

successful cyclopentanone formation from olefins as a general process. It may also prove possible to control product stereochemistry by suitable selection of carbonylating agents. Implicit in the proposed reaction pathways is the development of catalytic carbonylations.

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## $\sigma$ -Bonded Organic Derivatives of f Elements

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A new and exciting aspect of organometallic chemistry has been unveiled with the successful synthesis of a series of  $\sigma$ -bonded derivatives of the f elements. The f elements are the 14 elements that follow lanthanum and actinium in the periodic table and in which the 4f and 5f electrons are sequentially added to either the lanthanum or the actinium configuration. This Account deals with recent advances made in the synthesis and characterization of  $\sigma$ -bonded alkyl and aryl derivatives of organolanthanide and actinide compounds.

Because the lanthanide and actinide ions have such unique electronic and stereochemical properties, the synthesis of their  $\sigma$ -bonded derivatives has been a long-sought goal. The possible f-orbital participation in bonding, coupled with the unusually high coordination numbers and resultant coordination geometries, suggest that these compounds possess intriguing potential as organometallic reagents and catalysts. By providing the correct coordination geometries for the reacting species, a coordinatively unsaturated  $\sigma$ -bonded organic derivative of an f element can catalyze various chemical transformations.

The belief that  $\sigma$ -bonded organic derivatives of f elements could become important organometallic reagents and catalysts finds overwhelming support in the chemistry of  $\sigma$ -bonded organic derivatives of d-block transition metals. The current literature<sup>1</sup> reveals a large number of transition-metal-catalyzed processes of both industrial and biological significance which involve the

use of a  $\sigma$ -bonded organometallic derivative as the active catalyst. Preliminary reports by Lugli et al.<sup>2a</sup> and Marks<sup>2b</sup> have shown that  $\sigma$ -bonded organoactinide ( $\text{Cp}_3\text{UR}$ ,  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$  and  $\text{R} = \text{Me}, \text{Ph}, \text{PhCH}_2$ ) complexes can act as catalysts in olefin oligomerization reactions and as templates in cyclooligomerization reactions. These studies heighten our hopes that the investigation of these new types of organometallic derivatives may lead to more selective and efficient catalysts.<sup>2c</sup>

### Historical Background

Although attempts to synthesize organometallic derivatives of group 3B elements date back to Pletz<sup>3a</sup> in the late 1930's and to Gilman and Jones<sup>3b</sup> in the mid 1940's, the first successful synthesis of  $\pi$ -bonded organometallic compounds of the lanthanides<sup>4a</sup> and actinides<sup>4b</sup> was reported by Wilkinson et al. in the mid 1950's. In spite of a surge of interest in the early 1960's when a series of  $\pi$ -bonded cyclopentadienyl derivatives of the rare earth elements was reported,<sup>5-9</sup> the field remained relatively dormant until 1968 when Streitwieser et al.<sup>10</sup> reported the successful synthesis of ura-

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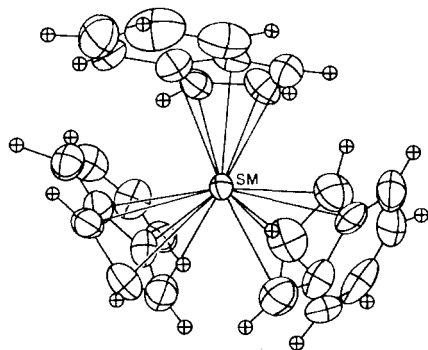
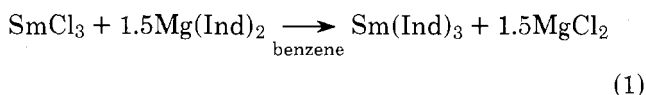


Figure 1. Structure of  $(\text{Ind})_3\text{Sm}$ .<sup>23</sup>

nocene (bis(cyclooctatetraene)uranium). Subsequently, cyclooctatetraene derivatives of the lanthanides<sup>11–13</sup> as well as of the actinides<sup>14,15</sup> were prepared. An allyl derivative<sup>16</sup> and a  $\pi$ -benzene<sup>17</sup> complex of uranium(III) have also been reported.

Tris(indenyl) derivatives were synthesized for the lanthanides,<sup>18</sup> and indenyl derivatives analogous to  $\text{Cp}_3\text{UCl}$  were prepared for U and Th.<sup>19</sup> Tsutsui and Gysling<sup>18</sup> examined the NMR spectrum of  $(\text{Ind})_3\text{La}\cdot\text{THF}$  (THF, tetrahydrofuran) and observed an  $A_2X$  pattern for the protons of the five-membered ring of the indenyl group, in agreement with the spectra observed for the  $\pi$ -bonded  $(\text{Ind})_2\text{Fe}$ ,<sup>20</sup>  $(\text{Ind})\text{Fe}(\text{Cp})$ ,<sup>21</sup> and  $(\text{Ind})_2\text{Ru}$ <sup>20</sup> complexes. However, examination of the NMR spectrum of  $(\text{Ind})_3\text{Sm}\cdot\text{THF}$  revealed an ABX pattern for the analogous protons, in agreement with the spectrum reported for the covalently  $\sigma$ -bonded  $\text{CpFe}(\text{CO})_2(1\text{-indenyl})$  complex.<sup>22</sup> Therefore, the authors<sup>18</sup> postulated that the indenyl groups of  $(\text{Ind})_3\text{Sm}\cdot\text{THF}$  were  $\sigma$ -bonded to the Sm(III) ion. If this claim could be substantiated, the  $(\text{Ind})_3\text{Sm}\cdot\text{THF}$  derivative might be the first truly  $\sigma$ -bonded derivative of a lanthanide element. The lanthanide contraction and the increased "hardness" of Sm(III) relative to La(III) were suggested as possible reasons for the different binding modes.



Although the structure of the monotetrahydrofuran complex is unknown at this time, Atwood et al.<sup>23</sup> reported the preparation (eq 1) and the crystal and molecular structure of  $(\text{Ind})_3\text{Sm}$  (Figure 1). They found

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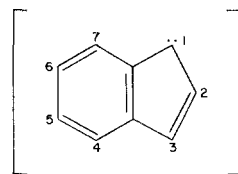
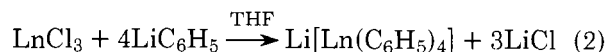


Figure 2. One of two resonance forms for the indenide ion showing localization at C-1.

that the five-membered rings have an approximate trigonal configuration about the samarium atom, and that the distances between Sm and all the carbon atoms of the five-membered rings (Figure 2) show no significant differences and therefore no evidence for enhanced covalent bonding to the carbon 1 position. Unfortunately, no comparison between  $(\text{Ind})_3\text{Sm}$  prepared in benzene and that resulting from the removal of THF in vacuo from  $(\text{Ind})_3\text{Sm}\cdot\text{THF}$  has yet been made.

Because earlier attempts<sup>24–27</sup> to prepare simple  $\sigma$ -bonded organometallic derivatives such as  $\text{U}(\text{CH}_3)_4$ <sup>26</sup> often resulted in poorly characterized or irreproducible products, these compounds have been less intensively investigated. However, in 1968, F. A. Hart et al. reported what appeared to be the first purely  $\sigma$ -bonded derivatives of the lanthanides<sup>28</sup> by treating anhydrous metal halides with phenyllithium as shown in eq 2.



In this manner lithium tetraphenyllanthanate and praseodymate were prepared. These complexes were weakly characterized by ir, elemental analysis for the metal, Michler's ketone test, and reaction with  $\text{HgCl}_2$ . The complexes were generally insoluble pyrophoric solids, which may have precluded better characterization.

The reaction of lanthanide halides with methyllithium was also reported. However, the reactive materials which were produced contained LiCl and could not be purified.

In 1972, Hart and coworkers reported the synthesis and single-crystal x-ray investigation of tetrakis(tetrahydrofuran)lithium tetrakis(2,6-dimethylphenyl)lutetate<sup>29</sup> prepared in a manner analogous to the complexes just mentioned. This was the first well-characterized example of a complex containing a lanthanide-carbon  $\sigma$  bond. The structure of the anion is shown in Figure 3. It was observed from the structure that the metal is surrounded by a tetrahedral array of ligands, making this the first known example of a four-coordinate lanthanide complex. The mean Lu-C  $\sigma$  bond distance of 2.45 Å is approximately 0.2 Å shorter than the mean  $\eta^5$  metal-carbon distance calculated for the  $\text{Lu}(\eta^5\text{-C}_5\text{H}_5)$  bonds. The analogous ytterbium complex was also prepared and found to be isostructural. However, attempts to prepare  $\sigma$ -bonded derivatives of the larger lanthanides were unsuccessful.

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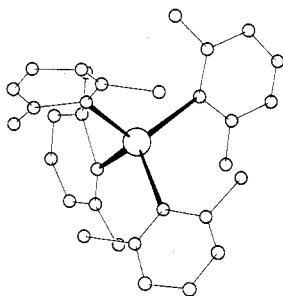


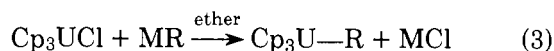
Figure 3. The tetrakis(2,6-dimethylphenyl)lutetiate anion.

Recent work<sup>30</sup> on isoleptic actinide alkyl and aryl complexes has determined that these "tetraalkyl" derivatives decompose rapidly on warming from  $-78^{\circ}\text{C}$  to room temperature. One possible reason for the instability or lack of existence of "tetraalkyl" complexes is that the ligands do not occupy enough coordination sites around the metal, thus leaving the metal in a reactive state. The significant amounts of both alkenes and alkanes found in the organic decomposition products indicate that these complexes decompose via  $\beta$  elimination. In contrast, NMR studies of  $\text{Cp}_3\text{U-R}$  complexes<sup>31</sup> show evidence that the uranium is coordinatively saturated and therefore resists  $\beta$  elimination.

However, a stable tetrabenzylthorium complex has apparently been synthesized from the reaction of  $\text{ThCl}_4 \cdot 3\text{THF}$  with benzyl lithium in THF at  $-20^{\circ}\text{C}$ .<sup>32</sup> The complex is stable to air and moisture, and decomposes above  $85^{\circ}\text{C}$ . The NMR spectrum and the ir spectrum, which is similar to that of tetrabenzylzirconium, indicate the presence of four  $\sigma$ -bonded benzyl moieties about the metal.

### Actinide Compounds

The great majority of organoactinide complexes with  $\sigma$  and  $\pi$  ligands are of the type  $\text{Cp}_3\text{U-R}$ , where R may be an alkyl, aryl, or alkynyl moiety. These complexes were first synthesized independently by three different research groups<sup>31,33-35</sup> by the reaction of  $\text{Cp}_3\text{UCl}$  with organolithium, -sodium, or -magnesium reagents in ethereal solution, as shown in eq 3. The known organoactinide complexes are listed in Table I.



All of these complexes are extremely sensitive to oxygen and moisture, and many are pyrophoric. However, they all have remarkably high thermal stabilities.<sup>31,33-38</sup>

Marks, Seyam, and Kolb have carried out thermolysis studies and found that the  $\sigma$ -bonded organouranium compounds decompose in a rather novel fashion.<sup>31</sup> Instead of the familiar  $\beta$  elimination of olefin, there is an intramolecular stereospecific abstraction of a proton from one of the Cp rings to give RH. The mass spectrum of the  $\text{Cp}_3\text{UC}_6\text{D}_5$  derivative revealed the loss of a  $\text{C}_5\text{H}_6$

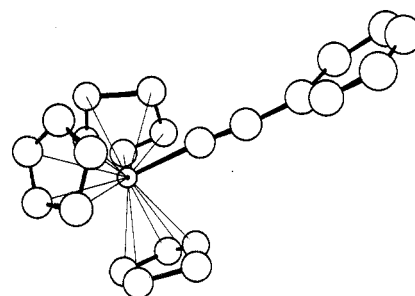


Figure 4. Structure of  $\text{Cp}_3\text{U-C}\equiv\text{C}-(\text{C}_6\text{H}_5)$ .

Table I  
 $\text{Cp}_3\text{U-R}$  Complexes

R	Color	Ref
Methyl	Yellow-brown	31, 34
Isopropyl	Dark red-brown	31
<i>n</i> -Butyl	Dark red-brown	23, 34
<i>tert</i> -Butyl	Dark green	31
Neopentyl	Dark red-brown	31
<i>cis</i> -2-Butenyl	Dark red-brown	31
<i>trans</i> -2-Butenyl	Dark red-brown	31
$\text{CH}_2$ - <i>p</i> - $\text{C}_6\text{H}_4\text{CH}_3$	Violet	31
Phenyl	Olive green	31, 33, 34
Pentafluorophenyl	Dark brown	31
Tolyl	Olive green	33, 34
Vinyl	Dark green	31
Allyl	Dark brown	31
$\text{CH}_3\text{C}(\text{CH}_2)_2$	Dark red-brown	46
Acetylide	Olive green	24
Phenylacetylide	Light olive green	33

ion which was given as further evidence that the mode of decomposition involved intramolecular proton abstraction.<sup>34</sup> This decomposition mechanism is further supported by the recently reported<sup>39</sup> isolation and structural characterization of  $[\text{Cp}_2\text{Th}(\text{C}_5\text{H}_4)]_2$  produced by the thermolysis of  $\text{Cp}_3\text{Th-}n\text{-C}_4\text{H}_9$ . The molecular structure is that of a dimeric complex in which each thorium is  $\pi$  ( $\eta^5$ ) bonded to three cyclopentadienyl rings as well as  $\sigma$  bonded to one of the cyclopentadienyl rings of the other thorium.

Recently, Tsutsui, Atwood, and colleagues<sup>40</sup> reported the crystal and molecular structure of tricyclopentadienylphenylethynyluranium(IV) and proved the  $\sigma$ -bonded nature of the phenylacetylide group (Figure 4). The U-C  $\sigma$  bond distance of 2.33 (2) Å is at least 0.3 Å shorter than the mean uranium-( $\eta^5$ - $\text{C}_5\text{H}_5$ ) distance (2.68 Å). The shortening can be attributed to enhanced covalency in the  $\sigma$  bond, supporting evidence for which was recently reported by Atwood<sup>41</sup> when he determined the U-C  $\sigma$  bond distance in  $\text{Cp}_3\text{U-C}\equiv\text{CH}$  to be 2.36 Å. Unfortunately, crystallographic difficulties limited the accuracy of the observed U-C  $\sigma$  bond distance in the acetylide derivative to  $\pm 0.03$  Å, thus precluding any definitive comparison between the two structures. Similar difficulties have been encountered in previous structural studies.<sup>40,41b,c</sup> The distances from the uranium atom to the centroids of the three Cp rings are

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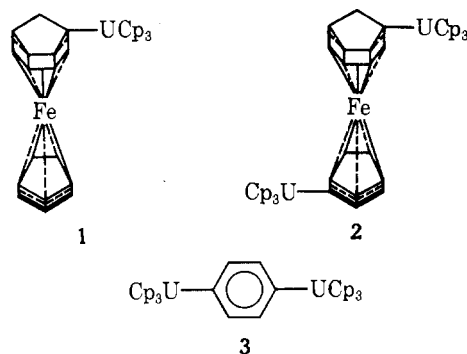
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Table II  
Variable-Temperature Magnetic Moments of Some Uranium(IV) Organometallics

Compound	$\mu_{\text{eff}}$ (288 K)	$\mu_{\text{eff}}$ (200 K)	$\mu_{\text{eff}}$ (150 K)	$\mu_{\text{eff}}$ (100 K)	$\mu_{\text{eff}}$ (80 K)
Cp <sub>3</sub> UCl	3.44	3.44	3.44	3.44	
Cp <sub>3</sub> U- <i>n</i> -C <sub>4</sub> H <sub>9</sub>	3.36	3.36	3.36		
1	3.01	2.78	2.50	2.14	1.98
2	3.57	3.33	3.09	2.70	2.47
3	3.50	3.34	3.17	2.80	2.60

2.42, 2.43, and 2.46 Å, and the angles made by the vectors so described are 116, 116, and 119°. Because of this, the uranium coordination site can be viewed as quite constrained for the R group.

Recently, Tsutsui and co-workers have been successful in synthesizing the following unusual bimetallic complexes: Cp<sub>3</sub>U-fer (fer, ferrocene) (1), (Cp<sub>3</sub>U)<sub>2</sub>-fer (2), and *p*-(Cp<sub>3</sub>U)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (3).<sup>35-38,41,42</sup> These are the only organoactinide complexes known which contain two Cp<sub>3</sub>U moieties bound to the same ligand and/or where the ligand is an organometallic moiety (ferrocene).



These complexes have a number of interesting properties. One of the decomposition products of 1 and 2 is ferrocene. This is viewed as further evidence that these Cp<sub>3</sub>U-R complexes decompose by the intramolecular proton abstraction mechanism previously mentioned. The mass spectrum of 1 reveals that a cyclopentadienyl ring is lost first (presumably from Cp<sub>3</sub>U) in preference to cleavage of the U-C  $\sigma$  bond.

The compounds were synthesized with the expectation that magnetic coupling via either the organic or organometallic bridge might be observed for the unpaired 5f electrons. It was of interest to us to compare the behavior of the "dimers" (2 and 3) to their "monomer" analogs 1 and Cp<sub>3</sub>UPh<sup>31,33,34</sup> with respect to the effect on the 5f electrons.

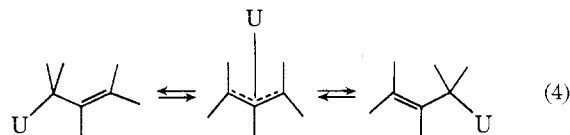
Magnetic susceptibility studies of these complexes have shown some interesting, anomalous results. All three continue to display temperature-dependent paramagnetism below 100 K. This is in sharp contrast to Cp<sub>3</sub>UCl and Cp<sub>4</sub>U,<sup>43</sup> as well as other Cp<sub>3</sub>U-R complexes<sup>31</sup> whose paramagnetism is independent of temperature below 100 K. These bimetallic complexes differ from all of the others mentioned in that they contain at least two metal ions (either iron or uranium). It has been postulated that this continued decrease in susceptibility is the result of increased spin-spin or coupling interactions which may even be ferromagnetic in nature.<sup>35</sup>

The values of  $\mu_{\text{eff}}$  for these complexes decreased markedly with decreasing temperature in the range studied. This behavior is in contrast to other uranium

organometallics. Representative values are given in Table II. The reasons for this unusual behavior have not as yet been elucidated. The possible explanations involve spin-spin interactions of the metals or electron coupling through the ligand. In addition, the mechanism must account for the fact that the magnitude of the observed reduction in 2 and 3 is of approximately the same amount. It should be noted, however, that Cp<sub>3</sub>U-C<sub>6</sub>H<sub>4</sub>-UCp<sub>3</sub> and its ferrocene analog are closely related since both have bridging groups which are "aromatic" closed-shell species.<sup>44</sup> Such a similarity might well account for the parallel behavior of compounds 2 and 3.

NMR spectra of the mononuclear organoactinide complexes have been examined by Tsutsui et al.<sup>33,35</sup> and Marks et al.<sup>31</sup> The most outstanding characteristic is that the signals for the protons of the R moieties have large chemical shifts. In all cases, the Cp protons appear as a sharp singlet between 9 and 12 ppm upfield from benzene. The isotropic chemical shifts for these compounds have been separated into contact and pseudo-contact effects.<sup>31</sup> The contact shift reflects the nature of the unpaired spin density (5f electrons for uranium) through the ligand system and can be related to covalency and bonding. The chemical shifts of the Cp<sub>3</sub>U-R complexes contain large contact contributions. This large contact contribution can be explained by a delocalization mechanism which transfers the ligand electron density into empty orbitals on the metal, and such a contact shift is therefore indicative of a covalent interaction between the metal and the ligand. This mechanism is the same as that proposed by Streitwieser et al. for the uranocenes.<sup>45</sup>

Two of these Cp<sub>3</sub>U-R complexes were found to be stereochemically nonrigid. The R = allyl compound is fluxional, as shown in eq 4, while in the R = *i*-C<sub>3</sub>H<sub>7</sub> complex there is restricted rotation about the U-C  $\sigma$  bond which can be observed in the NMR spectrum.<sup>31</sup>



The NMR spectra of the bimetallic complexes 2 and 3 would be very interesting to study for comparative purposes; however, these compounds have such poor solubility in common organic solvents (e.g., THF) that no spectra have as yet been obtained.

Recently, Halstead, Baker, and Raymond<sup>46</sup> reported the synthesis and structural analysis of an unusual ac-

(44) It must be emphasized, though, that these complexes have not been studied below 65 K. We are in the process of obtaining such data, which might provide a useful delineation of the magnetic properties of 2 and 3.

(45) A. Streitwieser, Jr., D. Dempf, G. N. La Mar, D. G. Karraker, and N. Edelstein, *J. Am. Chem. Soc.*, **93**, 7343 (1971).

(46) G. W. Halstead, E. C. Baker, and K. N. Raymond, *J. Am. Chem. Soc.*, **97**, 3049 (1975).

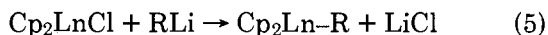
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tinide allyl complex,  $\text{Cp}_3\text{U}[\text{CH}_3\text{C}(\text{CH}_2)_2]$ . The most important feature of the structure is that the 2-methylallyl group is  $\sigma$  and not  $\pi$  bonded to the uranium atom. At first glance the  $\eta^1$  coordination of the allyl group is surprising, since in the analogous  $\text{Cp}_4\text{U}$  complex all four Cp rings are bonded in the  $\eta^5$  fashion.<sup>47</sup> Finally, a series of  $\text{Cp}_3\text{Th}-\text{R}$  complexes have been synthesized in a manner analogous to the  $\text{Cp}_3\text{U}-\text{R}$  compounds.<sup>48</sup> As expected, the properties of  $\text{Cp}_3\text{Th}-\text{R}$  complexes are similar to the analogous uranium derivatives (thorium(IV) is diamagnetic, however), though they are somewhat less stable kinetically.

### Lanthanide Compounds

Tsutsui and Ely<sup>36-38</sup> have recently extended the general method for preparing  $\sigma$ -bonded actinide complexes to the synthesis of compounds containing lanthanide-carbon  $\sigma$  bonds. Using the reaction shown in eq 5, they synthesized a number of alkyl, aryl, and alkynyl derivatives. The metals chosen vary from Gd to Yb. These new organolanthanide complexes are listed in Table III. Like their uranium analogs, they are oxygen and moisture sensitive, but they are surprisingly thermally stable.



Similar to the actinide "tetraalkyl" complexes,<sup>30</sup> isolectic lanthanide alkyl and aryl complexes have been found to be unstable or nonexistent. As in the actinide series, we felt that the cyclopentadienyl ligand in the  $\text{Cp}_2\text{Ln}-\text{R}$  complexes could be used to occupy coordination sites around the metal to reduce its reactivity, thus indirectly stabilizing  $\sigma$  bonds. That this approach has been successful is evidenced dramatically by the complex  $\text{CpHo}(\text{C}\equiv\text{CPh})_2$ ,<sup>38</sup> where a single Cp ligand has stabilized two  $\sigma$  bonds on the metal.

The question of covalency in lanthanide organometallic compounds is one of long and continuing interest. While little doubt exists that organoactinide compounds possess covalent character as evidenced by both crystallographic<sup>40,41</sup> and NMR results,<sup>31,33,35</sup> the covalent character of these new organolanthanide derivatives remains open to question.

Studies of the visible spectra and magnetic properties of the new organolanthanide complexes have shown that there appears to be more covalent character in the lanthanide-carbon  $\sigma$  bond than in the  $\pi$  bond. Visible spectra of all the  $\text{Cp}_2\text{Ln}-\text{R}$  complexes (except the Yb ones, which were not studied) show a charge-transfer band which is absent in the starting  $\text{Cp}_2\text{LnCl}$  complex.<sup>38</sup> This band shifts to lower energy as the reducing strength of the R moiety is increased, an effect consistent with its formulation as ligand to metal charge transfer.<sup>49</sup> Also, in the complexes  $\text{Cp}_2\text{Ho}(\text{C}\equiv\text{CPh})$  and  $\text{CpHo}(\text{C}\equiv\text{CPh})_2$ , the charge-transfer band is shifted to lower energy in the spectrum of the complex with two R moieties, again indicating that the charge transfer involves ligand to metal interactions and that the lanthanide-carbon  $\sigma$  bond is *not purely ionic*.

A number of the spectra displayed hypersensitive<sup>50</sup> transitions for some of the bands observed.<sup>38</sup> Although

Table III  
 $\sigma$ -Bonded Organolanthanide Complexes

Compound	Color	Ref
$\text{Cp}_2\text{Yb}-\text{C}\equiv\text{CPh}$	Orange	36, 38
$\text{Cp}_2\text{Yb}-\text{Ph}$	Orange	37, 38
$\text{Cp}_2\text{Yb}-\text{CH}_3$	Orange	37, 38
$\text{Cp}_2\text{Er}-\text{C}\equiv\text{CPh}$	Pink	36, 38
$\text{Cp}_2\text{Er}-\text{Ph}$	Pink	37, 38
$\text{Cp}_2\text{Er}-\text{CH}_3$	Pink	37, 38
$\text{Cp}_2\text{Ho}-\text{C}\equiv\text{CPh}$	Sand	38
$\text{CpHo}-(\text{C}\equiv\text{CPh})_2$	Sand	38
$\text{Cp}_2\text{Gd}-\text{C}\equiv\text{CPh}$	Yellow	36, 38
$\text{Cp}_2\text{Gd}-\text{Ph}$	Lavender	37, 38
$\text{Cp}_2\text{Gd}-\text{CH}_3$	Brown-lavender	37, 38

Table IV  
Variable-Temperature Magnetic Moments of Organolanthanide Complexes

Compound	$\mu_{\text{eff}}(295 \text{ K})$	$\mu_{\text{eff}}(195 \text{ K})$	$\mu_{\text{eff}}(77 \text{ K})$
$\text{Cp}_2\text{Er}-\text{CH}_3$	9.41	9.37	8.95
$\text{Cp}_2\text{Yb}-\text{CH}_3$	4.15	3.99	3.57
$\text{Cp}_2\text{Yb}-\text{Ph}$	3.86	3.75	3.47
$\text{Cp}_2\text{Ho}-\text{C}\equiv\text{CPh}$	10.14	10.00	9.85
$\text{CpHo}-(\text{C}\equiv\text{CPh})_2$	10.48	10.45	10.11
$\text{Cp}_3\text{Er}^3$	9.45	9.44	9.45
$\text{Cp}_3\text{Yb}^3$	4.00	4.00	4.00
$\text{Cp}_2\text{HoCl}^{\text{7a}}$	10.30	10.30	
$\text{CpErCl}_2 \cdot 3\text{THF}^{\text{7b}}$	9.68	9.68	

hypersensitivity has been related to either increased covalency or symmetry changes around the metal ion, the symmetry might remain essentially the same on going from the  $\text{Cp}_2\text{LnCl}$  complex to the  $\text{Cp}_2\text{Ln}-\text{R}$  complex. Therefore, the appearance of hypersensitivity in the spectra of some of the  $\text{Cp}_2\text{Ln}-\text{R}$  complexes may be an indication of enhanced covalency about the lanthanide arising from the  $\sigma$  bond.

Recent structural studies by Baker, Brown, and Raymond<sup>51</sup> have shown the dimeric nature of lanthanide dicyclopentadienyl halides. They reported that the molecular structure of  $[\text{Yb}(\text{C}_5\text{H}_4\text{CH}_3)_2\text{Cl}]_2$  consists of two ytterbium atoms, each with two  $\eta^5$ -bound methylcyclopentadienyl rings, which are nearly symmetrically bridged by the two chlorine atoms. However, the question of whether  $\sigma$ -bonded organolanthanide  $\text{Cp}_2\text{Ln}-\text{R}$  (R = alkyl, aryl) complexes exist as dimers in either the solid state or in solution remains unanswered at this time. While a complex such as  $\text{Cp}_2\text{LnPh}$  might exist as a "dimer" in the solid state with each Ph moiety simultaneously  $\sigma$  and  $\pi$  bonding to two discrete lanthanide ions, no concrete experimental evidence exists confirming the hypothesis. Consequently, more structural studies are needed to resolve this controversy.

Magnetic susceptibility studies of these complexes were performed, and the values of  $\mu_{\text{eff}}$  were found to be temperature dependent. Typical values are listed in Table IV. The temperature dependence of  $\mu_{\text{eff}}$  in the  $\text{Cp}_2\text{Ln}-\text{R}$  complexes appears to arise from a quenching of the orbital moment as a result of covalent interaction in the lanthanide-carbon  $\sigma$  bond.<sup>38</sup>

In an effort to prepare a  $\sigma$ -bonded allyl derivative analogous to  $\text{Cp}_3\text{UC}_3\text{H}_5$ ,<sup>16,31</sup> Tsutsui and Ely<sup>37</sup> prepared

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$\text{Cp}_2\text{LnC}_3\text{H}_5$  (Ln = Sm, Er, Ho) by reacting  $\text{Cp}_2\text{LnCl}$  with allylmagnesium bromide in THF–ether solution at  $-78^\circ\text{C}$ . Characterization of these new allyl derivatives revealed the formation of an  $\eta^3$ -allyl–lanthanide bond in preference to the  $\eta^1$ -allyl bond observed in the analogous actinide derivatives. It would appear from these results that the lanthanide alkyl and aryl complexes are coordinatively unsaturated and that given an opportunity (R = allyl) they will expand their coordination numbers and become coordinatively saturated.

### Bonding

The question of whether f orbitals of the lanthanide and actinide complexes are involved in covalent bonding is one of long-standing interest. For the lanthanides, it was believed that, besides being well shielded, the 4f orbitals did not extend far enough spatially to enter into covalent bonding or to be split by ligand fields to any great extent.<sup>52</sup> In the actinides, the 5f orbitals are much less shielded than the 4f orbitals and the binding energies are lower than in the lanthanides. These factors have been attributed to an increase in covalent bonding for the actinides.<sup>53</sup> Indeed, recent work has established that the bonding in a number of organolanthanide compounds is primarily ionic,<sup>3,54,55</sup> whereas covalency plays an important role in the bonding in complexes of U(IV) and Np(IV).<sup>54,56</sup> However, all of the complexes studied contain only  $\pi$ -bonded ligand in which the negative charge is delocalized over several carbon atoms. By contrast, an  $\eta^1$  ( $\sigma$ ) carbanion such as  $\text{CH}_3^-$  has its electron density concentrated on one carbon atom where it could be more readily available for some type of localized interaction with the metal and thus lead to greater covalency for a lanthanide–carbon  $\sigma$  bond than for a  $\pi$  bond.

A simple symmetry argument may be used to give some insight into the nature of the covalency in the  $\sigma$  bond. Let us assume that the symmetries of the

$\text{Cp}_2\text{Ln-R}$  and  $\text{Cp}_3\text{U-R}$  complexes are  $C_{2v}$  and  $C_{3v}$ , respectively.<sup>57</sup> The  $4f_{2,3}$  and  $5f_{2,3}$  orbitals on the metal and the  $p_z$  orbital on the carbon then both have  $A_1$  symmetry.<sup>58</sup> For the uranium complexes, these orbitals are of similar energy and it is probably this MO combination which accounts for the covalency observed in the uranium–carbon  $\sigma$  bond. These  $\text{Cp}_3\text{U-R}$  compounds can then be established as genuine f-transition-metal complexes.

However, for the lanthanide complexes, the problem is more complicated. Both the  $4f_{2,3}$  orbital and the  $5d_{z^2}$  orbital have  $A_1$  symmetry. In addition, the 4f and 5d orbitals are very similar in energy. The question of which orbital is involved in the covalent bonding is not readily answered. The data could be interpreted as being the result of 4f orbital involvement in the bonding or as perturbation of the 4f orbitals due to ligand interaction with the 5d orbitals. Either explanation appears equally plausible at this time. Although the ionic mode is still predominant,<sup>38</sup> there is increased covalent character in the lanthanide–carbon  $\sigma$  bond which establishes the  $\text{Cp}_2\text{Ln-R}$  compounds as a new class of lanthanide complexes where the ligands are not all bound in an essentially electrostatic manner.

While substantial progress has been made in elucidating the nature of  $\sigma$ -bonded organic derivatives of f elements, a number of important problems remain. First, the question of whether the 4f valence orbitals participate in covalent bonding has not yet been fully answered. Though preliminary studies by Tsutsui and colleagues give strong evidence of enhanced covalency in the bonding of organolanthanide complexes, more definitive data are needed to resolve the question. A thorough examination of the photoelectron spectra of a carefully selected series of  $\sigma$ -bonded organolanthanide complexes might provide the necessary insight by which the question of f-orbital participation in the bonding of  $\sigma$ -bonded organolanthanide derivatives might ultimately be resolved. Such studies are currently in progress in our laboratory.

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