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High Nuclearity Clusters Containing Methyl Groups. Synthesis and Structures of Pentaosmium-Gold Carbonyl Cluster Compounds

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### Abstract

The compounds  $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)_2$ , **2** and  $\text{Os}_5(\text{CO})_{14}[\mu_4\text{-Au}_3(\text{PPh}_3)_3](\mu_3\text{-AuPPh}_3)$ , **3** were obtained from the reaction of  $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$  using  $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ . Compound **2** contains two triply-bridging  $\text{Au}(\text{PPh}_3)$  groups. Compound **3** contains one triply-bridging  $\text{Au}(\text{PPh}_3)$  group and a quadruply-bridging  $\text{Au}_3(\text{PPh}_3)_3$  group. When the same reaction was performed in the presence of  $\text{CH}_3\text{Au}(\text{PPh}_3)$ , the new trigold compound  $\text{Os}_5(\text{CO})_{14}(\text{CH}_3)(\mu_3\text{-AuPPh}_3)_3$ , **4** was obtained. Compound **4** contains three triply-bridging  $\text{Au}(\text{PPh}_3)$  groups and one methyl group coordinated to one of the apical osmium atoms of the trigonal bipyramidal pentaosmium cluster. Compound **4** was not obtained by the direct reaction of **2** with  $\text{CH}_3\text{Au}(\text{PPh}_3)$  but it was obtained when  $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$  was added to the reaction solutions. Cationic digold species such as  $[\text{CH}_3\text{Au}_2(\text{PPh}_3)_2]^+$  have been proposed as a possible mechanism for the activation of  $\text{CH}_3\text{Au}(\text{PPh}_3)$  by  $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ . Compound **4** was also obtained albeit in a lower yield from the reaction of  $\text{Os}_6(\text{CO})_{18}$  with  $\text{MeAu}(\text{PPh}_3)$  following treatment with  $\text{Me}_3\text{NO}$ . Each of the pentaosmium products was characterized structurally by a single-crystal X-ray diffraction analysis.

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