Registry No. **1**, 89177-90-2; $\mathbf{1}^{2+}$, 89345-75-5; **2**, 12582-61-5; $\mathbf{2}^{2+}$, 72319-57-4; ((*p*-Et_2N)TPP)FeCl, 85529-39-1; [((*p*-Et_2N)TPP)Fe]$_2$O$^+$ClO$_4^-$, 89177-92-4; [((*p*-Et_2N)TPP)Fe]$_2$O^{2+}(ClO$_4^-$)$_2$, 89363-51-9.

Notes

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σ vs. π Bonding in Organoactinides and Possibilities of CO Coordination to Actinides

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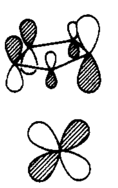
To find similarity or to search for differences, the antithetical and yet complementary lines of approach to science, are the ways in which organoactinide chemistry has been fostered, being weighed against d-block transition-metal chemistry.[1] Our extended Hückel analysis of the nature of actinide-to-carbon bonds follows the dual approach. In this communication, we concentrate our attention on the coordination of σ-methyl and π-cyclopentadienyl groups to iron and uranium. The study will then lead us to think that there is nothing wrong with a carbonyl ligand in actinide complexes.

Let us first examine the interaction between Cp and the naked Fe or U atoms, which will reveal the essence of M–Cp bonds.[2] We focus our discussion on $3d^6 4s^0 4p^0$ Fe(II) and $5f^0 6d^0 7s^0 7p^0$ U(VI) electron counts, so the charges on the hypothetical molecules are set to be 1+ for FeCp and 5+ for UCp. Figure 1 shows potential energy curves and changes in overlap populations as a function of the M–Cp separation, *L* or *R*. The potential curve for $FeCp^+$ finds a minimum at $R = 1.92$ Å, while a shallow minimum appears at $R = 2.83$ Å in the UCp^{5+} curve. These are fortuitously close to the experimentally observed distances of 2.0–2.1 Å (Fe)[3] and 2.7–2.8 Å (U)[4] in the actual complexes. Although we should not rely on the calculated energies too much because of the approximate nature of the calculations, the good agreement encourages our qualitative analysis.

The intriguing aspect of Figure 1 is the very small U–Cp overlap population. The largest value attained is merely 0.07 at around $R = 3.2$ Å. In the region of the observed U–Cp bond distances, it becomes nearly zero. This contrasts with the large positive overlap populations obtained for $FeCp^+$. The $FeCp^+$ curve shows that the maximum amounts to 0.69 at $R = 2.0$ Å. About 90% of the overlap population comes from the interactions of Cp e_1'' with Fe $3d_{xz}$ (**1**) and $3d_{yz}$ (**2**). For UCp^{5+}, the e_1''–$5f_{xz^2}$ and e_1''–$5f_{yz^2}$ interactions **3** and **4** are available in addition to **1** and **2**, but neither of them is great.



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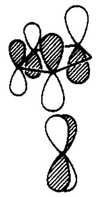

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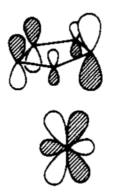

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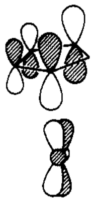

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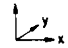
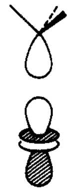
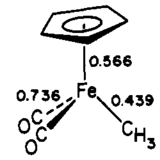


A similar calculation for d^8 $FeCH_3^-$ and f^0d^0 UCH_3^{5+} gives Figure 2. The $FeCH_3^-$ potential energy curve reproduces well the observed distances of 2.0–2.1 Å,[5] while the optimized U–CH_3 distance is at the longer limit of the broad range of observed U–R single bond distances, 2.4–2.7 Å.[6] The Fe–CH_3^- overlap populations are again notable, but more striking, in view of the MCp results, are the fairly large overlap populations calculated for U–CH_3^{5+}. Fe $3d_{z^2}$, 4s, and $4p_z$ all contribute to the Fe–CH_3 σ bond, and for UCH_3^{5+}, $5f_{z^3}$ (**5**) participates in the σ bond as well.

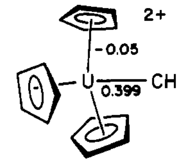


5

The interesting overlap population trends are not artifacts of the analysis based on the naked-metal models. They persist as well in calculations for more realistic molecules, CpFe(CO)$_2$CH$_3$ and $Cp_3UCH_3^{2+}$,[7] as displayed in **6** and **7**.



6



7

How do the results of the overlap population analysis reflect characteristics of actinide chemistry? The argument runs as follows. The root of the observed trends can be looked for in the nature of M–Cp and M–CH_3 bonds. From the small U–Cp overlap populations, one may deduce that the π bond carries very weak covalent character, if any, while covalency

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(1) (a) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989–997 and references therein. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics*, **1982**, *1*, 170.

(2) Atomic parameters are as follows. H_{ii}: Fe, 4s, −8.39 eV; Fe 4p, −4.74 eV; Fe 3d, −11.46 eV. Orbital exponents: Fe 4s, 1.9; Fe 4p, 1.9; Fe 3d, 5.35 (0.5366) + 1.8 (0.6678). The U parameters are taken from: Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656–2658.

(3) For example: (a) Krüger, C.; Barnett, B. L.; Brauer, D. In "The Organic Chemistry of Iron"; Koerner v. Gustorf, E. A., Grevels, F.-W., Fischler, I., Eds.; Academic Press: New York, 1978; pp 1–112 and references therein. (b) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1068–1074.

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(5) (a) Reference 3. (b) Goedken, V. L.; Peng, S.-M. *J. Am. Chem. Soc.* **1974**, *96*, 7826–7827.

(6) (a) Cramer, R. E.; Higa, K. T.; Pruskin, S. L.; Gilje, J. W. *Organometallics* **1982**, *1*, 869 and references therein. (b) For U–C bonds with multiple bond character, the distances are shorter, ranging from 2.29 to 2.36 Å: Atwood, J. L.; Hains, C. F., Jr.; Tsutsui, M.; Gebala, A. E. *J. Chem. Soc., Chem. Commun.* **1973**, 452–453. Atwood, J. L.; Tsutsui, M.; Ely, N.; Gebala, A. E. *J. Coord. Chem.* **1976**, *5*, 209–215. Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589–3590. (c) The longest U–C σ-bond distance was observed in CpU[$(CH_2)_2PPh_2$]$_3$: Cramer, R. E.; Maynard, R. B.; Gilje, J. W.; Tatsumi, K.; Nakamura, A., to be submitted for publication.

(7) The assumed geometries are as follows: Fe–C(Cp), 2.0 Å; Fe–C(CH_3) and Fe–C(CO), 2.0 Å; U–C(Cp), 2.81 Å, U–C(CH_3), 2.4 Å.

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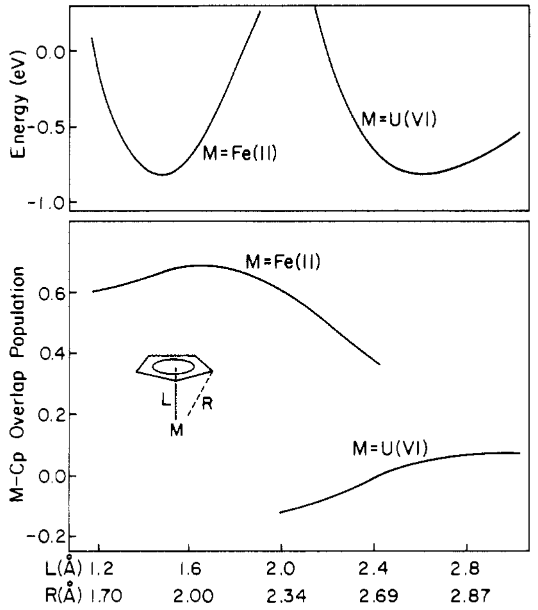

Figure 1. Potential energy curves (top) and M–Cp overlap populations (bottom) as a function of M–Cp separation for $FeCp^+$ and UCp^{5+}.

of the Fe–Cp bond is substantial. The lack of covalency in the U–Cp π bond relates to the fact that π coordinations to actinides have so far been limited to anionic π ligands,[8a–c] with the single exception of a π-arene complex of U(III).[8d] A very difficult task will thus be a synthesis of actinide compounds with neutral π ligands such as olefins and dienes etc., which are ubiquitous among Fe as well as the other d transition-metal complexes.

On the other hand, the presence of strong covalency in the $U-CH_3$ σ bond suggests the possibility of neutral σ ligands on actinides. Several experimental pieces of evidence corroborate this. Coordination of THF has occasionally been found in actinide complexes,[9] and a variety of O- and N-donor ligands in addition to THF are known to form adducts. These ligands include phosphine oxides, 1,2-dimethoxyethane, acetonitrile, amides, neutral pyrazole, 2,2′-bipyridyl, and 1,10-phenanthroline.[10] Also hydrogenolysis of $U(C_5Me_5)_2R_2$ in the presence of excess 1,2-bis(dimethylphosphino)ethane (dmpe) was found to give the first well-characterized uranium phosphine complex, $U(C_5Me_5)_2(dmpe)H$.[11]

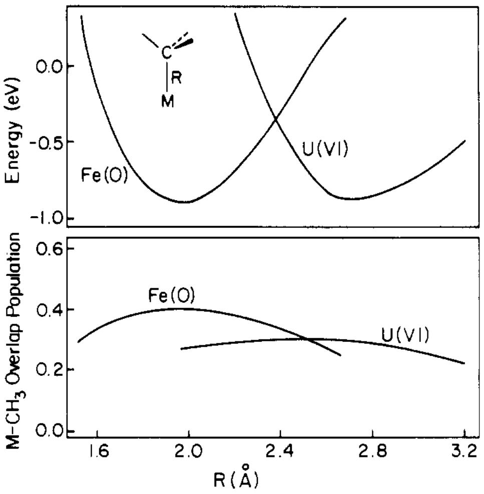

Figure 2. Potential energy curves (top) and $M-CH_3$ overlap populations (bottom) as a function of M–C distance for $FeCH_3^-$ and UCH_3^{5+}.

However, most attractive may be a complex with coordination of carbon monoxide, as yet a missing compound. The calculations on the hypothetical molecule Cp_3UCO^{3+} (**11**)[12] show that the U–CO overlap population is large, 0.468, even larger than that of $U-CH_3$. Facile migratory insertion of CO into An–C(alkyl),[13a] An–H,[13b] $An-NR_2$[13c] (An = Th and/or U), and $U{=}CHP(Ph)Me_2$[14] bonds probably starts with CO coordination to An. Certainly no strong π back-donation is expected for actinide carbonyl complexes, but we think that there is a good chance of making one.

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Registry No. **6**, 12080-06-7; **7**, 89746-37-2; **11**, 89746-38-3; $FeCp^+$, 61827-27-8; UCp^{5+}, 89746-34-9; $FeCH_3^-$, 89746-35-0; UCH_3^{5+}, 89746-36-1.

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(12) The U–C(CO) distance is assumed to be 2.4 Å.

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