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**Supplementary Material Available:** Atomic positional and thermal parameters (Tables 1 and 2) (2 pages). Ordering information is given on any current masthead page.

### Mixed-Metal Clusters by Metal Hydride Coupling. Crystal Structures of $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$ and $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$ . Direct Conversion of a Metalloligated Cluster to a Closed Polyhedron

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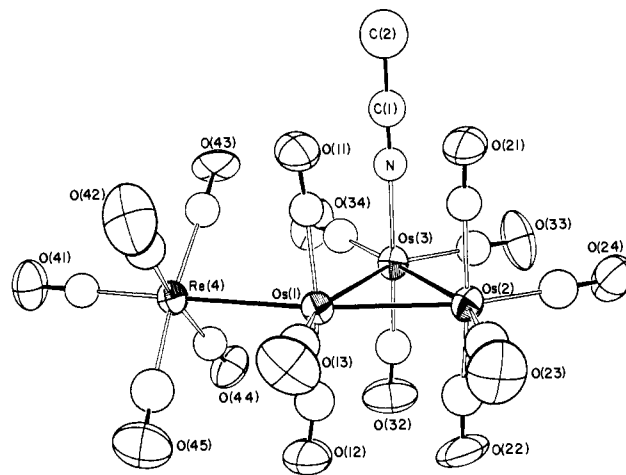
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The addition of a metal-containing species to a closed cluster of  $n$  metal atoms frequently yields a new closed cluster of  $n + 1$  metal atoms.<sup>1-3</sup> This process presumably involves stepwise formation of metal-metal bonds, but only in one case that we are aware of has an open-to-closed metal atom transformation been observed.<sup>4</sup> We previously reported the metalloligated clusters  $(\mu\text{-H})_n\text{Os}_3(\text{CO})_{12-n}[\text{Re}(\text{CO})_5]_n$  ( $n = 1, 2$ ), prepared by addition of  $n[\text{HRe}(\text{CO})_5]$  to  $\text{Os}_3(\text{CO})_{12-n}(\text{NCCH}_3)_n$ .<sup>5</sup> We have since found  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{16}$  and  $(\mu\text{-H})_2\text{Os}_3\text{Re}_2(\text{CO})_{20}$  to be related by a third, "lightly stabilized" species  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$ , which we now report can be induced to close to  $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$ .

The compound  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$ <sup>6</sup> is obtained quantitatively by heating  $(\mu\text{-H})_2\text{Os}_3\text{Re}_2(\text{CO})_{20}$  in acetonitrile. After isolation (TLC) and in hydrocarbon solution, treatment of  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$  with  $\text{HRe}(\text{CO})_5$  causes complete reversion to  $(\mu\text{-H})_2\text{Os}_3\text{Re}_2(\text{CO})_{20}$ . Similarly, stirring the solution under a carbon monoxide atmosphere leads exclusively to  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{16}$ .

We have undertaken an X-ray diffraction study of the complex  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$ . This crystallizes in the noncentrosymmetric monoclinic space group  $P2_1$  [ $C_2^2$ ; No. 4] with  $a = 9.132$  (1),  $b = 16.424$  (2),  $c = 9.457$  (1) Å;  $\beta = 114.61$  (1)°;  $V = 1289.7$  (3) Å<sup>3</sup>;  $\rho_{\text{calcd}} = 3.14$  g cm<sup>-3</sup> for  $M_r = 1219$  and  $Z = 2$ . Diffraction data were collected on a Syntex  $P2_1$  automated four-circle diffractometer (using Mo  $K\alpha$  radiation) as described previously.<sup>7</sup> The structure was solved by a combination of



**Figure 1.** Molecular geometry of  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$ , with hydrogen atoms omitted. The bridging hydride ligand lies in a diequatorial site across the  $\text{Os}(1)\cdots\text{Os}(3)$  vector (ORTEP-II diagram).

Patterson, difference-Fourier, and full-matrix least-squares refinement, the final discrepancy indices being  $R_F = 3.1\%$  and  $R_{wF} = 2.5\%$  for all 3376 data with  $4.5^\circ < 2\theta < 45^\circ$ . The molecular geometry is shown in Figure 1. The molecular core consists of a triangular array of osmium atoms, with a rhenium atom bound to one of the equatorial sites of an osmium atom. The  $\text{Os}(1)\text{-Re}(4)$  bond length is  $2.959$  (1) Å and the  $\text{Os}(1)\text{-Os}(2)$  and  $\text{Os}(2)\text{-Os}(3)$  distances are  $2.861$  (1) and  $2.885$  (1) Å. The third intratriangular vector,  $\text{Os}(1)\text{-Os}(3) = 3.032$  (1) Å, is  $0.159$  Å longer than the average of the two  $\text{Os-Os}$  distances and [taken in conjunction with the large cis-diequatorial angles adjacent to it— $\text{Os}(3)\text{-Os}(1)\text{-Re}(4) = 104.84$  (2)° and  $\text{Os}(1)\text{-Os}(3)\text{-C}(34) = 116.1$  (5)°] suggests that the bridging hydride ligand (which was, regrettably, not located directly) occupies an equatorial  $\mu_2$ -bridging site across the  $\text{Os}(1)\cdots\text{Os}(3)$  vector.

It is noteworthy that only the  $\text{Re}(\text{CO})_5$  moiety trans to a bridging hydride is eliminated in forming  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$  from  $(\mu\text{-H})_2\text{Os}_3\text{Re}_2(\text{CO})_{20}$ .<sup>8</sup> This may be due to a trans labilizing effect.

Treatment of a refluxing acetonitrile solution of  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$  under a hydrogen atmosphere with excess (3-4 equiv) trimethylamine *N*-oxide dihydrate leads to a pale yellow solution. Evaporation and preparative TLC yields >70%  $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$  as the only observable product.<sup>9</sup> No stable products are obtained in the absence of the hydrogen atmosphere.

We have also undertaken an X-ray diffraction study of  $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$ . This complex crystallizes in the centrosymmetric hexagonal space group  $P6_3/m$  [ $C_{6h}^2$ ; No. 176] with  $a = 19.087$  (5),  $c = 10.963$  (1) Å,  $V = 3459$  (3) Å<sup>3</sup>;  $\rho_{\text{calcd}} = 3.16$  g cm<sup>-3</sup> for  $M_r = 1098$  and  $Z = 6$ . Data were collected and the structure solved as described above, the resulting discrepancy indices being  $R_F = 8.0\%$  and  $R_{wF} = 7.1\%$  for 1425 reflections with  $|F| > \sigma(F)$  and  $4.5^\circ < 2\theta < 45.0^\circ$  (Mo  $K\alpha$  radiation). We attribute the high discrepancy indices to a combination of (a) the use of an extremely small crystal and (b) disorder, caused by an intrinsically asymmetric molecule lying on (and being disordered about) a crystallographic mirror plane. The gross molecular geometry and intermetallic distances in this molecule are shown in Figure 2. Our interpretation of these results is helped by the observation that the "thermal motion" of  $\text{Os}(1)$  and  $\text{Os}(1')$  [ $B_{\text{equiv}} = 3.21$  Å<sup>2</sup>] is greater than for  $\text{Os}(2)$  and  $\text{Re}(4)$  [ $B_{\text{equiv}} = 2.70$  and  $2.67$  Å<sup>2</sup>, respectively]. All  $\text{M}(\text{CO})_3$  groups are symmetrical, so no terminal hydride ligands are present. The five hydride ligands therefore bridge 5 of the 6 edges of the tetrahedron. The observed structure is therefore the composite of the structures I (in which

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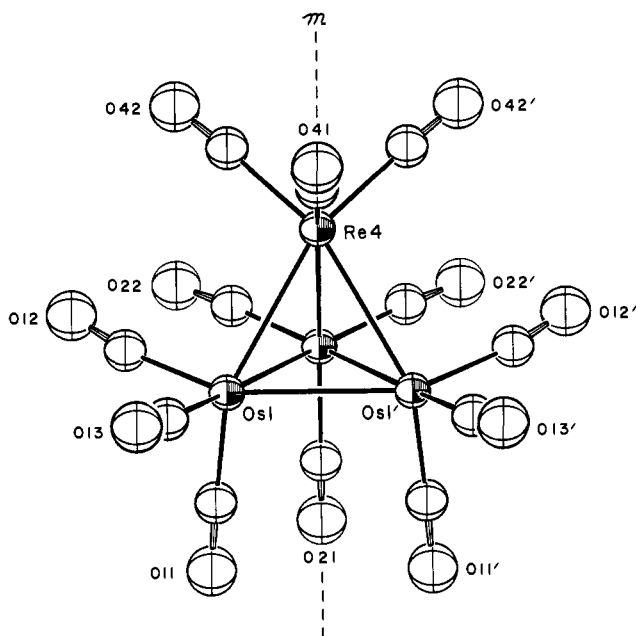
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(6) This compound was previously<sup>5</sup> reported as  $\text{HReOs}_3(\text{CO})_{15}$ . The present formulation is supported by later observation of a very weak parent ion in the field-desorption mass spectrum, a <sup>1</sup>H NMR signal for coordinated acetonitrile, and elemental analysis.

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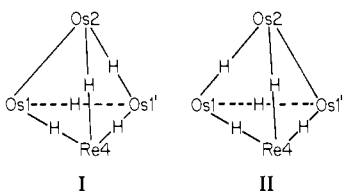
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(9) MS,  $m/e$  1104 ( $M^+$ ); IR  $\nu_{\text{CO}}$  ( $\text{CHCl}_3$ ) 2078 w, 2040 s, 2014 vs, 2002 sh, 1969 w, 1934 w  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR [25 °C,  $(\text{CH}_3)_2\text{CO}$ ]  $\tau$  29.2 (br s).



**Figure 2.** Molecular geometry of  $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$  (ORTEP-II diagram). Os(2) is not labeled. Relevant distances are as follows: Os(1)–Os(2) = Os(1')–Os(2) = 2.838 (3) Å, Os(1)–Os(1') = 2.964 (2) Å, Os(2)–Re(4) = 2.989 (4) Å, Os(1)–Re(4) = Os(1')–Re(4) = 3.017 (3) Å. Distinction between osmium and rhenium atoms rests on the relative metal–metal bond distances. Note that, in general, M–M and M–H–M bond lengths in tetrahedral species tend to be about 0.1 Å shorter than in triangular species.

Os(2)–Os(1) is the *nonbridged* bond and II (in which Os(2)–Os(1') is the *nonbridged* bond).



The compounds  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$  and  $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$  have one and three rhenium–osmium bonds, respectively. A possible precursor to the latter is another compound with three Re–Os bonds, namely,  $(\text{H})\text{Os}_3\text{Re}(\text{CO})_{15}$ , which has been prepared in low yield [from  $\text{Re}(\text{CO})_5^-$  and  $\text{Os}_3(\text{CO})_{12}^{10}$ ] and structurally characterized.<sup>11</sup> However, we have not been able to demonstrate conversion of  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$  to  $(\text{H})\text{Os}_3\text{Re}(\text{CO})_{15}$ . Another possible intermediate is a compound with two Re–Os bonds. In this case there may be a close analogy with the  $\text{Os}_3\text{C}$  portion of the  $\text{HOs}_3(\text{CO})_{10}\text{CH}_3/\text{H}_2\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)/\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})$  system.<sup>12</sup> In particular this comparison suggests that the formation of new Re–Os bonds in the closure of  $(\mu\text{-H})\text{Os}_3\text{Re}(\text{CO})_{15}(\text{NCCH}_3)$  to  $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$  may occur via *intramolecular* “oxidative” addition of M–H bonds analogous to the formation of new C–Os bonds by cleavage of C–H bonds. Attempts to isolate and characterize intermediates in the bimetallic polyhedral closure reaction are continuing.

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## $\eta^5$ -Benzyl: Crystal Structure, Nucleophilic Properties, and Electron-Transfer Reactions of $\text{CpFe}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)$ , an Intermediate in C–H Activation by $\text{O}_2$ via $\text{O}_2^{-\cdot}$

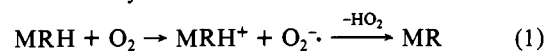
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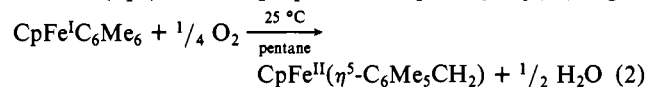
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The activation of C–H bonds, an important contemporary problem, has been approached by organic chemists through H–radical abstraction (autoxidation)<sup>2</sup> and then by organometallic chemists through oxidative addition.<sup>3</sup> We have recently proposed<sup>4</sup> an alternative way of using organometallics to achieve this activation by using  $\text{O}_2$  or air. If a neutral substrate MRH can transfer one electron to  $\text{O}_2$  (a ready process considering the low redox potential  $\text{O}_2/\text{O}_2^{-\cdot}$ ,  $-0.7$  V vs. SCE), further deprotonation by  $\text{O}_2^{-\cdot}$  is rendered possible through activation by the cationic organometallic moiety:

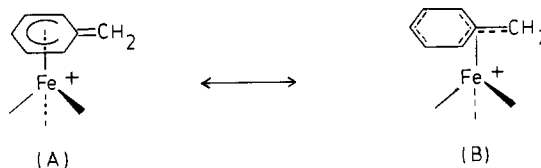


We have reported that the reaction of dioxygen with the 19–electron complex  $\text{CpFe}^{\text{I}}\text{C}_6\text{Me}_6$  (1)<sup>4</sup> gives rise to H-atom abstraction (eq 2) while  $\text{KO}_2$  deprotonates  $\text{CpFe}^{\text{I}}\text{C}_6\text{Me}_6$  ( $\text{I}^+$ ) to give



the same complex,  $\text{CpFe}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)$  (2) in which the  $\text{C}_6\text{Me}_5\text{CH}_2$  moiety is tentatively formulated as pentahapto coordinated (eq 2).

However, others<sup>5</sup> have depicted the same systems as zwitterionic, e.g.,  $\text{CpFe}^+(\eta^6\text{-C}_6\text{H}_n\text{Me}_{6-n}\text{CH}_2)^-$ . Indeed the crystal structure of  $\text{CpFe}^+(\text{fluorenyl})^-$  clearly suggests that it is a zwitterion<sup>6</sup> in which the arene ligand is  $\eta^6$  coordinated. It is now necessary to address the question of the nature of the ligand in unstabilized deprotonated arene complexes. Much interest in the benzyl ligand has arisen since the  $\eta^1 \rightleftharpoons \eta^3$  interconversion was shown to be responsible for the catalytic activity of complexes bearing it.<sup>7</sup> The possibility of pentahapto coordination of the benzyl cation (A) was first stressed by Hoffmann<sup>8</sup> in 1977 who also noted the lack of experimental evidence supporting this proposal and compared the structure with the  $\eta^4$ -trimethylenemethane as shown in (B).



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