Reactions of 1,4-diphenylbut-1-en-3-yne and 1,4-diferrocenylbuta-1,3-diyne with $Ru_3(CO)_{10}(\mu\text{-dppm})$. Unusual structures of the clusters $Ru_3(CO)_5(\mu\text{-CO})(\mu\text{-dppm})\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (two isomers) and $Ru_3(CO)_5(\mu\text{-CO})(\mu\text{-dppm})\{\mu_3\text{-}C_4Fc_2(C{\equiv}CFc)_2\}$

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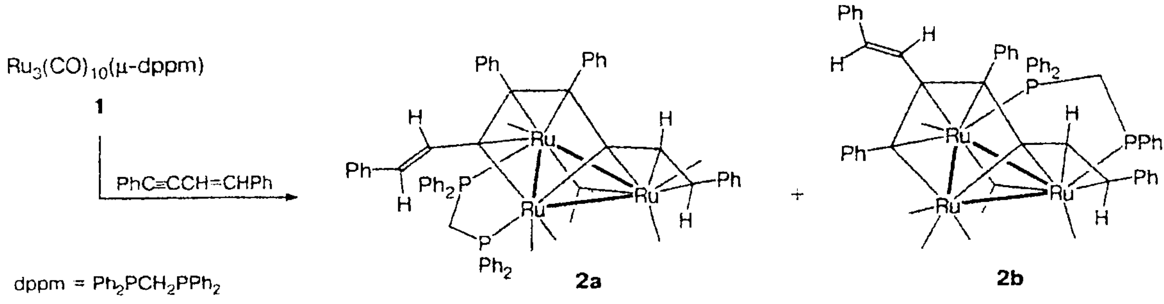
We found that the reaction of $Ru_3(CO)_{10}(\mu\text{-dppm})$ (**1**, dppm = $Ph_2PCH_2PPh_2$) with PhC≡CCH=CHPh (THF, 65 °C) afforded the cluster $Ru_3(CO)_5(\mu\text{-CO})(\mu\text{-dppm})\{\mu_3\text{-C(CHCHPh)C(Ph)C(Ph)C(CH=CHPh)}\}$ (**2a**) and the cluster $Ru_3(CO)_5(\mu\text{-CO})(\mu\text{-dppm})\{\mu_3\text{-C(CHCHPh)C(Ph)C(CH=CHPh)C(Ph)}\}$ (**2b**) with the unusual $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3$ mode of coordination of the dimerized enyne to the Ru_3 core (Scheme 1). This mode of coordination differs from those observed in metallacyclopentadiene derivatives of cluster carbonyls, including that found recently[1] for the related ruthenium complex of composition $Ru_3(CO)_8\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^4{:}\eta^2\text{-C(CH=CHPh)C(Ph)C(Ph)C(CH=CHPh)}\}$ (**3a**). Clusters **2a** and **2b** were characterized by spectral methods (^1H and ^{31}P NMR-and IR) and were studied by X-ray diffraction analysis.* In these clusters, the identical mode of coordination of the organic ligand to the Ru_3 core is realized.

In complex **2b**, the C(7) and C(10) atoms of the dimerized enyne form σ-bonds with the Ru(1) atom, giving rise to the five-membered ruthenacycle (Fig. 1). The C(7), C(8), and C(9) atoms of this ring are located at bonding distances (2.167—2.464(6) Å) from the Ru(2) atom, whereas the C(10) atom is substantially remote (the Ru(2)...C(10) distance is 2.534(5) Å). At the same time, the C(10) atom forms a normal bond with the Ru(3) atom (the Ru(3)—C(10) distance is 2.317(6) Å), which is coordinated by the PhCHCH group (the Ru(3)—C(31) and Ru(3)—C(32) distances are 2.237(6) and 2.371(6) Å, respectively). The data of X-ray diffraction analysis for cluster **2b** (as well as for **2a**) indicate that the organic ligand is involved in two π-allylic bonds (with the participation of the C(7), C(8), and C(9) atoms and the C(10), C(31), and C(32) atoms) and two σ-bonds with the Ru_3 core.

In cluster **2b**, the dppm and C(5)O(5) ligands form bridges between the Ru(2) and Ru(3) atoms. (In isomer **2a**, the dppm ligand is coordinated to the Ru(1) and Ru(2) atoms.) The Ru(2) and Ru(3) atoms are coordinated by one CO group each, whereas the Ru(1) atom is coordinated by three carbonyl groups, one of which is semibridging (the Ru(1)—C(3)—O(3) angle is 165.4(5)°).

Scheme 1



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* The complete X-ray diffraction data for compounds **2a**, **2b**, and **4** were deposited with the Cambridge Structural Database.

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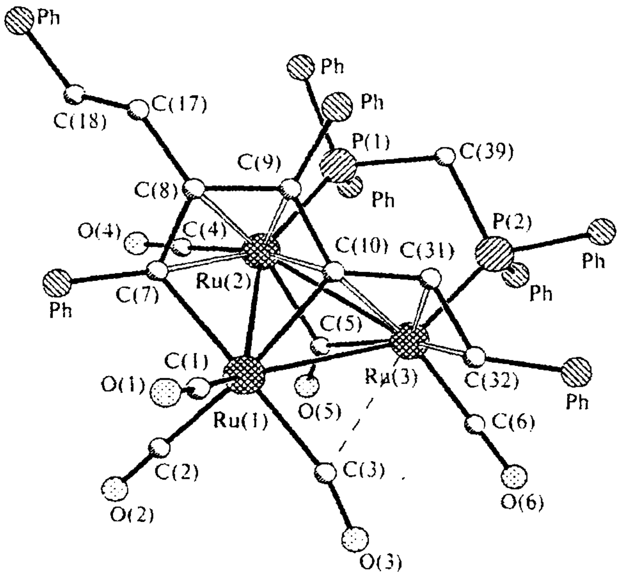

Fig. 1. Molecular structure of cluster **2b**.

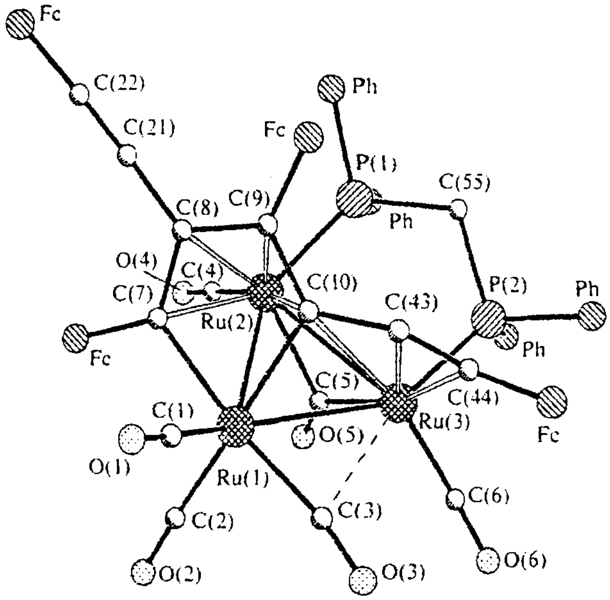

Fig. 2. Molecular structure of cluster **4**.

As a result, all Ru atoms in clusters **2a** and **2b** have 18-electron shells.

Hence, the modes of coordination of the eight-electron ligand $C_4Ph_2(CH=CHPh)_2$ to the $Ru_3(CO)_8$ and $Ru_3(CO)_5(\mu\text{-}CO)(\mu\text{-dppm})$ cores in complexes **3** and **2**, respectively, are different.

It was of interest to establish the structures of the clusters, which are related to compounds **2** and **3** and in which the ruthenacyclopentadiene fragment is formed by coupling of two 1,3-diyne molecules. Previous attempts to characterize the complex $Ru_3(CO)_6(\mu\text{-dppm})\{C_4Ph_2(C{\equiv}CPh)_2\}$ and the related complexes by X-ray diffraction studies failed.[2]

We succeeded in studying the cluster $Ru_3(CO)_5(\mu\text{-}CO)(\mu\text{-dppm})\{\mu_3\text{-}C_4Fc_2(C{\equiv}CFc)_2\}$ (**4**), which was prepared by the reaction of complex **1** with FcC≡CC≡CFc (Fc is ferrocenyl), by X-ray diffraction analysis. The modes of coordination and the coordination sites of the dppm ligand and the carbonyl groups in clusters **4** (Fig. 2) and **2b** are identical (the bridging C(5)O(5) group in **4** is less symmetrical than that in **2b**).

In cluster **4**, the distances between the carbon atoms of the ruthenacycle and the Ru(2) atom are in the range of 2.134—2.378(4) Å, the Ru(2)—C(10) distance being 2.337(4) Å, whereas the distance between the Ru(3) atom and the C(43) atom of the alkynyl group is typical of a π-bonded atom (2.312(4) Å). Two adjacent carbon atoms, *viz.*, C(10) and C(44), are located at large and virtually identical distances from the Ru(3) atom (Ru(3)—C(10), 2.519(4) Å; Ru(3)—C(44), 2.510(4) Å). The folding angles along the C(7)...C(10) line are 12.7° and 5.3° in clusters **4** and **2b**, respectively. It can be suggested that the elongated Ru(3)—C(10) and Ru(3)—C(44) bonds and the short Ru(2)—C(10) contact in cluster **4** appear due to the lower (compared to **2b**) capability of the dimerized ligand to form the "normal" $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3$ bond with the Ru_3 core. Apparently, this fact results from the linear geometry of the alkynyl group. To put it differently, the Ru(2)—C(10) contact is, probably, forced to be short. In this connection, it should be noted that all ruthenium atoms in cluster **4** acquire 18-electron shells, assuming that the organic ligand supplies the Ru(2) and Ru(3) atoms each with three electrons.

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References

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