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ELECTRONIC STRUCTURES OF TRIS(CYCLOPENTADIENYL)URANIUM(IV)-LIGAND COMPLEXES *

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Summary

We present a systematic molecular orbital study of the electronic and geometrical structure of complexes containing the Cp_3U fragment bonded to a variety of organic ligands. Nature of U–C bonding is variegated, as is incarnated in a remarkable range of U–C distances. As measured by overlap populations, covalency in the U–C(alkyl) σ bond is strong, but very weak in the case of the U–Cp π bond. Covalency in the U–$CHPR_3$ and U–CCR bonds is even enhanced due to additional interactions, more for the former, indicating the presence of partial multiple bond character.

Introduction

In modern organometallic chemistry, we often see one or two cyclopentadienyl ligands surrounding a metal atom, and forming the ubiquitous $CpML_n$ and Cp_2ML_n complexes. The size and electronic properties of the Cp anion are just right for stabilizing these metal complexes. The usefulness of Cp is by no means limited to *d*-transition metal chemistry, but it has aided recent development of organoactinide chemistry as well [1–3]. Besides the familiar $CpML_n$ and Cp_2ML_n stoichiometries, actinides frequently accommodate three Cp's at a metal center with an associated set of ligands, one or two in number. These are the Cp_3ML_n complexes (M = Th, U), and Cp_3UL is the subject of this theoretical study.

The majority of the known Cp_3ML complexes contain monodentate anionic ligands such as halogens and alkyls. M is typically U^{IV}. The molecules possess trigonal-pyramidal or pseudo-tetrahedral geometry **1**, and dozens of X-ray structures give us a good picture of this class [4–10]. More rarely, neutral donors are bound to Cp_3U, giving unusual U^{III} complexes of the type Cp_3UL [11,12]. An interesting facet of the Cp_3U fragment is that η^2-acyl [13], η^2-pyrazolate [14], and even η^5-cyclopentadienyl [15] can be bound to it, despite apparent steric congestion of the

* Dedicated to Professor Sei Otsuka, a pioneer in modern organometallic chemistry, on the occasion of his 65th birthday.

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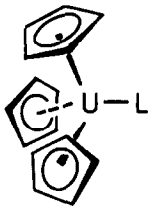

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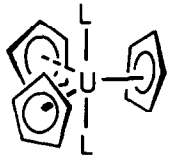

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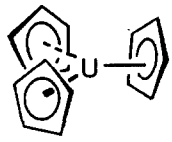
coordination sphere. With one more ligand, Cp_3UL_2, have been shown to exhibit trigonal-bipyramidal geometry **2**, where two L's occupy the axial positions [16,17].

In the present article we describe the basic features of the electronic structure of Cp_3UL compelxes, their geometry, and some aspects of bonding between U and ligands. Our study will then be extended to some specific topics, i.e., σ and π bonding capabilities of uranium with ligands and a possibility of U–L multiple bonds. The analysis relies on molecular orbital calculations of the extended Huckel type with parameters detailed in Appendix.

The tris(η^5-cyclopentadienyl)uranium fragment

Figure 1 shows a molecular orbital scheme for the tris(η^5-cyclopentadienyl)uranium fragment of the pseudotrigonal planar geometry. The orientation of three Cp rings is chosen to be **3** with the molecular symmetry of C_{3v}. At right of the



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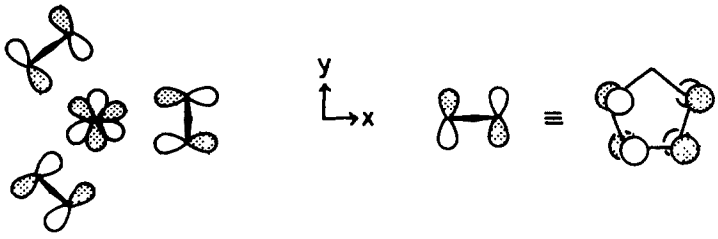
figure, the U atom carries $5f$, $6d$, $7s$, and $7p$ valence orbitals. Our calculations contain the inner $6p$ orbitals having the energy of -30.03 eV, but they are not shown in the figure. On the left, there are 15 frontier π orbitals resulting from three Cp ligands.

In the C_{3v} point group, two ligand orbitals have a_2 symmetry, which can overlap only with a uranium f orbital, $f_{y(3x^2-y^2)}$. The lower occupied a_2 in the π_2 set interacts



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with $f_{y(3x^2-y^2)}$ more strongly than the higher a_2 in the vacant π_3^* nest, and the net outcome is destabilization of $f_{y(3x^2-y^2)}$. **4** depicts the $a_2(\pi_2)-f_{y(3x^2-y^2)}$ bonding molecular orbital. Presence of *f*-orbital participation in bonding, to one degree or another, has occasionally been claimed in describing structures and chemical characteristic of lanthanide and actinide complexes [18–23]. For the Cp_3M complexes, the bonding interaction of a_2 symmetry, **4**, occurs only when the metal contains valence *f* orbitals. This symmetry requirement, in conjunction with the fact that the bulk of the Cp_3M complexes are within the *f*-transition metal series, might imply the

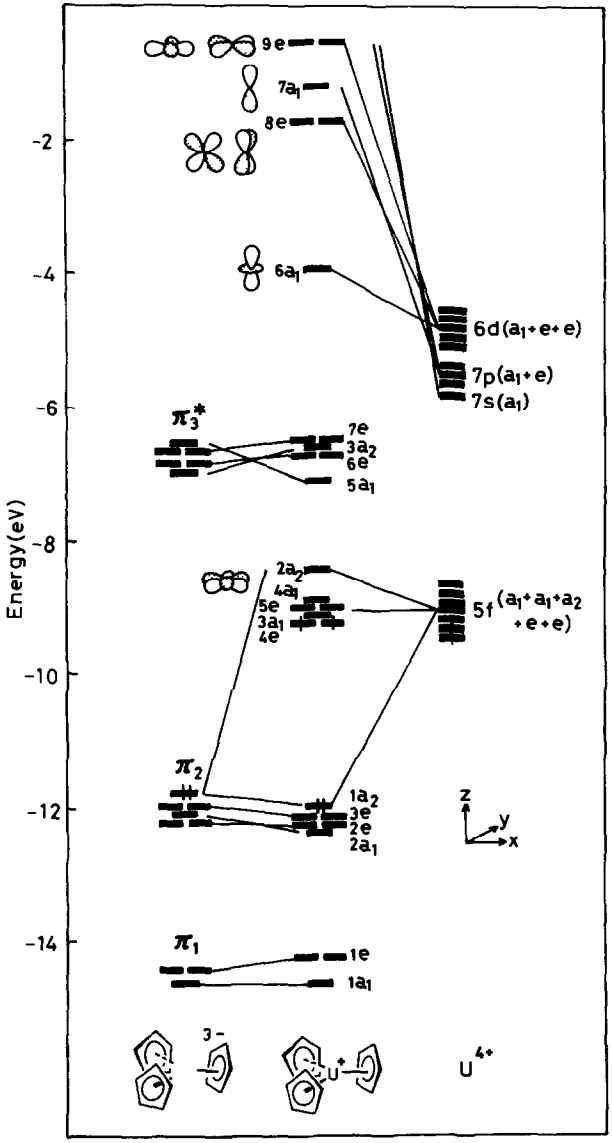

Fig. 1. Interaction diagram for the pseudo-trigonal-planar Cp_3U^+ fragment. The molecular symmetry is C_{3v}.

importance of f orbitals in stabilizing the M–Cp bonds. However, the degree of U f admixture in the bonding $1a_2$ molecular orbital is not great, amounting to 8% in our calculations. The rest of U f orbitals, having a_1 or e symmetry, remain essentially non-bonding.

The U $6d$, $7s$, and $7p$ orbitals all move up in energy through interactions with Cp π orbitals by different amounts. Of these levels, s, p_x, and p_y are strongly destabilized and are outside the energy range of Fig. 1. At somewhat lower energy, there are two degenerate e sets of $d_{xz} + d_{yz}$ and $d_{x^2-y^2} + d_{xy}$ character ($8e$ and $9e$), and $7a_1$ with p_z character. At still lower energy, $6a_1$ orbital consists mainly of d_{z^2} with 12% s admixture.

The Cp_3UL complexes are made of the pyramidalized Cp_3U fragment, and we wish to know how the Cp_3U orbitals vary their energy levels as a function of θ, the angle between the z axis and the normals to the Cp rings, **5**. In the motion which

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lowers θ from 90°, the C_{3v} molecular symmetry is retained. Figure 2 plots the energy changes of the frontier orbitals. We are interested in the bonding capability of Cp_3U with ligands, so only the molecular orbitals which comprise primarily the uranium orbitals are shown in the figure.

The basic trend noted in the figure is that the orbitals made of U d are stabilized with pyramidalization and the one made of p_z is destabilized. One reason for this trend is an increased p–d mixing as the fragment departs from the θ 90° geometry. The effect is particularly evident for the $6a_1$–$7a_1$ pair. As a consequence of the mixing, p_z–d_{z^2} (plus s) mixing in this case, they repel each other. Thus the higher orbital $7a_1$ goes up in energy while the lower one $6a_1$ moves down. The $6a_1$ hybrid directs along the z axis away from the three Cp ligands, and prepares itself for the interaction with an incoming ligand. Stabilization of $8e$ ($d_{xz} + d_{yz}$) with decreasing θ comes from mixing with $p_x + p_y$. The $9e$ set lacks ability to strongly hybridize with any p orbitals in the C_{3v} pyramidal structure, resulting in a slight downward curve. On the other hand, the U f orbitals stay approximatley constant in energy.

Before going into interactions of the Cp_3U fragment with various ligands, we briefly comment on the nature of U–Cp bonds. As Fig. 1 shows, U $6d$, $7s$, and $7p$ are pushed up due to the interactions with Cpπ orbitals. Nevertheless these uranium orbitals scarcely mix in the occupied Cpπ_2 orbitals, e.g. 3% in $3e$ and $2e$, and 6% in $2a_1$. We have mentioned that f-orbital participation was also not great, 8% in $1a_2$. Therefore, the calculated U–C_5(Cp) overlap population of the Mulliken type is fairly small, amounting to 0.05 for θ 90°. When the hydrogen atoms of Cp are included, the overall U–Cp overlap population is reduced to 0.01. This contrasts with the large M–Cp overlap populations, 0.57, obtained for a typical d transition metal Cp complex $CpFe(CH_3)(CO)_2$ [24]. From the small U–Cp overlap population, we deduce that the U–Cp bond has very weak covalent charachter, much weaker than the Fe–Cp bond in $CpFe(CH_3)(CO)_2$. The lack of covalency in the U–Cp π

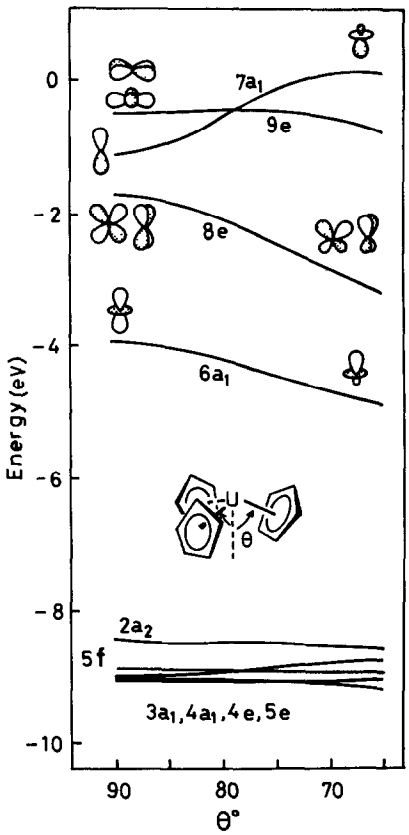


Fig. 2. Cp_3U orbitals as a function of the pyramidal angle θ. The molecular orbitals which comprise primarily uranium orbitals are shown in this diagram.

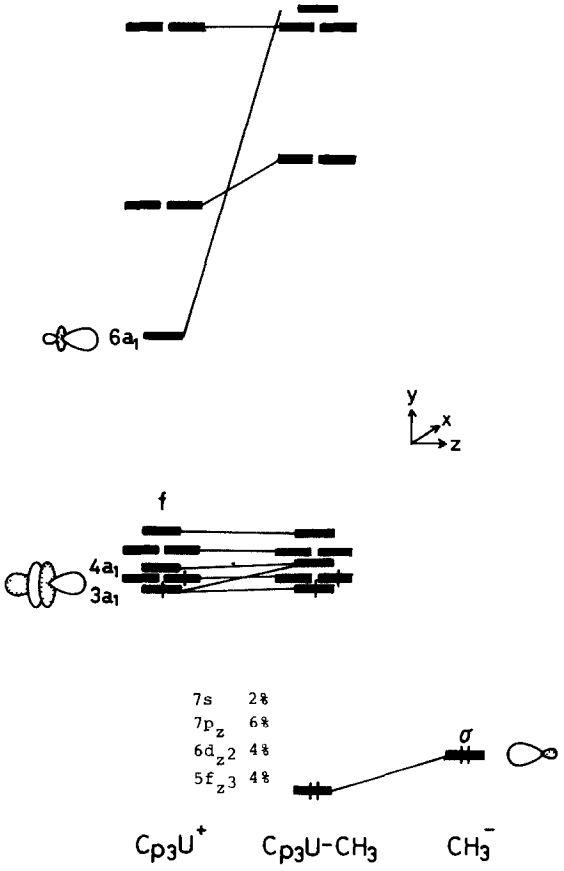
bond can be linked to the fact that π coordinations to actinides have so far been limited to anionic π ligands [4–10,21,25–26]. There are no actinide compounds with neutral ligands such as olefins and dienes etc., which are ubiquitous among *d* transition metal complexes. A single exception is the intriguing π arene complex of U^{III}, $U(AlCl_4)_3(C_6H_6)$. The molecule has rather long U–arene bond (U–C 2.91 Å), and even its existence is somewhat surprising [27].

Interactions between the pyramidalized Cp_3U and ligands

There are a good number of Cp_3UL complexes with a variety of ligands L. Aside from Cp_4U, the (Cp centroid)–U–(Cp centroid) angles open up from the ideal tetrahedral angle 109.47°, but only slightly, being typically 117°. The geometry may be termed a trigonally compressed tetrahedron. In our calculations on the Cp_3UL complexes, we fixed the Cp–U–Cp angle to be 109° and did not take its minor opening-up effect into account. Other geometrical parameters are summarized in Appendix.

Let us first study the model complex Cp_3UCH_3. The methyl ligand is a simple type of ligand to consider, for it can bond practically in a pure σ manner. The

interactions between the Cp_3U unit and CH_3 are given in **6**, where the energy levels are not drawn to scale. The methyl σ orbital overlaps very well with the fragment orbital $6a_1$, and somewhat with $3a_1$ and $4a_1$. The latter two fragment orbitals both have f_{z^3} character, and their interactions with the methyl σ are in practice due to the f_{z^3}–σ overlap. We have thus a reasonably strong σ bond between uranium and methyl. The presence of covalency in the bond is corroborated by the large U–C(CH_3) overlap population of 0.40. It is as large as the one (0.44) obtained for the Fe–C(CH_3) bond in $CpFe(CH_3)(CO)_2$, and contrasts with the very small U–Cp overlap population. The formation of strong U–C(CH_3) σ bond is also manifested in the composition of the bonding molecular orbital shown in **6**. U 7*s*, 7p_z, 6d_{z^2}, and



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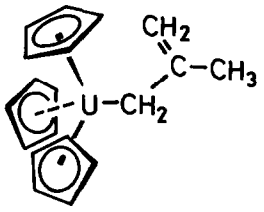
5f_{z^3} all contribute to the σ bond. Each contribution is small, but the total of them amounts to 16%.

Structures of the Cp_3ML complexes have been summarized by Raymond and Eigenbrot, Jr., [28] who presented an explanation for the observed metal-to-carbon(Cp) distances based on the ionic radii of the metal ion and the Cp anion. For the U–C(alkyl) bonds, three X-ray structures provide information. The uranium-to-carbon(alkyl or σ-allyl) distances in $Cp_3U(n\text{-}C_4H_9)$ [5], $Cp_3U(CH_2\text{-}p\text{-}CH_3C_6H_4)$ [5],

and $Cp_3U[\sigma\text{-}(CH_2)C(CH_3)CH_2]$ [6] are 2.43, 2.54, and 2.48 Å, respectively. These bond lengths are obviously shorter than those of the U–C(Cp) distances which range from 2.71 to 2.74 Å in the molecules. Closely related to Cp_3UR include $Cp_3U(C{\equiv}CH)$ [7], $Cp_3U(C{\equiv}CC_6H_5)$ [8], and $Cp_3UCHP(C_6H_5)(CH_3)_2$ [10], all of which have been studied by X-ray analyses. An interesting aspect of these three complexes is that they involve shorter uranium-to-carbon distances compared with the aforementioned alkyl complexes, being 2.36, 2.33, and 2.29 Å, respectively. Shortening of the U–C bonds will be addressed to their partial multiple bond character in the following section.

We now turn to Cp_3U complexes with cyclopentadienyl and allyl. Unlike alkyls, these ligands have multicoordination mode possibilities depending on the metal fragments with which they interact. The X-ray structure analysis of $Cp_3U[CH_2C(CH_3)CH_2]$ shows that the 2-methylallyl gorup is bound to uranium in a η^1-manner, **7** [29].



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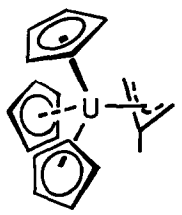

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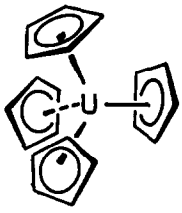
An alternative coordination mode, i.e. the π-allyl η^3-structure **8**, seems to be less stable. The steric reasoning cannot be applied to the geometrical choice, because in Cp_4U all rings are η^5. The Cp ring is bulkier than the allyl group, and yet favors the η^5-structure, **9** over η^1, **10**. Of the *d*-transition metal analogues, Cp_4Zr consists of



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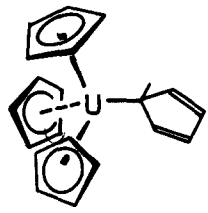

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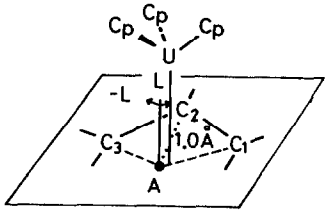
three η^5-Cp ligands and one η^1-Cp ligand, while Cp_4Ti and Cp_4Hf have two η^5-Cp's and two η^1-Cp's [30–34]. On an NMR time scale the molecules are fluxional with all four rings equivalent [35,36].

We have calculated two potential energy curves for $Cp_3U[(CH_2)_2CH]$, in an attempt to compare energies of its η^1 (**7**) and η^3 (**8**) structures. First consider the passage of the Cp_3U fragment across the face of an allyl molecule, moving as indicated in **11**. When Cp_3U is at right above the point A (L = 0), the allyl complex assumes an ideal π-allyl η^3-structure. From there, Cp_3U is allowed to slip sideways toward the point above either C_1 or C_3, keeping the U–allyl separation of 2.5 Å unchanged. The total energy profile for this movement is given by a solid curve at



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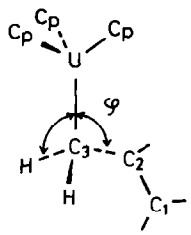

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left of Fig. 3. Then the allyl group is pyramidalized at the C_3 carbon, at above which Cp_3U resides (L = −1.25 Å). The dashed line in Fig. 3 left describes energetics of this pyramidalization. The energy minimum appears at $\varphi \approx 110°$, corresponding to a stable η^1-structure. Comparing energies of the two minima, one can see that the η^1-structure is indeed more stable than the η^3-structure. The energy difference was calculated to be 0.40 eV (9.2 kcal mol^{-1}). The ^1H NMR spectrum of $Cp_3U[(CH_2)_2CH]$ at 179 K has shown the A_2BCD pattern, characteristic of an η^1-allyl linkage. When the temperature goes up, the allyl group becomes fluxional through a $\sigma \rightleftharpoons \pi \rightleftharpoons \sigma$ interconversion as **13** [37]. The barrier to the 1,3-migration of

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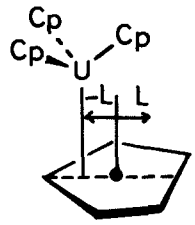
Cp_3U was estimated to be 8–9 kcal mol^{-1}, which accords quite well with our calculations in that a π-bonded η^3-intermediate lies 9.2 kcal mol^{-1} higher in energy than a σ-bonded η^1-structure.

We compare energies of $(\eta^5\text{-Cp})_3(\eta^1\text{-Cp})U$ in Fig. 3 right. The solid curve shows the total energy change for Cp_3U passing in a plane 2.55 Å above the Cp ring as defined in **14**. The energy minimum at L = 0 Å is for a geometry corresponding to



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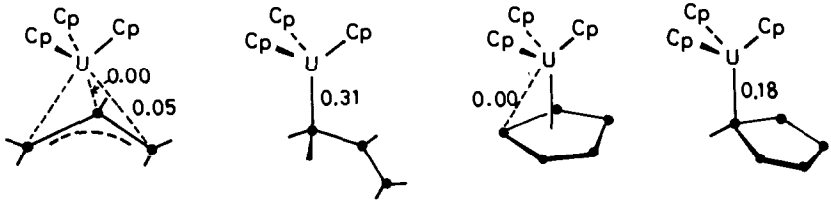
the $(\eta^5\text{-Cp})_4U$ complex. Optimization of an η^1-structure is performed again by pyramidalizing the Cp ring at a σ-coordination site. Its energy profile is give by the dashed line which has a minimum at $\varphi \approx 110°$. In contrast to the allyl case, the minimum is higher in energy than the minimum for Cp_4U. Thus the η^5-site of Cp is

where one better comes up with maximum stabilization for the Cp_3U fragment, as is experimentally observed in the X-ray structure.

Orbital symmetry arguments do not explain why Cp_3U(allyl) and Cp_4U choose the structures that they have. Instead, the geometrical contrast between the molecules is a consequence of delicate energy balance. In this respect, the good agreement between our calculations and the experimentally observed structures may be fortuitous, and yet there is a reason for it. The argument runs as follows. The overlap populations calculated for U–C bonds in the π- and σ-structures of $Cp_3U[(CH_2)_2CH]$ and Cp_4U are summarized in **15–18**. Comparing the two π-bonded structures, one



15 16 17 18

finds that the sum of U–C overlap populations in **15** is somewhat larger than that in **17**. Thus the covalent interactions can be stronger for the π-allyl complex. We think that the π-allyl structure itself is satisfactory, as far as bonding between U and the allyl part is concerned. Inspection of the orbital interactions shows that the filled NBMO of allyl anion finds a good overlap with one of the vacant Cp_3U 8*e* orbitals and overlaps with the vacant f_{xz^2} to some degree. These interactions are sketched in **19a** and **19b**, where the numbers denote the computed group overlap integrals. The outcome is the positive U–C (terminal) overlap population of 0.05. Then the

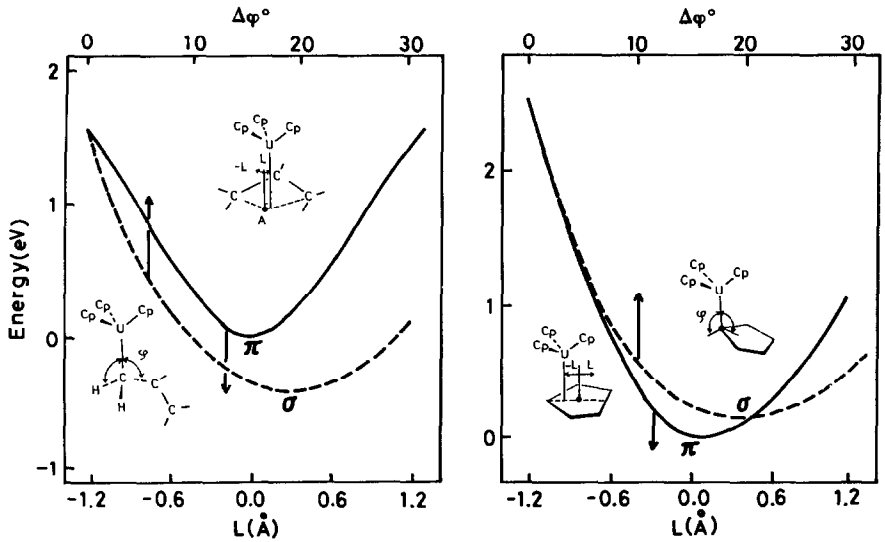
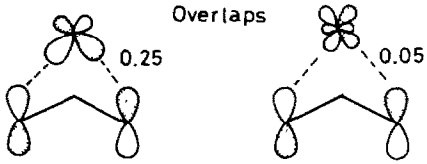


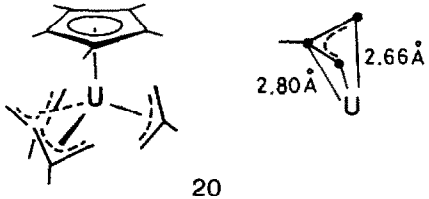
Fig. 3. Computed total energies for Cp_3U^+ moving across the face of an allyl (left, solid curve) and of a cyclopentadienyl (right, solid curve). The dashed curves are those for pyramidalization at a terminal carbon of allyl (left) and at a cyclopentadienyl carbon (right), where $\varphi = 90 + \Delta\varphi$. The marks, "$\pi$" and "$\sigma$", denote energy minima of π- and σ-structures of Cp_3U(allyl) and Cp_4U.



19a 19b

difference in σ-bond strength between **16** and **18** should account for the geometrical contrast between $Cp_3U(\sigma\text{-allyl})$ and $(\eta^5\text{-Cp})_4U$. The U–C(σ-allyl) overlap population is substantially larger than the U–C(σ-Cp) overlap population, indicating that allyl is a stronger σ-donor than Cp when coordinated to Cp_3U. The U–C(σ-allyl) bond seems to be sufficiently strong to let the molecule choose the η^1-structure, while the U–C(σ-Cp) bond is not strong enough to do so. The electron distribution in the free pyramidalized allyl and Cp anions corroborates the above trend. Negative charge (Q) of allyl anion is very well localized to the carbon atom at which U coordination occurs (Q −0.74e). To the contrary, accumulation of negative charge at the coordination site is less pronounced (Q −0.32e) in Cp^-, indicating a weak σ-donor character of the η^1-Cp ligand.

An interesting compound recently investigated is $(C_5Me_5)U[(CH_2)_2CCH_3]_3$, which has the structure shown in **20** [38]. This is the first well-characterized actinide



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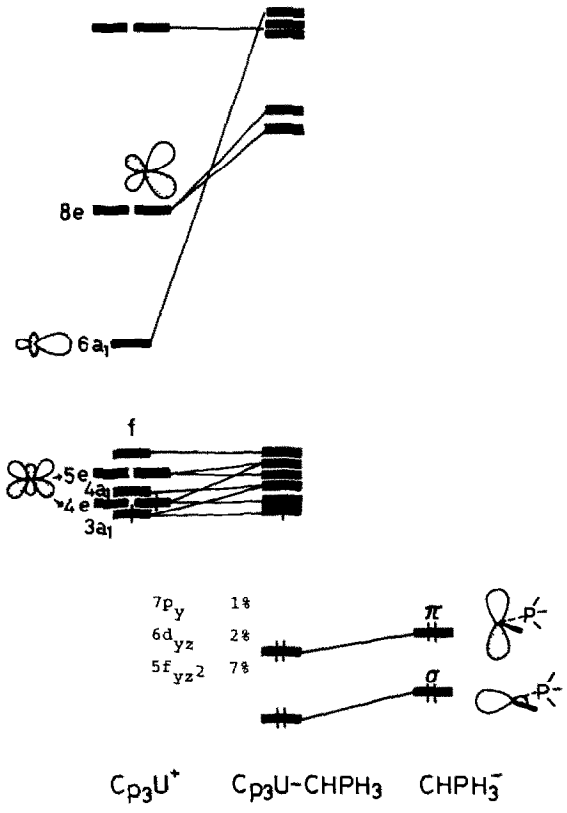
complex with η^3-allyl ligands, while the synthesis of $U(\eta^3\text{-}C_3H_5)_4$ was briefly reported in as early as 1969 [39]. Perhaps most intriguing is the long U–C(central) distance of 2.80 Å as compared with the average U–C(terminal) distance of 2.66 Å. The overlap populations calculated for $Cp_3U(\eta^3\text{-allyl})$ (**15**) shows a similar trend, i.e., less involvement of the central carbon in U–allyl bonding. It should be noted that the allyl central carbon is generally closest to a *d*-transition metal [40], except for the d^1 $Cp_2Ti(\eta^3\text{-2,3-dimethylallyl})$ complex [41].

Possibilities of uranium–carbon multiple bonds

In the preceding section, we briefly mentioned that U–C(L) distances in Cp_3UL (L = alkyls, acetylides, etc.) are diverse. They range from 2.29 in $Cp_3UCHP(C_6H_5)(CH_3)_2$ to 2.54 Å in $Cp_3U(CH_2\text{-}p\text{-}CH_3C_6H_4)$, the former of which is the shortest U–C distance konwn so far. In the related phosphoylide complex, $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, the U–C σ bond is as long as 2.66 Å [42]. The variation of distances is not simply related to steric crowding or ligand-ligand repulsion, because the complexes are all crowded molecules. Instead the root for the observed trend can be looked for in the nature of bonds, e.g. differences in covalent bond strengths. We here focus our attention on the short U–C distances in

$Cp_3U(C{\equiv}CR)$ and $Cp_3UCHP(C_6H_5)(CH_3)_2$. It will be shown that presence of U–C multiple bond character is responsible for the bond shortening.

Consider a model Cp_3UCHPH_3. The calculations were done using the observed U–C distance (2.29 Å) in $Cp_3UCHP(C_6H_5)(CH_3)_2$. The $CHPH_3$ ligand carries a $\pi(C\ p_y)$ orbital in addition to the σ lone-pair orbital as shown in the interaction diagram **21**. The σ orbital overlaps with the Cp_3U $6a_1$, $3a_1$ and $4a_1$, forming a U–C



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σ bond. This is quite similar to the U–CH_3 interaction given in **6**. Then another interaction comes in. The π orbital, being perpendicular to the σ, is nearly pure Cp_y and interacts well with Cp_3U $8e$ and f_{yz^2}. As a result, $CHPH_3^-$ is stabilized and now contains contribution from the U p_y (1%), d_{yz} (2%), and f_{yz^2} (7%) orbitals. The calculated U–C overlap population amounts to 0.61, where the π interaction **22**

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contributes 0.19 to it. Recall that the U–C(CH_3) overlap population was 0.40, which

was calculated for Cp_3UCH_3 assuming the U–C distance of 2.4 Å. The large overlap population for Cp_3UCHPH_3 is not a result of our choice of the short, 2.29 Å, U–C bond in the model compound. Calculations on Cp_3UCHPH_3 with distance of 2.4 Å reduces the overlap population only slightly to 0.57 (0.15 from the π interaction). It is still substantially larger than the one for $U–C(CH_3)$. The idea of U–C multiple bond character thus gains support from our theoretical analysis [10,13,43].

The $CHP(C_6H_5)(CH_3)_2^+$ ligand is electronically analogous to carbenes. One may categorize the numerous transition metal carbene complexes into the two classes; the Fischer type with electrophilic carbenes [44] and the Schrock type with nucleophilic carbenes [45]. Calculations on the model Cp_3UCHPH_3 place a highly negative charge of -1.38 on the ylide carbon and an electron population of 1.71 in the C p_y orbital. Nucleophilicity of the "ylide carbene" in Cp_3UCHPH_3 is evident. Probably its nucleophilic character is even stronger than Schrock type carbenes. Such a feature arises from the trend that uranium valence orbitals are high in energy and the C p_y orbital of $CHPH_3$ stays much lower than those.

It has been suggested that the short U–C distances in $Cp_3U(C{\equiv}CR)$ might reflect multiple metal carbon bonds [29]. Our calculations on $Cp_3U(C{\equiv}CH)$, with U–C distance of 2.4 Å, confirm this view. The computed U–C overlap population is 0.60, which is again much larger than the $U–C(CH_3)$ overlap population. However, the contribution from U–C π interactions (0.10) is smaller than the one obtained for Cp_3UCHPH_3. The degree of U–C multiple bond character in $Cp_3U(C{\equiv}CH)$ appears to be less pronounced than one might expect from the fact that the cylindrical $U–C(C{\equiv}CH)$ bond involves potentially two π interactions, perpendicular to each other.

Appendix

The extended Hückel parameters are listed in Table 1 [46]. Exponents of the Slater-type uranium orbitals were estimated from the relativistic Dirac-Fock wave functions of Desclaux [47]. The U 7*s* and 7*p* orbitals are of single-ζ type, exponents of which were determined from R_{max}, radius of maximum radial density, of the U $7s_{1/2}$ function. For the double-ζ parameters of U 6*d* and 5*f*, we used R_{max}, $\langle r \rangle$, and $\langle r^2 \rangle$ of U $6d_{5/2}$ and $6d_{3/2}$, and those of U $5f_{7/2}$ and $5f_{5/2}$, respectively. H_{ii} values

TABLE 1

EXTENDED HÜCKEL PARAMETERS

Orbital	H_{ii} (eV)	Exponent
U 7*s*	−5.50	1.914
7*p*	−5.50	1.914
6*d*	−5.09	2.581 (0.7608) + 1.207(04126)
5*f*	−9.01	4.943(0.7844) + 2.106(0.3908)
6*p*	−30.03	4.033
P 3*s*	−18.6	1.60
3*p*	−14.0	1.60
C 2*s*	−21.4	1.625
2*p*	−11.4	1.625
H 1*s*	−13.6	1.3

were also taken from the Desclaux's functions. In transforming the relativistic functions of U $6d$, $5f$, and $6p$ to non-relativistic ones, we took weighted averages of each multiplets. The parameters for the other elements are standard ones. The off-diagonal elements H_{ij} were calculated by a weighted Wolfsberg-Helmholtz formula with the standard K value of 1.75.

$$H_{ij} = K\frac{S_{ij}}{2}\left[(1+\Delta)H_{ii} + (1-\Delta)H_{jj}\right]$$

$$\text{where} = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}}$$

Geometrical assumptions included the following: Cp_3UCH_3; U–Cp(centroid) 2.54, C–C(Cp) 1.42, U–C(CH_3) 2.40, C–H 1.09 Å, Cp(centroid)–U–Cp(centroid) 109°: $Cp^3U[(CH_2)_2CH]$; C–C(allyl) 1.40 Å, C–C–C(allyl) 120°: Cp_4U; U–Cp(centroid) 2.55 Å, Cp(centroid)–U–Cp(centroid) 109.47°: Cp_3UCHPH_3; U–C 2.29, C–P 1.69, P–H 1.42 Å, U–C–P 142°, U–C–H 98°: $Cp_3U(C{\equiv}CH)$; U–C 1.40, C≡C 1.25, C–H 1.09 Å.

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