

SYNTHESIS OF LARGE CARBONYL CLUSTERS OF RUTHENIUM, OSMIUM
AND RHENIUM

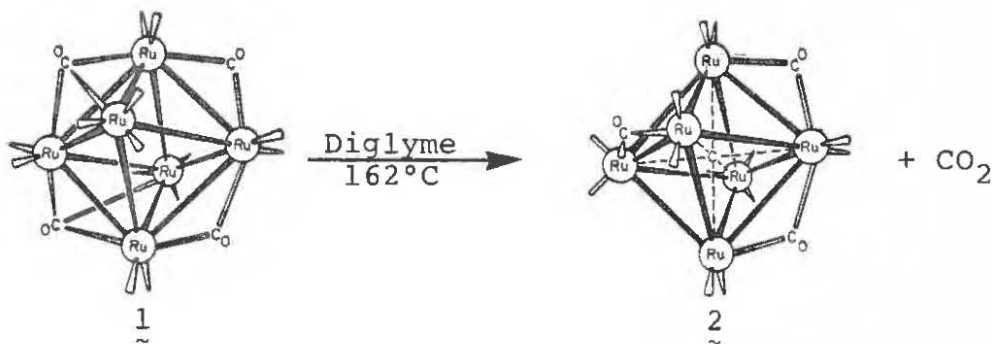
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Final Seminar

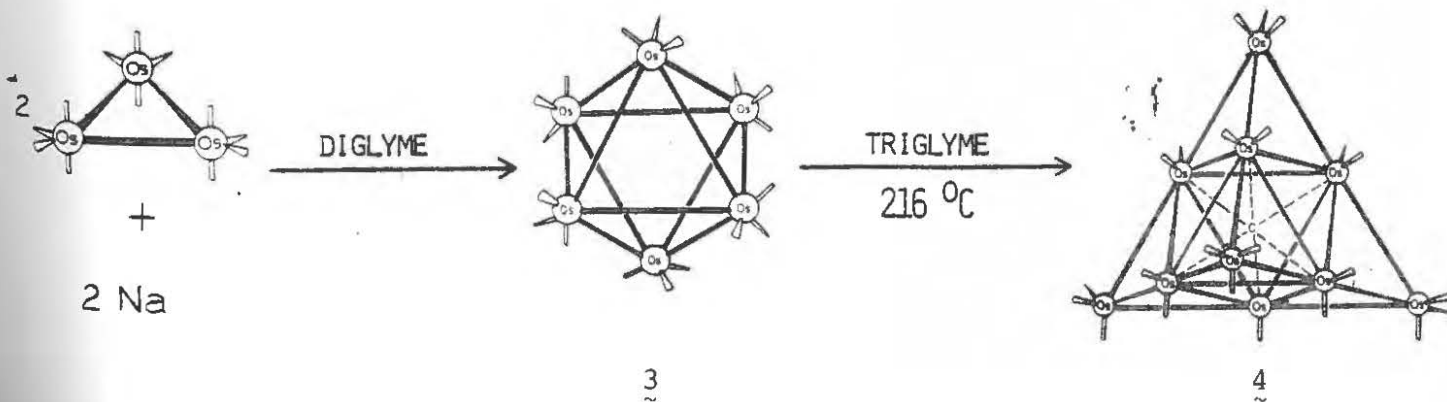
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The chemistry of metal carbonyl cluster compounds has been a subject of intense research activity over the past several years. Many studies have demonstrated that cooperation between metal centers leads to unique hydrocarbon ligand transformation in the chemistry of tri- and tetrametallic clusters [1]. Similar studies are desirable for larger clusters. Unfortunately, the lack of efficient synthetic procedures for many higher nuclearity Group VII and VIII metal clusters has limited the possibilities for further investigation of their reactivity.

We have found that the treatment of $M_3(CO)_4$ ($M = Ru, Os$) with sodium in ether solvents at various reaction temperatures provides selective formations of several large anionic carbonyl clusters of ruthenium and osmium [2]. This synthetic approach is analogous to the thermal condensation of a 5:1 mole ratio of $Fe(CO)_5$ and $Fe(CO)_4^{2-}$, which is obtained from the reduction of $Fe(CO)_5$ by sodium [3], to generate $Fe_5C(CO)_{16}^{2-}$ [4]. Thus, the reaction of $Ru_3(CO)_4$ and one equivalent of sodium ($Ru_3:Na = 1:1$) affords $Ru_6(CO)_{18}^{2-}$ (1) [5] in refluxing tetrahydrofuran ($66^\circ C$), but $Ru_6C(CO)_{16}^{2-}$ (2) [6] in refluxing diglyme ($162^\circ C$). Under the

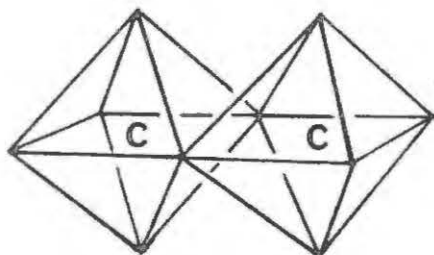


latter conditions $Ru_6(CO)_{18}^{2-}$ is converted quantitatively to $Ru_6C(CO)_{16}^{2-}$ with the evolution of carbon dioxide, which has been trapped as barium carbonate. Treatment of $Os_3(CO)_4$ with sodium ($Os_3:Na = 1:1$) in refluxing diglyme provides $Os_6(CO)_{18}^{2-}$ (3) [7]. Pyrolysis of 3 in triglyme ($216^\circ C$) gives $Os_{10}C(CO)_{24}^{2-}$ (4) [8] as the major product, which is formed also from the direct reaction of $Os_3(CO)_4$ with sodium in tetraglyme at $230-260^\circ C$. A compound



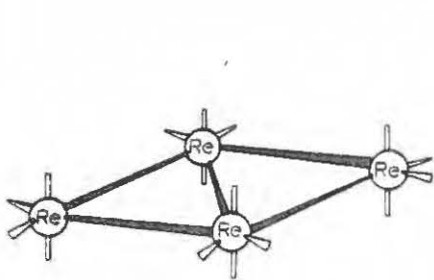
formulated as $\text{Os}_6\text{C}(\text{CO})_{17}$ is isolated in low yield from the oxidation of reaction mixtures produced upon prolonged pyrolysis of $\text{Os}_6(\text{CO})_{18}^{2-}$ (162°C). This is suggested as evidence for the formation of $\text{Os}_6\text{C}(\text{CO})_{16}^{2-}$ under the conditions for conversion of $\text{Os}_6(\text{CO})_{18}^{2-}$ to $\text{Os}_{10}\text{C}(\text{CO})_{24}^{2-}$.

Extended pyrolysis of $\text{Ru}_6\text{C}(\text{CO})_{16}^{2-}$ also provides a decanuclear cluster, but $\text{Ru}_{10}\text{C}_2(\text{CO})_{24}^{2-}$ (5) has two carbide ligands. The structural analysis of $\text{Ru}_{10}\text{C}_2(\text{CO})_{24}^{2-}$ [9] shows the carbido-metallic framework to have approximate D_2 symmetry and is based on two essentially octahedral moieties fused at a common equatorial edge. The limiting low temperature ^{13}C NMR spectrum of 5 shows a pattern fully consistent with the solid state structure.

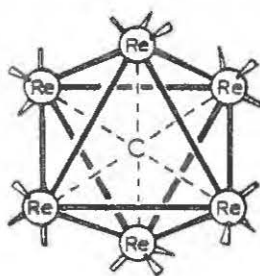


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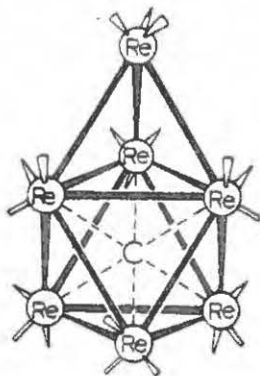
Treatment of $\text{Re}_2(\text{CO})_{10}$ with sodium ($\text{Re}_2:\text{Na} = 1:1$) in diglyme at 150°C affords $\text{Re}_4(\text{CO})_{16}^{2-}$ (6) [10], which in refluxing diglyme is converted predominantly to $\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}^{2-}$ (7) [11]. In the latter transformation $\text{Re}_7\text{C}(\text{CO})_{21}^{3-}$ (8) [12] and $\text{Re}_8\text{C}(\text{CO})_{24}^{2-}$ (9) [13] are obtained as minor products. These clusters have



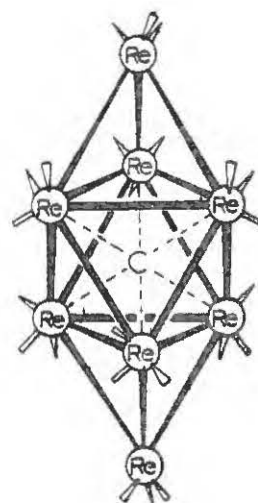
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been prepared selectively by employing the appropriate stoichiometric ratio of $\text{Re}_2(\text{CO})_{10}$ and sodium ($\text{Re}_2:\text{Na} = 3.5:3$ for 8 and $4:2$ for 9) in triglyme ($190-210^\circ\text{C}$). In both syntheses $\text{Re}_4(\text{CO})_{16}^{2-}$ and then $\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}^{2-}$ are the intermediates observed prior to the formation of 8 or 9. The evolution of carbon dioxide also is observed in the conversion of $\text{Re}_4(\text{CO})_{16}^{2-}$ to the three carbide clusters (7, 8, and 9).

References

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