These results confirm the theoretical prediction that loss of hydrogen occurs from an initial carbon-amine complex and is competative with N-H insertion.

Acknowledgment. We thank the Auburn University Computation Center for a generous allotment of computer time. M.L.M. thanks Auburn University of the award of a Grant-in-Aid (82-54). D.W.M. and P.B.S. gratefully acknowledge support of the experimental portion of this research by the National Science Foundation under Grant CHE-8103034.

Registry No. Carbon, 7440-44-0; ammonia, 7664-41-7; hydrocyanic acid, 74-90-8.

---

(16) The *N*-methylmethyleneimine (**5**) was trapped as the aminonitrile by adding an excess of HCN at 77 K. The aminonitrile was hydrolyzed to the amino acid which was derivatized and analyzed by GC-MS. The methylisocyanide (**4**) was detected among the volatile products by IR spectroscopy and quantitated by GC. Products of hydrogen abstraction by carbon and of C-H insertion are also observed in this system.[2b]

Valence Electronic Structures of the Organouranium Complexes $(\eta^5\text{-}C_5H_5)_2UX_2$ (X = Cl, CH_3)

Bruce E. Bursten* and Anne Fang

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received May 18, 1983

In recent years there has been a tremendous growth in the synthesis and structural characterization of organothorium and organouranium complexes.[1] Of particular interest have been the bis(pentamethylcyclopentadienyl) complexes $(\eta^5\text{-}C_5Me_5)_2M(X)(Y)$ (M = Th or U; X, Y = halide, alkyl, or acyl), the chemistry of which has been extensively developed by Marks and co-workers.[2] Some of these have been shown to activate CO toward hydrogenation or coupling,[3] and they are structurally analogous to the well-known dicyclopentadienyl complexes of early transition metals such as Ti, Zr, and Mo.[4] With the exceptions of thorocene and uranocene,[5] however, comparatively little is known about either the bonding in or the electronic demands of organoactinide systems and, in particular, how these might be related to their chemical reactivity. Here we report the first quantitative molecular orbital descriptions of two model nonactinocene organoactinide complexes, viz., $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$, as calculated by the X$\alpha$-SW method[6] including relativistic corrections. The recent He(I) and He(II) photoelectron spectroscopic studies of $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5Me_5)_2UCl_2$[7] will be used as a gauge of the effectiveness of the relativistic Xα method to calculate the electronic structure of organoactinide systems.

In order to make the calculation tractable, the $\eta^5\text{-}C_5Me_5$ ligands have been modeled with $\eta^5\text{-}C_5H_5$ ligands. Although the former have been used primarily to block formation of the tri- and tetracyclopentadienyl adducts, it is recognized that replacement of $\eta^5\text{-}C_5H_5$ by $\eta^5\text{-}C_5Me_5$ perturbs the electronic structure as well. The magnitude of this perturbation has been studied by ourselves[8] and others.[9] We find the effect to be small and uniform, and replacement of $\eta^5\text{-}C_5Me_5$ by $\eta^5\text{-}C_5H_5$ will not affect the conclusions presented here.

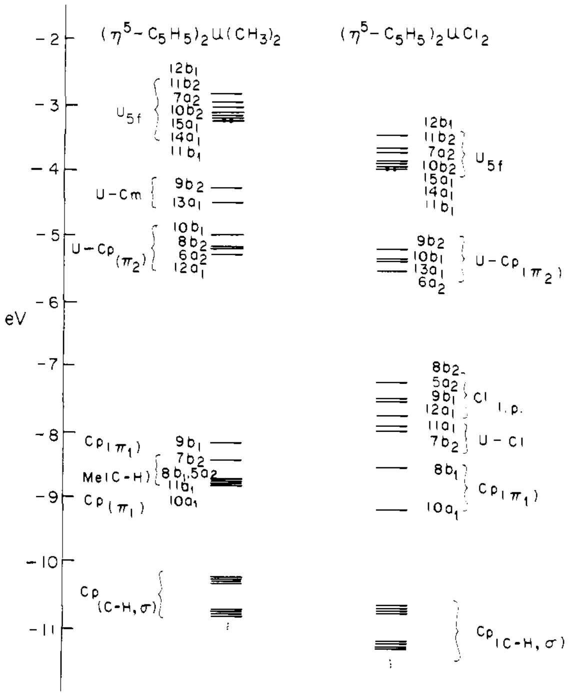


Figure 1. Converged RXα orbital energies for $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$. The principal contribution to each orbital is indicated.

Atomic coordinates for $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$ were taken from the crystal structures of the corresponding pentamethylcyclopentadienyl derivatives[10] and were idealized to C_{2v} symmetry. The calculations were first converged nonrelativistically via procedures analogous to other spin-restricted overlapping sphere Xα-SW calculations which we have reported.[11] The converged nonrelativistic potential was used as a starting point for the relativistic Xα (RXα) formalism of Wood and Boring.[12] This method, which includes the mass-velocity and Darwin terms of the Pauli Hamiltonian within a scattered-wave framework, was used to calculate orbital energies within the nonrelativistic single point group. Case and Yang have pointed out that the RXα method is generally a good approximation to a full Dirac-Slater treatment.[13] Spin-orbit splittings were not calculated for these molecules.

The valence orbital energies of $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$ are summarized in Figure 1. The bonding of the cyclopentadienyl ligands, both within the rings and to the uranium atom, is very similar in both compounds. The C-H and C-C σ bonds comprise a band of orbitals below -10 eV, and the totally symmetric π orbitals (π_1) are between -8.2 and -9.2 eV. None of these has a significant interaction with the uranium atom. Molecular orbitals that are bonding between the doubly degenerate π HOMO of $C_5H_5^-(\pi_2)$ and the U atom are clustered between -5.0 and -5.5 eV. These MO's contain from 12% to 26% U character with sizable contributions from both the 5f and 6d AO's of U. In the dimethyl complex, some of the C(Me)-H bonding levels are between -8.5 and -8.8 eV. The 9b$_2$ and 13a$_1$ MO's are the U-C(Me) bonds; these are the second- and third-highest occupied orbitals in the dimethyl complex and have energies of -4.3 and -4.5 eV, respectively. In the dichloro complex, four Cl lone pair levels appear at -7.5 to -7.8 eV, and the U-Cl σ bonds are slightly below these.

A comparison of the dimethyl and dichloro complexes leads to the expected conclusions that CH_3^- is a stronger σ donor than is Cl^- and that the U-C(Me) bonding orbitals have higher orbital

---

(1) Marks, T. J. *Prog. Inorg. Chem.* **1979**, *25*, 223.

(2) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989 and references therein.

(3) Marks, T. J.; Manriquez, J. M.; Fagan, P. J.; Day, V. W.; Day, C. S.; Vollmer, S. H. *ACS Symp. Ser.* **1980**, *No. 131*, 3.

(4) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

(5) Rösch, N.; Streitwieser, A. *J. Organomet. Chem.* **1978**, *145*, 195.

(6) Case, D. A. *Ann. Rev. Phys. Chem.* **1982**, *33*, 151.

(7) Ciliberto, E.; Condorelli, G.; Fagan, P. J.; Manriquez, J. M.; Fragala, I.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 4755.

(8) Bursten, B. E.; Fang, A.; Wilson, B. A., unpublished results.

(9) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H.; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839.

(10) Day, V. W.; Marks, T. J., private communication.

(11) Bursten, B. E.; Cotton, F. A. *Inorg. Chem.* **1981**, *20*, 3042.

(12) Wood, J. H.; Boring, A. M. *Phys. Rev. B* **1978**, *18*, 2701.

(13) Case, D. A.; Yang, C. Y. *J. Chem. Phys.* **1980**, *72*, 3443.

0002-7863/83/1505-6495$01.50/0

Table I. Calculated Transition-State Ionization Potentials for $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$

orbital	calculated IP, eV	assignment	exptl[a]
$11b_1$	5.58	U 5f	6.64 (x)
$9b_2$	6.30	$U\text{–}CH_3$	7.26 (a)
$13a_1$	6.50		
$10b_1$	7.08	$U\text{–}C_5H_5$ (π_2)	7.74
$8b_2$	7.22		8.16
$6a_2$	7.25		8.45 (b,c)
$12a_1$	7.30		
$9b_1$	10.24	C_5H_5 (π_1)	10.64 (d)

[a] Experimental values in eV for $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$ from ref 7. The band labels from that reference are given in parentheses.

Table II. Calculated Transition-State Ionization Potentials for $(\eta^5\text{-}C_5H_5)_2UCl_2$

orbital	calculated IP, eV	assignment	exptl[a]
$11b_1$	6.38	U 5f	6.85 (x)
$9b_2$	7.25	$U\text{–}C_5H_5$ (π_2)	7.47 (a)
$13a_1$	7.40		7.88 (a′)
$10b_1$	7.49		
$6a_2$	7.62		
$8b_2$	9.71	Cl lone pair	10.10 (b)
$5a_2$	9.92		10.65 (c)
$9b_1$	9.94		
$12a_1$	10.14		
$11a_1$	10.24	U–Cl	10.90 (c′)
$7b_2$	10.42		

[a] Experimental values in eV for $(\eta^5\text{-}C_5Me_5)_2UCl_2$ from ref 7. The band labels from that reference are given in parentheses.

energies than do the U–Cl bonds. There is no evidence that Cl^- acts as a π-donor to U in $(\eta^5\text{-}C_5H_5)_2UCl_2$.

The highest lying two electrons of each complex occupy orbitals that are essentially pure U 5f atomic orbitals. In order to simplify the calculations and to test the efficacy of the Xα-SW method applied to f orbital systems, we have required both of these electrons to occupy the same orbital, i.e., we have treated the complexes as closed-shell molecules. Even with this restriction the seven 5f orbitals are clustered quite closely together, and it is apparent that the molecule will prefer an open-shell, high-spin configuration for these last two electrons. This is consistent with the observed paramagnetism of the complexes.[14] As a further test, we have performed an Xα-SW calculation on the isostructural d^2 system $(\eta^5\text{-}C_5H_5)_2MoCl_2$, which is diamagnetic.[15] In this case, there is a healthy 2.2-eV gap between the HOMO and the LUMO, consistent with the preferred singlet spin properties of the Mo complex. Thus, the Xα-SW method correctly predicts the magnitude of both f and d orbital splitting in these bent metallocene molecules.

Ionization potentials for $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$ have been calculated using Slater's transition-state formalism.[16] The calculated ionization potentials are compared to the experimental values obtained by Fragala, Marks, et al.,[7] in Tables I and II. Even without the explicit inclusion of spin-orbit effects, the results are very satisfying. As is typical for Xα-SW calculations, the calculated ionization potentials are uniformly too low. The splittings between the various IP's are in excellent accord with the experimental ones, however, indicative that the RXα method properly estimates the extent of U-ligand interaction. The assignments presented here are in concurrence with those derived from the analysis of the relative He(I) and He(II) photoionization intensities with the exception of the band at 10.0–10.7 eV in the spectrum of $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$. This was proposed to be one of the ionizations due to the $U\text{–}CH_3$ bonds.[7] We find only a small splitting (~0.20 eV) between the two $U\text{–}CH_3$ ionizations and prefer that the band at 10.0–10.7 eV be assigned to ionizations from the totally symmetric π orbital of the $\eta^5\text{-}C_5Me_5$ rings.

Acknowledgment. We are grateful to Professors T. J. Marks and V. W. Day for results prior to publication. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$, 87136-09-2; $(\eta^5\text{-}C_5H_5)_2UCl_2$, 11077-15-9; $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$, 67605-92-9; $(\eta^5\text{-}C_5Me_5)_2U(Cl_2)$, 67506-89-2; $(\eta^5\text{-}C_5H_5)_2MoCl_2$, 12184-22-4.

---

(14) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

(15) Cooper, R. L.; Green, M. L. H. *J. Chem. Soc. A* **1967**, 1155.

(16) Slater, J. C. "Quantum Theory of Molecules and Solids. The Self-Consistent Field for Molecules and Solids"; McGraw-Hill: New York, 1974; Vol. 4.

Tricarbon Monoxide

Ronald D. Brown,* Frank W. Eastwood, Patricia S. Elmes, and Peter D. Godfrey

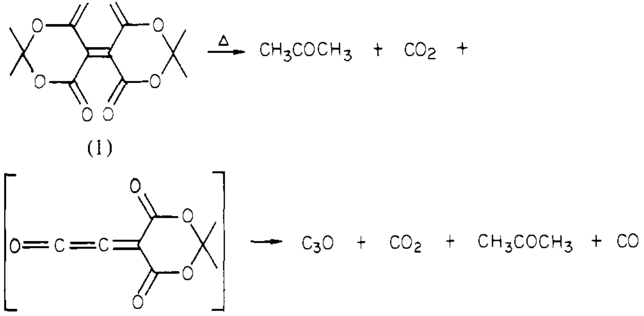
Monash University
Clayton, Victoria, Australia 3168

Received July 11, 1983

We wish to report the generation and identification of the gas-phase species C_3O. In 1971[1] DeKoch and Weltner reported the appearance of an IR absorption at 2241 cm^{-1} by reaction of C atoms with CO in an Ar matrix, attributing this band to C_3O. No further evidence in support of this assignment appears to have been forthcoming. Berke and Härter[2] described a chromium carbonyl complex containing C_3O as a ligand but did not observe C_3O as a separate species.

We set out to generate C_3O directly by an application of the pyrolytic decomposition pathway for Meldrum's acid and its derivatives[3] that has previously been exploited to generate and spectroscopically characterize propadienone, C_3H_2O.[4] Compound **1** was prepared[5] and pyrolyzed in a quartz tube of 20-mm i.d. × 400-mm length attached to a quadrupole mass spectrometer and microwave spectrometer cell.

As expected, at 500 °C **1** decomposed to yield acetone, CO_2, and some CO (detected in the QMS). At temperatures of 600 °C and higher a peak at m/z 52 appeared. At this temperature the mass spectrum showed some increase in peaks due to acetone, CO_2, and CO.



In the microwave spectrometer all of the stronger lines of acetone were observed under these conditions. In addition some weak lines, which increased in intensity as the pyrolysis tem-

---

(1) DeKock, R. L.; Weltner, W. *J. Am. Chem. Soc.* **1971**, *93*, 7106–7107.

(2) Berke, H.; Härter, P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 225–226.

(3) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Aust. J. Chem.* **1974**, *27*, 2373–2384.

(4) Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 7421–7422; *Aust. J. Chem.* **1977**, *30*, 179–193. Blackman, G. L.; Brown, R. D.; Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *J. Mol. Spectrosc.* **1977**, *68*, 488–491. Brown, R. D.; Godfrey, P. D.; Champion, R.; McNaughton, D. *J. Am. Chem. Soc.* **1981**, *103*, 5711–5715; **1982**, *104*, 6167. Brown, R. D. *J. Mol. Struct.* **1983**, *97*, 293–302.

(5) Snyder, H. R.; Kruse, C. W. *J. Am. Chem. Soc.* **1958**, *80*, 1942–1944.