ordinates and isotropic thermal parameters, and atomic coordinates and isotropic thermal parameters for **5** and **6** (12 pages); listings of structure factor amplitudes for **5** and **6** (47 pages). Ordering information is given on any current masthead page.

Clusters Containing Carbene Ligands. The Synthesis and Structural Characterization of a η^2 Triply Bridging Carbene Ligand and Its Transformation into a Terminal Carbene Ligand

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Summary: The reaction of $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$ with $CH_2(NMe_2)_2$ at 97 °C has yielded two isomeric cluster complexes with the formula $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (**1**, 52%; **2**, 25%). Both complexes were characterized by single-crystal X-ray diffraction analyses. Complex **1** contains a terminally coordinated secondary carbene ligand: δ +10.88 (*H*CNMe$_2$); C–N = 1.29 (2) Å. Complex **2** contains the first example of a C,N η^2 triply bridging carbene ligand: δ +7.62 (*H*CNMe$_2$); C–N = 1.54 (2) Å. Compound **2** was converted into **1** (60% yield) when refluxed in heptane under a CO atmosphere.

The first metal complexes containing carbene ligands were made in 1964.[1] Since then an enormous number and wide variety of complexes containing these ligands have been prepared and studied.[2] Curiously, however, although there are relatively few examples of metal cluster complexes that contain these ligands, both bridging and terminal coordination modes have already been characterized.[3-11] Polynuclear ligand coordinations have been shown to play an important role in the chemistry of metal cluster compounds.[12,13] To further illustrate the scope and diversity of polynuclear ligand coordination in clusters, we wish to report here the synthesis and characterization of the first cluster complex to contain a η^2 triply bridging (dialkylamino)carbene ligand.

The reaction of $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$ with $CH_2(NMe_2)_2$ in 100 mL of heptane for 6 h at reflux yielded two products with the formula $Os_3(CO)_9(OMe)(H)[C(H)NMe_2]$, **1** (52% yield) and **2** (25% yield). Both compounds were characterized by IR and ^{1}H NMR spectroscopies and by a single-crystal X-ray diffraction analysis.[14] An ORTEP drawing of **1** is shown in Figure 1.[15-17] The molecular structure of **1** is similar to that of the analogous benzenethiolato cluster $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}SPh)(\mu\text{-}H)$[18] and contains a terminally coordinated secondary (dimethylamino)carbene ligand: C–N = 1.29 (2) Å; δ (*H*CNMe$_2$) + 10.88.

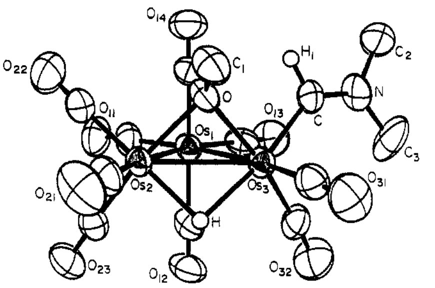

Figure 1. An ORTEP diagram of $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (**1**), showing 50% probability ellipsoids. The ellipsoids of the hydrogen atoms have been reduced for clarity.

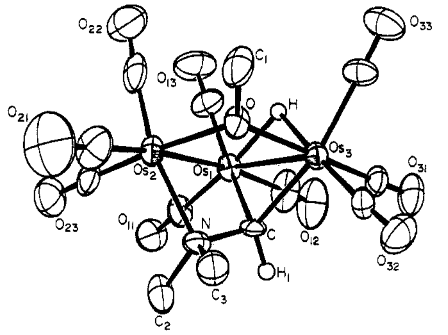

Figure 2. An ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (**2**), showing 50% probability thermal ellipsoids. The ellipsoids of the hydrogen atoms have been reduced for clarity.

An ORTEP diagram of the molecular structure of **2** is shown in Figure 2.[15,19,20] The structure consists of an open

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(14) Both compounds are air-stable and were isolated by TLC on silica gel by using a 40:60 CH_2Cl_2/hexane solvent mixture. For **1**: IR (ν(CO) in hexane) 2092 (m), 2051 (s), 2011 (vs), 2003 (m), 1996 (s), 1989 (m), 1982 (w), 1964 (m), 1937 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ) 10.88 (s, 1 H), 3.99 (s, 3 H), 3.61 (s, 3 H), 3.57 (s, 3 H), −12.92 (s, 1 H). For **2**: IR (ν(CO) in hexane) 2095 (m), 2071 (s), 2038 (s), 2011 (s), 1995 (vs), 1978 (m), 1970 (m), 1959 (w), 1935 (vw) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ) 7.62 (d, J_{H-H} = 1.38 Hz, 1 H), 4.01 (s, 3 H), 3.65 (s, 3 H), 3.03 (s, 3 H), −11.37 (d, J_{H-H} = 1.33 Hz, 1 H).

(15) Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo Kα radiation. Structure solutions and refinements were performed on a Digital Equipment Corp. MICROVAX II computer by using the Molecular Structure Corp. TEXSAN (V 2.0) program library. The data were corrected for absorption.

(16) Crystals of **1** were grown by slow evaporation of solvent from a CH_2Cl_2/hexane solution at 25 °C. Compound **1** crystallizes in the triclinic crystal system: space group $P\bar{1}$, a = 8.782 (1) Å, b = 16.042 (3) Å, c = 7.731 (1) Å, α = 100.00 (1)°, β = 109.79 (1)°, γ = 94.43 (2)°, Z = 2, ρ_{calcd} = 3.02 g/cm^3. The structure was solved by a combination of Patterson and difference Fourier techniques and was refined (2556 reflections) to the final residuals R = 0.0344 and R_w = 0.0341.

(17) Selected interatomic distances (Å) and angles (deg) for **1** are as follows: Os(1)–Os(2) = 2.8343 (9), Os(1)–Os(3) = 2.8423 (8), Os(2)–Os(3) = 2.7880 (9), Os(2)–H = 1.9 (1), Os(3)–H = 2.0 (1), Os(3)–C = 2.02 (1), C–N = 1.29 (2), C–H = 1.0 (1); Os(2)–H–Os(3) = 90 (4), Os(2)–Os(3)–C = 127.6 (4), Os(3)–C–N = 137 (1).

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trianglar cluster of three osmium atoms with two osmium-osmium bonds, Os(1)-Os(2) = 2.793 (1) Å and Os(1)-Os(3) = 2.873 (1) Å. The nonbonding osmium-osmium distance, Os(2)···Os(3) = 3.492 (1) Å, is bridged by the methoxide ligand. The hydride ligand, located crystallographically, bridges the Os(1)-Os(3) bond, Os(1)-H = 1.8 (1) Å and Os(3)-H = 2.0 (1) Å. The most interesting and unusual feature of this structure is the C,N η^2 triply bridging (dimethylamino)carbene ligand, H(1),C,N,C(2),C(3). The carbon atom symmetrically bridges the Os(1)-Os(3) bond on the side of the cluster opposite that of the bridging hydride ligand, Os(1)-C = 2.11 (2) Å and Os(3)-C = 2.15 (2) Å. The nitrogen atom is coordinated only to the third metal atom, Os(2)-N = 2.15 (1) Å. η^2-Carbene ligands are very unusual but have been observed previously in some mononuclear[21] and dinuclear[22] metal complexes. The compound $Ru_3(CO)_7(dppm)(\mu_3\text{-}CHPPh_2)(\mu_3\text{-}PPh)$ contains a triply bridging $C(H)PPh_2$ ligand which could be viewed as a (diphenylphosphino)carbene ligand.[23] The hydrogen atom H(1) was located crystallographically, but its position was not refined. It exhibits a low-field shift, δ +7.62, but this position is shifted upfield considerably from that of the terminal carbene ligand in 1 and related carbene complexes.[18,19] An interesting structural feature is the unusually long length of the C-N bond, 1.54 (2) Å, which is 0.25 Å longer than the corresponding distance in 1 and even longer than the C-N single bond lengths to the methyl groups, C(2)-N = 1.49 (2) Å and C(3)-N = 1.47 (2) Å in 2. The bond lengthening effects induced by polynuclear ligand coordination are well-known.[13]

Since compounds 1 and 2 are isomers, attempts were made to interconvert them. When 2 was heated to reflux in heptane under a CO atmosphere for 4 h, 1 was obtained in 60% yield. The pathway for this transformation has not yet been determined but by necessity must involve CO and hydride ligand shifts and a closing of the cluster. Further experiments to elucidate upon this are in progress.

Acknowledgment. These studies were supported by the Office of Basic Energy Science of the U.S. Department of Energy. We wish to thank Johnson Matthey Inc. for a loan of osmium tetraoxide. NMR measurements were made on a Brüker AM-300 spectrometer purchased with funds from the National Science Foundation under Grant No. CHE-8411172.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters and selected interatomic distances and angles for both structural analyses (14 pages); listings of structure factor amplitudes for both structural analyses (33 pages). Ordering information is given on any current masthead page.

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(19) Crystals of 2 were grown by slow evaporation of hexane solutions at -20 °C. Compound 2 crystallizes in the monoclinic crystal system: space group $P2_1/n$, a = 8.878 (2) Å, b = 26.287 (8) Å, c = 9.243 (2) Å, β = 115.19 (1)°. The structure was solved by direct methods (MULTAN) and was refined (2226 reflections) to the final residuals R = 0.0381 and R_w = 0.0387.

(20) Selected interatomic distances (Å) and angles (deg) for 2 as follows: Os(1)-Os(2) = 2.793 (1), Os(1)-Os(3) = 2.873 (1), Os(2)···Os(3) = 3.492 (1), Os(1)-H = 1.8 (1), Os(3)-H = 2.0 (1), Os(1)-C = 2.011 (2), Os(3)-C = 2.15 (2), Os(2)-N = 2.15 (1), C-N = 1.54 (2); Os(1)-H-Os(3) = 97 (5), Os(1)-C-Os(3) = 85.0 (6), Os(1)-C-N = 110 (1), Os(3)-C-N = 116 (1), Os(2)-N-C = 97.7 (9).

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New Hydrido-Carbonyl Rhenates by Reduction of $[Re_2(CO)_{10}]$ with Bases. X-ray Crystal Structure of the Anion $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$

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Summary: The reaction of $[Re_2(CO)_{10}]$ with OH^- gives first $[Re_2H(CO)_9]^-$ and then, under more drastic conditions, the novel anion $[Re_2H_2(CO)_8]^{2-}$, which can be reversibly protonated to give $[Re_2H_2(\mu\text{-}H)(CO)_8]^-$, whose structure has been elucidated by a X-ray investigation. Variable-temperature NMR spectra indicate that both the new hydrido carbonylates are fluxional in solution.

The reduction of $[Re_2(CO)_{10}]$ with bases was studied for the first time about 30 years ago,[1] and several compounds have been successively isolated by this route.[2] However, none of the products expected on the basis of the classical mechanism involving CO_2 elimination from an unstable hydroxycarbonyl intermediate was so far obtained. The use of the strong bases NR_4OH (R = Et or Bu) allowed us to fill in this gap and to discover a rapid and high yield route to two novel hydrido-carbonyl rhenates, the anions $[Re_2H_2(CO)_8]^{2-}$ and $[Re_2H_3(CO)_8]^-$, which can play a relevant role in the chemistry of polynuclear hydrido carbonylates of rhenium.

The first stable product expected from this type of reduction is the anion $[Re_2H(CO)_9]^-$ (compound 1), previously obtained[3] by photochemical decomposition of the formyl $[Re_2(CHO)(CO)_9]^-$. We have now found that on simply refluxing a tetrahydrofuran solution of $[Re_2(CO)_{10}]$ in the presence of a stoichiometric amount of NR_4OH, the anion 1 is rapidly and nearly quantitatively produced.[4]

Further attack of OH^- on 1 is obviously more difficult because of the negative charge. However, using highly concentrated tetraalkylammonium hydroxides, we succeeded in synthesizing, directly from $[Re_2(CO)_{10}]$, the species resulting from this second attack.[5] Depending on

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