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Synthesis of tetranuclear butterfly clusters $RuM_3(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}C_2Fc)$ (M = Ru, Os; Fc = ferrocenyl) and $RuOs_3(CO)_{12}(\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}HC_2Me)$ from trinuclear acetylide precursors. Fluctuation of μ_4-bonded acetylide ligand

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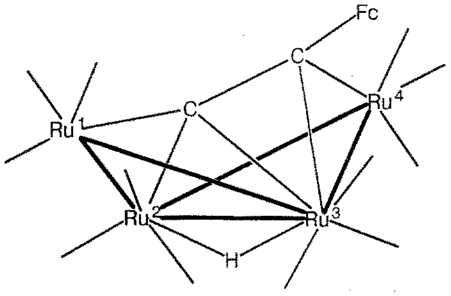
Being highly unsaturated and able to donate from one to five electrons, acetylide ligands show a diversity of bonding possibilities in transition metal clusters.[1] The study of molecular clusters with these ligands allows the processes of hydrocarbon C_2 group transformation on the polymetal centers of a catalytic surface to be clarified.

Previously, for the synthesis of acetylide derivatives of tri- and tetranuclear clusters we used an approach based on the interaction of mononuclear acetylide complexes with metal carbonyl clusters.[2–4] In this paper, the synthesis of tetranuclear butterfly clusters from trinuclear acetylide clusters is described.

Treatment of $Ru_3H(CO)_9(C{\equiv}CFc)$ (**1**, Fc = ferrocenyl) with dodecacarbonyltriruthenium in refluxing hexane gave the dark green $Ru_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}C_2Fc)$ complex (**2**) in 40 % yield. Cluster **2** can also be obtained by the interaction of ferrocenylacetylene with $Ru_3(CO)_{12}$, but the yield is lower.

The IR spectrum of **2** revealed the presence only of terminal CO ligands (νCO/cm^{-1}, hexane): 2090 w, 2062 vs, 2052 s, 2038 w, 2019 s, 1996 w (br), 1979 m (br). The ^1H NMR spectrum ($C_6D_5CD_3$, 25 °C) contains signals of the hydride ligand at δ −22.18 (1 H) and the ferrocenyl group at 4.31 (5 H), 4.76 (2 H), and 5.55 (2 H), the later being broadened.



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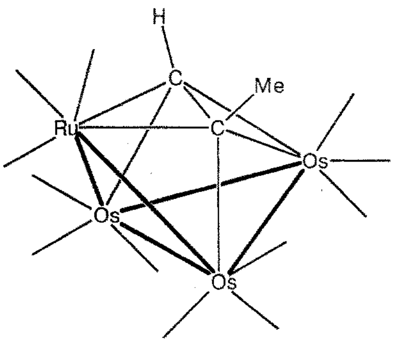

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A heterometallic analog of **2**, the green colored cluster $RuOs_3(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}C_2Fc)$ (**3**), was obtained by the reaction of the acetylide complex $Os_3H(CO)_9(C{\equiv}CFc)$ with $Ru_3(CO)_{12}$ in boiling benzene. ^1H NMR spectrum of **3** in $CDCl_3$ at 25 °C: δ −21.14 (1 H), 4.42 (5 H), 5.16 (2 H), 5.48 (2 H).

X-ray structural analysis, which details will be published later, showed the compound **2** to consist of Ru_4 cluster having butterfly type framework. Each ruthenium atom is coordinated by three terminal CO groups, the hydride ligand bridging Ru(2) and Ru(3) nodal atoms. Acetylide ligand is coordinated in the cluster in more complex way: with α-carbon atom binding three metal atoms, Ru(1), Ru(2), and Ru(3), and with β-carbon atom binding two, Ru(3) and Ru(4). The above coordination of acetylide ligand in tetranuclear butterfly clusters was recently found for $(C_5H_5)WOs_3(CO)_{11}(C{\equiv}CPh)$ (**4**) and $(C_5H_5)WRu_3(CO)_9(\mu\text{-}NPh)(C{\equiv}CPh)$ (**5**) obtained by the reaction of $(C_5H_5)W(CO)_5C{\equiv}CPh$ with $Os_3(CO)_{10}(NCMe)_2$ and $Ru_3(CO)_{10}(\mu\text{-}NPh)$, respectively.[5,6] However, unlike compounds **4** and **5**, the cluster **2** is a first example of homonuclear tetrametal cluster of butterfly type having besides acetylide, only carbonyl and hydride ligands.

^{13}C NMR of **2** enriched by ^{13}CO showed 12 carbonyl signals at −73 °C that is in accordance with the crystal structure of it, which does not possess any symmetry element: δ 199.3, 199.0, 198.9, 198.5, 196.6, 195.8, 192.0, 190.5, 189.0, 188.5 ($^2J_{CH}$ = 12.1 Hz); 188.1, 186.2 ($^2J_{CH}$ = 16.1 Hz). The protons H(2), H(5), H(3), and H(4) of substituted cyclopentadienyl ring of ferrocene moiety are diastereotopic in ^1H NMR of **2** at −73 °C: δ 5.83, 5.23 and 4.89, 4.75, respectively. Some exchange processes occur at higher temperatures: CO group migration (polytopal rearrangement of $Ru(CO)_3$ group, averaging ligands with δ 198.9, 198.5, and 188.5, has the lowest energy) and unknown previously fluctuation of $\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2$-acetylide ligand that includes the fast σ- and π-bond exchange with nodal atoms, Ru(2) and Ru(3), averaging the stereochemical environment of H(2), H(5) as well as H(3) and H(4) atoms in substituted cyclopentadienyl ring of ferrocenyl group.

To estimate the generality of the **2**, **3** formation reaction and the possible role of a substituent in the acetylide ligand in this process, we studied the reaction of other acetylide trinuclear clusters. The reaction of $Os_3H(CO)_9(C{\equiv}CMe)$ with ruthenium carbonyl in refluxing benzene led to the heteronuclear alkyne cluster $RuOs_3(CO)_{12}(\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}HC_2Me)$ (**6**). The ^1H NMR spectrum (C_6D_6, 25 °C) points out the transfer of a hydride ligand to the acetylide group during cluster **6** formation: δ 9.80 (s, 1 H) and 2.78 (s, 3 H). IR spectrum ($\nu CO/cm^{-1}$, hexane): 2099 w, 2072 vs, 2045 s, 2039 vs, 2019 m, 2012 m (sh), 2001 m, 1980 w, 1972 w, being similar to that of known $\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2$-alkyne butterfly clusters, $Os_4(CO)_{12}(HC_2R)$ (R = H, Et)[7] and $Ru_4(CO)_{12}(PhC_2Ph)$.[8]

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