Synthesis and Structural Characterization of a Series of High-Hydride Content Osmium-Rhodium Carbonyl Complexes

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Hydrido-transition metal clusters have been known for years, however few are reported in which the ratio hydride : metal exceeds unity. Such high hydrogen content of the clusters is important for the transition metal complexes to serve as hydrogenation catalyst and potential hydrogen storage materials. Hydrogenation of $[Os_5Rh_2(\eta^6\text{-}C_6H_5CH_3)(\mu\text{-}CO)\ (CO)_{16}]$ with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ in chloroform under reflux resulted in two hydrogen rich compounds $[\{Os_7Rh_3(\mu\text{-}H)_{11}(CO)_{23}\}\cdot CH_2Cl_2]$ **1** and $[\{Os_5Rh_3Cl(\mu\text{-}H)_8(CO)_{18}\}_2\cdot\ CH_2Cl_2]$ **2** in moderate yield. While treatment of $[Os_5Rh_2(\eta^6\text{-}C_6H_5CH_3)(\mu\text{-}CO)(CO)_{16}]$ with hydrogen in refluxing chloroform yielded another new cluster compound, $[Os_5Rh(\mu\text{-}H)_5(CO)_{18}]$ **3** in 20% yield, together with a known osmium-rhodium cluster, $[Os_6Rh(\mu\text{-}H)_7(\mu\text{-}CO)(CO)_{18}]$ as the major compound. The molecular structures of the three clusters have been established by single crystal X-ray diffraction, carried out on crystals of compounds **1**-**3** by slow evaporation of *n*-hexane into CH_2Cl_2. The metal core of **2** consists of two tetrahedral, Os(1), Os(2), Rh(2), Rh(1) and Os(4), Os(5), Rh(3), Rh(1) units fused together to form a bitetrahedron via the Rh(1) vertex. The bitetrahedron is additionally bonded to another Os(3) by Rh(2) and Rh(3), which form a triangular face with a Cl atom tri-capping the three metal atoms in a μ^3 mode. The corresponding Rh-Cl-Rh and Rh-Cl-Os bond angles fall in the range 70.1(3) to 73.0(3) °, which is comparable to that observed in a Cl face-bridged tritungsten cluster, $[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]^{3-}$.

Keywords: osmium-rhodium clusters, hydride content, single crystal x-ray diffraction