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The Reduction of Hydrated Ruthenium(III) Chloride with Zinc in the Presence of Cyclooctadiene: Molecular Structure of $Ru(C_8H_{10})(C_8H_{12})$ and Isolation and X-ray Structural Characterization of $Ru_2Cl_4(C_8H_{12})_2$, $RuH(C_8H_{11})(C_6H_6)$ and $Ru_3Cl_3(OCH_3)(C_8H_{12})_3$

K.-M. FROSIN and L. DAHLENBURG*

Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13 (F.R.G.)

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Abstract

The preparation of $Ru(C_8H_{10})(C_8H_{12})$ (1) by reduction of hydrated ruthenium trichloride with zinc in the presence of cyclooctadiene occasionally results in mixtures from which the addition compound $Ru_2Cl_4(C_8H_{12})_2 \cdot RuH(C_8H_{11})(C_6H_6) \cdot 0.5C_6H_6$ ($2 \cdot 3 \cdot 0.5C_6H_6$) and the trinuclear complex $Ru_3Cl_3(OCH_3)(C_8H_{12})_3$ (4) could be isolated. Complexes 1–4 were characterized by X-ray crystallography. Relevant crystallographic data are: 1: orthorhombic $Pna2_1$, $a = 2159.7(9)$, $b = 878.9(4)$, $c = 692.4(4)$ pm, $Z = 4$, $R = 0.029$, $R_w = 0.030$ (2281 data). $2 \cdot 3 \cdot 0.5C_6H_6$: triclinic $P\bar{1}$, $a = 773.8(2)$, $b = 1316.9(2)$, $c = 1766.9(6)$ pm, $\alpha = 72.40(2)$, $\beta = 79.70(3)$, $\gamma = 74.78(2)°$, $Z = 2$, $R = 0.051$, $R_w = 0.061$ (9564 data). 4: orthorhombic $Pna2_1$, $a = 1784.6(4)$, $b = 939.5(1)$, $c = 3076.3(7)$ pm, $Z = 8$, $R = 0.070$, $R_w = 0.075$ (2805 data).

Introduction

In recent years, cycloolefin complexes of ruthenium(0) such as Ru(COD)(COT) (COD = 1,5-cyclooctadiene, C_8H_{12}; COT = 1,3,5-cyclooctatriene, C_8H_{10}) have excited a lively interest both as starting materials for other ruthenium complexes, especially phosphine-substituted dihydrides or 'polyhydrides' containing molecular H_2-ligands [1–3], and as convenient precursors of catalytically active species promoting a series of novel organic syntheses [4], e.g. the linear co-dimerization of alkynes with 1,3-dienes, the [2 + 2] cross cycloaddition of norbornenes with dimethyl acetylene dicarboxylate and the addition of carboxylic acids to alkynes giving enol esters.

Ru(COD)(COT), first prepared in poor yield by interaction of isopropyl Grignard reagent with anhydrous $RuCl_3$ in 1:1 COD/COT mixtures under UV irradiation [5], is now more readily available by reduction of hydrated ruthenium trichloride with zinc dust, a reaction that has successfully been carried out either in EtOH/COD mixtures gently heated to 80 °C for 3 h [6, 7] or in a MeOH/COD solvent kept under ultrasonic vibration at 70 °C for approximately 2.5 h [8].

Our first experiments with Ru(COD)(COT) were directed towards the preparation of the *cis*-dihydride $[P(CH_2CH_2CH_2PMe_2)_3]RuH_2$, a compound we had previously shown to photochemically activate C–H bonds of free hydrocarbons [9, 10], by hydrogenation of the Ru(0) complex in the presence of the tripod tetradentate $P(CH_2CH_2CH_2PMe_2)_3$. In view of the successful use of this procedure for the synthesis of a number of tetrakis(phosphine) and bis(diphosphine) ruthenium dihydrides [1, 2], the Ru(COD)(COT)/$P(CH_2CH_2CH_2PMe_2)_3$ hydrogenation was expected to provide more convenient access to $[P(CH_2CH_2CH_2PMe_2)_3]RuH_2$ than the reaction between the dichloride $[P(CH_2CH_2CH_2PMe_2)_3]RuCl_2$ and $LiAlH_4$, which affords the dihydrido derivative in comparatively low yields only [11]. In agreement with observations described by other authors [8], our initial attempts at the preparation of the Ru(COD)(COT) precursor showed that reduction of ruthenium trichloride hydrate in alcohol/cyclooctadiene mixtures frequently results in the formation of complex mixtures of compounds apparently formed as intermediates or secondary products of the Ru(COD)(COT) synthesis. Since we succeeded in separating several of the chloro, cyclooctadiene, and (cyclooctadienyl)hydrido derivatives contained in these mixtures, we here report the results of the X-ray structural characterization of three of the complexes isolated, viz. $Ru_2Cl_4(COD)_2$ (2) $RuH(C_8H_{11})(C_6H_6)$ (3) and $Ru_3Cl_3(OCH_3)(COD)_3$ (4). The molecular structure of Ru(COD)(COT) (1), which according to our knowledge has not been described in previous work, is also presented.

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*Author to whom correspondence should be addressed.

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Experimental

General Procedures

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried according to recommended methods and were distilled under nitrogen prior to use.

Preparation of Complexes and Isolation of Single Crystals

Ru(COD)(COT) (1)

This compound was synthesized employing the procedure of Petici and Vitulli [7] under slightly modified conditions: 1.2 g (4.2 mmol) of hydrated ruthenium trichloride, obtained as '$RuCl_3 \cdot 3H_2O$' from Degussa (Hanau), was completely dissolved in 10 ml of ethanol. 1,5-Cyclooctadiene (33 ml), previously purified by chromatography on an alumina column (Merck product; activity I), and zinc dust (3 g) were added in that order and the mixture was stirred for 20 h at room temperature. After filtration, the resulting yellow solution was evaporated to dryness in an oil-pump vacuum at 50 °C and the residue obtained was extracted with hexane (3 X 30 ml). The combined extracts were concentrated and chromatographed with hexane on an Al_2O_3 column (2.5 X 20 cm; Merck product; activity III). Slow evaporation of the eluted yellow solution caused the deposition of pure **1** as beautifully shaped lemon crystals. Yield: 1.1 g (83%). *Anal.* Found: C, 60.8; H, 7.2. Calc. for $C_{16}H_{22}Ru$ (315.42): C, 60.93; H, 7.03%.

Single crystals of the addition compound $Ru_2Cl_4(COD)_2 \cdot RuH(C_8H_{11})(C_6H_6) \cdot 0.5C_6H_6$ ($2 \cdot 3 \cdot 0.5C_6H_6$)

The title compound was isolated by extracting the residue remaining after filtration of the original reaction mixture of the above preparation with benzene (25 ml). This produced a red solution, which was filtered and subsequently concentrated at elevated temperature (*c.* 70 °C). With slow cooling to room temperature, the formation of blackish-red single crystals containing complexes **2** and **3** as the addition compound $2 \cdot 3 \cdot 0.5C_6H_6$ was achieved.

Single crystals of $Ru_3Cl_3(OCH_3)(COD)_3$ (4)

This complex was separated from the residuals of the first filtration of the working-up procedure (*vide supra*) by washing with ethanol (2 X 20 ml) and extraction with THF (20 ml). The resulting red solution was filtered and evaporated to dryness. After re-dissolving the residue in hot methanol and filtering, the solvent was again removed *in vacuo*. Dissolution of the remaining blackish-brown solids in the minimum amount of hot THF and slow cooling of this solution to room temperature caused the formation of black complex **4** as single crystals.

X-ray Studies

Crystals of **1**, $2 \cdot 3 \cdot 0.5C_6H_6$ and **4** suitable for X-ray work were obtained as described above.

X-ray measurements were carried out at 20 ± 2 °C on a Syntex $P2_1$ diffractometer using Mo Kα radiation (λ = 71.07 pm). For each crystal, the orientation matrix and the final unit cell parameters were calculated by least-squares from the setting angles of several (>15) machine-centered reflections having $11° < 2\theta < 30°$. Diffraction intensities were measured by the $\omega/2\theta$ scan technique with variable scan rates (2.0°/min to 29.3°/min) determined from a fast prescan on each reflection. No significant decrease was observed in the intensities of three standard reflections monitored periodically during data collection. Data were corrected for Lorentz and polarization effects, but not for absorption or extinction.

In the structures, the ruthenium atoms as well as some of the chlorine positions of $2 \cdot 3 \cdot 0.5C_6H_6$ and **4** were readily located by comparison of the Patterson maps with the results of the TREF direct-methods attempts of SHELXS-86 [12]. Subsequent alternate cycles of difference Fourier synthesis and full-matrix least-squares refinement employing the SHELX-76 program package with scattering factors from the sources given therein [13] revealed the positions of the remaining non-hydrogen atoms.

The model resulting for structure **1** was refined with allowance for anisotropic thermal motion of all non-hydrogen atoms. The H atoms were included in the molecular model in geometrically idealized positions with C–H distances constrained to 96.0 pm. The final structural model of the addition compound $2 \cdot 3 \cdot 0.5C_6H_6$ used anisotropic temperature factors for the non-hydrogen atoms of the two complex molecules **2** and **3**, but isotropic thermal parameters for the C atoms of the solvent molecule. Hydrogen atoms were not included. The benzene of crystallization was detected in a position consistent with its occurrence, i.e. near the centre of symmetry of a triclinic $P\bar{1}$ cell containing two formula units of $Ru_2Cl_4(COD)_2$ and $RuH(C_8H_{11})(C_6H_6)$. The ring atoms were found to display a severe orientational disorder, which could only partially be resolved. Because of the limited number of data available, a mixed thermal model assigning anisotropic behaviour to the metal and chlorine atoms only was adopted for the refinement of structure 4. Again, hydrogen positions were not included.

A summary of relevant crystallographic information and results is collected in Table 1. Final positional and thermal parameters are presented in Tables 2–4. Selected bond lengths and angles are given in

TABLE 1. Crystallographic data

	1	$2 \cdot 3 \cdot 0.5C_6H_6$	4
M	315.43	886.75	765.16
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	$Pna2_1$	$P\bar{1}$	$Pna2_1$
a (pm)	2159.7(9)	773.8(2)	1784.6(4)
b (pm)	878.9(4)	1316.9(2)	939.5(1)
c (pm)	692.4(4)	1766.9(6)	3076.3(7)
α (°)	90	72.40(2)	90
β (°)	90	79.70(3)	90
γ (°)	90	74.78(2)	90
V ($\times 10^6$ pm^3)	1314	1646	5158
Z	4	2	8
D (g/cm^3)	1.595	1.790	1.971
μ (Mo Kα) (cm^{-1})	10.5	16.7	18.8
Max. 2θ (°)	65	65	48
No. of data			
collected	2766	12997	4810
independent	2564	11946	4317
used	2281	9564	2805
	($F_o > 4\sigma$)	($I > 3\sigma$)	($F_o > 4\sigma$)
No. paramaters refined	155	358	320
Data/parameters	14.7	26.7	8.8
R	0.029	0.051	0.070
R_w	0.030[a]	0.061[a]	0.075[b]

[a] $w = 1$. [b] $w = 1/(\sigma^2(F_o) + 0.001|F_o^2|)$.

TABLE 2. Positional and thermal parameters of Ru(COD)(COT) (1)

Atom	x/a	y/b	z/c	U_{eq}[a]
Ru	0.14101(1)	0.11465(3)	0.00000	0.0330(2)
C(1)	0.1408(3)	0.0014(7)	−0.2910(8)	0.065(6)
C(2)	0.1977(3)	0.0711(7)	−0.2615(10)	0.065(6)
C(3)	0.2374(4)	0.0776(7)	−0.1067(16)	0.064(8)
C(4)	0.2355(4)	0.0292(8)	0.0882(16)	0.067(7)
C(5)	0.1889(3)	−0.0520(6)	0.1830(9)	0.064(6)
C(6)	0.1431(3)	−0.1298(5)	0.0734(8)	0.055(5)
C(7)	0.1596(3)	−0.2245(5)	−0.985(10)	0.062(6)
C(8)	0.1258(3)	−0.1650(7)	−0.2683(11)	0.073(7)
C(9)	0.1259(3)	0.3488(6)	−0.0996(10)	0.048(5)
C(10)	0.1568(2)	0.3532(6)	0.0782(10)	0.051(5)
C(11)	0.1279(3)	0.3894(6)	0.2677(10)	0.064(6)
C(12)	0.0674(3)	0.3016(6)	0.3026(8)	0.057(5)
C(13)	0.0672(2)	0.1488(6)	0.2003(7)	0.046(4)
C(14)	0.0421(2)	0.1259(5)	0.0167(18)	0.049(5)
C(15)	0.0159(2)	0.2491(7)	−0.1110(9)	0.056(5)
C(16)	0.0573(2)	0.3899(6)	−0.1246(9)	0.059(5)

[a] U_{eq}: equivalent isotropic displacement parameter defined as one third of the trace of the orthogonalized U_{ij} tensor.

the captions to Figs. 1–4 showing SCHAKAL-drawn perspective views of the molecules [14]. See also 'Supplementary Material'.

TABLE 3. Positional and thermal parameters of $Ru_2Cl_4(COD)_2 \cdot RuH(C_8H_{11})(C_6H_6) \cdot 0.5C_6H_6$ ($2 \cdot 3 \cdot 0.5C_6H_6$)[a]

Atom	x/a	y/b	z/c	U_{eq}[b]
Ru(1)	1.19690(5)	0.31284(3)	0.24554(2)	0.0338(3)
Ru(2)	0.94575(6)	0.51212(3)	0.22210(3)	0.0402(4)
Cl(1)	0.8779(2)	0.3344(1)	0.2406(1)	0.057(1
Cl(2)	1.1045(2)	0.4240(1)	0.3411(1)	0.054(1)
Cl(3)	1.1925(3)	0.1520(1)	0.3568(1)	0.057(1)
Cl(4)	0.6726(3)	0.5589(2)	0.3060(1)	0.078(2)
C(1)	1.4749(7)	0.2677(5)	0.2653(4)	0.053(6)
C(2)	1.4472(7)	0.3674(5)	0.2056(4)	0.049(5)
C(3)	1.5132(9)	0.3724(7)	0.1170(4)	0.071(8)
C(4)	1.3877(11)	0.3491(7)	0.0734(4)	0.071(8)
C(5)	1.2455(8)	0.2924(5)	0.1257(4)	0.051(5)
C(6)	1.2837(8)	0.1887(5)	0.1826(4)	0.053(5)
C(7)	1.4715(10)	0.1216(6)	0.1964(5)	0.073(8)
C(8)	1.5704(9)	0.1591(6)	0.2471(6)	0.073(8)
C(9)	1.1221(9)	0.6261(4)	0.1835(4)	0.054(6)
C(10)	0.9566(9)	0.6763(4)	0.2160(4)	0.056(6)
C(11)	0.8136(12)	0.7632(5)	0.1660(6)	0.081(9)
C(12)	0.7002(11)	0.7194(6)	0.1296(6)	0.081(9)
C(13)	0.7684(9)	0.5988(5)	0.1306(5)	0.062(7)
C(14)	0.9362(9)	0.5567(5)	0.0934(4)	0.056(6)
C(15)	1.0630(12)	0.6302(7)	0.0471(4)	0.072(8)
C(16)	1.1867(12)	0.6500(6)	0.0966(4)	0.076(9)
Ru(3)	0.27146(6)	0.76797(3)	0.44150(3)	0.0395(3)
C(17)	0.5685(10)	0.7381(10)	0.4330(7)	0.094(12)
C(18)	0.5187(13)	0.6611(7)	0.4973(7)	0.092(11)
C(19)	0.3838(14)	0.6923(7)	0.5596(5)	0.089(10)

(continued)

TABLE 3. *(continued)*

Atom	x/a	y/b	z/c	U_{eq}[b]
C(20)	0.3088(11)	0.8039(7)	0.5518(4)	0.073(8)
C(21)	0.3680(12)	0.8813(6)	0.4861(6)	0.080(9)
C(22)	0.4940(12)	0.8497(9)	0.4262(6)	0.090(11)
C(23)	0.0022(8)	0.8748(5)	0.4315(4)	0.051(5)
C(24)	−0.0094(8)	0.7618(6)	0.4651(4)	0.057(6)
C(25)	0.0807(9)	0.6760(5)	0.4305(4)	0.057(6)
C(26)	0.2183(9)	0.6815(5)	0.3654(4)	0.057(6)
C(27)	0.2685(8)	0.7767(5)	0.3161(4)	0.052(5)
C(28)	0.1531(10)	0.8698(6)	0.2592(4)	0.061(7)
C(29)	−0.0418(10)	0.9040(5)	0.2870(4)	0.061(6)
C(30)	−0.0654(10)	0.9514(5)	0.3580(5)	0.064(7)
C(31)	−0.100(3)	0.057(2)	0.044(1)	0.034(4)
C(32)	0.144(4)	0.023(2)	0.047(2)	0.058(6)
C(33)	−0.216(3)	0.034(2)	0.005(2)	0.051(5)
C(34)	−0.035(3)	0.063(2)	0.056(1)	0.043(5)
C(35)	−0.156(4)	0.045(2)	0.022(2)	0.048(5)
C(36)	0.073(4)	0.016(2)	0.036(2)	0.058(6)

[a] $Ru_2Cl_4(COD)_2$ (2): atoms Ru(1) through C(16); $RuH(C_8H_{11})(C_6H_6)$ (3): atoms Ru(3) through C(30); solvate benzene: atoms C(31) through C(36) (s.o.f.s 0.25 each). [b] Equivalent isotropic displacement parameters (cf. Table 2) for the Ru, Cl, and C atoms of the two complex molecules; the solvent molecule was refined isotropically.

TABLE 4. Positional and thermal parameters of $Ru_3Cl_3(OCH_3)(COD)_3$ (4)

Atom	x/a	y/b	z/c	U_{eq}[a]
Molecule A				
Ru(1)	0.1037(1)	0.1512(3)	0.0000(0)	0.037(2)
Ru(2)	0.0007(1)	0.1415(3)	0.0669(1)	0.036(2)
Ru(3)	−0.0212(1)	−0.0923(2)	−0.0068(1)	0.032(2)
Cl(1)	−0.0354(5)	0.1754(9)	−0.0106(4)	0.058(6)
Cl(2)	0.0797(5)	−0.0386(9)	−0.0568(3)	0.050(6)
Cl(3)	−0.0943(4)	−0.0563(8)	0.0585(3)	0.044(6)
O(1)	0.068(1)	−0.030(2)	0.040(1)	0.051(4)
C(1)	0.110(2)	−0.123(3)	0.059(1)	0.076(4)
C(11)	0.206(2)	0.185(2)	0.035(1)	0.050(4)
C(12)	0.219(1)	0.097(2)	−0.001(1)	0.031(4)
C(13)	0.253(2)	0.147(3)	−0.045(1)	0.050(4)
C(14)	0.216(2)	0.282(3)	−0.064(1)	0.084(5)
C(15)	0.135(2)	0.301(3)	−0.047(1)	0.061(4)
C(16)	0.113(1)	0.371(2)	−0.008(1)	0.032(4)
C(17)	0.175(2)	0.453(3)	0.016(1)	0.085(5)
C(18)	0.229(2)	0.342(2)	0.036(1)	0.059(4)
C(21)	0.073(2)	0.162(2)	0.120(1)	0.060(4)
C(22)	0.009(1)	0.088(3)	0.135(1)	0.045(4)
C(23)	−0.057(2)	0.148(3)	0.161(1)	0.081(4)
C(24)	−0.115(2)	0.233(3)	0.134(1)	0.076(5)
C(25)	−0.084(2)	0.281(3)	0.089(1)	0.058(4)
C(26)	−0.019(1)	0.362(3)	0.080(1)	0.051(4)
C(27)	0.026(2)	0.419(3)	0.119(1)	0.073(4)
C(28)	0.089(2)	0.317(2)	0.133(1)	0.088(5)
C(31)	−0.035(1)	−0.315(3)	0.015(1)	0.040(4)
C(32)	0.019(1)	−0.311(3)	−0.018(1)	0.038(4)
C(33)	0.002(2)	−0.353(3)	−0.065(1)	0.063(4)
C(34)	−0.059(2)	−0.269(2)	−0.090(1)	0.062(4)
C(35)	−0.082(1)	−0.130(2)	−0.067(1)	0.039(4)
C(36)	−0.133(1)	−0.134(2)	−0.032(1)	0.041(4)
C(37)	−0.171(1)	−0.266(2)	−0.012(1)	0.066(4)
C(38)	−0.116(1)	−0.370(3)	0.010(1)	0.060(4)
Molecule B				
Ru(4)	0.3454(1)	0.3323(3)	0.7860	0.041(3)
Ru(5)	0.2399(2)	0.3538(3)	0.7210(1)	0.040(3)
Ru(6)	0.2246(1)	0.5797(3)	0.7977(1)	0.036(2)
Cl(4)	0.2071(5)	0.3155(10)	0.7990(4)	0.062(6)
Cl(5)	0.3280(5)	0.5185(9)	0.8453(4)	0.053(6)
Cl(6)	0.1469(5)	0.5579(9)	0.7343(3)	0.052(6)
O(2)	0.309(1)	0.522(2)	0.752(1)	0.049(4)
C(2)	0.349(2)	0.613(3)	0.731(1)	0.078(4)
C(41)	0.464(2)	0.373(3)	0.788(1)	0.076(4)
C(42)	0.443(2)	0.295(2)	0.751(1)	0.051(4)
C(43)	0.465(2)	0.137(2)	0.746(1)	0.072(4)
C(44)	0.406(2)	0.035(3)	0.765(1)	0.079(4)
C(45)	0.350(2)	0.115(3)	0.794(1)	0.063(4)
C(46)	0.375(2)	0.175(3)	0.834(1)	0.060(4)
C(47)	0.454(2)	0.199(3)	0.853(1)	0.089(5)
C(48)	0.499(2)	0.320(3)	0.831(1)	0.090(5)
C(51)	0.309(1)	0.329(2)	0.666(1)	0.051(4)
C(52)	0.245(1)	0.408(3)	0.655(1)	0.068(4)
C(53)	0.179(2)	0.348(3)	0.628(1)	0.081(4)
C(54)	0.118(2)	0.281(3)	0.658(1)	0.079(4)
C(55)	0.153(2)	0.227(3)	0.701(1)	0.055(4)
C(56)	0.218(1)	0.144(3)	0.707(1)	0.054(4)
C(57)	0.254(2)	0.087(3)	0.665(1)	0.076(4)
C(58)	0.324(2)	0.175(2)	0.652(1)	0.056(4)
C(61)	0.264(2)	0.793(3)	0.817(1)	0.043(4)
C(62)	0.218(1)	0.806(3)	0.780(1)	0.057(4)
C(63)	0.137(1)	0.857(3)	0.785(1)	0.058(4)
C(64)	0.088(2)	0.776(2)	0.818(1)	0.056(4)
C(65)	0.117(1)	0.627(2)	0.829(1)	0.043(4)
C(66)	0.171(2)	0.597(3)	0.861(1)	0.052(4)
C(67)	0.210(2)	0.711(2)	0.889(1)	0.070(4)
C(68)	0.239(2)	0.839(3)	0.863(1)	0.065(4)

[a] Equivalent isotropic displacement parameters (cf. Table 2) for the Ru and Cl atoms; the carbon positions were refined isotropically.

Results and Discussion

In the molecular structure of Ru(COD)(COT) (1) the coordinatively bonded triene part of the η^6-C_8H_{10} ligand is characterized by C–C bond lengths not differing significantly from each other. A similar bonding pattern indicating substantial electron delocalization within the conjugated π-system has previously been observed for the triene fragment of (cyclooctatriene)(bicyclo[4.2.0]octadiene)iron(0), which likewise does not exhibit a

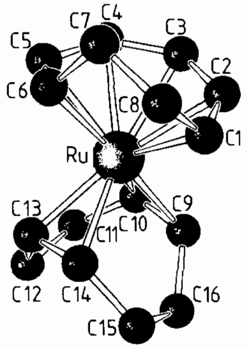

Fig. 1. Molecular arrangement and numbering scheme of the non-hydrogen atoms of 1. Bond lengths (pm) and angles (°) are: C(1)–Ru, 224.7(6); C(2)–Ru, 222.0(6); C(3)–Ru, 223.2(8); C(4)–Ru, 225.9(8); C(5)–Ru, 219.6(5); C(6)–Ru, 220.9(5); C(9)–Ru, 219.5(5); C(10)–Ru, 219.2(5); C(13)–Ru, 213.5(5); C(14)–Ru, 214.2(4); C(1)–C(2), 138.9(9); C(2)–C(3), 137.3(12); C(3)–C(4), 141.5(10); C(4)–C(5), 139.8(11); C(5)–C(6), 142.2(8); C(6)–C(7), 149.5(7); C(7)–C(8), 148.0(9); C(8)–C(1), 150.6(9); C(9)–C(10), 140.0(7); C(10)–C(11), 148.8(9); C(11)–C(12), 153.6(8); C(12)–C(13), 151.8(7); C(13)–C(14), 139.6(12); C(14)–C(15), 150.7(10); C(15)–C(16), 152.9(8); C(16)–C(9), 153.6(7). C(8)–C(1)–C(2), 127.1(5); C(1)–C(2)–C(3), 133.2(6); C(2)–C(3)–C(4), 135.6(9); C(3)–C(4)–C(5), 128.4(8); C(4)–C(5)–C(6), 119.7(6); C(5)–C(6)–C(7), 121.8(5); C(6)–C(7)–C(8), 108.6(4); C(7)–C(8)–C(1), 108.7(5); C(16)–C(9)–C(10), 123.5(5); C(9)–C(10)–C(11), 125.6(4); C(10)–C(11)–C(12), 112.8(5); C(11)–C(12)–C(13), 111.9(4); C(12)–C(13)–C(14), 123.6(5); C(13)–C(14)–C(15), 125.1(6); C(14)–C(15)–C(16), 113.5(4); C(15)–C(16)–C(9), 111.5(4).

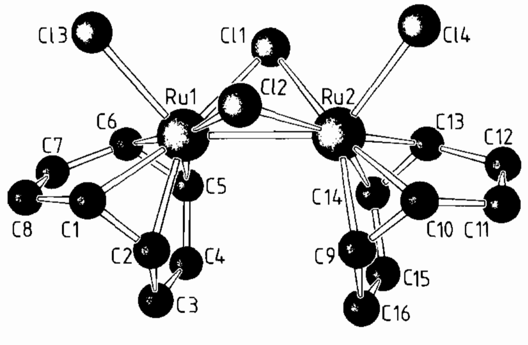

Fig. 2. The structure of molecule 2. Important interatomic distances (pm) and angles (°) are: Ru(1)–Ru(2), 279.1(1); Cl(1)–Ru(1), 242.4(1); Cl(2)–Ru(1), 245.3(1); Cl(3)–Ru(1), 241.9(2); C(1)–Ru(1), 213.9(5); C(2)–Ru(1), 216.8(5); C(5)–Ru(1), 216.9(5); C(6)–Ru(1), 214.8(5); Cl(1)–Ru(2), 244.5(1); Cl(2)–Ru(2), 244.5(2); Cl(4)–Ru(2), 240.7(2); C(9)–Ru(2), 216.9(5); C(10)–Ru(2), 215.5(5); C(13)–Ru(2), 215.8(6); C(14)–Ru(2), 218.1(6). Cl(1)–Ru(1)–Cl(3), 89.6(1); Cl(2)–Ru(1)–Cl(3), 88.5(1); Cl(1)–Ru(2)–Cl(4), 88.9(1); Cl(2)–Ru(2)–Cl(4), 89.5(1); Ru(1)–Cl(1)–Ru(2), 69.9(1); Ru(1)–Cl(2)–Ru(2), 69.5(1).

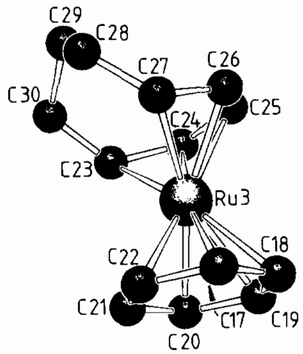

Fig. 3. Perspective view of complex 3. Pertinent bond lengths (pm) and angles (°) are: C(17)–Ru(3), 221.3(8); C(18)–Ru(3), 224.4(7); C(19)–Ru(3), 224.6(7); C(20)–Ru(3), 222.3(7); C(21)–Ru(3), 221.7(7); C(22)–Ru(3), 219.7(8); C(23)–Ru(3), 218.9(6); C(24)–Ru(3), 215.7(6); C(25)–Ru(3), 220.6(6); C(26)–Ru(3), 215.6(6); C(27)–Ru(3), 218.8(6); C(17)–C(18), 135(1); C(18)–C(19), 145(1); C(19)–C(20), 141(1); C(20)–C(21), 139(1); C(21)–C(22), 139(1); C(22)–C(17), 141(1); C(23)–C(24), 145(1); C(24)–C(25), 141(1); C(25)–C(26), 142(1); C(26)–C(27), 140(1); C(27)–C(28), 152(1); C(28)–C(29), 149(1); C(29)–C(30), 153(1); C(30–C(23), 147(1). C(22)–C(17)–C(18), 120.6(9); C(17)–C(18)–C(19), 120.4(7); C(18)–C(19)–C(20), 118.5(8); C(19)–C(20)–C(21), 119.6(8); C(20)–C(21)–C(22), 120.9(8); C(21)–C(22)–C(17), 119.9(9); C(30)–C(23)–C(24), 128.3(6); C(23)–C(24)–C(25), 124.8(6); C(24)–C(25)–C(26), 126.2(6); C(25)–C(26)–C(27), 125.9(5); C(26)–C(27)–C(28), 126.4(6); C(27)–C(28)–C(29), 117.6(6); C(28)–C(29)–C(30), 110.9(6); C(29)–C(30)–C(23), 115.8(5).

marked C–C/C=C alteration of its carbon–carbon bond lengths [15]. The $(1\text{–}6\text{-}\eta\text{-}C_8H_{10})$Ru metal-to-carbon distances vary between 219.6(5) and 225.9(8) pm and thus compare favourably with those measured for the 1–4-η-cyclooctatetraene compound $Ru(C_8H_8)(CO)_3$, 218.2(6) and 226.5(6) pm [16], but tend to be longer than the Ru–C distances of other C_8 cyclopolyolefin derivatives of Ru(0) such as $Ru(1\text{–}4\text{-}\eta\text{-}C_8H_8)(C_6Me_6)$ (212(1) and 223(1) pm [17]) or $Ru(1\text{–}4\text{-}\eta\text{-}C_8H_{10})(C_8H_{12})[P(OMe)_3]$ (204(2), 216(2), 218(2), and 223(2) pm [18]). The COD ligand of **1** displays the normal tub configuration which is also found in **2** and **4**.

In the structure of molecule **3** contained in the lattice of the addition compound $\mathbf{2}\cdot\mathbf{3}\cdot 0.5C_6H_6$, the benzene ring retains its planar geometry. The conformation of the C_8 ring, the metal-bonded part of which does not markedly deviate from planarity, as well as the presence of five carbon atoms within bonding distance of the central metal (bond lengths 218.9(6), 215.7(6), 220.6(6), 215.6(6), and 218.8(6) pm) clearly establish the coordination of a 1–5-η-cyclooctadienyl ligand (cf. Fig. 3). In keeping with an η^5-pentadienyl framework of the C_8 ring, the bond lengths between the five carbons attached to the ruthenium atom vary between 140 and 145 pm.

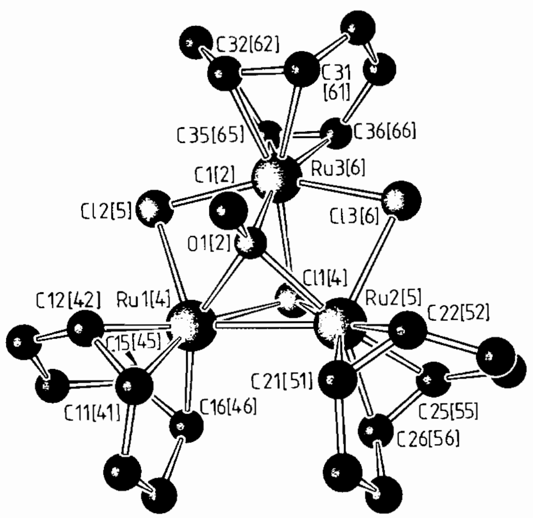

Fig. 4. Spatial arrangement and labelling scheme of the non-hydrogen atoms of the two crystallographically independent molecules of complex 4 (labels not put in brackets: molecule A; bracketed labels: molecule B). Selected interatomic distances (pm) and angles (°) of molecule A are: Ru(1)–Ru(2), 276.1(4); Ru(1)–Ru(3), 320.1(3); Ru(2)–Ru(3), 318.0(4); Cl(1)–Ru(1), 251.4(9); Cl(1)–Ru(2), 248.9(12); Cl(1)–Ru(3), 253.0(9); Cl(2)–Ru(1), 253.3(9); Cl(2)–Ru(3), 242.2(9); Cl(3)–Ru(2), 252.8(8); Cl(3)–Ru(3), 241.9(9); O(1)–Ru(1), 219(2); O(1)–Ru(2), 218(2); O(1)–Ru(3), 222(2); C(11)–Ru(1), 215(3); C(12)–Ru(1), 212(2); C(15)–Ru(1), 210(3); C(16)–Ru(1), 209(2); C(21)–Ru(2), 209(3); C(22)–Ru(2), 215(3); C(25)–Ru(2), 212(3); C(26)–Ru(2), 214(2); C(31)–Ru(3), 222(2); C(32)Ru(3), 221(2); C(35)–Ru(3), 218(2); C(36)–Ru(3), 218(2). Ru(1)–Cl(1)–Ru(2), 67.0(3); Ru(1)–Cl(1)–Ru(3), 78.8(3); Ru(2)–Cl(1)–Ru(3), 78.6(3); Ru(1)–Cl(2)–Ru(3), 80.4(3); Ru(2)–Cl(3)–Ru(3), 80.0(2); Ru(1)–O(1)–Ru(2), 78.3(7); Ru(1)–O(1)–Ru(3), 93.0(8); Ru(2)–O(1)–Ru(3), 92.7(8). Corresponding values for molecule B: Ru(4)–Ru(5), 275.5(4); Ru(4)–Ru(6), 319.1(4); Ru(5)–Ru(6), 318.6(4); Cl(4)–Ru(4), 250.4(9); Cl(4)–Ru(5), 249.5(12); Cl(4)–Ru(6), 250.2(10); Cl(5)–Ru(4), 254.6(9); Cl(5)–Ru(6), 242.5(9); Cl(6)–Ru(5), 256.8(9); Cl(6)–Ru(6), 240.1(9); O(2)–Ru(4), 217(2); O(2)–Ru(5), 221(2); O(2)–Ru(6), 212(2); C(41)–Ru(4), 215(3); C(42)–Ru(4), 208(3); C(45)–Ru(4), 207(3); C(46)–Ru(4), 214(3); C(51)–Ru(5), 211(3); C(52)–Ru(5), 209(3); C(55)–Ru(5), 206(3); C(56)–Ru(5), 205(3); C(61)–Ru(6); 221(2); C(62)–Ru(6), 220(3); C(65)–Ru(6), 220(2); C(66)–Ru(6), 219(3). Ru(4)–Cl(4)–Ru(5), 66.9(3); Ru(4)–Cl(4)–Ru(6), 79.2(3); Ru(5)–Cl(4)–Ru(6), 79.2(3); Ru(4)–Cl(5)–Ru(6), 79.8(3); Ru(5)–Cl(6)–Ru(6), 79.7(3); Ru(4)–O(2)–Ru(5), 77.9(7); Ru(4)–O(2)–Ru(6), 96.1(9); Ru(5)–O(2)–Ru(6), 94.5(8).

Similar η^5 bonding of the C_8H_{11} ring has previously been observed for $[Ru(1\text{–}5\text{-}\eta\text{-}C_8H_{11})(PMe_2Ph)_3][PF_6]$ [19] and $Ru(1\text{–}5\text{-}C_8H_{11})(\eta^6\text{-}1,4\text{-}CH_3C_6H_4SO_3)$ [20]. The molecular dimensions of these C_8H_{11} derivatives, like those of 3, also display longer metal-to-carbon distances for the central and terminal atoms of the pentadienyl skeleton than for those in between. It should be noted that the $1\text{–}5\text{-}\eta\text{-}C_8H_{11}$ coordination found for the three aforementioned ruthenium complexes is quite different from the pentahapto geometry of the cyclooctadienyl ligands in the formally related compounds $Ru(C_8H_{11})(\eta^6\text{-}C_6H_5BX_3)$ (X = F, Ph), which were observed to contain 1–3:5–6-η allyl-monoene anionic C_8H_{11} species [21]. The same pentadienyl/allyl-monoene isomerism has been described for the two cyclooctatrienyl ruthenium derivatives $[Ru(1\text{–}5\text{-}\eta\text{-}C_8H_9)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][PF_6]$ and $[Ru(1\text{–}3\text{:}6\text{–}7\text{-}\eta\text{-}C_8H_9)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][PF_6]$ [22]. The presence of the crystallographically undetected hydride ligand in molecule 3 is unequivocally established by a ^1H NMR singlet occurring at $\delta = -15.27$ (C_6D_6 solution).

Molecule 2, also being part of the lattice of the addition compound $2\cdot3\cdot0.5C_6H_6$, is remarkable in that it constitutes a structural isomer of the highly insoluble, but synthetically useful, polymeric $[Ru(COD)Cl_2]_x$ which normally results from cyclooctadiene and ethanolic ruthenium trichloride [23]. The metal–metal distance, 279.1(1) pm, is considerably shorter than the non-bonded Ru–Ru distances observed for double halide-bridged binuclear Ru(II) complexes containing six-coordinate central atoms, such as $[RuCl_2(PPh_3)(DPF)]_2$, DPF = 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene, (*d*-(Ru–Ru = 368.3(1) pm [24]) or $[RuBr_2(CO)_3]_2$, (*d*(Ru–Ru) = 375.2(4) pm [25]). The *d*(Ru–Ru) value found for 2 hence indicates significant metal–metal interaction, although it remains somewhat long for the Ru=Ru double bond formally required if each ruthenium atom is assigned the closed-shell 18e configuration.

The original product of the reaction leading to complex 4, $Ru_3Cl_3(OCH_3)(C_8H_{12})_3$, is presumably the ethoxy derivative which is converted to the methoxy derivative during work-up. Compound 4 is best regarded as a mixed-valence triruthenium compound containing one coordinatively saturated Ru(II) centre, Ru(3) or Ru(6) of Fig. 4, and two Ru(I) centres achieving their 18e count by formation of one metal–metal linkage in addition to five metal-to-ligand bonds (atoms Ru(1) and Ru(2) or Ru(4) and Ru(5) of Fig. 4). In accordance with this description of 4 as a Ru_3(I,I,II) derivative, which to the best of our knowledge has no structurally characterized precedent, the two crystallographically independent molecules of $Ru_3Cl_3(OCH_3)(C_8H_{12})_3$ reveal non-bonding distances between Ru(3) and Ru(1), 320.1(3) pm, and Ru(3) and Ru(2), 318.0(4) pm, as well as between Ru(6) and Ru(4), 319.1(4) pm, and Ru(6) and Ru(5), 318.6(4) pm, bonding interactions of 276.1(4) and 275.5(4) pm being measured for Ru(1)–Ru(2) and Ru(4)–Ru(5), respectively.

The Ru–Cl bond lengths observed for both the terminal and bridging Ru–Cl linkages of **2** and **4** – 240.7(2) and 241.9(2) pm for the terminal units in **2**, 242.4(1) to 245.3(1) pm for the μ_2-bridges of **2**, 240.1(9) to 256.8(9) pm for the doubly bridging chloro ligands of **4** with the shorter bonds to the Ru(II) centres and the longer ones to the metal(I) atoms, and 248.9(9) to 253.0(9) pm for the triple bridges of **4** – compare reasonably with previously reported d(Ru–Cl) values, which appear to fall into the range 238 to 255 pm [24, 26].

As has recently been stated by others [20], the formation of ruthenium trichloride reduction products persistently retaining chloro ligands attached to Ru(II) centres, e.g. **2** and **4**, can be attributed to the inertness of the Ru(II)–Cl bond rendering the chloride ion difficult to remove even by strong reducing agents such as zinc powder. $RuH(C_8H_{11})(C_6H_6)$, **3**, can be regarded as a trapped form of $RuH(C_8H_{11})(COT)$ where the cyclooctatriene ligand has been displaced by benzene. Cyclooctadienyl hydrides of composition $RuH(C_8H_{11})(COT)$ containing either 1–5-η-C_8H_{11} or 1–3:5–6-η-C_8H_{11} ligands have been postulated as common key intermediates for the formation of the various $C_{16}H_{22}Ru$ isomers that are accessible by zinc reduction of alcoholic $RuCl_3$ in the presence of cyclooctadiene under varying conditions [8].

Supplementary Material

Further crystallographic details including tables of thermal parameters and calculated hydrogen positions as well as F_o/F_c listings are available from the Fachinformationszentrum Energie, Physik, Mathematik GmbH (cooperating with the Cambridge Crystallographic Data Centre), D-7514 Eggenstein-Leopoldshafen 2, F.R.G. Any request should be accompanied by the registration number CSD-53626 as well as by the full literature citation for this communication.

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