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Reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)$ with Diazomethane. The First Example of a Trimetallic Cluster Containing a μ-Methylidene and a σ-Methyl

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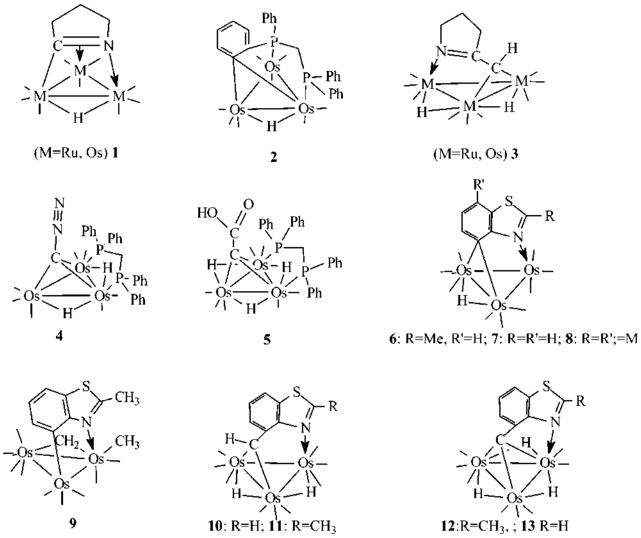
*Summary: The electronically unsaturated cluster $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)$ (**6**) reacts with excess CH_2N_2 at −10 to +25 °C to give $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\mu\text{-}CH_2)CH_3$ (**9**), a rare example of a triosmium cluster containing an edge-bridging methylene group and a σ-bound methyl group. On thermolysis in refluxing heptane **9** affords $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHC_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)_2$ (**11**) and $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}CC_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)_3$ (**12**). In contrast, $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_7H_4NS)(\mu\text{-}H)$(**7**) reacts with diazomethane under exactly similar conditions to afford $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHC_7H_4NS)((\mu\text{-}H)_2$ (**10**), which on thermolysis in refluxing heptane gives $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}CC_7H_4NS)(\mu_3\text{-}H)_3$ (**13**).*

Diazomethane is an efficient source of methylene and is a versatile reagent in organometallic chemistry.[1] Trimetallic clusters containing both bridging methylene and σ-bonded methyl groups are unknown. Interest in these complexes has been stimulated by the idea that the surface-bound μ-CH_2 groups are intermediates in the conversion of CO into hydrocarbons in Fischer−Tropsch chemistry.[2−4] The reactions of diazoalkanes with trimetallic clusters of osmium, ruthenium, and iron have been investigated over the last two decades and have given many interesting compounds with various coordination modes, including insertion of CH_2 into metal−metal and metal−carbon bonds with N_2 extrusion.[5−10] We have previously investigated the reactions of diazomethane with the μ_3-imidoyl clusters $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}NCH_2CH_2CH_2)(\mu\text{-}H)$ (M = Ru, Os; **1**) and the electronically unsaturated cluster $Os_3(CO)_8(Ph_2PCH_2P(Ph)C_6H_4)(\mu\text{-}H)$ (**2**) and observed a remarkable variety of structures depending on the metal carbonyl cluster (Chart 1).[10,11] For example, diazomethane reacts with **1** to give $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHC{=}NCH_2CH_2CH_2)(\mu\text{-}H)_2$ (M = Ru, Os; **3**), whereas with **2** $Os_3(CO)_7(\mu_3\text{-}CNN)(\mu\text{-}dppm)(\mu\text{-}H)_2$ (**4**) and $Os_3(CO)_7(\mu_3\text{-}CCOOH)(\mu\text{-}dppm)(\mu\text{-}H)_3$ (**5**) are obtained (Chart 1). As a continuation of our studies on the reactivity of electronically unsaturated triosmium clusters, we have examined the behavior of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_2(2\text{-}R)(5\text{-}R')NS)(\mu\text{-}H)$ (**6**, R = Me, R′ = H; **7**, R = R′ = H; **8**, R = R′ = Me) toward diazomethane (Chart 1).

Chart 1



(M=Ru, Os) **1**

2

(M=Ru, Os) **3**

4

5

6: R=Me, R'=H; **7**: R=R'=H; **8**: R=R';=M

9

10: R=H; **11**: R=CH$_3$

12:R=CH$_3$, ; **13** R=H

Treatment of **6** with excess ethereal diazomethane at −10 to +25 °C gives $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\mu\text{-}CH_2)CH_3$ (**9**) in 35% yield (Chart 1).[12] Compound **9** is presumably formed by the insertion of a methylene group into one of the metal−metal bonds, followed by formation of a methyl group by reaction of the second

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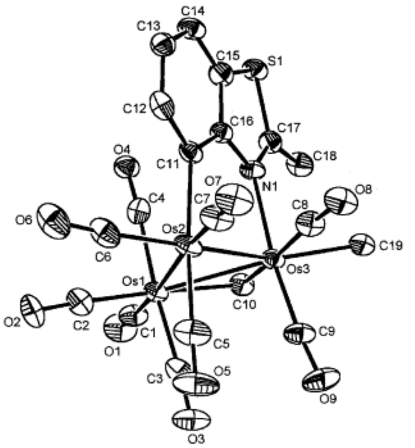

Figure 1. Molecular structure of **9**. Selected bond lengths (Å) and angles (deg): Os(1)−Os(2) = 2.9952(5), Os(1)−Os(3) = 2.8680(4), Os(2)−Os(3) = 2.7463(4), Os(1)−C(10) = 2.265(8), Os(3)−C(10) = 2.041(8), Os(3)−C(19) = 2.177(8), Os(2)−C(11) = 2.148(7), Os(3)−N(1) = 2.189(6); Os(3)−Os(1)−Os(2) = 55.809(11), Os(3)−Os(2)−Os(1) = 59.750(11), Os(2)−Os(3)−Os(1) = 64.441(11), C(10)−Os(1)−Os(3) = 45.0(2), C(10)−Os(3)−Os(2) = 116.0(2).

methylene with the cluster-bound bridging hydride and loss of a carbonyl ligand. The reverse sequence, formation of the methyl group followed by reaction with a second methylene, is also possible. Although individual examples of triosmium clusters containing bridging methylene and σ-bonded methyl groups are known, to our knowledge compound **9** provides the first example of a triosmium cluster containing both bridging methylene and σ-bonded methyl groups.[7] The solid-state structure of **9**[13] (Figure 1) consists of an Os_3 triangle with three distinctly different metal−metal bonds (Os(1)−Os(2) = 2.9952(5) Å, Os(2)−Os(3) = 2.7463(4) Å, and Os(1)−Os(3) = 2.8680(4) Å). An intriguing structural feature of **9** is the asymmetric nature of the methylene bridge on the Os(1)−Os(3) edge (Os(1)−C(10) = 2.265(8) Å and Os(3)−C(10) = 2.041(8) Å). Such a large difference in methylene-bridged Os−C bond lengths has never been observed before in methylene-bridged triosmium complexes.[7] For example, the Os−C bond lengths of the methylene bridges in $Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}H)_2$ are 2.151(5) and 2.150(6) Å;[7] in $Os_3(CO)_9(PPh_3)(\mu\text{-}CH_2)(\mu\text{-}H)_2$ they are 2.140(6) and 2.171(6) Å, and in $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CH_3C_2CH_3)(\mu\text{-}CH_2)$ they are 2.17(2) and 2.15 Å.[10] It is difficult to pinpoint the origin of this asymmetry. Asymmetry in bridging hydride ligands has been observed where the hydride bridges the same edge as a μ-σ-C,N-bound heterocycle. The shorter Os−H distance is always associated with the nitrogen-bound Os atom.[14] The bond length of the σ-bonded methyl group terminally coordinated at an equatorial site on Os(3) has a fairly typical value (Os(3)−C(12) = 2.177(8) Å). The bridging 2-methylbenzothiazolide ligand is nearly perpendicular to the plane of the osmium triangle, as has been previously noted in related complexes.[10,11] The Os(3)−N(1) bond length of 2.189(6) Å is similar to the corresponding Os−N distance in **6** (2.172(10) Å), but the Os(2)−C(11) distance (2.148(7) Å) is significantly shorter than the related bond distance in **6** (2.27(2) Å), as expected on going from an electron-deficient three-center−two-electron bond to an electron-precise two-center−two-electron bond. Another remarkable structural feature of **9** is the exceptionally long Os(1)−Os(2) bond. A local electron count reveals that Os(1) has $19e^-$, Os(2) has $17e^-$, and Os(3) has $18e^-$, formally making the Os(1)−Os(2) bond a donor−acceptor bond. Similarly elongated bonds have been reported for osmium and ruthenium clusters and have been attributed to a donor−acceptor interaction.[15]

The spectroscopic data for **9**[16] are in good agreement with the structure shown in Figure 1. The infrared spectrum indicates that all the carbonyl groups are terminal. In addition to the usual resonances for the heterocyclic ligand, the ^1H NMR spectrum of **9** shows two equal-intensity doublets at δ 7.21 and 6.66 ($J = 6.6$ Hz) for the bridging methylene group and a singlet at δ 1.03 for the σ-bonded methyl group. The mass spectrum contains the highest peak at m/z 984 ($M^+ - CH_3$), and fragment ions showed the successive loss of one CH_2 and nine carbonyl groups.

In contrast, the reaction of **7** with excess ethereal diazomethane affords $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHC_7H_4NS)(\mu\text{-}H)_2$ (**10**) in 44% yield (Chart 1),[12,17] in which a methylene fragment has inserted into the metal−carbon σ bond of the heterocyclic ligand and undergone a C−H oxidative addition, analogous to the same reaction with **1**, which gives **3** (Chart 1). No detectable reaction products were obtained from the reaction of **8** with diazomethane, and only unreacted starting material was recovered from the reaction mixture.

The thermolysis of **9** in refluxing heptane results in the formation of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHC_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)_2$ (**11**) and $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}CC_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)_3$ (**12**) in 7 and 39% yields, respectively (Chart 1).[18,19] Compound **11** is presumably formed by insertion of the methylene group into the metal−carbon σ bond of the heterocyclic ligand followed by C−H activation and loss of the σ-bonded methyl group as methylene. Loss of methylene is required in order to account for the presence of two hydrides in the final product, **11**. Thermolysis of **11** in refluxing heptane affords **12**, indicating that the formation of **12** takes place via the intermediate formation of **11**. Thermolysis of **10** in refluxing heptane gives the trihydrido compound $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}CC_7H_4\text{-}$

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(13) Crystal data for **9**: $C_{19}H_{11}NO_9Os_3S$, $M_r = 999.95$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.2852(4)$ Å, $b = 10.3219(4)$ Å, $c = 13.4911(5)$ Å, $\alpha = 97.974(3)°$, $\beta = 105.797(3)°$, $\gamma = 112.489(2)°$, $V = 1105.82(8)$ Å^3, $Z = 2$, $D_c = 3.003$ g/cm^{-3}, μ(Mo Kα) = 17.339 mm^{-1}, $\lambda = 0.710\ 73$ Å, $T = 150(2)$ K, crystal size 0.15 × 0.15 × 0.10 mm. R1 = 0.0412, wR2 = 0.0931 ($I > 2\sigma(I)$); R1 = 0.0536, wR2 = 0.0991 (all data). Crystal data for **12**: $C_{17}H_9NO_8Os_3S$, $M_r = 957.91$, monoclinic, space group $P2_1/c$, $a = 16.1881(4)$ Å, $b = 11.2807(4)$ Å, $c = 11.8325(4)$ Å, $\beta = 100.692(2)°$, $V = 2123.26(12)$ Å^3, $Z = 4$, $D_c = 2.997$ cm^{-3}, μ(Mo Kα) = 18.050 mm^{-1}, $T = 293(2)$ K, crystal size 0.30 × 0.20 × 0.05 mm. R1 = 0.0459, wR2 = 0.0980 ($I > 2\sigma(I)$); R1 = 0.0729, wR2 = 0.1083 (all data). Intensity data were collected on a FAST area detector diffractometer. The structures were solved by direct methods (SHELXS-86) and refined on F^2 by full-matrix least squares (SHELXL-96) using all unique data with intensities >0. The CIF files for **9** and **12** have been deposited at the Cambridge Crystallographic Data Center with the reference numbers 179622 and 179623, respectively.

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(16) See Supporting Information for spectroscopic data for **9**.

(17) See Supporting Information for spectroscopic data for **10**.

(18) See Supporting Information for spectroscopic data for **11** and experimental procedure for **11** and **13**.

(19) See Supporting Information for spectroscopic and analytical data for **12**.

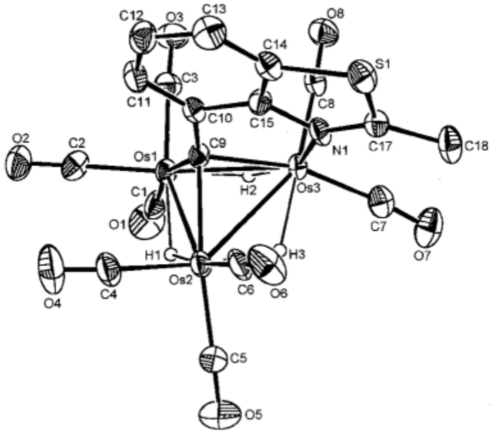

Figure 2. Molecular structure of **12**. Selected bond lengths (Å) and angles (deg); Os(1)−Os(3) = 2.8607(5), Os(2)−Os(3) = 2.8892(5), Os(1)−Os(2) = 2.8915(6), Os(1)−C(9) = 2.045(9), Os(2)−C(9) = 2.144(10), Os(3)−C(9) = 2.108(10), Os(3)−N(1) = 2.183(8); Os(3)−Os(1)−Os(2) = 60.299(13), Os(1)−Os(3)−Os(2) = 60.379(13), Os(3)−Os(2)−Os(1) = 59.322(13), Os(1)−C(9)−Os(3) = 87.1(4), Os(1)−C(9)−Os(2) = 87.3(4), Os(3)−C(9)−Os(2) = 120.2(7), Os(3)−C(9)−C(10) = 114.3(6), Os(2)−C(9)−C(10) = 120.2(7), Os(1)−C(9)−C(10) = 145.0(7).

NS)(μ-H)$_3$ (**13**) in 31% yield, which is apparently isostructural with **12**.[20]

The proposed structure of **12** (Figure 2) has been confirmed by a solid-state structural investigation.[13] It consists of an Os$_3$ triangle with two almost equal metal−metal bonds (Os(1)−Os(2) = 2.8915(6) Å, Os(2)−Os(3) = 2.8892(5) Å) and one shorter metal−metal bond (Os(1)−Os(3) = 2.8607(5) Å). The structure is related to that observed for Os$_3$(CO)$_{10}$(μ_3-CR)(μ-H) (R = H,[21] Ph,[22]) with the additional Os−N(1) interaction replacing one radial carbonyl. The 2-methylbenzothiazolide ligand is nearly perpendicular to the plane of the osmium triangle. The μ_3-methylidyne atom C(9) bridges three osmium atoms with three distinctly different metal−carbon bonds (Os(1)−C(9) = 2.045(9) Å, Os(2)−C(9) = 2.144(10) Å, and Os(3)−C(9) = 2.108(10) Å). A key feature of **12** is that the μ_3-CC$_7$H$_3$(2-CH$_3$)NS ligand has significant bonding interactions with all the three osmium atoms, in contrast to the related compounds Os$_3$(CO)$_{10}$(μ_3-CR)(μ_3-CR). (R = H,[21] Ph,[22] CH$_2$CHMe[23]), where the bonding is viewed as semi-triply bridging. The C(9)−C(10) bond vector is nearly perpendicular to the Os$_3$ plane but is tilted slightly toward Os(3) (∠Os(3)−C(9)−C(10) = 114.3(6)°, ∠Os(2)−C(9)−C(10) = 120.2(7)°, ∠Os(1)−C(9)−C(10) = 145.0(7)°). The three bridging hydrides H(1), H(2), and H(3), located but not refined, are trans to CO(3) and CO(6), CO(2) and N(1), and CO(4) and CO(8), respectively, maintaining approximately octahedral geometry around each osmium atom.

The fate of the initial adduct formed from the reaction of **6** and **7** with methylene is apparently subject to some very subtle effects. The isolation of **10** from **7** is contrary to what one would expect on the basis of steric grounds. If one assumes that the initial reaction yields a 48e$^-$ methylene−hydride complex, it seems reasonable to propose that three possible processes can occur from this intermediate: (1) reductive elimination to form a 46e$^-$ σ-methyl, (2) coordination of a second mole of methylene, and (3) C−H oxidative addition. It could be argued that the presence of a σ-electron donating group in the 2-position might promote reductive elimination or coordination of an electron-deficient triplet carbene, while in the absence of the methyl group, a σ-C−H complex formed with the already bound methylene would be more favorable. Alternatively, the difference in reactivity between **6** and **7** could arise from a difference in the site of attack. If the methylene group is added across the Os(1)−Os(2) edge (opposite the Os atom bound to the N donor atom, with the hydride on the Os(1)−Os(3) edge), it would be set up for reductive elimination of CH$_2$ with the Os−heterocycle carbon bond. On the other hand, methylene addition across the Os(1)−Os(3) or Os(2)−Os(3) bond would set up reductive elimination with the hydride ligand to give a methyl group. In the case of **8**, the presence of two methyl groups ortho and para to the nitrogen may slow the reactivity of electron-deficient species with the initially formed singlet carbene. We have previously noted a marked sensitivity in the reactivity of complexes related to **6**−**8** toward substitutions at the heterocyclic ring and the metal core in the coordination chemistry of such complexes.[24] Further studies with a wider range of related heterocycles are underway in order to test these hypotheses. The factors controlling the relative rates of the processes observed here are very important to our understanding of such processes in catalytic systems.

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Supporting Information Available: Text and tables giving details of the X-ray crystallographic structure determination for **9** and **12** and experimental details and spectroscopic and analytical data for **9**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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