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Photoelectron Spectroscopy of f-Element Organometallic Complexes. 4. Comparative Studies of Bis(pentamethylcyclopentadienyl) Dichloride and Dimethyl Complexes of Uranium(IV), Thorium(IV), and Zirconium(IV)

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Abstract: This paper presents the first comparative study of the photoelectron spectra of a series of transition-metal and actinide organometallic compounds with exactly the same ligand array, i.e., $M[\eta^5\text{-}(CH_3)_5C_5]_2X_2$ where M = Zr, Th, and U and X = CH_3 and Cl. Studies were performed with both He I and He II photon energies. It is found that the bonding in these complexes is rather similar, and differences within the series are smaller than would be encountered in changing to M = Nb or Mo. The major differences between Zr and the actinides appear to arise from metal–ligand bonding involving metal 5f orbitals. A distinctive $5f^2$ ionization signal is observed in the spectra of both uranium complexes.

A major goal today in actinide organometallic chemistry[2] is to understand and to correlate chemical reactivity patterns with molecular and electronic structure. Furthermore, it is essential to develop meaningful comparisons between the properties of actinide complexes and those of analogous d-element organometallic complexes. In regard to elucidating the electronic structure of actinide organometallic and coordination compounds, photoelectron (PE) spectroscopy utilizing variable photon energies, i.e., He I (21.2 eV) and He II (40.8 eV), has provided valuable information on metal–ligand bonding.[3-5]

Recently, considerable interest in f-element organometallic chemistry has focused on the properties of thorium and uranium bis(pentamethylcyclopentadienyl) compounds, $M[\eta^5\text{-}(CH_3)_5C_5]_2X_2$.[6] These are some of the most reactive organoactinides prepared to date, and a rich stoichiometric and catalytic chemistry is emerging. Moreover, these compounds represent the first series of organoactinides which contain a ligand array *identical* with that of a well-characterized d-element system (M = Ti, Zr, Hf).[7] Thus detailed comparisons of many chemical as well as physicochemical observables should be possible. For these reasons we have carried out a comparative investigation of the He I and He II photoelectron spectra of a series of $M[(CH_3)_5C_5]_2X_2$ complexes. By variation of the metal ion from M = Zr(IV) ($4d^0$) to Th(IV) ($5f^0$) to U(IV) ($5f^2$) and of the X substituent from Cl to CH_3, it is possible to examine trends in metal–ligand bonding for transition-metal and actinide ions, while systematically varying important aspects of electronic configuration and ligand identity.

Experimental Section

Materials. The organoactinides employed in this study were prepared as described elsewhere.[6,8] All compounds were purified by multiple recrystallization under a rigorously anaerobic atmosphere. The compounds $Zr[(CH_3)_5C_5]_2Cl_2$ and $Zr[(CH_3)_5C_5]_2(CH_3)_2$ were prepared by the literature procedure[9] and were also multiply recrystallized. The purity of all organometallics used for this study was ascertained by elemental analysis, as well as by ^1H NMR and IR spectroscopy. Samples were handled under inert atmosphere at all times.

Measurements. PE spectra were obtained with a Perkin-Elmer PS-18 spectrometer modified for He II measurements by including a hollow cathode lamp producing a high photon flux at the He II wavelength (Helectros Developments Co.). Spectra were recorded at temperatures ranging from ca. 120 °C in the case of the dichlorides to 140 °C for the dimethyls. Several scans were made of each sample to check for possible thermal decomposition. The ionization energy (IE) scale in the spectra was calibrated by reference to peaks arising from admixed inert gases and He $1s^{-1}$ self-ionization. Quantitative evaluation of spectral band intensities was not always possible due to the complexity of the spectra. Thus, intensity arguments in He I vs. He II comparisons are only made when relative variations in peak height are clear and unambiguous.

Results and Discussion

X-ray diffraction structural data are now available for a large number of actinide and transition-metal $M[(CH_3)_5C_5]_2X_2$ compounds[6d,h,10] as well as $M(C_5H_5)_2X_2$ and $M(CH_3C_5H_4)_2X_2$ analogues.[6d,11] On the basis of these results as well as spectral and

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(1) (a) Università di Catania. (b) Northwestern University. (c) Camille and Henry Dreyfus Teacher-Scholar.

(2) (a) Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, in press. (b) Marks, T. J.; Fischer, R. D., Eds. "Organometallics of the f-Elements"; D. Reidel Publishing Co.: Dordrecht, Holland, 1979. (c) Marks, T. J. *Prog. Inorg. Chem.* **1979**, *25*, 224–333. (d) Cotton, S. A. *J. Organomet. Chem. Libr.* **1977**, *3*, 189–217. (e) Baker, E. C.; Halstead, G. W.; Raymond, K. N. *Struct. Bonding (Berlin)* **1976**, *25*, 23–68. (f) Marks, T. J. *Acc. Chem. Res.* **1976**, *9*, 223–230.

(3) Fragalà, I. In ref 2a, pp 421–466.

(4) (a) Cyclooctatetraene complexes: Fragalà, I.; Condorelli, G.; Zenella, P.; Tondello, E. *J. Organomet. Chem.* **1976**, *122*, 357–363. (b) Cyclopentadienyl complexes: Fragalà, I.; Ciliberto, E.; Fischer, R. D.; Sienel, G. R.; Zanella, P. *Ibid.* **1976**, *120*, C9–C12. (c) Indenyl complexes: Fragalà, I.; Goffart, J.; Condorelli, G. "Abstracts of the papers", The Eighth International Conference on Organometallic Chemistry, 4C04 (to be submitted for publication in *Inorg. Chem.*).

(5) Fragalà, I.; Condorelli, G.; Tondello, E.; Cassol, A. *Inorg. Chem.* **1978**, *17*, 3175–3179.

(6) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J. In ref 2a, pp 113–148. (b) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939–3941. (c) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Ibid.* **1978**, *100*, 7112–7114. (d) Marks, T. J.; Manriquez, J. M.; Fagan, P. J.; Day, V. W.; Day, C. S.; Vollmer, S. H. *ACS Symp. Ser.* **1980**, *No. 131*, 1–29. (e) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5396. (f) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Day, V. W.; Vollmer, S. H. *Ibid.*, in press. (g) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.*, in press. (h) Day, V. W., private communication.

(7) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127 and references therein.

(8) Fagan, P. J.; Manriquez, J. M.; Marks, T. J., manuscript in preparation.

(9) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.

(10) (a) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218–219. (b) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975** *102*, 457–466.

0002-7863/81/1503-4755$01.25/0

Table I. Symmetry Classification of Atomic and Molecular Orbitals in C_{2v} $M(C_5H_5)_2X_2$ Compounds ($X = CH_3$, Cl)[a,b]

symmetry	5f set	6d set	CH_3 σ set	Cl 3p set	Cp π set
a_1	$f_{z^3}, f_{z(x^2-y^2)}$	$d_{z^2}, (d_{x^2-y^2})$	$a_1(\sigma)$	$a_1(\sigma)^*$	$a_1(\pi)$
b_1	$f_{xz^2}, (f_{x(x^2-3y^2)})$	d_{xz}	$b_1(\sigma)$	$b_1(\sigma)$, $^*b_1(\pi)^*$	$b_1(\pi)$
a_2	f_{xyz}	(d_{xy})		$a_2(\pi)^{**}$	$a_2(\pi)$
b_2	$f_{yz^2}, (f_{y(3x^2-y^2)})$	d_{yz}		$b_2(\pi)^*$	$b_2(\pi)$

[a] Orbitals in parentheses are not expected to have appreciable overlap with the X_2 set. [b] For the Cl 3p set, the asterisk denotes orbitals providing comparable group overlap with metal 6d and 5f orbitals, while the double asterisk denotes orbitals providing specific interactions with metal 5f orbitals.

Table II. Ionization Energy Data and Assignments for $M[(CH_3)_5C_5]_2Cl_2$ Compounds

	ionization energies, eV				
band label	$Zr(C_5H_5)_2Cl_2$[a]	$Zr[(CH_3)_5C_5]_2Cl_2$	$Th[(CH_3)_5C_5]_2Cl_2$	$U[(CH_3)_5C_5]_2Cl_2$	assignment
x				6.85	$^2F_{5/2}$
a	8.60 9.08	7.55	7.43	7.47	a_1,b_1 } Cpπ
a′	9.84	7.97	7.90	7.88	a_2,b_2 } Cpπ
b	10.45	9.96	10.2	10.10	$b_1(\pi)$
c		10.85	10.73	10.65	$a_1(\pi),b_2(\pi)$ } Cl3p[b]
c′	11.12	11.06	11.00	10.90	$a_2(\pi),b_1(\sigma)$ } Cl3p[b]
d	11.33	11.52	11.32	11.35	$a_1(\sigma)$ } Cl3p[b]

[a] Taken from ref 12a. [b] Strict σ and π separation is precluded in C_{2v} symmetry. The σ notation indicates orbitals quantized along the M–Cl axes.

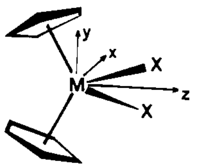

Figure 1. Schematic structure of $M[(CH_3)_5C_5]_2X_2$ complexes.

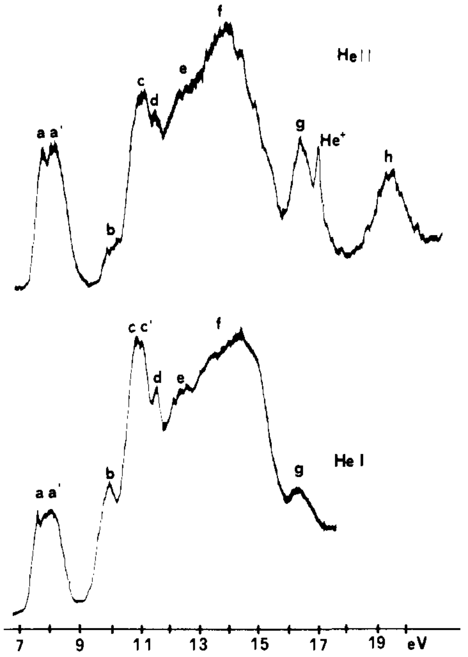

Figure 2. Full He I and He II spectra of $Zr[(CH_3)_5C_5]_2Cl_2$. The narrow peak at 17.03 eV represents He ($1s^{-1}$) self-ionization excited by He II (β) radiation.

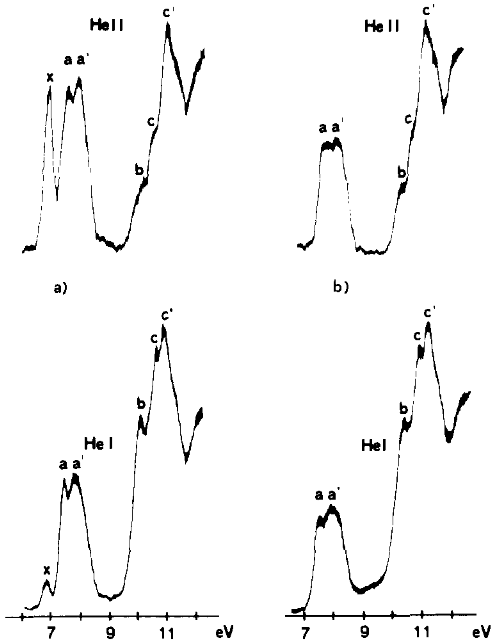

Figure 3. (a) He I and He II spectra of $U[(CH_3)_5C_5]_2Cl_2$ (low IE region). (b) He I and He II spectra of $Th[(CH_3)_5C_5]_2Cl_2$ (low IE region). The regions above 12 eV are identical with those in Figure 2 and are not shown.

molecular weight data,[6] the bent-sandwich C_{2v} structure shown in Figure 1 is assigned to all complexes employed in this study. When the present PE spectroscopic results are interpreted, reference is made to previous, detailed studies of d-element $M(C_5H_5)_2X_2$ and $M(CH_3C_5H_4)_2X_2$ compounds[12] as well as of other d-element and main-group organometallics.[13] The present organoactinide analyses also draw upon results for 5f cyclopentadienyl ($M(C_5H_5)_3X$[4b]) and cyclooctatetraene ($M(C_8H_8)_2$[4a,14])

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(11) (a) Fronczek, F. R.; Baker, E. C.; Sharp, P. R.; Raymond, K. N.; Alt, H. G.; Rausch, M. D. *Inorg. Chem.* **1976**, *15*, 2284–2289 and references therein. (b) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422–6433. (c) Prout, K.; Cameron, T. S.; Forder, R. A.; Crichley, S. R.; Denton, B.; Rees, R. V. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290–2304 and references therein.

(12) (a) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragalà, I.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 61–73. (b) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433–6441. (c) Condorelli, G.; Fragalà, I.; Centineo, A.; Tondello, E. *J. Organomet. Chem.* **1975**, *87*, 311–315.

(13) (a) Egdell, R. G.; Fragalà, I.; Orchard, A. F. *J. Electron. Spectrosc. Relat. Phenom.* **1978**, *14*, 467–475. (b) Fragalà, I.; Ciliberto, E.; Egdell, R. G.; Granozzi, G. *J. Chem. Soc., Dalton Trans.* **1980**, 145–148. (c) Cauletti, C.; Green, J. C.; Kelly, M. R.; Powell, P.; van Tilborg, J.; Robbins, J.; Smart, J. *J. Electron. Spectrosc. Relat. Phenom.* **1980**, *19*, 327–353. (d) Energy and intensity data for early members of the $M[(CH_3)_5C_5]_2$ sandwich series[13c] suggest that some tailing of the ring ionization might underlie other, more intense features in the 11-eV region of the present compounds.

(14) Clark, J. P.; Green, J. C. *J. Chem. Soc., Dalton Trans.* **1978**, 505–508.

systems. From these investigations and other work, several important generalizations can be made about how the spectral intensities of ionizations associated with various atomic orbitals (or molecular orbitals composed thereof) depend on increasing photon energy. When carbon 2p is taken as a reference, cross-sections for electrons ejected from halogen p orbitals decrease on going from He I to He II, while cross-sections for metal d orbitals show a moderate to zero increase (the enhancement effect falling off with increasing atomic number) and those for metal f orbitals a very large increase.

In the discussion which follows, reference is made to symmetry-adapted linear combinations (SALCs) of atomic orbitals appropriate for the C_{2v} point group. This information is compiled in Table I.

$M[(CH_3)_5C_5]_2Cl_2$ Compounds. PE spectra for the various dichlorides are presented in Figures 2 and 3. Data are set out in Table II. Taking the $Zr[(CH_3)_5C_5]_2Cl_2$ spectrum as an example, earlier studies[12,13] of cyclopentadienyl and pentamethylcyclopentadienyl complexes have identified spectral features having energies greater than ca. 11.5 eV as ionizations from orbitals which predominantly compose the cyclopentadienyl σ-bond and inner π-bond framework. Band e, however, is peculiar to η^5-$(CH_3)_5C_5$ systems and is likely related to molecular orbitals (MOs) localized primarily on the ring methyl groups. Furthermore, from previous work, the broad band f is attributed to σ MOs with predominant C 2p character.[3,12,13] This transition is likely to include ionization from low-lying π MOs arising from symmetry combinations of $(CH_3)_5C_5^-$ a_1 MOs (under D_{5h} symmetry). Band g is assigned to ionization from ring σ MOs with considerable C 2s character ($a'_1 + e'_1 + e'_2$ under D_{5h} symmetry); the increase in intensity of this band with He II radiation is the expected[3] cross-section change for C 2s. Finally, band h must also be related to σ MOs with high C 2s character (e(σ) in $(CH_3)_5C_5^-$). These bands at energies higher than 12 eV involve MOs which are not significantly involved in metal–ligand bonding and will not be considered in greater detail.

Turning now to the ionization region below 11.5 eV, two major envelopes are present in the PE spectra of the $M[(CH_3)_5C_5]_2Cl_2$ compounds. These are labeled a, a′ and b, c, c′, d, respectively. In addition, the uranium complex exhibits a low-energy ionization band labeled x. It is noted that the change from He I to He II ionization causes marked band intensity changes in this spectral region. Relative to the C 2p ionizations, the a, a′ bands increase slightly in intensity, the b, c, c′, d bands decrease in intensity, and the intensity of the x band increases enormously. From studies on similar $M(C_5H_5)_2X_2$ complexes, the a, and a′ transitions can be related to ionizations from π MOs (C 2p) which are composed of symmetry combinations of $(CH_3)_5C_5^-$ e_1'' (under D_{5h} symmetry) orbitals.[3,12,13] Under C_{2v} symmetry (Figure 1) these combinations transform as a_2, b_1, a_1, and b_2 (Table I). The a, a′ cross-section increases observed relative to b–d with He II radiation indicate that detectable mixing with metal d or f orbitals may occur; however, some of the effect is surely also due to the large C 2p/Cl 3p He II cross-section ratio[12a,13b] (vide infra). The ionization energies from the ring π MOs are slightly lower for $Zr[(CH_3)_5C_5]_2Cl_2$ than for $Zr(C_5H_5)_2Cl_2$ (Table II), reflecting the electron-releasing effect of the methyl substituents.[15] The $Zr[(CH_3)_5C_5]_2Cl_2$ a, a′ ionization energies are slightly higher (ca. 0.3 eV) than the corresponding ionizations for the early members of the transition-metal $M[(CH_3)_5C_5]_2$ series,[13c] consistent with the greater positive charge of the tetravalent metal ion. The envelope in the a, a′ region is also narrower and less structured in the present case than in $M(C_5H_5)_2Cl_2$ analogues (e.g., M = Zr).[12a] The energy separation of the ring a_2, b_1, a_1, and b_2 π MOs no doubt reflects both metal–ring bonding interactions as well as ring–ring nonbonding interactions. That the a, a′ envelope is essentially insensitive to metal ion identity (M = Zr, Th, U) in the present series where both 4d as well as 6d/5f orbitals are involved, suggests that, in contrast to the case of simpler $M(C_5H_5)_2Cl_2$ complexes, metal–ring interactions are of little importance in determining the relative energies of these ring molecular orbitals. A reduction in this differentiation may also reflect a somewhat smaller interligand nonbonding interaction because of the slightly greater ring–ring separations in the complexes of the bulkier pentamethylcyclopentadienyl ligand. For example, ring centroid–metal–ring centroid angles in $M(C_5H_5)_2X_2$ compounds are typically in the range of 126–132°,[11] while in $M[(CH_3)_5C_5]_2X_2$ compounds the angle is slightly larger (130–138°) for comparable M and X entities.[6b,g,10] As this angle increases, the $a_2 + b_1$ and $a_1 + b_2$ orbital pairs are transformed into the degenerate e_{1g} and e_{1u} symmetry species of the D_{5d} metallocene.[13c,15] We note in this context that the doublet structure presently observed is strongly reminiscent of that observed in $M(C_5H_5)_2$ and $M[(CH_3)_5C_5]_2$ sandwich complexes. For a given metal ion, some reduction of ring–ring interactions is also expected from the longer M–C distances (ca. 0.05–0.1 Å) in pentamethylcyclopentadienyl complexes.[6g,10,11] It is interesting to note that the $(CH_3)_5C_5$ π MO ionization pattern is qualitatitively so similar for the transition-metal and actinide ions. This result indicates a strong similarity in the bonding (vide infra).

The bands at 9.5–11.5 eV in the dichloride spectra can be assigned to ionizations from MOs of predominantly Cl 3p character.[12,13] These transitions are not observed in the spectra of the corresponding dimethyl complexes (vide infra) and display the expected Cl 3p diminution in cross-section at higher photon energy. It has been previously noted that the energy differences among the various σ and π Cl 3p symmetry combinations are a sensitive function of metal–ligand bonding interactins as well as ligand–ligand nonbonding interactions.[12] Turning first to the $Zr[(CH_3)_5C_5]_2Cl_2$ spectrum (Figure 1) it can be seen that the b, c, c′, d band pattern is very similar to that in $Zr(C_5H_5)_2Cl_2$ (Table II) and that b, c, c′, d can be assigned, in a localized bonding model,[16,17] to ionization from the $b_1(\pi)$, $a_1(\pi)$ $b_2(\pi) + a_2(\pi) + b_1(\sigma)$ (irrespective of ordering), and $a_1(\sigma)$ MOs, respectively. The major difference between the $Zr(C_5H_5)_2Cl_2$ and $Zr[(CH_3)_5C_5]_2Cl_2$ spectra in this region is that band b, the ionization from the essentially nonbonding $b_1(\pi)$ MO, occurs at appreciably lower energy for the ring-methylated derivative. This effect has been ascribed to extra-atomic relaxation[18] in the $^2B_1$ ion state due to enhanced $(CH_3)_5C_5^-$ polarization by the highly localized positive hole produced on ionization.[19]

Although the spectra of the thorium and uranium dichlorides are strongly similar to that of the zirconium dichloride in the 9.5–11.5-eV region (Figure 3) and can be assigned by analogy, there are also some notable differences. Relative to the zirconium complex, bands b and d (the ionizations from the Cl 3p $b_1(\pi)$ and $a_1(\sigma)$ orbitals, respectively) shift inward toward the c, c′ doublet in the actinide complexes. Some of this effect presumably reflects differences in metrical parameters, due to the larger ionic radii of the actinide ions. Thus, the greater Cl–Cl distance no doubt reduces nonbonded interactions and decreases the energy dispersion of the various Cl 3p ionizations. Also, the increased $(CH_3)_5C_5$–Cl distances are likely to reduce the importance of the aforementioned relaxation effects and thus to raise the energy of band b. An examination of the spectral alterations on changing from He I to He II radiation indicates that other effects also contribute to differences between zirconium and the actinides. Thus, for thorium and uranium, band c′ does not decrease as greatly in intensity as for zirconium. The previous distance-related effects do not appear adequate to explain these differences. Rather, within the

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(15) Evans, S.; Green, M. L. H.; Jewitt, B.; Orchard, A. F.; Pygall, C. F. *J. Chem. Soc., Faraday Trans. 2*, **1972**, 68, 1847–1865.

(16) Cox, P. A.; Evans, S.; Orchard, A. F.; Richardson, N. V.; Roberts, P. J. *Faraday Discuss. Chem. Soc.* **1972**, *No. 54*, 26–40.

(17) As far as the $>MCl_2$ network is concerned, no significant variations in bond distances and bond angles have been observed on passing from analogous transition-metal $M(C_5H_5)_2Cl_2$ to $M[(CH_3)_5C_5]_2Cl_2$ complexes (see ref 10 and 11 and references cited therein). This necessarily implies nearly identical interligand and metal–ligand group overlaps.

(18) Fadley, C. S. In "Electron Spectroscopy: Theory, Techniques and Applications", Brundle, C. R.; Baker, A. D., Eds.; Academic Press: London 1978; pp 1–156.

(19) Fragalà, I.; Marks, T. J.; Fagan, P. J.; Manriquez, J. M. *J. Electron. Spectrosc. Relat. Phenom.* **1980**, *20*, 249–252.

Table III. Ionization Energy Data and Assignments for $M[(CH_3)_5C_5]_2(CH_3)_2$ Compounds

	ionization energies, eV			
band	$Zr[(CH_3)_5C_5]_2(CH_3)_2$	$Th[(CH_3)_5C_5]_2(CH_3)_2$	$U[(CH_3)_5C_5]_2(CH_3)_2$	assignment
x			6.64	${}^2F_{5/2}$
a	7.18	7.00	7.26	$b_1\,(\sigma_{M-C})$
b	7.85	7.30	7.74	$\left.\begin{matrix}a_1,b_1\\a_2,b_2\end{matrix}\right\}Cp\pi$
b′		7.73	8.16	
c		8.03	8.45	
d	10.27	10.22	10.64	$a_1\,(\sigma_{M-C})$

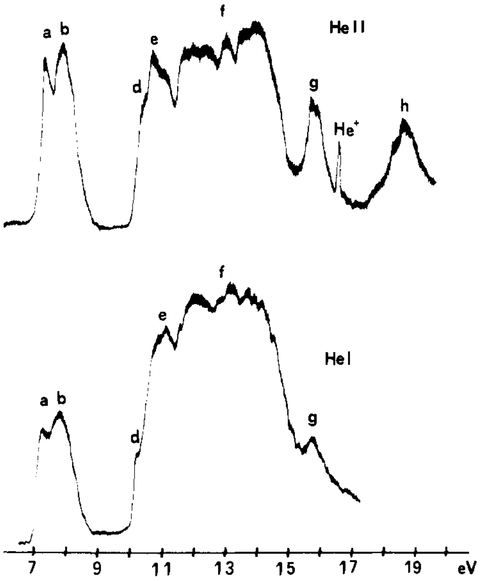

Figure 4. Full He I and He II spectra of $Zr[(CH_3)_5C_5]_2(CH_3)_2$.

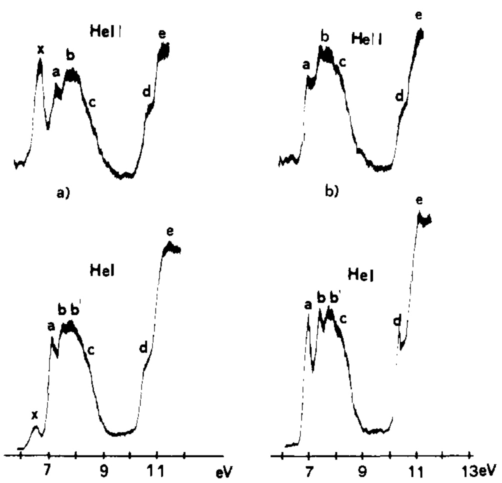

Figure 5. (a) He I and He II spectra of $U[(CH_3)_5C_5]_2(CH_3)_2$ (low IE region). (b) He I and He II spectra of $Th[(CH_3)_5C_5]_2(CH_3)_2$ (low IE region). The regions above 12 eV are identical with those in Figure 4 and are not shown.

framework of the Gelius model,[20] a more plausible explanation is admixture of metal 5f orbitals (besides 6d[21]) into the Cl 3p set. In Table I are given Cl 3p combinations of appropriate symmetry to overlap with both 6d and 5f orbitals (asterisk) and with only 5f orbitals (double asterisk). It can be seen that only the chlorine $a_2(\pi)$ orbital is uniquely suited for mixing with a metal 5f orbital, thus plausibly accounting for the enhanced He II intensity of band c′ in the actinide complexes.

The remaining band to be assigned in the dichloride spectra is the low-energy ionization in the uranium compound (band x). The energy as well as the marked increase in intensity of this band at higher photon energy is characteristic of a 5f electron ionization.[3]

$M[(CH_3)_5C_5]_2(CH_3)_2$ Compounds. PE spectra of the zirconium and actinide dimethyls are shown in Figures 4 and 5. Data are tabulated in Table III. Turning first to the He I and He II spectra of $Zr[(CH_3)_5C_5]_2(CH_3)_2$, it can be seen that the Cl 3p ionizations observed in the dichlorides are absent and that the low-energy ionization envelope (bands a and b) has broadened somewhat and shifted to lower energy. This band no doubt includes ionizations from π $(CH_3)_5C_5$ MOs (a_2, b_1, a_1, and b_2). Some of the observed shift to lower energy in the dimethyl compound may reflect the greater electron-releasing tendency of the two methyl ligands. It is also probable that the locally antisymmetric (b_1) symmetry combination of the Zr–CH_3 bonding MOs falls within the a and b multiplet. On the basis of these observations and results for $M(C_5H_5)_2(CH_3)_2$ compounds (M = Mo, W),[22a] band a is the most plausible selection for this transition. The totally symmetric (a_1) metal–carbon σ combination is expected at higher ionization energy[22b] and band d appears to be the ionization from this MO. The absence of this feature in the PE spectra of early decamethylmetallocenes[13c] and of the bent sandwich compound $Sn[(CH_3)_5C_5]_2$[23] supports this assignment. The average of the assigned a_1 and b_1 ionization energies, 8.7 eV, is in reasonable agreement with data for other transition-metal alkyls.[22b]

The PE spectra of $Th[(CH_3)_5C_5]_2(CH_3)_2$ and $U[(CH_3)_5C_5]_2(CH_3)_2$ differ significantly from the zirconium dimethyl in the 7.5–10-eV region. The differences are much greater than in the analogous series of dichlorides. In particular, the observed envelopes are considerably broader and more structured for the actinide complexes. It is reasonable to again assign band a to the antisymmetric b_1 σ M–C combination and, correspondingly, band d to the a_1 combination. It is noted that ΔIE (a_1–b_1) for the actinide dimethyls (ca. 3.2 eV) is nearly identical with that for the zirconium dimethyl, indicating considerable similarity in bonding. In contrast, ΔIE for $Mo(C_5H_5)_2(CH_3)_2$ and $W(C_5H_5)_2(CH_3)_2$[22a] is on the order of ca. 1.5 eV, reflecting considerable dissimilarity in electronic/molecular structure for the d^2 systems. The dispersion of bands b, b′, and c in the actinide spectra as compared to the zirconium spectrum is not explained by ring–ring nonbonded interactions since this effect is reasonably smaller for the actinide complexes. Rather, the best explanation appears to be enhanced metal–ring interaction, probably involving 5f orbitals of appropriate symmetry (Table I).

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(20) Gelius, U. In "Electron Spectroscopy"; Shirley, D. A., Ed.; North-Holland, Publishing Co.: Amsterdam, 1972; pp 311–334.

(21) (a) It has been shown that 6d orbitals are important in actinide–ligand bonding.[14,21b,c] The differences in the He II spectra of $Zr[(CH_3)_5C_5]_2Cl_2$ and the actinide dichlorides cannot, however, be interpreted simply in terms of 6d instead of 4d metal–ligand bonding. Recent evidence indicates that 6d cross-sections are smaller than 4d cross-sections at He II photon energies.[4,14,21c] (b) Rosch, N.; Streitwieser, A., Jr. *J. Organomet. Chem.* **1978**, *145*, 195–200. (c) Thornton, G.; Edelstein, N.; Rösch, N.; Egdell, R. G.; Woodwark, D. R. *J. Chem. Phys.* **1979**, *70*, 5218–5221.

(22) (a) Green, J. C.; Jackson, S.; Higginson, B. *J. Chem. Soc., Dalton Trans.* **1975**, 403–409. IE's: 8.3 ($2b_1$), 9.6 ($1a_1$) eV. (b) Cowley, A. H. *Prog. Inorg. Chem.* **1979** *26*, 133–139. The spread between the ionizations for the various M–C bonding combinatins is frequently on the order of 2 eV ($Re(CH_3)_6$) to 5 eV ($Ge(CH_3)_4$). For transition-metal organometallics, the weighted average of these ionizations is usually near 9 eV. Functionalization of a methyl group (e.g., $CH_3 \rightarrow CH_2C(CH_3)_3$) generally lowers the ionization energy.

(23) Fragalà, I.; Jützi, P. "Proceedings of the 3rd International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin, and Lead", Dortmund, West Germany, 1980.

J. Am. Chem. Soc. **1981,** *103,* 4759–4763

The lowest energy ionization in the $U[(CH_3)_5C_5]_2(CH_3)_2$ spectrum (x) is assigned, as in the uranium dichloride, to the $^2F_{5/2}$ final state component derived from the $5f^2$ ground-state configuration. The other spin–orbit component, $^2F_{7/2}$, expected for a one-electron ionization of the U(IV) $^3H_4$ ground term, is not observed. The probability of reaching this state is small,[3] and the weak transition is likely to be obscured by other spectral features. There is also no evidence of ligand field splitting of the x transition. With the exception of $U(C_5H_5)_3BH_4$,[4b] such effects have been too small to be observed in organouranium PE spectra.[3,4] The $5f^2$ ionization in the uranium dimethyl compound is at lower energy than in the dichloride, as expected because of the electron-releasing properties of the σ-bonded methyl groups. However, the IE difference ($\Delta IE = 0.21$ eV) is much smaller than would have been expected from considering a similar d^2 system. For instance, on passing from $Mo(C_5H_5)_2Cl_2$[12b] to $Mo(C_5H_5)_2(CH_3)_2$[22] the IE shift of the d^{-1} ionization is 2.5 eV. Although the smaller organoactinide ΔIE may reflect π bonding involving chlorine lone pairs, an equally plausible explanation can be advanced in terms of extraatomic relaxation in the $^2F_{5/2}$ ion state. Namely, the electrostatic polarization of the nonbonding electron density of chlorine groups by the strongly localized positive hole produced upon ionization of 5f subshells stabilizes the $^2F_{5/2}$ state to a greater degree.

Conclusions

This study provides the first comparison of He I/He II PE spectra for a series of transition-metal and actinide organometallic compounds with an identical ligand array. The most striking result of this comparison is that the spectra, hence many of the bonding characteristics, are so similar. To put this similarity in perspective, it is instructive to contrast the rather modest differences in orbital ionization energies observed in the present series with the changes observed in the series $Zr(C_5H_5)_2Cl_2$, $Nb(C_5H_5)_2Cl_2$, $Mo(C_5H_5)_2Cl_2$.[12a] As the d^0, d^1, d^2 series is traversed, far more drastic changes are observed. There is a reversal in level ordering with the ionization energy of the predominantly ring π orbitals increasing by ca. 1.5 eV and the ionization energy of the predominantly halogen 3p orbitals falling by ca. 1.5 eV. These trends reflect major changes in the metal orbital energies and metal–ligand bonding which are not observed in the Zr, Th, U series.

Differences within the Zr, Th, U series are observed. Within the $M[(CH_3)_5C_5]_2Cl_2$ group, there is some evidence for π interaction between Cl 3p-based $b_1(\pi)$ MOs and actinide $5f_{xyz}$ orbitals. While there appears to be no corresponding, conspicuous interaction with the $(CH_3)_5C_5^-$ π MOs in the dichlorides, the situation appears opposite in the actinide $M[(CH_3)_5C_5]_2(CH_3)_2$ compounds. Here, the methyl substituents are not suited for a π dative interaction with the metal ions, and possible as a consequence, the deviation from the zirconium system is this time observed in the ring π MO ionizations. Further investigations in this area, including calculations,[24] are in progress.

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(24) (a) Bursten, B. E., unpublished results. (b) Fagan, P. J.; Fragalà, I.; Marks, T. J., unpublished results.

The Ambidentate Thiocyanate Ligand. Niobium-93 Nuclear Magnetic Resonance Detection of (Thiocyanato)- and (Isothiocyanato)niobium(V) Complexes

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Abstract: Niobium-93 NMR investigation of acetonitrile solutions containing six-coordinate niobium(V) complexes with thiocyanate ion and chloride ion ligands has revealed 16 magnetically nonequivalent niobium environments (i.e., different complexes) within a chemical shift range of 1342 ppm. Use of the pairwise additivity model has enabled the assignment of these spectral lines to 16 of the 56 different configurations possible for the system $[Nb(NCS)_n(SCN)_mCl_{6-(n+m)}]^-$. The ligand redistribution reaction which gives rise to these complexes produces both S-bonded and N-bonded thiocyanate complexes with about equal frequency. The previously unreported $[Nb(SCN)_6]^-$ represents the first case of a homogeneous complex in which thiocyanate ion bonds through its sulfur atom to a class a metal. Some new questions are raised about the hard–soft acid–base generalization for chemical bonding.

The study here reported deals with a metal–ligand system made highly complex by virtue of linkage isomerism, with a novel spectroscopic technique the discriminating power of which matches the complexity of the system under study, and with the limitations to a metal–ligand bonding generalization that has come to enjoy widespread currency among inorganic chemists.

The Metal–Ligand System. The pioneering work of Werner on cobalt complexes done in the early part of this century established the beauty, symmetry, and simplicity of six-coordination. If the six ligands surrounding a metal atom are of three different types, however, much of the simplicity disappears. A complex $MX_2Y_2Z_2$ has 5 geometric isomers, and if the lability of this complex in solution gives intermolecular redistribution of ligands, the resulting system of $MX_nY_mZ_{6-(n+m)}$ complexes permits 28 different stoichiometries encompassing 56 different configurations. The niobium(V) complexes reported in this study undergo slow ligand redistribution to give an equilibrium mixture of identifiably discrete configurations in solution, all belonging to the $[Nb(NCS)_n(SCN)_mCl_{6-(n+m)}]^-$ system.

Pairwise Additivity and ^{93}Nb Chemical Shifts. There are few analytical techniques capable of identifying the presence of one specific configuration in a solution mixture which may contain

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