for 18 h as described in the previous experimental. The solvent was blown off with N_2 to yield 0.58 mg of an orange solid. The solid was vacuum sublimed to give 0.050 g (0.16 mmol, 87%) of crystalline $(CO)_5MnI$ (IR (hexane, cm^{-1}) 2131 (w), 2050 (s), 2009 (m)) which was identical with an authentic sample[30] by TLC.

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Registry No. 1, 81831-11-0; 2, 81846-86-8; 7, 81831-12-1; $(CO)_5MnCH_2OCH_3$, 71147-66-5; $K[(CO)_5Mn]$, 15693-51-3; $(CO)_5MnI$, 14879-42-6; H_2CO, 50-00-0; $(CH_3)_3SiI$, 16029-98-4.

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[30] Quick, M. H.; Angelici, R. J. *Inorg. Synth.* 1979, *19*, 161.

Photoelectron Spectroscopy of f-Element Organometallic Complexes. 5. Comparative Study of Ring-Substituted Uranocenes

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This paper presents the first data obtained on the electronic structure of 1,1′-ring-substituted uranocenes studied by He I and He II photoelectron spectroscopy. Quite unexpectedly, differences of the electron donor–acceptor properties of substituents do not result in any significant change of spectral patterns, the photoelectron data thus pointing to the same bonding model adopted for the unsubstituted complex. Ring substitution leads to the lifting of degeneracy of π orbitals in the electroneutral free ligand. By contrast similar effects, due to the lowering of the symmetry, are not evident in the spectra of 1,1′-ring-substituted complexes neither in the form of splitting nor broadening of ligand-centered photoelectron bands. Within the proposed molecular orbital model, this observation is evidence of comparable involvement of U 5f and U 6d orbitals in the metal–ligand bonding. The values associated with ionizations of ligand-centered π molecular orbitals in the ring-substituted uranocenes do not depend upon the nature of a particular substituent. This observation suggests an almost unique ability of the central uranium atom to restore electronic charge variation induced on the ligand.

Introduction

Great efforts in recent years devoted to an understanding of the metal–ligand bonding in actinoid organometallics have resulted in a revision of some aspects of the bonding model previously adopted.[1] Thus the photoelectron (PE) spectra of the highly symmetrical cyclooctatetraenide complexes, $An(C_8H_8)_2$ (An = Th(IV), U(IV)), have provided evidence of a substantial participation of 6d as well as 5f orbitals in the bonding,[2] and analogous conclusions have been arrived at by high-level theoretical calculations.[3] In the case of actinide complexes of considerably lower symmetry, the use of combined He I and He II PE techniques as well as the comparison with the spectra of analogous *n*d transition-metal complexes have indicated specific metal–ligand covalency effects due not only to 5f metal subshells but also to 6d orbitals as well.[4,5]

In order to gain a further insight into the problem, we have extended our research on the bonding in actinoid sandwich compounds to the PE spectra of two 1,1′-ring-substituted uranocene derivatives, namely, $U(C_8H_7R)_2$ (R = $Si(CH_3)_3$, $P(t\text{-}C_4H_9)_2$.

Another motivation for this study has been the expectation of a substantial perturbation of the ligand electronic structure by the ring substituent which should allow an estimate as to what extent the resulting spectral variations fit into the framework of the current bonding hypotheses.

Experimental Section

The complexes under study were purified by vacuum sublimation and always handled under argon atmosphere. Spectra were run on a Perkin-Elmer PS 18 spectrometer modified by inclusion of a hollow cathode discharge lamp giving high yields of He II photons. Energy calibration of spectra was obtained by reference to peaks of Ar and Xe gases allowed into the target chamber and to He ls^{-1} self-ionization. Spectra were run in the 100–120 °C temperature range.

Results and Discussion

Figure 1a shows the PE spectrum of the electroneutral ligand $C_8H_7Si(CH_3)_3$, which is of some relevance to the understanding of the spectrum of its uranium complex, $(C_8H_7Si(CH_3)_3)_2U$ (hereafter $U(cotSi)_2$). The general ap-

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[1] See, for example: "Organometallic of f Elements"; Marks, T. J., Fischer, R. D., Eds.; D. Reidel Publishing Co.: Dordrecht, 1979.

[2] Clark, J. P.; Green, J. C. *J. Chem. Soc., Dalton Trans.* 1977, 555.

[3] See: Streitwieser, A., Jr., in ref 1.

[4] See: Fragalà, I., in ref 1.

[5] Fragalà, I.; Condorelli, G.; Tondello, E.; Cassol, A. *Inorg. Chem.* 1978, *17*, 3175. Ciliberto, E.; Fagan, P. I.; Manriquez, J. M.; Fragalà, I.; Marks, T. J. *J. Am. Chem. Soc.* 1981, *103*, 4755. Fragalà, I.; Goffard, J.; Granozzi, G.; Zerbo, M. A. *Inorg. Chem.*, to be submitted for publication.

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Table I. Relevant Spectral Data and Assignments of Studied Complexes

U(cot)$_2$				U(cotSi)$_2$				U(cotP)$_2$				
	intensities				intensities				intensities			
IE, eV	He I	He II	half-width, eV	IE, eV	He I	He II	half-width, eV	IE, eV	He I	He II	half-width, eV	assignt
6.15	0.15	1	0.28	6.05	0.13	0.80	0.27	6.15	0.18		0.26	e_{3u} ($5f_{\pm3}$)
6.80	0.83	1.27	0.36	6.70	0.80	1.20	0.38	6.74	0.90		0.38	e_{2u} (π)
								7.46	2.00			p (lone pair)
7.75	1	1	0.44	7.69	1	1	0.44	7.84				e_{2g} (π)
9.80				9.75				9.44				e_{1u}, e_{1g}
10.20				10.14				10.03				σ(Si–C)
10.60				10.23								
11.40				11.22				11.39				onset of ring structure

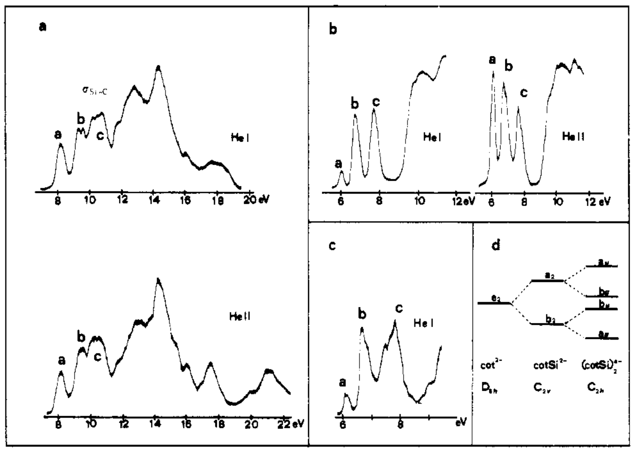

Figure 1. (a) PE spectra of the ligand $C_8H_7Si(CH_3)_3$. (b) PE spectra of U(cotSi)$_2$ (low IE region). (c) He I spectrum of U(cotP)$_2$ (low IE region). (d) Qualitative scheme of splitting of MO's in the low-symmetry compound $C_8H_7Si(CH_3)_3$.

pearance of this spectrum resembles that of unsubstituted C_8H_8.[6]

Major differences are the splittings into two components (b in Figure 1) of the band present in C_8H_8 at 9.78 eV and also a new feature c in the 10–11-eV region. No remarkable differences are, however, observed in the IE's associated with various bands, contrary to what one would expect because of the trimethylsilyl substitution. In the He II spectrum the band b increases moderately in relative intensity.

The He I spectrum of the complex U(cotSi)$_2$ is shown in Figure 1b. It is similar to that of the simpler U(C_8H_8).[2] The IE's associated with various bands are no longer influenced by ring substitution. Relative intensity variations when passing to He II spectra are reported in Table I. The spectrum of U(C_8H_7P(t-Bu)$_2$)$_2$ (hereafter U(cotP)$_2$) reveals (Figure 1c) noteable differences compared with that of the trimethylsilyl-substituted complex, the band c being more intense and somewhat more structured. The He II spectrum of the former complex is not reported. The lesser resolution inherent in the use of He II radiation results in a structure where relevant intensity variations are hardly understandable.

The assignment of bands in the spectrum of the ligand $C_8H_7Si(CH_3)_3$ is quite straightforward. By comparison with the PE data of the parent compound C_8H_8,[6] it is evident that the structures a and b represent ionizations from molecular orbitals (MO's) related to the $4a_1$ and 7e molecular orbitals of C_8H_8.

The splitting into two components of the band b is certainly due to the lifting of the twofold degeneracy of the MO 7e because of the trimethylsilyl substitution. The higher IE structures up to 11.5 eV must involve, analogously to C_8H_8, the ionization of the remaining π MO's ($4b_2$ in C_8H_8). Moreover, ionization from the σ(Si–C) orbital must be expected in this region. Comparison with data on some closely related compounds suggests[7] an assignment of the 10.4-eV band to this particular ionization. The remaining bands above 11.5 eV are attributed to ring σ MO's and devoid of any relevance to the bonding ability of the unsaturated hydrocarbon.

Finally, we comment on the slight shifts to lower IE's observed when passing from the simple C_8H_8 to its trimethylsilyl derivative. As mentioned, somewhat larger variations would have been expected, owing to the inductive effect of the substituent. However, detailed ab initio calculations[8] on related molecules suggest significant (C 2p → Si 3d) π bonding which stabilizes the ring π orbital system.[9] Such a stabilization is likely to counterbalance effectively the shift toward lower IE's, as opposed to what we expected as a result of the inductive effect of the Si(CH_3)$_3$ group.

Turning to the spectra of U(cotSi)$_2$ (Figure 1b), a surprising analogy with those of U(cot)$_2$[2,10] is noted. Relevant spectral data such as IE's, relative intensities, and half-widths are almost coincident (Table I). This feature should clearly imply an analogous assignment (Table I) and, hence, a completely analogous bonding model as for unsubstituted uranocene. Thus the bands a, b, and c in Figure 1b represent, respectively, ionizations of MO's corresponding to the metal e_{3u} ($5f_{\pm3}$) and to the "ligand" π e_{2u} and e_{2g} orbitals (labeling refers to D_{8h} symmetry). An obvious implication of this sequence is that, analogous to U(cot)$_2$,[2,3] covalent interactions between ring π and actinoid 6d orbitals are a substantial source of bonding also in U(cotSi)$_2$.[2,3] There is, however, evidence of covalent involvement of 5f orbitals in the bonding. The relative increase of intensity of band b accompanying the change from He I to He II excitation (Table I) confirms a $5f_{\pm2}$–e_{2u} interaction of similar extent to that in U(cot)$_2$. It might appear that the present data are devoid of any further information on the relative preponderance of 6d and 5f orbitals for complex stability. This question has remained a controversial point even in the treatment of U(cot)$_2$.[2] We believe, however, that a closer examination of variations of the band widths can be of some guidance. Actually in

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(6) Batich, C.; Bischop, P.; Heilbronner, E. *J. Electron Spectrosc. Relat. Phenom.* **1972**, *1*, 333.

(7) Evans, S.; Green, J. C.; Joachim, P. J.; Orchard, A. F.; Turner, D. W.; Maier, J. P. *J. Chem. Soc., Faraday Trans. 2* **1972**, 905.

(8) Cradock, S.; Finlay, R. H.; Palmer, M. H. *J. Chem. Soc., Dalton Trans.* **1974**, 905.

(9) The increase of relative intensity in the region b of the He II spectrum can be accounted for by such (p → d)π interaction, the silicon 3d cross-section being larger than C_{2p} at He II wavelength.

(10) Fragalà, I.; Condorelli, G.; Zanella, P.; Tondello, E. *J. Organomet. Chem.* **1977**, *122*, 357.

the planar dianion $(C_8H_7Si(CH_3)_3)^{2-}$ of C_{2v} symmetry the degeneracy of each of the orbitals e_{1-3} of the D_{8h} system $(C_8H_8)^{2-}$ is removed, thus giving rise to three pairs of orbitals of a_2 and b_2 symmetry. The actual energy separations $\Delta E(a_2 - b_2)$ depend upon the magnitude of d_π–p_π interactions between the $(CH_3)Si$ group and the C_8H_7 π orbital systems. In view of results already discussed for the neutral ligand $C_8H_7Si(CH_3)_3$, $\Delta E(a_2 - b_2)$ values somewhat higher than 0.3 eV are expected.[11] Furthermore, when two such ligands are arranged in the complex $U(cotSi)_2$ in a fixed staggered sandwich structure of C_{2h} symmetry about the uranium atom, the corresponding pairs of a_2 and b_2 orbitals will give rise to symmetric and antisymmetric combinations. Figure 1d shows, as an example, the case of orbitals related to the e_2 MO in $U(C_8H_8)$ which proved to be the main bonding orbital. The energy separation between the last-mentioned symmetry combinations $(\Delta E(a_u - b_g))$ depends upon nonbonded inter-ring repulsion and is expected to be of the same order of magnitude as $\Delta E(a_2 - b_2)$. As a consequence, a greater (than in the unsubstituted $U(C_8H_8)_2$ intrinsic energy dispersion of potentially bonding ligand electronic levels holds for the 1,1′-trimethylsilyl-substituted complex.[12] Therefore we should expect a greater energy spread (and, thence, a different band width) of the PE band responsible for g- and u-type orbitals, unless both sets were strongly and equally perturbed by metal orbitals of appropriate symmetry (U 5f and U 6d, respectively). In that case, such a stronger perturbation will act as a leveling effect upon intrinsic energy dispersion of ligand orbitals. Actually, the analysis of band-widths collected in Table I indicates that values in the spectrum of $U(cotSi)_2$ are no longer different from those in $U(cot)_2$ and, in any case, are comparable for both sets of orbitals of u and g symmetry.

Within the proposed qualitative model, this observation becomes evidence of an equally strong involvement of both U 5f and U 6d orbitals into the metal–ligand bonding.

Finally, turning to the PE spectrum of $U(cotP)_2$ we shall consider first structure c. This spectral feature is, unlike the case of both $U(cot)_2$ and $U(cotSi)_2$, structured into two components, the total intensity of which being approximately twice that of corresponding bands in the two former complexes (Table I). Actually in the low IE region we expect some additional bands due to ionization from the phosphorus 3p lone pairs. In C_{2h} symmetry, two different symmetry combinations are expected which should, however, be almost completely degenerate because of the great distance between the two P atoms. The corresponding ionization has been detected at 7.70 eV in the simple $P(t\text{-}Bu)_3$[13] while it is firmly established that substitution by aromatic rings results in a shift toward lower IE's.[14]

Therefore we favor the lower energy band at 7.46 eV for an assignment to the phosphorous lone-pair ionizations. Given this assignment, we arrive at a spectral pattern for the remaining low energy bands completely analogous to that observed for both $U(cot)_2$ and $U(cotSi)_2$ (Table I). Therefore we propose, also in the case of $U(cotP)_2$, the same MO sequence, e_{3u} $(5f_{\pm 3})$, e_{2u}, e_{2g} (ligand π), found in previous cases (Table I) and, consequently, an identical bonding scheme.

Conclusions

The results presented appear rather unexpected. We embarked on a PE study of ring substitution effects on uranocenes with the fair conviction that different donor–acceptor abilities of ring substituents would cause marked differences in the PE spectra of corresponding uranium complexes. Our experimental results, however, do not reflect any noteworthy variations in the relevant data. Obvious implications of these results are identical electronic structure as well as the assumption of an almost comparable involvement of both 6d and 5f uranium orbitals in the bonding. The absence of any IE shift of the corresponding PE bands associated to ligand-centered π ionizations by varying the nature of ring substituents is of particular relevance for still another reason. Clearly the different donor–acceptor characteristics of the two ring substituents presently considered should result in nonnegligible variations of the gross electronic charge localized on the rings.[15] The experimental fact that the IE's associated with relevant bands remain almost constant seems to indicate a unique ability of the uranium atom to "buffer" charge variation. This "charge buffering" should, in turn, imply a different transfer of free spin density onto ligand atoms which may be revealed by complementary NMR measurements. Finally, it would be of interest to test the generality of the conclusion drawn in this paper by studying further examples of ring-substituted uranocenes.

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Registry No. $U(cot)_2$, 11079-26-8; $U(cotSi)_2$, 68868-62-2; $U(cotP)_2$, 81939-61-9.

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[11] A higher value than in neutral $C_8H_7Si(CH_3)_3$ is expected in the planar aromatic dianion because of a minor σ–π mixing. For example, the energy splitting is 0.3 eV in the (trimethylsilyl)benzene. See: McLean, R. A. N. *Can. J. Chem.* **1973**, *51*, 2089.

[12] Actually, several conformational rotomers can be populated in the vapor phase at the temperature at which the spectra have been recorded. However, the final energy dispersion of ring centered ligand π orbitals does not depend upon the particular conformation adopted since the energy values are mainly mediated by inter-ring overlaps which, in turn, almost depend upon inter-ring distances. For instance, in the eclipsed C_{2v} conformation (the less favorable because of the bulky ring substituents) the symmetric and antisymmetric combinations of orbitals related to the e_2 in the C_8H_8 dianion transform as $a_1 + b_2$ and $a_2 + b_1$. Their energy dispersion is, however, comparable with that of related combinations in the staggered conformation since overlaps between C_{2p}-based ring π orbitals are mainly dependent upon inter-ring distances. Such geometrical parameters are likely to be similar to that in $U(cot)_2$ whatever the adopted conformation.

[13] Lappert, M. F.; Graffenil, M.; Labarre, J. F.; Leibovici, C.; Stelzer, O. *J. Chim. Phys.* **1975**, *72*, 799.

[14] Debies, T. P.; Rabelais, J. W. *Inorg. Chem.* **1974**, *13*, 308.

[15] For instance, the average IE of ionization in C_6H_5–$Si(CH_3)_3$ and C_6H_5–$P(CH_3)_2$ are respectively 9.25 and 9.0 eV. A greater IE difference of ring π ionizations would be expected when passing from C_8H_7–$Si(CH_3)_3$ to C_8H_7–$P(t\text{-}Bu)_2$ because of the electron-releasing effect of *t*-Bu groups.