Preliminary Communication

Reactions of dodecacarbonyltriruthenium with enones.
Five-membered oxaruthenacycles

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(Received April 15, 1994)

Abstract

Tri- and hexanuclear ruthenium complexes, $Ru_3(CO)_8(\mu$-RCOCH=CPh$)_2$ and $Ru_6(CO)_{12}(\mu$-CO$)_2(\mu$-H$)_2(\mu_4$-O$)(\mu$-RCOCH=CPh$)_2$, are formed in the reactions of $Ru_3(CO)_{12}$ with oxadienes RCOCH=CHPh (R = $p - MeC_6H_4$ or Me); in both complexes, the X-ray diffraction studies revealed a common structural motif involving the five-membered chelate RuC=CC=O ring capable of coordinating additional metal atoms by its C=C double bond and by the lone pair of the O atom.

Key words: Ruthenium

Previously, we reported [1] that thermal reactions of $Ru_3(CO)_{12}$ with enones (oxadienes) RCOH=CHPh (1) (R = $p - MeC_6H_4$ (a), R = Me (b)) yield mixtures of carbonylruthenium complexes of various nuclearities. Several complexes have been isolated from these mixtures by preparative chromatography. The structures of two complexes, binuclear $Ru_2(\mu$-H$)(CO)_6(\mu$-MeCOCH=CPh) (2b) and tetranuclear $Ru_4(\mu$-H$)(\mu$-CO$)(CO)_7(p$-MeC$_6$H$_4$COCH=CPh$)(\mu$-p-MeC$_6$H$_4$COCH=CPh$)(\mu_4$-p-MeC$_6$H$_3$COCHCHPh) (3a) (cf. Scheme 1), have been determined by X-ray diffraction studies. The structures of other complexes were suggested on the basis of their IR and NMR spectra.

The present communication reports the structures of two more complexes of this series, $Ru_3(CO)_8(\mu$-MeC$_6$H$_4$COCH=CPh$)_2$ (4a) and $Ru_6(CO)_{12}(\mu$-CO$)_2(\mu$-H$)_2(\mu_4$-O$)(\mu$-MeC$_6$H$_4$COCH=CPh$)_2$ (5a), which are formed in the reaction of $Ru_3(CO)_{12}$ with 1a

(molar ratio 1:4, under reflux in heptane, 4 and 2.5 h, respectively).

Complex 4a was isolated by chromatography of the reaction products (silica gel, hexane/CH_2Cl_2 10:1) in the form of orange–red crystals; yield 18% [1].

The X-ray structural study of 4a has shown that its molecule (Fig. 1) features a chain of three Ru atoms in which two peripheral atoms are involved in the oxaruthenacyclopentadienyl rings [2]. The central Ru atom is η^3-coordinated by the ruthenaallyl moieties of both rings. Molecule 4a has thus a local twofold symmetry, although it occupies a general position in the crystal. Previously, by analogy with azaruthenarutheno-cenes prepared by reaction of $Ru_3(CO)_{12}$ with azadienes [2], we had suggested, as one of the possibilities, the bis(η^5-oxaruthenacyclopentadienyl)ruthenium structure for 4a. However, the C=O bond order decrease on formation of oxaruthenacyclopentadiene significantly reduced its ability for π-coordination of the metal atom. That is why, in 4a, η^3-ruthenaallyl is observed rather than the expected more symmetrical η^5-oxaruthenacyclopentadienyl system.
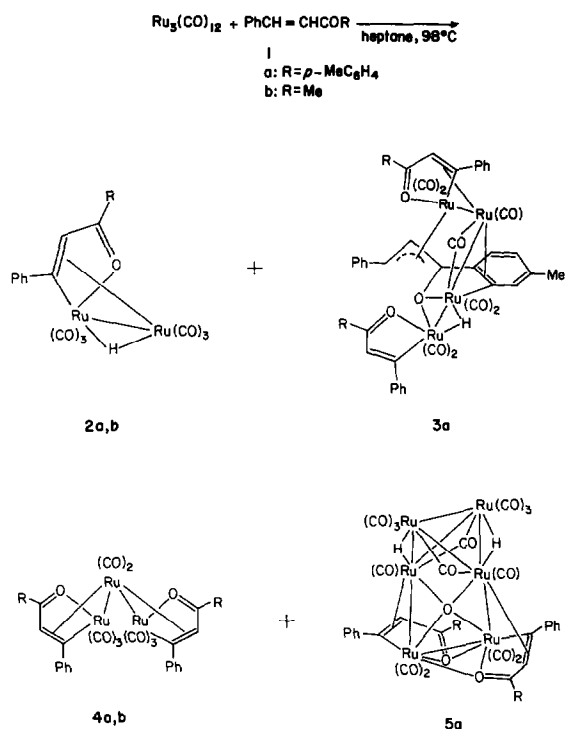
Complex 4b [3], structurally similar to 4a, is formed in the reaction of $Ru_3(CO)_{12}$ with 1b (molar ratio 1:4, refluxing heptane, 4 h). It was isolated from the reac-

Ru₃(CO)₁₂ + PhCH = CHCOR $\xrightarrow{\text{heptane, 98°C}}$

a: R = p-MeC₆H₄
b: R = Me

Scheme 1.

Fig. 2. The molecular structure of Ru₆(CO)₁₂(μ-CO)₂(μ-H)₂(μ_4-O)(μ-MeC₆H₄COCH=CPh)₂ (5a) (the atomic numbering in the aromatic rings is omitted for clarity). Selected bond distances (Å): Ru(1)–Ru(2) 3.114(1), Ru(1)–Ru(3) 3.016(1), Ru(1)–Ru(3a) 2.901(1), Ru(2)–Ru(2a) 3.081(1), Ru(3)–Ru(3a) 2.934(1), Ru(1)–C(7) 1.966(9), Ru(3)–C(7a) 2.287(7), Ru(1)–H(1) 1.89(11), Ru(3)–H(1) 1.74(9), Ru(1)–O(9) 2.097(4), Ru(2)–O(9) 2.098(4), Ru(1)–C(9) 2.234(6), Ru(1)–C(10) 2.151(6), Ru(2)–O(8) 2.127(5), Ru(2)–O(8a) 2.316(4), Ru(2)–C(10) 2.058(6), O(8)–C(8) 1.304(7), C(8)–C(9) 1.422(9), C(9)–C(10) 1.46(1), C(8)–C(11) 1.47(1), C(10)–C(18) 1.480(9).

tion mixture in 7% yield in the form of orange–red crystals by chromatography on silica gel with hexane/CH₂Cl₂ (10 : 1) as eluent.

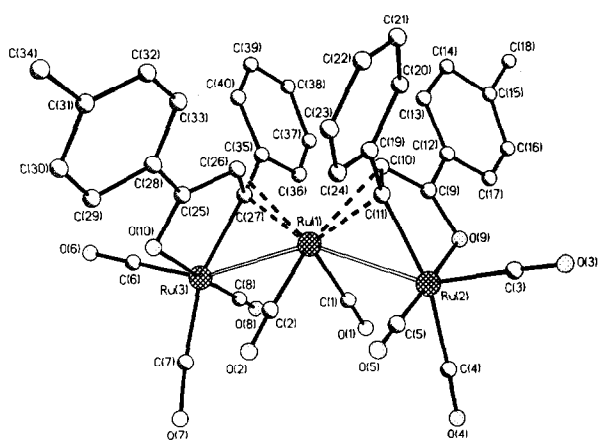Another product of the reaction of Ru₃(CO)₁₂ with 1a was isolated in the form of brown crystals (complex

5a [4]), which was recrystallized from heptane (yield 2%).

The X-ray diffraction study of 5a has shown this complex to be a hexanuclear cluster (Fig. 2), occupying a special position in the crystal [5]. The twofold symmetry axis passes through the central O(9) oxo-atom and the midpoints of the Ru(2)–Ru(2a) and Ru(3)–Ru(3a) bonds. The Ru(1), Ru(1a), Ru(3) and Ru(3a) atoms form a butterfly-type core, the tips of the butterfly wings Ru(1) and Ru(1a) being η^3-coordinated by

Fig. 1. The molecular structure of Ru₃(CO)₈(μ-MeC₆H₄-COCH=CPh)₂ (4a). Selected bond distances (Å): Ru(1)–Ru(2) 2.796(2), Ru(1)–Ru(3) 2.807(2), Ru(1)–C(10) 2.25(2), Ru(1)–C(11) 2.17(2), Ru(1)–C(26) 2.25(2), Ru(1)–C(27) 2.14(2), Ru(2)–O(9) 2.12(1), Ru(2)–C(11) 2.08(2), O(9)–C(9) 1.24(3), C(9)–C(10) 1.46(3), C(10)–C(11) 1.45(3), C(9)–C(12) 1.47(3), C(11)–C(19) 1.47(3), Ru(3)–O(10) 2.12(1), Ru(3)–C(27) 2.06(2), O(10)–C(25) 1.32(3), C(25)–C(26) 1.39(3), C(26)–C(27) 1.46(3), C(25)–C(28) 1.48(3), C(27)–C(35) 1.46(3).
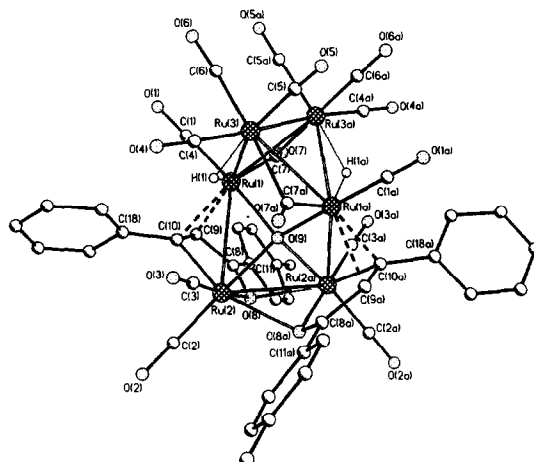
ruthenaallyl systems of chelate five-membered oxaruthenacycles.

In molecule **5a** there is one crystallographically independent asymmetrically bridging carbonyl group (supporting the Ru(1)–Ru(3a) bond) as well as one μ-hydride ligand bridging the Ru(1)–Ru(3) bond. The existence of μ-hydride atom located in the X-ray diffraction study is consistent with the ^{1}H NMR data. The significant (about 0.1 Å) elongation of the Ru(1)–Ru(3) bond (as compared to Ru(1)–Ru(3a)) provides additional evidence for the presence of a μ-hydride bridge, which is known to give rise to the weakening of the corresponding metal–metal bond in the cluster.

In contrast to **4a**, the Ru(2) and Ru(2a) atoms involved in the oxaruthenacycles in **5a** are directly bonded to each other, which results in the closure of the overall polycyclic system of metallic core. Both Ru(2) and Ru(2a) atoms also form coordination Ru ←O bonds with the oxygen atoms O(8) and O(8a) of the alternative five-membered cycles. Thus, compound **5a** exhibits a rather complex system of fused ruthenacycles.

One of the most unexpected features of the structure **5a** is the central O(9) oxo-atom coordinated by four metals. Although its origin seems at the moment not quite obvious, its nature as an oxygen atom was unambiguously proved by X-ray experiment; attempts to refine it as, say, carbon yielded insensible thermal parameters and much worse discrepancy factors.

In spite of the apparent complexity of the structures of clusters formed in the reactions of $Ru_3(CO)_{12}$ with enones **1a** and **1b** one can, nevertheless, discern one and the same building block, namely, the five-membered chelate oxaruthenacycle, which is obviously formed in the first stages of the reaction. Further complication of the structure is evidently associated with the ability of these cycles to coordinate additional metal atoms both by the ruthenaallyl moiety and by the uninvolved (in coordination with other Ru atom) lone electron pair of the oxygen atom.

Acknowledgements

References

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