Journal of Organometallic Chemistry 485 (1995) 253–255

Reactions of dodecacarbonyltriruthenium with enones: η^3-coordinated dihydropyranyl rings

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Received 14 May 1994

Abstract

Further studies of reactions of $Ru_3(CO)_{12}$ with enones PhCH=CHC(R)=O (R = Me or p-MeC_6H_4) revealed the formation of binuclear and tetranuclear complexes, whose molecules involve the η^3-coordinated six-membered dihydropyranyl ring; X-ray structures of both complexes are reported.

Keywords: Ruthenium

Previously [1,2] we have shown that thermal reactions of $Ru_3(CO)_{12}$ with enones (oxadienes) PhCH=CHC(R)=O (R = p-MeC_6H_4 (**1a**) or R = Me (**1b**)) give rise to mixtures of carbonylruthenium complexes of different nuclearities. All products studied were found to involve the same structural arrangement namely a five-membered chelate oxaruthenacycle, η^3 coordinated by the second metal atom. Moreover, the lone electron pair of the O atom, uninvolved in the cyclic bond, may be engaged in further coordination by the third ruthenium atom. Such diverse coordination capabilities of the oxaruthenacycle are the prerequisite for the formation of various complexes **2**–**5** (Scheme 1) with rather complicated structures, which were elucidated by X-ray diffraction studies.

In the present paper we report the isolation and X-ray structures of two more complexes **6a** and **7b** [3], formed in the reactions of $Ru_3(CO)_{12}$ with **1a** and **1b** respectively. Although the overall structures of **6** and **7** are quite different, both of them feature the same typical structural moiety, namely six-membered η^3-coordinated dihydropyranyl ring, which was not observed in the earlier products **2**–**5** of the same reactions.

The binuclear complex **6a** represents a yellow crystalline precipitate formed in the reaction of $Ru_3(CO)_{12}$ with **1a** in refluxing heptane (molar ratio 1:4; 9 h; yield, 10%). Selected spectroscopic data for **6a**; IR spectrum (CH_2Cl_2): ν(CO) 2076w, 2064s, 2004s cm^{-1}. It has a rather peculiar structure (Fig. 1), involving two η^3-dihydropyranyl rings. The molecule of **6** occupies a special position over the crystallographic inversion centre coinciding with the centre of the four-membered Ru_2O_2 cycle. Its oxygen atoms may be considered to be 3e donors, each of them forming one shorter covalent σ bond (Ru(1)–O(4), 2.069(2) Å) and one longer coordination bond (Ru(1)–O(4′), 2.199(3) Å) with ruthenium atoms, which are additionally coordinated with the 2,3,4-allyl moieties of the dihydropyranyl rings.

The tetranuclear complex **7b** was obtained in the reaction of $Ru_3(CO)_{12}$ with **1b** (molar ratio, 1:4), refluxing in heptane for 4 h with subsequent chromatography on silica gel (eluent, 10:1 heptane CH_2Cl_2) and crystallization from heptane (yield, 4%). IR spectrum (heptane); ν(CO) 2040m, 2036m, 2006s, 2002s, 1998vs, 1964s, 1948s, 1936vs cm^{-1}. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 7.77–7.00 (m, 20H, arom), 5.168 (s, 1H, =CH), 5.062 (s, 1H, =CH), 3.824 (s, 1H, allyl-H), 3.06–2.50 (m, 3H, $-CHCH_2$), 1.907 (s, 6H, $-CH_3$), 1.743 (s, 3H, $-CH_3$), 0.887 (s, 3H, $-CH_3$). Complex **7b** combines both typical features characteristic for the structures of carbonylruthenium complexes with enone ligands. Its molecule (Fig. 2) has two five-membered oxaruthenacycles similar to those found in **2**–**5**, as well

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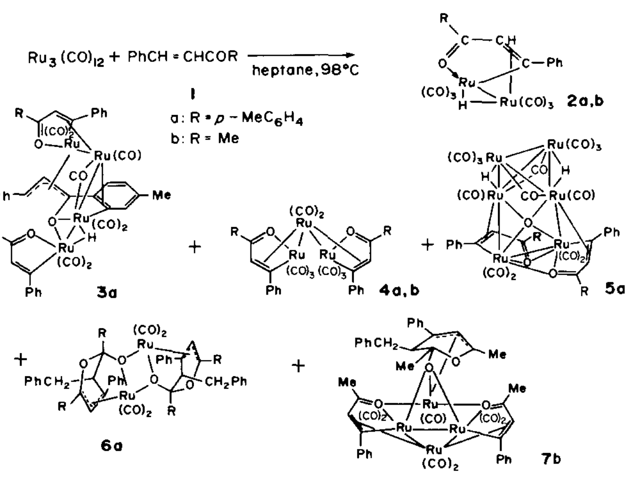
SSDI 0022-328X(94)24779-1



Scheme 1.

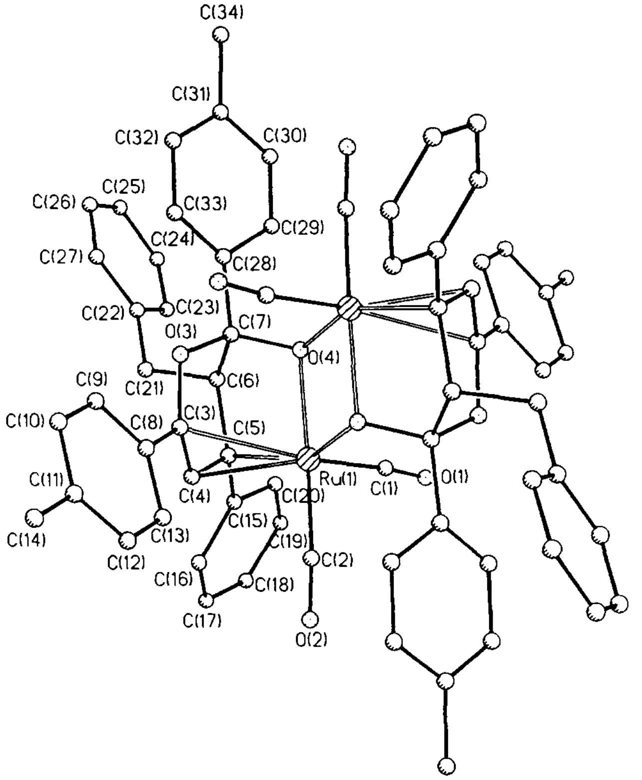


Fig. 1. Molecular structure of **6a**. Selected bond distances (Å): Ru(1)–O(4), 2.069(2); Ru(1)–O(4'), 2.199(3); Ru(1)–C(3), 2.531(4); Ru(1)–C(4), 2.229(4); Ru(1)–C(5), 2.158(4); O(3)–C(3), 1.374(3); C(3)–C(4), 1.395(5); C(4)–C(5), 1.437(6); C(5)–C(6), 1.536(3); C(6)–C(7), 1.550(6); C(7)–O(3), 1.460(5); C(7)–O(4), 1.393(4); C(3)–C(8), 1.479(6); C(5)–C(15), 1.492(5); C(6)–C(21), 1.546(6); C(7)–C(28), 1.510(3).

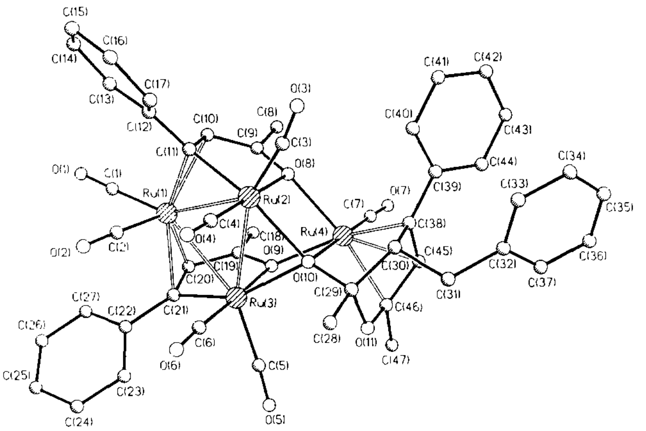
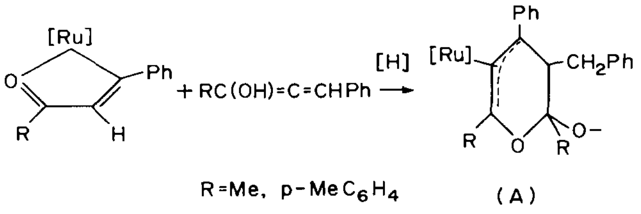


Fig. 2. Molecular structure of **7b**. Selected bond distances (Å): Ru(1)–Ru(2), 2.916(2); Ru(1)–Ru(3), 2.908(2); Ru(2)–Ru(3), 2.864(1); Ru(1)–C(10), 2.31(1); Ru(1)–C(11), 2.15(1); Ru(1)–C(20), 2.27(1); Ru(1)–C(21), 2.22(1); Ru(2)–O(8), 2.131(6); Ru(2)–C(11), 2.07(1); O(8)–C(9), 1.30(2); C(9)–C(10), 1.40(2); C(10)–C(11), 1.46(1); Ru(3)–O(9), 2.137(6); Ru(3)–C(21), 2.05(1); O(9)–C(19), 1.31(2); C(19)–C(20), 1.40(2); C(20)–C(21), 1.43(1); Ru(2)–O(10), 2.224(8); Ru(3)–O(10), 2.215(8); Ru(4)–O(8), 2.234(8); Ru(4)–O(9), 2.221(9); Ru(4)–O(10), 2.114(6); Ru(4)–C(38), 2.18(1); Ru(4)–C(45), 2.11(1); Ru(4)–C(46), 2.17(1); O(10)–C(29), 1.44(2); O(11)–C(29), 1.44(1); O(11)–C(46), 1.42(1); C(29)–C(30), 1.51(2); C(30)–C(38), 1.55(1); C(38)–C(45), 1.41(2); C(45)–C(46), 1.43(2).

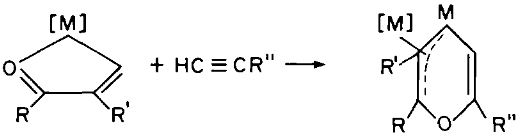
as one dihydropyranyl ring, the same as in **6a**. The Ru(2) and Ru(3) atoms are involved in two five-membered oxaruthenacycles, both of which coordinate the Ru(1) atom. In this case, in contrast with **4**, the Ru(2)–Ru(3) bond (2.864(1) Å) is retained. The fourth ruthenium atom, Ru(4), η^3 coordinated with dihydropyranyl ring, is bound to the metal triangle via the O(8), O(9) and O(10) atoms. The last oxygen atom, in distinction to its analogue in **6a**, forms three bonds with metal atoms, two of which (Ru(2)–O(10), 2.224(8); Ru(3)–O(10), 2.215 (8) Å) being significantly longer than the third (Ru(4)–O(10), 2.114(6) Å). Formally considering this atom as a 5e donor and the O(8) and O(9) atoms as 3e donors, one may easily find each of the Ru atoms in **7b** to have a closed 18e shell; the same is true for **6a**.

Both dihydropyranyl rings in **6a** and **7b** have a chair conformation considerably flattened at its allyl side: the folding angles along the lines C(3)...C(5) in **6a** and C(38)...C(46) in **7b** (25° and 32° respectively) are much smaller than the folding angles along the lines O(3)...C(6) and O(11)...C(30) (52° and 49°) in **6a** and **7b** respectively.

Taking into account the rather complex structures of **6a** and **7b**, it is difficult to put forward, at least at present, any sufficiently well-substantiated assumption on the mechanisms of their formation. It may still be suggested that η^3-dihydropyranyl rings (**A**) are formed from the five-membered oxaruthenacycles as a result of initial insertion of the second enone molecule in its dieneol form RC(OH)=C=CHPh and subsequent hydrogen addition:



This assumption is in agreement with the transformation of oxametallacycles into η^3-pyranyl complexes in the reaction with alkynes reported in [5]:



The results on the reactions of $Ru_3(CO)_{12}$ with oxadienes reported in the present and earlier papers [1,2] allow one to compare these heterodienes with their nitrogen analogues, azadienes, whose reactions with $Ru_3(CO)_{12}$ were studied in detail in [6]. The similarity of both heterodienes is limited to the formation of five-membered metallacycles [Ru]–C(R)=CH–C(R')=X (X = O or NR'') in both cases. However, the chemical behaviour of the cycles is quite different. Thus oxaruthenacycles coordinate additional metal atoms predominantly by η^3 type, whereas the azaruthenacycles are normally η^5 coordinated. The coupling of the ligands with formation of η^3-tetrahydropyridinyl rings, nitrogen analogues of rings **A**, has never been observed. The additional lone electron pair on the oxygen atom is capable of formation of metal–oxygen n bond, thus enhancing the complexity of the polynuclear molecular systems formed.

Acknowledgements

One of the author (A.I.Y.) acknowledges the financial support of the American Crystallographic Association and the US National Committee for Crystallography (the ACA–USNCCr grants program).

This work was in part supported by the Russian Foundation for Fundamental Research (Grants 93-03-4028 and 94-03-08338).

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[3] Crystal data for **6a**: $C_{66}H_{56}O_8Ru_2$; $M = 1203.3$; triclinic; space group, $P\bar{1}$; $a = 11.864(4)$, $b = 12.355(3)$, $c = 12.393(6)$ Å; $\alpha = 112.39(2)$, $\beta = 115.30(2)$, $\gamma = 100.02(2)°$; $V = 1389.9(7)$ Å^3; $Z = 1$, $D_c = 1.438$ g cm^{-3}.
Crystal data for **7b**: $C_{47}H_{38}O_{11}Ru_4 \cdot \frac{1}{2}n\text{-}C_6H_{14}$; $M = 1219.1$; monoclinic; space group, $P2_1/n$; $a = 13.183(3)$, $b = 19.175(3)$, $c = 20.180(4)$ Å; $\beta = 109.06(2)°$; $V = 4822(1)$ Å^3; $Z = 4$; $D_c = 1.679$ g cm^{-3}.
The X-ray diffraction experiments were carried out with a Siemens P3/PC diffractometer ($T = 293$ K; graphite-monochromated Mo Kα radiation; $\lambda = 0.71069$ Å; θ–2θ scan technique; $2\theta \leqslant 56°$ and 46° for **6a** and **7b** respectively). The structures were solved by direct methods using SHELXTL PLUS programs (PC version) [4]. Anisotropic least-squares refinement (H atoms refined isotropically for **6a** and included in calculated positions with the common refined $U_{iso} = 0.062(7)$ Å^2 for **7b**) converged at $R = 0.037$ and 0.062, $R_w = 0.047$ and 0.066 for 5423 and 4654 observed independent reflections with $I \geqslant 3\sigma(I)$ for **6a** and **7b** respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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