

FORMATION OF μ -CARBONYLMETHYLIDENE MOIETY FROM μ_3 -METHYLIDYNE MOIETY ON THE TRIOSMIUM CLUSTER FRAMEWORK

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Reaction of the μ_3 -methylidyne cluster $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CC}_9\text{H}_5(4\text{-Me})\text{N})]$ **1** with CO at 80 °C gives $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-C}(\text{CO})\text{C}_9\text{H}_5(4\text{-Me})\text{N})]$ **2** in 31% yield. Compound **2** contains a μ -carbonylmethylidene carbon moiety formed from the coupling between μ_3 -methylidyne carbon moiety of compound **1** and CO ligand.

The nature and reactivity of exposed carbon atoms on the surface of the metal carbide clusters have attracted considerable interest for a long time.⁽¹⁻⁴⁾ The μ_3 -methylidyne and μ_4 -carbido ligands are vulnerable to attack by nucleophiles and the low-coordinate carbon atoms, especially $\mu_4\text{-C}$, is the most reactive, perhaps best modeling carbon species on metal surfaces which was supported by the observed reactivities.⁽⁵⁻⁹⁾ The first triosmium cluster containing a μ_3 -carbonylmethylidyne ligand, $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_3(\mu_3\text{-CCO})]$, was synthesized by Shapley and coworkers.⁽¹⁰⁾ Recently, we have reported a series of μ_3 -methylidyne clusters of the general formula $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_3\{\mu_3\text{-C}(\text{benzoheterocycle})\}]$, synthesized by the thermolysis of the corresponding μ -methylidene clusters $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_2\{\mu_3\text{-CH}(\text{benzoheterocycle})\}]$.⁽¹³⁾ Another class of $\mu_3\text{-C}$ clusters contains carbon radicals generated from stable $\mu_3\text{-CX}$ compounds which have been proposed as intermediates in the reactions of $[\text{Co}_3(\text{CO})_9(\mu_3\text{-CX})]$ ⁽¹⁴⁾ as well as in the reduction of $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_3(\mu_3\text{-CBr})]$ by $(n\text{-Bu})_3\text{SnH}$.⁽¹⁵⁾

Among the various reactions of μ_3 -methylidyne and μ_4 -carbido ligands, the carboxylation of these ligands by nucleophiles is the most widely investigated one.^(5-9, 13) The first triosmium compound containing $\mu_3\text{-CCO}_2\text{H}$ ligand, $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_3(\mu_3\text{-CCO}_2\text{H})]$, was synthesized from the reaction of $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-CCO}_2\text{H})]$ with an $\text{H}_2\text{O-HCl}$ mixture.⁽⁶⁾ Recently, we reported that the reaction of the μ_3 -diazomethylidyne complex $[\text{Os}_3(\text{CO})_7(\mu\text{-H})_2(\mu\text{-dppm})(\mu_3\text{-CN}_2)]$ with 1 atm of CO and H_2O results in the quantitative and instantaneous conversion into the μ_3 -carboxymethylidyne complex $[\text{Os}_3(\text{CO})_7(\mu\text{-H})_3(\mu\text{-dppm})(\mu_3\text{-CCO}_2\text{H})]$.⁽¹³⁾ This paper is a continuation of our investigation on the behavior of triosmium cluster containing μ_3 -methylidyne carbon atom towards nucleophiles and describes the synthesis and characterization of a unique example of a triosmium cluster containing a μ -carbonylmethylidene carbon atom.

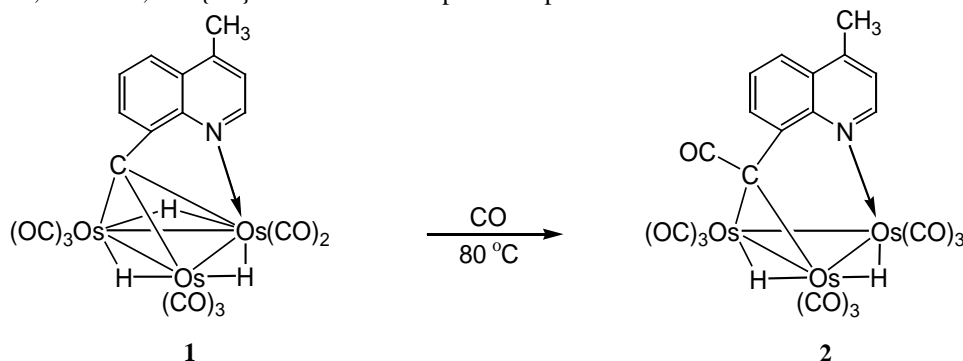
All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Reagent-grade solvents were dried by standard procedures and were distilled from appropriate drying agents prior to use. The starting cluster $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CC}_9\text{H}_5(4\text{-Me})\text{N})]$ **1** was prepared according to the published procedure.⁽¹²⁾

Reaction of 1 with carbonmonoxide: CO was bubbled through a refluxing cyclohexane solution (20 mL) of **1** (55 mg, 0.058 mmol) for 1 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel.

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Elution with hexane/CH₂Cl₂ (2:1, v/v) developed two bands. The faster moving band gave unreacted **1** (36 mg) while the slower moving band afforded [Os₃(CO)₉(μ-H)₂(μ₃-η²-C(CO)C₉H₅(4-Me)N)] **2** (18 mg, 31%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at 4 °C (Anal. Calcd. for C₂₁H₁₀NO₁₀Os₃: C, 25.05; H, 1.00, N, 1.39. Found: C, 25.23; H, 1.01; N, 1.45). IR (νCO, CH₂Cl₂): 2157 m, 2128 m, 2064 s, 2038 vs, 2003 m, 1981 m cm⁻¹; ¹H NMR (CDCl₃): δ 9.76 (d, 1H, *J* = 5.6 Hz), 7.81 (d, 1H, *J* = 7.2 Hz), 7.72 (d, 1H, *J* = 7.2 Hz), 7.63 (t, 1H, *J* = 7.2 Hz), 7.41 (d, 1H, *J* = 5.6 Hz), 3.05 (s, 3H), -15.29 (d, *J* = 2.0 Hz), -17.01 (d, *J* = 2 Hz); ¹³C-¹H} NMR (CDCl₃): δ 185.6, 176.8, 173.4, 173.1, 169.5, 169.4, 169.3, 168.9, 168.2, 168.1, 165.6, 163.4, 156.4, 149.9, 130.1, 129.3, 124.9, 123.1, 120.3, 29.7, 19.1; mass spectrum: *m/z* 1008 (M⁺), 980 (M⁺-CO), 952 (M⁺-2CO), 924 (M⁺-3CO), 896 (M⁺-4CO), 868 (M⁺-5CO), 840 (M⁺-6CO), 812 (M⁺-7CO), 784 (M⁺-8CO), 756 (M⁺-9CO).

The reaction of [Os₃(CO)₈(μ-H)₃(μ₃-η²-CC₉H₅(4-Me)N)] **1** with CO in refluxing cyclohexane, followed by usual workup and chromatographic separation as mentioned in the experimental section, resulted in the isolation of [Os₃(CO)₉(μ-H)₂(μ₃-η²-C(CO)C₉H₅(4-Me)N)] **2** in 31% yield (Scheme 1). We were unable to obtain X-ray quality crystals of **2**, therefore its characterization is based on elemental analysis, IR, ¹H NMR, ¹³C-¹H} NMR and mass spectroscopic data.



Scheme 1

The elemental analysis and mass spectral data of compound **2** suggest a trinuclear formulation for it. The infrared spectrum of **2** in the carbonyl stretching region is similar to those of triosmium clusters having a 3,3,3 distribution of carbonyl ligands.^(10, 12) The ¹H NMR spectrum of compound **2** displays two hydride resonances at δ -15.29 (d, *J* = 2.0 Hz) and -17.01 (d, *J* = 2 Hz) indicating that one of the hydride ligand is eliminated from **1** during product formation. Furthermore, in addition to the methyl proton resonance at δ 3.05 the ¹H NMR spectrum in the aromatic region displays four doublets at δ 9.76 (*J* = 5.6 Hz), 7.81 (*J* = 7.2 Hz), 7.72 (*J* = 7.2 Hz), 7.41 (*J* = 5.6 Hz) and a triplet at δ 7.63 (*J* = 7.2 Hz) suggesting that the heterocyclic ligand remains intact in the product. It is clear from the *J*_{H-H} values that the doublets at δ 7.81 and 7.72 and the triplet at δ 7.63 are due to the protons of the carbocyclic ring while the doublets at δ 9.76 and 7.41 are due to that of the heterocyclic ring. On the other hand, the ¹³C-¹H} NMR spectrum shows twenty one resonances which are consistent with the assigned formulation. The carbonyl region of this spectrum exhibits ten sharp resonances for ten carbonyl groups within the

molecule. The resonances at δ 185.6 is probably due to the carbonyl group bonded to the μ -methylidene carbon. Since the molecule possesses a pseudo mirror plane of symmetry,⁽¹²⁾ we observe four close pairs of resonances due to eight carbonyl groups bonded to osmium. In addition to this, the spectrum displays a markedly upfield low intense resonance at δ 29.7 for the μ -methylidene carbon atom.⁽¹⁰⁾ The FAB mass spectrum shows the parent molecular ion peak at m/z 1008 and peaks due to the sequential loss of nine carbonyl groups which are consistent with the proposed structure. To our knowledge compound **2** is the first reported example of triosmium cluster that contains a μ -carbonylmethylidene carbon moiety.

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