a Pd–H intermediate is unlikely since isotope effect determinations in metal–hydride bond cleavage by external species give values of 0.4 at 65–100 °C.[15] The assumption that there is no significant contribution of tunneling to the observed isotope effects is established by plots of log k_H/k_D vs. $1/T$ which have slope and intercept corresponding to ΔE_a and A_H/A_D of 1.075 kcal and 0.844, respectively.[14b]

In summary, the present isotope effects, if analyzed under the model of More O'Ferrall, suggest that the formal insertion of palladium into the allylic carbon–hydrogen bond of methylenecyclohexane proceeds by removal of the hydrogen as a proton by a base which can be either internal or external to the palladium complex. The use of this information for improved preparation of (π-allyl)palladium complexes and the extension of this mechanistic approach to other insertions is under study.

Acknowledgment. We are grateful to the National Science Foundation for support of this work, to Professor L. M. Stephenson for information about work in his laboratory, and to Professor Jack Halpern for a helpful discussion.

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Preparation of the First Molecular Carbon Monoxide Complex of Uranium, $(Me_3SiC_5H_4)_3UCO$

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Received September 30, 1985

Migratory insertion of an anionic group onto coordinated carbon monoxide or an isocyanide is an important mechanistic postulate in organoactinide chemistry.[1] In contrast to transition metals, where carbon monoxide complexes abound, only three examples of carbon monoxide coordination to uranium have been observed in matrix isolation studies at cyrogenic temperatures. These studies showed that $U(CO)_6$ can exist below ca. 20 K and that ν_{CO} of 1961 cm^{-1} is similar to that found for $W(CO)_6$, ν_{CO} is 1987 cm^{-1} under similar conditions.[2a,b] The ν_{CO} is lowered substantially from gaseous CO (ν = 2145 cm^{-1}) which implies that uranium metal is a π-donor, though the bonds are either kinetically labile, thermodynamically weak, or both. In $UF_4(CO)$ the ν_{CO} of 2182 cm^{-1} at 20 K[2c] shows that the tetravalent compound does not engage in π-back-bonding to CO.[3] In another study, UO_2 has been shown to absorb CO at temperatures below 20 K; the CO stretching frequency was not measured.[2d] In this paper, we give evidence for $(Me_3SiC_5H_4)_3UCO$, the first molecular actinide complex of carbon monoxide, in solution and solid phase.

We have determined, on the basis of equilibrium constant measurements, that the ligand displacement series toward $(MeC_5H_4)_3U$ is $PMe_3 \approx P(OMe)_3$ > pyridine > tetrahydrothiophene > tetrahydrofuran and toward $(Me_3SiC_5H_4)_3U$ the series is EtNC > EtCN.[4a] The observation that phosphite and isocyanide ligands, which are generally classified as π-acceptor ligands,[4b] are good ligands toward the trivalent uranium metallocenes suggests that the uranium center can act as a π-donor. The extent of π-acceptance is difficult to judge on the basis of the infrared spectrum[5] as ν_{CN} of 2160 cm^{-1} in $(Me_3SiC_5H_4)_3UCNEt$[6a] is slightly higher in energy than that in free CNEt of 2151 cm^{-1}. In Cp_3UCN(cyclohexyl),[6c] ν_{CN} increases by 25 cm^{-1} on coordination. The purported π-base character of $(RC_5H_4)_3U$ led us to expose $(Me_3SiC_5H_4)_3U$ to one of the best π-acids known, carbon monoxide.

The deep green solution of $(Me_3SiC_5H_4)_3U$ in either pentane or hexane turned burgundy on exposure to carbon monoxide at 1 atm and 20 °C. Volumetric studies showed that the metallocene absorbs 1.0 ± 0.05 M equivalents of carbon monoxide at 25 °C. Exposure of the burgundy carbon monoxide complex to vacuum or purging the solution with argon regenerates the green, carbon monoxide free $(Me_3SiC_5H_4)_3U$. The carbon monoxide, vacuum cycle may be repeated several times without detectable decomposition. In addition, the burgundy solution may be stored for at least 2 years at −80 °C. Clearly, $(Me_3SiC_5H_4)_3U$ reversibly adsorbs a molar equivalent of carbon monoxide in hydrocarbon solution. Examination of the infrared spectrum of the burgundy solution using ^{12}CO shows ν_{CO} at 1976 cm^{-1}, with ^{13}CO ν_{CO} is 1935 cm^{-1}, and with $C^{18}O$ ν_{CO} is 1932 cm^{-1}. The predicted values for ν ^{13}CO and $C^{18}O$ are 1931 and 1930 cm^{-1}, respectively.[7]

The $(Me_3SiC_5H_4)_3U$ also reversibly absorbs ^{12}CO in the solid state. Exposure of $(Me_3SiC_5H_4)_3U$ in a KBr wafer to ^{12}CO at 1 atm results in the appearance of an absorption at 1969 cm^{-1} which completely disappears when the sample is evacuated for 1.5 h. Using ^{13}CO (99%) causes the absorption to shift to 1922 cm^{-1}.

We assume that the complex is carbon-bonded, as are all CO complexes, and the U–C–O unit is linear. Some support for this is derived from the X-ray crystal structure determination of $(Me_3SiC_5H_4)_3UCNEt$.[8] The averaged U–C(Cp) distance is 2.81 ± 0.03 Å, the U–Cp ring centroid distance is 2.53 Å, the U–C-(CNEt) distance is 2.57 (3) Å, the ring centroid–U–ring centroid angle is 118.6°, the ring centroid–U–C(CNEt) angle is 97°, and, most importantly, the U–C–N angle is 173.6 (2.0)° and the C–N–C (Et) angle is 170.2 (2.6)°.

A very crude molecular orbital model, based upon the symmetry orbitals, may be constructed that accounts for the reduction in the C–O stretching frequency in the complex. Assume that the molecule has C_{3v} symmetry. The e_1 and a $p\pi$ SALC'S for $(Cp)_3$ transform as $2a_1 + a_2 + 3e$. In C_{3v} symmetry the metal AO's transform as $a_1[s, z, z^2, z^3, x(x^2 - 3y^2)]$, $a_2[y(3x^2-y^2)]$, and $e[x, y, x^2 - y^2, xy, xz, yz, xz^2, yz^2, xyz$, and $z(x^2 - y^2)]$. If we let the nine Cp orbitals overlap with the available metal AO's then we have left over $3a_1 + 2e$ symmetry orbitals that contain three electrons to overlap with the filled σ-orbitals and the empty π-

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orbitals on CO. Since the π-orbitals on CO are C–O antibonding, population of these orbitals results in lowering of ν_{CO}. The lowering of ν_{CO} may be expressed in valence bond language by the two resonance structures.

$$Cp_3U\leftarrow\overset{-}{C}\equiv\overset{+}{O} \leftrightarrow Cp_3U{=}C{=}O$$

Acknowledgment. The work at Berkeley is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy, under Contract DE-AC03-76SF00098. We also thank Dr. F. J. Hollander, staff crystallographer at CHEXRAY, for solving the structure of $(Me_3SiC_5H_4)_3UCNEt$.

Supplementary Material Available: Listing of postional parameters, general temperature factors, and rms amplitudes of thermal vibration, ORTEP diagrams of the four molecules in the unit cell, tables of bond lengths and angles, crystal data and method of solution, and structure factor tables for $(Me_3SiC_5H_4)_3UCNEt$ (48 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of $[Au_6(o\text{-}CH_3C_6H_4CS_2)_6]$, a Novel Gold Cluster Compound

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Received August 22, 1985

Gold cluster compounds have been known for two decades, but only recently has research accelerated in this area, spurred on perhaps by the potential catalytic activity of such clusters. Beyond the relatively common dinuclear compounds containing two univalent linearly coordinated gold species, there is a growing number of compounds containing the Au_n^{x+} species with Au–Au bonds and an average oxidation state <1, where n = 4, 5, 6, 8, 9, 11, 13 (and at least one compound with n = 55) and x = 2 or 3.[1] The attached ligands are organophosphines and occasionally halide. Very recently[2] a tetranuclear dithioacetate (dta) complex, $[Au_4(dta)_4]$, was prepared and its X-ray structure showed it to contain four nearly equivalent Au–Au distances (averaging 3.013 Å) with the four gold(I) atoms at the vertices of a rhombus. An analogous dithiobenzoate (dtb) complex, Au(dtb), was also prepared,[2] but its structure could not be obtained.

Previously known compounds containing an Au_6 cluster have been either octahedra, as in $Au_6[P(p\text{-}CH_3C_6H_4)_3]_6^{2+}$,[3] or edge-sharing bitetrahedra, as in $\{Au_6[P(C_6H_5)_3]_6\}(NO_3)_2$,[4] and molecular orbital calculations have been completed[5] for such clusters where the metal atoms are situated on the surface of a regular polyhedron.

We now report the synthesis and crystal structure[6] of an entirely new type of gold cluster in which the six gold atoms in the (o-methyldithiobenzoato)gold(I) complex, $[Au_6(o\text{-}CH_3C_6H_4CS_2)_6]$, lie nearly in a plane with the bidentate ligands each attached to neighboring gold atoms and lying alternately above and below the plane.

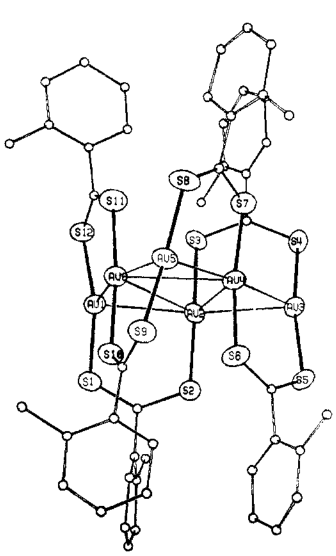

Figure 1. Gold hexamer, giving numbering scheme for Au and S. C atoms are arbitrarily small, and H atoms are omitted.

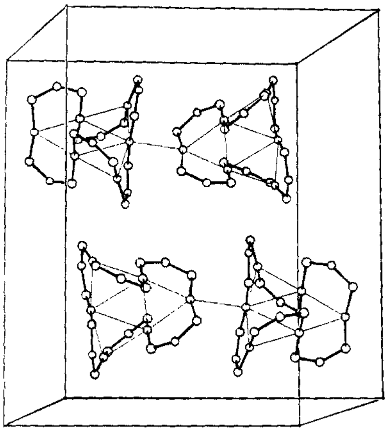

Figure 2. Unit cell, illustrating chains of hexamers along c axis, horizontal. Only S–C–C portions of ligands are shown.

The new gold compound was prepared by addition of $NaAuCl_4{\cdot}2H_2O$ to the $(n\text{-}Pr)_4N^+$ salt of the ligand, each dissolved in DMF, in a 2:1 ligand-to-metal molar ratio. A reddish orange solid separated after the warmed, stirred solution stood overnight. Dark red needles of the hexamer were formed by slow evaporation of a CS_2 solution.

The gold hexamer is illustrated in Figure 1. The six gold atoms of the central cluster are coplanar to within 0.14 Å. The odd-numbered Au atoms lie at the vertices of a triangle which is approximately equilateral with side 5.94 Å. The even-numbered Au atoms lie slightly outside the lines connecting these vertices, such that Au–Au distances around the periphery average 2.987 Å and alternate angles average 169.3° and 69.5°. The even-numbered Au atoms thus form a central triangle with edges Au2–Au4 3.240 (1), Au2–Au6 3.547 (1), and Au4–Au6 3.421 (1) Å. Each Au(I) forms two bonds in near linear fashion (S–Au–S angles range 160.7 (2)–174.6 (2)° and average 167.3°) to bridging ligands alternately above and below the cluster plane. Au–S distances range 2.283 (5)–2.305 (5) Å and average 2.296 Å. This ligand bridging pattern is analogous to that found in the tetramer $Au_4(dta)_4$, in which Au–Au distances average 3.013 Å, Au–S distances average 2.296 Å, and S–Au–S angles average 167.7°.[2]

The ligands are distinctly nonplanar. Aromatic rings are rotated with respect to dithiocarboxylate planes by angles ranging 60.4–87.1°, presumably as a result of the steric effects of 2-methyl substitution.

In addition to the multitude of Au–Au interactions within the hexameric cluster, a close intermolecular contact (Au3–Au6′, 3.195 (1) Å) exists, forming chains of hexamers along the direction

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(6) $(AuC_8H_7S_2)_6$, monoclinic $P2_1/c$, a = 14.803 (2) Å, b = 22.070 (3) Å, c = 17.464 (4) Å, β = 104.45 (1)°, Z = 4, R = 0.039 for 4250 observations.

0002-7863/86/1508-0336$01.50/0