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Uranocenes with Hydrocarbon Substituents[1]

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In this article are described the preparation and physical and chemical properties of uranocene (bis(π-cyclooctatetraene)-uranium) derivatives from the following cyclooctatetraenes: ethyl, *n*-butyl, vinyl, phenyl, cyclopropyl, and 1,3,5,7-tetramethyl. The alkyl-substituted uranocenes show bathochromic shifts in the visible spectrum interpreted as charge-transfer transitions. A mixture of 1,1′-diethyl- and 1,1′-di-*n*-butyluranocenes gave no 1-ethyl-1′-*n*-butyluranocene on heating. 1,1′-Divinyluranocene is converted to 1,1′-diethyluranocene by hydrogenation and to 1,1′-dicyclopropyluranocene with the Simmons-Smith reagent. These results are consistent with the formulation of uranocene as an f-orbital metallocene.

Bis(cyclooctatetraene)uranium(IV) was first prepared in 1968 as a proposed f-orbital aromatic system justifying the trivial name, uranocene, a system homologous to the class of d-transition cyclopentadienylmetallocenes.[2,3] The establishment of such unique ligand(π MO)-metal(f orbital) bonding is clearly an important fundamental problem in chemistry, but one that does not lend itself to simple approaches. We have adopted the approach of examining a range of chemistry for such compounds in order to determine how well the varied pattern of results can be accommodated by our simple bonding hypothesis. Our systematic study in this regard includes examination of other central metals (lanthanides,[4] other actinides, etc.) and various ligands (substituted cyclooctatetraenes, other π ligands, etc.). As part of this systematic study of the chemistry of a new class of rare earth organometallic compounds, we report here the preparation and properties of several uranocenes symmetrically substituted in both rings by hydrocarbon substituents.

The general preparation followed that of the parent compound.[2,3] The substituted cyclooctatetraene[5] was converted to the dianion with potassium in THF at −40°. A solution of uranium tetrachloride in THF was added, solvent was removed, and the residue was extracted into a suitable solvent. The substituted cyclooctatetraene, yield of isolated and purified complex, and extraction solvent are respectively as follows: ethyl, 92%, cyclohexane; *n*-butyl, 90%, hexane; phenyl, 87%, hexane; vinyl, 97%, cyclohexane; cyclopropyl, 88%, hexane; 1,3,5,7-tetramethyl, 53%, THF. Bis(1,3,5,7-tetramethylcyclooctatetraene)uranium(IV) has been reported previously.[6] 1,1′-Diethyl- and 1,1′-di-*n*-butyluranocene have also been prepared and characterized by Karraker.[7] Physical and chemical properties are generally similar to the parent system, but the differences found are notable. The substituted compounds are much more soluble in organic solvents than is uranocene itself. This important difference makes these new derivatives more convenient for studies of chemical reactivity. The solutions have a characteristic green color and react readily with oxygen to regenerate the free ligand quantitatively. The crystalline solids are less sensitive to oxygen than is uranocene; the phenyl-substituted complex is stable in air for several minutes before decomposition sets in.

Spectral data for the substituted uranocenes are summarized in Table I. Uranocene has a distinctive infrared pattern; the substituted compounds show only slight changes in these absorption frequencies in addition to the substituent absorptions.

The mass spectra of these compounds are summarized in Table I and show distinctive patterns. Important *m/e* peaks include P (parent), P − L (ligand), and L, as in the case of uranocene itself.[2] However, all of the compounds except octamethyluranocene give a significant peak at *m/e* 446, corresponding to $(C_8H_8)_2U^+$. A sample of *n*-butylcyclooctatetraene was carefully purified by gc to ensure absence of COT, yet the 1,1′-dibutyluranocene prepared from this ligand still gave a substantial peak at *m/e* 446. This and other careful control experiments establish that this peak comes from stripping off the side chains during electron impact and not from any uranocene impurity. 1,1′-Diphenyluranocene gives a peak at *m/e* 521 $[(C_6H_5C_8H_7)(C_8H_7)U^+]$ which is larger than the uranocene peak. 1,1′-Dibutyluranocene gives a significant peak at *m/e* 515 $[(n\text{-}BuC_8H_7)(C_8H_7CH_2)U^+?]$.

Visible Spectrum. Uranocene has a characteristic absorption in the 600–700-nm range consisting of four sharp absorptions of decreasing intensity going to longer wavelength. The substituted compounds show a similar four-band absorption (except for the bis-vinyl compound, which shows only three bands) (Figure 1). An important observation is the small but significant shifts to longer wavelength displayed by electron-donating alkyl substituents. These results combined with the relatively high magnitude of the extinction coefficients provide ample evidence that these visible bands are not the result of simple f–f transitions.

The results can be accounted for simply as charge-transfer transitions from ligand to metal. Alkyl groups increase the ability of the rings to donate electrons and result in bathochromic shifts. The simple MO model proposed earlier[2,3] is consistent with these spectral results. As illustrated schematically in Figure 2, substantial ring-metal bonding results from covalent interaction of the highest occupied e_{2u} ligand MO's of two cyclooctatetraene dianion rings with vacant $5f_{xyz}$ and $5f_{z(x^2-y^2)}$ orbitals of the central uranium. Alkyl substituents raise the energies of the ligand π MO's and should increase the bonding interaction of the e_{2u}-f ($l_z = \pm 2$) combination. The increased stability of the substituted uranocenes observed qualitatively is in agreement with this corollary. We expect to obtain quantitative data in subsequent experiments. We suggest that the visible absorption can be described approximately as a charge-transfer transition from the highest occupied e_{2g} ligand MO's to metal f orbitals. Transitions to the $l_z = \pm 1$ (f_{xz^2}, f_{yz^2}) or $l_z = \pm 3$ ($f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$) f orbitals

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[1] This work was supported in part by National Science Foundation Grants No. GP-31803 and GP-13369.

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Table I. Spectral Data on Substituted Uranocenes, $(RCOT)_2U$

R	Visible spectrum,[a] nm ($\epsilon \times 10^{-3}$)
H	616 (1.8), 643 (0.72), 661 (0.41), 671 (0.12)
C_2H_5	619 (1.5), 644 (0.54), 666 (0.36), 682 (0.30)
n-C_4H_9	622 (1.6), 651 (0.60), 671 (0.37), 681 (0.23)
C_6H_5	625 (1.1), 652 (0.45), 671 (0.30), 684 (0.19)
$CH{=}CH_2$	617 (1.1), 645 (0.33), 664 (0.20)
c-C_3H_5	619 (1.5), 647 (0.52), 662 (0.37), 683 (0.16)
1,3,5,7-$(CH_3)_4$	650 (0.90), 689 (0.47), 704 (0.44), 718 (0.33)

R	Infrared spectrum, cm^{-1} (Nujol mull)
H	1320 w, 1260 w, 900 m, 780 w, 775 w, 745 m, 700 s
C_2H_5	1321 w, 1247 m, 940 m, 900 m, 720 s, 682 m
n-C_4H_9	1320 w, 1245 m, 941 m, 907 m, 727 s, 684 m
C_6H_5	1590 w, 1330 w, 1254 m, 925 w, 765 w, 750 w, 725 s, 700 s
$CH{=}CH_2$	1615 w, 1333 w, 1296 w, 1256 m, 987 m, 935 m, 750 m, 722 s
c-C_3H_5	1322 w, 1260 m, 798 m, 720 m, 710 m
1,3,5,7-$(CH_3)_4$	1250 m, 907 m, 836 m, 728 s

R	Mass spectrum, m/e of major identifiable peaks
H	446 $(C_8H_8)_2U^+$, 342 $(C_8H_8)U^+$, 104 $(C_8H_8)^+$
C_2H_5	502 $(EtC_8H_7)_2U^+$, 446 $(C_8H_8)_2U^+$, 370 $(EtC_8H_7)U^+$
n-C_4H_9	558 $(BuC_8H_7)_2U^+$, 515 $(BuC_8H_7)(C_8H_7CH_2)$-U^+, 502 $(BuC_8H_7)(C_8H_8)U^+$, 446 $(C_8H_8)_2U^+$, 398 $(BuC_8H_7)U^+$
C_6H_5	598 $(C_6H_5C_8H_7)_2U^+$, 521 $(C_6H_5C_8H_7)(C_8H_7)$-U^+, 446 $(C_8H_8)_2U^+$, 418 $(C_6H_5C_8H_8)U^+$, 180 $(C_6H_5C_8H_8)^+$
$CH{=}CH_2$	498 $(C_{10}H_{10})_2U^+$, 446 $(C_8H_8)_2U^+$, 368 $(C_{10}H_{10})U^+$, 130 $(C_{10}H_{10})^+$
c-C_3H_5	526 $(C_{11}H_{12})_2U^+$, 485 $(C_{11}H_{12})(C_8H_7)U^+$, 446 $(C_8H_8)_2U^+$, 382 $(C_{11}H_{12})U^+$
1,3,5,7-$(CH_3)_4$	558 $(C_{12}H_{16})_2U^+$, 398 $(C_{12}H_{16})U^+$, 160 $(C_{12}H_{16})^+$

R	Solvent	Nmr spectrum, δ^b at 34°
H	THF[c]	−35.2
C_2H_5	THF	0.2 (CH_3), −16.3 (CH_2), −31.8, −33.3, −35.0, −38.1
n-C_4H_9	C_6D_6	1.23 (CH_2), 0.54 (CH_3), −25.9 (CH_2), −32.0, −33.5, −35.6, −39.2
$CH{=}CH_2$	C_6D_6	−8.7 (quartet), −10.4 (d), −13.6 (d), −33.4 (d), −35.1, −37.2
1,3,5,7-$(CH_3)_4$	THF	−3.8, −34.5

[a] Spectra taken in THF. [b] Referenced to TMS with minus sign indicating upfield. [c] At 29°.

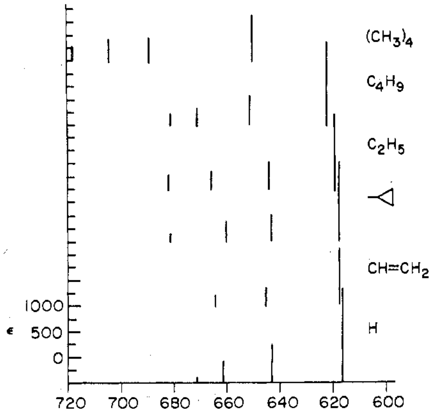

Figure 1. Visible spectra of 1,1′-disubstituted uranocenes.

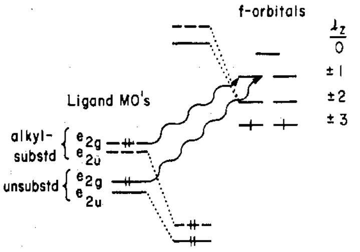

Figure 2. Schematic interpretation of the effect of alkyl substituents on the visible spectrum of uranocene. The electron-donating alkyl groups increase the energies of ligand π MO's and result in a bathochromic shift in the postulated charge-transfer transition between ligand e_{2g} and uranium f orbitals.

are both allowed by symmetry, but the $l_z = \pm 1$ orbitals are expected to provide better spatial overlap. This description can only be approximate because l_z is not a true quantum number if covalent interaction is significant and spin-orbit configuration interaction mixes the f orbitals. Furthermore, the substituted uranocenes are no longer of D_{8h} symmetry and the substituents will remove the degeneracy of the e levels. Nevertheless, this simple picture serves as a suitable framework and helps to rationalize this spectral region. The extension to electron-attracting substituents is obvious; hypsochromic shifts are expected and are found in compounds to be reported later. These spectra thus provide a further and independent demonstration of the essential validity of our electronic structure hypotheses of uranocene as a f-orbital metallocene[2,3] homologous to the d-orbital cyclopentadienylmetallocenes.

The nmr spectra of uranocene[8] and 1,3,5,7,1′,3′,5′,7′-octamethyluranocene[6] have been reported and interpreted. The nmr spectra of the present compounds (Table I) are straightforward extensions of the earlier spectra and are completely consistent with the interpretations based on pseudocontact shifts from the uranium 5f electrons and contact shifts derived from spin density in the ligand π systems. Alkyl protons not α to the ligand ring show upfield pseudocontact shifts that diminish with distance from the ring. The α protons show superposed downfield shifts analogous to those interpreted in octamethyluranocene as an effect of ligand π-spin density. The vinyl protons show an upfield shift that can be interpreted as a spin-density effect in the conjugated vinyl π system exactly as for the ligand protons.[6] These interpretations can only be qualitative. Although structural hypotheses can be constructed from the known structure of octamethyluranocene,[9] lack of data relating to conformations precludes meaningful calculation of the pseudocontact shifts of the larger side-chain substituents.

Reactions. The substituted uranocenes show the same stability as the parent toward mild acidic conditions such as acetic acid. With stronger acids they decompose to give polymeric products. The sensitivity to oxidation includes even rather mild reagents. Attempted oxidation of the side chains of 1,1′-diethyluranocene with manganese dioxide gave only oxidation of the metal with liberation of ethylcyclooctatetraene.

In an important reaction to test the strength and character of the ligand-metal bond, a mixture of 1,1′-diethyluranocene and 1,1′-dibutyluranocene was refluxed in diglyme (bp 161°) for 5 hr. Examination of the product showed only the two reactants with no observable amount of mixed sandwich complex. This reaction demonstrates conclusively that ring-metal bonding in uranocene compounds is covalent in nature and substantial in magnitude. It also demonstrates the absence of equilibria of the type

$$(C_8H_8)_2U \rightleftharpoons (C_8H_8)U^{2+}\cdot\text{solvent} + C_8H_8^{\ 2-}$$

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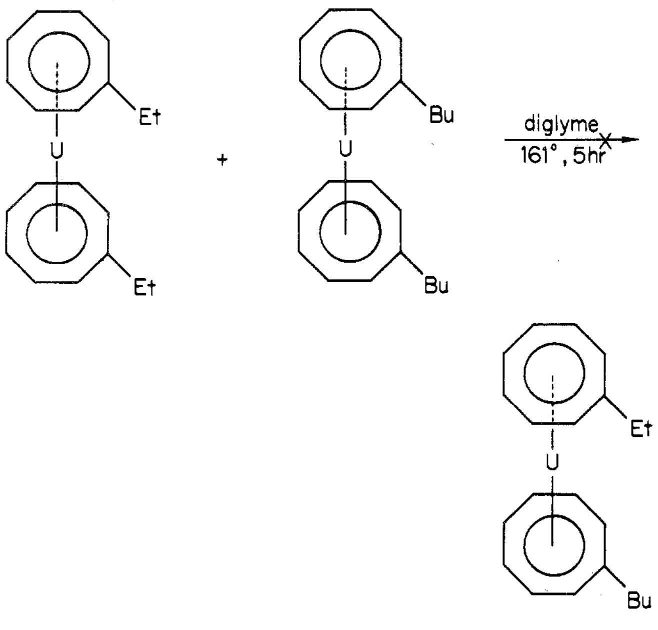
[8] N. Edelstein, G. N. La Mar, F. Mares, and A. Streitwieser, Jr., *Chem. Phys. Lett.*, 8, 399 (1971).

[9] K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, 12, 458 (1973).



Subject to the limitations imposed by the uranocene structure, normal reactions could be accomplished on the substituent functional groups. For example, uranocene is stable to hydrogenation conditions with Pd/C;[3] 1,1′-divinyluranocene is readily hydrogenated to 1,1′-diethyluranocene in moderate yield. Similarly, the vinyl compound reacts with the Simmons-Smith reagent to give a low (5%) yield of 1,1′-dicyclopropyluranocene identical with that synthesized from cyclopropylcyclooctatetraene. The low yield is undoubtedly caused by the strong Lewis acid character of the zinc iodide formed during the reaction.

Experimental Section

All reactions were carried out under an inert atmosphere of argon. Infrared and visible spectra were obtained with a Cary 14 recording spectrometer. Nmr spectra were recorded with a Varian HA-100 instrument.

Materials. In all reactions, reagent grade solvents were used after being distilled from lithium aluminum hydride and subsequently degassed to remove oxygen. Anhydrous uranium tetrachloride was prepared from the reaction of uranium trioxide with hexachloropropene.[10] Monosubstituted cyclooctatetraenes were prepared in good yield (60–98%) from the reaction of lithium diorganocuprates(I) with bromocyclooctatetraene.[5] Tetramethylcyclooctatetraene was prepared by the method of de Mayo and Yip.[11] However, no experimental details were given in their communication, and we include our procedure.

1,3,5,7-Tetramethylcyclooctatetraene.[12] A solution of 17 g of 4,6-dimethylcoumalin[13] in 26 ml of benzene was photolyzed for 2 weeks in a conventional Pyrex photoreactor with a medium-pressure mercury lamp (Hanovia 654A 36, 200 W). After 2 days a white solid began to appear on the walls of the reactor. Daily scraping of the solid from the reactor wall was required to allow adequate light transmission. The solid was removed by filtration and air-dried, giving 2.6 g of the reported dimers (the benzene solution could be photolyzed again to obtain additional product). The solid was placed in a small flask equipped with a reflux condenser and heated under nitrogen to 280° for 10 minutes to decarboxylate the dimers. The tetramethylcyclooctatetraene was extracted with 10 ml of ether and separated from a brown residue by filtration. Evaporation of the ether followed by chromatography of the residual solid over silica gel with pentane gave 1.0 g of white crystalline tetramethylcyclooctatetraene (mp 69°; lit.[12] mp 69–70°). This method appears to be more convenient and less time consuming than that suggested by Cotton, Faller, and Musco.[14]

General Preparation of Substituted Uranocenes. To a potassium dispersion (0.04 g-atom) in 150 ml of THF at −40° was added 0.02 mol of substituted cyclooctatetraene. The mixture was stirred at −40° until all of the potassium went into solution, indicating the formation of dianion. Then 0.01 mol of uranium tetrachloride dissolved in 75 ml of THF was added to the brown dianion solution. The resulting thick green slurry was stirred for 8 hr at −40° and allowed to come to room temperature. The solvent and unreacted ligand were removed under vacuum, and the remaining solid was extracted with a suitable solvent in the apparatus described previously.[3] Spectral properties are summarized in Table I.

Oxidation of 1,1′-Diethyluranocene. Air was slowly introduced at 0° into an nmr tube containing 0.50 ml of 1.0 *M* benzene in carbon tetrachloride and 50 mg (0.10 mmol) of 1,1′-diethyluranocene. After the black solid had settled, the nmr spectrum was taken and showed a benzene:ethylcyclooctatetraene ratio of 2.63, or 0.19 mmol of ethylcyclooctatetraene. This corresponds to an ethylcyclooctatetraene:uranium ratio of 1.9, with an estimated uncertainty of 5%.

Attempted Ligand Exchange between 1,1′-Diethyluranocene and 1,1′-Di-*n*-butyluranocene. A solution of 0.50 g (0.001 mol) of 1,1′-diethyluranocene and 0.56 g (0.001 mol) of 1,1′-di-*n*-butyluranocene in 150 ml of diglyme was refluxed for 5 hr. The diglyme was removed by vacuum transfer and the remaining green solid was analyzed by mass spectroscopy. The results showed no fragment of mass 530, which would correspond to a ligand-exchange product.

Hydrogenation of 1,1′-Divinyluranocene. Hydrogen gas (40 psi) was introduced into a hydrogenation vessel containing a solution of 1.0 g (0.002 mol) of 1,1′-divinyluranocene in 100 ml of benzene containing 1.0 g of 5% Pd/C. The mixture was shaken for 6 hr and transferred to the glove box, where the green suspension was filtered to remove the catalyst. The benzene was vacuum-transferred, leaving a green solid (0.8 g). The visible spectrum and mass spectral analysis of the green product showed the solid to be primarily 1,1′-diethyluranocene. Nmr analysis of an oxidized sample of the solid showed 6% vinylcyclooctatetraene and 94% ethylcyclooctatetraene.

Reaction of 1,1′-Divinyluranocene with Simmons-Smith Reagent. Methylene iodide (5 ml) was added dropwise to 5 g of zinc–copper in 100 ml of an ether solution containing 1.0 g (0.002 mole) of 1,1′-divinyluranocene. The mixture was stirred for 24 hr at room temperature and filtered. Degassed water (100 ml) was added to remove zinc iodide, and the green ether fraction was dried over Linde 4A molecular sieves. Ether removal followed by sublimation (140° (10^{-3} mm)) gave 50 mg of a green solid which was found by mass spectral analysis to be 1,1′-dicyclopropyluranocene (*m/e* 526).

Manganese Dioxide Oxidation of 1,1′-Diethyluranocene. Freshly prepared manganese dioxide[15] (0.9 g, 0.01 mol) was added at room temperature to 100 ml of benzene containing 1.0 g (0.002 mol) of 1,1′-diethyluranocene. One hour after the addition of the manganese dioxide, decomposition of the uranocene was complete, as indicated by the color of the solution turning from green to yellow. The visible spectrum of this solution showed that no diethyluranocene remained. The yellow mixture was filtered and the filtrate was concentrated under vacuum. An infrared spectrum of the concentrate showed no carbonyl absorption. Gc separation of the yellow oil (SE-30, 5 ft) followed by mass spectral analysis showed the product to be ethyl-

Registry No. $U(RCOT)_2$; R = H, 11079-26-8; $(RCOT)_2U$; R = C_2H_5, 37274-10-5; $(RCOT)_2U$; R = *n*-C_4H_9, 37274-12-7; $(RCOT)_2U$; R = C_6H_5, 37274-13-8; $(RCOT)_2U$; R = CH = CH_2, 37274-09-2; $(RCOT)_2U$; R = *c*-C_3H_5, 37274-11-6; $(RCOT)_2U$; R = 1,3,5,7-$(CH_3)_4$, 12715-87-6.

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