Synthesis and Characterisation of Heptaosmium Carbido Clusters; Crystal and Molecular Structures of $[Os_7(\mu\text{-}H)_2C(CO)_{19}]$ and $[Os_7(\mu\text{-}H)C(CO)_{19}]^-$

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The compound $[Os_7(\mu\text{-}H)_2C(CO)_{19}]$ (**1**) was isolated in good yield by vacuum pyrolysis of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}COMe)]$, deprotonation of (**1**) gives $[Os_7(\mu\text{-}H)C(CO)_{19}]^-$ (**2**); the structures of (**1**) and (**2**) have been established by *X*-ray crystallography.

The chemistry of Os_7 carbonyl clusters has been studied in recent years,[1—3] but the chemistry of Os_7 carbido clusters remains unexplored. The only report[4] of the Os_7 carbido clusters is the early work on $Os_3(CO)_{12}$ pyrolysis in the presence of a trace amount of water that leads to the formation of a green compound formulated as $[Os_7(H)_2C(CO)_{19}]$ (based on mass spectra and ^1H NMR spectra). The yield from this method is usually prohibitively poor (less than 2%).

We report a new synthetic route to this compound that gives good yield and a full characterisation by spectroscopic and crystallographic methods. Vacuum pyrolysis of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}COMe)]$[5] at 240 °C gives a mixture of high-nuclearity osmium clusters. A typical distribution of products is $[Os_4H_4(CO)_{12}]$ (12%), $[Os_6(CO)_{18}]$ (10%), $[Os_7(H)_2C(CO)_{19}]$ (50%), $[Os_8C(CO)_{21}]$ (15%), $[Os_{10}(H)_2C(CO)_{24}]$ (3%) and other unidentified products at low yields. All known compounds were identified from their IR spectra and mass spectra. The major green product gives a mass spectrum M^+ 1877 consistent with $[Os_7(H)_2C(CO)_{19}]$. However, the IR spectrum† is distinctly different from the

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† Spectroscopic data for (**1**): IR ν (CO) (n-hexane): 2109vw, 2080s, 2067vs, 2039s, 2029s, 2012m, 1993w, 1979w, 1960w cm^{-1}; FAB MS: M^+ (obs.) m/z 1877 (calc.) 1877; ^1H NMR (CD_2Cl_2): δ −13.15 (s, 1 H), δ −22.56 (s, 1 H); ^{13}C NMR (CD_2Cl_2): δ 379.9 (μ_5-carbide), 160.3, 168.9, 169.3, 169.4, 169.8, 170.1, 170.2, 171.1, 171.9, 172.9, 173.0, 173.5, 177.0, 178.1, 179.4, 180.0, 181.3, 183.3, 186.2 (19 CO). The Ph_3MeP^+ salts of (**2**): IR ν (CO) (CH_2Cl_2): 2090vw, 2065m, 2051vs, 2029s, 2012m, 1995s, br, 1967w, 1913vw; FAB MS: M^+ (obs.) m/z 1876 (calc.) 1876; ^1H NMR (CD_2Cl_2) δ 7.73 (m, 15 H, Ph_3MeP$^+$), δ 2.69 (d, 13 Hz, 3 H, Ph$_3$*Me*P$^+$), δ −13.07 (s, 1 H, MH).

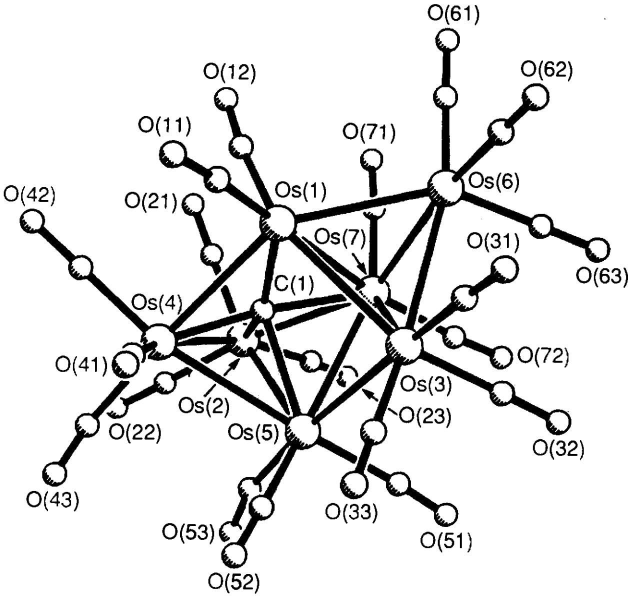


Figure 1. The molecular structure of $[Os_7(\mu\text{-}H)_2C(CO)_{19}]$ (**1**).

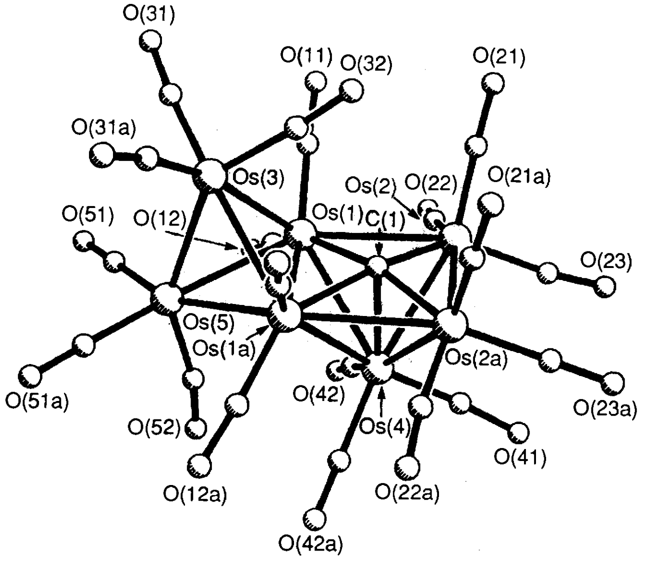
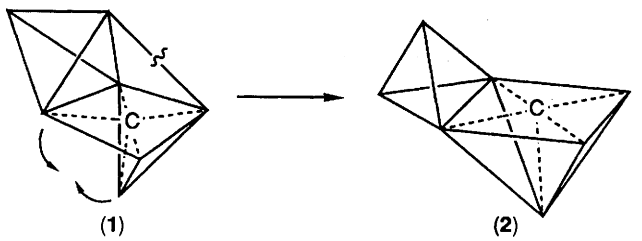


Figure 2. The molecular structure of $[Os_7(\mu\text{-}H)C(CO)_{19}]^-$ (**2**).

reported compound. Therefore, *X*-ray structure analysis‡ was undertaken to characterise the compound. Its molecular structure is shown in Figure 1. The metal core may be



Scheme 1. Conversion of $[Os_7(\mu\text{-}H)_2C(CO)_{19}]$ to $[Os_7(\mu\text{-}H)C(CO)_{19}]^-$.

described as a bridged butterfly [Os(1), Os(2), Os(4), Os(5), Os(7)] fused with a butterfly [Os(1), Os(3), Os(5), Os(7)] and a tetrahedron [Os(1), Os(3), Os(6), Os(7)] with two edges and one face sharing. The carbide carbon is bonded to five osmium atoms of the bridged butterfly with distance to Os(5) significantly longer than all others which may reflect the electron richness of Os(5). All carbonyl ligands are terminally bonded and essentially linear except C(53)–O(53), which shows a slight tilt towards Os(2) [Os(5)–C(53)–O(53) 164.8 (3)°, Os(2) ··· C(53) 2.78 (3) Å], such incipient bridging carbonyl may reflect an electronic imbalance between Os(2) and Os(5). The two hydrides, as evident from ^{1}H NMR, cannot be located directly by *X*-ray analysis. However, potential-energy calculations[6] suggest that one bridges Os(1)–Os(3), and the other bridges Os(1)–Os(6).

Reaction of (**1**) with a base, such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or Et_3N, gives the red monohydrido anion $[Os_7(\mu\text{-}H)C(CO)_{19}]^-$ (**2**) in quantitative yield. *X*-Ray analysis of the Et_4N^+ salt of (**2**) reveals a more symmetrical metal core geometry than the parent compound. The molecular structure of (**2**) is depicted in Figure 2. The metal-core geometry of (**2**) consists of a square-based pyramid and a tetrahedron sharing a common edge. The carbide carbon sits at the basal plane of the square pyramid with a slight displacement out of the plane (0.16 Å) away from the vertex. The position of the hydride ligand cannot be determined. Potential-energy calculations yield two possible alternatives either bridging Os(3)–Os(5) or Os(2)–Os(2a). All 19 carbonyls are terminally bonded and the bond parameters are within the expected ranges.

Both structures contain 13 metal–metal bonds which fits the EAN rule with 100 valence electrons in the clusters. The structure of (**1**) is related to (**2**) in the way that one metal–metal bond in (**1**) breaks [Os(3)–Os(5)] and one metal–metal bond reforms [Os(1)–Os(2)] to give (**2**). See Scheme 1.

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‡ *Crystal data* for (**1**): $C_{20}H_2O_{19}Os_7$, $M = 1877.6$, Monoclinic, Space group $P2_1/n$ (non-standard setting of $P2_1/c$ No. 14), $a = 9.828(2)$, $b = 20.580(8)$, $c = 15.430(3)$ Å, $\beta = 91.06(1)°$, $U = 3120.3$ Å^3, $Z = 4$, $D_c = 3.997$ g cm^{-3}, $F(000) = 3224$, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 285.11 cm^{-1}, 3035 observed diffractometer data [$F > 4\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Os anisotropic) to $R = 0.062$, $R_w = 0.077$.

Crystal data for (**2**): $C_{28}H_{21}NO_{19}Os_7$, $M = 2006.9$, Monoclinic, Space group $P2_1/m$, $a = 9.573(3)$, $b = 13.641(4)$, $c = 15.911(5)$ Å, $\beta = 91.47(1)°$, $U = 2077.1$ Å^3, $Z = 2$, $D_c = 3.209$ g cm^{-3}, $F(000) = 1760$, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ (Mo-K_α) = 214.27 cm^{-1}, 2109 observed diffractometer data [$F > 4\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Os anisotropic) to $R = 0.047$, $R_w = 0.059$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.