

Reactions of diacetylene ligands with trinuclear clusters

II. Reactions of hexa-2,4-diyne-1,6-diol and 1,4-diphenyl-1,3-butadiyne with $\text{Ru}_3(\text{CO})_{12}$

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Received 3 July 1996; accepted 12 August 1996

Abstract

Thermal reactions of $\text{Ru}_3(\text{CO})_{12}$ with hexa-2,4-diyne-1,6-diol and 1,4-diphenyl-1,3-butadiyne were studied. Reaction of the triruthenium cluster with $\text{HOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OH}$ results in substitution of two CO groups and coordination of the diyne ligand to a ruthenium triangle in parallel μ_3, η^2 -mode via one of the conjugated triple bonds. The structure of the final product $\text{Ru}_3(\text{CO})_{10}(\mu_3, \eta^2\text{-HOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OH})$ was determined by a single-crystal X-ray study. The analogous reaction with $\text{PhC}_2\text{C}_2\text{Ph}$ affords the binuclear ruthenium complex $\text{Ru}_2(\text{CO})_6(\mu_3, \eta^4\text{-C(Ph)C(C}_2\text{Ph)C(C}_2\text{Ph)C(Ph)})$. The starting diyne ligand in this complex is dimerized forming a ruthenacyclopentadiene ring $\text{Ru-C(Ph)=C(R)C(R)=C(Ph)}$. As a whole, the structural unit obtained can be rationalized as a cluster skeleton containing two d- and four p-elements arranged into nido pentagonal bipyramid with eight skeletal electron pairs; this cluster pattern is very typical for the iron subgroup alkyne polynuclear complexes. © 1997 Elsevier Science S.A.

Keywords: Ruthenium; Clusters; Diacetylene derivatives; X-ray structure

1. Introduction

Reactions of alkynes with trinuclear ruthenium and osmium clusters have been studied extensively over the last two decades [1–5]. Various modes of alkyne coordination were obtained depending on the reaction conditions and nature of the starting reagents, in many cases the ligand coordination being accompanied by considerable rearrangement of the ligand structure. Reactions of poly-yne ligands with carbonyl clusters were less extensively studied and the examples reported in literature display interesting and unusual transformations of conjugated diynes in the process of coordination, including single C–C bond rupture [6], intramolecular cyclization of ligand [7], and the ligands coupling [8]. In our previous paper [7] we reported the reactions of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with hexa-2,4-diyne-1,6-diol and its derivatives. In the present paper we describe the results of $\text{Ru}_3(\text{CO})_{12}$ reaction with two conjugated diynes that afford products which differ in the composition of the

final cluster core and in the nature of the coordinated organic moiety.

2. Experimental

Commercial grade $\text{Ru}_3(\text{CO})_{12}$, 1,4-diphenyl-1,3-butadiyne and hexa-2,4-diyne-1,6-diol were used without additional purification. All solvents were dried over appropriate reagents and distilled prior to use. All reactions were carried out under dry argon. The NMR spectra were recorded on a Bruker AM 500 instrument, using $\text{Cr}(\text{acac})_3$ as a relaxation agent in the case of ^{13}C spectra. The IR spectra were recorded on a Specord M80 spectrophotometer. Mass spectra were measured on an MX-1321 instrument (electron impact, ionizing potential 70 eV).

2.1. Reaction of $\text{Ru}_3(\text{Co})_{12}$ with hexa-2,4-diyne-1,6-diol

Hexa-2,4-diyne-1,6-diol (45 mg, 0.41 mmol) was dissolved in 0.5 ml of methanol and diluted with 5 ml of chloroform. This solution was then added to a boiling

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solution of $\text{Ru}_3(\text{CO})_{12}$ (75 mg, 0.12 mmol) in 20 ml of chloroform. The mixture obtained was left to cool to room temperature. Prolonged heating of the reaction mixture results in decrease of the product yield. The solvent was then removed under reduced pressure, and the residue was extracted with 2×2 ml portions of chloroform, and the extract was separated by column chromatography (2×7 cm, Silica 5/40 mesh). Elution with hexane–ether (4/1) mixture gave the yellow band of unreacted $\text{Ru}_3(\text{CO})_{12}$ (24.9 mg). Changing the eluent polarity to hexane–ether (1/2) gave the orange band of the product (**I**) $\text{Ru}_3(\text{CO})_{10}(\mu_3, \eta^2\text{-HOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OH})$ (3 mg, 14% with respect to $\text{Ru}_3(\text{CO})_{12}$ consumed). IR, $\nu(\text{CO})$, cm^{-1} , CHCl_3 : 2101_w, 2070_s, 2055_s, 2032_m, 2015_{sh}, 1882_{w,br}; NMR ^1H , 297 K, CDCl_3 , δ , ppm: 4.40 (d, 4 Hz, CH_2), 4.32 (d, 2 Hz, CH_2), 2.12 (broad, OH), 1.55 (broad, OH); ^{13}C 297 K, CDCl_3 , δ , ppm: 196.5 (s, 10CO), 177.2 (s, C_{alkyne}), 136.2 (s, C_{alkyne}), 96.3 (s, C_{alkyne}), 90.5 (s, C_{alkyne}), 71.9 (t, 141 Hz, CH_2), 51.7 (t, 151 Hz, CH_2); ^{13}C , 215 K, carbonyl signals: 194.1 (1CO), 192.3 (1CO), 188.8 (1CO), and a broad signal in the range 205–185 ppm corresponding to the rest of the CO groups taking part in a fast exchange process. The mass spectra of the cluster displayed the molecular ion (m/e 693, Ru_3 303) and signals corresponding to the loss of ten CO groups. Single crystals of (**I**) suitable for an X-ray analysis were grown by slow diffusion of heptane in dichloromethane at 2°C.

2.2. Reaction of $\text{Ru}_3(\text{CO})_{12}$ with 1,4-diphenyl-1,3-butadiyne

$\text{Ru}_3(\text{CO})_{12}$ (159 mg, 0.25 mmol) and 1,4-diphenyl-1,3-butadiyne (130 mg, 0.64 mmol) were dissolved in 75 ml of hexane and refluxed under Ar for 3 h. The solution was then reduced in volume to 15 ml under vacuum and chromatographed on a column (1.5×14 cm) packed with Silica 5/40 mesh. Elution with hexane gave the unreacted ligand and $\text{Ru}_3(\text{CO})_{12}$ (60.2 mg). Subsequent elution with the hexane–ether (9/1) mixture gave a bright-yellow band of the main product, $\text{Ru}_2(\text{CO})_6(\mu_2, \eta^4\text{-C}(\text{Ph})\text{C}(\text{C}_2\text{Ph})\text{C}(\text{C}_2\text{Ph})\text{C}(\text{Ph}))$ (**II**) (70 mg), along with a few bands containing trace amounts of unidentified compounds. IR, $\nu(\text{CO})$, cm^{-1} , hexane: 2084_m, 2058_s, 2020_s, 2004_m, 1974_{sh}, 1958_{sh}. Single crystals of (**II**) suitable for an X-ray analysis were grown from the heptane solution at 2°C.

2.3. Crystal structure determination

X-ray diffraction studies of the crystals of **I** and **II** were carried out with a Siemens P3/PC diffractometer (293 and 148 K, graphite monochromated $\text{Mo K}\alpha$ radiation, $\lambda = 0.71073$ Å, $\theta/2\theta$ scan technique, $\theta \leq 25$ and

27°, 7276 and 7164 unique reflections collected for **I** and **II** respectively).

Crystals of **I** ($\text{C}_{17}\text{H}_9\text{O}_{12.5}\text{Ru}_3$, $M = 716.45$, $F(000) = 2744$) are monoclinic, space group $P2_1/c$, at 293 K $a = 21,514(9)$, $b = 9,368(4)$, $c = 24,419(10)$ Å, $\beta = 113.86(3)$, $V = 4501(3)$ Å³, $Z = 8$, $d_{\text{calc}} = 2.115$ g cm⁻³.

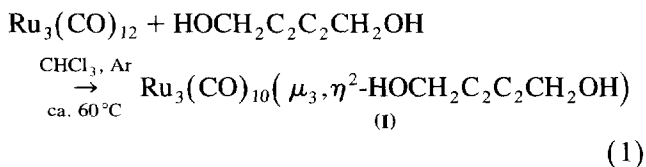
Crystals of **II** ($\text{C}_{38}\text{H}_{20}\text{O}_6\text{Ru}_2$, $M = 774.68$, $F(000) = 3072$) are orthorhombic, space group $Pna2_1$, at 148 K $a = 24,703(11)$, $b = 7,458(4)$, $c = 34,96(2)$ Å, $V = 6442(6)$ Å³, $Z = 8$, $d_{\text{calc}} = 1.598$ g cm⁻³.

The values of $\mu(\lambda\text{Mo K}\alpha) = 20.5$ cm⁻¹ and 9.8 cm⁻¹ (for **I** and **II** respectively) indicated no necessity for absorption corrections.

The structures were solved by direct methods and refined by the full matrix least squares technique with anisotropic thermal displacement parameters assigned to all non-H atoms for **I** and ruthenium atoms for **II**. The H atoms in **I** were not taken into account. All Ph-rings in **II** were treated as rigid fragments with C–C = 1.36 and C–H = 0.97 Å. Final discrepancy factors were: $R1 = 0.0610$ (on F^2 for 4235 reflections with $I > 2\sigma(I)$), $wR2 = 0.1524$ (on F^2 for all 7256 reflections used in the refinement of 586 parameters) for **I**; $R1 = 0.1282$ (on F^2 for 4956 reflections with $I > 2\sigma(I)$), $wR2 = 0.4370$ (on F^2 for all 6959 reflections used in the refinement of 293 parameters) for **II**. Rather low precision of structure **II** may be attributed to the poor quality and weak diffracting ability of the single crystals. All calculations were carried out with an IBM PC using the SHELXTL PLUS 5 (gamma version) programs. The absolute structure of **II** was determined by means of the refinement of the Flack x parameter [9], which yielded the value of 0.1(2). The coordinates of atoms in the structures of **I** and **II** are given in Tables 1 and 2. Selected bond lengths and angles in the structures of **I** and **II** are given in Tables 3 and 4. A complete list of bond lengths and angles, and tables of anisotropic thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

The starting ruthenium cluster reacts with hexa-2,4-diyne-1,6-diol in chloroform at 60°C yielding the only isolable product (**I**)



The molecular structure of (**I**) was determined by an X-ray diffraction study. Fig. 1 shows one of the two geometrically similar independent molecules A and B.

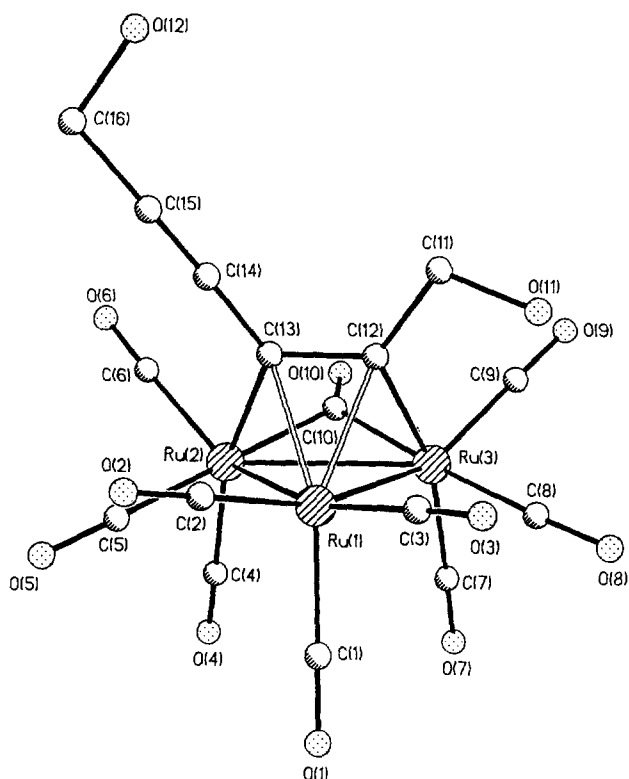


Fig. 1. Molecular structure of $\text{Ru}_3(\text{CO})_{10}(\mu_3, \eta^2\text{-HOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OH})$ (**I**).

Selected bond lengths and angles are given in Table 3. The diyne ligand in (**I**) is bound to the triruthenium core via only one triple bond coordinated in parallel μ^3, η^2 -mode. The other alkyne group remains uncoordinated and the ligand as a whole is not rearranged. This behaviour is not typical of the α -hydroxyalkynes reactions with ruthenium and osmium clusters. In the reactions of this type there is a tendency to transfer the hydrogen atom both from the α -carbon atom to the metal skeleton and in the reverse direction [7,10–12], the parent alkyne forming a completely rearranged coordinated ligand as a result of the transfer processes. In contrast, the coordination observed in the case of (**I**) is closer to the reaction products of dialkyl and diaryl acetylenes with activated derivatives of $\text{Ru}_3(\text{CO})_{12}$ [3–5]. These reactions proceed under mild conditions and give as one of the main products the compound $\text{Ru}_3(\text{CO})_{10}(\mu_3, \eta^2\text{-RC}_2\text{R})$ with a substantially similar structure.

The coordinated alkyne moiety in (**I**) is oriented parallel to the $\text{Ru}(2)\text{--Ru}(3)$ bond bridged by the $\text{C}(10)\text{O}(10)$ carbonyl group (the angle between the $\text{Ru}(2)\text{--Ru}(3)$ and $\text{C}(12)\text{--C}(13)$ vectors is equal to 0.9° and 1.6° in A and B respectively). The length of the coordinated $\text{C}(12)\text{--C}(13)$ bond (1.39(2) and 1.38(2) Å) is typical for the triply bridged alkynes and is considerably longer than the other non-coordinated $\text{C}(14)\text{--C}(15)$ triple bond, 1.19(2) and 1.20(2) Å. As usual, of the three

metal–metal bonds in the ruthenium triangle the bond bridged by a CO ligand is longer ($\text{Ru}(2)\text{--Ru}(3)$ 2.825(2) and 2.849(2) Å) than the other two $\text{Ru}\text{--Ru}$ bonds ($\text{Ru}(1)\text{--Ru}(2)$ 2.724(2) and 2.715(2) Å, $\text{Ru}(1)\text{--Ru}(3)$ 2.731(2) and 2.751(2) Å). The $\text{Ru}\text{--C}_{\text{alkyne}}$ bonds differ significantly, and those to $\text{Ru}(2)$ and $\text{Ru}(3)$ atoms are shorter ($\text{Ru}(2)\text{--C}(13)$ 2.097(11) and 2.097(11) Å, $\text{Ru}(3)\text{--C}(12)$ 2.077(11) and 2.094(11) Å) than the corresponding $\text{Ru}(1)\text{--C}(12)$, $\text{Ru}(1)\text{--C}(13)$ bonds (2.237(11), 2.239(11) Å and 2.243(11), 2.253(11) Å respectively). The geometry of the bridging carbonyl group is different in the two independent molecules. Thus, in molecule A the $\text{Ru}(2)\text{--C}(10)$ and $\text{Ru}(3)\text{--C}(10)$ distances are almost equal (2.14(2) Å and 2.151(14) Å respectively), whereas molecule B shows significant asymmetry in the bridging CO group coordination ($\text{Ru}(2)\text{--C}(10)$ 2.362(13) Å and $\text{Ru}(3)\text{--C}(10)$ 1.989(13) Å). This difference between the two independent molecules, strange though it may seem, nevertheless is reflected in the noticeably unequal $\text{Ru}(1)\text{--Ru}(2)$ and $\text{Ru}(1)\text{--Ru}(3)$ bonds in molecule B (see above). It even finds an analogy in the structure of $\text{Ru}_3(\text{CO})_{10}(\text{MeC}\equiv\text{CMe})$ [4], wherein two independent molecules exhibit quite similar geometric differences. The bridging CO group in both independent molecules of **I** is displaced from the Ru_3 plane in the direction of the coordinated acetylene; the dihedral angles $\text{Ru}(1)\text{Ru}(2)\text{Ru}(3)/\text{Ru}(2)\text{C}(10)\text{Ru}(3)$ in both molecules are almost equal (15.5° and 14.5° in A and B respectively).

Crystal **I** is characterized by a complicated H-bond system, which involves three of the four independent OH-groups of both cluster molecules (the $\text{O}(11)\text{H}$ -group of molecule A does not take part in the H-bonding) and the OH-group of the solvating ethanol. Three H-bonds ($\text{O}(12\text{A}) \cdots \text{O}(12\text{B})$ 2.68(3), $\text{O}(12\text{A}) \cdots \text{O}(1)$ 2.74(4) and $\text{O}(12\text{B}) \cdots \text{O}(1\text{S})$ 2.65(4) Å) are responsible for the formation of six-membered H-bonded cycles, which are linked into infinite chains along the y -axis of the crystal by means of the fourth H-bond ($\text{O}(12\text{A}) \cdots \text{O}(11\text{B})$ 2.85(3) Å).

The ^1H , ^{13}C NMR spectroscopic data for cluster (**I**) are compatible with the structure found in the solid state. The non-carbonyl part of the ^{13}C spectrum consists of two triplets of the CH_2 groups, two singlets of the free alkyne carbons (96.3 and 90.5 ppm), and two signals of the coordinated alkyne moiety (177.2 and 136.3 ppm). The latter signals are significantly downfield shifted compared with those corresponding to the free alkyne carbons and differ substantially from each other. The spectral pattern described remains unchanged in the temperature range 215–297 K; this points to stereochemical rigidity of the coordinated diyne in the temperature range studied. In contrast, carbonyl ligands appear in the room temperature spectrum as a single averaged resonance due to the fast exchange, which is evidently caused by carbonyl scrambling over the ruthenium

dent molecules is manifested in the inequality of the Ru(1)···C(4) distances involving the semi-bridging carbonyl group (C(4)O(4) (2.49(3) Å and 2.69(3) Å in A and B respectively). This inequality is most probably associated with different orientations of Ph-groups, which provide different steric environments of the C(4) atom in both independent molecules. Indeed, the C(4) atom in molecule A forms the only intramolecular short contact with the atoms of the Ph groups (C(4A)···C(16A) 4.17(4) Å), whereas the C(4) atom in molecule B is involved in two noticeably shorter contacts (C(4B)···C(16B) 3.63(4) Å and C(4B)···C(34B) 4.08(4) Å), which cause the semi-bridging group to move further away from the Ru(1) atom in molecule B than in molecule A.

The semi-bridging carbonyl group is a typical feature of the binuclear complexes $\text{Ru}_2(\text{CO})_6(\text{RCCR}')_2$ with substituted acetylenes RCCR' . Of the four structurally characterized complexes of this type, the semi-bridging CO ligand was found in three structures (R = R' = CH_2OH (**III**) [24]; R = $\text{CH}_2\text{CH}_2\text{OH}$, R' = C_2H_5 (**IV**) [24]; R = R' = CO_2Me (**V**) [25]). Only in the fourth case (R = Fc, R' = H (**VI**) [26]) was not semi-bridging group observed. It is noteworthy that the Ru(1)···C(4) distances in both molecules of **II** are significantly shorter than the corresponding distances in structures **III–V**, which is also well correlated with the most pronounced deviations of the semi-bridging carbonyl group from linearity (Ru(2)C(4)O(4) 157(3)° and 161(3)° in molecules A and B of **II** respectively, compared with the average value of 171° for the analogous angle in **III–V**). Astier et al. [24], however, express some doubts as to the existence of attractive Ru···C(O) interactions with the semi-bridging group in these complexes, and tend to attribute the short Ru···C(O) distance to steric rather than electronic effects.

The butadiene moieties C(7)C(8)C(9)C(10) in both independent molecules of **II** are planar within 0.015 Å and 0.022 Å for molecules A and B respectively; the Ru(1) atom is displaced from the mean plane of the butadiene moiety by 0.41 and 0.38 Å in the direction opposite to the Ru(2) atom. The same direction of the displacement of the metal atom was found in structures **III–V**; however, the actual values of displacements in these previously studied complexes (0.24–0.28 Å) are significantly smaller than in **II**. It is noteworthy that in molecule **VI**, which has no semi-bridging carbonyl group, the Ru(1) is displaced from the mean plane of the butadiene moiety (by 0.13 Å) in the opposite direction, i.e. towards then η^5 -coordinated Ru(2) atom.

The C(17)≡C(18) and C(25)≡C(26) acetylene fragments naturally do not show significant displacements from the C(7)C(8)C(9)C(10) plane, as is also the case with the 'terminal' Ph-rings which form dihedral angles of 9–14° with this plane.

Acknowledgements

We thank Johnson-Matthey for the generous loan of the starting ruthenium chloride. This work was in part supported by the Russian Foundation for Basic Research (Project No 94-03-08338) and International Science Foundation (Grant No M04300).

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