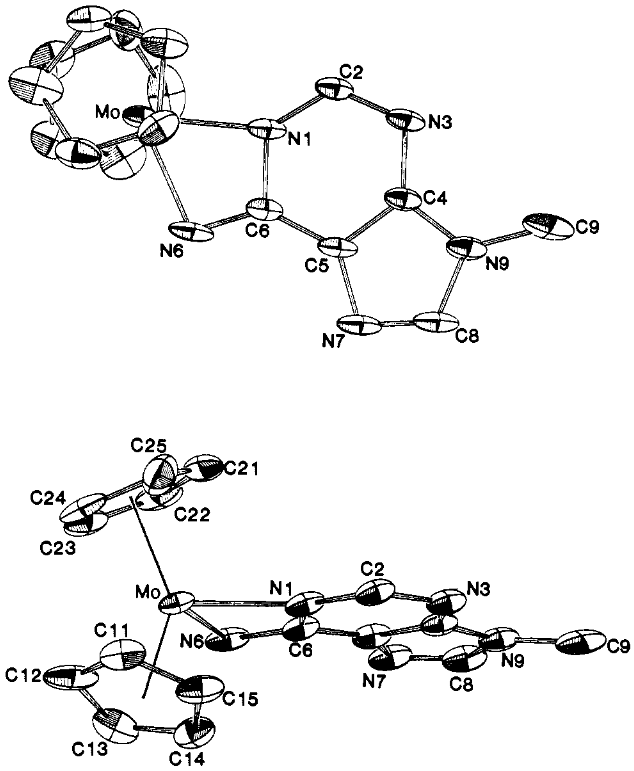

Figure 2. Two perspective views of the molecular structure of $Cp_2Mo(9\text{-methyladenyl})^+PF_6^-$ (**3**) showing the cationic portion. Important bond distances (Å) and angles (deg) are as follows: Mo–N(1) = 2.173 (3), Mo–N(6) = 2.145 (3), C(6)–N(1) = 1.382 (5), C(6)–N(6) = 1.314 (5), Mo–ring centroid = 2.005 (5) (av), N(1)–Mo–N(6) = 60.9, N(6)–C(6)–N(1) = 108.5 (3), ring centroid–Mo–ring centroid = 128.9 (2), Mo–N(6)–C(6) = 97.0 (2), Mo–N(1)–C(6) = 93.5 (2).

be separated by fractional crystallization.[14] Complex **3** can be quantitatively converted to **4** by heating at 80 °C, suggesting that **3** is the kinetic product. ^1H NMR spectral parameters (Table I)[15] indicate $N(6)H_2$ deprotonation and HN6⁻,N1 and HN6⁻,N7 chelation in **3** and **4**, respectively. Diffraction results on **3**[16] confirm this unusual chelation mode (Figure 2). While the Cp_2Mo portion of **3** is unexceptional,[17] the four-membered chelate ring contains a highly acute (60.9 (1)°) N(1)–Mo–N(6) angle and short (vide infra) Mo–N(6) (2.145 (3) Å) and Mo–N(1) (2.173 (3) Å) distances. The N(6)–C(6)–N(1) angle has contracted 11° (toward Mo) from that in free 9-MeAd.[18] These results can be compared with ∠O–Mo–N values of 74.1 (5)° and 73.4 (6)° in $(Cp_2MoNH_2\text{-}CH_2COO)^+Cl^-$ and $(Cp_2MoNH(CH_3)CH_2COO)^+Cl^-$, respectively.[16a] The corresponding Mo–N distances in these latter complexes are 2.26 (1) and 2.23 (2) Å, respectively, and that in $[Cp_2MoNH_2CH(CH_2S)CO_2H]^+Cl^-$, 2.256 (7) Å.[16a] The recent elucidation of 1-methylcytosine HN4⁻,N3–Pt(IV) coordination[19] constitutes the only other diffractometric report of such a four-membered nucleobase chelate ring.

Table I. NMR Spectroscopic Data for Free Ligands and Molybdenum Complexes[a]

compound	H2[d]	H8[d]	C_5H_5[d]	N(6)H[d]	P
5′-dAMP[b]	7.92 (1)	8.32 (1)			4.8
Cp_2Mo(5′-dAMP) (**2**)[b]	7.97 (1)	8.11 (1)	5.31 (5)		38.0
			5.68 (5)		
5′-dAMP[c]	8.12 (1)	8.44 (1)		7.30 (2)	4.8
Cp_2Mo(5′-dAMP) (**2**)[c]	8.13 (1)	8.30 (1)	5.76 (5)	7.26 (2)	42.0
			5.71 (5)		
9-methyladenine[c]	8.14 (1)	8.08 (1)		7.17 (2)	
$Cp_2Mo(9\text{-}MeAd^-)^+PF_6^-$ (**3**)[c]	7.64 (1)	8.00 (1)	5.84 (10)	6.90 (1)	
$Cp_2Mo(9\text{-}MeAd^-)^+PF_6^-$ (**4**)[c]	8.16 (1)	8.32 (1)	5.88 (10)	6.46 (1)	

[a] ^1H data vs TMS; ^{31}P data vs 85% H_3PO_4. [b] In D_2O at pD ~ 7.4. [c] In DMSO-d_6. [d] Number in parentheses denotes number of protons by integration.

These results illustrate the considerable kinetic and architectural fine structure of Cp_2MX_2–nucleobase/nucleotide complexation. Complementary studies with oligo- and polynucleotides are now in progress.

Acknowledgment. This research was supported by NSF (Grant CHE8306255). L.Y.K. is a Dee and Moody Fellow.

Supplementary Material Available: X-ray experimental details including positional and anisotropic displacement parameters and bond lengths and angles (8 pages); listings of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(14) (a) **3**: Anal. Calcd for $C_{16}H_{16}N_5MoPF_6$: C, 37.01; H, 3.11; N, 13.49; P, 5.97. Found: C, 35.80; H, 3.00; N, 13.32; P, 5.94. **4**: Found: C, 36.89; H, 3.07; N, 13.38; P, 5.89.

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(16) Crystals of **3** from ether diffusion into an acetone solution are triclinic ($P\bar{1}$) with cell dimensions as follows: a = 10.682 (3) Å, b = 11.619 (5) Å, c = 7.701 (5) Å, α = 106.93 (4)°, β = 96.32 (3)°, and γ = 86.98 (3)°; V = 908.64 Å^3, Z = 2, d_{calcd} = 1.73 g cm^{-3}. With use of a crystal of dimensions 0.30 × 0.20 × 0.15 mm, 4212 reflections were measured at values of $h,\pm k,\pm l$ in the range 3.0° ≤ 2θ ≤ 55°, using Mo Kα radiation. Of these, 3614 had $F_o > 3\sigma(F_o)$. The structure was solved by direct methods and Fourier techniques. Full-matrix least-squares refinement on 280 variables, using the SHELX76 package of programs with the Mo, and all C and N atoms anisotropic, converged with residuals R = 0.045 and R_w = 0.05. The PF_6^- anion is threefold disordered around the nondisordered phosphorus atom.

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Synthesis and X-ray Crystal Structure of a Heterobimetallic Ethyl-Bridged Organoaluminum Complex: $(C_5Me_5)_2Sm(\mu\text{-}C_2H_5)_2Al(C_2H_5)_2$[1]

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Since the discovery of Ziegler–Natta catalytic polymerization of alkenes,[2] the chemistry of organoaluminum complexes in association with other metallic species has been of great interest. Numerous heterobimetallic organoaluminum containing molecules have been synthesized, structurally characterized,[3–6] and studied

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(1) Presented in part at the 2nd International Conference on the Chemistry and Technology of the Lanthanides and Actinides, Libson, Portugal, April 1987; L(II)I and at the 193rd National Meeting of the American Chemical Society, Denver, Co, April 1987; Paper INOR 227.

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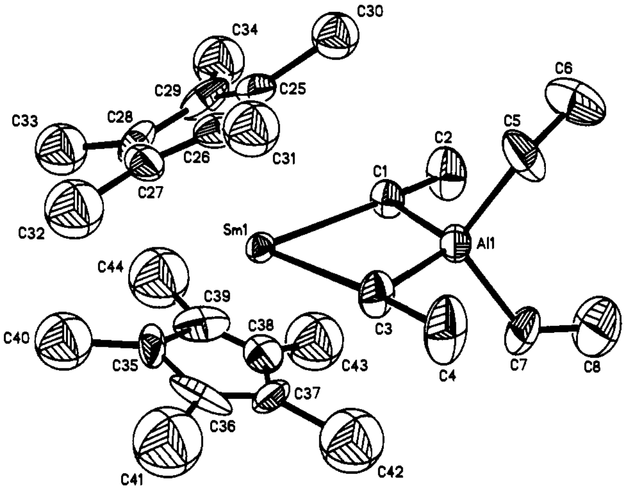

Figure 1. ORTEP diagram of molecule 1 of $(C_5Me_5)_2Sm(\mu\text{-}Et)_2AlEt_2$, **1**.

in efforts to learn more about the catalytic process.[1-7] A key role for the organoaluminum reagent in many mechanistic schemes is the alkylation of a transition-metal center. Intermediates which involve bridging, three-center, electron deficient M–(μ-R)–Al linkages (R = alkyl) have been envisioned for this reaction and structurally characterized model compounds are known for R = CH_3.[4,5] Although triethylaluminum is frequently used in Ziegler–Natta systems, no crystallographic studies have been reported for species containing a three-center, electron deficient *ethyl* bridge between aluminum and a transition or f orbital metal.[8] Exploratory synthetic studies of the chemistry of the unusual bent metallocene $(C_5Me_5)_2Sm$[9] have provided such a species, and we report here the details of its synthesis and structure.

Addition of excess $AlEt_3$ [2 mL, 0.25 M in hexane] by syringe to an emerald green toluene solution of $(C_5Me_5)_2Sm$[9] (150 mg, 0.356 mmol) in an ether-free glovebox caused no immediate reaction. However, after approximately 3 h the solution turned a deep red color, and an aluminum mirror was deposited on the glassware. The reaction mixture was centrifuged, the clear red solution was decanted, and the solvent was removed by rotary evaporation to provide the product as a red oil. Cooling a hexane solution of the red oil to −20°C allowed isolation of deep red crystals of $(C_5Me_5)_2SmAlEt_4$ (**1**) in approximately 55% isolated yield (110 mg) according to eq 1. Red crystals of **1** were examined by spectroscopic, magnetic, and analytical methods which provided data consistent with the above formulation.[10]

$$(C_5Me_5)_2Sm + \text{excess } AlEt_3 \rightarrow \underset{\mathbf{1}}{(C_5Me_5)_2SmAlEt_4} + Al \qquad (1)$$

The room temperature ^{1}H NMR spectrum[10] of **1** in toluene-d_8 is complex, exhibiting a peak at δ 0.38 ppm ($\Delta\nu_{1/2}$ = 7.2 Hz) for C_5Me_5 and a series of broad, featureless peaks in the range of 0 to −4 ppm ($\Delta\nu_{1/2}$ = 170–620 Hz). The peak width is not only partially dependent on the paramagnetic nature of Sm^{3+} but also is indicative of dynamic exchange processes in solution. As the temperature is raised, the upfield peaks are observed to shift and coalesce, reaching high-temperature saturation at 80 °C. Unfortunately, the 80 °C spectrum is not definitive since the peaks remain broad and featureless. At −10 °C, **1** precipitates from solution, precluding a thorough low-temperature analysis. Likewise, the ^{13}C NMR spectrum is not definitive, although resonances consistent with the C_5Me_5 and ethyl carbon atoms are observed.[10]

A single-crystal X-ray diffraction study unequivocally determined the rare ethyl-bridged structure of this molecule.[13] As shown in Figure 1, the structure consists of a $(C_5Me_5)_2Sm$ bent metallocene unit coordinated to an $Et_2Al(\mu\text{-}Et)_2$ moiety via two bridging methylene carbon atoms. The structure has three crystallographically independent $(C_5Me_5)_2Sm(\mu\text{-}Et)_2AlEt_2$ molecules in the asymmetric unit whose averages are used in the following discussion.

The samarium portion of **1** is typical of trivalent $(C_5Me_5)_2Sm(X)(Y)$ complexes.[14] The 2.712 (2) Å average Sm–C(C_5Me_5) distance and the 134.2° average (C_5Me_5 centroid)–Sm–(C_5Me_5 centroid) angle are normal, and the two bridging methylene carbon atoms lie in a plane which bisects the (C_5Me_5 centroid)–Sm–(C_5Me_5 centroid) angle. The average Sm–C(CH_2) distance [i.e., Sm(1)–C(1), Sm(1)–C(3), etc.] of 2.662 (4) Å is longer than the Sm–C terminal distances in $(C_5Me_5)_2Sm(C_6H_5)(THF)$,[15] 2.511 (8) Å, and $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$,[16] 2.528 (8) Å, as expected for bridging versus terminal lanthanide–carbon bonds.[17] The Sm–C distances are clearly within bonding range, however. Hence **1** is not simply a $[(C_5Me_5)_2Sm]^+[AlEt_4]^-$ ion pair. The Sm–C–C angle is a remarkable 170 (4)°.[18]

The structural parameters involving aluminum fall into two sets: one for the bridging ethyl groups and one for the terminal ethyl ligands. The average Al–C(CH_2) bridging distance (i.e., Al(1)–C(1), Al(1)–C(3), etc.) of 2.106 (5) Å is significantly longer than the Al–C(CH_2) terminal distance (i.e., Al(1)–C(5), Al(1)–C(7), etc.) of 2.032 (6) Å. The latter terminal distance is comparable to the Al–C(CH_2) distance of 2.023 (6) Å found in $(LiAlEt_4)_n$ (**2**), which was described as an array of alternating Li^+ and Et_4Al^- ions.[20] The 104° average Al–C–C angle in the bridging ethyl groups of **1** [e.g., Al(1)–C(1)–C(2)] is smaller than the 121° average Al–C–C angle in the terminal ethyl ligands [e.g., Al(1)–C(5)–C(6)]. In **2**, the Al–C–C angle is intermediate between these values: 109.2 (5)°. The average C–Al–C angle in **1**, 109.3 (2)°, is similar to that in **2** 110.1 (6)°.

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(10) $\chi_M = 1110 \times 10^{-6}$ cgs; $\mu_{eff} = 1.6\ \mu_B$ which is typical for Sm(III);[11] ^{1}H NMR (toluene-d_8) shift ($\Delta\nu_{1/2}$ in Hz) 0.38 (7) (s, C_5Me_5), −1.5 (620), −2.7 (150), −3.7 (170); ^{13}C NMR (toluene-d_8) 19.75 (C_5*Me*$_5$), 120.22 (*C*$_5$Me$_5$). Anal. Calcd for $SmAlC_{28}H_{50}$: Sm, 26.66; Al, 4.78; C, 59.63; H, 8.93. Found: Sm, 26.78; Al, 6.75; C, 58.74; H, 9.30. Attempts to find the ethyl carbons using DEPT NMR techniques[12] did not prove conclusive. However, peaks were located at 19.24, 24.54, and 70.33 ppm, which may indeed be the signals for the bridging CH_2 (70.33), terminal CH_2 (24.54), and terminal methyl (19.24) carbon atoms. IR (KBr) 2870 s, 2905 s, 2940 sh, 1760 br, m, 1445 m, 1410 w, 1382 w, 1265 w, 1230 w, 1185 w, 1090 w, 1020 sh, 990 m, 945 w, 755 m, 700 w, cm^{-1}.

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The mechanism by which **1** is formed may parallel the reaction of alkali metals with AlR_3 to form AlR_4^- salts (eq 2; M = alkali metal).[21] Parallels between the alkali metals and $(C_5Me_5)_2Sm$

$$3M + AlR_3 \rightarrow Al + 3RM \xrightarrow{3R_3Al} 3MAlR_4 + Al \qquad (2)$$

and its solvated analogue $(C_5Me_5)_2Sm(THF)_2$ have been noted previously.[22] If the formation of **1** follows the sequence in eq 2, the intermediate analogous to RM would be $(C_5Me_5)_2SmC_2H_5$. This complex would be expected to be highly reactive and could readily decompose via β-hydrogen elimination. The less than quantitative yield of **1** from reaction 1 may be the result of decomposition of a $(C_5Me_5)_2SmEt$ intermediate. Consistent with this is the fact that when the reaction was run on a vacuum line attached to a Toepler pump, small amounts of ethene were obtained (0.2 equiv per equivalent of $(C_5Me_5)_2Sm$).

The synthesis of **1** provides an opportunity to study the chemistry of a fully characterized ethyl bridged organoaluminum complex. The reactivity of **1**, which includes polymerization of ethylene and interaction with CO, is under study.

Acknowledgment. We thank the National Science Foundation for support of this research and the University of California for a Presidential Postdoctoral Fellowship (to L.R.C.). Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495.

Supplementary Material Available: Tables of crystal data, bond distances, angles, final fractional coordinates, thermal parameters, fully numbered plots of molecules 1–3 (12 pages); listing of observed and calculated structure factor amplitudes (56 pages). Ordering information is given on any current masthead page.

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Fast Interfacial Electron Transfer between Cytochrome *c* Peroxidase and Graphite Electrodes Promoted by Aminoglycosides: Novel Electroenzymic Catalysis of H_2O_2 Reduction

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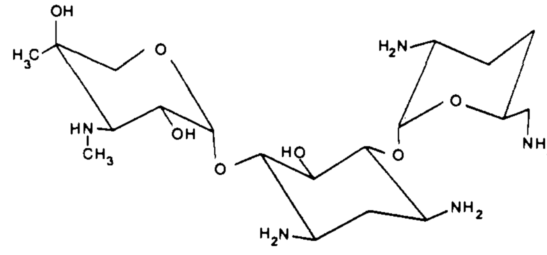
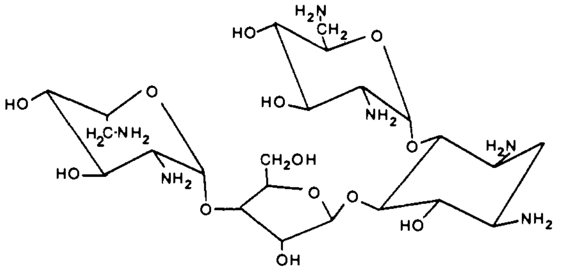
We have achieved fast interfacial electron transfer between cytochrome *c* peroxidase (CCP) and an electrode, thus establishing a fully operational *electrochemical* analogue of the archetypal biological redox system. In the latter,[1-3] CCP reacts rapidly with H_2O_2 to give a two-equivalent oxidized form (compound I) containing oxyferryl heme (Fe^{IV}=O) and a protein-bound radical; two rapid reactions with cytochrome *c* (II) then regenerate the Fe(III) form via an oxyferryl intermediate, compound II. Long-range electron transfer occurs across specific 1:1 complexes[4-6] stabilized by complementary polar interactions between lysines ($-NH_3^+$) located around the partly exposed heme edge region of cytochrome *c* and a ring of acidic ($-CO_2^-$) residues on CCP. In our electrochemical system we use aminoglycosides, gentamycin or neomycin, which contain spatial arrangements of $-NH_3^+$ groups on a quasi-rigid framework, to promote the docking of CCP at a pyrolytic graphite edge (PGE) surface. As demonstrated by DC voltammetry (Figure 1), the system reductively exhausts H_2O_2 at high potentials.



gentamycin C_{1a} base



neomycin B base

A. In electrolyte alone (0.1 M KCl, 5 mM HEPES, pH 7.0) H_2O_2 shows no faradaic activity at a polished PGE between +850 and +250 mV vs NHE.[7] Upon addition of CCP[8] (0.2 μM) and gentamycin (5 mM) at 0 °C, a cathodic wave develops, ultimately (with 56 μM H_2O_2) to peak sharply at +575 mV.[9] Times required to achieve optimal peak potential vary with [CCP], being typically >15 min (0.1 μM) to <3 min (1.0 μM). Corresponding peak currents, corrected for background, are remarkably invariant. No response occurs without gentamycin, and 1 or 5 mM levels yield the same result, indicating saturation. Neomycin acts similarly but $Cr(NH_3)_6^{3+}$, a potent promoter of the electrochemistry of small electron-transfer proteins,[10] is much less effective.[11] Free protoporphyrin IX, substituted for CCP, is inactive. Alone, neither aminoglycoside responds or catalyzes H_2O_2 reduction between −800 and +950 mV.

B. Peak currents are proportional to $[H_2O_2]$ up to at least 70 μM. Peak potentials *increase* with decreasing $[H_2O_2]$, reaching typically ca. +750 mV at 11 μM (scan rate = 10 mV s^{-1}, [CCP] = 0.2 μM).

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(9) Between sweeps the diffusion layer was replenished by brief "microflea" stirring at open circuit potential. The electrochemistry is stable for at least 1 h at 0 °C, but instability is a problem at 25 °C. This may be due to thermal denaturation at the electrode surface or perhaps formation of excessive enzyme coverage which restricts efficient movement of electrons and substrate.

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(11) A broad ill-defined response developed during incubation times of 15–60 min with use of $Cr(NH_3)_6^{3+}$ in the concentration range 1–15 mM.

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