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Clusters Containing Carbene Ligands. Novel Example of Carbene Ligand Transfer from a Metal Atom to a Carbon Atom

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Summary: The reaction of the new carbene-containing cluster complex $Os_3(CO)_{11}[C(Et)NMe_2]$ (**2**) with $PhC{\equiv}CH$ has yielded the complex $Os_3(CO)_9[\mu_3\text{-}PhC_2\{C(Et)(NMe_2)\}](\mu\text{-}H)$ (**3**, 35%), which contains a triply bridging alkyne ligand with phenyl and ethyl(dimethyliminio)methyl substituents. The product is believed to have been formed by the transfer of the $C(Et)NMe_2$ carbene ligand in **2** to the α-carbon atom of a bridging $PhC{\equiv}C$ ligand in an intermediate formed by the activation of $PhC{\equiv}CH$ by the cluster.

Metal complexes containing carbene ligands have recently been used with great success as reagents in a variety of new organic syntheses.[1,2] The transfer of the carbene ligand from the metal atom to an organic substrate is a central feature of these reactions. The relative paucity of metal cluster complexes containing carbene ligands has resulted in a lag in the development of their organic chemistry.[3] One might anticipate that the multicenter environment of the cluster complex could produce modifications of the organic substrates that are not readily achieved by mononuclear metal complexes[4] and thus open new directions into the organic chemistry of carbene ligands.[5]

We have recently reported that the reaction of certain cluster complexes containing ynamine ligands with hydrogen can lead to the formation of aminocarbene ligands.[6] From the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with MeC_2NMe_2 we have obtained the complex $Os_3(CO)_{10}[\mu\text{-}EtCN(Me)CH_2](\mu\text{-}H)$ (**1**), which contains an *N*-methyl-metalated ethyl(dimethylamino)carbene ligand.[7] We have now found that treatment of **1** with CO (1300 psi/110 °C) yields the CO addition product $Os_3(CO)_{11}[C(Et)NMe_2]$ (**2**) in good yield (68%).[8] Compound **2** was characterized by single-crystal X-ray diffraction analysis.[9,10] An ORTEP drawing of the molecular structure of **2** is shown in Figure 1. Compound **2** contains a normal ethyl(dimethylamino)carbene ligand in an equatorial coordination site of a triosmium carbonyl cluster and is the first example of a simple carbene derivative of $Os_3(CO)_{12}$.[4]

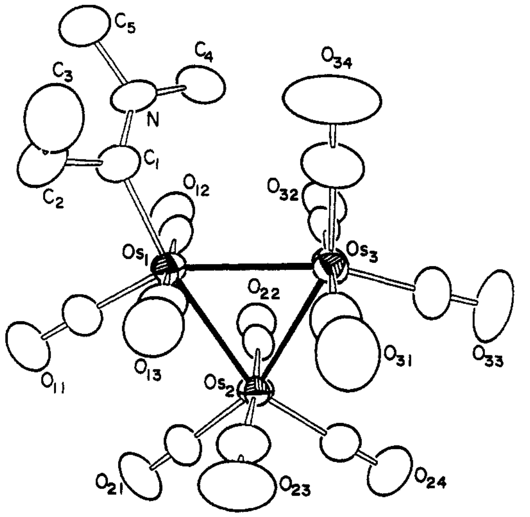

Figure 1. ORTEP diagram of $Os_3(CO)_{11}[EtC(NMe_2)]$ (**2**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Os(1)-Os(2) = 2.9043 (9), Os(1)-Os(3) = 2.9026 (9), Os(2)-Os(3) = 2.8913 (8), Os(1)-C(1) = 2.09 (1), C(1)-N = 1.32(1); Os(3)-C(1)-N = 129 (1).

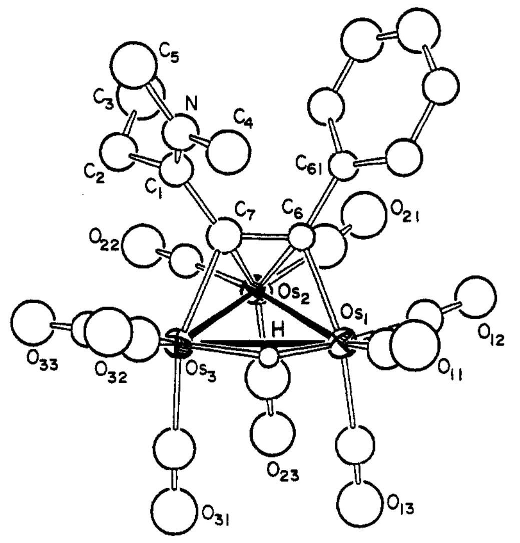

Figure 2. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}PhC_2\{C(Et)(NMe_2)\}](\mu\text{-}H)$ (**3**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Os(1)-Os(2) = 2.774 (1), Os(1)-Os(3) = 2.981 (1), Os(2)-Os(3) = 2.774 (1), C(6)-C(7) = 1.40 (2), C(1)-C(7) = 1.51 (3), C(1)-N = 1.29 (2); C(7)-C(1)-N = 120 (2).

It was formed, obviously, by a simple reductive elimination of the CH_2 grouping and the bridging hydride ligand

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[8] Spectroscopic data for **2** are as follows. IR (ν(CO) in hexane, cm^{-1}): 2105 (w), 2051 (s), 2025 (s, sh), 2016 (vs), 1997 (vw), 1986 (m), 1973 (m), 1956 (vw), 1949 (w). ^1H NMR (δ in $CDCl_3$): 3.75 (s, NMe), 3.40 (s, NMe), 3.28 (q, CH_2, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.12 (t, CH_3, $J_{H\text{-}H}$ = 7.6 Hz). Satisfactory elemental analyses have been obtained.

[9] Yellow crystals of **2** were grown from solutions in a CH_2Cl_2/hexane solvent mixture by slow evaporation of solvent at 0 °C. The crystals belonged to the triclinic crystal system: space group $P\bar{1}$, a = 11.407 (2) Å, b = 12.332 (2) Å, c = 8.602 (1) Å, α = 103.92 (1)°, β = 110.56 (1)°, γ = 82.57 (1)°, Z = 2. The structure was solved by a combination of direct methods and difference Fourier techniques and was refined (2627 reflections) to the final R values R = 0.031 and R_w = 0.036.

[10] Diffraction data were collected on a Rigaku AFC6S diffractometer by using Mo Kα radiation. Calculations were performed on a MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Data were corrected for absorption.

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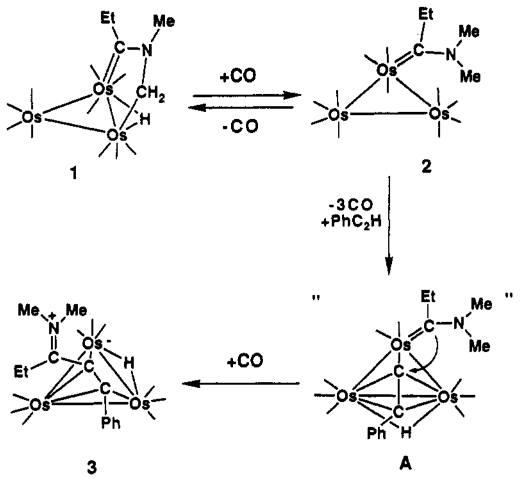
Scheme I



in 1 and an addition of a CO ligand to the resultant vacant site. The carbene ligand exhibits no unusual structural features. This reaction is reversible, and when 2 is heated to 97 °C for 3 h, in heptane solvent, compound 1 is regenerated in 59% yield.[11] To investigate the potential for new chemistry involving the carbene ligand, we carried out the reaction of 2 with PhC≡CH.

From the reaction of 2 with PhC≡CH in refluxing heptane solvent, we have obtained the new compound $Os_3(CO)_9[\mu_3\text{-}PhC_2\{C(Et)(NMe_2)\}](\mu\text{-}H)$ (3) in 35% yield.[12] The structure of 3 was also established by a single-crystal X-ray diffraction analysis, and an ORTEP drawing of 3 is shown in Figure 2.[10,13] The molecule contains a phenyl- and ethyl(dimethyliminio)methyl-substituted acetylene ligand bridging the triosmium cluster in the μ_3-|| coordination mode.[14,15] The imino substituent contains a planar nitrogen atom and a C-N double bond (1.29 (2) Å). The molecule is zwitterionic with a formal positive charge on the nitrogen atom and the negative charge delocalized in the cluster of metal atoms. A single hydride ligand (located, but not refined), with δ −19.52 ppm, was found bridging the long Os(1)–Os(3) metal–metal bond (Os(1)–Os(3) = 2.981 (1) Å).

It is known that terminal acetylenes readily react with $Os_3(CO)_{12}$ to yield the acetylide complexes $Os_3(CO)_9(\mu_3\text{-}CCR)(\mu\text{-}H)$ by cleavage of the acetylenic C—H bond.[5,16] Thus, a possible mechanism for the formation of 3 could involve an activation of the acetylenic C—H bond of a PhC≡CH ligand and a CO-induced shift of the carbene ligand to the carbon atom of the resultant acetylide ligand in an intermediate such as A, containing a μ_3-CCPh ligand and a *metal*-coordinated carbene ligand (see Scheme I).[17]

The reactions of terminal alkynes with mononuclear metal carbene complexes generally yield annulation products without cleavage of the acetylenic C—H bond.[1,2] The tendency of the cluster to react with terminal alkynes by activation of the C—H bond thus permits a new pathway to alkyne–carbene-derived products. Studies of the reactivity of 2 with other substrates are in progress, in hopes of combining other examples of cluster-specific substrate activation with carbene addition reactions.

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Supplementary Material Available: Tables of crystal data, positional parameters, intramolecular bond distances and angles, and anisotropic thermal parameters for the structural analysis of compounds 2 and 3 (16 pages); tables of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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(11) A small amount (4% yield) of $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}H)_2$[7] was also obtained in this reaction.

(12) A heptane solution (35 mL) containing 12.6 mg of 2 and 0.20 mL of PhC_2H was heated to reflux for 1.5 h. Separation by TLC on silica gel with a CH_2Cl_2/hexane (1/4) solvent mixture yielded 3.3 mg of 1, 1.2 mg of 2, and 4.6 mg of 3, 35%. Spectroscopic data for 3 are as follows. IR (ν(CO) in hexane, cm^{-1}): 2080 (m), 2050 (s), 2027 (vs), 2003 (s), 1986 (m), 1975 (w, sh), 1968 (s), 1948 (w). ^1H NMR (δ in $CDCl_3$): 7.20–6.90 (5 H, m, Ph), 3.04 (3 H, s, NMe), 2.91 (1 H, dq, $^1J_{H-H} = 13.4$ Hz, $^3J_{H-H} = 7.7$ Hz, C*H*H), 2.75 (1 H, dq, $^1J_{H-H} = 13.4$ Hz, $^3J_{H-H} = 7.7$ Hz, CH*H*), 2.60 (3 H, s, NMe), 1.45 (3 H, t, $^3J_{H-H} = 7.7$ Hz, Me), −19.52 (1 H, s, OsH). Compound 3 can also be obtained in 18% yield from 1 and PhC_2H under the same conditions. We think the lower yield indicates that 1 is not an intermediate in the reaction of 2 with PhC_2H. If 1 were an intermediate, the yield of 3 should be higher than that from 2. Instead, we think that the formation of 3 from 1 and PhC_2H indicates simply that ligands other than CO are also capable of producing a terminal carbene by reductive elimination of a C—H bond in 1.

(13) Yellow crystals of 3 were grown for hexane/CH_2Cl_2 solutions by slow evaporation of solvent at 0 °C. Compound 3 crystallized in the monoclinic crystal system: space group $P2_1/n$, $a = 9.027$ (3) Å, $b = 16.051$ (4) Å, $c = 17.769$ (3) Å, $\beta = 93.17$ (2)°, $Z = 4$. The structure was solved by a combination of direct methods and difference Fourier techniques and was refined (1804 reflections) to the final values of the residuals $R = 0.035$ and $R_w = 0.036$.

(14) Cluster complexes containing iminio-substituted alkyne ligands have also been prepared by other methods.[15]

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(17) Alternatively, the loss of only two CO ligands from the cluster would allow the formation of a $\mu\text{-}\eta^2$-acetylide ligand,[4] which could then accept the carbene ligand and transform to 3 without the need of a CO addition step.