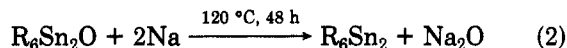


Table I. Reduction of Organotin Oxides into Ditins

reducing agent	solvent	ditin	yield, <sup>a,b</sup> %
TiCl <sub>3</sub> , K	THF	<i>n</i> -Bu <sub>6</sub> Sn <sub>2</sub>	70
K	THF	<i>n</i> -Bu <sub>6</sub> Sn <sub>2</sub>	62
K	toluene	<i>n</i> -Bu <sub>6</sub> Sn <sub>2</sub>	71
K	none	<i>n</i> -Bu <sub>6</sub> Sn <sub>2</sub>	60
Na	none	<i>n</i> -Bu <sub>6</sub> Sn <sub>2</sub>	71
Na	none	<i>i</i> -Bu <sub>6</sub> Sn <sub>2</sub>	62
Na	none	<i>n</i> -Pen <sub>6</sub> Sn <sub>2</sub>	77
Na	none	<i>n</i> -Oct <sub>6</sub> Sn <sub>2</sub>	68
Mg	THF	<i>n</i> -Bu <sub>6</sub> Sn <sub>2</sub>	81
Mg	none	<i>n</i> -Bu <sub>6</sub> Sn <sub>2</sub>	58
Mg	THF	<i>i</i> -Bu <sub>6</sub> Sn <sub>2</sub>	82
Mg	THF	<i>n</i> -Oct <sub>6</sub> Sn <sub>2</sub>	82

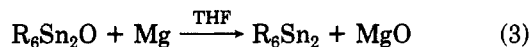
<sup>a</sup> Pure isolated products. <sup>b</sup> Reaction mixtures and ditins were analyzed by reversed-phase HPLC and <sup>119</sup>Sn NMR spectroscopy.<sup>6</sup>

Since titanium powder was prepared from titanium trichloride and potassium in THF, we checked if potentially unreacted potassium could have any influence on the course of the reaction. If the reduction is performed directly with a stoichiometric amount of potassium (2 mol for 1 mol of bis(tri-*n*-butyltin) oxide), it works nearly as well (see Table I), although the cleavage of ditins with metals to give tin-metal derivatives is known.<sup>3</sup> This unobserved cleavage is probably the result of the higher reactivity of the oxide toward potassium. The results with sodium were equally good (see Table I). Finally, we found that the reaction could be carried out in the absence of solvent (eq 2) (see Table I).



Byproducts, mainly tetraalkyltin (1-5%) and unconverted (R<sub>3</sub>Sn)<sub>2</sub>O (5-15%), are present in small amounts and can be removed easily: (R<sub>3</sub>Sn)<sub>2</sub>O by filtration of the mixture (10 g diluted in 200 mL of pentane) through a short SiO<sub>2</sub> column (100 g, 230-400 mesh) and R<sub>4</sub>Sn by distillation. With bis(triphenyltin) oxide, <sup>119</sup>Sn NMR analysis of the crude mixture showed that tetraphenyltin is the main product of the reaction, hexaphenyltin being formed in 20% yield.

The reduction with magnesium has also been studied: bis(trialkyltin) oxides react cleanly with magnesium powder which has been activated by 1,2-dibromoethane or iodine, in the presence of a small amount of THF (eq 3). In this case no tetraalkyltin is formed, the only possibly present byproduct being some unreacted (R<sub>3</sub>Sn)<sub>2</sub>O.



Ditins are obtained as pure materials after distillation. For instance, for R = *n*-Bu, this reaction gives a better yield than the coupling of tri-*n*-butyltin chloride by magnesium.<sup>12</sup> The reaction occurs also in the absence of solvent, but the yield is lower. No reaction was observed with iron powder, and with aluminium, large amounts of tetraalkyltin, together with hexaalkylditins, are recovered.

In conclusion, we have shown that bis(triorganotin) oxides (often easily available from industrial sources) react readily with metals. This reduction provides a convenient new route to ditins. In particular, the preparation of hexa-*n*-butylditin from bis(tri-*n*-butyltin) oxide and magnesium is an especially attractive method on the laboratory scale.

**Experimental Procedure.** A solution of bis(tri-*n*-butyltin) oxide (59.6 g, 100 mmol) in 60 mL of dry THF was added dropwise to a suspension of magnesium powder

(98%, 70 mesh) (3.6 g, 150 mmol), activated by a few drops of 1,2-dibromoethane (or a crystal of iodine) in 20 mL of dry THF. The mixture was heated at reflux for 15 h. At this time the characteristic Sn-O-Sn IR absorption at 755 cm<sup>-1</sup> has disappeared. An <sup>119</sup>Sn NMR spectrum of the crude hexa-*n*-butylditin showed only one signal at -83.2 ppm (C<sub>6</sub>D<sub>6</sub>, Me<sub>4</sub>Sn as external standard). Then, after addition of 200 mL of petroleum ether, filtration, and evaporation of the solvents, the product was recovered by distillation: yield 47 g (81%); bp 145 °C (0.05 torr) (*i*-Bu<sub>6</sub>Sn<sub>2</sub>, bp 136-138 °C (0.05 torr); *n*-Oct<sub>6</sub>Sn<sub>2</sub>, bp 180-185 °C (0.01 torr)).

**Registry No.** *n*-Bu<sub>6</sub>Sn<sub>2</sub>, 813-19-4; *i*-Bu<sub>6</sub>Sn<sub>2</sub>, 3750-18-3; *n*-Pen<sub>6</sub>Sn<sub>2</sub>, 21227-23-6; *n*-Oct<sub>6</sub>Sn<sub>2</sub>, 21227-24-7; *n*-Bu<sub>6</sub>Sn<sub>2</sub>O, 56-35-9; *i*-Bu<sub>6</sub>Sn<sub>2</sub>O, 6208-26-0; *n*-Pen<sub>6</sub>Sn<sub>2</sub>O, 25637-27-8; *n*-Oct<sub>6</sub>Sn<sub>2</sub>O, 2787-93-1.

### Facile Activation of Hydrogen by an Unsaturated Metal Carbonyl Cluster. The Addition of H<sub>2</sub> to Os<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-S)(μ<sub>4</sub>-HC<sub>2</sub>CO<sub>2</sub>Me)

Richard D. Adams\* and Suning Wang

Department of Chemistry, University of South Carolina  
Columbia, South Carolina 29208

Received February 3, 1986

**Summary:** The unsaturated cluster Os<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-S)(μ<sub>4</sub>-HC<sub>2</sub>CO<sub>2</sub>Me) (1) has been synthesized and structurally characterized. Compound 1 readily adds hydrogen to form two isomeric hydride containing clusters of formula Os<sub>4</sub>(CO)<sub>11</sub>(μ<sub>3</sub>-S)(μ<sub>3</sub>-HC<sub>2</sub>CO<sub>2</sub>Me)(μ-H)<sub>2</sub> (2a and 2b). These will subsequently add CO to form Os<sub>4</sub>(CO)<sub>12</sub>(μ<sub>3</sub>-S)(μ<sub>3</sub>-HC<sub>2</sub>CO<sub>2</sub>Me)(μ-H)<sub>2</sub> (3). Compounds 1, 2b, and 3 have been characterized structurally.

The inability of metal carbonyl cluster complexes to add and activate hydrogen under mild conditions has been a major impediment in the development of these compounds as hydrogenation catalysts.<sup>1,2</sup> Unsaturated clusters would seem to offer a potential solution to the problem, but the number of fully characterized unsaturated clusters is very small.<sup>2</sup> An important class of unsaturated clusters are the polyphosphine complexes of rhodium and platinum.<sup>3,4</sup> These compounds activate hydrogen very readily and even serve as hydrogenation catalysts.<sup>3,5</sup> We wish to report that we have synthesized the new unsaturated carbonyl cluster Os<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-S)(μ<sub>4</sub>-HC<sub>2</sub>CO<sub>2</sub>Me) (1) and have found that it activates hydrogen, reversibly, under unusually mild conditions.

When the compound Os<sub>4</sub>(CO)<sub>12</sub>[μ<sub>4</sub>-SC(CO<sub>2</sub>Me)CH]<sub>6</sub> is refluxed in octane solvent for 40 min, it loses 1 mol of CO and is transformed into the new cluster Os<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-S)(μ<sub>4</sub>-HC<sub>2</sub>CO<sub>2</sub>Me) (1) in 88% yield.<sup>7</sup> The molecular structure of 1 was determined by a single-crystal X-ray diffraction analysis, and an Ortep diagram of the molecule

(1) Vahrenkamp, H. *Adv. Organomet. Chem.* 1983, 22, 169.

(2) Kaesz, H. D. In *Metal Clusters in Catalysis*; Knozinger, H., Gates, B. C., Guzzi, L., Eds.; Elsevier: Amsterdam, 1986, in press.

(3) Muetterties, E. L. *Catal. Rev.—Sci. Eng.* 1981, 23, 69.

(4) Goodfellow, R. J.; Hamon, E. M.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G. *J. Chem. Soc., Chem. Commun.* 1984, 1604.

(5) Burch, R. R.; Shusterman, A. J.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* 1983, 105, 3546.

(6) Adams, R. D.; Wang, S. *Organometallics* 1985, 4, 1902.

(7) IR ν(CO) in CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>: 2106 (w), 2077 (w), 2070 (w), 2043 (vs), 2022 (s), 1976 (w), 1804 (w, br), 1712 (w, br); <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>) 7.73 (s, CH), 3.48 (s, CH<sub>3</sub>). Anal. Calcd: C, 15.19; H, 0.34. Found: C, 15.45; H, 0.31. Compound 1 was isolated by TLC on silica gel by using a CH<sub>2</sub>Cl<sub>2</sub>/hexane solvent mixture.

(12) Shirai, H.; Sato, Y.; Niwa, N. *Yakugaku Zasshi* 1970, 90, 59; *Chem. Abstr.* 1970, 72, 90593.

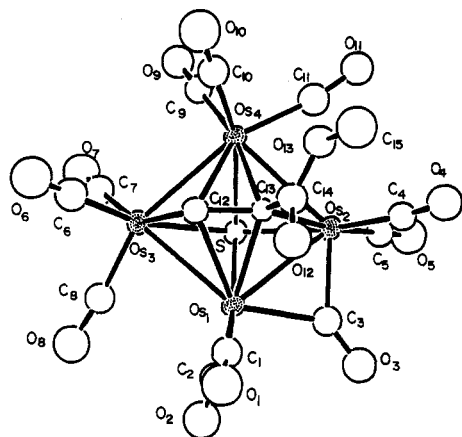


Figure 1. An Ortep drawing of  $\text{Os}_4(\text{CO})_{11}(\mu_4\text{-S})(\mu_4\text{-HC}_2\text{CO}_2\text{Me})$  (1) showing 50% probability thermal ellipsoids.

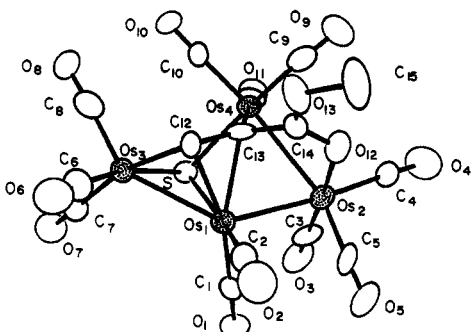


Figure 2. An Ortep drawing of  $\text{Os}_4(\text{CO})_{11}(\mu_3\text{-S})(\mu_4\text{-HC}_2\text{CO}_2\text{Me})(\mu\text{-H})_2$  (2b) showing 50% probability thermal ellipsoids.

is shown in Figure 1.<sup>8,9</sup> The molecule consists of a square of four osmium atoms with quadruply bridging sulfido and acetylene ligands on opposite sides of the cluster. The Os(1)–Os(2) bond distance is significantly shorter than the other three Os–Os bonding distances, but this could be caused by the influence of the bridging carbonyl ligand.<sup>10</sup> Compound 1 contains 62 electrons. With only four metal–metal bonds it is, according to the EAN rule, electron deficient by the amount of two electrons. It is, however, stable and can be isolated in air by TLC. The stability of 1 may be due to the fact that it adopts a structure that conforms to the skeletal electron pair bonding theory.<sup>11,12</sup>

(8) Diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer by the Molecular Structure Corp., College Station, TX. Structure solutions and refinements were performed on a Digital Equipment Corp. VAX 11/782 computer by using the Enraf-Nonius program library SDP-Plus at the University of South Carolina. Diffraction data were corrected for the effects of absorption.

(9) Platelike yellow crystals of 1 were grown from solutions in a  $\text{C}_6\text{H}_6/\text{CH}_2\text{Cl}_2/\text{hexane}$  (5/5/90) solvent mixture by cooling to 0 °C: space group  $P2_1/c$ ;  $a = 13.867$  (2) Å,  $b = 9.087$  (3) Å,  $c = 17.814$  (2) Å;  $\beta = 96.17$  (1)°;  $Z = 4$ ;  $\rho_{\text{calcd}} = 3.56$  g/cm<sup>3</sup>. The structure was solved by a combination of direct methods and difference Fourier techniques and was refined with 2428 reflections to the final values for the residuals  $R = 0.043$  and  $R_w = 0.047$ . The acetylenic hydrogen atom on carbon C(12) was not observed crystallographically.

(10) Selected interatomic distances (Å) and angles (deg) for 1 are as follows: Os(1)–Os(2) = 2.744 (1), Os(1)–Os(3) = 2.850 (1), Os(2)–Os(4) = 2.845 (1), Os(3)–Os(4) = 2.831 (1), Os(1)–C(12) = 2.32 (2), Os(1)–C(13) = 2.295 (13), Os(2)–C(13) = 2.192 (15), Os(3)–C(12) = 2.12 (2), Os(4)–C(12) = 2.33 (2), Os(4)–C(13) = 2.262 (15), C(12)–C(13) = 1.43 (2); Os(2)–Os(1)–Os(3) = 96.84 (2), Os(1)–Os(2)–Os(4) = 81.80 (2), Os(2)–Os(4)–Os(3) = 95.02 (2), Os(1)–Os(3)–Os(4) = 80.23 (2).

(11) (a) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980. (b) Johnson, B. F. G.; Benfield, R. E. In *Top. Stereochem.* 1981, 12.

(12) Compound 1 is very similar to the cluster  $\text{Ru}_4(\text{CO})_9(\mu\text{-CO})(\mu\text{-CO})_2(\mu\text{-PPh})(\mu\text{-C(Ph)C(Ph)})$  that was recently reported by Carty.<sup>13</sup>

(13) Lunnis, J.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E., *Organometallics* 1985, 4, 2066.

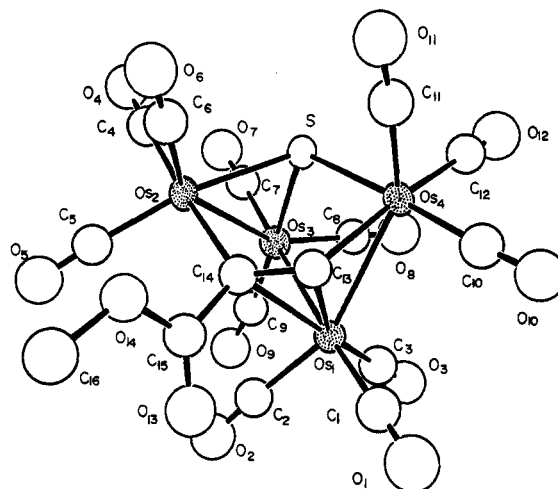
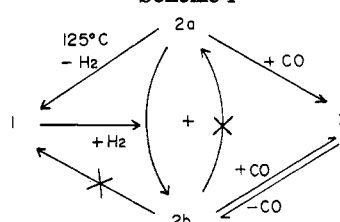


Figure 3. An Ortep drawing of  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-S})(\mu_3\text{-HC}_2\text{CO}_2\text{Me})(\mu\text{-H})_2$  (3) showing 50% probability thermal ellipsoids.

### Scheme I



Nevertheless, compound 1 is unusually reactive toward certain ligand addition reactions.<sup>14</sup> For example, it reacts with hydrogen at 25 °C (1 atm) over 12 h to yield two new hydride containing complexes that have been formulated as isomers of  $\text{Os}_4(\text{CO})_{11}(\mu_3\text{-S})(\text{HC}_2\text{CO}_2\text{Me})(\mu\text{-H})_2$  (2a and 2b) in 69% and 7% yields, respectively.<sup>16</sup> The formation of 2a is partially reversible. When heated to 125 °C, it is converted back to 1, 66% yield, but significant amounts of 2b, 16% yield, are also formed. The formation of 2b is not reversible, and a structural analysis of it has been completed. An Ortep drawing of  $\text{Os}_4(\text{CO})_{11}(\mu_3\text{-S})(\mu_4\text{-HC}_2\text{CO}_2\text{Me})(\mu\text{-H})_2$  (2b) is shown in Figure 2.<sup>17,18</sup> The molecule consists of a planar cluster of four osmium atoms connected by three metal–metal bonds.<sup>19</sup> The very long

(14) Compound 1 readily and reversibly adds 1 mol of CO to form the new compound  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-S})(\mu_4\text{-HC}_2\text{CO}_2\text{Me})$ .<sup>15</sup>

(15) Adams, R. D.; Wang, S., to be submitted for publication.

(16) Compounds 2a and 2b can be separated by TLC on silica gel by using a  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (10/90) solvent mixture. IR ( $\nu(\text{CO})$  in hexane,  $\text{cm}^{-1}$ ): for 2a, 2113 m, 2091 vs, 2070 vs, 2041 vs, 2030 s, 2024 m, 2014 s, 2005 s, 1978 m, 1707 w; for 2b, 2118 w, 2087 s, 2081 vs, 2034 s, 2016 vs, 2009 s, 1997 m, 1947 m, 1558 w. <sup>1</sup>H NMR studies of 2a show that it exists in solution as a mixture of two rapidly interconverting isomers in a 2/1 ratio. At –20 °C separate resonances are observed for each isomer. In  $\text{CDCl}_3$  at –20 °C: major isomer,  $\delta$  11.85 (s, CH), 3.79 (s,  $\text{CH}_3$ ), –10.00 (s, OsH), –13.15 (s, OsH); minor isomer,  $\delta$  11.82 (s, CH), 3.78 (s,  $\text{CH}_3$ ), –8.96 (s, OsH), –14.53 (s, OsH). At 25 °C the CH resonances and  $\text{CH}_3$  resonances of the two isomers are averaged and the hydride resonances are broad. At +55 °C the hydride resonances have averaged in pairs and exist as two broad singlets at –9.51 and –13.72 ppm. Variable temperature <sup>1</sup>H NMR spectra were run at 400 MHz on a Bruker WH-400 spectrometer. For 2b in  $\text{CDCl}_3$ :  $\delta$  8.07 (s, cH), 3.67 (s,  $\text{CH}_3$ ), –13.09 (s, OsH), –13.29 (s, OsH). Satisfactory elemental analyses have been obtained for both compounds.

(17) Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo K $\alpha$  radiation. Structure solutions and refinements were performed on a Digital Equipment Corp. MICROVAX I computer by using the Molecular Structure Corp. TEXSAN program library. The data were corrected for absorption.

(18) Pale yellow crystals of 2b were grown by slow evaporation of solvent from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  solutions at –20 °C; space group  $P\bar{1}$ ;  $a = 11.780$  (2) Å,  $b = 11.019$  (1) Å,  $c = 9.620$  (2) Å;  $\alpha = 97.92$  (1)°,  $\beta = 72.64$  (1)°,  $\gamma = 100.41$  (1)°;  $Z = 2$ ;  $\rho_{\text{calcd}} = 3.38$  g/cm<sup>3</sup>. The structure was resolved by the heavy-atom method and was refined with 3149 reflections to the final values for the residuals,  $R = 0.045$  and  $R_w = 0.050$ . The hydrogen atoms were not observed and were ignored.

Os(3)–Os(4) bond at 3.092 (1) Å is believed to contain one of the two unobserved bridging hydride ligands. The second hydride ligand is believed to bridge the Os(1)–Os(3) bond.<sup>20</sup> There is a triply bridging sulfido ligand on one side of the cluster and a quadruply bridging acetylene ligand on the other side. The acetylene ligand is bonded to three of the metal atoms at the unsaturated C(12)–C(13) bond and is coordinated to the fourth metal through the oxygen atom O(12) of the carboxylate group, Os(2)–O(12) = 2.18 (1) Å. Thus, the acetylene ligand serves as a six-electron donor and the 66-electron complex is electron-precise.

Compound **2a** has not yet yielded crystals suitable for a structural analysis, but it reacts rapidly (30 min) with CO (25 °C) (1 atm) to form the adduct Os<sub>4</sub>(CO)<sub>12</sub>(μ<sub>3</sub>-S)-(μ-HC<sub>2</sub>CO<sub>2</sub>Me)(μ-H)<sub>2</sub> (**3**) in 86% yield.<sup>8,21,22</sup> Compound **3** has been analyzed by a X-ray diffraction analysis, and an Ortep drawing of this molecule is shown in Figure 3. The molecule consists of a chain of four osmium atoms with three metal–metal bonds.<sup>23</sup> The external bonds Os(1)–Os(4) = 2.941 (1) Å, and Os(2)–Os(3) = 2.924 (1) Å which are longer than the internal bond Os(1)–Os(3) = 2.803 (1) Å are believed to contain the two inequivalent bridging hydride ligands. There is a triply bridging sulfido ligand and triply bridging acetylene ligand that serve as four-electron donors. Thus, compound **3** like **2b** is electron-precise. When heated to 125 °C, **3** loses both CO and hydrogen to regenerate **1** in 34% yield but also yields a small amount of **2b** by loss of CO alone. Compound **2b** adds CO to form **3**, but the reaction is much slower: 8 days; 25 °C (1 atm); 39% yield. The transformations observed for these compounds are summarized in Scheme I.

Details of the structure of **2a** have not been established yet, but the high stretching frequency (1712 cm<sup>-1</sup>) of the carboxylate C=O bond indicates that this group is not coordinated in this molecule. The relatively low-field chemical shift (–8 to –10 ppm) for one of the hydride ligands in this molecule could be indicative of the presence of a terminally coordinated hydride ligand.<sup>16</sup>

The unsaturated clusters M<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-PR)<sub>2</sub> (M = Fe,<sup>24</sup> Ru<sup>25</sup>) also undergo unusually facile ligand additions, but

studies of their reactivity toward hydrogen have not been reported. The fact that **1** readily adds both hydrogen and donors would seem to make it a most attractive subject for hydrogenation catalysis.<sup>2</sup> These studies are in progress.

**Acknowledgment.** This research was supported by the National Science Foundation under Grant No. CHE-8416460. We wish to thank Johnson-Matthey for a generous loan of osmium tetroxide.

**Registry No.** **1**, 102110-06-5; **2b**, 102110-07-6; **3**, 102110-08-7; Os<sub>4</sub>(CO)<sub>12</sub>[μ<sub>4</sub>-SC(CO<sub>2</sub>Me)CH], 97919-67-0.

**Supplementary Material Available:** Tables of fractional atomic coordinates and thermal parameters, interatomic distances, selected interatomic angles, and structure factor amplitudes for the structural analyses of compounds **1**, **2b**, and **3** (61 pages). Ordering information is given on any current masthead page.

### Reactivity of Unsaturated Clusters. Multiple Additions of Unsaturated Hydrocarbons to Os<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-S)(μ<sub>4</sub>-HC<sub>2</sub>CO<sub>2</sub>Me)

Richard D. Adams\* and Suning Wang

Department of Chemistry, University of South Carolina  
Columbia, South Carolina 29208

Received February 24, 1986

**Summary:** The unsaturated cluster Os<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-S)(μ<sub>4</sub>-HC<sub>2</sub>CO<sub>2</sub>Me) (**1**) undergoes facile multiple addition reactions with phenylacetylene or allene at 25 °C to form the products Os<sub>4</sub>(CO)<sub>11</sub>[μ-C(Ph)=CH<sub>2</sub>][μ<sub>4</sub>-η<sup>3</sup>-SC(Ph)=C(H)-C≡CCO<sub>2</sub>Me] (**2**) or Os<sub>4</sub>(CO)<sub>11</sub>[μ-C(CH<sub>2</sub>)<sub>2</sub>][μ<sub>3</sub>-η<sup>5</sup>-(MeO<sub>2</sub>C)C=C(H)C(CH<sub>2</sub>)<sub>2</sub>](μ<sub>3</sub>-S) (**3**) in 34% and 46% yields, respectively. Compounds **2** and **3** have been characterized by X-ray diffraction analyses and were found to consist of opened clusters of metal atoms in which the methyl acetylenecarboxylate ligand in **1** has been coupled to one of the added ligands by carbon–carbon bond formation.

Coordination unsaturation in metal complexes is a feature that has played a very critical role in the development of the field of homogeneous catalysis.<sup>1</sup> Coordination unsaturation in polynuclear metal complexes is uncommon because electron deficiencies are usually eliminated by the formation of metal–metal bonds.<sup>2</sup> Recent reports have described the synthesis and reactivity of the new tetranuclear clusters M<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-L)(μ<sub>4</sub>-L') (M = Fe, Ru; L = L' = PR) which consist of a square-planar arrangement of four metal atoms.<sup>3</sup> These compounds contain only 62 valence electrons and are thus electron deficient (EAN rule) by the amount of two electrons. Accordingly, they readily engage in ligand addition reactions and may be the prototypes for a general class of cluster complexes that exhibit high reactivity toward ligand additions.<sup>3</sup> In our recent studies we have synthesized the new tetraosmium cluster Os<sub>4</sub>(CO)<sub>11</sub>(μ<sub>4</sub>-S)(μ<sub>4</sub>-HC<sub>2</sub>CO<sub>2</sub>Me) (**1**).<sup>4</sup> This cluster

(19) Selected interatomic distances (Å) and angles (deg) for **2b** are as follows: Os(1)–Os(2) = 2.803 (1), Os(1)–Os(3) = 2.803 (1), Os(2)–Os(4) = 3.092 (1), Os(3)–Os(4) = 3.943 (1), Os(1)–C(12) = 2.31 (2), Os(3)–C(12) = 2.11 (2), Os(1)–C(13) = 2.29 (2), Os(4)–C(13) = 2.14 (2), Os(2)–O(12) = 2.18 (1), C(12)–C(13) = 1.40 (2), C(14)–O(12) = 1.22 (2), Os(2)–Os(1)–Os(3) = 137.31 (3), Os(1)–Os(2)–Os(4) = 70.12 (2).

(20) This hydride ligand is believed to bridge the Os(1)–Os(3) bond in the large cavity that is circumscribed by the carbonyl ligands C(1)–O(1), C(2)–O(2), C(6)–O(6), and C(7)–O(7).

(21) Compound **3** was isolated by TLC on silica gel plates using a CH<sub>2</sub>Cl<sub>2</sub>/hexane (20/80) solvent mixture. IR (ν(CO) in hexane, cm<sup>-1</sup>): 2113 w, 2093 s, 2082 vs, 2059 s, 2035 m, 2022 m, sh, 2018 s, 2005 w, 1995 w, 1989 w, 1709 w, br. Compound **3** exists in CDCl<sub>3</sub> solution as a mixture of two slowly interconverting isomers in a 3/4 ratio. <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>): minor isomer, 8.06 (s, CH), 3.74 (s, CH<sub>2</sub>), –16.48 (s, OsH), –18.28 (s, OsH); major isomer, 7.83 (s, CH), 3.79 (s, CH<sub>2</sub>), –16.52 (s, OsH), –18.22 (s, OsH). Satisfactory elemental analyses have been obtained.

(22) Yellow platelike crystals of **3** were grown by slow evaporation of solvent from CH<sub>2</sub>Cl<sub>2</sub>/hexane solutions at –20 °C: space P2<sub>1</sub>/n; a = 13.674 (5) Å, b = 10.253 (5) Å, c = 17.746 (4) Å; β = 103.42 (2)°; Z = 4; ρ<sub>calcd</sub> = 3.34 g/cm<sup>3</sup>. The structure was solved by direct methods (MULTAN) and was refined with 2366 reflections to the final values of the residuals R = 0.040 and R<sub>w</sub> = 0.042. The hydrogen atoms were not observed and were thus ignored.

(23) Selected interatomic distances (Å) and angles (deg) for **3** are as follows: Os(1)–Os(3) = 2.867 (1), Os(1)–Os(4) = 2.941 (1), Os(2)–Os(3) = 2.924 (1), Os(1)–C(13) = 2.31 (2), Os(1)–C(14) = 2.43 (2), Os(2)–C(14) = 2.16 (2), Os(4)–C(13) = 2.11 (2), C(13)–C(14) = 1.37 (2), Os(3)–Os(1)–Os(4) = 83.66 (3), Os(1)–Os(3)–Os(2) = 81.19 (3).

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