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Preliminary communication

THE SYNTHESIS AND MOLECULAR STRUCTURE OF η^6-CARBIDOHEXADECACARBONYLHEXARUTHENATE(−2): A HIGH YIELD ROUTE INTO Ru_6C CHEMISTRY [1]

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Summary

$Ru_6C(CO)_{16}^{2-}$ is produced in reproducibly high yield by the reduction of $Ru_3(CO)_{12}$ with $Mn(CO)_5^-$ in refluxing diglyme. ^{13}C NMR evidence identifies carbon monoxide as the source of the encapsulated carbon atom. The facile prototype synthesis of an organometallic derivative of the Ru_6C core is described.

The first carbidocarbonyl clusters of ruthenium were described a decade ago by Lewis and co-workers in their reports of the synthesis and structures of $Ru_6C(CO)_{17}$ and $Ru_6C(CO)_{14}(arene)$ [2,3]. These compounds were the first hexaruthenium clusters known, but despite their novelty remarkably little has been reported on the chemistry of the Ru_6C system, especially when compared to the voluminous literature on triruthenium cluster chemistry. This is undoubtedly a result of the low and sometimes erratic yields encountered in the syntheses of the larger clusters, whose formation by pyrolysis of $Ru_3(CO)_{12}$ in an appropriate solvent is generally accompanied by extensive metal deposition. As part of an investigation of the chemistry of transition metal carbidocarbonyl clusters we required a reliable, high yield route to Ru_6C derivatives, and we report here the synthesis of $[Ru_6C(CO)_{16}]^{2-}$, obtainable in consistent yields of ~60% from the high temperature reduction of $Ru_3(CO)_{12}$ by manganese pentacarbonyl anion. The procedure is, in fact, similar to that reported for the synthesis of the analogous $Fe_6C(CO)_{16}^{2-}$ [4].

$Ru_3(CO)_{12}$ (5 g) was added to a solution of $NaMn(CO)_5$ (3 g) in dry diglyme (150 ml) and the mixture refluxed under nitrogen. After several minutes the initially deep red solution became a brown suspension, which probably contained the mixture of anions from which $Ru_6(CO)_{18}^{2-}$ was isolated in 11% yield by Lewis et al. in a similar reaction in THF [5]. However, on refluxing for several hours an intense red solution formed, from which $[Ru_6C(CO)_{16}]^{2-}$ was isolated as either the R_4N^+, Ph_4As^+ or $(Ph_3P)_2N^+$ salt*. Bright red crystals of the slightly air sensitive product (3.1 g of the Et_4N^+ salt, 60% based on $Ru_3(CO)_{12}$) were obtained by recrystallization from methylene chloride; IR (cm^{-1}, CH_2Cl_2): 2048w, 2032w, 1977s, 1952(sh)m, 1918m, 1820(sh)m, 1780m. ^1H NMR exhibits only resonances due to the cation. A ^{13}CO enriched sample, prepared using enriched $Ru_3(CO)_{12}$, showed ^{13}C resonances at 213 ppm (carbonyls) and 288 ppm downfield from TMS. Those carbidocarbonyl clusters for which ^{13}C NMR has been reported have shown characteristically low field resonances for the interstitial carbon atom (e.g. 266.7 ppm for $Rh_6C(CO)_{15}^-$ [6]. The 228 ppm resonance, in the appropriate intensity ratio to that at 213 ppm, therefore confirmed not only the presence of an encapsulated carbon atom, but also the fact that it was derived from carbon monoxide. This fact has been inferred for $Ru_6C(CO)_{17}$ from chemical evidence [7], but spectroscopic evidence has not apparently been reported.

The new cluster was thus tentatively identified as $Ru_6C(CO)_{16}^{2-}$, and confirmation of this assignment was obtained by an X-ray crystallographic study. Crystals of the tetramethylammonium salt were grown from methylene chloride/ethanol solution and diffraction data were obtained by Dr. J.M. Troup, Molecular Structure Corporation, College Station, Texas. The salt crystallizes in the orthorhombic space group *Pnma*, *a* 10.144(4) Å, *b* 19.416(6) Å, *V* 7275 Å^3,

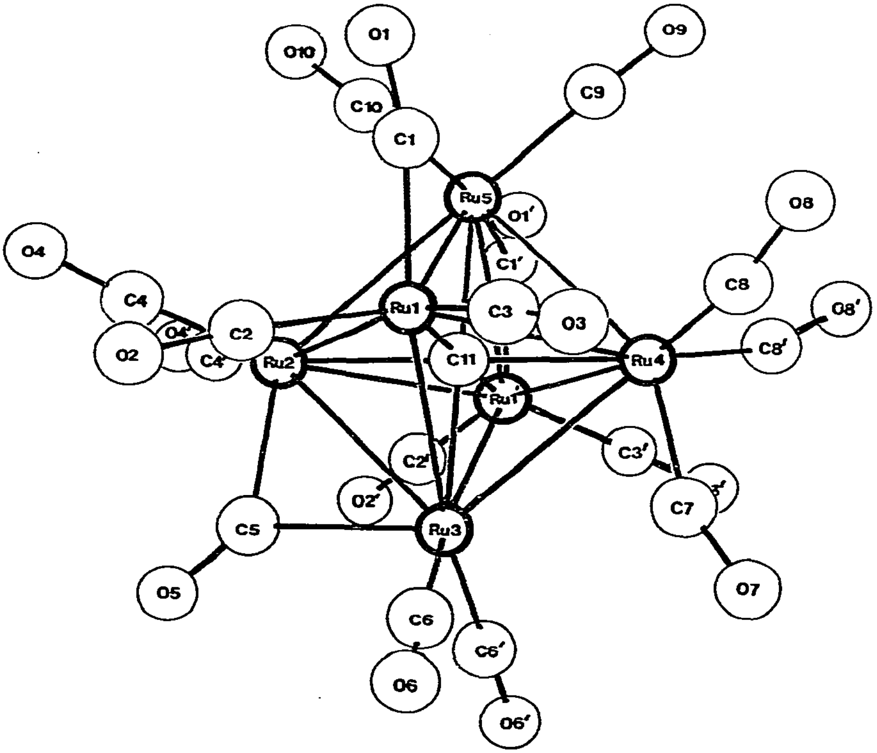

Fig. 1. The $Ru_6C(CO)_{16}^{2-}$ anion.

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*Satisfactory elemental analyses were obtained for Et_4N^+, Ph_4As^+ and PPN^+ salts.

$F_0^2 > 3\sigma(F_0^2)$ were used in the refinement of the structure to $R = 0.054$. The structure comprises two similar but crystallographically non-equivalent $Ru_6C(CO)_{16}^{2-}$ ions, one of which is shown in Fig. 1. Each contains thirteen terminal and three bridging carbonyls. The average Ru—Ru distance is 2.864 ± 0.04 Å, and the mean ruthenium to encapsulated carbon distance is 2.045 ± 0.007 Å; the structure bears a close resemblance to that of the iron analog [8].

The ready availability of this potentially useful starting material has enabled us to investigate further the chemistry of Ru_6C clusters. Protonation of the dianion occurs readily in a stepwise fashion, and mild oxidation in the presence of CO yields $Ru_6C(CO)_{17}$. Similar oxidations in the presence of organic ligands result in the formation in good yield of organometallic Ru_6C derivatives, as exemplified by the reaction between the dianion and tropylium bromide to yield an η^6—μ^3-bitropyl cluster [1,9]:

$$Ru_6C(CO)_{16}^{2-} + 2C_7H_7^+ \rightarrow Ru_6C(CO)_{14}(C_{14}H_{14})$$

in which one C_7 ring is bonded to one triangular face of the cluster [10].

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