 7·821$ (2), $c = 12·715$ (3) Å, $V = 2260$ (1) Å^3, $Z = 8$, $D_x = 1·68$ Mg m^{-3}. The lattice parameters were determined based on 12 2θ values ($18 < 2\theta < 25°$) with $\lambda(\text{Mo } K\alpha) = 0·70926$ Å at 295 (2) K. Final $R = 0·050$ for 855 observed unique reflections. The molecular structure is almost identical to that of the monoclinic modification. Detailed description of this modification is omitted because of the lower accuracy of the intensity data, the result of severe sublimation induced by X-ray irradiation.

Discussion. Table 2 lists atomic coordinates and Table 3 bond lengths and angles.* Perspective views of (I) and (II) are shown in Fig. 1(*a*) and (*b*), respectively. Information on the least-squares planes through each of the Cp rings has been deposited.* The e.s.d.'s of distances of atoms from a plane and of the dihedral angles between the best planes were calculated by the program *BP*70 (Ito, 1982). The deviation of the ring C atoms from the best plane is less than 0·004 (3) Å for (II), whereas that of (I) is in the range –0·007 (2) to 0·008 (2) Å (greater than 3σ), suggesting slight out-of-plane deformation of the Cp rings of (I). The ring C(1) atom of (I) deviates from the plane through the C(2), C(3), C(4) and C(5) atoms by 0·020 (5) Å on the other side of the Ru atom. The deviation of ring C(9) atom of (I) from the plane defined by C(10), C(11), C(12) and C(13) atoms is 0·019 (6) Å on the same side of the Ru atom. The distances of the Ru atom to the best planes of the Cp rings are 1·802 (2) and 1·796 (2) Å for (I) and 1·816 (2) and 1·813 (2) Å for (II). The C—C bond axes attached to the Cp ring of (I) are bent inside the ring planes by 4·6 (2) ~ 5·0 (2)°. On the other hand, those of (II) are bent outside the ring planes by 2·5 (2) ~ 2·9 (2)°.

Table 1. *Experimental conditions and refinement details*

	(I)	(II)
Habit of crystals	Prismatic *a*	Prismatic *c*
Solvent used for recrystallization	*n*-Hexane	Benzene
Size of specimen (mm)	0·5 × 0·25 × 0·2	0·5 × 0·4 × 0·1
Number of reflections and 2θ range (°) used for measuring lattice parameters	20 $55 < 2\theta < 59$	25 $34 < 2\theta < 40$
$2\theta_{\max}$(°)	60	55
Range of *h*, *k* and *l*	+ *h*, + *k*, ± *l*	± *h*, + *k*, + *l*
Systematic absences	*h*0*l*, *h* odd	0*k*0, *k* odd; *h*0*l*, *l* odd
Variation of $\lvert F_o\rvert$ amplitudes of 5 standard reflections, $\sum(\lvert F_o\rvert/\lvert F_o\rvert_{\text{initial}})/5$	0·972 ~ 1·005	0·907 ~ 1·000
No. of reflections measured	1540	2789
No. of reflections observed	1454	2190
No. of zero reflections	84	579
Weak reflections with $\lvert F_o\rvert \leq 3\sigma(\lvert F_o\rvert)$	2	20
R	0·016	0·033
wR	0·021	0·041
Weight $w^{-1}=\sigma^2(\lvert F_o\rvert) + (c\lvert F_o\rvert)^2$	$c = 0·015$	$c = 0·020$
S	1·19	1·73
No. of observed unique reflections	1389	2025
No. of parameters	183	200
$(\Delta\rho)_{\min}$ in final difference density map (e Å^{-3})	–0·8	–2·4
$(\Delta\rho)_{\max}$ (e Å^{-3})	0·2	0·6
$(\Delta/\sigma)_{\max}$	< 1	< 1

Table 2. *Positional parameters* ($\times 10^4$; *for* Ru $\times 10^5$) *and equivalent isotropic thermal parameters* (*Hamilton*, 1959)

$$B_{\text{eq}} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij}\, \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
(I)				
Ru	0	38225 (2)	0	1·9
C(1)	156 (3)	5677 (4)	2743 (5)	2·7
C(2)	–348 (3)	6632 (4)	642 (5)	2·8
C(3)	576 (3)	6564 (4)	–389 (6)	3·1
C(4)	1627 (3)	5552 (4)	1042 (5)	2·7
C(5)	1365 (3)	4979 (3)	3001 (5)	2·5
C(6)	2145 (4)	3740 (3)	4864 (6)	3·1
C(7)	2431 (3)	1909 (4)	4078 (6)	3·2
C(8)	1323 (3)	591 (4)	3164 (5)	2·9
C(9)	348 (3)	1070 (3)	887 (6)	2·4
C(10)	–949 (3)	1438 (4)	438 (6)	2·8
C(11)	–1531 (3)	2014 (4)	–1889 (5)	3·0
C(12)	–600 (3)	1982 (4)	–2908 (5)	3·0
C(13)	541 (4)	1392 (4)	–1216 (6)	2·9
(II)				
Ru	67967 (2)	935 (2)	33132 (3)	2·4
C(1)	6260 (3)	867 (2)	691 (4)	3·3
C(2)	5673 (3)	1341 (3)	1829 (5)	3·8
C(3)	6508 (4)	1788 (3)	3322 (6)	4·9
C(4)	7635 (3)	1589 (2)	3085 (5)	3·9
C(5)	7478 (3)	1013 (2)	1459 (5)	3·2
C(6)	8400 (3)	673 (3)	624 (6)	4·7
C(7)	8643 (3)	–506 (3)	697 (5)	4·2
C(8)	9334 (3)	–915 (3)	2559 (5)	4·0
C(9)	8727 (3)	–1771 (3)	3321 (5)	4·2
C(10)	7730 (3)	–1400 (2)	3970 (4)	3·0
C(11)	6517 (3)	–1605 (2)	3130 (5)	3·8
C(12)	5877 (3)	–1166 (3)	4239 (5)	4·2
C(13)	6674 (3)	–692 (3)	5758 (5)	4·3
C(14)	7814 (3)	–832 (3)	5581 (4)	3·5

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* Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms, bond lengths and bond angles involving H atoms, least-squares planes through the Cp rings and deviations of atoms from them, and projections of the crystal structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38856 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The dihedral angle of the two Cp rings in (I) is 14·8 (2)° and larger than that of 1·7 (2)° in (II), as expected from the PMR spectra. (I) has a larger signal splitting of α- and β-H atoms in the Cp rings than that of (II) (Kamiyama *et al.*, 1978). The pairs of C···C distances between the rings (Fig. 1) show a trend in which the rings are skewed to one side. C(4)···C(13) is shorter than C(1)···C(10) by 0·066 (6) Å for (I). The corresponding value for (II) is 0·026 (6) Å. The C—C bond lengths next to the Cp ring are in the range 1·498 (6) to 1·506 (4) Å, significantly shorter than the other C—C bonds in the bridge [1·521 (6) ~ 1·545 (4) Å]. Mean bond distances from the Ru to the ring C atoms are 2·172 (3) and 2·180 (4) Å, respectively. These values are a little shorter than that of 2·21 (1) Å in ruthenocene (Hardgrove & Templeton, 1959). The mean C—C bond distance in the Cp rings is 1·430 (6) and 1·420 (6) Å for (I) and (II), respectively.

Table 3. *Bond lengths* (Å) *and bond angles* (°)

(I)		(II)	
Ru—C(1)	2·169 (3)	Ru—C(1)	2·173 (3)
Ru—C(2)	2·208 (3)	Ru—C(2)	2·178 (4)
Ru—C(3)	2·199 (3)	Ru—C(3)	2·183 (4)
Ru—C(4)	2·167 (3)	Ru—C(4)	2·183 (3)
Ru—C(5)	2·145 (3)	Ru—C(5)	2·185 (4)
Ru—C(9)	2·137 (2)	Ru—C(10)	2·188 (3)
Ru—C(10)	2·161 (3)	Ru—C(11)	2·184 (3)
Ru—C(11)	2·192 (3)	Ru—C(12)	2·181 (4)
Ru—C(12)	2·190 (3)	Ru—C(13)	2·179 (4)
Ru—C(13)	2·152 (4)	Ru—C(14)	2·166 (3)
C(1)—C(2)	1·425 (4)	C(1)—C(2)	1·412 (6)
C(1)—C(5)	1·433 (5)	C(1)—C(5)	1·419 (5)
C(2)—C(3)	1·427 (6)	C(2)—C(3)	1·407 (5)
C(3)—C(4)	1·430 (4)	C(3)—C(4)	1·439 (6)
C(4)—C(5)	1·433 (5)	C(4)—C(5)	1·418 (5)
C(5)—C(6)	1·506 (4)	C(5)—C(6)	1·498 (6)
C(6)—C(7)	1·534 (4)	C(6)—C(7)	1·525 (5)
C(7)—C(8)	1·545 (4)	C(7)—C(8)	1·526 (5)
C(8)—C(9)	1·502 (4)	C(8)—C(9)	1·521 (6)
C(9)—C(10)	1·434 (5)	C(9)—C(10)	1·502 (6)
C(9)—C(13)	1·435 (6)	C(10)—C(11)	1·433 (5)
C(10)—C(11)	1·433 (4)	C(10)—C(14)	1·417 (5)
C(11)—C(12)	1·428 (5)	C(11)—C(12)	1·421 (6)
C(12)—C(13)	1·422 (4)	C(12)—C(13)	1·413 (5)
		C(13)—C(14)	1·425 (5)
C(2)—C(1)—C(5)	109·8 (3)	C(2)—C(1)—C(5)	108·9 (3)
C(1)—C(2)—C(3)	106·5 (3)	C(1)—C(2)—C(3)	108·5 (3)
C(2)—C(3)—C(4)	109·1 (3)	C(12)—C(3)—C(4)	107·1 (4)
C(3)—C(4)—C(5)	107·9 (3)	C(3)—C(4)—C(5)	108·5 (3)
C(1)—C(5)—C(4)	106·7 (3)	C(1)—C(5)—C(4)	106·9 (3)
C(1)—C(5)—C(6)	126·1 (3)	C(1)—C(5)—C(6)	125·6 (3)
C(4)—C(5)—C(6)	126·9 (3)	C(4)—C(5)—C(6)	127·4 (3)
C(5)—C(6)—C(7)	116·0 (3)	C(5)—C(6)—C(7)	115·2 (3)
C(6)—C(7)—C(8)	116·7 (3)	C(6)—C(7)—C(8)	114·5 (3)
C(7)—C(8)—C(9)	115·2 (3)	C(7)—C(8)—C(9)	114·8 (3)
C(8)—C(9)—C(10)	126·3 (3)	C(8)—C(9)—C(10)	115·0 (3)
C(8)—C(9)—C(13)	127·2 (3)	C(9)—C(10)—C(11)	126·4 (3)
C(10)—C(9)—C(13)	106·3 (3)	C(9)—C(10)—C(14)	126·5 (3)
C(9)—C(10)—C(11)	108·9 (3)	C(11)—C(10)—C(14)	107·0 (3)
C(10)—C(11)—C(12)	107·7 (3)	C(10)—C(11)—C(12)	108·2 (3)
C(11)—C(12)—C(13)	107·7 (3)	C(11)—C(12)—C(13)	108·3 (3)
C(9)—C(13)—C(12)	109·4 (4)	C(12)—C(13)—C(14)	107·6 (3)
		C(10)—C(14)—C(13)	108·9 (3)

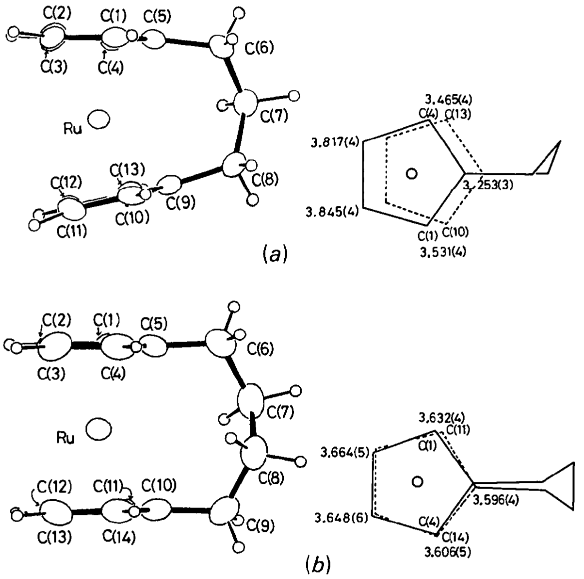

Fig. 1. *ORTEP* drawings of (*a*) (I) and (*b*) (II) with thermal ellipsoids scaled at the 50% probability level (Johnson, 1965). H atoms are represented by circles of radius 0·08 Å. Projections of the molecules on the Cp ring containing the C(1) atom are also given with the C···C distances (Å) between the rings. An open circle denotes the Ru atom.

The crystal structure consists of discrete molecules separated by normal van der Waals distances.* The shortest intermolecular distances are 3·412 (4) Å for C(2)···C(9)($1+x$, $1+y$, z) and 3·557 (5) Å for C(1)···C(3)(x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) for (I) and (II), respectively.

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* See deposition footnote.

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