Synthesis of $H_3Ru_3(CO)_9CCH_3$, a Ruthenium Ethylidyne Complex

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Summary A ruthenium ethylidyne complex, $H_3Ru_3(CO)_9$-CMe, has been obtained from the reaction of α-$H_4Ru_4(CO)_{12}$ with ethylene; spectroscopic data indicate C_{3v} symmetry with bridging hydrido-ligands.

COBALT alkylidyne complexes, $Co_3(CO)_9CR$, have been known for several years.[1] Except for a recent report of some nickel complexes, $(\pi$-$C_5H_5)_3Ni_3CR$,[2] complexes of this type involving other metal atoms have not been isolated. The formation of tetranuclear and trinuclear organometallic complexes from the reactions of α-$H_4Ru_4(CO)_{12}$ and cyclic olefins[3] has led us to study the reactivity of this cluster towards simple olefins, resulting in isolation of a ruthenium ethylidyne complex.

Treatment of α-$H_4Ru_4(CO)_{12}$ with ethylene at 65—75° (1 atm, closed system, 45 min) in cyclohexane yields a dark red suspension. Chromatography on silica gel with hexane as eluant gave, as the major soluble products, α-$H_2Ru_4(CO)_{13}$ (*ca.* 30%) and a yellow crystalline complex characterized by analysis and mass, i.r., ^1H, and ^{13}C n.m.r. spectroscopy as $H_3Ru_3(CO)_9CMe$ (*ca.* 12%).

The ^1H n.m.r. spectrum in $CDCl_3$ shows two sharp singlets of equal intensity at τ 5·88 and 27·63. The high-field signal is in the region normally observed for bridging hydrido-ligands in trinuclear ruthenium cluster complexes, and remains unchanged in line shape from −50° to 70°, indicating that it almost certainly results from equivalence of environments, rather than rapid intramolecular exchange of inequivalent hydrido-ligands. The absorption at τ 5·88 is in the region previously observed for an alkylidyne grouping in the cobalt complexes $Co_3(CO)_9CR$ [τ 6·35 (R = Me) and 5·98 (R = CH_2Ph)].[4] The ^1H n.m.r. spectrum is therefore consistent with the presence of a methyl group and three hydrido-ligands. In the mass spectrum a parent ion $Ru_3(CO)_9C_2H_6^+$ is observed, together with ions corresponding to loss of nine CO groups.

A high symmetry is suggested by the i.r. spectrum in the carbonyl region which exhibits only three terminal ν (C–O) absorptions. This is confirmed by the ^{13}C n.m.r. spectrum in C_6D_6. In the presence of 0·04M-$Cr(acac)_3$ as a shiftless relaxation reagent,[5] two carbonyl ligand environments are indicated, with absorptions at 190·1 and 189·3 p.p.m. downfield from Me_4Si. Two absorptions are expected for C_{3v} symmetry. If one assumes that Overhauser enhancement of carbonyl groups in a cluster of this sort will be negligible, especially in the presence of Cr^{III},[5] and that relaxation by $Cr(acac)_3$ does not discriminate among different types of carbonyl carbons, the observed 2:1 intensity ratio should reflect relative abundances and permit assignment to carbonyl groups A and B, respectively (see Figure). A resonance at 47·2 p.p.m. is near those found for methyl and methylene carbon atoms bound to a quaternary carbon in the related ruthenium complex, $HRu_3(CO)_9C_6H_9$.[6] As found for $HRu_3(CO)_9C_6H_9$,[6] observation of a resonance for the quaternary carbon was not possible.

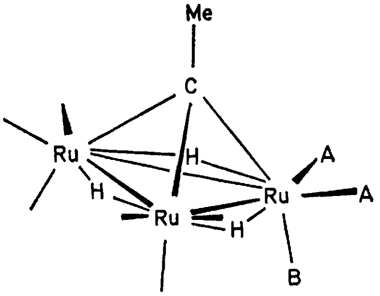

FIGURE. *Molecular structure of* $H_3Ru_3(CO)_9CMe$ *showing* C_{3v} *symmetry.*

The presence of C_{3v} symmetry, a methyl group, and three equivalent bridging hydrido-ligands indicates the structure shown in the Figure. This is closely related to that found for cobalt alkylidyne complexes, with the effective atomic number rule satisfied by addition of three hydrido-ligands to the cluster when passing from cobalt to ruthenium. This study indicates that the metal–ligand arrangement and bonding found in cobalt and nickel alkylidyne complexes may well be accessible for other transition elements.

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