Hydrolysis of the Metal-Chloride Bonds in (η^5-C_5Me_5)$TaCl_4$ Leading to Stepwise Formation of Binuclear and Trinuclear Tantalum Oxide Clusters

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Summary: Cp*$TaCl_4$ (**1**) (Cp* = η^5-C_5Me_5) reacts with H_2O in the solid state and in solution to give the bridging oxide complexes [Cp*$TaCl_3$]$_2$(μ-O) (**2**) and [Cp*$TaCl_2$(OH)]$_2$(μ-O) (**3**). Complex **2** reacts with MeLi to form [Cp*$TaMe_3$]$_2$(μ-O) (**6**) and with H_2O to form **3**. Complex **3** then loses H_2O and HCl upon heating to form the trinuclear cluster Cp*$_3Ta_3$(μ_2-O)$_3$(μ_3-O)(μ-Cl)Cl_3 (**4**) which in turn reacts further with water to yield [Cp*$_3Ta_3$(μ_2-O)$_3$(μ_3-O)$_2$Cl(H_2O)$_2$]Cl (**5**). Complexes **4**, **5**, and **6** have been structurally characterized.

The complex Cp*$TaCl_4$ (**1**, Cp* = C_5Me_5) is a versatile starting material for the preparation of many interesting complexes containing the Cp*Ta moiety.[1] Although it is generally recognized that complex **1** is air-sensitive, there have been no indications as to the extent of this sensitivity[2] nor what the reactions are that the complex undergoes. In the course of developing a program to prepare new examples of μ-NR and μ-O complexes as an extension of our previous μ-PR_2 complex studies,[3] we have found that complex **1** undergoes a unique stepwise hydrolysis to yield a series of oxide-bridged Ta_2 and Ta_3 complexes (Scheme I), and that these complexes readily re-form **1** when exposed to HCl.

Exposure of solid samples of **1** to the ambient atmosphere for 2 days gave complete conversion to a ~1:3 mixture of complexes **2** and **3**, as evidenced by the quantitative replacement of the δ 2.73 ^1H NMR Cp* resonance of freshly prepared **1** with the corresponding resonances of **2** and **3** at δ 2.41 and 2.32 ($CDCl_3$ solution). Hydrolysis is more rapid in solution where total loss of **1** occurs within several hours at 22 °C following addition of excess water. ^1H NMR monitoring of the reaction of $CDCl_3$ solutions of **1** with limited amounts of H_2O in sealed NMR tubes show the existence of a complex equilibrium between **1**, **2**, **3**, and another complex believed to be the mononuclear hydroxo complex Cp*$TaCl_3$(OH) (**7**, Scheme I; δ 2.51 (s)),[4] with the ratios of these species critically dependent on the amount of H_2O used. For example, reaction of **1** with 2 equiv of H_2O gave a mixture of **1**, **2**, **3**, and **7** in a 42/33/21/4 ratio. Complex **3** can be obtained pure by use of excess H_2O, and it was isolated in 84% yield as a canary yellow solid from such reaction in THF by evaporation of the solvent, dissolution of the residue in CH_2Cl_2, and slow concentration of the filtered CH_2Cl_2 solution. Complex **3** is far more soluble in THF than **2**, allowing **2** to be obtained as a pure yellow crystalline solid, albeit in low yield (8%), by washing the residue from a reaction of **1** with 1.6 equiv of H_2O with dry THF.

Both complexes have been analytically and spectroscopically characterized,[5] with the determined molecular weight of 836 for **3** (calcd 824.2) particularly indicative of its formulation. They each show Ta-O-Ta vibrations in their IR spectra (KBr: **2**, 687 vs cm^{-1}; **3**, 644 vs, 594 vs cm^{-1}) which shift the expected amount when $^{18}OH_2$ is used in their synthesis (KBr: **2**, 656 vs cm^{-1}; **3**, 629 vs, 577 vs cm^{-1}).[6] Complex **3** further shows a strong, sharp OH vibration at 3584 cm^{-1} which shifts to 2645 cm^{-1} upon deuteriation and to 3574 cm^{-1} upon incorporation of ^{18}O.

Complex **2** has been further defined by its quantitative (by ^1H NMR) conversion into the hexamethyl complex **6**[7] (eq 1). Complex **6** has been isolated as a yellow crystalline

$$\underset{\mathbf{2}}{[\mathrm{Cp^*TaCl_3}]_2(\mu\text{-O})} + 6\mathrm{MeLi} \rightarrow \underset{\mathbf{6}}{[\mathrm{Cp^*TaMe_3}]_2(\mu\text{-O})} + 6\mathrm{LiCl} \quad (1)$$

solid in 32% yield, and an ORTEP drawing is shown in Scheme I.[8] Noteworthy is the linear Ta-O-Ta linkage similar to that found in other Ta_2(μ-O) complexes.[9]

Although complex **3** is stable in the solid state under ambient conditions, it quantitatively transforms upon heating in air (6 h, 185 °C) into Cp*$_3Ta_3O_4Cl_4$ (**4**;[10] Scheme

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(1) See for example: (a) Gibson, V. C.; Bercaw, J. E.; Bruton, W. J.; Sanner, R. D. *Organometallics* **1986**, *5*, 976. (b) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 6409. (c) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

(2) Herrmann, W. A.; Kalcher, W.; Biersack, H.f Bernal, I.; Creswick, M. *Chem. Ber.* **1981**, *114*, 3558. This reference states that **1** can be handled for short periods in air, but we have observed that reaction with atmospheric moisture begins immediately upon air exposure.

(3) (a) Targos, T. S.; Geoffroy, G. L. *Organometallics* **1986**, *5*, 12. (b) Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1418. (c) Rosenberg, S.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1184.

(4) (a) Consistent with this assumption is the observation of a strong ν_{O-H} stretch at 3588 cm^{-1} (KBr) in the IR spectrum of the solid residue from a solution which showed only ^1H NMR resonances due to **1** and **2** along with the δ 2.51 singlet assigned to **7**.

(5) **2**: IR (KBr) 1495 m, 1437 m, 1301 s, 1022 m, 687 vs, 598 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (s, $C_5(CH_3)_5$). Anal. Calcd for $C_{20}H_{30}Cl_6OTa_2$: C, 27.91; H, 3.51. Found: C, 27.51; H, 3.73. **3**: IR (KBr) 3584 s, 1491 m, 1437 m, 1381 s, 1024 m, 833 vs, 644 vs, 609 s, 594 vs, 474 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.59 (s, 2 H, O*H*), 2.32 (s, 30 H, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 128.94 (s, $C_5(CH_3)_5$), 12.08 (s, $C_5(CH_3)_5$). Anal. Calcd for $C_{20}H_{32}Cl_4O_3Ta_2$: C, 29.14; H, 3.91; Cl, 17.20. Found: C, 29.32; H, 4.14; Cl, 17.00.

(6) For comparison see: Chen, G. J.-J.; McDonald, J. W.; Bravard, D. C.; Newton, W. E. *Inorg. Chem.* **1985**, *24*, 2327.

(7) **6**: IR (KBr) 795 vs, 475 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.96 (s, 15 H, $C_5(CH_3)_5$), 0.22 (s, 6 H, Ta*Me*$_2$), 0.18 (s, 3 H, Ta*Me*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 116.69 (s, $C_5(CH_3)_5$), 55.62 (s, Ta*Me*), 53.96 (s, Ta*Me*$_2$), 11.10 (s, $C_5(CH_3)_5$); mass spectrum *m/z* (FD), 723 ($M^+ - CH_3$), 708 ($M^+ - 2CH_3$).

(8) **4**: orthorhombic, *Pbcm*, a = 10.645 (3) Å, b = 17.224 (5) Å, c = 19.084 (6) Å, V = 3499 (5) Å^3, Z = 4. The structure is disordered with interpenetrating sets of Ta_3 frameworks in two orientations offset by a 30° interplanar angle. All atoms of the major orientation (70%) were reliably located except the Cp* methyl groups on Ta(1). Only the Ta, Cl, and O atoms of the minor orientation could be located. R_F = 9.06% and R_{wF} = 9.56%. The following distances (Å) are considered reliable: Ta(1)-Cl(2), 2.37 (1); Ta(3)-Cl(1), 2.65 (1); Ta(3)-Cl(3), 2.41 (1); Ta(1)-O(1), 2.22 (2); Ta(1)-O(3), 1.81 (2); Ta(3)-O(2), 1.95 (2); Ta(3)-O(3), 1.96 (2). The major orientation is shown in Scheme I. **5**·0.5H_2O: monoclinic, *C*2/c, a = 34.96 (1) Å, b = 11.494 (4) Å, c = 18.458 (6) Å, β = 94.08 (3)°, V = 7399 (4) Å^3, Z = 8. The structure refined to $R(F)$ = 0.058 and $R(wF)$ = 0.061 for 4208 reflns with $F_o \geq 3\,\sigma(F_o)$. Bond distances (Å): Ta-(μ_2-O)$_{av}$, 2.01; Ta-(μ_3-O)$_{av}$, 2.13; Ta(1)-O(6), 1.92 (1); Ta(2)-O(7), 1.91 (1); Ta···Ta$_{av}$, 3.092. Bond angles: Ta(1)-O(3)-Ta(2), 97.5 (4)°; Ta(1)-O(4)-Ta(3), 102.4 (5) °; Ta(2)-O(5)-Ta(3), 102.2 (5)°; Ta-(μ_3-O)-Ta$_{av}$, 92.7°. **6**: monoclinic, $P2_1/c$, a = 8.540 (3) Å, b = 21.010 (7) Å, c = 8.807 (3) Å, β = 118.50(3)°, V = 1388.7 (9) Å^3, Z = 2. The structure refined to $R(F)$ = 0.0405 and $R(wF)$ = 0.0485 for 1955 reflections with $F_o \geq 3\sigma(F_o)$. Bond distances (Å): Ta-O, 1.909 (7); Ta-C(11), 2.22 (2); Ta-O(12), 2.26 (1); Ta-C(13), 2.23 (1). Bond angles: Ta-O-Ta′, 180°; C(11)-Ta-O, 128.6 (4)°; C(12)-Ta-O, 86.6 (3)°; C(13)-Ta-O, 85.5 (3)°; CNT(1)-Ta-O, 123.1 (3)°.

(9) (a) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981**, *20*, 1866. (b) Chisholm, M. H.; Huffman, J. C.; Tan, L.-S. *Inorg. Chem.* **1981**, *20*, 1859.

(10) **4**: IR (KBr) 1493 ms, 1437 ms, 1377 s, 1169 w, 1073 m, 1026 ms, 959 w, 870 w, 808 m, 689 vs, 608 vs, 522 s, 477 m, 409 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23 (s, 1 $C_5(CH_3)_5$), 2.21 (s, 2 $C_5(CH_3)_5$); mass spectrum, *m/z* (EI, based on ^{35}Cl), 1152 (M^+), 1117 ($M^+ - Cl$), 1017 (M^+ - Cp*). Anal. Calcd for $C_{30}H_{45}Ta_3O_4Cl_4$: C, 31.21; H, 3.94; Cl, 12.28. Found: C, 31.21; H, 3.75; Cl, 11.55.

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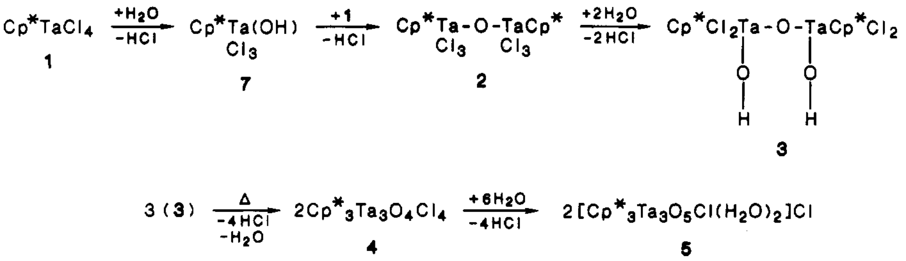
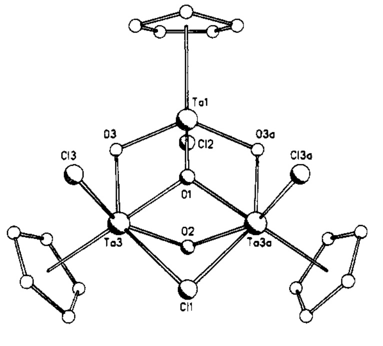
Scheme I



$$\underset{\mathbf{1}}{\mathrm{Cp^*TaCl_4}} \xrightarrow[-\mathrm{HCl}]{+\mathrm{H_2O}} \underset{\mathbf{7}}{\mathrm{Cp^*Ta(OH)Cl_3}} \xrightarrow[-\mathrm{HCl}]{+\mathbf{1}} \underset{\mathbf{2}}{\mathrm{Cp^*Ta{-}O{-}TaCp^*Cl_3\ Cl_3}} \xrightarrow[-2\mathrm{HCl}]{+2\mathrm{H_2O}} \underset{\mathbf{3}}{\mathrm{Cp^*Cl_2Ta(OH){-}O{-}TaCp^*Cl_2(OH)}}$$

$$3(\mathbf{3}) \xrightarrow[-4\mathrm{HCl},\ -\mathrm{H_2O}]{\Delta} \underset{\mathbf{4}}{\mathrm{2Cp^*_3Ta_3O_4Cl_4}} \xrightarrow[-4\mathrm{HCl}]{+6\mathrm{H_2O}} \underset{\mathbf{5}}{\mathrm{2[Cp^*_3Ta_3O_5Cl(H_2O)_2]Cl}}$$



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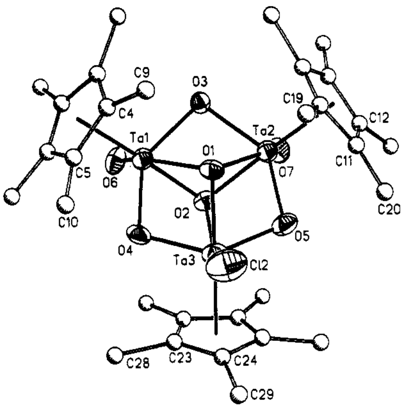

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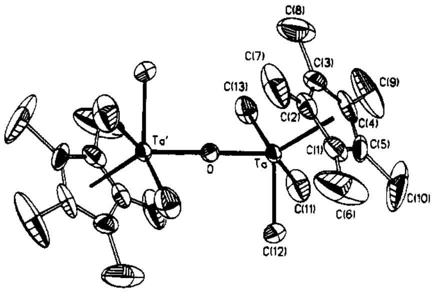

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I). This species was isolated as a pale yellow microcrystalline solid in 85% yield from dry Et_2O recrystallization and has been structurally characterized (Scheme I).[8] The molecule has a triangle of Cp*Ta units with each edge bridged by an oxide ligand and the triangular face capped by a single μ_3-oxide ligand. Each Ta also bears a chloride ligand, and two of the Ta atoms are bridged by a fourth chloride.

Complex 4 in turn reacts with excess H_2O in Et_2O (22 °C, 17 h) to quantitatively form (by ^1H NMR) the salt $[Cp^*_3Ta_3O_5Cl(H_2O)_2]Cl$ (5).[11] This species was isolated as a white crystalline solid in 80% yield, and an ORTEP drawing is shown in Scheme I.[8] The cation consists of a triangle of Cp*Ta units with each edge bridged by an oxide ligand and the triangular face capped above and below by two μ_3-oxide ligands. Water molecules are coordinated to two Ta atoms and a chloride to the third.

All of the hydrolysis products 2–5 smoothly convert back into 1 upon reaction with gaseous HCl (~2 atm, $CDCl_3$, 22 °C). In each case, the reactions are complete within 2–5 min as evidenced by the immediate color change to that of orange yellow 1 and the observation of only the Cp* ^1H NMR resonance of 1 after 10 min.

The initial product of hydrolysis of 1 is presumably the mononuclear hydroxide complex 7 (Scheme I). This species has not been definitely characterized, although we believe it responsible for the δ 2.51 ^1H NMR resonance seen in incompletely hydrolyzed samples which contain a mixture of complexes 1–3 (see above). Complex 2 could form by condensation of two molecules of 7, although a more likely reaction involves elimination of HCl from combination of 7 with 1. Complex 3 derives from subsequent hydrolysis of 2 as shown by the quantitative conversion of 2 into 3 upon reaction with H_2O, either in the solid state or in solution. This latter transformation may proceed via the initial formation of $[Cp^*TaCl_3(H_2O)]_2(\mu\text{-}O)$ (8) since the Nb analogue of 8 has been fully characterized.[12]

The formation of 4 from 3 represents an unusual solid-state synthesis of an organometallic oxide cluster. Complex 4 can conceptually be assembled from the fragments $Cp^*Ta(O)Cl_2$ (9) and $Cp^*(O)ClTa{-}O{-}TaCl(O)Cp^*$ (10), both of which can derive from 3. Species 10 would result by loss of two HCl molecules from 3 while heterolytic cleavage of 3 into $Cp^*Ta(O)Cl_2$ and $Cp^*Ta(OH)_2Cl_2$, followed by loss of H_2O from the latter, would give two molecules of 9.

The most important aspect of this study is the demonstration that oxide ligands can be progressively introduced in a controlled fashion into increasingly more complex organometallic clusters. Although other metal halide complexes undergo similar hydrolyses,[13] no other system has permitted the *stepwise* incorporation of oxide ligands to the extent reported here. Also significant is the near quantitative preparation of complexes 3, 4, and 5, a feature which should facilitate the use of these species in further syntheses. Such studies are in progress.

Acknowledgment. We thank the National Science Foundation (CHE-8501548) for support of this research and for contributing funds toward the purchase of the diffractometer at the University of Delaware, and R. Minard, G. Steinmetz, and R. Hale for assistance in obtaining mass spectra.

Supplementary Material Available: Tables of bond distances and angles, anisotropic temperature factors, H-atom co-

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(11) 5: IR (KBr) 3384 br s, 1497 m, 1439 ms, 1377 ms, 1265 w, 1073 w, 1026 m, 1007 m, 939 w, 774 s, 743 ms, 681 s, 640 s, 592 sh, 573 s, 517 ms, 469 ms, 424 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (s, 1 $C_5(CH_3)_5$), 2.08 (s, 2 $C_5(CH_3)_5$). Anal. Calcd for $C_{30}H_{49}Ta_3O_7Cl_2 \cdot 0.5H_2O$: C, 31.48; H, 4.41; Cl, 6.19. Found C, 31.16; H, 4.39; Cl, 7.52.

(12) Bunker, M. J.; De Cian, A.; Green, M. L. H.; Moreau, J. J. E.; Siganporia, N. *J. Chem. Soc., Dalton Trans.* **1980**, 2155.

(13) (a) Wieghardt, K.; Ventur, D.; Tsai, Y. H.; Kruger, C. *Inorg. Chim. Acta* **1985**, *99*, L25. (b) Blanco, S. G.; Sal, M. P. G.; Carreras, S. M.; Mena, M.; Royo, P.; Serrano, R. *J. Chem. Soc., Chem,. Commun.* **1986**, 1572. (c) Skapski, A. C.; Troughton, P. G. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 716. (d) Petersen, J. L. *Inorg. Chem.* **1980**, *19*, 181. (e) Caulton, K. G.; Huffman, J. C.; Stone, J. G.; Krusell, W. C. *J. Am. Chem Soc.* **1977**, *99*, 5829. (f) Klemperer, W. G.; Babcock, L. M.; Day, V. M., submitted for publication, private communication.

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 (HCNMe$_2$); 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 (HCNMe$_2$); 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 ^1H 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 (HCNMe$_2$) + 10.88.

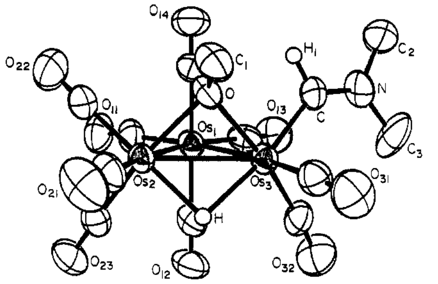

Figure 1. An ORTEP diagram of $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (1), showing 50% probability ellipsoids. The ellipsoids of the hydrogen atoms have been reduced for clarity.

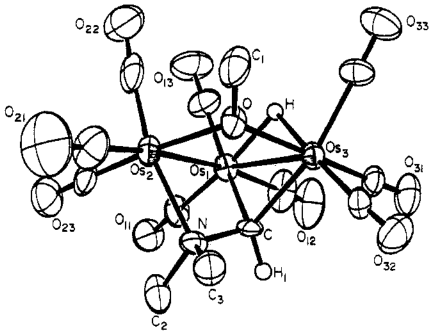

Figure 2. An ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (2), showing 50% probability thermal ellipsoids. The ellipsoids of the hydrogen atoms have been reduced for clarity.

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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(1) Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645.

(2) Dotz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Chemistry*; Verlag Chemie: Weinheim, West Germany, 1983. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

(3) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1985**, *107*, 6107.

(4) Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1615.

(5) Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1982**, *104*, 4679.

(6) Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926.

(7) Jensen, C. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 6969.

(8) Shapley, J. R.; Yeh, W. Y.; Churchill, M. R.; Li, Y. *Organometallics* **1985**, *4*, 1898.

(9) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 729.

(10) Adams, R. D.; Babin, J. E.; Kim, H. S. *Inorg. Chem.* **1986**, *25*, 4319.

(11) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

(12) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127.

(13) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.

(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}; ^1H 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}; ^1H 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).

(18) Adams, R. D.; Babin, J. E.; Kim, H. S. *Organometallics* **1986**, *5*, 1924.

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