Surface-mediated Organometallic Synthesis: Formation of $[Os_5C(CO)_{14}]^{2-}$ from $[Os_3(CO)_{12}]$ on MgO

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$[Os_3(CO)_{12}]$ is converted on the surface of partially dehydroxylated MgO under 1 bar of flowing CO at 550 K into $[Os_5C(CO)_{14}]^{2-}$; this one-step synthesis is far simpler and gives much higher yields (65%) than the conventional synthesis.

The best known syntheses of high-nuclearity metal carbonyl clusters proceed by condensation of reactive fragments generated photochemically or pyrolytically, by redox condensations of anionic and neutral clusters, or by reduction of high-nuclearity clusters.[1,2] These syntheses typically suffer from lack of reproducibility and low yields, with the attendant problems of separation. Here we report the use of a novel synthetic method involving reactions on the basic surface of a porous, high-area solid, MgO; $[Os_3(CO)_{12}]$ is simply converted to $[Os_5C(CO)_{14}]^{2-}$ in high yield on this surface in the presence of CO.

$[Os_3(CO)_{12}]$ was slurried from dry hexane solution, using Schlenk techniques, onto the surface of partially dehydroxylated MgO powder (75 $m^2 g^{-1}$, MCB MX-65, reagent) which had been calcined and evacuated at 675 K. The slurry was stirred for 4—6 h until uptake of $[Os_3(CO)_{12}]$ was complete. The solvent was evaporated and the solid dried overnight *in vacuo*. The resulting yellow powder, containing 0.97% Os as determined by *X*-ray fluorescence, had an i.r. spectrum (ν_{CO} 2075m, 2006s,br, and 1949s,br cm^{-1}; Figure 1a) agreeing closely with that reported for a complex formulated as $[Os_3(CO)_{11}]^{2-}$ tightly ion-paired to the MgO surface.[3]

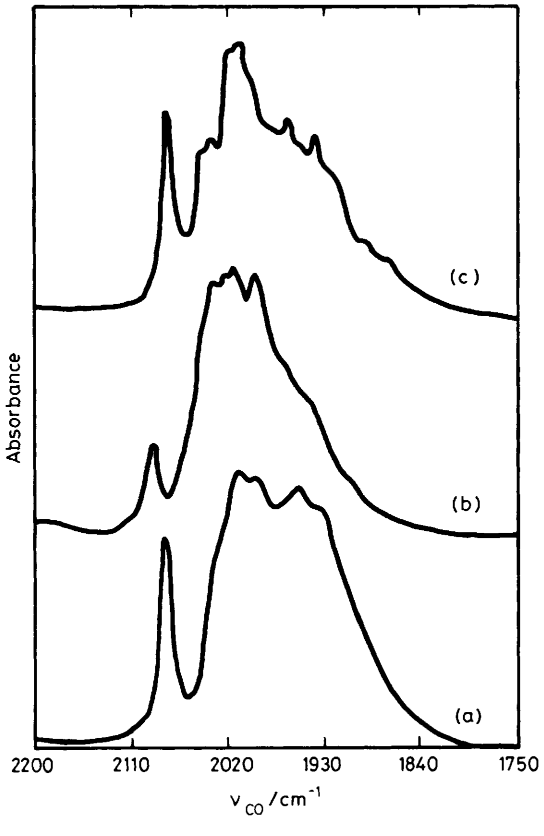

Figure 1. I.r. spectra in ν_{CO} region of samples (a) prepared by adsorption of $[Os_3(CO)_{12}]$ on MgO under N_2; (b) after 2 h exposure to CO at 1 bar and 420 K; (c) after 4 h exposure to CO at 1 bar and 550 K.

$[Os_5C(CO)_{14}]^{2-}$ was formed on the surface by exposing 2 g of this sample to flowing CO for 4 h in a tube at 550 K and 1 bar. The sample was cooled in flowing CO to room temperature and removed in a nitrogen-filled glovebox. The carbonyl bands in the i.r. spectrum of the bright yellow powder revealed the formation of a new surface complex (Figure 1c). Extraction of the powder with $[(Ph_3P)_2N]Cl$ (PPNCl) in acetone gave a golden yellow solution with an i.r. spectrum (ν_{CO} 2039w, 2023w, 1991s, 1977vs, 1970vs, 1947s, 1926w, and 1891w cm^{-1}) indicative of $[PPN]_2[Os_5C(CO)_{14}]$.[4] The identity of this cluster was confirmed by fast atom bombardment mass spectrometry as well as by characterization of the $[PPh_3Au]^+$ derivative, prepared by addition of $[AuPPh_3]Cl$ in the presence of Tl_2SO_4 to the bright yellow extract solution. Within 10 min, the solution turned red–orange, giving an i.r. spectrum (ν_{CO} 2085w, 2051vs, 2036m,sh, 1965w, 1936w, and 1902w cm^{-1}) indicative of authentic $[Os_5C(CO)_{14}\{AuPPh_3\}_2]$.[4] Further characterization of $[Os_5C(CO)_{14}]^{2-}$ was carried out by reaction with concentrated sulphuric acid to yield $[H_2Os_5C(CO)_{15}]$[4] and by oxidation with ferrocinium tetrafluoroborate in the presence of CO to give $[Os_5C(CO)_{15}]$ and $[Os_5C(CO)_{16}]$, which were identified by i.r. spectroscopy. The yields of $[Os_5C(CO)_{14}]^{2-}$ were >65%.

The formation of $[Os_5C(CO)_{14}]^{2-}$ on the MgO surface in a controlled environment cell at 1 bar was monitored by i.r. spectroscopy. Upon heating of the sample formed by adsorption of $[Os_3(CO)_{12}]$ to 360 K under CO, the peaks broadened, and distinct new bands appeared at 2103w, 2088w, 2028s,sh, and 1945m,sh cm^{-1}. At 420 K, the starting material was almost completely converted, as shown by the disappearance of the 2075 cm^{-1} band (Figure 1b). At 475 K, the spectrum consisted of one strong band at 2011 cm^{-1} with shoulders at 2081w, 2051m, 1973m, and 1943m cm^{-1}. After 4 h at 550 K followed by cooling to room temperature under CO, the i.r. spectrum of the surface species and the species extracted with [PPN]Cl in acetone confirmed the formation of $[PPN]_2[Os_5C(CO)_{14}]$.

In an attempt to determine the nature of intermediate surface species formed in the reaction of the chemisorbed triosmium carbonyl cluster with CO, a separate experiment was conducted for a shorter time at lower temperature. The evolution of the starting material was followed by *in situ* i.r. spectroscopy as the temperature was increased to 420 K with the sample under flowing CO for 2 h. The resulting yellow material was then extracted with [PPN]Cl in acetone. The yellow solution exhibited i.r. bands at 2049s, 2042m,sh, 2023s, 2002vs, 1996sh, 1981m, 1968sh, 1950w,sh, and 1922w cm^{-1}.

The bands at 2042m,sh, 1996sh, 1981m, 1968sh, 1950w,sh, and 1923w cm^{-1} are assigned to $[Os_5C(CO)_{14}]^{2-}$ and the other three bands to $[H_3Os_4(CO)_{12}]^-$.[5] The presence of $[H_3Os_4(CO)_{12}]^-$ on the MgO surface suggests its role as an intermediate condensation product.

In summary, the results demonstrate a simple one-step, high-yield synthesis of $[Os_5C(CO)_{14}]^{2-}$ from readily available starting materials, $[Os_3(CO)_{12}]$ and MgO, under mild conditions. In contrast, in the heretofore best known synthesis,[4,6] this cluster has been isolated as a minor product after a multistep synthesis requiring tedious separations. Both procedures involve pyrolytic conversion of $[Os_3(CO)_{12}]$ and rely on the presence of basic media [$Na_2(CO)_3$ for the traditional method, the MgO surface for the new synthesis]. When the basic surface is used as the reaction medium, the synthesis is facilitated, the yield is greatly increased, and the product purification is markedly simplified. Surface-mediated syntheses may find wide application in organometallic chemistry.

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