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 \([\text{Os}_3(\text{CO})_9(\mu-H)_3(\mu_3-\eta^2-\text{CC}_9\text{H}_5(4-\text{Me})\text{N})]\) 1 with CO at 80 °C gives \([\text{Os}_3(\text{CO})_9(\mu-H)_2(\mu_3-\eta^2-\text{C}>(\text{CO})\text{C}_9\text{H}_5(4-\text{Me})\text{N})]\) 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. The µ 3-methylidyne and µ 4-carbido ligands are vulnerable to attack by nucleophiles and the low-coordinate carbon atoms, especially µ 4-C, is the most reactive, perhaps best modeling carbon species on metal surfaces which was supported by the observed reactivities. The first triosmium cluster containing a µ 3-carbonylmethylidyne ligand, \([\text{Os}_3(\text{CO})_9(\mu-H)_3(\mu_3-\text{CCO})]\), was synthesized by Shapley and coworkers. Recently, we have reported a series of µ 3-methylidyne clusters of the general formula \([\text{Os}_3(\text{CO})_9(\mu-H)_2(\mu_3-C(\text{benzoheterocycle}))]\), synthesized by the thermolysis of the corresponding µ-methylidene clusters \([\text{Os}_3(\text{CO})_9(\mu-H)_2(\mu_3-\text{CH}(\text{benzoheterocycle}))]\). Another class of µ 3-C clusters contains carbon radicals generated from stable µ 3-CX compounds which have been proposed as intermediates in the reactions of \([\text{Co}_3(\text{CO})_9(\mu_3-CX)]\) as well as in the reduction of \([\text{Ru}_3(\text{CO})_9(\mu-H)_3(\mu_3-\text{CBr})]\) by \((n-\text{Bu})_3\text{SnH}\).

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. The first triosmium compound containing µ 3-CO_2H ligand, \([\text{Os}_3(\text{CO})_9(\mu-H)_2(\mu_3-CO_2H)]\), was synthesized from the reaction of \([\text{Os}_3(\text{CO})_9(\mu-H)_2(\mu_3-CO_2H)]\) with an \(\text{H}_2\text{O}-\text{HCl}\) mixture. Recently, we reported that the reaction of the µ 3-diazoalkylidyne complex \([\text{Os}_3(\text{CO})_7(\mu-H)_2(\mu_3-\text{dppm})(\mu_3-\text{CN}_2)]\) with 1 atm of CO and \(\text{H}_2\text{O}\) results in the quantitative and instantaneous conversion into the µ 3-carboxymethylidyne complex \([\text{Os}_3(\text{CO})_7(\mu-H)_3(\mu_3-\text{CO}_2\text{H})]\). 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 \([\text{Os}_3(\text{CO})_9(\mu-H)_3(\mu_3-\eta^2-\text{CC}_9\text{H}_5(4-\text{Me})\text{N})]\) 1 was prepared according to the published procedure.

Reaction of 1 with carbon monoxide: 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)₈(µ-H)₂(µ₂-η⁴-C(CO)C₆H₄(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, 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)₂(µ₃-η⁴-C(CO)C₆H₄(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-η⁴-C(CO)C₆H₄(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.

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. 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 Jₜₜ 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

![Scheme 1](image-url)
molecule. The resonances at $\delta$ 185.6 is probably due to the carbonyl group bonded to the $\mu$-methyldiene carbon. Since the molecule possesses a pseudo mirror plane of symmetry,\(^\text{(12)}\) 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 $\delta$ 29.7 for the $\mu$-methyldiene carbon atom.\(^\text{(10)}\) 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 trisodium cluster that contains a $\mu$-carbonylmethyldiene carbon moiety.

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REFERENCES
