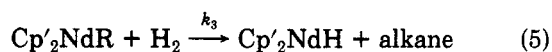
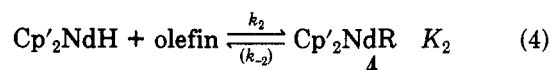
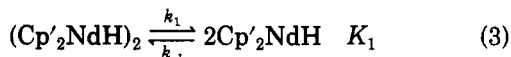


scrupulously anaerobic vacuum line conditions in toluene or cyclohexane solution (25 °C, 1-atm pressure), $N_t > 80\,000\text{ min}^{-1}$ for ethylene polymerization¹⁸ (product $\bar{M}_n = 233\,000\text{--}590\,000$, $\bar{M}_w/\bar{M}_n = 1.91\text{--}4.50$);¹⁹ even at -78 °C , $N_t > 16\,000\text{ min}^{-1}$. Such rates are comparable to or exceed those of the most active "homogeneous" ethylene polymerization catalysts known.^{4,20} For $(\text{Cp}'_2\text{UH})_n$,^{3d} $N_t = 144\text{ min}^{-1}$, while 1 is inactive. At 25 °C, 1-atm pressure, 1-hexene is hydrogenated by 3 with $N_t = 77\,000\text{ h}^{-1,21}$ vs. 6400 h^{-1} for $\text{Ir}(\text{COD})\text{P}(\text{c-Hex})_3(\text{py})^+\text{PF}_6^-$ (0 °C),²² 650 h^{-1} for $\text{Rh}(\text{PPh}_3)_3\text{Cl}$,²² and $63\,000\text{ h}^{-1}$ for $(\text{Cp}'_2\text{UH})_n$.³ Kinetically, hexene hydrogenation is first order in catalyst (0.10–2.50 mM), first order in P_{H_2} (0.3–1.5 atm), and zero order (over ca. 99% of the reaction) in olefin. These observations can be most simply accommodated by a scheme^{23,24} as in eq 3–5 where [olefin] is high, k_2 and K_2 are large (kinetically¹⁵



and thermodynamically^{15,25} reasonable; verified by NMR), and hydrogenolysis (k_3) is rate limiting. Note that classical oxidative addition/reductive elimination sequences^{22,26} are inappropriate for Nd(III). At 31% conversion, 4.1% of the olefin is present as 2-hexene, suggesting β -H elimination can occur from 4 (2- or 3-hexyl); under D_2 , this 2-hexene is predominantly d_1 , the unreacted 1-hexene predominantly d_0 , and the hexane predominantly 1,2- d_2 .²⁷ For cyclohexene, $N_t(\text{max}) = 8300\text{ h}^{-1}$, and the reaction is first order in olefin, $1/2$ order in catalyst (0.58–11.6 mM), and zero order in P_{H_2} (0.55–1.4 atm). Equations 3–5 accommodate this observation if k_2 is now rate limiting (sterically, kinetically, and thermodynamically²⁵ reasonable; verified by NMR). To our knowledge, these data represent some of the first detailed kinetic/mechanistic observations on early transition^{26,28} and f-element^{1,2,17} homogeneous hy-

drogenation catalysis. The efficiency with which eq 4 and 5 can be coupled is particularly remarkable, as is, for both polymerization and hydrogenation, the increase in overall activity over the uranium analogue.

The present results offer new synthetic routes to highly reactive early (and other^{29a}) organolanthanides and the first opportunities to acquire comparative 4f/5f mechanistic information. Further studies are in progress and will be reported in due course.^{10a,29}

Acknowledgment. We thank Molycorp for support of this research and Prof. R. L. Burwell, Jr., and G. Jeske and H. Lauke for helpful discussions.

Registry No. 1, 93383-00-7; 3, 93303-98-1; $\text{Cp}'_2\text{NdCl}_2\text{-Li}(\text{ether})_2^+$, 78128-14-0; $\text{LiCH}[\text{Si}(\text{CH}_3)_3]_2$, 41823-71-6; $\text{CH}_2[\text{Si}(\text{C}_2\text{H}_5)_3]_2$, 2117-28-4; ethylene, 74-85-1; polyethylene, 9002-88-4; 1-hexene, 592-41-6; cyclohexene, 110-83-8.

Supplementary Material Available: Structure report and tables of fractional atomic coordinates and anisotropic thermal parameters as well as bond distances and angles and structure factors (61 pages). Ordering information is given on any current masthead page.

(29) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J., submitted for publication ($\text{Cp}'_2\text{MCH}[\text{Si}(\text{CH}_3)_3]_2$, M = La, Nd, Sm, Lu). (b) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J., submitted for publication. (c) **Note added in proof.** The new complexes $\text{Cp}'_2\text{YCH}[\text{Si}(\text{CH}_3)_3]_2$ and $(\text{Cp}'_2\text{YH})_2$ have been recently reported and appear to have very similar structures: Den Haan, K. H.; Teuben, J. H., NATO Advanced Study Institute "Fundamental and Technological Aspects of Organo-Element Chemistry", Maratea, Italy, Sept 10–21, 1984.

Chemical and Electrochemical Reactivity of Some Unsaturated Hexanuclear Osmium–Gold Clusters†

Caroline M. Hay, Brian F. G. Johnson, Jack Lewis,*
Roderick C. S. McQueen, Paul R. Ralby,
Robert M. Sorrell, and Michael J. Taylor

University Chemical Laboratory, Lensfield Road
Cambridge, CB2 1EW, Great Britain

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Summary: The unsaturated clusters $\text{Os}_4(\text{CO})_{12}(\text{AuPR}_3)_2$ [$\text{PR}_3 = \text{PEt}_3$ (I), PPh_3 (II), PMePh_2 (III)] may be prepared by the thermal decarbonylation of $\text{Os}_4(\text{CO})_{13}(\text{AuPR}_3)_2$ [$\text{PR}_3 = \text{PEt}_3$ (IV), PPh_3 (V), PMePh_2 (VI)] which have been obtained previously by the reaction of $[\text{Os}_4\text{H}(\text{CO})_{13}]^-$ with 2 equiv of $\text{Au}(\text{PR}_3)\text{Cl}$. The former reaction is reversible, and clusters I, II, and III readily add a range of nucleophiles as well as undergoing facile sequential, electrochemical reductions, to $[\text{Os}_4(\text{CO})_{12}(\text{AuPR}_3)_2]^-$ and $[\text{Os}_4(\text{CO})_{12}(\text{AuPR}_3)_2]^{2-}$. The existence of the monoanionic species is confirmed by the observation of an ESR spectrum, while X-ray crystallographic studies on III and IV show "open" bicapped butterfly and dedge-bridged tetrahedral metal frameworks, respectively.

Substitution reactions at metal centers in low-valent carbonyl clusters generally proceed via a dissociative

(18) Measured aliquots of catalyst solution were injected into a rapidly stirred, solvent-filled Morton flask maintained at 1 atm of ethylene. After a measured time interval, polymerization was quenched with methanol, and polyethylene was collected, washed, and dried.

(19) GPC in $o\text{-C}_6\text{H}_4\text{Cl}_2$. The dependence of molecular weight and polydispersity upon reaction conditions will be discussed elsewhere.^{29a} We thank Dr. Mark Delaney (Dow Central Research) for these measurements.

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(21) (a) An extensively modified version of the constant volume apparatus described elsewhere^{21b} was employed. Mass transport effects were shown to be unimportant under the present conditions. (b) Kung, H. H.; Pellet, R. J.; Bruwell, R. L., Jr. *J. Am. Chem. Soc.* 1976, 98, 5603–5611.

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† Dedicated to the memory of Earl L. Muettterties.

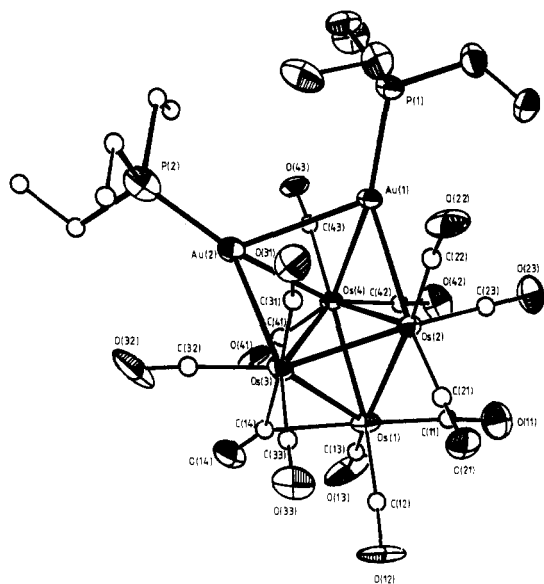


Figure 1. The molecular structure of $\text{Os}_4(\text{CO})_{13}(\text{AuPEt}_3)_2$ (IV).

mechanism and require considerable thermal or photochemical activation.¹ This problem may be overcome if addition reactions are carried out by using formally unsaturated clusters as starting materials, and in this context $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ has proved a versatile reagent.² The introduction of a heterometal unit into a cluster may also increase reactivity because of the inherent polarity in mixed-metal bonds. Two unsaturated triosmium clusters containing gold-phosphine ligands, $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-AuPR}_3)_3$ and $\text{Os}_3(\text{CO})_{10}(\mu\text{-AuPR}_3)_2$,⁴ are known, and the chemistry of these molecules closely parallels that of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ from which they are derived.⁴ In this communication we report the synthesis and reactivity of a new unsaturated osmium-gold cluster, $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-AuPR}_3)_2$ [$\text{PR}_3 = \text{PEt}_3$ (I), PPh_3 (II), PMePh_2 (III)], based on a tetraosmium unit, which has no known hydrido equivalent.

The unsaturated $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-AuPR}_3)_2$ cluster is obtained by the thermal decarbonylation of the saturated cluster $\text{Os}_4(\text{CO})_{13}(\mu\text{-AuPR}_3)_2$ [$\text{PR}_3 = \text{PEt}_3$ (IV), PPh_3 (V), PMePh_2 (VI)], which is analogous to the hydrido species $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}$, and is prepared by the standard techniques for introducing gold-phosphine groups into cluster species.⁵ The reaction of $[(\text{Ph}_3\text{P})_2\text{N}][\text{Os}_4(\mu\text{-H})(\text{CO})_{13}]$ with the appropriate gold-phosphine chloride, in the presence of $\text{Ti}[\text{BF}_4]$, which acts as a chloride abstractor, for 0.5 h affords IV, V, or VI in good yield.⁶

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(6) For $\text{Os}_4(\text{CO})_{13}(\text{AuPEt}_3)_2$ (IV): IR ν_{CO} (CH_2Cl_2) 2074 (s), 2032 (vs), 2030 (vs), 2009 (s), 1985 (w), 1970 (m), 1899 (w) cm^{-1} ; ^{31}P NMR (CH_2Cl_2) -61.5 ppm. Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{O}_{13}\text{Os}_4\text{P}_2\text{Au}_2$: C, 17.11; H, 1.72. Found: C, 17.22; H, 1.89. For $\text{Os}_4(\text{CO})_{13}(\text{AuPPh}_3)_2$ (V): IR ν_{CO} (CH_2Cl_2) 2077 (s), 2037 (vs), 2030 (vs), 2015 (s), 1992 (s), 1975 (m), 1908 (w) cm^{-1} . For $\text{Os}_4(\text{CO})_{13}(\text{AuPMePh}_2)_2$ (VI): IR ν_{CO} (CH_2Cl_2) 2035 (vs), 2032 (vs), 2015 (s), 1990 (w), 1975 (m), 1909 (w) cm^{-1} .

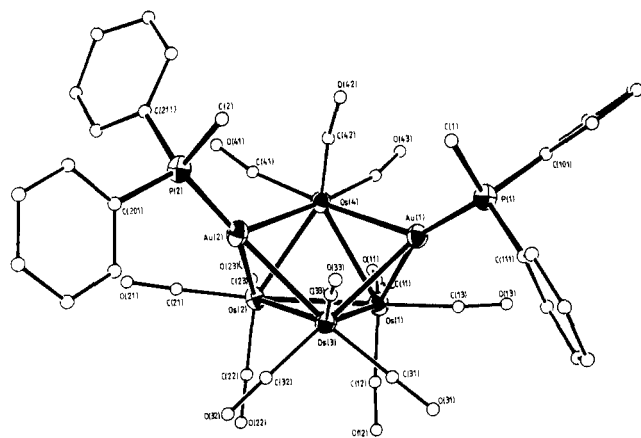
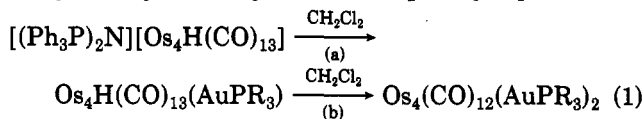


Figure 2. The molecular structure of $\text{Os}_4(\text{CO})_{12}(\text{AuPMePh}_2)_2$ (III).

These clusters are thermally unstable in the solid state and in solution and lose CO to form $\text{Os}_4(\text{CO})_{12}(\text{AuPR}_3)_2$ [$\text{PR}_3 = \text{PEt}_3$ (I), PPh_3 (II), PMePh_2 (III)] (eq 1).⁷ This



(a) $\text{Au}(\text{PR}_3)\text{Cl}/\text{TIBF}_4$, room temperature, 30 min;

(b) $\text{Au}(\text{PR}_3)\text{Cl}/\text{TIBF}_4/\text{NEt}_3$, room temperature, 15 h

is in contrast to $\text{Os}_4(\text{CO})_{13}(\text{AuPR}_3)\text{H}$ and $\text{Os}_4\text{H}_2(\text{CO})_{13}$ which do not lose CO readily, and where prolonged refluxing in xylene results in a mixture of products, indicating that cluster fragmentation occurs.⁸

It has been common in mixed-metal cluster chemistry to consider the "AuPR₃" unit as a one-electron donor, drawing an analogy with a hydride. In this case the clusters $\text{Os}_4(\text{CO})_{13}(\text{AuPR}_3)_2$ are electron-precise 60-electron systems, while the loss of a carbonyl group to generate the $\text{Os}_4(\text{CO})_{12}(\text{AuPR}_3)_2$ species reduces the electron count to 58 electrons, and thus these species are formally unsaturated.

In order to establish the geometry of the saturated and unsaturated clusters and discover whether the unsaturation is localized or delocalized over the cluster framework, X-ray crystal structure analyses on the compounds III and IV have been performed. In the structure of IV⁹ (Figure 1) the four Os atoms define a tetrahedron and the AuPEt₃ groups bridge two adjacent Os-Os edges.¹⁰ The Au-Au

(7) For $\text{Os}_4(\text{CO})_{12}(\text{AuPEt}_3)_2$ (I): IR ν_{CO} (CH_2Cl_2) 2063 (m), 2017 (s), 2008 (vs), 1957 (m, br) cm^{-1} ; ^{31}P NMR (CH_2Cl_2) -68.5 ppm. Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{O}_{12}\text{Os}_4\text{P}_2\text{Au}_2$: C, 16.69; H, 1.75. Found: C, 16.76; H, 1.69. For $\text{Os}_4(\text{CO})_{12}(\text{AuPPh}_3)_2$ (II): IR ν_{CO} (CH_2Cl_2) 2061 (m), 2016 (s), 2009 (vs), 1954 (m, br) cm^{-1} . For $\text{Os}_4(\text{CO})_{12}(\text{AuPMePh}_2)_2$ (III): IR ν_{CO} (CH_2Cl_2) 2062 (m), 2017 (s), 2009 (vs), 1955 (m, br) cm^{-1} .

(8) Johnson, B. F. G.; Lewis, J.; Taylor, M. J., unpublished results.

(9) Crystal data for $\text{Os}_4(\text{CO})_{13}(\text{AuPEt}_3)_2$ (IV): unit cell dimensions, $a = 12.459$ (1) Å, $b = 17.655$ (2) Å, $c = 16.950$ (2) Å, $\alpha = 95.59$ (1)°, $\beta = 3711$ (3) Å³, space group $P2_1/a$ ($Z = 4$, $d(\text{calcd}) = 3.14$ g cm^{-3}); Mo radiation, $\lambda = 0.710$ 69 Å, $\mu(\text{Mo K}\alpha) = 250.33$ cm^{-1} ; 4743 observed reflections were collected by using ω - θ scan mode. The structure was solved by a combination of direct methods and Fourier difference techniques and refined by blocked full-matrix least squares to a final agreement factor $R = 6.1\%$.

(10) Selected bond parameters for IV: Os(1)-Os(2) = 2.830 (1), Os(1)-Os(3) = 2.784 (1), Os(1)-Os(4) = 2.829 (1), Os(2)-Os(3) = 2.824 (1), Os(2)-Os(4) = 2.887 (1), Os(3)-Os(4) = 2.958 (1), Au(1)-Os(2) = 2.863 (1), Au(1)-Os(4) = 2.739 (1), Au(2)-Os(3) = 2.853 (1), Au(2)-Os(4) = 2.740 (1), Au(1)-Au(2) = 3.128 (1), Au(1)-P(1) = 2.315 (5), Au(2)-P(2) = 2.291 (8), Os(1)-C(14) = 2.22 (3), and Os(3)-C(14) = 2.07 (2) Å; Os(2)-Au(1)-Os(4) = 62.0 (1), Os(2)-Au(1)-Au(2) = 88.2 (1), Os(4)-Au(1)-Au(2) = 55.2 (1), Os(2)-Au(1)-P(1) = 136.0 (1), Os(4)-Au(1)-P(1) = 161.8 (1), Au(2)-Au(1)-P(1) = 119.3 (1), Os(3)-Au(2)-Os(4) = 63.8 (1), Os(3)-Au(2)-Au(1) = 85.5 (1), Os(4)-Au(2)-Au(1) = 55.2 (1), Os(3)-Au(2)-P(2) = 137.2 (2), Os(4)-Au(2)-P(2) = 158.0 (2), and Au(1)-Au(2)-P(2) = 122.5 (2)°.

separation is ca. 0.34 Å longer than the value of 2.793 (4) Å for the equivalent interaction in the isoelectronic cluster $\text{Os}_4\text{H}_2(\text{CO})_{12}(\text{AuPPh}_3)_2$ where the two AuPR_3 groups bridge the same Os–Os edge^{5b} but similar in length to the Au–Au distance of 3.176 (1) Å in $\text{Ru}_3\text{H}(\text{CO})_9(\text{COMe})(\text{AuPPh}_3)_2$.¹¹ Although no direct Au–Au bond is required in the simplest electron counting scheme, it is probable that the observed distance is indicative of some Au–Au interaction in a multicenter, multielectron bonding scheme, possibly involving tangentially orientated orbitals as proposed in other cluster systems.¹² There are also short contacts between the two Au atoms and a number of the Os–bonded carbonyl groups [$\text{Au}(1)\cdots\text{C}(22) = 2.72$ (2) Å, $\text{Os}(2)\text{---}\text{C}(22)\text{---}\text{O}(22) = 168$ (2)°, $\text{Au}(1)\cdots\text{C}(43) = 2.63$ (2) Å, $\text{Os}(4)\text{---}\text{C}(43)\text{---}\text{O}(43) = 165$ (2)°, $\text{Au}(2)\cdots\text{C}(31) = 2.84$ (2) Å, $\text{Os}(3)\text{---}\text{C}(31)\text{---}\text{O}(31) = 165$ (2)°, and $\text{Au}(2)\cdots\text{C}(43) = 2.72$ (2) Å] which may help to balance the electron distribution over the cluster framework.

In the structure of the electron deficient cluster (III)¹³ (Figure 2) the Os_4 framework has opened up to form a "butterfly" arrangement, and each Au atom μ_3 -caps the two "wing-tip" Os atoms and one of the "hinge" Os atoms. The Au...Au separation across the cluster is 4.046 (2) Å, so there is no direct interaction in this case.¹⁴ This Os_4Au_2 framework closely resembles the equivalent fragment in $\text{Os}_8(\text{CO})_{22}(\text{AuPPh}_3)_2$,¹⁵ a cluster that is formally isoelectronic with binary carbonyl $\text{Os}_8(\text{CO})_{23}$ ¹⁶ that has not been considered as unsaturated. The bond parameters within the structure of III do not indicate a specific site of unsaturation as in $\text{Os}_3\text{H}_2(\text{CO})_{10}$ ¹⁷ but, presumably, the delocalization is accommodated within a bonding scheme involving the six metal atoms such as that proposed for the hexagold cluster $\text{Au}_6(\text{PH}_3)_6$.¹⁸

However, the clusters I–III behave chemically as unsaturated species and react with CO to regenerate IV, V, and VI while warming the latter complexes to 80 °C in the absence of CO reforms the unsaturated clusters. Many cycles are possible before decomposition of the reactants occurs.

The clusters I–III also add dihydrogen to afford the known complex $\text{Os}_4\text{H}_2(\text{CO})_{12}(\text{AuPR}_3)_2$,^{5b} but the reaction requires fairly forcing conditions (100 °C, 50 atm), is complicated by the formation of other low yields products, and is irreversible.

These reactions of I, II, and III with CO and H_2 may be contrasted with similar reactions of *closo*-triosmium-

platinum clusters.¹⁹ The cluster $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_{11})_3\}$ forms 1:1 adducts with CO and H_2 , under mild reaction conditions, to give $\text{Os}_3\text{Pt}(\mu\text{-H})_4(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_{11})_3\}$, respectively. These two complexes readily revert to the starting material under a stream of dinitrogen and do not require the forcing conditions described above for the OsAu clusters.

Nucleophilic reagents such as trimethyl phosphite and butyl isocyanide add to I at room temperature. With $\text{P}(\text{OMe})_3$ the initial product is $\text{Os}_4(\text{CO})_{12}\text{P}(\text{OMe})_3(\text{AuPEt}_3)_2$ (VII),²⁰ but prolonged reaction results in the substitution of a carbonyl ligand to give $\text{Os}_4(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}_2(\text{AuPEt}_3)_2$ (VIII).²¹ With *t*-BuNC the reaction is rapid and the only product isolated is $\text{Os}_4(\text{CO})_{11}(t\text{-BuNC})_2(\text{AuPEt}_3)_2$ (IX).²²

The chemical reduction of II is achieved by treatment of a tetrahydrofuran solution of the cluster with an excess of 4% Na/Hg amalgam, under a dinitrogen atmosphere. The product $\text{Na}_2[\text{Os}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]$ (X)²³ is very air sensitive, rapidly reverting to II. The reduction may also be performed electrochemically, and the clusters I–III all show two reversible, one-electron reductions at room temperature (CH_2Cl_2 , Ag/AgCl electrode, FeCp_2 internal calibrant).²⁴ An ESR spectrum of the monoanion $[\text{Os}_4(\text{CO})_{12}(\text{AuPR}_3)]^-$ exhibits a signal at $g = 1.775$ which indicates that the unpaired electron does not couple with the P nuclei and may be consistent with electron being located within the metal framework. At –40 °C the clusters I–III undergo two irreversible, one-electron oxidations.

In conclusion, the introduction of gold–phosphine groups to tetranuclear osmium clusters leads to the formation of stable unsaturated mixed-metal clusters for which there is no direct hydridoosmium clusters analogy. These clusters readily undergo addition reactions with nucleophiles and may be reduced to give reactive anionic species. This suggests that compounds such as I, II, and III should prove to be very versatile starting materials for reactions with a wide variety of organic molecules and monometal complexes to produce a range of novel addition compounds, and work in this area is continuing.

Acknowledgment. We thank the Science and Engineering Research Council for financial support and British Petroleum p.l.c. for an award (C.M.H.).

Registry No. I, 93474-77-2; II, 93474-78-3; III, 93474-79-4; IV, 93474-80-7; V, 93474-81-8; VI, 93474-82-9; $[(\text{Ph}_3\text{P})_2\text{N}][\text{Os}_4(\mu\text{-H})(\text{CO})_{13}]$, 76468-65-0; $\text{Au}(\text{PEt}_3)\text{Cl}$, 15529-90-5; $\text{Au}(\text{PPh}_3)\text{Cl}$, 14243-64-2; $\text{Au}(\text{PPh}_2\text{Me})\text{Cl}$, 38686-38-3; TIBF_4 , 28625-02-7; $\text{Os}_4\text{H}_2(\text{CO})_{13}$, 21349-95-1; $\text{P}(\text{OMe})_3$, 121-45-9; *t*-BuNC, 7188-38-7; Os, 7440-04-2; Au, 7440-57-5.

Supplementary Material Available: Complete listings of

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(12) Stone, A. J., *Inorg. Chem.* **1981**, *20*, 563.

(13) Crystal data for $\text{Os}_4(\text{CO})_{12}(\text{AuPMePh}_2)_2$ (III): unit cell dimensions, $a = 18.510$ (5) Å, $b = 17.503$ (5) Å, $c = 27.000$ (12) Å, $V = 8748$ (4) Å³, space group *Pbca* ($Z = 8$, $d(\text{calcd}) = 2.87$ g cm⁻³); Mo radiation, $\lambda = 0.710$ 69 Å, $\mu(\text{Mo K}\alpha) = 183.49$ cm⁻¹; 3900 observed reflections were collected by using ω scan mode. The structure was solved by a combination of direct methods and Fourier difference techniques and refined by blocked full-matrix least squares to a final agreement factor $R = 7.4\%$.

(14) Selected bond parameters for III: Os(1)–Os(2) = 2.918 (2), Os(1)–Os(3) = 2.737 (2), Os(1)–Os(4) = 2.791 (2), Os(2)–Os(3) = 2.785 (2), Os(2)–Os(4) = 2.732 (2), Os(3)–Os(4) = 3.250 (2), Au(1)–Os(1) = 2.819 (2), Au(1)–Os(3) = 2.819 (2), Au(1)–Os(4) = 2.802 (2), Au(1)–P(1) = 2.283 (8), Au(2)–Os(1) = 2.828 (2), Au(2)–Os(2) = 2.784 (2), Au(2)–Os(4) = 2.831 (2), and Au(2)–P(2) = 2.279 (9) Å; Os(1)–Au(1)–Os(3) = 58.1 (1), Os(1)–Au(1)–Os(4) = 59.5 (1), Os(3)–Au(1)–Os(4) = 70.6 (1), Os(2)–Au(2)–Os(3) = 59.5 (1), Os(2)–Au(2)–Os(4) = 57.7 (1), and Os(3)–Au(2)–Os(4) = 70.7 (1)°.

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(20) For $\text{Os}_4(\text{CO})_{12}\text{P}(\text{OMe})_3(\text{AuPEt}_3)_2$ (VII): IR ν_{CO} (CH_2Cl_2) 2054 (m), 2016 (vs), 2004 (m), 1983 (w), 1963 (w) cm⁻¹; ¹H NMR (CD_2Cl_2) δ 1.23 (dt, 18 H, $J_{\text{PH}} = 18.0$ Hz), 1.97 (dq, 12 H, $J_{\text{PH}} = 8.0$ Hz, $J_{\text{HH}} = 7.5$ Hz), 3.8 (d, 9 H, $J_{\text{PH}} = 12.0$ Hz); ³¹P NMR (CH_2Cl_2) δ –62.6 (2P), –30.3 ppm (1P).

(21) For $\text{Os}_4(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}_2(\text{AuPEt}_3)_2$ (VIII): IR ν_{CO} (CH_2Cl_2) 2056 (m), 2018 (vs), 2016 (sh), 1987 (w), 1966 (w), 1964 (w) cm⁻¹; ¹H NMR (CD_2Cl_2) δ 1.23 (dt, 18 H, $J_{\text{PH}} = 18.0$ Hz), 1.99 (dq, 12 H, $J_{\text{HH}} = 8.0$ Hz), 3.84 (d, 9 H, $J_{\text{PH}} = 11.5$ Hz), 3.79 (d, 9 H, $J_{\text{PH}} = 13.0$ Hz).

(22) For $\text{Os}_4(\text{CO})_{11}(t\text{-BuNC})_2(\text{AuPEt}_3)_2$ (IX): IR ν_{CO} (CH_2Cl_2) 2173 (m, br), 2054 (m), 2018 (vs), 2000 (s), 1991 (m), 1963 (m, br), cm⁻¹; ¹H NMR (CD_2Cl_2) δ 1.24 (dt, 18 H, $J_{\text{PH}} = 18.0$ Hz), 1.98 (dq, 12 H, $J = 3.0$ Hz, $J_{\text{HH}} = 7.5$ Hz), 1.56 (s, 9 H), 1.55 (s, 9 H); ³¹P NMR (CH_2Cl_2) δ –62.3.

(23) For $\text{Na}_2[\text{Os}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]$ (X): IR ν_{CO} (THF) 2027 (m), 1964 (vs), 1905 (m, br) cm⁻¹.

(24) All cyclic voltammograms were recorded in the presence of 0.2 M supporting electrolyte [$[\text{C}_6\text{H}_5)_4\text{N}][\text{BF}_4]$] in CH_2Cl_2 at 20 °C. All potentials are referred to the normal hydrogen electrode: (I) $E_{1/2}(1) = -0.605$ (65 mV), $E_{1/2}(2) = -0.890$ (60 mV); (II) $E_{1/2}(1) = -0.580$ (70 mV), $E_{1/2}(2) = -0.810$ (65 mV); (III) $E_{1/2}(1) = -0.570$ (60 mV), $E_{1/2}(2) = -0.790$ (65 mV).

positional parameters, anisotropic thermal parameters, bond angles, bond distances, and observed and calculated structures for III and IV (63 pages). Ordering information is given on any current masthead page.

Preparation of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2[\text{AlMe}_3]_2$. A Complex with Four Yb-Me-Al Interactions[†]

James M. Boncella and Richard A. Andersen*

Chemistry Department and Materials and Molecular Research Division of Lawrence Berkeley Laboratory University of California, Berkeley, California 94720

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Summary: Trimethylaluminum reacts with base-free ytterbium bis[bis(trimethylsilyl)amide] to give $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2[\text{AlMe}_3]_2$. The X-ray crystal structure provides evidence for four Yb-Me-Al and two Yb-Me-Si bridging interactions.

Bridging alkyl compounds formed by interaction of aluminum alkyls with early d- and f-element organometallic compounds are of interest relative to structure and bonding¹ as well as to the mechanism of Ziegler-Natta polymerization processes.² Several compounds have been isolated in which two methyl groups of an aluminum alkyl forms bridges between the main-group and f-block metal,³ as in $\text{Me}_4\text{Al}_2(\mu\text{-Me})_2$,⁴ viz., the methyl group contributes one σ -type molecular orbital and a single electron to the bridge bonding.

Base-free $\text{Yb}_2[\text{N}(\text{SiMe}_3)_2]_4$ ⁵ is a dimer with two terminal and two bridging silylamide groups and both ytterbium atoms are three-coordinate. The overall geometry is similar to that found for $\text{Mn}_2[\text{N}(\text{SiMe}_3)_2]_4$ ^{6a,b} and $\text{Co}_2[\text{N}(\text{SiMe}_3)_2]_4$.^{6b} The Yb-N-Yb bridge in $\text{Yb}_2[\text{N}(\text{SiMe}_3)_2]_4$ can be cleaved by Lewis bases, such as phosphines, to give $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)$,^{7a} and by molecules that have Lewis acidic and basic sites present in the same

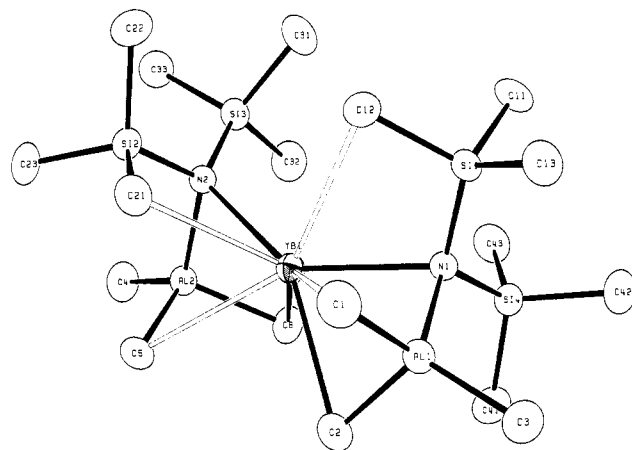


Figure 1. An ORTEP drawing of I, $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2[\text{AlMe}_3]_2$, showing the divalent ytterbium atom in eight-coordination.

molecule, such as $\text{NaN}(\text{SiMe}_3)_2$ to give $\text{NaYb}[\text{N}(\text{SiMe}_3)_2]_3$.^{7b} The latter complex contains two silylamide groups that bridge the metal atoms with the lone pair of electrons on the nitrogen atoms acting as donors toward the alkali and lanthanide metal atoms. In this communication we describe a complex formed between $\text{Yb}_2[\text{N}(\text{SiMe}_3)_2]_4$ and the Lewis acid Me_3Al_2 that contains two bridging and two semibringing Yb-Me-Al interactions.

Two molar equivalents of Me_3Al_2 react with $\text{Yb}_2[\text{N}(\text{SiMe}_3)_2]_4$ in pentane to give a bright yellow solution from which yellow plates of diamagnetic $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{Me}_3\text{Al})_2$ (I) were obtained by crystallization from pentane at -20°C in essentially quantitative yield.⁸ Triethylaluminum behaves similarly giving the yellow, low melting $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{Et}_3\text{Al})_2$.⁹ Figure 1 shows an ORTEP of I. The complex can be thought of as being derived from a monomeric $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2$ fragment in which each lone pair of electrons on the nitrogen atoms is coordinated to aluminum atoms so that the coordination number of the nitrogen and aluminum atoms is four. The averaged Al-N distance of 1.963 (5) Å and the averaged Yb-N-Al angle of $80.5(7)^\circ$ are similar to those found in $\text{Me}_4\text{Al}_2(\mu\text{-NPh}_2)(\mu\text{-Me})$ ^{10a} of 2.003 (3) Å and $85.6(1)^\circ$ and $\text{Me}_4\text{Al}_2(\mu\text{-NMe}_2)$ ^{10c} of 1.96 (1) Å and $91.6(2)^\circ$, respectively. The Yb-N(1) and Yb-N(2) bond lengths of 2.510 (2) and 2.573

[†] This paper is dedicated to the memory of the late Professor E.L. Muettterties with thanks for his wisdom and guidance.

* To whom correspondence should be addressed at the Chemistry Department, University of California.

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(8) (a) NMR: ¹H, δ 0.28 (s, 36 H), -0.25 (s, 18 H), temperature independent to -85°C ; ¹³C{¹H}, δ 5.36 and 0.85 due to Me₃Si and Me₃Al, respectively; IR (Nujol) 1260 (m), 1250 (s), 1212 (w), 1185 (w), 880 (s), 832 (s), 775 (m), 755 (m), 725 (m), 715 (w), 625 (s), 615 (w), 532 (w), 505 (w), 442 (m), 360 (w) cm⁻¹, MS (CI CH₃⁺): 637 (M - 1)⁺, the experimental (M - 1)⁺ ion matched the simulated spectrum beautifully. Crystal data (-95°C): triclinic, $P\bar{1}$, $a = 9.8707(17)$ Å, $b = 12.9348(17)$ Å, $c = 13.1081(20)$ Å, $\alpha = 68.12(11)^\circ$, $\beta = 83.19(15)^\circ$, $\gamma = 84.39(14)^\circ$, $V = 1539.5$ Å³, $Z = 2$, $d(\text{calcd}) = 1.39$ g cm⁻³, $\mu = 32.456$ cm⁻¹, crystal size, $0.33 \times 0.36 \times 0.22$ mm, Mo K α ($\lambda = 0.71073$ Å). The 4012 raw intensity data were reduced to structure factor amplitudes and their ead's by correction for background, scan speed, and Lorentz and Polarization effects.^{8d} A 2.75% linear decay in three standard reflections was observed, and the data were corrected. A three-dimensional Patterson synthesis revealed the position of the Yb, Al, and Si atoms, and the remaining atoms were located by Fourier techniques. An empirical absorption correction using azimuthal scan data was applied.^{8d} The final residuals for 245 variables refined against 3814 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0169$, $R_w = 0.0258$, and GOF = 1.857. The R for all 4012 data was 0.019. (c) The hydrogen atoms on C(2) and C(6) were located in the Fourier difference maps, but they were not refined since we did not collect high angle data ($2\theta > 45^\circ$). (d) Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* 1984, 23, 432.

(9) NMR: ¹H (PhMe-*d*₈, +30 °C), δ 1.38 (t, $J = 7.8$ Hz, 18 H), 0.34 (q, $J = 7.8$ Hz, 12 H), 0.27 (s, 36 H). Lowering the temperature resulted in severe line broadening by -40°C . Further cooling did not result in better resolution. The infrared spectrum was essentially identical with that of the trimethylaluminum homologue.

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