to the plane of the metal surface and *a bulk packing density*.

Further evidence for lipid organization comes from the measured site density of **1**. Treatment of the lipid-modified surface with 5.4 M HCl for 6 h at 40 °C and subsequent analysis of the solution for phosphorus[12] indicated the presence of $2.7 \times 10^{14} \pm 1.4 \times 10^{14}$ lipids cm^{-2} of geometric surface [average of six preparations, using three different batches of gold-coated slides and lipid concentrations in the range of 4×10^{-7} to 4×10^{-5} M]. By use of one freshly prepared batch of slides and a constant lipid concentration (4×10^{-5} M), five independent surface treatments afforded a phosphorus content of 1.8 ± 0.25 lipids/cm^2. In a control experiment, a gold-coated slide was treated with a 10^{-5} M methanolic solution of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine; examination by ellipsometry and phosphorus analysis indicated negligible lipid association.

Scanning electron microscopy of untreated and **1**-modified gold slides (70000×) did not reveal any detectable morphology. To a first approximation, the true area of these surfaces can be estimated to be within a factor of 2 of the geometrical surface.[7] Based on the measured collisional area of **1** (82 Å^2/molecule, film balance determination), a tightly packed monolayer contains 1.2×10^{14} lipids cm^{-2}. While the uncertainty of the true surface area for each gold sample precludes a quantitative assessment of the compactness of monolayers of **1** on gold, the observed loading is clearly in the range expected for a packed monolayer.

Attempted "horizontal lifting"[13] of a monolayer of **1**, formed at the air-water interface with a surface pressure of 16 dyn/cm and a subphase temperature of 20 °C (collapse point is ca. 33 dyn/cm), onto a gold slide resulted in a severe and unavoidable disruption (observable waves) of the quiet liquid surface, due to the strong hydrophilicity of the surface. The observed film thickness and Θ_a for the transferred monolayer were 17 ± 3 Å and 58 ± 6°, respectively. Taken together; this lower film thickness, higher value of Θ_a, and higher standard deviation of Θ_a, relative to the spontaneously assembled monolayer of **1** on gold, indicate a less organized and less homogeneous assembly. In view of the hydrophilic nature of the gold, meaningful monolayer transfer, via vertical dipping from air into water, was precluded. Interestingly, however, monolayers of **1** transferred to gold slides via pulling from water into air exhibited an initial Θ_a of 44°; after 42 h in air, Θ_a reached a limiting value of 25 ± 5°. In contrast, when a clean hydrophilic glass slide was used as the substrate, a *stable* surface ($\Theta_a = 55°$) was obtained. These results imply that **1** "flips over" on gold with time, to form a more thermodynmically favored assembly in which the thiol moiety binds to gold and the more polar choline head group extends away from the surface.

In preliminary studies, we have found that spontaneous assembly of 1-palmitoyl-2-(16-mercaptohexadecanoyl)-*sn*-glycero-3-phosphocholine (**2**) on gold using a 4×10^{-6} M methanolic solution of the lipid resulted in a loading, Θ_a, and film thickness of 1.0×10^{14} lipids cm^{-2}, 47 ± 6°, and 17.7 Å, respectively (CPK models predict a maximum length of 28 Å). These results imply a looser packed monolayer compared with **1** and that each "leg" of the lipid needs to be adsorbed onto the gold surface for maximal chain packing.

Efforts which are now in progress are aimed at gaining further insight into the degree of compactness, uniformity, and orientation of monolayers of **1** and **2** (and related analogues) on gold and exploiting such surfaces as biomembrane models.[14]

Acknowledgment. We thank Drs. Ralph Nuzzo (Bell Laboratories) and Dave Allara (Bell Communications Research) for essential discussions concerning the adsorption properties and surface chemistry of gold.

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Synthesis and X-ray Crystal Structure of a Soluble Pentametallic Organoyttrium Alkoxide Oxide Complex, $(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)$[1]

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As part of a general program to make oxygen-stabilized organoyttrium and organolanthanide complexes, we have examined synthetic routes to the simple prototypical organometallic alkoxide complex dicyclopentadienylyttrium methoxide (**1**). Although **1** can be produced in the reaction of $[(C_5H_5)_2Y(\mu\text{-}H)(THF)]_2$ with CH_3OH or CH_2O, the potentially more direct synthesis from $(C_5H_5)_2YCl(THF)$ and alkali-metal methoxides can take a different course. A remarkable polymetallic oxide complex can be obtained whose synthesis and structure may have important implications in organometallic oxide/alkoxide chemistry.

$(C_5H_5)_2YCl(THF)$[3] reacts with desolvated $KOCH_3$[5] in THF overnight at 30 °C to form a mixture of products containing some dicyclopentadienylyttrium methoxide.[6] By use of the solvate $KOCH_3 \cdot CH_3OH$,[5] complex **1** can also be obtained from $(C_5H_5)_2YCl(THF)$ at −78 °C, but when the reaction is run at 30 °C for a 2-day period, the formation of complex **1** is not observed. Instead, a complex, **2**, which is a minor component at low temperature, is obtained as the predominant product. **2** can be isolated in 60–70% yield by removing THF from the reaction mixture and extracting with toluene.[7] The ^1H NMR spectrum of **2** contains two cyclopentadienyl resonances in a 4:1 ratio and two methoxide resonances of equal intensity corresponding to a total of eight methoxide ligands per five cyclopentadienyl groups.[8] **2** is soluble in hexane and sublimes at 260 °C at 10^{-5} torr.

X-ray quality crystals of **2** were grown from toluene at 30 °C and the complex was identified as $(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)$ by X-ray diffraction.[9] Figure 1 shows that **2** is comprised of a square pyramid of yttrium atoms each of which is coordinated to one C_5H_5 group. Upon each triangular face of the square pyramid is a triply bridging methoxide ligand and attached to each edge of the square base is a doubly bridging

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(1) Presented in part at the 191st National Meeting of the American Chemical Society, New York, NY, April 1986; paper INOR 291.

(2) Alfred P. Sloan Research Fellow.

(3) Prepared from YCl_3 and NaC_5H_5 as previously described[4] except for the following. Solvent is removed from the crude reaction mixture and the solids are washed with hexane. The solids are extracted with THF and the THF extract is filtered or centrifuged leaving the NaCl behind.

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(5) The potassium methoxide is prepared in THF by adding potassium to CH_3OH previously distilled from a vessel containing CH_3OH which was dried first with CaH_2 and then with sodium. Removal of THF and excess CH_3OH by rotary evaporation leaves $KOCH_3 \cdot CH_3OH$. This can be desolvated by heating at 80–90 °C under vacuum for several hours. The methoxides were characterized by ^1H NMR and elemental analysis.

(6) Anal. Calcd for $YC_{11}H_{13}O$: Y, 35.54. Found (complexometric analysis[4]): Y, 35.0. ^1H NMR (THF-d_8) δ 6.17 (s, 10 H, C_5H_5), 3.34 (s, 3 H, OCH_3); (C_6D_6) δ 6.14 (s, 10 H, C_5H_5), 2.84 (s, 3 H, OCH_3).

(7) Typically, in the glovebox, $[(C_5H_5)_2YCl]_2$ (250 mg, 0.49 mmol) dissolved in 8 mL of THF was added to a stirred suspension of $KOCH_3 \cdot CH_3OH$ (69 mg, 0.68 mmol) in 8 mL of THF. After 2 days, the mixture was centrifuged, the supernatant was decanted, the solvent was removed, and the solids were extracted with toluene. Removal of toluene gives **2** (127 mg, 63%). The yield and purity of the product is quite sensitive to reaction time, reaction temperature, purity of starting materials, and the alkali-metal salt used.

(8) ^1H NMR (C_6D_6) δ 6.26 (s, 20 H, C_5H_5), 6.16 (s, 5 H, C_5H_5), 3.67 (s, 12 H, μ_3-OCH_3), 3.47 (s, 12 H, μ-OCH_3). IR (KBr) 3090 w, 2920 s br, 2810 s, 1457 m, 1258 m, 1154 w, 1072 s br, 1018 s br, 770 s br cm^{-1}. Anal. Calcd for $Y_5C_{33}H_{49}O_9$: Y, 42.98%. Found: Y, 41.0%. Attempts to obtain a melting point resulted in decomposition at 320 °C.

(9) The space group is monoclinic $P2_1/c$ with $a = 11.402$ (2) Å, $b = 19.502$ (3) Å, $c = 20.922$ (5) Å, $\beta = 95.41$ (2)°, $U = 4631$ (2) Å^3, and $D_{calcd} = 1.48$ g cm^{-3} for $Z = 4$. Full-matrix least-squares refinement on the basis of 2477 unique reflections with $I > 3\sigma(I)$ yielded a final $R = 0.087$, $R_w = 0.108$. All non-hydrogen atoms except those of the cyclopentadienyl rings and C1 were refined with anisotropic temperature factors.

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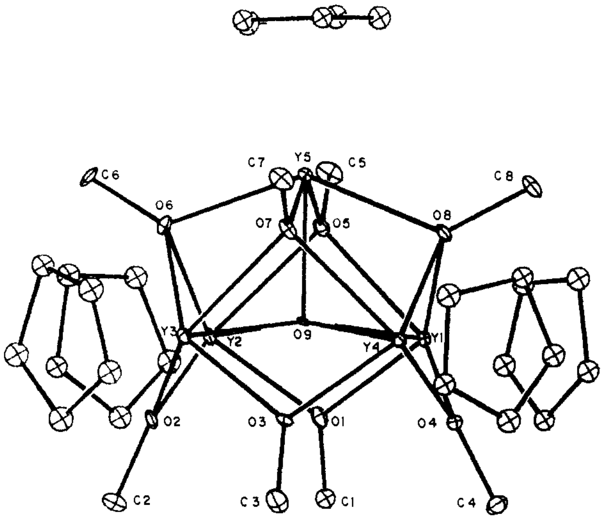

Figure 1. ORTEP drawing of the molecular structure of $(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)$. The probability ellipsoids have been reduced to 5% for clarity.

methoxide group. An oxide ligand is in the interior of the structure. Each metal interacts with five oxygen atoms and one cyclopentadienyl group for a formal coordination number of eight.

The structure is very regular. The four basal yttrium atoms are coplanar to within 0.006 Å. The four oxygen atoms associated with the μ_3-OCH_3 groups and the four oxygen atoms of the μ-OCH_3 ligands also form planes with coplanarity within 0.006 and 0.018 Å, respectively. These three planes are parallel as evidenced by the fact that the vector between the apical yttrium and the oxide ligand is perpendicular to each plane to within 0.9°. The oxide ligand in **2** is located 0.258 Å from the plane of the four basal yttrium atoms in the direction of the apical yttrium.

The Y–O distances in this pentametallic species can be compared with the 2.275 (3) and 2.290 (3) Å Y–O lengths in $[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$,[10] in which the yttrium atoms are also eight-coordinate. Also worth noting are distances of 2.299 (8) and 2.443 (8) Å in YVO_4[11] (eight-coordinate yttrium), 2.28 Å in Y_2O_3[12] (six-coordinate yttrium), and 2.305 Å in $UO_3{\cdot}3Y_2O_3$[13] (six-coordinate yttrium). The longest Y–O distances in **2** involve the connections of the basal yttrium atoms, Y(1)–Y(4), to the μ_3-OCH_3 groups with a range of 2.40 (2)–2.46 (2) Å (2.43 Å average). The μ_3-OCH_3 groups lie closer to apical yttrium atom, Y(5), with Y(5)–O lengths from 2.30 (2) to 2.35 (2) Å (2.33 Å average). As expected the doubly bridging distances are shorter: the eight Y(basal)–O(μ-OCH_3) distances average 2.22 Å with a 2.19 (2)–2.25 (2) Å range. The internal oxide is within 2.34 (2)–2.41 (2) Å of the basal yttrium vertices and is located 2.27 (2) Å from apical Y(5).[14]

The yttrium oxygen framework in complex **2** resembles a metal oxide lattice in which one metal vertex has been removed from the set of metals surrounding an oxide ion in an octahedral hole. As such, this soluble molecule may provide an interesting model for chemistry in a polymetallic oxide environment. From another point of view, this molecule can be compared to B_5H_9.[16] Both molecules have a square-pyramidal arrangement of trivalent element vertices with one terminal ligand each and both have four doubly bridging units around the base of the square. It remains to be determined if this is anything more than a structural coincidence.[17]

In any case, this molecule provides an interesting new example of inorganic self-assembly.[19] We find that this species appears in a variety of cyclopentadienyl yttrium alkoxide systems. The generality of such structures, the reactivity of this complex, and the origin of the oxide ligand are under investigation.

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Supplementary Material Available: Tables of crystal data, bond distances, angles, final fractional coordinates, and thermal parameters and a fully numbered ORTEP plot of **2** (8 pages); table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(17) For example, is there an electronic correlation? If one ignores, for electron counting purposes, the exopolyhedral doubly bridging groups in **2** and B_5H_9, does the $(\mu_3\text{-}OR)_4O$ unit hold five $(C_5H_5Y)^{2+}$ units together in a manner analogous to the way in which the $2n + 4 = 14$ electrons hold five BH^{2+} units in a nido conformation?[18]

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Observation of "Intramolecular" Ion–Molecule Reactions within Ionized Hetero Clusters of Methyl Chloride–Acetone

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Upon ionization,[1,2] large polyatomic molecules (such as halocarbons[3-5]) are usually excited and the ions undergo unimolecular decay. One might therefore expect a nascent cluster ion to fragment simply into a small ion and neutral molecular constituents, i.e., the "solvent" molecules. In contrast, as reported for methyl halide clusters,[6,7] extensive bond reformation (not merely "evaporation") can take place within the ionized clusters. This suggests that bimolecular (and possibly termolecular) reactions are occurring rapidly *within* a cluster ion. The major pathways observed can indeed be accounted for by known bimolecular ion–molecule reactions, previously studied by ICR[8-12] (and other methods).

Here we report the extension of our methyl halide cluster beam

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