these highly delocalized covalent compounds, we do so here only for the sake of simplicity. In terms of an MO model we are arguing that the make up of the filled bonding orbitals is mainly ligand in character. Therefore, in the resulting complexes the effective charge on the metal is high.

- (29) The previously characterized V(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub><sup>2-</sup> was also found not to undergo oxidation.<sup>30</sup>
- (30) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 4, 55 (1965).
- (31) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972.
- (32) D. A. Miller and R. D. Bereman, *Coord. Chem. Rev.*, 9, 107 (1973).
  (33) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 88, 3235 (1966).
- (34) A recent photoelectron study by Finster, et al.,<sup>35</sup> of Mo[S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub>]<sub>3</sub><sup>2-</sup>, Mo[S<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, and Mo(S<sub>2</sub>C<sub>2</sub>H<sub>2</sub>)<sub>3</sub> seemingly favors Schrauzer's MO scheme by concluding that the electrons added in forming the reduced Mo(mnt)<sub>3</sub><sup>2-</sup> complex go into primarily ligand orbitals and specifically onto the sulfurs, thus breaking down the interligand S-S

bonding found in neutral trigonal prismatic complexes and leading to octahedral geometry for the 2- and 3- complexes. We wish to point out that Gray's<sup>21</sup> scheme can equally well accommodate the experimental results. The maleonitrile dithiolate ligand, as a result of its stable orbitals, will render the 4e' MO more ligand in character and as a result addition of two electrons into the 3a' MO, which is mainly metal in character, can still result. The change in geometry is also readily explained; addition of electrons to the 3a' orbital, which is antibonding with respect to the metal ligand ( $m_h$ ) overlap, and the increase in ligand character of the 4e' orbital both tend to reduce the delocalized bonding between the metal and dithiol and consequently disfavor the trigonal prismatic geometry. Indeed, it will be shown further in the discussion that we believe this delocalized bonding to be primarily responsible for the stabilization of the trigonal prism.

- (35) J. Finster, N. Meusel, P. Muller, W. Dietzsch, A. Meisel, and E. Hoyer, Z. Chem., 13, 146 (1973).
- (36) J. L. Martin and J. Takats, manuscript in preparation.
- (37) Personal communication from M. J. Bennett.

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

# Organoactinides and Organolanthanides. XII. Bimetallic Tris(cyclopentadienyl)uranium Derivatives with Uranium–Carbon $\sigma$ Bonds

# MINORU TSUTSUI,\*1 NEAL ELY,2 and ALLEN GEBALA

# Received July 23, 1974

New  $\sigma$ -bonded organouranium complexes of the type Cp<sub>3</sub>U-R (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>; R = acetylide, ferrocenyl) and (Cp<sub>3</sub>U)<sub>2</sub>-R (R = ferrocenyl, *p*-phenyl) have been prepared from Cp<sub>3</sub>U-Cl and the respective RLi, RNa, or RLi<sub>2</sub> reagents in THF. The ferrocenyl complexes are the first  $\sigma$ -bonded organoactinide compounds where the R group is an organometallic moiety and the (Cp<sub>3</sub>U)<sub>2</sub>-R complexes are the only organometallics known to contain two organoactinide moieties bound to the same R group. Infrared and proton nmr spectra support the presence of the R groups as being  $\sigma$  bonded. A mechanism based on large contact effects is used to explain the large isotropic shifts in the nmr spectra. All of the complexes have marked thermal stability and a mass spectrum of the Cp<sub>3</sub>U-ferrocene derivative is reported. Magnetic susceptibility studies at various temperatures indicate enhanced spin-spin interactions present in the (Cp<sub>3</sub>U)<sub>2</sub>-R complexes which are absent in their Cp<sub>3</sub>U-R analogs. Other differences between the Cp<sup>3</sup>U-R complexes and their "dimeric" analogs are noted.

Within the past few years, the organometallic chemistry of the actinide elements (especially uranium) has received renewed attention.<sup>3</sup> Emphasis has been on covalent bonding and the role of the 5f electrons in bonding. Streitwieser, et al.,4 have presented evidence for a covalent  $\pi$  bond involving the 5f electrons in "uranocene," (C8H8)2U. However, it has only been relatively recently that compounds containing  $\sigma$ -bonded ligands have been prepared and studied. These new types of  $\sigma$ -bonded organoactinide complexes are of the type ( $\eta^{5}$ - $C_5H_5$ )<sub>3</sub>U-R<sup>5</sup> and  $[(\eta^5-C_5H_5)_3U]_2$ -R,<sup>6</sup> where R is an alkynyl, aryl, alkyl, or organometallic ligand. It is becoming clear that these  $\sigma$ -bonded organoactinide compounds will become a wide and varied area of research, especially with regard to covalency<sup>7,8</sup> and 5f electron involvement in the bonding. With respect to our continuing research in this new area, we wish to report the preparation and properties of several new  $\sigma$ bonded derivatives.

### **Experimental Section**

All reactions and operations were performed using Schlenk techniques or in an inert-atmosphere drybox using dried oxygen-free argon or helium. Tetrahydrofuran (THF) was dried and freed of oxygen by distilling under argon from blue sodium-benzophenone. Other solvents were degassed prior to use and distilled under argon from finely divided lithium aluminum hydride. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Melting points were determined in sealed argon-filled capillaries and are uncorrected.

 $Tris(\eta^{5}$ -cyclopentadienyl)(acetylenyl)uranium. Into a centrifuge Schlenk tube were placed 2.35 g (5.0 mmol) of  $(\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>U-Cl<sup>9</sup> and 0.26 g (5.4 mmol) of ethynylsodium.<sup>10</sup> Approximately 80 ml of THF was transferred into the tube and the resulting suspension was allowed to stir overnight at room temperature. During this time, the solution changed from dark red-brown to dark green-brown. After centri-

# AIC405018

fugation, the solution was transferred into a large Schlenk tube and the THF was removed by distillation *in vacuo* leaving a dark green-brown solid; yield ~95%. One gram of this material was continuously extracted with 50 ml of pentane for 10 hr, leaving a dark red-brown residue on the frit. The resulting pentane suspension was centrifuged and the bright yellow-green product was washed once with 25 ml of pentane and dried *in vacuo* at room temperature to yield 0.78 g of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>UC=CH. Anal. Calcd for C<sub>17</sub>H<sub>16</sub>U: C, 44.55; H, 3.52; U, 51.98. Found: C, 43.99; H, 3.65; U, 51.93.

**Tris**( $\eta^{5}$ -cyclopentadienyl)(ferrocenyl)uranium. Into a centrifuge Schlenk tube were placed 0.87 g (4.5 mmol) of ferrocenyllithium<sup>11</sup> and 2.10 g (4.5 mmol) of ( $\eta^{5}$ -CsH5)<sub>3</sub>U-Cl. Approximately 60 ml of THF was cooled to  $-78^{\circ}$  and transferred onto the solids. After stirring at  $-78^{\circ}$  for 1 hr, all of the insoluble material had dissolved and the solution, intensely red, was allowed to warm gradually to room temperature and to stir overnight. The THF was removed *in vacuo* and the brown solid dried as before. The solid was then placed in a Schlenk–Soxhlet extractor equipped with a frit and continuously extracted with hexane for 18 hr. At this time, the extraction being complete, the solution was centrifuged and the hexane transferred away leaving a brown solid which was washed with hexane and dried leaving 2.1 g (75%) of ( $\eta^{5}$ -CsHs)<sub>3</sub>U-(CsH4)Fe(CsHs). *Anal.* Calcd for C2sH24FeU: C, 48.56; H, 3.90; Fe, 9.03; U, 38.49. Found: C, 47.56; H, 5.21; Fe, 8.62; U, 38.13.

**1,1'-Bis[tris**( $\eta^{5}$ -cyclopentadienyl)uranium]ferrocene. Into a centrifuge Schlenk tube were weighed 1.95 g (4.16 mmol) of ( $\eta^{5}$ -C5H<sub>5</sub>)<sub>3</sub>U-Cl and 0.66 g (2.10 mmol) of ( $\eta^{5}$ -C5H<sub>4</sub>Li)<sub>2</sub>Fe-C6H<sub>16</sub>N<sub>2</sub>.<sup>12</sup> Approximately 60 ml of THF, cooled to  $-78^{\circ}$ , was transferred onto the solids and the resulting suspension was allowed to stir with gradual warming. At  $-50^{\circ}$ , all of the solid had dissolved and the solution was then warmed to between -20 and  $-30^{\circ}$ . Stirring was maintained for 4 hr during which time a voluminous green precipitate appeared in solution. At this point the tube was warmed to room temperature and centrifuged, and the THF was transferred off. The green solid was washed three times with 20-ml portions of THF and then dried *in vacuo*. It was further purified by continuous extraction with THF

#### Organoactinides and Organolanthanides

to yield 1.25 g (60%) of  $[(\eta^{5}-C_{5}H_{5})_{3}U]_{2}(C_{5}H_{4})_{2}Fe.$  Anal. Calcd for C<sub>40</sub>H<sub>38</sub>FeU<sub>2</sub>: C, 45.73; H, 3.64; Fe, 5.32; U, 45.31. Found: C, 45.52; H, 3.70; Fe, 4.97; U, 45.52.

p-Bis[tris( $\eta^5$ -cyclopentadienyl)uranium]benzene. Into a 200-ml Schlenk tube were placed 0.47 g (2.0 mmol) of sublimed pdibromobenzene and  $\sim 0.28$  g (40 mmol, a tenfold excess) of lithium metal in the form of small chunks; the lithium metal had been melted and allowed to cool and the clean metal core was used. Approximately 50 ml of THF was cooled to -78° and transferred into the Schlenk tube, 2 drops of *n*-butyl bromide was added, and the mixture was stirred for 2 hr at  $-30^{\circ}$  during which a red color developed. The mixture was cooled to -78° and filtered to remove excess lithium metal into a centrifuge Schlenk tube containing 1.85 g (4.0 mmol) of  $(\eta^{5}-C_{5}H_{5})_{3}U-C_{1}$ . The resulting solution was allowed to warm to room temperature and stirred for 1 hr, during which time glistening red-orange platelets precipitated from the red-brown solution. The suspension was then centrifuged, the solution decanted, and the bright red-orange solid washed twice with 20-ml portions of THF and dried in vacuo at room temperature to yield 0.45 g (25%) of p-[( $\eta^{5}$ -C5H5)3U]2C6H4. Further purification was attained by continuous extraction into THF as previously described. Anal. Calcd for C<sub>36</sub>H<sub>34</sub>U<sub>2</sub>: C, 45.87; H, 3.64; U, 50.49. Found: C, 45.54; H, 3.66; U, 50.78.

Attempts to Prepare Bis[tris( $\eta^5$ -cyclopentadienyl)uranium]acetylide. Several methods were attempted, most of which involved trying to displace the acetylenic proton of  $(\eta^5$ -CsH5)<sub>3</sub>UC=CH.

A. With NaH. A 460-mg (0.1-mmol) amount of  $(\eta^{5}-C_{5}H_{5})_{3}UC=CH$  and 55 mg (1.1 mmol) of NaH (50% oil dispersion) were placed in a small Schlenk tube and ~10 ml of THF, cooled to  $-78^{\circ}$ , was added. The solution was allowed to warm to room temperature with stirring and bubbles were observed to come out of solution, which turned red-brown. The THF was removed *in vacuo* and the solid extracted with pentane. During the extraction, a green precipitate appeared in the pentane which was identified as starting material. The residue remaining on the frit was extracted with THF but the product isolated from this was found to be devoid of a C=C linkage.

**B.** With *n*-Butyllithium. A 1.83-g (4-mmol) sample of  $(\eta^5 - C_5H_5)_3UC = CH$  was dissolved in 50 ml of THF. The resulting solution was cooled to  $-78^\circ$  and 9.6 ml of 0.42 *M n*-butyllithium in hexane was added, causing the solution to become deep red-brown immediately. The solution was allowed to come to room temperature, the THF removed, and the solid extracted with pentane as before. Beautiful red crystals formed in the pentane, which were identified as  $(\eta^5-C_5H_5)_3U(C_4H_9).^{5b}$  No other uranium species could be isolated and no evidence for a C C linkage could be found.

C. Lithium Carbide.  $(\eta^5-C_5H_5)_3U-Cl$  and Li<sub>2</sub>C<sub>2</sub> were allowed to stir in THF at room temperature for several days but no reaction occurred.

**Physical Measurements.** Proton nmr spectra of the complexes were recorded at room temperature on Varian T-60 and HA-100 spectrometers. Spectra were obtained in THF and benzene solutions.

Infrared spectra in the 4000-625 cm<sup>-1</sup> region were recorded with a Beckman IR-8 spectrophotometer. Samples were prepared as Nujol and Fluorolube mulls and examined between NaCl plates.

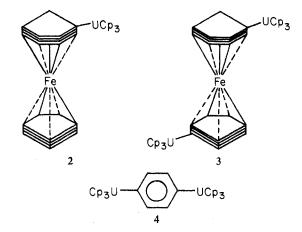
Mass spectra were measured at low ionizing voltage and samples were studied by the direct-inlet method.

Magnetic susceptibilities were done by the Faraday method using  $Hg[Co(SCN)_4]$  as a standard.

#### Results

In the course of our studies, the following complexes were prepared:  $(\eta^5-C_5H_5)_3UC\equiv CH(1), (\eta^5-C_5H_5)_3U(C_5H_4)$ -Fe(C5H5) (2),  $(\eta^5-C_5H_5)_3U(C_5H_4)$ Fe(C5H4)U( $\eta^5-C_5H_5$ )\_3 (3), and  $(\eta^5-C_5H_5)_3U(p-C_6H_4)U(\eta^5-C_5H_5)_3$  (4). All of the compounds studied are sensitive to oxygen and moisture. Compounds 1 and 2 have properties similar to other Cp<sub>3</sub>U-R (Cp =  $\eta^5-C_5H_5$ ) derivatives in terms of solubilities and decomposition products. However, as we reported in an earlier communication,<sup>6</sup> 2 and 3 represent the only known examples of Cp<sub>3</sub>U-R type complexes where R is an organometallic moiety. Also, 3 and 4 are the only organoactinide complexes which contain two actinides "bridged" by (attached to) the same ligand.

It was of interest to us to study the behavior of the "dimers"



(3 and 4) in comparison to their "monomer" analogs 2 and  $(\eta^5-C_5H_5)_3U-C_6H_{5^5}$  (5). In this context, we also attempted to prepare  $[(Cp_3U)_2](C \equiv C)$ , 6, but are so far unsuccessful. We wanted to study the effects of having two metals on the same ligand vs. one and especially how the 5f electrons would be affected.

It should be mentioned at this point that -: C==C:- and

-:::

are isoelectronic with  $N \equiv N$  and



respectively. Taube has studied the compounds  $(NH_3)_5O_8N \equiv NO_8(NH_3)_5$  and

and found that there are electronic metal-metal interactions across the ligand systems.<sup>13,14</sup> In this context, we wanted to prepare analogous f transition metal complexes of isoelectronic ligands similar to Taube's d transition metal complexes. We then anticipated examination of these compounds for f-f interactions between the metals across the ligand systems and information about the extent of f-electron participation in the bonding.

Synthesis. The new organoactinide complexes were prepared according to reactions 1-3. The complexes were purified by

$$Cp_{3}U-Cl + RNa \to Cp_{3}U-R + NaCl$$
(1)

$$Cp_{3}U-Cl + RLi \rightarrow Cp_{3}U-R + LiCl$$
<sup>(2)</sup>

$$2$$

$$2Cp_{3}U-Cl + RLi_{2} \rightarrow (Cp_{3}U)_{2}-R + 2LiCl \qquad (3)$$

$$3.4$$

continuous extraction and all gave satisfactory elemental analyses. In the solid state, all of them appear to be stable indefinitely in an atmosphere of Ar. In benzene and THF solutions, there is only slight decomposition after several weeks. 1 and 2 are highly soluble in THF and fairly soluble in aromatic and hydrocarbon solvents. By contrast, the "dimers" 3 and 4 are virtually insoluble in these solvents, being only very sparingly soluble in THF.

As has been noted earlier,<sup>5</sup> the thermal stability of these compounds is quite high; all are stable *in vacuo* to at least 180°. The decomposition products of 2 and 3 are ferrocene and a brown intractable solid containing cyclopentadiene and uranium. Thus the mode of decomposition, even in the

**Table I.** Infrared Spectra of  $Cp_3U-R$  and  $(Cp_3U)_2R^{\alpha}$ 

		1 = 5 + 2	
1	2	3	4
3120 w	3145 w	3125 w	3106 m
3100 m	3115 m	3106 m	3020 m
2062 m, br	3096 m	3096 m	1440 s
1439 s	3086 m	3086 m	1063 m
1282 w	1437 m	1988 w	1058 m
1026 s, sh	1370 m	1684 w	1012 vs
1012 vs	1149 w	1447 s	840 w
896 m	1106 vs	1339 w	805 vs)
840 m	1067 w	1143 w	780 vs >br
823 m	1052 m	1105 s	765 vs)
811 vs, s br	1017 vs	1065 w	
792 vs	1000 m	1052 m	
779 vs 🕴	816 s)	1010 vs	
657 vs	797 s}br	840 w	
645 vs	778 s)	816 vs)	
		795 vs >br	
		778 vs)	

<sup>a</sup> Key: w, weak; m, medium; s, strong; vs, very strong; br, broad.

complexes where R is an organometallic ligand, appears one of proton abstraction by R from a Cp group on uranium to give the free ligand RH (or RH<sub>2</sub>), which is in agreement with the results obtained by Marks in studies of the decomposition products of tricyclopentadienyluranium alkyls and aryls.<sup>5b</sup> This is in contrast to d transition metals, whose  $\sigma$ -bonded complexes decompose by the more familiar  $\beta$  elimination or homolytic bond scission.

However, it appears that this unusual result may be peculiar to the Cp<sub>3</sub>U system. In our attempts to prepare other  $\sigma$ -bonded derivatives of uranium, we ran the reaction shown in scheme 4. Instead of isolating a  $\sigma$ -bonded complex, we obtained large

$$(indenyl)_{3}U-Cl^{15} + Li(p-tolyl) \xrightarrow{\text{TH F}} ?$$
 (4)

yields of bitolyl and a compound tentatively identified as  $(indenyl)_3 U^{III}$ ;<sup>16,17</sup> the  $\sigma$ -bonded complex apparently formed and decomposed during the course of the reaction, but decomposition occurred by homolytic bond cleavage with radical coupling rather than proton abstraction.

Thus, it appears that putting substituents on the cyclopentadienyl ligands causes noticeable changes in the stability of the uranium–carbon  $\sigma$  bond.<sup>18–20</sup>

The infrared spectra of these compounds are consistent with our formulation of them as Cp<sub>3</sub>U–R or (Cp<sub>3</sub>U)<sub>2</sub>–R, where R is  $\sigma$  bonded. The major absorptions are listed in Table I. Bands are present in all of the complexes at ~3100, 1440, 1010, and 810 cm<sup>-1</sup> indicative of an  $\eta^{5}$ -cyclopentadienyl moiety.<sup>21</sup> The C==C band in 1 appears at 2062 cm<sup>-1</sup> and is a broad band of medium intensity similar to the band for the uranium-phenylacetylide derivative (2072 cm<sup>-1</sup>).<sup>5a</sup>

The ferrocene complexes, 2 and 3, show a band above 3000 cm<sup>-1</sup> in addition to those present for the  $\eta^5$ -cyclopentadienyl group. This arises from the less symmetrical Cp ring on ferrocene to which the uranium is bonded and lends further support to the  $\sigma$  nature of this bond.

In 4, the band at 3020 cm<sup>-1</sup> is indicative of the C–H stretching for phenyl groups. Also, the band at 840 cm<sup>-1</sup> arises from the presence of a para-disubstituted phenyl group; in this case,  $\sigma$  bonded to two Cp<sub>3</sub>U moieties.

One of the purposes in preparing these compounds was to study them by proton nmr and compare the effects of one Cp<sub>3</sub>U group per ligand vs. two. However, as previously mentioned, we were unable to prepare the "dimer" of the acetylide derivative, and 3 and 4 are so insoluble that no spectra could be obtained. Nmr results for 1 and 2 are listed in Table II.

As we communicated previously,<sup>6</sup> a mechanism based on large contact shift contributions rather than pseudocontact effects seems to predominate for 2, to account for the large upfield shifts. This will also explain the downfield shift for

Table II. Proton Nmr of  $Cp_3 U-R^{a,b}$ 

Compd	Signal <sup>c</sup>	Chem shift	Assignment	
$1^d$	S	-1.53 (15)	Cp <sub>3</sub> U	
	S	14.74 (1)	C≡CH	
$2^e$	S	-1.65 (5)	CpFe	
	s	-2.33(15)	Cp <sub>3</sub> U	
	m	-13.46 (2)	$\beta$ protons on the substituted Cp	
	m	-30.59 (2)	$\alpha$ protons	

<sup>a</sup> Pmr data in ppm based on TMS occurring at  $\delta$  0; a minus sign indicates an upfield shift. <sup>b</sup> All data at 25°. All signals were originally referenced to internal solvent. <sup>c</sup> Key: s, singlet; m, multiplet. <sup>d</sup> Nmr taken in benzene. <sup>e</sup> Nmr taken in THF.

**Table III.** Mass Spectrum of  $Cp_3U(C_5H_4)Fe(C_5H_5)$  (2)

		-				
_	m/e	Intens	Assignment	m/e	Intens	Assignment
	618	57.1	 M+	303	14.3	CpU <sup>+</sup>
	553	85.7	$M - Cp^+$	186	31.0	Cp,Fe <sup>+</sup>
	552	100.0	$M - C_{5}H_{6}^{+}$	121	23.8	CpFe+
	433	52.3	Cp₄U <sup>*</sup>	56	19.0	Fe <sup>+</sup>
	368	88.1	Cp <sub>2</sub> U*			

the acetylenic proton in 1, and we believe that the same mechanism is operative here as well. Contact shifts reflect the nature of the unpaired spin density (5f electrons for uranium) through the ligand system and can be related to covalency and bonding. Marks has studied this for other Cp<sub>3</sub>U–R complexes<sup>5b</sup> and Streitwieser, *et al.*, have studied this in the "uranocenes."<sup>4a</sup> Their data indicate that similar effects are responsible for the chemical shifts in the two systems. For our compounds 1 and 2 (as well as the other Cp<sub>3</sub>U–R complexes<sup>5b</sup>), this mechanism is charge transfer from filled ligand MO's to vacant f orbitals on the metal and seems to involve at least some degree of covalency.<sup>22</sup>

One of the properties affected on going from one Cp<sub>3</sub>U group to two is the volatility: 2 sublimes nicely under vacuum at about  $180^{\circ}$  and 5 will sublime with decomposition, but 3 and 4 are nonvolatile. On heating under reduced pressure, they blacken and decompose.

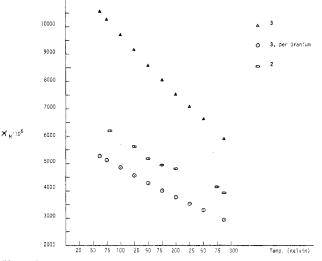
In fact, 2 is rather volatile (more so than other Cp<sub>3</sub>U-R complexes) and its mass spectrum was obtained with no difficulty. A summary of the major ion fragments is given in Table III. The parent ion at m/e 618 was present as was a peak at 433 corresponding to the Cp<sub>3</sub>U<sup>+</sup> ion. This ion shows successive loss of two cyclopentadienyl groups, but no ion at m/e 238 (U<sup>+</sup>) was observed. The ion at m/e 186 is for the ferrocene ion and it shows successive loss of the two rings to give peaks at m/e 121 and 56.

A peak at m/e 552 (M - C<sub>5</sub>H<sub>5</sub><sup>+</sup>) was observed. This fragment was also observed in **5** and its deuteriophenyl analog.<sup>5c</sup> This fragment is further evidence for a mode of decomposition involving intramolecular transfer of H from one of the cyclopentadienyl rings. Also, this fragment at m/e 552 was the base peak in the spectrum.

The absence of a peak at m/e 238 (U<sup>+</sup>) is not unusual as other cyclopentadienyl complexes of uranium are without it.<sup>23</sup> Like Cp<sub>3</sub>U–Cl and Cp<sub>4</sub>U, where the cyclopentadienyl ligands are successively more difficult to remove,<sup>24</sup> the Cp<sub>2</sub>U<sup>+</sup> ion in 2 is more intense. The loss of the ferrocene moiety (m/e 186) from uranium is not very intense relative to the loss of the first two cyclopentadienyl groups and suggests that the ferrocenyl ligand is not readily dissociated from the uranium and is relatively strongly bound.

The new compounds were studied by magnetic susceptibility at various temperatures to see what effects, if any, two Cp<sub>3</sub>U groups would have on the ligand vs. one. The results for the ferrocene compounds, 2 and 3, will be discussed, although they are pertinent to the phenyl compounds, 4 and 5, as well.

Several interesting observations were noted as a result of the work performed. The results are plotted in Figure 1. It





is apparent that these compounds  $(4 \text{ as well})^{24}$  continue to display temperature-dependent paramagnetism below 100°K unlike Cp<sub>3</sub>U-Cl<sup>25</sup> or other Cp<sub>3</sub>U-R compounds.<sup>5</sup> The susceptibility was measured as low as 65°K and the results seem to indicate that the susceptibility would continue to be temperature dependent even at lower temperatures. Compounds 2-4 differ from the others mentioned in that the former all contain at least two metal atoms (either uranium or iron). The metal atoms may "see" each other in space giving rise to some spin-spin or coupling interaction which is ferromagnetic in nature and hence temperature dependent.<sup>26</sup>

A second anomaly which we observed is that the susceptibility per uranium, in 3, is lower than that for 2 (see Figure 1). The reason(s) for this is (are) not immediately obvious. This phenomenon could arise from increased spin-spin interactions for 3 in the crystal lattice as opposed to 2. Also, since the molecular symmetries in 2 and 3 are different, increased ligand field distortions could possibly arise in 3 which would help quench orbital angular momentum and hence reduce the susceptibility.

It was also interesting to us that at lower temperatures the overall susceptibility of **3** was less than **4**. If the geometries of the compounds are as we predict, it is easy to visualize that in **3**, the metals are aligned much better for spin interactions (*i.e.*, the molecular orbitals of the metals extend spatially in a more favorable way toward each other) than in **4** (where the metals are parallel to each other across the phenyl moiety).<sup>27</sup> If this is so, there should be enhanced spin interactions in **3** and hence a lower susceptibility, which is the observed case. It thus appears that metal-metal interactions through the organic ligand systems are, at most, not very strong. If this were not the case, one would expect to notice enhanced spin-spin interactions in **4**, more so than **3**, which is not the observed case.

X-Ray crystallographic studies would be invaluable in helping to interpret further the magnetic data. It would also be useful in determining the degree of covalency involved in the  $\sigma$  bond. The bonding mechanism which is proposed for these compounds involves the ligand donating electron density into vacant f orbitals on the uranium. If, for instance, this is the case for 2, there should be less electron density on the substituted ferrocenyl cyclopentadienyl ring to bond with the iron. This should result in a weaker bond and the resulting ring to iron bond distance should be longer than in free ferrocene or even in the unsubstituted cyclopentadienyl group of the ferrocenyl moiety. Acknowledgment. We wish to thank the United States Air Force Office of Scientific Research (Grant AFOSR 71-2017) for financial support. We thank Dr. Erik Pedersen and Mrs. Solveig Kallesoe for assistance with the magnetic susceptibilities.

**Registry No.** 1, 52827-35-7; 2, 52827-36-8; 3, 52827-37-9; 4, 52827-38-0; ( $\eta^{5}$ -CsH<sub>5</sub>)<sub>3</sub>UCl, 1284-81-7; ethynylsodium, 1066-26-8; ferrocenyllithium, 1271-15-4; ( $\eta^{5}$ -CsH<sub>4</sub>Li)<sub>2</sub>Fe·C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>, 32677-77-3; *p*-dibromobenzene, 106-37-6.

### **References and Notes**

- (1) To whom correspondence should be addressed.
- (2) Work done in partial fulfillment for the requirements of the Ph.D. degree at Texas A&M University.
- (3) For a review see (a) H. Gysling and M. Tsutsui, Advan. Organometal. Chem., 9, 361 (1970); (b) R. G. Hayes and J. L. Thomas, Organometal. Chem. Rev., Sect. A, 7, 1 (1971); (c) B. Kanellakopulos and K. W. Bagnall, MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One, 7, 299 (1972).
- (4) (a) A. Streitwieser, Jr., D. Dempf, G. N. La Mar D. G. Karraker, and N. Edelstein, J. Amer. Chem. Soc., 93, 7343 (1971); (b) A. Streitwieser, Jr., U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, *ibid.*, 95, 8644 (1973).
  (5) (a) A. E. Gebala and M. Tsutsui, J. Amer. Chem. Soc., 95, 91 (1973);
- (5) (a) A. E. Gebala and M. Tsutsui, J. Amer. Chem. Soc., 95, 91 (1973);
  (b) T. J. Marks, A. M. Seyam, and J. R. Kolb, *ibid.*, 95, 5529 (1973);
  (c) G. Brandi, M. Brunelli, G. Lugii, and A. Mazzei, *Inorg. Chim. Acta*, 7, 319 (1973).
- (6) M. Tsutsui and N. Ely, J. Amer. Chem. Soc., 96, 3650 (1974).
- (7) Outside of several actinide(IV) compounds,<sup>4-6</sup> it appears as though most organometallic compounds of the actinides, as well as those of the lanthanides, are bound in principally an ionic mode.<sup>8</sup>
  (8) L. J. Nugent, P. G. Laubereau, G. K. Werner, and K. L. Vander Sluis,
- (8) L. J. Nugent, P. G. Laubereau, G. K. Werner, and K. L. Vander Sluis, J. Organometal. Chem., 27, 365 (1971).
- (9) L. T. Reynolds and G. Wilkinson, J. Inorg. Nucl. Chem., 2, 246 (1956).
- (10) K. W. Greenlee and A. L. Henne, *Inorg. Syn.*, 2, 75 (1946).
   (11) M. D. Rausch, G. A. Moser, and C. F. Meade, *J. Organometal. Chem.*,
- (11) M. D. Katsell, G. A. Mosel, and C. P. Meade, J. Organometal. Crem. 51, 1 (1973).
- (12) J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, *J. Organometal. Chem.*, 27, 241 (1971).
   (13) C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, 91, 3988 (1969).
- (13) C. Cleutz and H. Taube, J. Amer. Chem. Soc., 91, 5988 (1909).
   (14) R. Magnuson and H. Taube, J. Amer. Chem. Soc., 94, 7213 (1972).
- (15) P. G. Laubereau, L. Ganguly, J. H. Burns, B. M. Benjamin, and J. L. Atwood, *Inorg. Chem.*, **10**, 2274 (1971).
- (16) This is based on comparing the infrared spectra from this product with product obtained from the reaction 3 K(indenide) + UCl<sub>3</sub>.<sup>17</sup>
- (17) A. Gebala, N. Ely, and M. Tsutsui, unpublished results. Whether the  $\sigma$  bond in the tolyluranium(IV) indenide case did not form due to steric or electronic factors is not yet known. This one instance, however, does not preclude the formation of (indenyl)<sub>3</sub>U-R complexes with different R groups under other reaction conditions. The important point is the different method of decomposition.
- (18) The crystal structure of (indenyl)<sub>3</sub>U-Cl has been done: J. H. Burns and P. G. Laubereau, *Inorg. Chem.*, **10**, 2789 (1971). The molecule is essentially tetrahedral like Cp<sub>3</sub>U-Cl<sup>19</sup> and the metal is bonded symmetrically in a n<sup>5</sup> fashion to the five-membered ring. The indenyl moiety can be loosely viewed in this case as a cyclopentadienyl ring with a phenyl group fused to the 4 and 9 positions. Of course electronic differences between this and, say, methylcyclopentadiene have to be considered. In the indenyl group, electrons in both cyclic systems of the moiety are shared in the aromatic system, and electron differences between this and klyl substituents are not negligible.<sup>20</sup> In fact, methyl-substituted cyclopentadiene should form a stronger ring to metal bond as methyl group will have some of the electron density from the five-membered ring in aromatic ligand MO's (with the fused phenyl group) and, overall, there should be less electron density available to bond to the metal.
- (19) C. H. Wong, Y. M. Yen, and T. Y. Lee, Acta Crystallogr., 18, 340 (1965).
- (20) Tris(methylcyclopentadienyl)uranium-R complexes have been prepared and do not behave much differently from their unsubstituted analogs: N. Ely, A. Gebala, and M. Tsutsui, unpublished results.
- (21) F. A. Cotton and T. J. Marks, J. Amer. Chem. Soc., 91, 7281 (1969).
  (22) A similar mechanism, though not as strongly covalent, appears to be operative in some lanthanide-carbon σ bonds: M. Tsutsui and N. Ely, in press.
- (23) M. L. Anderson and L. R. Crisler, J. Organometal. Chem., 17, 345 (1969).
- (24) This is important because it rules out the possibility of this phenomenon arising only from some interaction with the Fe atom.
- (25) D. G. Karraker and J. A. Stone, Inorg. Chem., 11, 1742 (1972).
- (26) It should be noted that there does not have to be any formal bonding between metals for this to occur.(27) This is, of course, only one possibility. Since the measurements were
- done in the solid state, there could be *interm*olecular as well as *intram*olecular interactions operating in the lattice.