



# Lanthanide and Actinide Chemistry and Spectroscopy

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*Lawrence Berkeley Laboratory*

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## PREFACE

The last published symposium on lanthanide and actinide chemistry, sponsored by the Division of Inorganic Chemistry and the Division of Nuclear Chemistry and Technology of the American Chemical Society, was held in 1966. The purpose of this earlier symposium was "to summarize the significant areas of current chemical research. . . ." The same statement may be made about the present symposium; however, the topics covered differ considerably. For example, there was not one chapter on organolanthanide or organoactinide chemistry in the earlier symposium, while in the present volume a goodly fraction of the chapters are on this topic. Further, the availability of significant amounts of the transcurium elements have led to the elucidation of the properties of the elements and their compounds with atomic numbers greater than 96. Also, as in other areas of science, new, sophisticated instrumentation is in the process of revolutionizing the quality and type of data obtained on the *f*-block elements and compounds.

This volume is intended to introduce the nonspecialist chemist to recent trends in lanthanide and actinide chemistry and spectroscopy, to summarize this work, and to identify directions for future studies. Inevitably, the chapters in this collection reflect (to some extent) the tastes of the organizer.

I would like to thank the participants in the symposium for their contributions, Dr. William T. Carnall for his help in organizing the spectroscopy part of the symposium, and Drs. John Fackler, Gary Long, and Leonard Interrante of the Division of Inorganic Chemistry for their efforts on behalf of the symposium and the publication of the proceedings. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this symposium.

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December 21, 1979.

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ORGANOACTINIDE AND  
ORGANOLANTHANIDE CHEMISTRY



# Nonclassical Activation of Carbon Monoxide by Organoactinides

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## Abstract

This article reviews recent results on the carbonylation chemistry of bis(pentamethylcyclopentadienyl) thorium and uranium hydrocarbyl and dialkylamide complexes. Facile migratory insertion of carbon monoxide into metal-carbon and metal-nitrogen bonds is observed. In several cases bihaptoacyl and bihapto-carbamoyl complexes were isolated and characterized by single crystal X-ray diffraction. The great strength of the metal-oxygen bonding in these species is evident in metrical and spectral data, as well as in the reaction chemistry, which is decidedly alkoxycarbene-like. In the case of the bis(pentamethylcyclopentadienyl) actinide dialkyls, the final carbonylation products are C-C coupled cis-1,2-enediolate complexes, while for the corresponding bis(dialkylamides), the products are bis(carbamoyl) species. Both types of compound have been characterized by X-ray diffraction. The carbon monoxide chemistry observed here may be of relevance to mechanistic discussions of catalytic CO reduction, especially that involving actinide oxide or actinide oxide supported catalysts.

## Introduction

Our recent research in actinide organometallic chemistry (1-5) has sought to exploit those features of f-element ions which differ from transition metal ions. The goal of our effort has been to discover and to understand to what degree the large ionic radii and f valence orbitals might foster a unique new organometallic chemistry. Exploration has been at both the chemical and physicochemical levels with the central issues concerning the properties of actinide-to-carbon sigma bonds and related functionalities. We have learned that the thermal stability and chemical reactivity of these linkages can be modulated to a considerable degree (and often in opposite directions) by changes in the supporting ligands within the actinide ion coordination sphere.

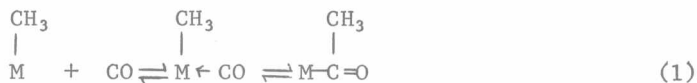
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Thus, while the coordinative saturation of the triscyclopentadienyl alkyls, alkenyls, alkynyls, and aryls (hydrocarbyls) of thorium and uranium,  $M(\eta^5\text{-C}_5\text{H}_5)_3\text{R}$  (6,7,8,9), affords considerably enhanced thermal stability over that of the simple homoleptic derivatives (10,11,12), it is at the expense of chemical reactivity.

In an effort to more finely tune the coordinative saturation of actinide hydrocarbyls and to provide greater than one metal-carbon bond for reaction, we have initiated an investigation of biscyclopentadienyl thorium and uranium chemistry (6,13,14). Systems based upon the pentamethylcyclopentadienyl ligand have proved to be some of the most interesting and form the basis of this article. The advantages of the  $\eta^5\text{-(CH}_3)_5\text{C}_5$  ligand are that it makes far greater steric demands than  $\eta^5\text{-C}_5\text{H}_5$  (thus reducing the number of large, bulky ligands which can be accommodated at the metal center) while imparting far greater solubility and crystallizability. It also appears that the methyl  $\text{C(sp}^3\text{)-H}$  bonds of this ligand are more inert with respect to scission than cyclopentadienyl  $\text{C(sp}^2\text{)-H}$  bonds; this has the effect of hindering a common thermal decomposition process, intramolecular hydrogen atom abstraction (7,8,15,16,17), hence of preserving the metal-to-carbon sigma bond for other chemical transformations. The net result is that pentamethylcyclopentadienyl actinide hydrocarbyls form the basis for an elaborate and extremely reactive new class of organometallic compounds.

The purpose of this article is to review the chemical, physicochemical, and structural properties of bis(pentamethylcyclopentadienyl) actinide compounds with respect to one reagent: carbon monoxide. The interaction of organometallic complexes with carbon monoxide is a subject of enormous technological importance. Vast quantities of acetic acid, alcohols, esters, and other important chemicals are presently produced using organic feedstocks, carbon monoxide, and homogeneous catalysts of the Group VIII transition metals (18,19,20). Much of this chemistry is now well-understood from model studies and is based upon the "classical" migratory insertion reaction of carbon monoxide into a metal-to-carbon sigma bond to form an acyl derivative (A) (equation (1)) (21,22,23). An industrially important example of this type of chemistry is the rhodium catalyzed hydroformylation cycle illustrated in Figure 1 (18). It is not clear, however, that the



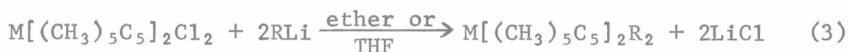
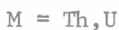
A

classic picture of CO activation established for low-valent, "soft", mononuclear, Group VIII metal complexes is complete or accurate in describing the mechanisms of Fischer-Tropsch (24-28), methanation (24-28), ethylene glycol synthesis (29), and other

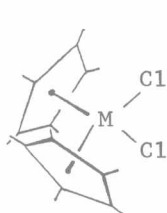
reactions in which drastic changes in the CO molecule such as facile deoxygenation and homologation are occurring. Clearly there is a necessity to develop new carbon monoxide chemistry and to elucidate new reaction patterns. Such research is essential to understanding the fundamental aspects of processes which will be of ever-increasing importance in an economy shifting to coal-based feedstocks. It will be seen that the carbonylation reactions of bis(pentamethylcyclopentadienyl) actinide hydrocarbyls and related compounds differ dramatically from the "classical" pattern and afford a better insight into the reactivity of carbon monoxide at metal centers which exhibit both high oxygen affinity and high coordinative unsaturation. In the sections which follow we consider first the chemical and then the structural aspects of this problem.

### Synthesis and Chemistry

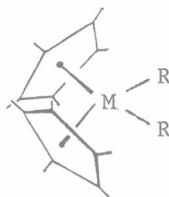
The sequence shown in equations (2) and (3) offers an effective route to monomeric, highly crystalline, thermally stable thorium and uranium organometallics with either one or two metal-



carbon sigma bonds (6,30,31). All compounds shown in these and subsequent reactions were thoroughly characterized by elemental analysis, cryoscopic molecular weight in benzene (solubility permitting), infrared and NMR spectroscopy, and, in several cases, by single crystal X-ray diffraction. Structures B and C are proposed for these new compounds in solution.



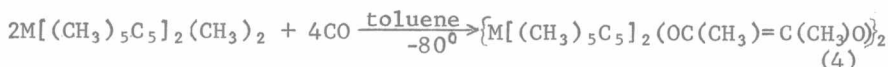
B



C



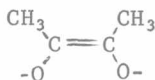
The reaction of  $\text{Th}[(\text{CH}_3)_5\text{C}_5]_2(\text{CH}_3)_2$  and  $\text{U}[(\text{CH}_3)_5\text{C}_5]_2(\text{CH}_3)_2$  with carbon monoxide is quite rapid (6,32,33). At  $-80^\circ\text{C}$  in toluene solution, these compounds absorb 2.0 equivalents of carbon monoxide (at less than one atmosphere pressure) within 1 hour. Upon warming to room temperature, the dimeric products (1) are isolated in essentially quantitative yield (equation (4)). The infrared spectra ( $\nu_{\text{C}=\text{C}} = 1655 \text{ cm}^{-1}$ ;  $\nu_{\text{C}-\text{O}} = 1252, 1220 \text{ cm}^{-1}$ ) as well as the single methyl resonance in the  $^1\text{H}$  NMR spectrum strongly suggests that C-C coupling of the inserted carbon monoxide



1a M = Th (colorless crystals)

1b M = U (brown crystals)

molecules has occurred to form enediolate moieties (D). Confirmation of this hypothesis was achieved by single crystal X-ray dif-



D

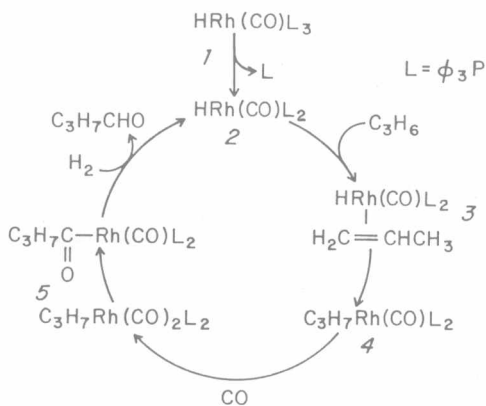
fraction studies on 1a (6,32,33). As can be seen in Figure 2, four carbon monoxide molecules have been coupled to form four thorium-oxygen bonds and, stereospecifically, two cis-substituted carbon-carbon double bonds. Two  $\text{Th}[(\text{CH}_3)_5\text{C}_5]_2$  units in the common "bent sandwich" configuration (34) are components of a ten-atom metallocycle. The enediolate ligands are essentially planar with genuine C-C double bonds ( $\text{C}_1-\text{C}_2 = \text{C}_1'-\text{C}_2' = 1.33(2)\text{\AA}$ ). Further structural remarks are reserved for the following section.

As a prelude to discussing additional f-element chemistry, it is at this point worth noting the results of carbonylation experiments with the biscyclopentadienyls of early transition metals. As is the case for the actinides, these elements in the higher oxidation states exhibit a great affinity for oxygen-donating ligands (35,36), and their chemistry will place further actinide results in a more meaningful perspective. Floriani and coworkers have carried out an extensive investigation of the reaction of biscyclopentadienyl titanium, zirconium, and hafnium bis-hydrocarbyls and halohydrocarbyls with carbon monoxide (equations (5) and (6)) (37,38,39). Only monocarbonylation is observed. Similar



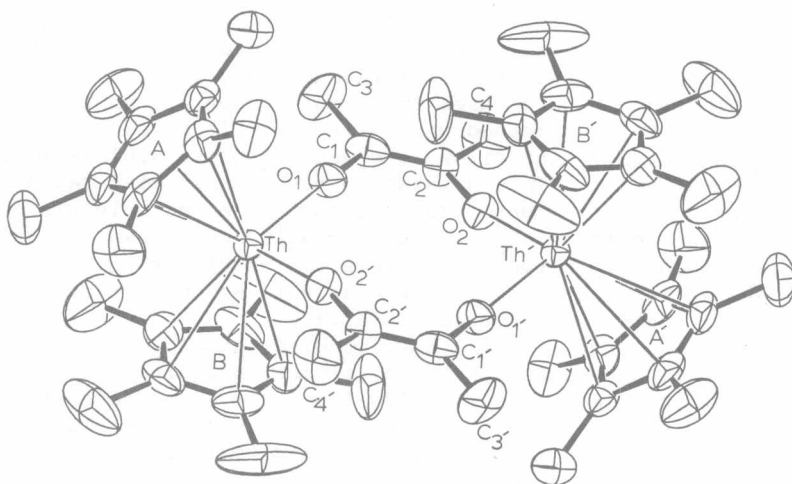
M = Zr, Hf

R =  $\text{CH}_3$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ , ( $\text{C}_6\text{H}_5$  not reversible)



Journal of Molecular Catalysis

Figure 1. A proposed mechanism for the rhodium-catalyzed hydroformylation of propylene (18)



Journal of the American Chemical Society

Figure 2. ORTEP drawing of the nonhydrogen atoms for the  $[Th(\eta^5-(CH_3)_5-C_5)_2(\mu-O_2C_2(CH_3)_2)_2]$  molecule, 1a. All atoms are represented by thermal vibrational ellipsoids drawn to encompass 50% of the electron density. Atoms of a given type labelled with a prime (') are related to those labelled without by the crystallographic inversion center midway between the two thorium atoms. The crystallographically independent pentamethylcyclopentadienyl ligands are labelled A and B, respectively (32).



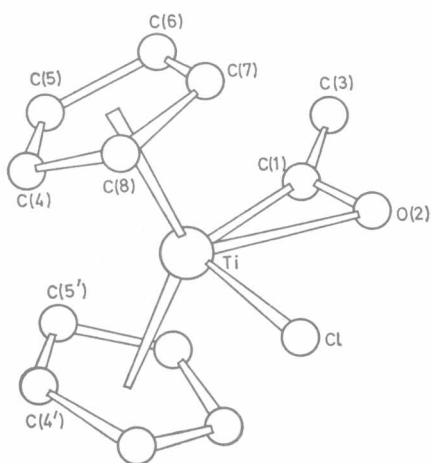
results have recently been reported by Lappert, *et. al.* (40). The insertion products are not simple acyls as A, but are bihaptoacyls (E, F) in which both carbon and oxygen atoms are bound to the metal ion. Such bonding is evidenced in the vibrational spectra of



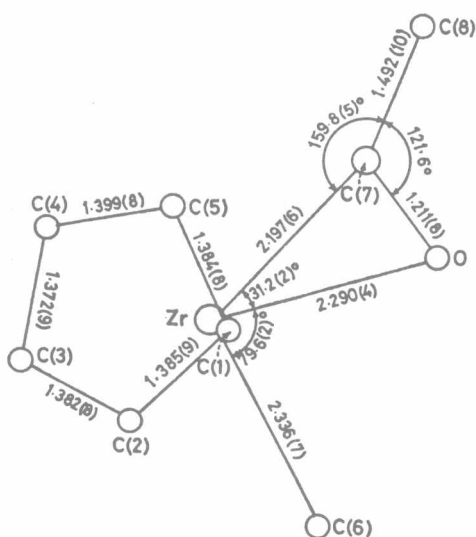
metal acyls by a lowering of the C-O stretching frequency. Thus, typical frequencies for nonconjugated transition metal monohaptoacyls fall in the range  $1630-1680 \text{ cm}^{-1}$  (41,42) while nonconjugated transition metal bihaptoacyls are generally in the range  $1530-1620 \text{ cm}^{-1}$  (37,38,39). This decrease in C-O force constant and presumably bond order can be rationalized in terms of the contribution of valence bond resonance hybrid F. The molecular structures of  $Ti(C_5H_5)_2(COCH_3)Cl$  (38) and  $Zr(C_5H_5)_2(COCH_3)CH_3$  (37) have been studied by X-ray diffraction and the results are presented in Figures 3 and 4, respectively. Although the acyl coordination is clearly bihapto, in both cases the metal-carbon distance is ca.  $0.1 \text{ \AA}$  shorter than the metal-oxygen distance. It should be noted that oxygen coordination allows the metal ions to achieve 18 electron valence shells. This saturation may be a crucial reason for the reluctance of the monoacyls to insert a second molecule of CO. Trends in the position of the equilibria in equations (5) and (6) can be explained in terms of the relative metal-carbon bond strengths in reactants and products as well as the extent of conjugation in the insertion product (37,38).

Lauher and Hoffmann (43) have studied the  $M(C_5H_5)_2R_2 + CO$  insertion reaction by extended Hückel molecular orbital calculations. The approach of the carbon monoxide lone pair is expected to be most favorable in the direction where there is best overlap with the  $M(C_5H_5)_2R_2$  lowest unoccupied molecular orbital. This direction is along the perpendicular to the ring centroid-metal-ring centroid plane (34,43,44,45) and is expected, after R migration, to yield a product of structure G, i.e., with the C-O vector pointing away from the unreacted R ligand. An unsolved problem concerning this insertion process is why only products of structure H have so far been identified (cf. Figures 3 and 4). A fleeting intermediate, very possibly of structure G, has been noted in the reaction of  $Zr(C_5H_5)_2(p-CH_3C_6H_4)_2$  with carbon monoxide (46).





Journal of the Chemical Society, Dalton Translation

Figure 3. Molecular structure of  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-COCH}_3)\text{Cl}$  (38)

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Figure 4. Molecular structure of  $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-COCH}_3)\text{CH}_3$  (37) viewed perpendicular to the  $\text{Zr}(\text{COCH}_3)(\text{CH}_3)$  plane (37)