Lawrence Berkeley National Laboratory
Recent Work

Title
Sandwiches, Half-Sandwiches and Related f-element Organometallics

Permalink
https://escholarship.org/uc/item/0p37w0c9

Authors
Streitweiser, A.
Boussie, T.R.

Publication Date
1990-10-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Sandwiches, Half-Sandwiches and Related f-element Organometallics

A. Streitwieser and T.R. Boussie

October 1990

DISCLAIMER

Sandwiches, Half-Sandwiches and Related f-element Organometallics*

Andrew Streitwieser and Thomas R. Boussie

Department of Chemistry, University of California and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley CA 94720 USA

ABSTRACT.-This survey of recent organo-f-element chemistry emphasizes the cyclooctatetraene compounds of the f-elements that now include sandwich structures of central actinides in the +3 and +4 oxidation states and lanthanides of +2, +3 and +4, as well as half-sandwich structures of uranium(IV). A new application of a bis-cyclopentadienyllanthanide compound is as a catalyst for a Mukaiyama reaction of silyl enolates with aldehydes.

The organometallic compounds of the f-elements involve mostly the use of cyclopentadienyl and cyclooctatetraene ([8]annulene] π-ligands. Much of the f-organometallic chemistry in our group has emphasized the [8]annulene ligand starting with the synthesis of uranocene, 1, in 1968.[1] Since the last comprehensive review of the f-organometallic chemistry of this ligand[2] the subject has expanded along several avenues. Today, [8]annuleneyl complexes of actinide, lanthanide, early transition-metal, alkali and alkaline earth elements in oxidation states ranging from +4 to +1 have been synthesized and many examples have been structurally characterized. The variety of

---

metals that bind cyclooctatetraene dianion as a ligand reflects the diversity of structural types that these compounds assume. Note that in the survey to follow at least seven structural classes of cyclooctatetraene dianion complexes are identified. Note also that in formula representations "COT" is intended to represent a general cyclooctatetraene dianion ligand; we do not distinguish between cyclooctatetraene itself and the variety of substituted cyclooctatetraenes also found in these complexes.

Survey of [8]annulenyl Metal Complexes

Among tetravalent metals the [8]annulenyl complexes fall into two categories: bis[8]annulenyl sandwich and mono-[8]annulenyl half-sandwich compounds. Sandwich compounds of the type $(COT)_2M$ have been reported for M = Th, Pa, U, Np, Pu, Ce and Zr. Crystal structures of Th, U and Ce complexes confirm their isostructural nature; the metal atom is sand-wiched between two planar (or nearly planar) cyclo-octatetraene dianion rings. The half-sandwich compounds can be grouped into the parent dichlorides $(COT)MCl_2(L)_n$, where M = Th, U and Zr, and their derivatives. These compounds are discussed in greater detail below.

The [8]annulene complexes of trivalent metals incorporate a wide range of structural types. Potassium salts of bis[8]annulene sandwich complexes of the type $K[(COT)_2M]$ have been reported for actinides (U, Np, Pu, Am) and lanthanides (Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, Lu) while the corresponding mono[8]annulene half-sandwich dimers, $[(COT)MCl.L]_2$ are reported only for lanthanides. Mixed ring systems of the type $(COT)MCp(L)_x$ and $(COT)MCp*(L)_x$, $(Cp* = C_5Me_5)$ which can be viewed as half-sandwich derivatives, are reported for Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Lu, Ti, Zr, Sc and Y. An additional half-sandwich derivative incorporating an internally-chelating ligand, $(COT)Lu(o-C_6H_4CH_2NMe_2).OC_4H_8$, has also been synthesized. Two additional structures round out this diverse group of compounds, $(COT)_3Ce_2$ and $(COT)_3Nd_2(THF)$.

For divalent metals only two structural classes have been confirmed. The first are the dipotassium salts of bis[8]annulene sandwich complexes, $K_2[(COT)_2M]$, M = Yb, Ca; for the second there is a single example of a mono[8]annulene half-sandwich complex, $(COT)Yb(NC_5H_5)3 \cdot NC_5H_5$.

The last class of [8]annulene complexes are the alkali metal salts. Their importance is underscored by the frequency of their use in the synthesis of many of the compounds described above. Dianion salts of all of the alkali metals have been reported. However, few structural analyses of this class of compound have been performed. Within those complexes for which structural information is known there is significant diversity of structural type, dependent primarily on the nature and stoichiometry of neutral coordinating ligands incorporated into the crystal. The general stoichiometry is $(COT)M_2(L)_x$. Structures have been reported where the coordinating ligands are diglyme, for example $[K(diglyme)]_2(COT)$ and $(COT)M_2.$-(diglyme) where M = K and Rb, and for tetrahydrofuran in $(COT)K_2\cdot(OC_4H_8)$.

The growing body of x-ray structure analyses of [8]annulenyl complexes facilitates a comparison of some of their structural features. Raymond and Eigenbrot[3] first analyzed [8]annulenyl complexes by invoking an effective "COT radius", calculated by subtracting the metal ionic radius (corrected for charge and coordination number) from the metal-ring carbon distance. This allowed direct comparison of the effect on structural parameters of a change in metal or metal oxidation state. In their analysis, both cyclopentadienyl and [8]annulenyl complexes were considered. Stockwell and Hanusa[4] have recently extended Raymond's qualitative analysis of cyclopentadienyl complexes to a rigorous statistical analysis. We have updated[5] the analysis of [8]annulenyl complexes to include a number of new structures and also included in the analysis the effects of long-range electrostatic and steric interactions. Some relevant compounds and their M-ring carbon distances are listed in Table 1.

There is significant variation in the values of r_{COT} in the complexes listed in Table 1, but within roughly homologous compounds there is some agreement. For example, note the similarity in r_{COT} in related compounds **1 - 5, 6 - 8, 9** and **10** and **11 - 13**. On the other hand, comparison of the bis-([8]annulenyl) complexes **1** and **3** with their mono-([8]annulenyl) derivatives **6, 7** and **8** reveals an apparent inconsistency. Since the ionic radius of nine-coordinate U(IV) is approximately 0.04 Å less than that of ten-coordinate U(IV),[20] one would expect a shorter metal-carbon distance in ten-coordinate **1** and **3** than in their nine-coordinate counter

Table 1 Comparison of M-C bond lengths and r_{COT} for several [8]annulene complexes

Compound[a]	M	M C.N.	M-C Dist.	r_M[b]	r_{COT}	Ref.
1. U(C$_8$H$_8$)$_2$	U^{4+}	10	2.647(4)	1.08	1.57	6
2. U(Me$_4$C$_8$H$_4$)$_2$	U^{4+}	10	2.658(4)	1.08	1.58	7
3. U(C$_8$H$_7$TMS)$_2$	U^{4+}	10	2.659(13)	1.08	1.58(1)	8
4. Th(C$_8$H$_8$)$_2$	Th^{4+}	10	2.701(4)	1.13	1.57	9
5. Ce(MeC$_8$H$_7$)$_2$	Ce^{4+}	10	2.692(6)	1.07	1.62	5
6. (C$_8$H$_8$)UCl$_2$(py)$_2$	U^{4+}	9	2.683(6)	1.05	1.63	10
7. (C$_8$H$_8$)U(acac)$_2$	U^{4+}	9	2.694(4)	1.05	1.64	10
8. (C$_8$H$_8$)ThCl$_2$(thf)$_2$[c]	Th^{4+}	9	2.72(1)	1.09	1.63(1)	11
			2.71(2)	1.09	1.62(2)	
			2.72(2)	1.09	1.63(2)	
9. (C$_8$H$_8$)Cp*Th[CH(TMS)$_2$]	Th^{4+}	9	2.746(10)	1.09	1.66(1)	12
10. (C$_8$H$_8$)Cp*Th[N(TMS)$_2$]	Th^{4+}	9	2.758(12)	1.09	1.67(1)	8
11. [K(dg)][U(MeC$_8$H$_7$)$_2$][d]	U^{3+}	10	2.732(8)	1.22	1.51	5
	U^{3+}	10	2.707(7)	1.22	1.49	
	K$^+$	8	3.263(14)	1.51	1.75(1)	
12. [K(dg)][Ce(C$_8$H$_8$)$_2$][d]	Ce^{3+}	10	2.733(4)	1.25	1.48	13
	Ce^{3+}	10	2.746(6)	1.25	1.50	
	K$^+$	8	3.166(17)	1.51	1.66(2)	
13. [K(dg)][Yb(C$_8$H$_8$)$_2$][d]	Yb^{3+}	10	2.610(8)	1.10	1.51	5
	Yb^{3+}	10	2.598(4)	1.10	1.50	
	K$^+$	8	3.191(14)	1.51	1.68(1)	
14. [K(gl)]$_2$[Yb(C$_8$H$_8$)$_2$]	Yb^{2+}	10	2.741(10)	1.26	1.48(1)	14
	K$^+$	7	3.017(6)	1.46	1.56	
15. (C$_8$H$_8$)LuCp*	Lu^{3+}	8	2.433(1)	0.977	1.46	15
16. (C$_8$H$_8$)Lu(o-PhCH$_2$NMe$_2$)·(thf)	Lu^{3+}	8	2.549(15)	0.977	1.57(1)	16
17. [(C$_8$H$_8$)CeCl(thf)$_2$]$_2$	Ce^{3+}	9	2.710(2)	1.20	1.51	17
18. (C$_8$H$_8$)Yb(py)$_3$·1/2(py)	Yb^{2+}	8	2.64(3)	1.14	1.50	18
19. [K(dg)]$_2$(Me$_4$C$_8$H$_4$)	K$^+$	8	3.003(8)	1.51	1.49	19

a) thf=tetrahydrofuran; dg=diglyme; gl=glyme; py=pyridine.
b) From the tables of Shannon.[20] For coordination numbers for which ionic radii are not known, values are obtained from linear interpolation from known coordination numbers.
c) The molecule adopts more than one conformation in the crystal.
d) The [8]annulene rings are in different coordination environments.

parts **6, 7** and **8**. What is observed, however, is an increase in the metal-carbon distance on going from bis- to mono-([8]annulene complexes. In another example, consider the K-C distances in compounds **11, 12, 13** and **19**. In each case the coordination environment of the potassium atom is identical; a dianion coordinates one face of the potassium ion while a single diglyme coordinates the other face. One might then expect the K-C distances to be approximately the same. However, in each of the sandwich complexes the K-C distance is significantly longer than that in **19**.

These observations are rationalized by including effects of electrostatic interaction of more than just nearest neighbors. In an ionic model of **19** each potassium is attracted to the central dianion and is repelled by the other cation. In **11, 12**, and **13**, however, the potassium is repelled by the more highly charged metal +3 cation, which also attracts the dianion more strongly. Accordingly, the K^+-ring distances are greater in the latter compounds. Similarly, in the half-sandwich compounds, **6, 7** and **8** the metal-Cl and -O anion distances are less than the metal-ring distances and ring-ligand repulsions will be greater than the ring-ring repulsions in **1-4**. Additional repulsions in the half-sandwich compounds of **6** and **8** come from the dipoles of coordinated pyridine and THF, respectively.

Hydrolysis of Uranocenes

Protonation of the dianion rings of uranocene is one of the reactions that this compound undergoes and a mechanistic study of this reaction was undertaken.[21] Pseudo-first order kinetics was measured by monitoring the λ_{max} (600 - 650 nm) of 10^{-3} M solutions of the uranocenes in 1 M H_2O-THF. The electronic effect of ring substitution was determined by a study of the rates of hydrolysis of a series of aryl-substiututed uranocenes, $(XC_6H_4COT)_2U$ (Table 2) in THF with 1 M water at 25 °C.

Table 2. Hydrolysis of Diaryluranocenes $(XC_6H_4COT)_2U$

X	$k \times 10^5 \ s^{-1}$
p-NMe2	0.835
p-OMe	2.27
H	4.39
o-Me	5.10
m-F	21.0

The corresponding Hammett plot correlation (ρ = 2.1) is excellent between the hydrolysis rate and a set of σ° values that reflect only inductive effects. Hydrolysis of disubstituted uranocenes appears to be dominated by electronic effects. The direction of the effect is that electron-attracting substituents increase the hydrolysis rate. This direction is expected if the rate-determining step involves coordination at uranium because such substituents increase the effective Lewis acidity of the uranium.

The use of D_2O in place of H_2O gives large primary isotope effects; k_H/k_D = 8 - 12 for different uranocenes. Thus, the rate-determining step cannot be attack of water at uranium but must include the proton-transfer step itself. Alcohols and phenol are less reactive than water, and acetic acid is just slightly more reactive than water.

Consistent with these experiments is a mechanism for the hydrolysis of uranocene that involves a pre-equilibrium coordination of water to the uranium center followed by rate-determining proton transfer to the ring. The substituent effects are then rationalized on the basis that stabilization of the dianion rings by electron-withdrawing groups is offset by the increased Lewis acid character imparted to the U metal center, and results in a higher concentration of water-coordinated uranocene.

New Syntheses of Bis[8]annulene Sandwich Compounds

Full characterization of ([8]annulene)$_2$Ce complexes, or cerocenes, an interesting and unusual class of Ce(IV) organometallics, has been restricted by the difficulty of their synthesis. We have recently reported[22] an improved synthesis of this class of compounds via the oxidation of their corresponding Ce(III) salts, K[(RCOT)$_2$Ce], by AgI. This method, however, is still erratic and occasional over-oxidation has been observed. A new route makes use of allyl bromide as the oxidizing agent.[23] The reaction is homogeneous and reproducible and gives easily purified product. The higher yields and greater reproducibility have allowed complete characterization of several cerocenes, including an x-ray structure of 1,1'-dimethylcerocene,[5] the first organocerium(IV) compound structurally characterized.

Bridged Uranocene

In recent years organometallic complexes have been increasingly utilized in catalytic systems. These include several f-element organometallic catalysts with cyclopentadienyl ligands.[24] The ability of a substrate to reversibly bind to an open coordination site on the metal center is an intrinsic feature of organometallic catalysts, a feature conspicuously absent in the bis[8]annulene metal complexes. We have taken two approaches toward modification of the uranocene morphology in order to provide open coordination space on the uranium. One involves mono[8]annulene complexes, discussed below, and the other involves the synthesis of bridged-ligand uranocenes. As shown in Figure 1, variation of the length of the tether connecting the ligand rings will dictate the tilt angle between the rings and consequently the degree of coordination space made available on the uranium metal center.
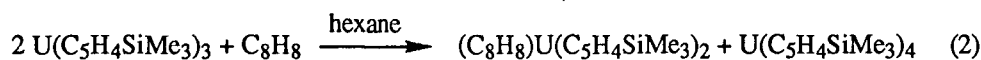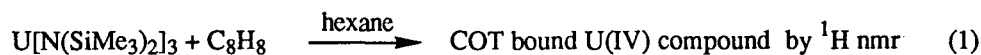
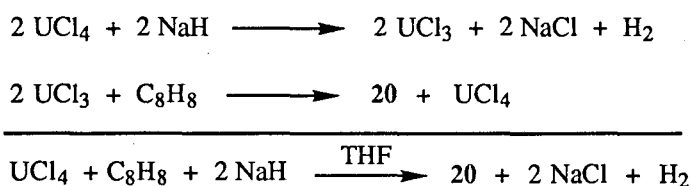Figure 1. Uranocene and a Bridged Uranocene

1
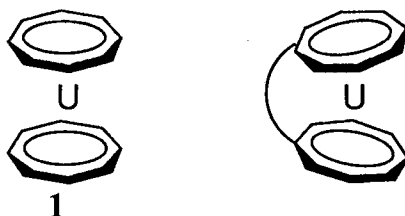
The first such bridged uranocene has recently been synthesized.[25] Reduction with K metal of the linked di-COT ligand, $C_8H_7SiMe_2CH_2CH_2SiMe_2C_8H_7$, to its tetraanion followed by slow addition of UCl_4 generated the desired monomeric uranocene. This material readily sublimes at high vacuum and has been characterized by ^{1}H NMR and high-resolution mass spectroscopy. Variable temperature ^{1}H NMR reveals a fluxional molecule whose resonances broaden and begin to coalesce at low temperatures. This is indicative of a rather loose tether, reflected in its ease of synthesis and high stability.

Mono[8]annulene U(IV) Half-sandwich Chemistry

Brennan showed that reduction of COT by U(III) complexes such as $U[N(SiMe_3)_2]_3$ and $[C_5H_4(SiMe_3)]_3U$ produces mono([8]annulene) U(IV) complexes (eq. 1,2). By direct analogy to reactions 1 and 2, $(C_8H_8)UCl_2(THF)_2$ **(20)** was generated by the reduction of COT with UCl_3 (eq. 3).[10]

$$U[N(SiMe_3)_2]_3 + C_8H_8 \xrightarrow{\text{hexane}} \text{COT bound U(IV) compound by } {}^1H \text{ nmr} \quad (1)$$

$$2\,U(C_5H_4SiMe_3)_3 + C_8H_8 \xrightarrow{\text{hexane}} (C_8H_8)U(C_5H_4SiMe_3)_2 + U(C_5H_4SiMe_3)_4 \quad (2)$$

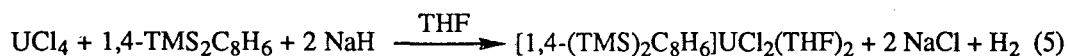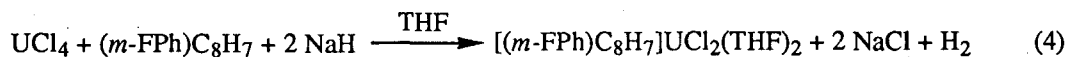$$2\,UCl_3 + C_8H_8 \xrightarrow{\text{THF}} 20 + UCl_4 \quad (3)$$

This direct synthesis of **20** is handicapped by the generation of an equivalent amount of UCl_4 as a by-product. Incorporating into reaction 3 of a reducing agent capable of selectively reducing UCl_4 to UCl_3 in the presence of COT and **20** allowed direct synthesis of **20** with minimal UCl_4 contamination. A convenient such reducing agent is NaH (Scheme 1).[10]

$$2\,UCl_4 + 2\,NaH \longrightarrow 2\,UCl_3 + 2\,NaCl + H_2$$

$$2\,UCl_3 + C_8H_8 \longrightarrow 20 + UCl_4$$

$$\overline{UCl_4 + C_8H_8 + 2\,NaH \xrightarrow{\text{THF}} 20 + 2\,NaCl + H_2}$$

Scheme 1.

Unfortunately, the direct synthesis of uranium half-sandwich complexes is not general for all substituted COTs; it would appear dependent on the reduction potential of the . Whereas there is no reaction between UCl_3 and a COT with an electron-donating substituent, e.g. n-butyl, COTs bearing electron-withdrawing substituents [such as m-fluorophenyl or 1,4-di(trimethylsilyl))] react smoothly to form the corresponding substituted [8]annulene half-sandwichs (eq. 4,5).

$$UCl_4 + (m\text{-FPh})C_8H_7 + 2\,NaH \xrightarrow{\text{THF}} [(m\text{-FPh})C_8H_7]UCl_2(THF)_2 + 2\,NaCl + H_2 \quad (4)$$

$$UCl_4 + 1,4\text{-TMS}_2C_8H_6 + 2\,NaH \xrightarrow{\text{THF}} [1,4\text{-}(TMS)_2C_8H_6]UCl_2(THF)_2 + 2\,NaCl + H_2 \quad (5)$$

In the absence of coordinating ligands such as THF or pyridine, uranium half-sandwich complexes tend to be insoluble in non-polar solvents. This insolubility can be exploited in an alternative synthesis of half-sandwich complexes through their corresponding uranocenes. Slow addition of I_2 to a solution of a substituted uranocene in hexane
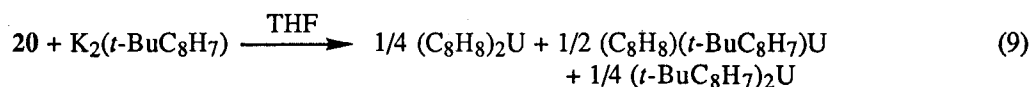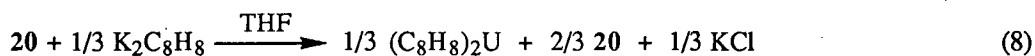
allows selective oxidation of one dianion ring and precipitation of the mono[8]annulene uranium diiodide formed (eq. 6).[26] This represents a complementary syntheses to the method described above and allows the synthesis of half-sandwich complexes from COT's bearing electron-donating substituents.

$$(RCOT)_2U + I_2 \xrightarrow{\text{hexane}} (RCOT)UI_2 + RCOT \qquad (6)$$

Replacement of the THF ligands on **20**, which are relatively weakly coordinating and desolvate from the solid state rapidly at ambient pressure, with more strongly coordinating pyridine molecules (eq. 7) generated $(C_8H_8)UCl_2(NC_5H_5)_2$ (**6**). An x-ray structure analysis of **6** (Figure 1) shows a compound analogous to the known mono[8]annulene thorium analog $(C_8H_8)UCl_2(THF)_2$.[11]

$$\textbf{20} + xs\ C_5H_5N \xrightarrow{\text{PhMe}} \textbf{6} \qquad (7)$$
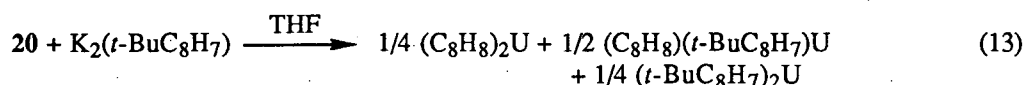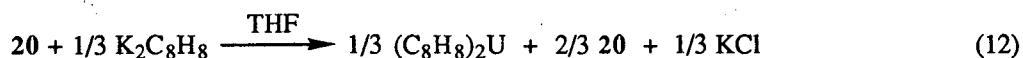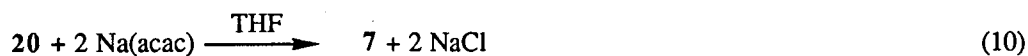
Reaction of **20** with one-third equivalent of $K_2C_8H_8$ results in smooth conversion to one-third equivalent of uranocene (eq. 8). However, the lability of the dianion ligand of **20** in the presence of free COT dianion is demonstrated in the reaction with one equivalent of $K_2(t\text{-BuC8H7})$ (eq. 9).

$$\textbf{20} + 1/3\ K_2C_8H_8 \xrightarrow{\text{THF}} 1/3\ (C_8H_8)_2U + 2/3\ \textbf{20} + 1/3\ KCl \qquad (8)$$

$$\textbf{20} + K_2(t\text{-BuC}_8\text{H}_7) \xrightarrow{\text{THF}} 1/4\ (C_8H_8)_2U + 1/2\ (C_8H_8)(t\text{-BuC}_8\text{H}_7)U \qquad (9)$$
$$+ 1/4\ (t\text{-BuC}_8\text{H}_7)_2U$$

Sattelberger has reported the synthesis of $(C_8H_8)U[N(SiMe_3)_2]$[8] via the metathesis of **20** with two equivalents of $NaN(SiMe_3)_2$. He has also reported[12] several thorium half-sandwich derivatives, for example $(C_8H_8)(C_5Me_5)ThCl$, $(C_8H_8)(C_5Me_5)ThN(SiMe_3)_2$ and $(C_8H_8)(C_5Me_5)ThCH(SiMe_3)_2$, but has also been unable to isolate thorium or uranium half-sandwich σ-bonded derivatives containing less sterically demanding ligands.

In addition to complexes containing Cp* and Cp' $(C_5H_4SiMe_3)$, two additional half-sandwich derivatives containing delocalized, multidentate ligands have been isolated. These are the acetylacetonate (acac) derivative $(C_8H_8)U(acac)_2$ **7** (eq. 10) and the tropylate (trop) derivative $(C_8H_8)U(trop)_2$

(8) (eq. 11). An x-ray structural analysis of **7** has been obtained. However, metathesis reactions with a variety of other reagents has not been successful (eq. 11 and 12).

$$20 + 2\,Na(acac) \xrightarrow{THF} 7 + 2\,NaCl \tag{10}$$

$$20 + 2\,Na(trop) \xrightarrow{THF} 8 + 2\,NaCl \tag{11}$$

$$20 + 1/3\,K_2C_8H_8 \xrightarrow{THF} 1/3\,(C_8H_8)_2U + 2/3\,20 + 1/3\,KCl \tag{12}$$

$$20 + K_2(t\text{-}BuC_8H_7) \xrightarrow{THF} 1/4\,(C_8H_8)_2U + 1/2\,(C_8H_8)(t\text{-}BuC_8H_7)U + 1/4\,(t\text{-}BuC_8H_7)_2U \tag{13}$$

Electron Transfer in Bis[8]annulene f-element Systems

The rate of electron exchange between dipotassium bis(*t*-butyl[8]annulenyl)ytterbate(II) and potassium bis(*t*-butyl-[8]annulenyl)ytterbate(III) has been measured[27] by dynamic NMR techniques. This system was chosen because the *t*-butyl substituents serve as convenient NMR markers for these paramagnetic species for which line broadening of the [8]annulenyl ring protons can be severe. Typical second order rate constants are 5×10^7 $M^{-1}s^{-1}$ at 19.3 °C in THF and 1×10^7 $M^{-1}s^{-1}$ in THF with sufficient diglyme to solvate the potassium cations in solution. Activation parameters were measured for both systems. In THF, $\Delta H^{\ddagger} = 11.0 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 14 \pm 6$ eu and in THF/diglyme, $\Delta H^{\ddagger} = 9.0 \pm 1.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = 4 \pm 4$ eu. Addition of excess diglyme did not significantly reduce the rate of exchange. These observations are consistent with a mechanism that involves in the rate determining step loss of or reduction in the number of solvating THF molecules; for the THF/diglyme system the low entropy of activation and the independence of the rate on diglyme concentration are consistent with a mechanism in which coordination of the diglyme molecule changes from η^3 to η^1 in the rate determining step.

Bis[8]annulenyl f-element complexes of the type K[(COT)$_2$M] and (COT)$_2$M are known for M = U, Np, Pu and Ce and, in principle, their rates of electron exchange can be measured in a fashion analogous to that described above for the Yb(II)/Yb(III) system. The first ^{1}H NMR spectra have been obtained[28] for organoneptunium and -plutonium compounds. The NMR spectrum of (*t*-BuC$_8$H$_7$)$_2$Pu shows temperature

independent paramagnetism. The spectra of K(t-BuC$_8$H$_7$)$_2$Pu, (t-BuC$_8$H$_7$)$_2$Np, and K(t-BuC$_8$H$_7$)$_2$Np show normal temperature dependent paramagnetism. The spectra of mixtures of (t-BuC$_8$H$_7$)$_2$Pu with K(t-BuC$_8$H$_7$)$_2$Pu and of (t-BuC$_8$H$_7$)$_2$Np with K(t-BuC$_8$H$_7$)$_2$Np show rapid electron transfer. Similar rapid electron transfer was found for mixtures of (C$_8$H$_7$Me)$_2$U and K(C$_8$H$_7$Me)$_2$U. Thus, rapid electron transfer between COT derivatives of f-elements in different oxidation states appears to be general.

Organolanthanide Catalysis of a Mukaiyama Reaction

In attempted applications to aldol-type reactions of a lanthanide with Cp* ligands we found in preliminary work that the Cp* ligand is apparently too basic and further work was done with the 1,3-C$_5$H$_3$(SiMe$_3$)$_2$, Cp", ligand. (Cp"$_2$YbCl)$_2$ has been prepared by the Lappert group.[29] We have found that it serves as a useful catalyst for the reaction of silyl enolates of esters with aldehydes and shows useful diasterioselectivity.[30] The reaction can be run over a range of temperatures and in several solvents, although CH$_2$Cl$_2$ is particularly convenient. A key discovery was that the presence of additional trimethylsilyl chloride leads to a reproducible and convenient experimental procedure. A kinetic study of the reaction has been reported; the derived mechanism readily rationalizes the observed diasterioselectivity.[31]

Acknowledgment

REFERENCES

[1] A. STREITWIESER and U. T. MÜLLER-WESTERHOFF, *J. Am. Chem.Soc.* 1968, **90**, 7364.

[2] S. A. KINSLEY and A. STREITWIESER, *Organometallics of the f-Elements*, T. J. MARKS and I. L. FRAGALA, eds., D. Reidel Publishing Co., Dordrecht, Holland (1985), p. 77-114.

[3] (a) E. C. BAKER; G. W. HALSTEAD; K. N. RAYMOND *Structure and Bonding* 1976, **25**, 23. (b) K. N. RAYMOND; C. W. EIGENBROT, Jr. *Accts. Chem. Res.* 1980, **13**, 276.

[4] S. C. STOCKWELL; T. P. HANUSA *Inorg. Chem.* 1990, **29**, 76-80.

[5] T. R. BOUSSIE; D. C. EISENBERG; J. G. RIGSBEE; A. STREITWIESER; A. ZALKIN *Organometallics*, submitted.

[6] A. ZALKIN; K. N. RAYMOND *J. Amer. Chem. Soc.* 1969, **91**, 5667.

[7] K. O. HODGSON; K. N. RAYMOND *Inorg. Chem.* 1973, **12**, 450.

[8] A. P. SATTELBERGER, personal communication.

[9] A. AVDEEF; K. N. RAYMOND; K. O. HODGSON; A. ZALKIN *Inorg. Chem.* 1972, **11**,1083.

[10] T. R. BOUSSIE; R. M. MOORE, Jr.; A. STREITWIESER; A. ZALKIN; J. BRENNAN; K. A. SMITH *Organometallics*, 1990, **9**, 2010-2016.

[11] A. ZALKIN; D. H. TEMPLETON; C. LE VANDA; A. STREITWIESER *Inorg. Chem.* 1980, **19**, 2560.

[12] a) T. M. GILBERT; R. R. RYAN; A. P. SATTELBERGER *Organometallics* 1989, **8**, 857.   b) M-C distances from a personal communication.

[13] K. O. HODGSON; K. N. RAYMOND *Inorg. Chem.* 1972, **11**, 3030.

[14] S. A. KINSLEY; A. STREITWIESER; A. ZALKIN *Organometallics* 1985, **4**, 52.

[15] H. SCHUMANN; R. D. KÖHN; F. -W. REIER; A. DIETRICH; J. PICKART *Organometallics* 1989, **8**, 1388.

[16] A. L. WAYDA; R. D. ROGERS *Organometallics* 1985, **4**, 1440.

[17] K. O. HODGSON; K. N. RAYMOND *Inorg. Chem.* 1972, **11**, 171.

[18] A. L. WAYDA; I. MUKERJI; J. L. DYE *Organometallics* 1987, **6**, 1328.

[19] S. G. GOLDBERG; K. N. RAYMOND; C. A. HARMON; D. H. TEMPLETON *J. Amer. Chem. Soc.* 1974, **96**, 1348.

[20] R. D. SHANNON *Acta Crystallogr.* 1976, **A32**, 751.

[21] R. M. MOORE, Jr., Dissertation, University of California, 1985.

[22] A. STREITWIESER; S. A. KINSLEY; J. A.RIGSBEE; I. L. FRAGALÀ; E. CILIBERTO; N. RÖSCH *J. Am. Chem. Soc.* 1985, **107**, 7778.

[23] C. JENSEN, unpublished results.

[24] For some examples see P. L. WATSON and G. W. PARSHALL, *Acc. Chem. Res.*, 1985, **18**, 51; G. JESKE, H. LAUKE, H. MAUERMANN, P. N. SWEPSTON, H. SCHUMANN and T. J. MARKS, *J. Am. Chem. Soc.* 1985, **107**, 8091.

[25] H. K. WANG; T. BARROWS; T. R. BOUSSIE unpublished results.

[26] T. R. BOUSSIE unpublished results.

[27] D. C EISENBERG; S. A. KINSLEY; A. STREITWIESER *J. Am. Chem. Soc.* 1989, **111**, 5769.

[28] D. C EISENBERG; A. STREITWIESER; W. K. KOT *Inorg. Chem.*, 1990, **29**, 10-14.

[29] M. F. LAPPERT, A. SINGH, J. L. ATWOOD and W. E. HUNTER, *J. C. S. Chem. Comm.* 1981, 1190.

[30] L. GONG and A. STREITWIESER, *J. Org. Chem.* submitted.

[31] L. GONG and A. STREITWIESER, *Eur. J. Solid State Inorg. Chem.*, in press

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720