Cover Essay

Uranocene. The First Member of a New Class of Organometallic Derivatives of the f Elements

I. Organouranium Chemistry: The Beginnings

The first organouranium compound mentioned in the literature was $(C_2H_5)_2UO_2$.[1] However, this compound had not been prepared by Hallwachs and Schafarik—they merely suggested it as a possible organometallic compound that might be accessible by the reaction of Frankland's newly discovered diethylzinc with UO_2Cl_2. Partington, in his discussion of organometallic compounds, mistakenly reported it as a bona fide, isolated compound.[2] Shortly after the report by Victor Grignard of the reagents which came to bear his name, Sand and Singer[3] reported (without providing any details) that they had carried out a reaction of CH_3MgI with UO_2Cl_2 in diethyl ether. They merely said that UO_2Cl_2 "reacted favorably" but that the product appeared to be decomposed by water. Their conclusion was that the U−C bond was hydrolytically unstable, and they did not pursue that matter any further.

During World War II the need for uranium compounds that were volatile and thermally stable for use in $^{235}U/^{238}U$ isotope separation in the Manhattan Project made organic derivatives of uranium of interest. Henry Gilman, in a review of his research in organometallic chemistry that spanned more than 50 years, noted that attempts in his laboratories at Iowa State College to prepare organouranium compounds such as tetramethyluranium had been unsuccessful, presumably because they were unstable.[4] In view of this, Gilman and his students in their World War II program focused their efforts on the preparation of uranium compounds in which the organic groups were linked to uranium through oxygen, nitrogen, or sulfur.[5] In the Ethyl Corporation laboratories during World War II, Calingaert et al. attempted the preparation of a volatile uranium carbonyl by various procedures: direct reaction of CO with uranium metal or UH_3, reaction of $Ni(CO)_4$ with UH_3, reaction of uranium halides with CO in the presence of organometallic reagents ($RMgX$, BuLi, R_2Zn) or metals (Zn, Na), and reaction of CO with $U(OC_2H_5)_5$ and uranium borohydride. None of these reactions gave any evidence of a uranium carbonyl.[5]

The prospects for the development of an organometallic chemistry of uranium seemed bleak in the late 1940s.

II. Organoactinide Chemistry Takes Off. Preparation of Cyclopentadienyl Derivatives

The discovery of ferrocene in 1951 and the recognition of its novel structure and bonding in the following year were followed by rapid development of the chemistry of the cyclopentadienyl derivatives of the transition metals by E. O. Fischer at the Technische Hochschule München and Geoffrey Wilkinson at Harvard University and their respective research groups. John Birmingham and Wilkinson prepared ionic $(C_5H_5)_3M$ compounds of some lanthanide elements.[7] That 4f elements formed such compounds suggested that cyclopentadienyl derivatives of the 5f actinide elements might be accessible and stable as well. In 1956 Todd Reynolds and Wilkinson reported the first preparation of some cyclopentadienyl compounds of uranium.[8] The reaction of anhydrous UCl_3 with sodium cyclopentadienide in THF, followed by removal of solvent and heating of the dried reaction mixture under vacuum, gave a low yield of a red sublimate. The latter was exceedingly air-sensitive and thermally unstable. Its analysis showed it to be Cl-free and to have the approximate composition $C_{15}H_{15}U$. In view of these properties, no further work was done with this compound. However, the reaction of 1.8 molar equiv of sodium cyclopentadienide in THF with 1 molar equiv of UCl_4 (slow addition of the sodium reagent to UCl_4 followed by rapid stirring for a few hours while the reaction mixture was heated at reflux) gave $(C_5H_5)_3UCl$ as dark red-black crystals which sublimed at 245 °C at 10^{-4}−10^{-5} mm in 82−85% yield. The product melted

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[1] Hallwachs, H.; Schafarik, A. *Ann.* **1859**, *33*, 206.

[2] Partington, J. R. *A History of Chemistry*; Macmillan: London, 1964; Vol. 4, p 511.

[3] Sand, J.; Singer, F. *Justus Liebigs Ann. Chem.* **1903**, *329*, 190.

[4] Gilman, H. *Adv. Organomet. Chem.* **1968**, *7*, 33.

[5] For instance, volatile 1,3-dicarbonyl chelates, $U(RC(O)CHC(O)R')_4$ and uranium(V) alkoxides were prepared: (a) Gilman, H.; Jones, R. G.; Bindschadler, E.; Blume, D.; Karmas, G.; Martin, G. A., Jr.; Nobis, J. F. *J. Am. Chem. Soc.* **1956**, *78*, 2790. (b) Jones, R. G.; Bindschadler, E.; Blume, D.; Karmas, G.; Martin, G. A., Jr.; Thritle, J. R.; Gilman, H. *J. Am. Chem. Soc.* **1956**, *78*, 6027.

[6] Calingaert, G.; Soroos, H.; Dykstra, F. J.; Hnizda, V.; Capinjola, J. C. *U. S. At. Energy Comm.* TID-5290, Book 1, 350−363 1958; *Chem. Abstr.* **1959**, *53*, 16779. However, in later years, matrix isolation experiments at cryogenic temperatures showed that $U(CO)_6$ was accessible below ∼20 K (Slater, J. L.; Sheline, R. K.; Lin, K. C.; Welter, W. *J. Chem. Phys.* **1971**, *55*, 5129. Sheline, R. K.; Slater, J. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 309), as was $UF_4(CO)$ at ∼20 K (Kunze, K. R.; Hauge, R. H.; Hamill, D.; Margrave, J. L. *J. Phys. Chem.* **1977**, *81*, 1664). In 1986, R. A. Andersen and co-workers reported that $(\eta^5\text{-}Me_3SiC_5H_4)_3U$ reversibly binds 1 molar equiv of CO in solution and in the solid state at room temperature to give $(\eta^5\text{-}Me_3SiC_5H_4)_3UCO$, which was stable at room temperature but too labile to isolate (Brennan, J. G.; Andersen, R. A.; Robbins, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 335). In later work, it was found that $(\eta^5\text{-}Me_4C_5H)_3UCO$ is sufficiently stable to permit its isolation as a dark red-purple, crystalline solid whose X-ray crystal structure was determined at −123 °C (Conejo, M. d. M.; Parry, J. S.; Carmona, E.; Schultz, M.; Brennan, J. G.; Beshouri, S. M.; Andersen, R. A.; Rogers, R. D.; Coles, S.; Hursthouse, M. *Chem. Eur. J.* **1999**, *5*, 3000).

[7] (a) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 6210. (b) *J. Am. Chem. Soc.* **1956**, *78*, 422.

[8] Reynolds, L. T.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 246.

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at 260−265 °C and was thermally stable to 300 °C but was exceedingly air-sensitive. It was soluble in THF and pyridine and, with some difficulty, in water. Addition of silicotungstic acid, chloroplatinic acid, Reinecke's salt, and potassium triiodide to aqueous solutions of $(C_5H_5)_3UCl$ resulted in formation of precipitates. The Reineckate, $(C_5H_5)_3U[Cr(NH_3)_2(SCN)_4]\cdot 3H_2O$, was characterized by elemental analysis. No ferrocene was formed when $(C_5H_5)_3UCl$ was treated with $FeCl_2$ in THF at room temperature, and there was no apparent reaction between $(C_5H_5)_3UCl$ and maleic anhydride. The observed lack of reactivity spoke against an ionic formulation with $[C_5H_5]^-$ ligands, as found in the lanthanide tricyclopentadienides, and against η^1-C_5H_5 bonding. Sandwich-type covalent bonding (i.e., η^5) of the three C_5H_5 groups was suggested. Support for this was provided by a molecular orbital treatment by Professor William Moffitt of Harvard (incorporated in ref 8), in which the C_5H_5 ligands were treated as neutral π-species (as they had been considered in Moffitt's MO treatment of ferrocene) and in which there was extensive participation of uranium 5f orbitals in the bonding. Nine years later an X-ray crystal structure determination showed $(C_5H_5)_3UCl$ to have a distorted-tetrahedral structure.[9] The U−Cl bonding was stated to be "essentially ionic" and the U−C_5H_5 sandwich bond to be covalent.

Reynolds and Wilkinson also tried to prepare an organouranium compound by starting with UO_2Cl_2, but neither sublimation of the C_5H_5Na/UO_2Cl_2 reaction mixture nor its treatment with aqueous acid produced an identifiable product. In a similar manner, their attempts to prepare a cyclopentadienylthorium compound were in the main unsuccessful. As noted:

> "From the dried reaction mixture of anhydrous thorium tetrachloride with an excess of sodium cyclopentadienide, a white sublimate, in yields of the order of 1%, can be obtained by heating the mixture in vacuum at 250 °C."

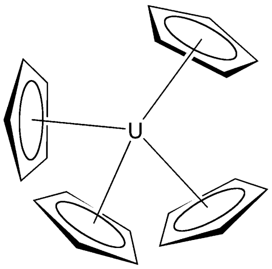
The product was too air-sensitive and too thermally unstable on attempted purification by sublimation to permit its isolation in pure form. A thorium analysis suggested "the approximate composition $(C_5H_5)_4Th$." Attempts to prepare a cyclopentadienylthorium chloride of the type $(C_5H_5)_2ThCl_2$ by using a 2:1 molar ratio of C_5H_5Na to $ThCl_4$ were equally unsuccessful. The treatment of the evaporated reaction mixture with 6 N HCl and addition of Reinecke's salt to the resulting aqueous solution did give a precipitate which, however, could not be isolated in pure form.

This then was the beginning of organoactinide chemistry. The yield per effort expended was so meager that Wilkinson did no further work in the area. However, organoactinide chemistry was a potentially interesting area and within a few years other groups in the USA and, especially, in Germany were actively investigating this field.

The two groups most active in the development of transition-metal−cyclopentadienyl chemistry in the 1950s and 1960s, as noted above, were those of G. Wilkinson and E. O. Fischer; thus, it was no surprise that the latter became very active in the development of cyclopentadienylactinide chemistry. The tetracyclopentadienyl compounds of niobium, tantalum, and molybdenum had been prepared earlier in Fischer's laboratories, and the procedure used was found to be applicable to the synthesis of $(C_5H_5)_4U$ (eq 1).[10a]

$$UCl_4 + 4C_5H_5K\ (\text{excess}) \xrightarrow[\text{reflux}]{C_6H_6} (C_5H_5)_4U + 4KCl \quad (1)$$

Sublimation in vacuo, after removal of solvent, destroyed the product, but extraction of the residue under purified nitrogen with pentane for several days gave red crystals of $(C_5H_5)_4U$, albeit in only ∼6% yield. The red crystals were air-stable in the solid state, but their solution in benzene was extremely air-sensitive. The dipole moment of $(C_5H_5)_4U$ in benzene was 0; its infrared spectrum indicated that the C_5H_5 ligands were "sandwich-bonded" (**1**).



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In a paper immediately following the $(C_5H_5)_4U$ report, Fischer and Treiber described the preparation of $(C_5H_5)_4Th$.[10b] The reaction was carried out between a large excess of C_5H_5K and $ThCl_4$ in diethyl ether for 2 days. Repeated sublimation of the residue at 250−290 °C in vacuo and washing of the sublimate gave $(C_5H_5)_4Th$ as white crystals in low yield. A tetrahedral arrangement of the sandwich-bonded C_5H_5 ligands about Th was indicated by the IR and proton NMR spectra.

In the Ethyl Corporation laboratories in Detroit, the attempt by Ter Haar and Dubeck to prepare tricyclopentadienyluranium by the reaction of C_5H_5Na with UCl_3 in THF at reflux for 3 days resulted in the isolation of green crystals of $(C_5H_5)_3UOC_4H_9$-n in unspecified yield, rather than the desired product.[11] Presumably the formation of the butoxide resulted in a redox process in which THF solvent molecules underwent ring-opening cleavage. A rational procedure for the preparation of the n-butoxide and $(C_5H_5)_3UOCH_3$ based on the reaction of UCl_4 in dimethoxyethane, first with 2 molar equiv of RONa and then with 4 molar equiv of C_5H_5Na, was developed. Also prepared during the course of this study were $(C_5H_5)_3ThCl$ and the white tricyclopentadienylthorium methoxide and n-butoxide.

A collaboration between E. O. Fischer and his student P. Laubereau at the Technische Hochschule München and F. Baumgärtner and B. Kanellakopulos at the Nuclear Research Center in Karlsruhe and at the

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[9] Wong, C.-H.; Yen, T.-M.; Lee, T.-Y. *Acta Crystallogr.* **1965**, *18*, 340.

[10] (a) Fischer, E. O.; Hristidu, Y. *Z. Naturforsch.* **1962**, *17b*, 275. (b) Fischer, E. O.; Treiber, A. *Z. Naturforsch.* **1962**, *17b*, 276. (c) The X-ray crystal structures of $(C_5H_5)_4U$ and $(C_5H_5)_4Th$ were later determined. In both molecules the C_5H_5 ligands are η^5-bonded and tetrahedrally arranged around the central metal atoms. U: Burns, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 3815. Th: Maier, R.; Kanellakopulos, B.; Apostolidis, C.; Meyer, D.; Rebizant, J. *J. Alloys Compd.* **1993**, *190*, 269.

[11] Ter Haar, G.; Dubeck, M. *Inorg. Chem.* **1964**, *3*, 1648.

University of Heidelberg from 1965 to 1970 resulted in the preparation of cyclopentadienyl derivatives of protoactinium and the transuranium elements through curium. Laubereau, continuing this work in collaboration with John H. Burns at the Transuranium Research Laboratory at Oak Ridge National Laboratory, extended this cyclopentadienyl transuranium series to berkelium and californium. The transuranium elements involved, neptunium, plutonium, americium, curium, berkelium, and californium, all are highly radioactive, and all the preparative and characterization experiments required use of the special laboratory facilities needed for handling highly radioactive materials. The first preparation of $(C_5H_5)_3NpCl$ was achieved by a radiochemical method (eq 2).[12] Since ^{239}Np has a half-life (β^- emission) of 2.3

$$^{239}\mathrm{U}(\mathrm{C}_5\mathrm{H}_5)_3\mathrm{X} \xrightarrow[23\ \mathrm{min}]{\beta^-} {}^{239}\mathrm{Np}(\mathrm{C}_5\mathrm{H}_5)_3\mathrm{X} \qquad (2)$$

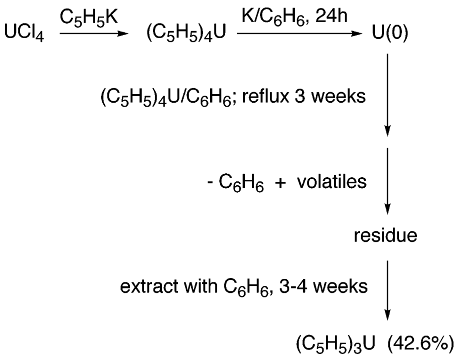
$$\mathrm{X} = \mathrm{Cl},\ \mathrm{F}$$

days, a sample of the product could be isolated by sublimation at 230 °C. For the synthesis of tricyclopentadienylplutonium a new method was developed which found extensive use in the synthesis of other transuranium metal cyclopentadienyls (eq 3).[13] The reaction was

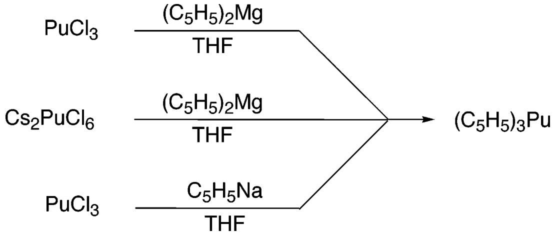
$$2\mathrm{PuCl}_3 + 3(\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Be} \rightarrow 2(\mathrm{C}_5\mathrm{H}_5)_3\mathrm{Pu} + 3\mathrm{BeCl}_2 \qquad (3)$$

carried out in molten $(C_5H_5)_2Be$ at around 70 °C; excess $(C_5H_5)_2Be$ was removed by sublimation. The moss green product was readily hydrolyzed and was extremely air-sensitive. The dicyclopentadienylberyllium method was used to prepare flesh pink tricyclopentadienylamericium from $AmCl_3$,[14] $(C_5H_5)_3NpCl$ from $NpCl_4$,[15] and orange-yellow tetracyclopentadienylprotoactinium from $PaCl_4$.[16] Potassium cyclopentadienide in a benzene suspension served in the preparation of reddish brown $(C_5H_5)_4Np$ from $NpCl_4$.[17] At Oak Ridge, Laubereau and Burns applied the $(C_5H_5)_2Be$ method to the preparation of tricyclopentadienylberkelium and tricyclopentadienylcalifornium.[18] In a subsequent study it was found that, in the $^{249}BkCl_3/(C_5H_5)_2Be$ reaction, a mixture of $(C_5H_5)_2BkCl$ and $(C_5H_5)_3Bk$ actually was formed.[19] For these reactions of radioactive substances, special techniques and quartz or platinum apparatus for organometallic syntheses on a microgram scale were developed.[18] For the preparation of tricyclopentadienylcurium from $^{248}CmCl_3$,[20] molten $(C_5H_5)_2Mg$, a reagent that had been used by Reid and Wailes in 1966 to prepare $(C_5H_5)_4Th$ and $(C_5H_5)_4U$ from the respective tetrafluorides,[21] was used.

Scheme 1



Scheme 2



Tricyclopentadienylcurium (244) also was prepared on a 10 μg scale; larger scale reactions using $(C_5H_5)_2Be$ or $(C_5H_5)_2Mg$ were unsuccessful.[22]

The elusive tricyclopentadienyluranium was prepared in 1970 by the German group by the reduction of $(C_5H_5)_4U$ with highly reactive elemental uranium (Scheme 1).[23] The bronze-colored $(C_5H_5)_3U$ also could be prepared by reaction of C_5H_5K with UCl_3 in benzene, but the yield was only 10%. In THF solution the brown THF adduct $C_5H_5)_3U{\cdot}THF$ was obtained in 96% yield. Displacement of THF from the adduct by other Lewis bases gave the respective $(C_5H_5)_3U{\cdot}D$ compounds with cyclohexyl isocyanide and L-nicotine. Highly reactive uranium powder, obtained by thermal decomposition of a uranium amalgam (which had been prepared electrolytically from an aqueous solution), was found to react directly with cyclopentadiene in benzene solution to give $(C_5H_5)_3U$ in 30% yield.[24]

Also prepared was $(C_5H_5)_3Th$, a violet, crystalline solid (eq 4). Italian workers also prepared $(C_5H_5)_3U$ by

$$(\mathrm{C}_5\mathrm{H}_5)_3\mathrm{ThCl} + \mathrm{Na} \xrightarrow[\mathrm{THF}]{\text{naphthalene}} (\mathrm{C}_5\mathrm{H}_5)_3\mathrm{Th} + \mathrm{NaCl} \qquad (4)$$

reduction of $(C_5H_5)_3UCl$ with sodium hydride in benzene.[26] The $(C_5H_5)_2Mg$ method was used by workers at

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(12) Baumgärtner, F.; Fischer, E. O.; Laubereau, P. *Naturwissenschaften* **1965**, *52*, 560.

(13) Baumgärtner, F.; Fischer, E. O.; Kanellakopulos, B.; Laubereau, P. *Angew. Chem.* **1965**, *77*, 866.

(14) Baumgärtner, F.; Fischer, E. O.; Kanellakopulos, B.; Laubereau, P. *Angew. Chem.* **1966**, *78*, 112.

(15) Fischer, E. O.; Laubereau, P.; Baumgärtner, F.; Kanellakopulos, B. *J. Organomet. Chem.* **1966**, *5*, 584.

(16) Baumgärtner, F.; Fischer, E. O.; Kanellakopulos, B.; Laubereau, P. *Angew. Chem.* **1969**, *81*, 182; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 202.

(17) Baumgärtner, F.; Fischer, E. O.; Kanellakopulos, B.; Laubereau, P. *Angew. Chem.* **1968**, *80*, 661; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 634.

(18) Laubereau, P. G.; Burns, J. H. *Inorg. Chem.* **1970**, *9*, 1091.

(19) Laubereau, P. G. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 611.

(20) Laubereau, P. G.; Burns, J. H. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 59.

(21) Reid, A. F.; Wailes, P. C. *Inorg. Chem.* **1966**, *7*, 1213.

(22) Baumgärtner, F.; Fischer, E. O.; Billich, H.; Dornberger, E.; Kanellakopulos, B.; Roth, W.; Stieglitz, L. *J. Organomet. Chem.* **1970**, *22*, C17.

(23) (a) Kannelakopulos, B.; Fischer, E. O.; Dornberger, E.; Baumgärtner, F. *J. Organomet. Chem.* **1970**, *24*, 507. (b) A later X-ray crystal and molecular structure determination of $(C_5H_5)_3U{\cdot}THF$ showed a distorted-tetrahedral arrangement of the four ligands around the uranium atom with η^5 binding of the C_5H_5 groups: Wasserman, H. J.; Zozulin, A. J.; Moody, D. C.; Ryan, R. R.; Salazar, K. V. *J. Organomet. Chem.* **1983**, *254*, 305.

(24) Chang, C. C.; Sung-Yu, N. K.; Hseu, C. S.; Chang, C. T. *Inorg. Chem.* **1979**, *18*, 885.

(25) Kanellakopulos, B.; Dornberger, E.; Baumgärtner, F. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 155.

(26) Zanella, P.; Rosetto, G.; De Paoli, G. *Inorg. Chim. Acta* **1980**, *44*, L155.

Dow Chemical Co. to prepare $(C_5H_5)_3Pu$ rapidly in gram quantities (Scheme 2).[27]

In addition to the known organouranium compounds of types $(C_5H_5)_3U$, $(C_5H_5)_4U$, and $(C_5H_5)_3UX$, di- and monocyclopentadienyl compounds of uranium have been prepared (eqs 5 and 6). $(C_5H_5)_2UCl_2$ is not stable and rapidly disproportionates to $C_5H_5UCl_3$ and $(C_5H_5)_3UCl$. Its dmpe adduct, however, could be isolated and characterized.

$$UCl_4 + 2C_5H_5Tl \xrightarrow[\text{room temp}^{28}]{CH_3OCH_2CH_2OCH_3} (C_5H_5)_2UCl_2 + 2\ TlCl \quad (5)$$

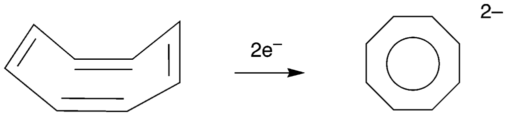
$$UCl_4 + C_5H_5Tl \xrightarrow[\text{room temp}^{29}]{CH_3OCH_2CH_2OCH_3} C_5H_5UCl_3{\cdot}CH_3OCH_2CH_2OCH_3 \quad (6)$$

These, then, are the organoactinide compounds that contain only C_5H_5 ligands. Others containing substituted cyclopentadienyl ligands such as $CH_3C_5H_4$, $PhCH_2C_5H_4$, $Me_3SiC_5H_4$, $(CH_3)_5C_5$, etc., as well as indenyl ligands, are known. The pentamethylcyclopentadienyl derivatives are of special interest: they are more soluble and crystallize more readily. The steric properties of this ligand, which make complete substitution by $(CH_3)_5C_5$ (Cp*) more difficult, have allowed the development of the chemistry of $Cp^*_2MX_2$ and Cp^*MX_3 complexes as well: i.e., a functional chemistry at uranium and thorium.

All cyclopentadienylactinide complexes are very air-sensitive; therefore, all work must be carried out with rigorous exclusion of air using degassed solvents. Their chemistry, their spectroscopic and magnetic properties, their structures, and related questions of bonding (i.e., ionic vs covalent; involvement of 6d and 5f orbitals) have received much attention. Among the cyclopentadienyluranium compounds of special interest may be noted alkyl, aryl, and hydride compounds of the types $(C_5H_5)_3UR$,[30] $[(CH_3)_5C_5]_2U(R)Cl$,[31] $[(CH_3)_5C_5]_2U(CH_3)_2$,[32] and $[(C_5H_5)_3UR]Li$,[33] the tris(allyl) compound $(CH_3)_5C_5U(\eta^3\text{-}C_3H_5)_3$,[34] hydrides, both neutral, e.g., $(RC_5H_4)_3UH$ (R = Me_3Si, Me_3C),[35] and anionic, e.g., $[(C_5H_5)_3U(\mu\text{-}H)U(C_5H_5)_3]Na(THF)_2$,[36] and anionic chlorides of the types $[(C_5H_5)_3U(\mu\text{-}Cl)U(C_5H_5)_3]Na$ and $[Bu_4N][(C_5H_5)_3UCl]$.[37] These examples serve to show that a well-developed chemistry of cyclopentadienyluranium compounds exists. Many chemists have contributed to the rapid progress in cyclopentadienyluranium chemistry in recent years, and it is the work of Tobin J. Marks at Northwestern University and Richard A. Andersen at the University of California at Berkeley, and their respective co-workers, and of the group at the Los Alamos National Laboratory which has provided the most numerous and notable advances in this field. A more detailed discussion of cyclopentadienylactinide chemistry is beyond the scope of this essay, and the reader is referred to the pertinent review literature.[38]

III. Cyclooctatetraene Dianion as a New Ligand for f-Orbital Metals. Preparation of Uranocene by Streitwieser and Müller-Westerhoff

The uranocene story begins 20 years before its first preparation when evidence began to accumulate suggesting that a stable dianion, $[C_8H_8]^{2-}$, could be formed by addition of two electrons to cyclooctatetraene (eq 7).



(7)

The source of these electrons could be alkali metals in ether[39] or liquid ammonia[40] or (triphenylmethyl)sodium.[41] Hydrolysis of such dianion solutions yielded cyclooctatrienes, treatment with CO_2 gave dicarboxylic acids, and reaction with benzophenone resulted in formation of a diol.[39−41] The 2-electron reduction to the dianion also could be effected electrochemically.[42] In 1960, Thomas J. Katz of Columbia University reported the first isolation and the ^1H NMR spectrum of the dipotassium salt of the cyclooctatetraene dianion, prepared by reaction of potassium metal with cyclooctatet-

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(27) Crisler, L. R.; Eggerman, W. G. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1424.

(28) Zanella, P.; Faleschini, S.; Doretti, L.; Faraglia, G. *J. Organomet. Chem.* **1971**, *26*, 353.

(29) Doretti, L.; Zanella, P.; Faraglia, G.; Faleschini, S. *J. Organomet. Chem.* **1972**, *43*, 339.

(30) (a) Marks, T. J.; Sevam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529. (b) Analogous $(C_5H_5)_3ThR$: Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 703.

(31) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170.

(32) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939 (also the analogous Th compound).

(33) (a) Foyentin, M.; Folcher, G.; Ephritikhine, M. *J. Organomet. Chem.* **1987**, *335*, 201. (b) Arnaudet, L.; Charpin, P.; Folcher, G.; Lance, M.; Nierlich, M.; Vigner, J. *Organometallics* **1986**, *5*, 270.

(34) Cymbaluk, T. H.; Ernst, R. D.; Day, V. W. *Organometallics* **1983**, *2*, 963.

(35) (a) Berthet, J.-C.; Le Maréchal, J.-F.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1991**, 360. (b) Berthet, J.-C.; Le Maréchal, J.-F.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1992**, *9*, 1523.

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(41) Wittig, G.; Wittenberg, D. *Justus Liebigs Ann. Chem.* **1957**, *606*, 1.

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raene in THF solution, and of the dilithium salt.[43] A single sharp singlet

> "insignificantly displaced from the resonance of cyclooctatetraene itself"

was observed. Katz interpreted this as evidence for a planar, aromatic $[C_8H_8]^{2-}$ species, one that obeyed the Hückel $[2n + 4]$ rule. He pointed out that

> "Increased proton shielding would be expected on addition of electrons to the molecule and in this case must be compensated if the ring flattens or aromatizes by the displacement to low fields characteristic of aromatic molecules due to at least in part to the diamagnetic ring current induced in the applied magnetic field."

Thus, it appeared that $[C_8H_8]^{2-}$ is a flat 8-membered ring with 10 π electrons that is highly resonance stabilized.

The conceptual makings of uranocene were now in hand: (1) the demonstrated existence of the planar, dianionic, aromatic $[C_8H_8]^{2-}$ ligand and (2) the U(IV) atom in $(C_5H_5)_4U$ and $(C_5H_5)_3UCl$, whose 5f orbitals Moffitt had shown play an important part in the η^5 sandwich bonding in these compounds. However, another 8 years went by before the preparation of uranocene was accomplished.

In the meantime, in 1963, R. Dieter Fischer at the University of Hamburg published a theoretical paper in which he considered the metal–ring bonding in sandwich complexes.[44] In the final section of this paper he discussed the C_8H_8 ligand. In addition to transition-metal complexes containing a planar C_8H_8 ligand[45] such as $(C_8H_8)_2Ti$, he suggested the possibility of a stable uranium complex, $(C_8H_8)_2U$, noting that there might be

> "a possible additional gain in energy due to the participation of the f-orbitals of heavy central atoms."

Further considerations did not lead him to any firm conclusions concerning the stability of the hypothetical $(C_8H_8)_2U$, his final sentence on the subject being

> "If these considerations at this time do not permit a reliable prediction, they do, however, justify further preparative work with the C_8H_8 ligand."

$(C_8H_8)_2U$ was a potentially interesting molecule; however, synthetic chemists normally don't read *Theoretica Chimica Acta*, so no one took him up on his suggestion.

The story of the conception and the preparation of $(C_8H_8)_2U$, which was christened "uranocene", is told in Andrew Streitwieser's autobiography.[46] But first a bit about Streitwieser (Figure 1). He was born in Buffalo, NY, in 1927, the son of German immigrant parents. A move to New York City in the late 1930s allowed him to attend Stuyvesant High School, where his interest in chemistry began. His undergraduate education at Columbia was interrupted by 18 months' service in the US Army Medical Corps, and he subsequently returned to Columbia and stayed there to obtain his Ph.D. During his graduate years (1948–1951), he carried out his dissertation research under the guidance of William von Eggers Doering, working on quantitative studies of various solvolysis reactions. Postdoctoral study at the Massachusetts Institute of Technology in the research group of J. D. Roberts followed. Streitwieser began his independent career at the University of California at Berkeley in 1952 as an instructor in chemistry. He proceeded up the academic ladder and is still a member of the Berkeley chemistry faculty today as professor emeritus. Over the years his research has ranged broadly in organic chemistry—stereochemistry of the primary carbon atom, solvolytic displacement reactions, secondary deuterium isotope effects, Hückel molecular orbital theory (with the publication of an important book, *Molecular Orbital Theory for Organic Chemists*, in 1961), C–H bond acidity (a major program), carban-

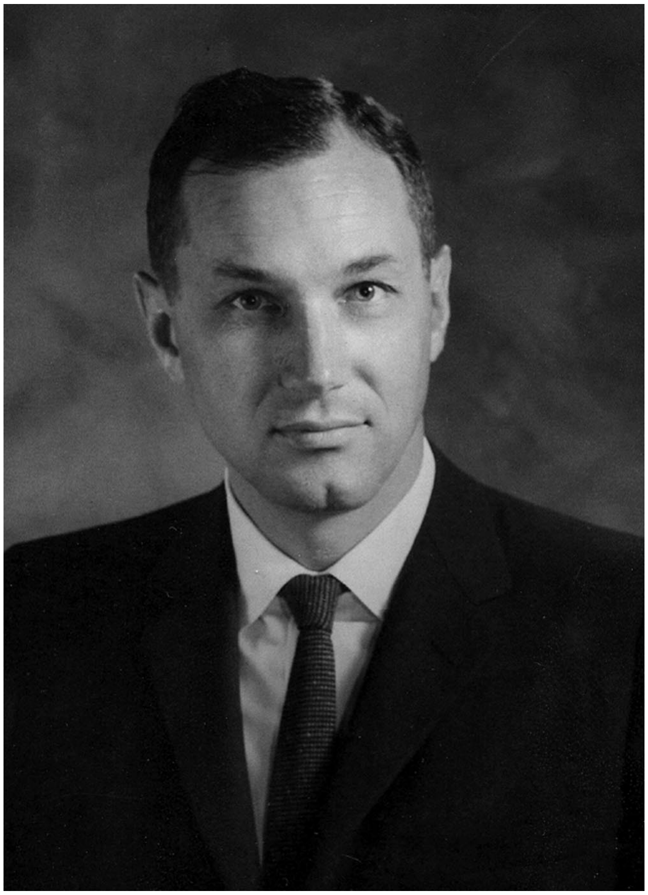

Figure 1. Andrew Streitwieser, 1967 (photo by Barry Evans Studio; reproduced by permission of Barry Evans Studio and Andrew Streitwieser).

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[43] Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3784. (Thomas J. Katz, b. 1936 in Prague; B.A., Wisconsin, 1956; Ph.D., Harvard, 1959; at Columbia since 1959. Many innovative and imaginative fundamental contributions to mechanistic and synthetic organic and organometallic chemistry, including syntheses of 10-π-aromatic anions, the benzene isomers benzvalene and prismane, the first pentaalkylphosphoranes, and the first cyclobutenyl cations. Seminal contributions to the mechanism of the transition-metal-catalyzed olefin metathesis reaction and the first general procedure for effecting ring-opening metathesis polymerizations stereospecifically. Katz spent the Spring 1965 semester at Berkeley as a visiting lecturer, substituting for Andrew Streitwieser, who was Miller Research Professor during that year.)

[44] Fischer, R. D. *Theor. Chim. Acta* **1963**, *1*, 418.

[45] For a brief account of transition-metal complexes containing the C_8H_8 and $[C_8H_8]^{2-}$ ligands, see the literature cited in ref 44.

[46] Streitwieser, A. *A Lifetime of Synergy with Theory and Experiment*; Profiles, Pathways, and Dreams: Autobiographies of Eminent Chemists, Seeman, J. I., Series Ed.; American Chemical Society: Washington, DC, 1997.

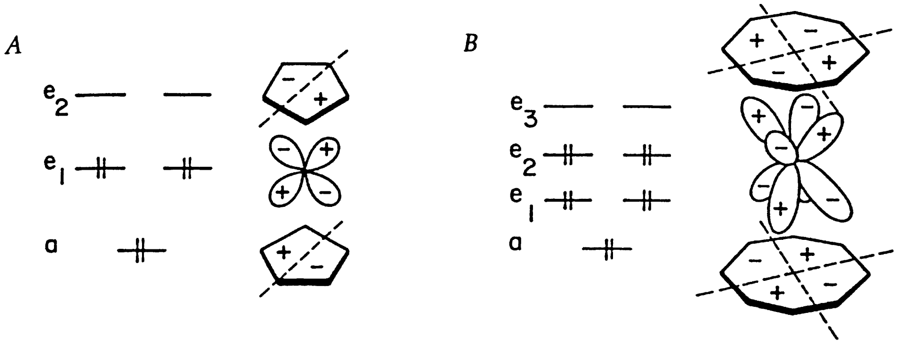

Figure 2. HOMO–LUMO interactions in metallocenes: (A) the ligand π-MOs of two cyclopentadienyl anions and corresponding d orbitals of Fe^{2+} of e_{1g} symmetry have one shared nodal plane; (B) the HOMO π-MOs of two cyclooctatetraene dianions and $f_{\pm 2}$ orbitals of a central U^{4+} of e_{1g} symmetry have two shared nodal planes. (from Streitwieser, A., Jr. *A Lifetime of Synergy with Theory and Experiment*, Profiles, Pathways, and Dreams: Autobiographies of Eminent Chemists; Seeman, J. I., Series Ed.; American Chemical Society: Washington, DC, 1996; p 183).

ion chemistry, ab initio quantum organic chemistry, f-orbital organometallic chemistry, and heterocyclic polycations, as the chapter headings in his autobiography tell us—mostly involving physical organic chemistry but also some first-rate synthetic chemistry, including the synthesis of our cover molecule.

Streitwieser had become acquainted with cyclooctatetraene and its dianion through his attempted synthesis of octalene, a compound consisting of two fused cyclooctatetraene rings. As Streitwieser reports in his autobiography, in late summer 1968 he attended a seminar at Berkeley on the bonding in ferrocene. As he recalls, this seminar

> “had caused me to muse one evening about this bonding interpretation. With all of our recent experimental work with cyclooctatetraene, I chanced to wonder about the possibility of a similar type of bonding with the next higher Hückel $4n + 2$ ring system with 10 π-electrons instead of 6. This thought process was clearly stimulated by our extensive use of cyclooctatetraene dianion in synthetic studies during the several preceding years. I quickly recognized that ring-metal bonding comparable to that in ferrocene would require an 8-lobed atomic orbital that I realized had to be one of the f-orbitals (Figure 2). f-Orbitals immediately suggest the actinide and lanthanide elements. I mentioned this suggestion to Ullie Müller-Westerhoff who had been working with me for almost a year in continuing our fruitless attempt to prepare octalene. ... [Ullie] had a long interest in organometallic chemistry. Thus, after all those months in unproductive organic synthesis he was ready for a change and in one of his first experiments only a few days later treated cyclooctatetraene dianion with uranium tetrachloride and obtained beautiful green crystals of the compound we then named uranocene” (eq 8).

$$2C_8H_8 + 4K \xrightarrow{THF} 2K_2[C_8H_8] \xrightarrow{UCl_4} (C_8H_8)_2U^{IV} + 4KCl \quad (8)$$

Ulrich Müller-Westerhoff (Figure 3) has provided an account[48] of his first preparation of uranocene:

> “In my first attempt to prepare $(COT)_2U$, the reaction of UCl_4 with K_2COT in THF under nitrogen produced a deep green solid. Solvolysis by methanol and water showed that the complex was inert to protic solvents. However, I almost made a mess and lost my product because I had no idea that my product could be pyrophoric. In my ignorance, I vacuum filtered my reaction product through a regular Büchner funnel and washed out the byproduct with methanol and water. That something was amiss became rapidly clear to me: each time the solvent had been sucked through, the Büchner funnel got warm! Evidently, air did something bad to my product. Because it now was late at night of the first attempted uranocene synthesis, I washed my product under nitrogen into a flask, kept it under N_2 and went home.
>
> The next day, I filtered the product under nitrogen and purified it by continuous extraction under nitrogen with THF at reflux. Because the experience of the previous day had forewarned me, the resulting shiny green, small crystals were stored under nitrogen and treated with caution. They certainly showed their reactivity toward oxygen rather easily. One favorite lab demonstration was to take a small sample on a spatula and count to five. The microscale fireworks always were a success. A more negative effect showed up when I tried to record a proton NMR spectrum: despite careful efforts to exclude air from the sample, I only saw the peak of free COT. A controlled preparative scale reaction with air, by bubbling air through a THF solution of the complex, led to quantitative formation of UO_2 and COT. Despite this reactivity, I was able to record a VIS spectrum and was thrilled by the cascade of sharp peaks I saw.
>
> We were so confident that this was indeed the desired sandwich complex that Andy Streitwieser came to the labs with a bottle of champagne to celebrate and christen the new compound uranocene, to highlight its similarity to ferrocene.”

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(47) Ulrich Müller-Westerhoff, born 1937 in Düsseldorf, Germany. Initial chemistry studies at University of Marburg; Diplom (with G. N. Schrauzer) at Universität München, 1964; Ph.D., 1967 with K. Hafner, beginning in Universität München, continuing at University of Darmstadt. Postdoctoral studies (theory and synthesis) at University of California at Berkeley with A. Streitwieser, 1967–1968. On technical staff of IBM Research Laboratory in San Jose, 1968–1982. Professor of Chemistry at University of Connecticut, Storrs, CT since 1982.

(48) Müller-Westerhoff, U. “How Uranocene Happened”, unpublished account, March 2003.

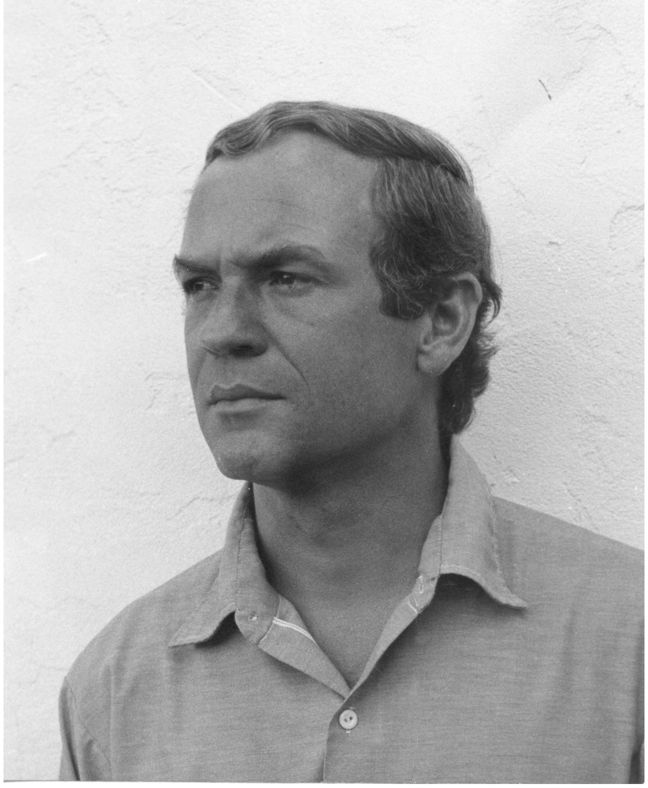

Figure 3. Ulrich Mueller-Westerhoff (photo by Eda Easton; reproduced by permission of Eda Easton and Ulrich Mueller-Westerhoff).

The identity of the green crystalline product was based on its thermal stability (it sublimes at 180 °C at 0.03 mmHg) and its mass spectrum, which showed the molecular ion, $(C_8H_8)_2U^+$, as well as peaks due to $C_8H_8U^+$ and $C_8H_8^+$. Uranocene was an exciting discovery: a very interesting and theoretically important molecule whose preparation presaged the existence of a completely new field of organometallic chemistry. This result was published in the same year in a brief Communication to the Editor in the *Journal of the American Chemical Society* (Figure 4).[49] A full paper on uranocene, after more detailed studies had been carried out, was published in 1973.[50] The preparative procedure was improved, and a special Soxhlet extraction unit (Figure 5) was devised for use in the purification of uranocene. Uranocene is extremely air-sensitive, enflaming in air, and it is essential to exclude all traces of air during all operations. It is rapidly decomposed by aqueous bases and by strong acids but is hydrolyzed only slowly in neutral water. It was not possible to lithiate uranocene or to effect electrophilic substitution with $[CH_3C(O)][SbCl_6]$. A working hypothesis of the electronic structure of uranocene (Figure 6) was given, the essential feature of which is the interaction of the uranium f_{xyz} and $f_{z(x^2-y^2)}$ orbitals with e_{2u} ligand orbitals. As the authors noted, if this bonding picture is correct and there is significant covalent bonding between the C_8H_8 ligands and the uranium 5f orbitals, then uranocene "represents a new class of metallocene-like compounds homologous to the d transition metal metallocenes and could be regarded as a new "aromatic" organometallic system." That the chemical properties of uranocene are very different from those of ferrocene was ascribed to the fact that in its bonding scheme both the highest occupied and the lowest vacant orbitals are predominantly uranium orbitals. Thus, reactions with many reagents will occur at the metal, resulting in cleavage of the metal−ligand bonds.

Once uranocene had been prepared, its structure, of course, was of interest. How the structure determination was accomplished is described by Streitwieser in his autobiography:[51]

> "Ken Raymond had just been appointed, beginning July 1968, as an Assistant Professor at Berkeley. Ken is an inorganic chemist and an expert X-ray crystallographer. He recalls my telling him about our new uranocene synthesis over lunch at the Faculty Club one day that Fall and asking about the feasibility of doing a structure determination. I was aware that uranium would dominate the X-ray diffraction and that the electron density about the much lighter carbon might be difficult to detect. Ken thought it might be feasible; however, at Berkeley he planned to downplay his crystal structure work and to emphasize other research interests. I thereupon took from my pocket a vial with some beautiful uranocene crystals and he was hooked. He determined the structure in collaboration with Allen Zalkin, a research chemist and X-ray structure expert at the Lawrence Berkeley Laboratory (LBL), and proved the D_{8h} structure with two planar octagonal rings having uranium at the center (Figure 7). It is amusing that they had trouble publishing their result. A referee objected that the contribution of carbon to the diffraction compared to the much heavier uranium would be too small to determine, exactly the fear that prompted me to consult Ken in the first place. Only when Ken pointed out to the referee that the symmetry of uranocene was such that the uranium could not contribute to many of the reflections was the communication published."[52]

As expected, the structure of uranocene (Figure 8) showed it to be a π-bonded sandwich complex with D_{8h} molecular symmetry. The C_8 rings are planar, and the alternate C−C bond lengths are equal. Zalkin and Raymond concluded that there is

> "no question that this is a pseudo-aromatic ring and that di-π-cyclooctatetraeneuranium or 'uranocene' is an authentic π sandwich complex of the 5f transition series."[52a]

At this point, a note on nomenclature is appropriate. Uranocene has been called di- (or bis) [π-(or η^8)cyclooctatetraene]uranium, bis(cyclooctatetraenyl)uranium, and, in some of Streitwieser's later papers, bis([8]annulene)uranium. The ligand in uranocene is not cyclooctatetraene, the neutral C_8H_8 molecule, nor is it cyclooctatet-

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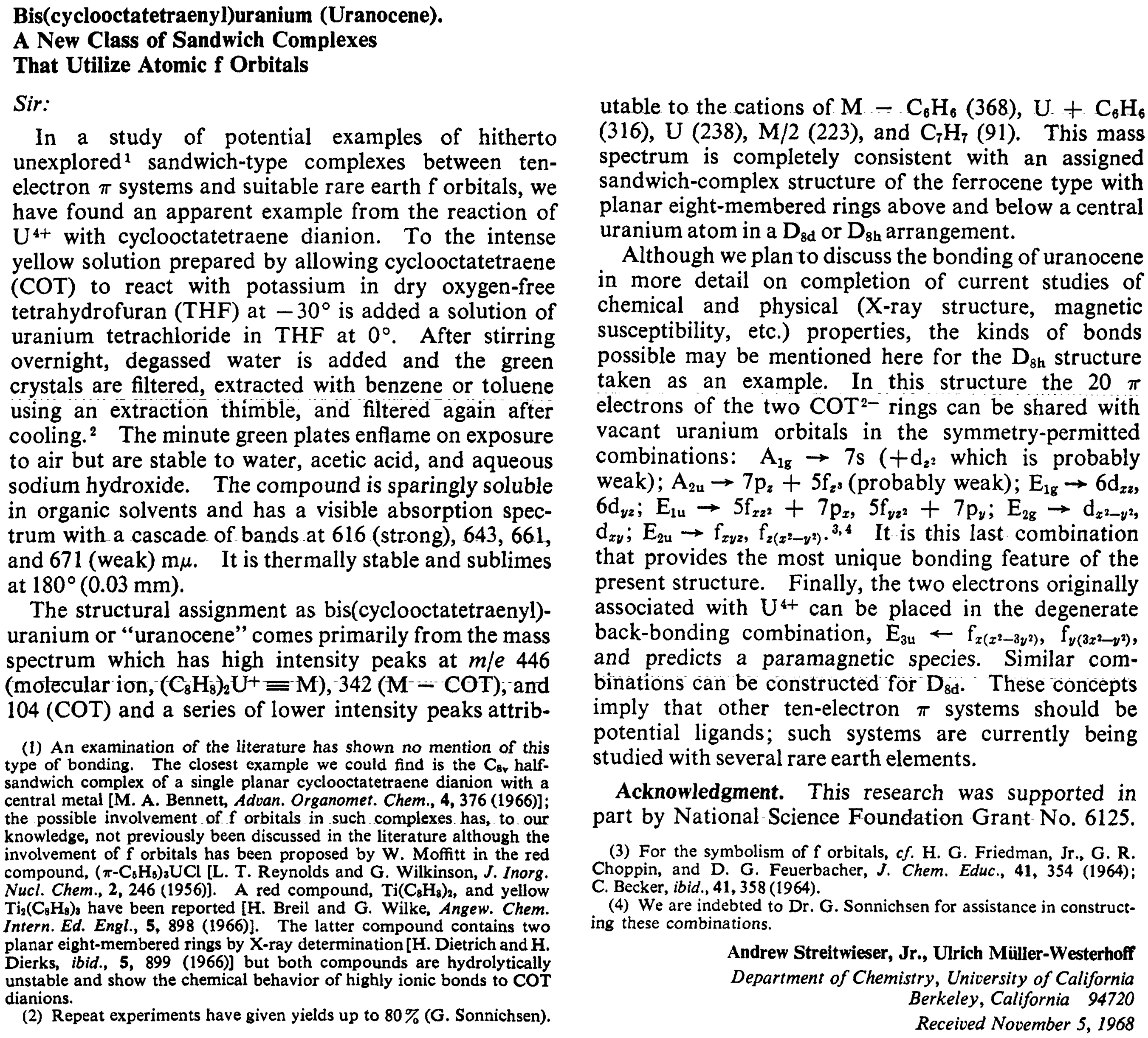
[49] Streitwieser, A., Jr.; Müller-Westerhoff, U. *J. Am. Chem. Soc.* **1968**, *90*, 7364.

[50] (a) Streitwieser, A., Jr.; Müller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8644. (b) Streitwieser, A., Jr.; Mueller-Westerhoff, U.; Mares, F.; Grant, C. B.; Morrell, D. G. *Inorg. Synth.* **1979**, *19*, 148.

[51] Reference 46, pp 185−186.

[52] (a) Zalkin, A.; Raymond, K. N. *J. Am. Chem. Soc.* **1969**, *91*, 5667. (b) Avdeef, A.; Raymond, K. N.; Hodgson, K. O.; Zalkin, A. *Inorg. Chem.* **1972**, *11*, 1083.



Bis(cyclooctatetraenyl)uranium (Uranocene). A New Class of Sandwich Complexes That Utilize Atomic f Orbitals

Sir:

In a study of potential examples of hitherto unexplored[1] sandwich-type complexes between ten-electron π systems and suitable rare earth f orbitals, we have found an apparent example from the reaction of U^{4+} with cyclooctatetraene dianion. To the intense yellow solution prepared by allowing cyclooctatetraene (COT) to react with potassium in dry oxygen-free tetrahydrofuran (THF) at −30° is added a solution of uranium tetrachloride in THF at 0°. After stirring overnight, degassed water is added and the green crystals are filtered, extracted with benzene or toluene using an extraction thimble, and filtered again after cooling.[2] The minute green plates enflame on exposure to air but are stable to water, acetic acid, and aqueous sodium hydroxide. The compound is sparingly soluble in organic solvents and has a visible absorption spectrum with a cascade of bands at 616 (strong), 643, 661, and 671 (weak) mμ. It is thermally stable and sublimes at 180° (0.03 mm).

The structural assignment as bis(cyclooctatetraenyl)-uranium or "uranocene" comes primarily from the mass spectrum which has high intensity peaks at *m/e* 446 (molecular ion, $(C_8H_8)_2U^+ \equiv M$), 342 (M − COT), and 104 (COT) and a series of lower intensity peaks attributable to the cations of M − C_6H_6 (368), U + C_6H_6 (316), U (238), M/2 (223), and C_7H_7 (91). This mass spectrum is completely consistent with an assigned sandwich-complex structure of the ferrocene type with planar eight-membered rings above and below a central uranium atom in a D_{8d} or D_{8h} arrangement.

Although we plan to discuss the bonding of uranocene in more detail on completion of current studies of chemical and physical (X-ray structure, magnetic susceptibility, etc.) properties, the kinds of bonds possible may be mentioned here for the D_{8h} structure taken as an example. In this structure the 20 π electrons of the two COT^{2-} rings can be shared with vacant uranium orbitals in the symmetry-permitted combinations: $A_{1g} \rightarrow 7s$ ($+d_{z^2}$ which is probably weak); $A_{2u} \rightarrow 7p_z + 5f_{z^3}$ (probably weak); $E_{1g} \rightarrow 6d_{xz}$, $6d_{yz}$; $E_{1u} \rightarrow 5f_{xz^2} + 7p_x$, $5f_{yz^2} + 7p_y$; $E_{2g} \rightarrow d_{x^2-y^2}$, d_{xy}; $E_{2u} \rightarrow f_{xyz}$, $f_{z(x^2-y^2)}$.[3,4] It is this last combination that provides the most unique bonding feature of the present structure. Finally, the two electrons originally associated with U^{4+} can be placed in the degenerate back-bonding combination, $E_{3u} \leftarrow f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$, and predicts a paramagnetic species. Similar combinations can be constructed for D_{8d}. These concepts imply that other ten-electron π systems should be potential ligands; such systems are currently being studied with several rare earth elements.

Acknowledgment. This research was supported in part by National Science Foundation Grant No. 6125.

(1) An examination of the literature has shown no mention of this type of bonding. The closest example we could find is the C_{8v} half-sandwich complex of a single planar cyclooctatetraene dianion with a central metal [M. A. Bennett, *Advan. Organomet. Chem.*, **4**, 376 (1966)]; the possible involvement of f orbitals in such complexes has, to our knowledge, not previously been discussed in the literature although the involvement of f orbitals has been proposed by W. Moffitt in the red compound, $(\pi\text{-}C_5H_5)_3UCl$ [L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956)]. A red compound, $Ti(C_8H_8)_2$, and yellow $Ti_2(C_8H_8)_3$ have been reported [H. Breil and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **5**, 898 (1966)]. The latter compound contains two planar eight-membered rings by X-ray determination [H. Dietrich and H. Dierks, *ibid.*, **5**, 899 (1966)] but both compounds are hydrolytically unstable and show the chemical behavior of highly ionic bonds to COT dianions.

(2) Repeat experiments have given yields up to 80% (G. Sonnichsen).

(3) For the symbolism of f orbitals, *cf.* H. G. Friedman, Jr., G. R. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, **41**, 354 (1964); C. Becker, *ibid.*, **41**, 358 (1964).

(4) We are indebted to Dr. G. Sonnichsen for assistance in constructing these combinations.

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Figure 4. The Streitwieser/Mueller-Westerhoff *J. Am. Chem. Soc.* Communication to the Editor reporting the preparation of uranocene (*J. Am. Chem. Soc.* **1968**, *90*, 7364).

raenyl as used by some others (which implies C_8H_7, i.e., loss of a hydrogen substituent). It is the cyclooctatetraene dianion, obtained by addition of two electrons, $[C_8H_8]^{2-}$, and thus is cyclooctatetraenide(2−). Using this name in the case of $(C_8H_8)_2Ce$, bis(cyclooctatetraenide)cerium, is suitable, as the compound is ionic, but would give the impression that the mostly covalent uranocene is ionic. Thus, nomenclature is a problem and the trivial name "uranocene" seems preferable. Extended to the other actinide elements, the general name would be "actinocene", specifically, thorocene, neptunocene, plutonocene, etc.

Uranocene and substituted uranocenes have been the subjects of extensive studies aimed at obtaining a detailed understanding of the bonding: proton NMR spectroscopy[53] (uranocene, with two unpaired 5f electrons, is paramagnetic), He I/He II photoelectron[54] and X-ray photoelectron[55] spectroscopy, optical spectroscopy,[56] vibrational spectroscopy,[38h] electronic Raman spectroscopy,[57] and magnetic susceptibility,[58] as well as theoretical studies.[59] Marks and Streitweiser in 1986[38a] summarized the results of these experimental and theoretical studies as follows:

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(53) Review: Luke, W. D.; Streitwieser, A., Jr. *ACS Symp. Ser.* **1980**, *No. 131*.

(54) (a) Amberger, H.-D.; Fischer, R. D.; Kanellakopulos, B. *Theor. Chim. Acta* **1975**, *37*, 105. (b) Edelstein, N.; Streitwieser, A., Jr.; Morrell, D. G.; Walker, R. *Inorg. Chem.* **1976**, *15*, 1397.

(55) (a) Clark, J. P.; Green, J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 505. (b) Green, J. C.; Payne, M. P.; Streitwieser, A., Jr. *Organometallics* **1983**, *2*, 1707. (c) Fragalà, I.; Condorelli, G.; Zanella, P.; Tondello, E. *J. Organomet. Chem.* **1976**, *122*, 357. (d) Brennan, J. G.; Green, J. C.; Redfern, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 2373.

(56) Beach, D. B.; Bomben, K. D.; Edelstein, N. M.; Eisenberg, D. C.; Jolly, W. L.; Shinomoto, R.; Streitwieser, A., Jr. *Inorg. Chem.* **1986**, *25*, 1735.

(57) (a) Harmon, C. A.; Bauer, D. P.; Berryhill, S. P.; Hagiwara, K.; Streitwieser, A., Jr. *Inorg. Chem.* **1977**, *16*, 2143. (b) Streitwieser, A., Jr.; Harmon, C. A. *Inorg. Chem.* **1973**, *12*, 1102.

(58) Dallinger, R. F.; Stein, P.; Spiro, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 7865.

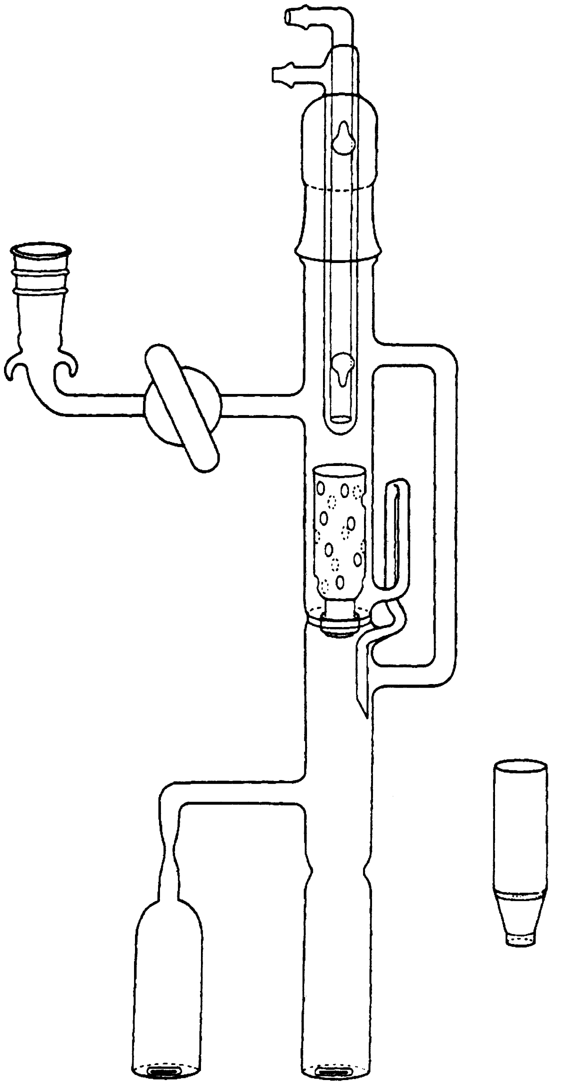


Figure 5. Diagram of the sidearm Soxhlet extractor used for purification of actinide cyclooctatetraene complexes (from Streitwieser, A., Jr. et al. *J. Am. Chem. Soc.* **1973**, *95*, 8644).

> "There is now reasonable agreement in the interpretation of most of these results. The picture emerging for uranocene is one in which there is significant metal–ligand bond covalence. While metal 5f orbitals are doubtless involved in the bonding, the role of 6d orbitals is probably comparable or greater. Furthermore, there is greater metal–ligand bond covalence in uranocene than in thorocene."

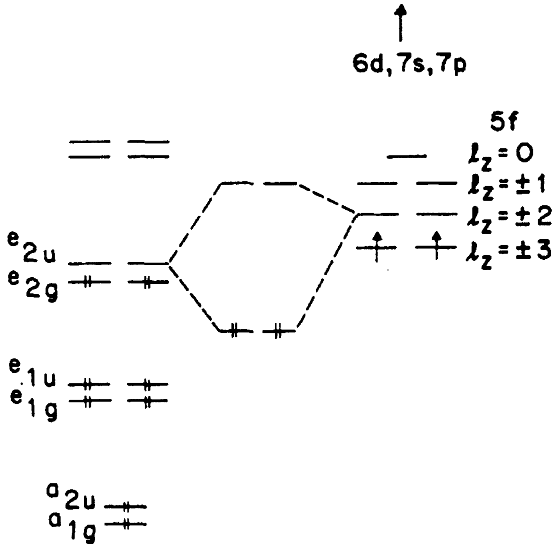


Figure 6. Working hypothesis of the electronic structure of uranocene (from Streitwieser, A., Jr. et al. *J. Am. Chem. Soc.* **1973**, *95*, 8644).

Figure 7. Kenneth Raymond and Andrew Streitwieser in 1978, at the celebration of the 10th anniversary of the discovery of uranocene (unknown photographer; reproduced by permission of Kenneth Raymond and Andrew Streitwieser).

In their recent paper and review on the application of relativistic density functional theory to the actinocenes, Bursten and co-workers have provided a qualitative energy-level diagram for $(C_8H_8)_2Pa^{59h,i}$ (Figure 9). As Li and Bursten point out, the main interactions in $(C_8H_8)_2Pa$ are those of the protoactinium 5f and 6d orbitals with the eight C_8H_8 π molecular orbitals as shown in Figure 9, with the principal bonding interactions being those between the protoactinium 6dδ and C_8H_8 $3e_{2g}$ and the metal 5fδ and the C_8H_8 $3e_{2u}$ combinations. The available electrons (16 C_8H_8 π electrons and 4 Pa electrons) fill all the MOs up to the π_{2g} and π_{2u} pairs. The interactions involving the Pa 6d orbitals are stronger than are those involving the 5f orbitals. The extra metal electrons not used in bonding to the C_8H_8 ligands are localized in the 5f-based MOs.

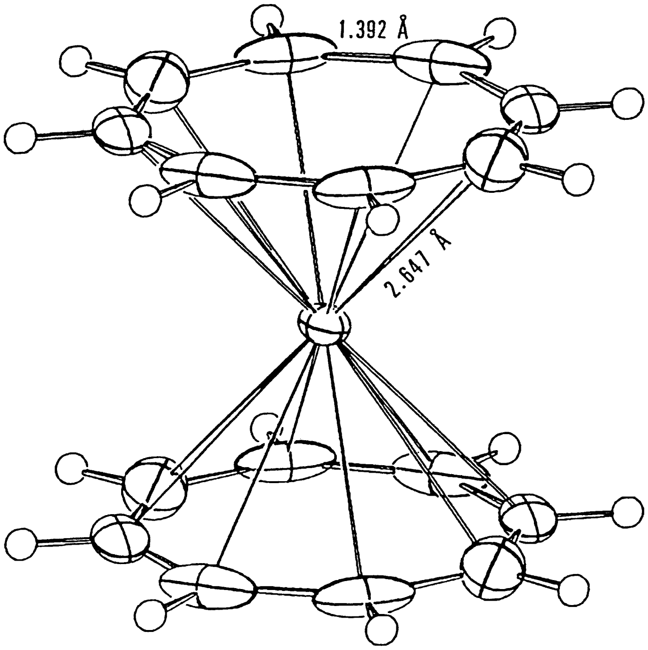


Figure 8. X-ray crystal structure of uranocene (from Zalkin, A.; Raymond, K. N. *J. Am. Chem. Soc.* **1969**, *91*, 5667).

The preparation of uranocene was followed by extensive synthetic studies, whose goal was the further development of this interesting new area of actinide organometallic chemistry, for the most part carried out at Berkeley in Streitwieser's laboratories but also by chemists in other laboratories in the USA and Europe. Other routes to uranocene were developed (eqs 9 and 10). The synthesis in eq 10 requires the use of finely divided, highly reactive metallic uranium. This may be generated by various methods: by thermal decomposition of UH_3 (which gives pyrophoric uranium)[61] and of "(n-C_4H_9)$_4$U",[62] by reduction of UCl_4 with Na/K alloy,y[63] and by electrolysis.[24] Of interest is the observation that metallic mercury in trace amounts catalyzes the reaction of cyclooctatetraene with metallic uranium.[61]

$$UF_4 + 2MgC_8H_8 \xrightarrow[\text{no solvent}]{\text{ref 60}} (C_8H_8)_2U + 2MgF_2 \quad (9)$$

$$U(s) + 2C_8H_8 \rightarrow (C_8H_8)_2U \quad (10)$$

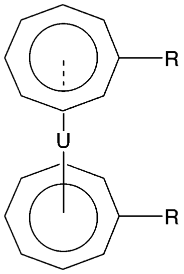
Actinocene complexes of other actinides also were prepared: yellow $(C_8H_8)_2Th$, by the cyclooctatetraene dianion route[64] and by reaction of cyclooctatraene with finely divided metallic thorium (from thorium hydride);[61] red $(C_8H_8)_2Np$, as shown in eq 11;[65] red $(C_8H_8)_2Pu$, also by the cyclooctatetraene dianion route[65] (eq 12); yellowish $(C_8H_8)_2Pa$, in a similar manner (eq 13).[66] The plutonium complex also was prepared by the reaction of cyclooctatetraene with finely divided plutonium (via PuH_3 thermolysis).[61] The thorium[65] and plutonium[65] cyclooctatetraene complexes were shown to be isomorphous with uranocene. The research on uranocene was carried out using depleted uranium from which the ^{235}U isotope content had been separated. The radioactivity of such depleted uranium is low, and it could be handled using normal precautions without problem in the chemistry laboratories at Berkeley. Work with the highly radioactive actinides neptunium, plutonium, and protoactinium was carried out in the special facilities for work with highly radioactive materials in the Nuclear Division of the Lawrence Berkeley Laboratory.

$$NpCl_4 + 2K_2C_8H_8 \xrightarrow{\text{THF}} (C_8H_8)_2Np + 4KCl \quad (11)$$

$$[Et_4N]_2PuCl_6 + 2K_2C_8H_8 \xrightarrow{\text{THF}} (C_8H_8)_2Pu + 2[Et_4N]Cl \quad (12)$$

$$PaCl_4 + 2K_2C_8H_8 \xrightarrow{\text{THF}} (C_8H_8)_2Pa + 2KCl \quad (13)$$

Many substituted uranocenes have been prepared, the most numerous being the 1,1′-disubstituted derivatives **2**.[68] Functional disubstituted uranocenes also could be prepared: R = $CO_2C_2H_5$,[69] OCH_3, OC_2H_5, OCH_2-$CH{=}CH_2$, $N(CH_3)_2$, $CH_2N(CH_3)_2$, $(CH_2)_3N(CH_3)_2$, $N^+(CH_3)_3I^-$, $CH_2N^+(CH_3)_3I^-$.[70] More highly substituted uranocenes have been reported: 1,1′,5,5′-tetra-*tert*-butyluranocene,[71] 1,1′,3,3′,5,5′,7,7′-octamethyluranocene,[72a] and 1,1′,3,3′,5,5′,7,7′-octaphenyluranocene.[72b] The last species is of particular interest. Its uranium atom is so hindered to attack by external reagents that its air oxidation required keeping it at 120 °C in air for 4 days (in contrast to the facile oxidation of unhindered uranocenes) and it sublimed unchanged at 400 °C.



2 R = CH_3, C_2H_5, n-C_4H_9, $CH_2{=}CH$, *cyclo*-C_3H_5, C_6H_5, t-C_4H_9, mesityl

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(59) This has been a very active area, and a complete listing and discussion of the many papers dealing with the electronic structure of the actinocenes is beyond the scope of this essay. Some of these papers are cited below, but the list is not all-inclusive. (a) Rösch, N.; Streitwieser, A., Jr. *J. Organomet. Chem.* **1978**, *145*, 195. (b) Rösch, N.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 7237. (c) Rösch, N. *Inorg. Chim. Acta* **1984**, *94*, 297. (d) Hayes, R. G.; Edelstein, N. *J. Am. Chem. Soc.* **1972**, *94*, 8688. (e) Warren, K. D. *Struct. Bonding* **1977**, *33*, 98. (f) Chang, A. H. H.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500. (g) Parry, J. A.; Cloke, F. G. N.; Coles, S. J.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 6867. (h) Kaltsoyannis, N.; Bursten, B. E. *J. Organomet. Chem.* **1997**, *528*, 19. (i) Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 11456. (j) Boerrigter, P. M.; Baerends, E. J.; Snijders, J. G. *Chem. Phys.* **1988**, *122*, 357. (k) Li, J.; Bursten, B. E. In *Computational Organometallic Chemistry*; Cundari, T. R., Ed.; Marcel Dekker: New York, 2001, Chapter 14, pp 345−379, and references therein. (l) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719 (a general review of the electronic structures of actinide-containing molecules).

(60) Starks, D. F.; Parson, T. C.; Streitwieser, A., Jr.; Edelstein, N. *Inorg. Chem.* **1974**, *13*, 1307.

(61) Starks, D. F.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 3423.

(62) Cernia, E.; Mazzei, A. *Inorg. Chim. Acta* **1974**, *10*, 239.

(63) Rieke, R. D.; Rhyne, L. D. *J. Org. Chem.* **1979**, *44*, 3445.

(64) Streitwieser, A., Jr.; Yoshida, N. *J. Am. Chem. Soc.* **1969**, *91*, 7528.

(65) Karraker, D. G.; Stone, J. A.; Jones, E. R.; Edelstein, N. *J. Am. Chem. Soc.* **1970**, *92*, 4841.

(66) (a) Goffart, J.; Fuger, J.; Brown, D.; Duyckaerts, G. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 413. (b) Starks, D. F.; Parsons, T. C.; Streitwieser, A., Jr.; Edelstein, N. *Inorg. Chem.* **1974**, *13*, 1307.

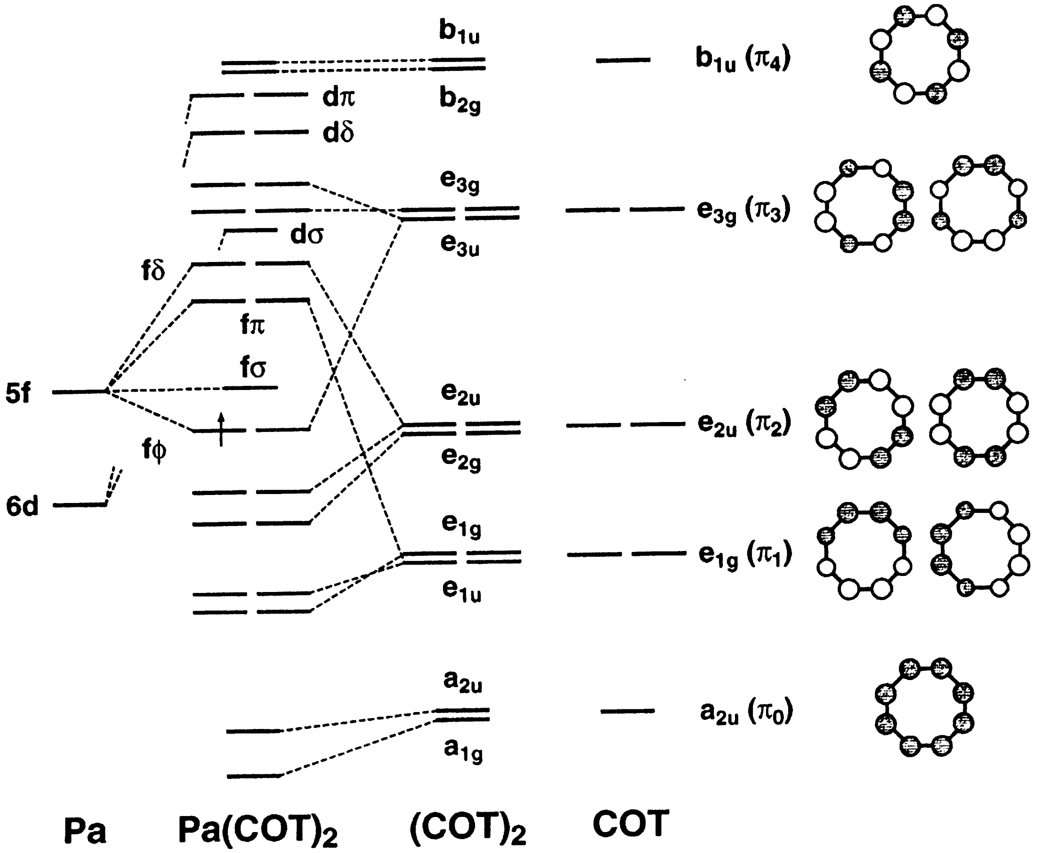
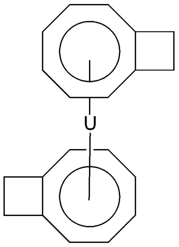


Figure 9. Qualitative molecular orbital diagram for protoactinocene, $(C_8H_8)_2Pa$, under the D_{8h} single group, showing the principal interactions of the Pa 6d and 5f orbitals with the π orbitals of the C_8H_8 rings (from Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 11456).

Also prepared were uranocenes that contain exocyclic organic substituents: bis(cyclobuteno)uranocene (**3**),[73] bis(cyclopenteno)uranocene (**4**),[74] and dibenzouranocene (**5**).[75]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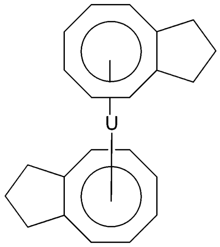
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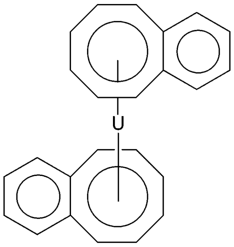
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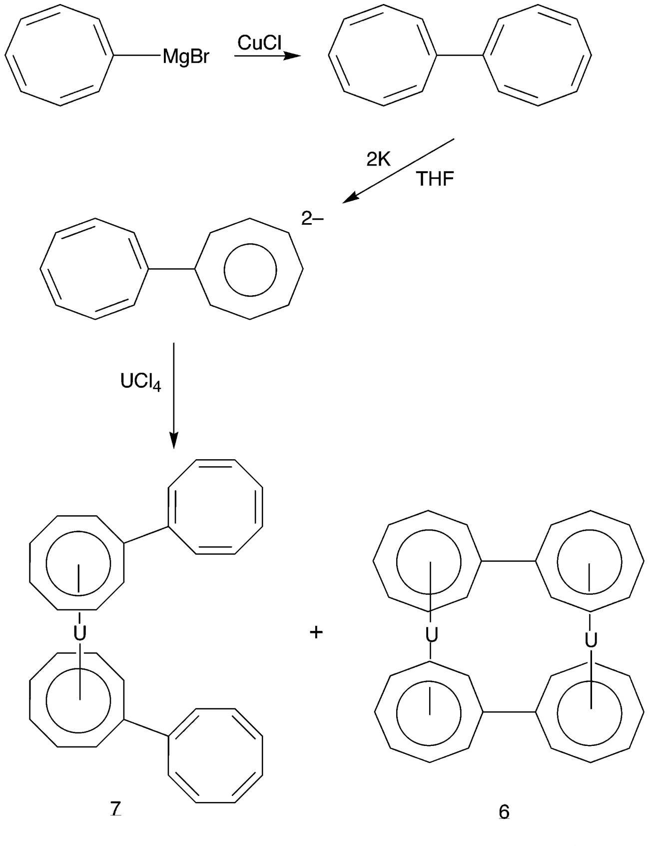
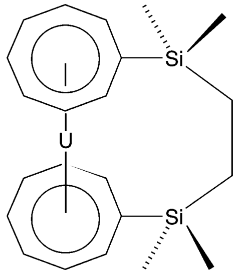
The novel biuranocene (bis(dicyclooctatetraenyl)diuranium; **6**) was obtained as a byproduct in the synthesis of 1,1′-dicyclooctatetraenyluranocene (**7**) (Scheme 3).[76] Compound **7** also was prepared by a Grignard procedure by Spiegl and Fischer.[77] Compound **7** could be converted to **6** by treatment with finely divided uranium in THF.[76]

Uranocenes containing heteroatoms other than oxygen and nitrogen include silyl and phosphino derivatives. Edelmann, Kanellakopulos, and their co-workers have prepared 1,1′,3,3′,5,5′-hexakis(trimethylsilyl)uranocene by the dianion route by starting with 1,3,5-tris(trimethylsilyl)cyclooctatetraene,[78] while Streitwieser et al. reported bis[1,2-bis(cyclooctatetraenyldimethylsilyl)ethane]uranium (**8**) as the first *ansa*-uranocene.[79] Spiegl has prepared the silyl and stannyl derivatives $(Me_3SiC_8H_7)_2U$ and $(Me_3SnC_8H_7)_2U$,[80] but no details are available.

Scheme 3



Bis(substituted cyclooctatetraene) compounds of other actinide metals have been reported: $(RC_8H_7)_2Th$ (R =



8

CH_3, C_2H_5, *n*-C_4H_9, *t*-C_4H_9, C_6H_5) and also (1,4-$(Bu^t)_2$-$C_8H_6)_2$Th and (1,3,5,7-$Me_4C_8H_4)_2$Th;[81] $(RC_8H_7)_2M$ (M = Np, Pu; R = C_2H_5, *n*-C_4H_9);[68f] (1,3,5,7-$Me_4C_8H_4)_2$M (M = Np,[73,82] Pa, Pu;[82] (1,3,5-$(Me_3Si)_3C_8H_5)_2$M (M = Th, Np).[78]

In comparison with the broad and varied reactivity of ferrocene, the reactivity of uranocene is very limited. As already noted, uranocene did not react with organolithium reagents or Friedel−Crafts acylating reagents to give any isolable products. However, Harmon and Streitwieser found that appropriately substituted uranocenes could be alkylated by organolithium reagents, apparently via a "uranocyne" mechanism.[70,83] Thus, reaction of 1,1′-dimethyoxyuranocene with *n*- and *tert*-butyllithium (in excess) in cyclohexane at room temperature gave 1,1′-di-*n*-butyluranocene and 1,1′-di-*tert*-butyluranocene, respectively, in good yield. Methyl- and phenyllithium did not react with 1,1′-dimethoxyuranocene, but uranocenes bearing alkylammonium substituents were more reactive. Phenylation and methylation of $U(C_8H_7NMe_3{}^+I^-)_2$ with the respective organolithium reagent were successful, giving 1,1′-diphenyl- and 1,1′-dimethyluranocene, respectively. A metalation chain reaction was the suggested mechanism of these reactions (Scheme 4), which seems quite reasonable in view of the known analogous reactions in benzene and ferrocene chemistry.

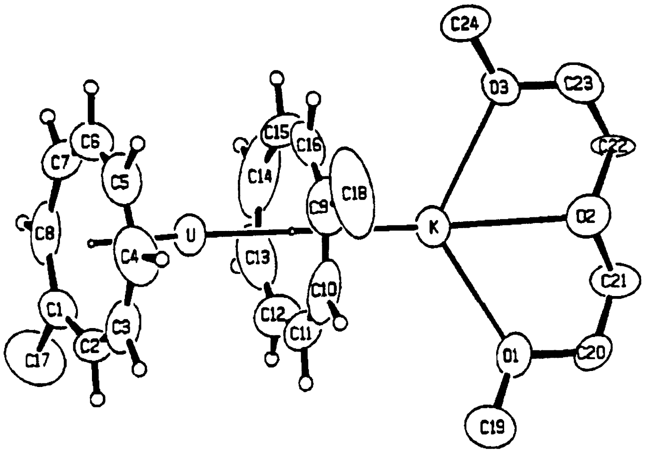
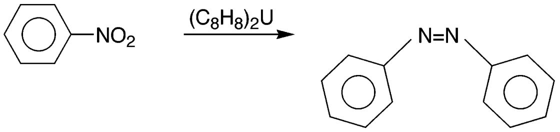


Figure 10. X-ray crystal structure of [K(diglyme)][$(C_8H_7CH_3)_2U(III)$] showing the asymmetric displacement of the uranium atom between the two C_8 rings (from Boussie, T. R.; Eisenberg, D. C.; Bigsbee, J.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1991**, *10*, 1922).

Uranocene acts as a reducing agent in its reactions with aromatic nitro compounds (eq 14).[84]



(14)

Perhaps the most interesting reaction of uranocene and of other actinocenes is their reduction from the tetravalent to the trivalent state. The reaction of uranocene with potassium in the presence of a small amount of naphthalene in THF at room temperature (color change from green to brown) gave, after appropriate workup and addition of diglyme, the U(III) salt [K(diglyme)][$(C_8H_8)_2U^{III}$] as reddish brown crystals. Such reduction of 1,1′-dimethyluranocene proceeded more readily because it is more soluble in THF.[85] 1,1′-Di-*tert*-butylneptunocene and 1,1′-di-*tert*-butylplutonocene were reduced to the Np(III) and Pu(III) bis-$C_8H_7CMe_3$ complexes as well. Mixtures of the respective actinocene(III) and -(IV) complexes showed rapid electron transfer on the NMR time scale. The crystal structure of [K(diglyme)][$(C_8H_7CH_3)_2U^{III}$] has been determined.[86] There is an asymmetrical displacement of the uranium atom between the two C_8 rings, and the ring centroid−U−ring centroid angle is nonlinear (176°) (Figure 10). Neptunocene(III) and plutonocene(III) had been prepared earlier by Karraker and Stone[87] as the bis-THF solvates by reaction of the trivalent actinide bromides or iodides with $K_2[C_8H_8]$. More recently, the thorocene(IV) $Th[C_8H_6(SiMe_2Bu^t)_2]_2$ has been reduced with potassium to $[K(DME)_2][C_8H_6(SiMe_2Bu^t)_2Th]$ (Scheme 5). The analogous uranium(III) complex also was prepared.[88] In an interesting application of this chemistry, partial reduction of biuranocenylene (**6**)[76] by potassium

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[67] Goffart, J.; Fuger, J.; Gilbert, B.; Kanellakopulos, B.; Duyckaerts, G. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 403.

[68] (a) Streitwieser, A., Jr.; Harmon, C. A. *Inorg. Chem.* **1973**, *12*, 1102. (b) Miller, J. T.; DeKock, C. W. *Inorg. Chem.* **1979**, *18*, 1979. (c) Miller, M. J.; Lyttle, M. H.; Streitwieser, A., Jr. *J. Org. Chem.* **1981**, *46*, 1977. (d) Streitwieser, A., Jr.; Lyttle, M. H.; Wang, H.-K.; Boussie, T.; Weinländer, A.; Solar, J. P. *J. Organomet. Chem.* **1995**, *501*, 245. (e) Spiegl, A.; Fischer, R. D. *Chem. Ber.* **1979**, *112*, 116. (f) Karraker, D. G. *Inorg. Chem.* **1973**, *12*, 1105.

[69] Streitwieser, A., Jr.; Burghard, H. P. G.; Morrell, D. G.; Luke, W. D. *Inorg. Chem.* **1980**, *19*, 1863.

[70] Harmon, C. A.; Bauer, D. P.; Berryhill, S. R.; Hagiwara, K.; Streitwieser, A., Jr. *Inorg. Chem.* **1977**, *16*, 2143.

[71] Lyttle, M. H.; Streitwieser, A., Jr.; Miller, M. J. *J. Org. Chem.* **1989**, *54*, 2331.

[72] (a) Streitwieser, A., Jr.; Dempf, D.; LaMar, G. N.; Karraker, D. G.; Edelstein, N. *J. Am. Chem. Soc.* **1971**, *93*, 7343. (b) Streitwieser, A., Jr.; Walker, R. *J. Organomet. Chem.* **1975**, *97*, C41.

[73] Luke, W. D.; Berryhill, S. R.; Streitwieser, A., Jr. *Inorg. Chem.* **1981**, *20*, 3086.

[74] Zalkin, A.; Templeton, D. H.; Luke, W. D.; Streitwieser, A., Jr. *Organometallics* **1982**, *1*, 618.

[75] Streitwieser, A., Jr.; Kluttz, R. O.; Smith, K. A.; Luke, W. D. *Organometallics* **1983**, *2*, 1873.

[76] Miller, M. J.; Streitwieser, A., Jr. *J. Organomet. Chem.* **1981**, *209*, C52.

[77] Spiegl, A. W.; Fischer, R. D. *Chem. Ber.* **1979**, *112*, 116.

[78] Apostolidis, C.; Edelmann, F. T.; Kanellakopulos, B.; Reissmann, U. *Z. Naturforsch.* **1999**, *54b*, 960.

[79] Streitwieser, A., Jr.; Barros, M. T.; Wang, H.-K.; Boussie, T. R. *Organometallics* **1993**, *12*, 5023.

[80] Spiegl, A. W. Dissertation, Universität Erlangen, 1978; mentioned in ref 77.

[81] LeVanda, C.; Streitwieser, A., Jr. *Inorg. Chem.* **1981**, *20*, 656.

[82] Solar, J. P.; Burghard, H. P. G.; Banks, R. H.; Streitwieser, A., Jr.; Brown, D. *Inorg. Chem.* **1980**, *19*, 2186.

[83] Harmon, C. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 8926.

[84] Grant, C. B.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 2433.

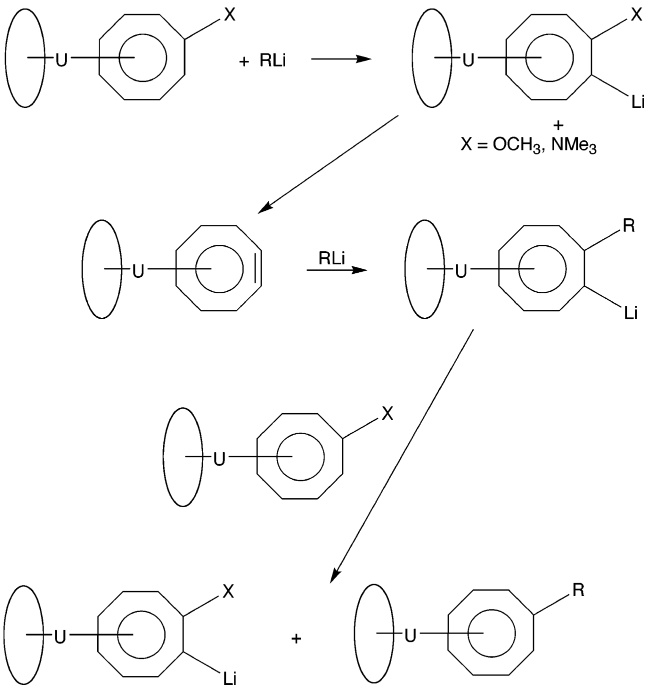
[85] Eisenberg, D. C.; Streitwieser, A., Jr.; Kot, W. K. *Inorg. Chem.* **1990**, *29*, 10.

[86] Boussie, T. R.; Eisenberg, D. C.; Bigsbee, J.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1991**, *10*, 1922.

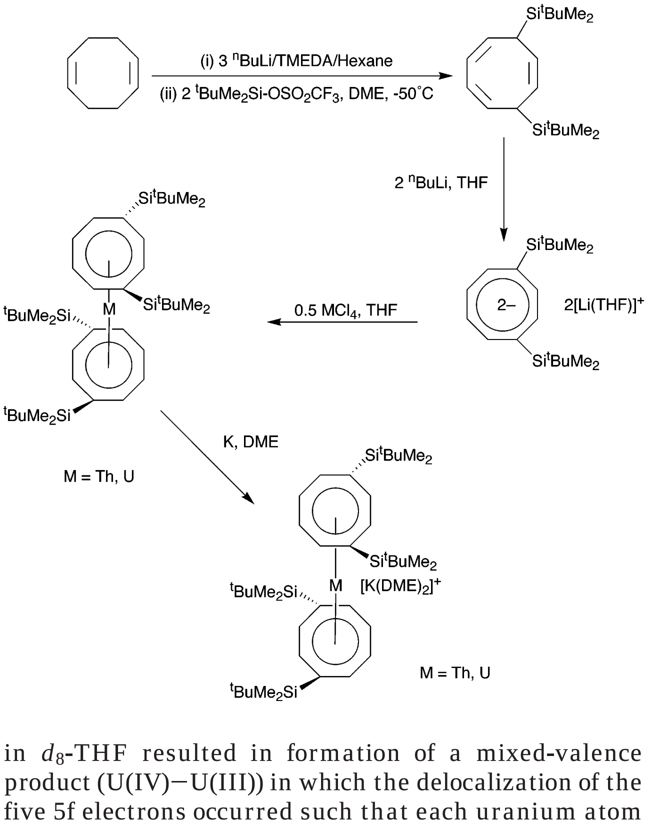
[87] Karraker, D. G.; Stone, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 6885.

[88] Parry, J. A.; Cloke, F. G. N.; Coles, S. J.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 6867.

Scheme 4



Scheme 5



in d_8-THF resulted in formation of a mixed-valence product (U(IV)−U(III)) in which the delocalization of the five 5f electrons occurred such that each uranium atom has an intermediate oxidation state of 3.5.[89]

The rather limited chemistry of uranocene and substituted uranocenes was disappointing and it was the mono-C_8H_8 uranium(IV) compounds, half-sandwich complexes of type η^8-$C_8H_8UX_2$, that opened new vistas for cyclooctatetraene−uranium chemistry.

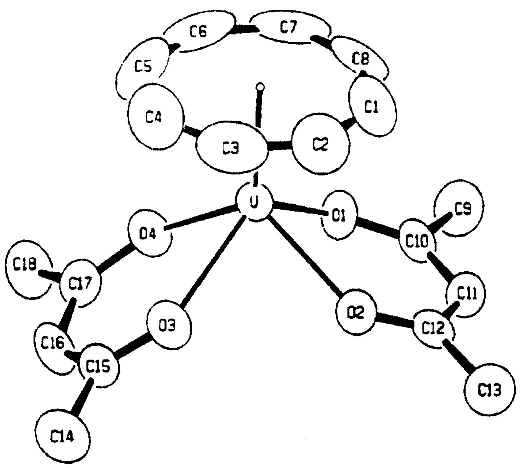


Figure 11. X-ray crystal structure of C_8H_8U bis(acetylacetonate) (from Boussie, T. R.; Moore, R. M., Jr.; Streitwieser, A., Jr.; Zalkin, A.; Brennan, J.; Smith, K. A. *Organometallics* **1990**, *9*, 2010).

IV. Mono-C_8H_8 Half-Sandwich Complexes. First Preparation by Streitwieser and Further Development by Ephritikhine and Their Respective Co-Workers

Initially, the mono-C_8H_8 half-sandwich complexes of uranium(IV) of the type η^8-$C_8H_8UX_2$ did not seem to be all that promising in terms of the reactivity of the inorganic functionality bonded to uranium. A few such compounds of uranium and thorium were prepared by Streitwieser and co-workers. Both $C_8H_8UCl_2$ and $C_8H_8ThCl_2$ could be prepared as 2:1 THF solvates by a redistribution reaction between the respective $(C_8H_8)_2M$ compound and MCl_4 (eq 15).[90] The thorium compound

$$(C_8H_8)_2M + MCl_4 \xrightarrow{\text{THF}} 2C_8H_8MCl_2{\cdot}2THF \quad (15)$$

also was prepared by a 1:1 $K_2[C_8H_8]$ + $ThCl_4$ reaction, but in the case of UCl_4 the product was uranocene. The THF molecules of $C_8H_8UCl_2{\cdot}2THF$ are loosely coordinated and easily displaced by pyridine to give $C_8H_8UCl_2{\cdot}2py$. Attempted alkylation or arylation of $C_8H_8UCl_2{\cdot}2THF$ with a variety of organolithium and Grignard reagents was unsuccessful; no products could be isolated. This also was the case with alkali metal alkoxides. However, $C_8H_8UCl_2{\cdot}2THF$ did react with sodium acetylacetonate to give a stable product (eq 16)[90]

$$\begin{aligned} &C_8H_8UCl_2{\cdot}2THF +\\ &\qquad 2Na[CH_3C(O)CHC(O)CH_3] \xrightarrow[-20\ ^\circ C]{\text{THF}}\\ &\qquad C_8H_8U[CH_3C(O)CHC(O)CH_3]_2 + 2NaCl \quad (16)\end{aligned}$$

and with $NaN(SiMe_3)_2$ to give $C_8H_8U[N(SiMe_3)_2]_2$.[91]The structures of the bis(pyridine) adduct and the acetylacetonate were determined by X-ray diffraction. The structure of the former is shown in the ORTEP plot in Figure 11. Other thorium half-sandwich complexes were prepared by the redistribution procedure—(n-C_4H_9-

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[89] Streitwieser, A., Jr.; Eisenberg, D. C. *Inorg. Chim. Acta* **1987**, *139*, 193.

[90] Boussie, T. R.; Moore, R. M., Jr.; Streitwieser, A., Jr.; Zalkin, A.; Brennan, J.; Smith, K. A. *Organometallics* **1990**, *9*, 2010.

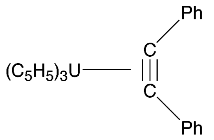
[91] Gilbert, T. M.; Ryan, R. R.; Sattelberger, A. P. *Organometallics* **1988**, *7*, 2514.

Figure 12. Michel Ephritikhine (unknown photographer; reproduced by permission of Michel Ephritikhine).

$C_8H_7)ThCl_2{\cdot}2THF$ and $(1,3,5,7\text{-}Me_4C_8H_4)ThCl_2{\cdot}2THF$—and it was found that $C_8H_8ThCl_2$ also can be prepared by reaction of thorocene with dry HCl.[92] The structure of $C_8H_8ThCl_2{\cdot}2THF$ is essentially the same, in terms of the coordination about Th, as that of $C_8H_8UCl_2{\cdot}2py$.[93]

In 1984 Michel Ephritikhine (Figure 12) joined the research program of molecular chemistry of the Commissariat à l'Energie Atomique (CEA) in Saclay near Paris. Not surprisingly, his research became focused on uranium chemistry with major attention to the development of organouranium chemistry. Ephritikhine was born in 1947 in Algiers. He studied chemistry at the University of Nancy in France and carried out his graduate work at the University of Paris 6, obtaining his initial doctor's degree in 1971 and his Doctorat d'État in 1974. His doctoral research, carried out under the guidance of Professor J. Levisalles, was concerned with the synthesis and properties of A-homocholestanones and with the fluorination of alkenes using PbF_4 as fluorinating agent. His introduction to organometallic chemistry came in 1975–1976 during a postdoctoral stay at Oxford in the laboratories of Malcolm Green, where he carried out research on the metallacyclobutane complexes of molybdenum and tungsten. The next 8 years were spent with Hugh Felkin at the Institute of Chemistry of Natural Products of the CNRS at Gif-sur-Yvette, France, where he continued research in the organometallic chemistry area—studies of organorhenium hydrides and on C−H bond activation. 1984 brought the abrupt change to organouranium chemistry. Since 1992 he has been Directeur de Recherche (first class) at the CNRS, the French government research organization. He lists his current interest and activites as coordination and organometallic chemistry of uranium and lanthanide elements, applications of uranium complexes in organic synthesis and catalysis, magnetic properties of heterobimetallic complexes of uranium, and differentiation of trivalent lanthanides and actinides.

During the 19 years since he began research in organouranium chemistry, Ephritikhine and co-workers in the Laboratoire de Chimie de l'Uranium have been very productive in the further development of uranium chemistry and have made some outstanding contributions to the field. Their first publication on organouranium chemistry in 1985, on the synthesis and crystal structure of the volatile $C_5H_5U(BH_4)_3$,[94] reported a uranium borohydride, a compound type which was to be crucial in their subsequent successful development of mono-C_8H_8−uranium chemistry. Further studies on cyclopentadienyl and substituted-cyclopentadienyl uranium compounds followed. Of special interest was the synthesis of the first stable organouranium hydride, $(Me_3SiC_5H_4)_3UH$, by reaction of the chloride with $KBEt_3H$. Reaction of the hydride with $[Et_3NH]BPh_4$ gave the cationic complex $[(Me_3SiC_5H_4)_3U]BPh_4$.[95] Also prepared was $(Me_3CC_5H_4)_3UH$, whose structure was determined by X-ray diffraction.[96] Reduction of $(C_5H_5)_3UCl$ with NaH in THF produced the novel hydrogen-bridged anion $[(C_5H_5)_3U{-}H{-}U(C_5H_5)_3]^-$ (isolated as the $[Na{\cdot}2THF]^+$ salt).[97] Ephritikhine's prior interest in rhenium hydride chemistry led to the preparation of the bright red, crystalline $(C_5H_5)_3UH_6Re[P(C_6H_4F\text{-}p)_3]_2$ by reaction of $[(p\text{-}FC_6H_4)_3P]_2ReH_6K$ with $(C_5H_5)_3UCl$.[98] The first U(III) cationic complex, $[(Me_5C_5)_2U(THF)_2]BPh_4$, was isolated and structurally characterized. The action of $[NH_4]BPh_4$ on $[(Me_5C_5)_2UN(SiMe_3)_2]$ served in its preparation.[99] An alkyne complex, **9**, also was prepared, by reaction of $(C_5H_5)_3U{\cdot}THF$ with diphenylacetylene.[100] Its reactions with the organolithium reagents CH_3Li and *n*-BuLi gave the alkyl complexes $(C_5H_5)_3URLi$. Of interest also are the (tetramethylphospholyl)uranium complexes, the tet-



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(95) (a) Berthet, J.-C.; Le Maréchal, J.-F.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1991**, 360. (b) Berthet, J.-C.; Ephritikhine, M. *New J. Chem.* **1992**, *16*, 767 (reaction of the hydride).

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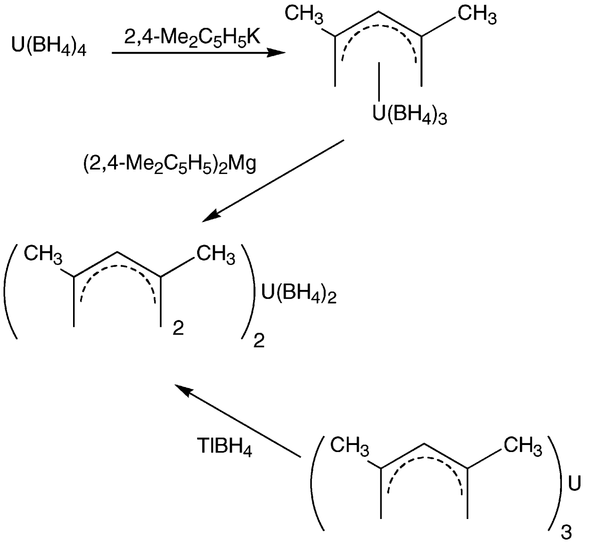
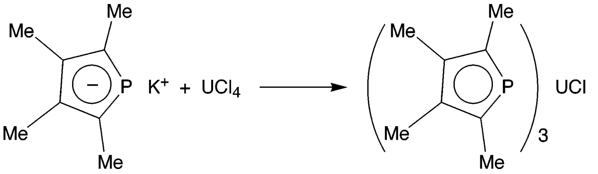
Scheme 6



ramethylphospholyl ligand being a steric mimic of the Me_5C_5 ligand. Their preparation was accomplished as shown in eq 17.[101] The structure of the chloride,



(17)

determined by X-ray diffraction, showed the planar phospholyl ligands to be η^5-bonded to uranium. Reactions of the chloride with the appropriate reagents gave the respective tris(tetramethylphospholyl)uranium hydride, methyl, and isopropoxide. Mono- and bis(tetramethylphospholyl) complexes of uranium also were prepared.[102]

In addition to studies of the chemistry of cyclopentadienyluranium complexes, Ephritikhine and co-workers have reported interesting new types of organouranium compounds.

(1) Weakly coordinated η^6-mesitylene– and hexamethylbenzene–$U(BH_4)_3$ complexes[103] (see also the earlier work of others on π-arene–uranium complexes[104]).

(2) The urana[1]ferrocenophane $Li_2[(py)U(fc)_3]$ (fc = 1,1′-ferrocenylene), in which the average U–Fe distance of 3.14(2) Å suggested the presence of a U–Fe bond.[105]

(3) (η^5-2,4-Dimethylpentadienyl)uranium borohydride complexes, prepared as shown in Scheme 6.[106] ($U(2,4\text{-}Me_2C_5H_5)_3$ had been prepared earlier by Ernst and co-workers.[107])

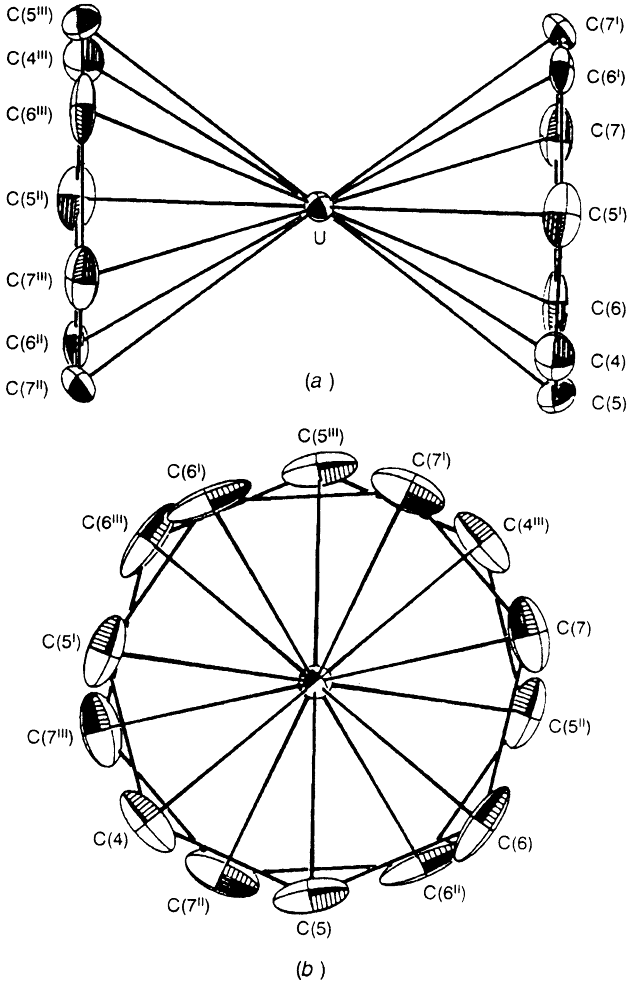
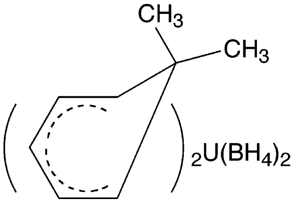


Figure 13. X-ray crystal structure of the anion in $[K(18\text{-crown-}6)][(\eta^7\text{-}C_7H_7)_2U]$: (a) view showing the planarity of the C_7H_7 rings; (b) view along the ring centroid–U–ring centroid axis (from Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1995**, 183; reproduced by permission of the Royal Society of Chemistry).

(4) (η^5-6,6-Dimethylcyclohexadienyl)uranium complexes,[106a,b,108] e.g., **10** and **11**, prepared in much the same manner.



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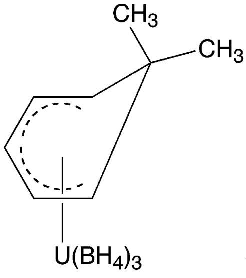

11

(5) (η^7-Cycloheptatrienyl)uranium compounds: $[K(18\text{-crown-}6)][(\eta^7\text{-}C_7H_7)_2U]$ (Figure 13)[109] and the novel inverted cycloheptatrienyluranium sandwich complexes $[X_3U(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)UX_3]^-$ (X = NEt_2, BH_4) (Figure 14).[110] These anions were prepared by reaction of $K[C_7H_9]$ with the respective UX_4. The cation in $[U(BH_4)_2{\cdot}5THF][(BH_4)_3U(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)U(BH_4)_3]$ was obtained by reaction of $U(BH_4)_3(THF)_3$ with $[Et_3NH]BPh_4$ in THF.

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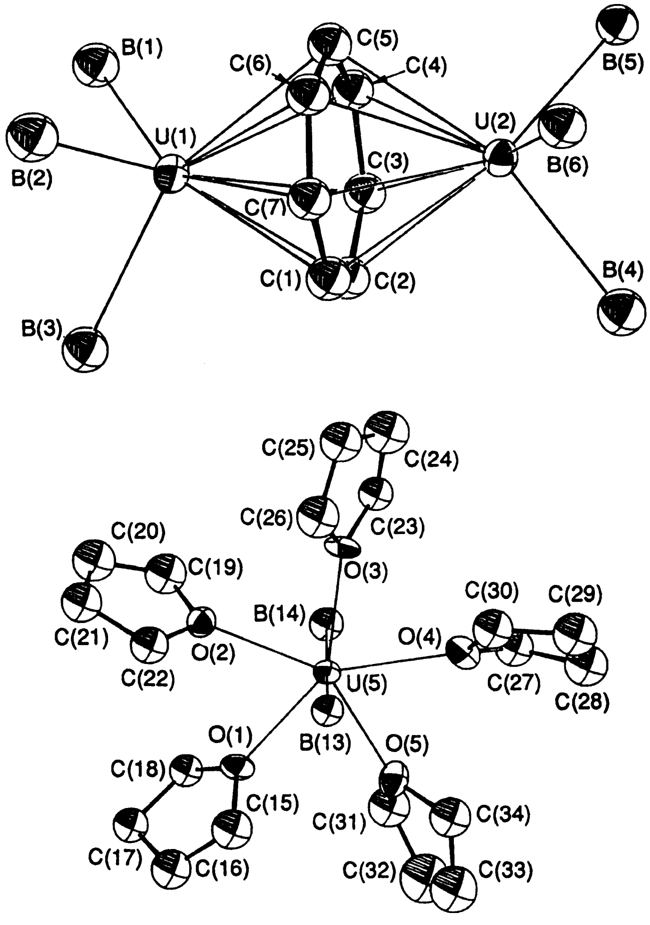

Figure 14. X-ray crystal structure of the anion in the inverse cyclohetatrienyl uranium sandwich complex $[U(BH_4)_2(THF)_5][(H_4B)_3U(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)U(BH_4)_3]$ (from Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1994**, 847; reproduced by permission of the Royal Society of Chemistry).

Some of Ephritikhine's major efforts in organouranium chemistry have been devoted to the synthesis and study of $C_8H_8UX_2$ and derived complexes. As noted earlier, $C_8H_8UCl_2{\cdot}2THF$ seemed not to be very promising, as far as its use in the further development of mono-C_8H_8 uranium chemistry was concerned. It was the preparation of $C_8H_8U(BH_4)_2$[111] and $C_8H_8UI_2{\cdot}2THF$[112] (eqs 18 and 19) by Ephritikhine and co-workers that

$$(C_8H_8)_2U + U(BH_4)_4 \rightarrow 2C_8H_8U(BH_4)_2 \qquad (18)$$

$$(C_8H_8)_2U + I_2 \xrightarrow{THF} C_8H_8UI_2{\cdot}2THF \qquad (19)$$

provided the reactive starting materials needed for an extensive development of mono-C_8H_8 uranium chemistry. As discovered by Cloke and co-workers at the University of Sussex, $C_8H_8U(BH_4)_2$ also may be prepared by the photolysis or thermolysis of $U(BH_4)_4$ in toluene or mesitylene in the presence of a slight excess of cyclooctatetraene. The reaction of $K_2[1,4\text{-}(Me_3Si)_2C_8H_6]$ with a mixture of UCl_4 and 2 $LiBH_4$ gave $1,4\text{-}(Me_3Si)_2C_8H_6U(BH_4)_2$.[113]

Both the Streitwieser and Los Alamos groups had been unsuccessful in their attempts to prepare alkyl derivatives, $C_8H_8UR_2$. The French workers also failed to isolate stable uranium alkyls of this type from reaction mixtures in which $C_8H_8UI_2{\cdot}2THF$ or $C_8H_8U(BH_4)_2$ had been treated with alkyllithium and alkyl Grignard reagents (R = $PhCH_2$, Me_3SiCH_2). However, when $C_8H_8UI_2{\cdot}2HMPA$ (HMPA = $(Me_2N)_3PO$) was used as the starting material, a reaction with Me_3SiCH_2Li in toluene at 20 °C gave $C_8H_8U(CH_2SiMe_3)_2{\cdot}HMPA$ as stable orange microcrystals in 45% yield.[112,114] Other alkyl derivatives were not as stable. When 3 equiv of Me_3SiCH_2Li was used in THF, an "ate" complex, $[Li(THF)_3][C_8H_8(CH_2SiMe_3)_3]$, was obtained. Reactions of $C_8H_8UI_2{\cdot}2THF$ with 1 equiv of C_5H_5Tl and Me_5C_5K in THF resulted in the mixed-ring complexes $C_8H_8(C_5H_5)UI$ and $C_8H_8(Me_5C_5)UI$, respectively.[112] Reaction of the latter with Me_3SiCH_2Li gave $C_8H_8(Me_5C_5)UCH_2SiMe_3$. Similar reactions of $C_8H_8UI_2{\cdot}2THF$ were used to prepare the complexes $C_8H_8(C_5H_3(SiMe_3)_2)UI{\cdot}HMPA$ and $C_8H_8(C_5H_5)UN(SiMe_3)_2$. The Los Alamos group prepared the trivalent complex $C_8H_8(Me_5C_5)U{\cdot}THF$ by the route shown in eq 20.[115] A mixed-ligand, Cl-bridged complex of thorium,

$$Me_5C_5UI_2{\cdot}3THF + K_2C_8H_8 \xrightarrow{THF} C_8H_8(Me_5C_5)U{\cdot}THF + 2KI \qquad (20)$$

$[C_8H_8(Me_5C_5)ThCl]_2$, had been prepared by Gilbert, Ryan, and Sattelberger in 1989 by the action of $Me_5C_5MgCl{\cdot}THF$ on $C_8H_8ThCl_2{\cdot}2THF$. Reaction of the chloride with $(Me_3Si)_2CHLi$ gave the alkyl derivative, whose structure was determined. The C_8 and C_5 rings are not coplanar.[116]

Ephritikhine and co-workers extended the class of uranium-functional half-sandwich C_8H_8U compounds to alkoxides, $C_8H_8U(BH_4)(OR)$ (OR = OC_2H_5, $OCH(CH_3)_2$) and $C_8H_8U(OR)_2$ (OR = OC_2H_5, $OCH(CH_3)_2$, $OC(CH_3)_3$), by the action of ROH on $C_8H_8U(BH_4)_2$, using the appropriate stoichiometry.[112,117] The alkoxy derivatives are alkoxy-bridged dimers in the solid state but are monomeric in donor solvents such as THF and pyridine. A similar route gave thiolate derivatives, $C_8H_8U(SPr^i{}_2)_2$ (a SPr^i-bridged dimer in the solid and in solution) and $[C_8H_8U(SPr^i)_3]^-$ (as the [Na(THF)] salt).[118] Also prepared by the French workers was the first uranium

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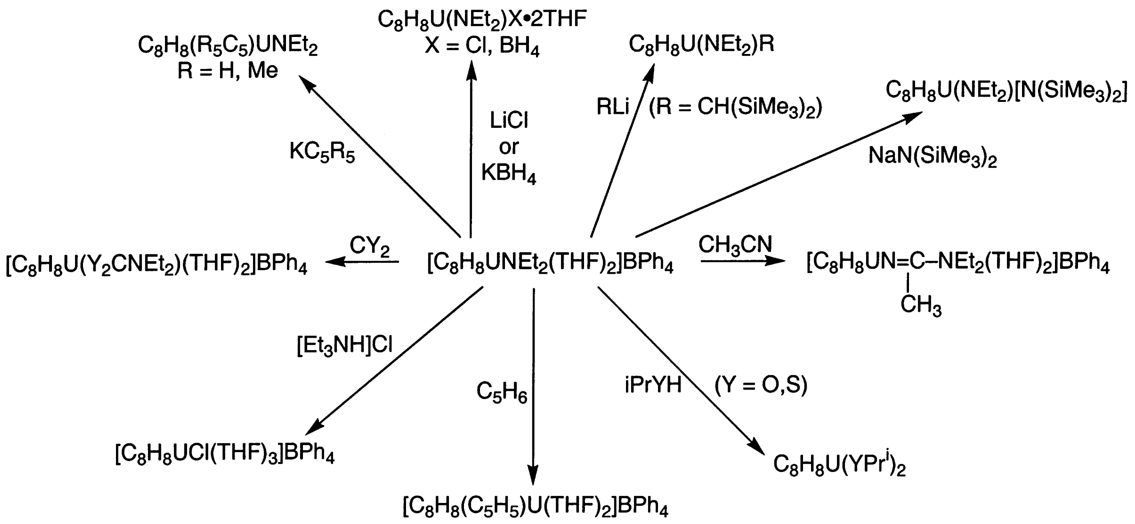
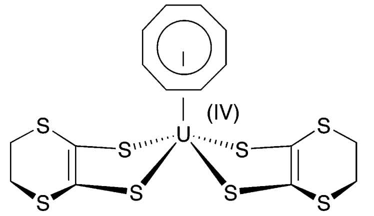
(117) Arliguie, T.; Baudry, D.; Ephritikhine, M.; Nierlich, M.; Lance, M.; Vigner, J. *J. Chem. Soc., Dalton Trans.* **1992**, 1019.

Scheme 7





[Na(18-crown-6)]$_2$

12

dithiolene complex, **12**, which could be oxidized with Ag(I) compounds to the corresponding U(V) compound.[119] As Ephritikhine and co-workers reported,[120,121] C_8H_8U diethylamino derivatives can be prepared by different routes (eqs 21 and 22). Reaction of

$$\left.\begin{array}{l}[U(NEt_2)_3]BPh_4 + K_2C_8H_8 \rightarrow \\ [U(NEt_2)_4] + K_2C_8H_8 \rightarrow \\ UCl_4 + 4Et_2NLi + K_2C_8H_8 \rightarrow \\ U(NEt_2)_2Cl_2 + Et_2NLi + K_2C_8H_8 \rightarrow \end{array}\right\} K[C_8H_8U(NEt_2)_3] \quad (21)$$

$$K[C_8H_8U(NEt_2)_3] + [Et_3NH]BPh_4 \xrightarrow{THF} C_8H_8U(NEt_2)_2{\cdot}THF \quad (22)$$

$C_8H_8U(NEt_2)_2{\cdot}THF$ with thallium cyclopentadienide resulted in oxidation to the U(V) complex $C_8H_8(C_5H_5)U(NEt_2)_2$.

Tl(I) also oxidized $K[C_8H_8U(NEt_2)_3]$ to a U(V) compound (eq 23).

$$K[C_8H_8U(NEt_2)_3] + TlBPh_4 \xrightarrow{THF} C_8H_8U(NEt_2)_3 + Tl + KBPh_4 \quad (23)$$

Protonolysis of $C_8H_8U(NEt_2)_2$ with $[Et_3NH]BPh_4$ in THF formed the cation $[C_8H_8UNEt_2(THF)]BPh_4$,[121,122] whose high reactivity toward nucleophiles gave a variety of addition, substitution, and insertion products (Scheme 7).

Another type of cationic C_8H_8 uranium complex was prepared by the action of $[Et_3NH]BPh_4$ on $C_8H_8U(BH_4)_2{\cdot}THF$ (eq 24).[123] The monocation could be

$$C_8H_8U(BH_4)_2{\cdot}THF + [Et_3NH]BPh_4 \xrightarrow{THF} [C_8H_8UBH_4{\cdot}(THF)_2]BPh_4 + H_3B{\cdot}NEt_3 + 0.5H_2 \quad (24)$$

converted to the novel dication $[C_8H_8U(HMPA)_3]^{2+}$ by reaction with $[Et_3NH]BPh_4$ in the presence of HMPA in refluxing THF solution.[124]

V. C_8H_8 as an η^8:η^8 Bridging Ligand in Dinuclear Uranium Complexes: Ephritikhine, Cummins, and Evans

The C_8H_8 ligand also can bridge two uranium atoms in an η^8:η^8 manner to give an "inverted" uranocene. The first evidence for this novel bonding mode was reported by Baudry et al. in 1990.[111] Proton NMR evidence for the molecule $(H_4B)_3U(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)U(BH_4)_3$ (**13**) was provided (δ 80.57 (q, 80, 24 H); 24.98 (s, 8 H)), but pure samples could not be obtained from the stable, red THF solutions that contained it. Compound **13** was formed by treating $(C_8H_8)_2U$ with an excess of $U(BH_4)_4$, by preparing an equilibrium mixture of $U(BH_4)_4$ and $C_8H_8U(BH_4)$, and by treating $U(BH_4)_4{\cdot}$(mesitylene) with cyclooctatetraene. An apparently mobile equilibrium (Scheme 8) made isolation of pure **13** impossible. The singlet resonance of the C_8H_8 protons of **13** suggests the presence of a planar η^8:η^8 bridging C_8 ring.

A complex of this type, **14**, was prepared, isolated, and structurally characterized by Diaconescu and Cummins at MIT,[125] as shown in Scheme 9. Reaction of KN=C(Bu^t)(Mes) (Mes = mesityl, 2,4,6-trimethylphenyl) with $UI_3{\cdot}DME$ gave the tris(ketimido)uranium

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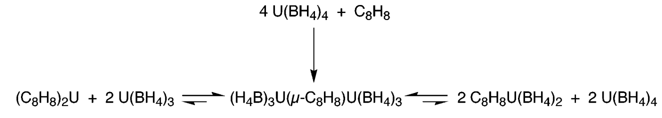
Figure 15. Christopher C. Cummins (photo by Atlantic Photo Service, Inc.; reproduced by permission of Atlantic Photo Service, Inc., and Christopher C. Cummins).

Scheme 8



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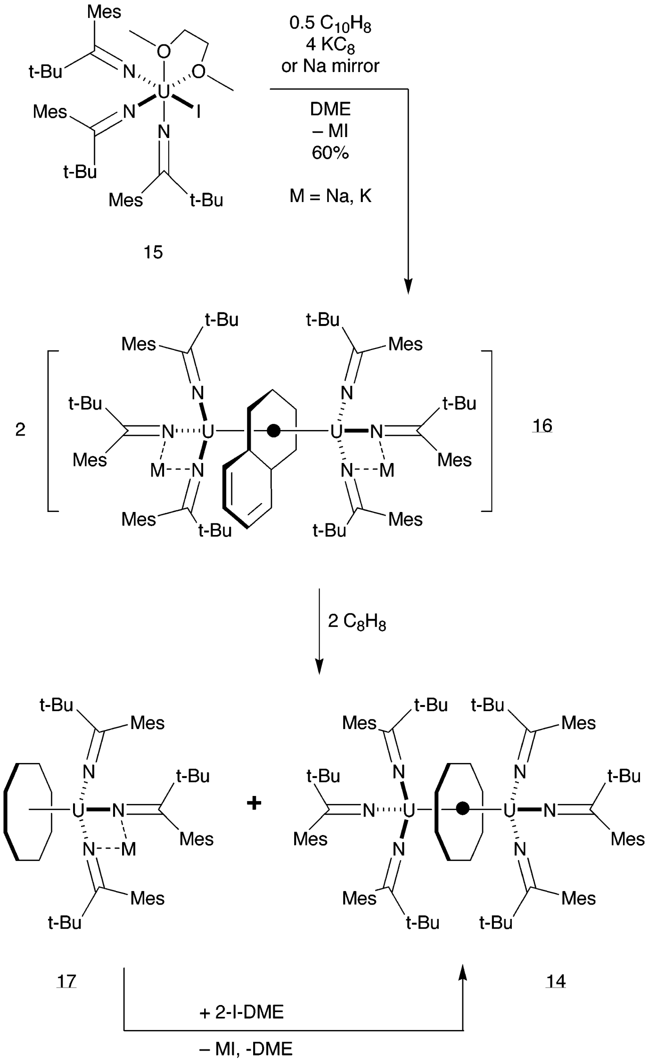
Scheme 9



iodide **15**. Reduction of the latter with a sodium mirror in DME in the presence of ca. 0.5 molar equiv of naphthalene resulted in formation of the bridging naphthalene complex $M_2[(Mes(Bu^t)C{=}N)_3U(\mu\text{-}\eta^6{:}\eta^6\text{-}C_{10}H_8)U(N{=}C(Bu^t)Mes)_3]$ (**16**; M = Na). Similar reduction with KC_8 gave the potassium salt of **16** (M = K). Reaction of the sodium salt **16** with cyclooctatetraene in diethyl ether provided an ∼1:1 mixture of the bridging C_8H_8 complex **14** and $[Na(Et_2O)][C_8H_8U(N{=}C(Bu^t)Mes)_3]$ (**17**). When the potassium salt **16** was used, **17** was the main product and the yield of **14** was negligible. However, the reaction of **17** (either the K or Na salt) with the iodide **15** was found to provide a high-yield synthesis of **14**. Alternatively, **14** was the only product formed when cyclooctatetraene reacted with $Na_2[(Mes(Bu^t)C{=}N)_3U(\mu\text{-}\eta^6{:}\eta^6\text{-biphenyl})U(N{=}C(Bu^t)Mes)_3]$, although a longer reaction time was required. The structures of **14** and **17** were determined by X-ray diffraction; that of **14** is shown in Figure 16. The average $U{-}C_{COT}$ distance in **14**, 2.822 Å, is longer than that in $C_8H_8U(NEt_2)_2{\cdot}THF$[121b] and in other $C_8H_8U^{IV}$ complexes, ∼2.68 Å, indicating a poorer covalent overlap in **14**. DFT calculations carried out on the model compound $(H_2C{=}N)_3(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)(N{=}CH_2)_3$ indicated that there were δ bonds involving U f orbitals and the C_8H_8 HOMO.[125b] Oxidation of the alkali-metal salts **17** with $TiCl_4{\cdot}2THF$ in THF gave the neutral U(V) ketimide $C_8H_8U(N{=}C(Bu^t)Mes)_3$.[125b]

Christopher (Kit) Cummins[126] is a relative newcomer to organouranium chemistry but has already made significant contributions to this field, in addition to the discovery of the bridging C_8H_8 complex **14**. Notable also have been the syntheses of a number of $\mu\text{-}\eta^6{:}\eta^6$-arene-bridged diuranium complexes, $X_3U(\mu\text{-}\eta^6{:}\eta^6\text{-arene})UX_3$ (X = a sterically encumbered group such as $-N(Bu^t)(3,5\text{-}Me_2C_6H_3)$ or $-N(adamantyl)(3,5\text{-}Me_2C_6H_3)$) by action of KC_8 on the respective iodides, IUX_3.[127] Also prepared were $\mu\text{-}\eta^6{:}\eta^6$-arenediuranium hexakisketimide com-

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(126) Christopher C. Cummins, b. 1966; undergraduate studies and research (with Peter Wolczanski) at Cornell, B.S., 1989; graduate studies and research (with Richard R. Schrock) at MIT, Ph.D., 1993. Appointment at MIT as assistant professor in 1993; full professor, 1996. Major research efforts on the use of bulky anilide substituents to stabilize low-coordinate transition-metal complexes, which because of “site isolation” can show unusual reactivity, e.g., activation of N_2, N_2O, NO. Outstanding new chemistry including the cleavage of N_2 by a molybdenum tris(anilide) in 1995.

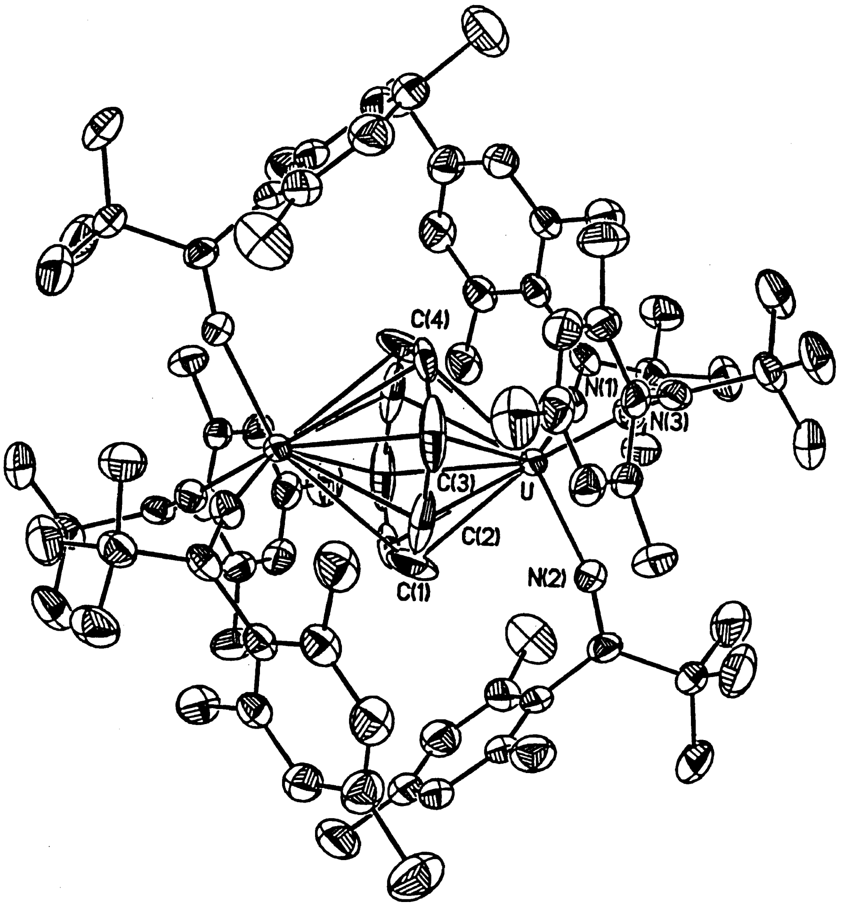
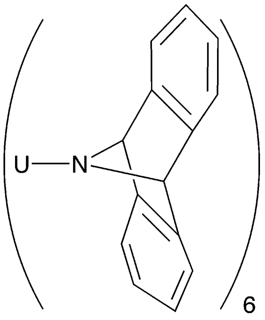


Figure 16. X-ray crystal structure of the anion on $K_2[(Mes(Bu^t)C{=}N)_3U(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)U(N{=}C(Bu^t)Mes)_3]$ (Diaconescu, Paula L. Ph.D. Thesis, p 111, Figure 21; Massachusetts Institute of Technology Department of Chemistry, 2003; reproduced by permission of Massachusetts Institute of Technology and Paula L. Diaconescu).

plexes of the type $M_2[(Mes(Bu^t)C{=}N)_3U(\mu\text{-}\eta^6{:}\eta^6\text{-arene})\text{-}U(N{=}C(Bu^t)Mes)_3]$ (M = K, Na; arene = naphthalene (i.e., **16**), biphenyl, *trans*-stilbene, *p*-terphenyl) and $K[(Mes(Bu^t)C{=}N)_3U(\mu\text{-}\eta^6{:}\eta^6\text{-arene})U(N{=}C(Bu^t)Mes)_3]$.[128] Cummins' research in organouranium chemistry started with the preparation of a U(III) anilide, $U[N(Bu^t)(3,5\text{-}Me_2C_6H_3)]_3{\cdot}THF$, by reduction of the U(IV) tris(anilide) iodide. When the tris(anilide) was stirred in toluene with an equimolar quantity of $Mo[N(Bu^t)(C_6H_5)]_3$ under 1 atm of N_2, the remarkable heterodinuclear dinitrogen complex **18**, whose structure was confirmed by an X-ray diffraction study, was formed. Also notable were the hexamidouranium(VI) compound **19**, which was obtained by oxidation of the hexamidouranium anion with silver triflate in air,[130] and the uranium silyl complex $[(3,5\text{-}Me_2C_6H_3)(Bu^t)N]_3USi(SiMe_3)_3$.[131]

$$[(3,5\text{-}Me_2C_6H_3)(Bu^t)N]_3U{-}N{=}N^+{=}Mo^-[(Bu^t)(C_6H_5)]_3$$

18



19

As William J. Evans and co-workers at the University of California at Irvine have reported,[132] the C_8H_8 ligand also can bridge two uranium atoms in a different manner. Reaction of the sterically crowded $(Me_5C_5)_3U$ with C_8H_8 in a 2:3 molar stoichiometry (eq 25) or of $(Me_5C_5)_2UH(Me_2PCH_2CH_2PMe_2)$ with C_8H_8 in benzene[133] resulted in formation of the diuranium complex **20**, which contains a C_8H_8 bridging ligand that is not planar and is bonded to the uranium atoms in an unprecedented $\mu\text{-}\eta^3{:}\eta^3$ manner such that one carbon

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(127) Diaconescu, P. L.; Arnold. P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2000**, *122*, 6108.

(128) Diaconescu, P. L.; Figueroa, J. S.; Cummins, C. C. *Organometallics*, in press.

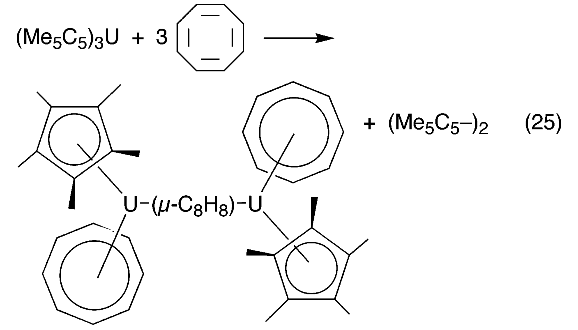
(129) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836.

(130) Meyer, K.; Mindiola, D. J.; Baker, T. A.; Davis, W. M.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2000**, *39*, 3063.

(131) Diaconescu, P. L.; Odom, A. L.; Agapie, T.; Cummins, C. C. *Organometallics* **2001**, *20* 4993.

(132) Evans, W. J.; Nyce, G. W.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 240. Evans has been very active in research on the organometallic chemistry of the f elements, mostly of the lanthanides but also of the actinides, since 1978 and has made important contributions to this area.

(133) Evans, W. J.; Nyce, G. W.; Forrestal, K. J.; Ziller, J. W. *Organometallics* **2002**, *21*, 1050.

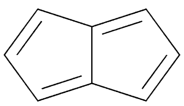


20

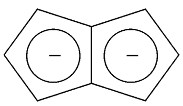
atom of the bridging ligand is common to both of the pseudo-allyl bonding segments (Figure 17). The reaction in eq 25 involves a three-electron reduction: one U(IV)/U(III) couple and two $Me_2C_5/Me_5C_5^-$ couples.

VI. The Pentalene Dianion as Another 8-Carbon Cyclic π Ligand in Uranium Chemistry. Geoffrey Cloke at the University of Sussex

The cyclooctatetraene dianion is not the only C_8 cyclic dianion. Pentalene (**21**), the transannularly bridged-



21



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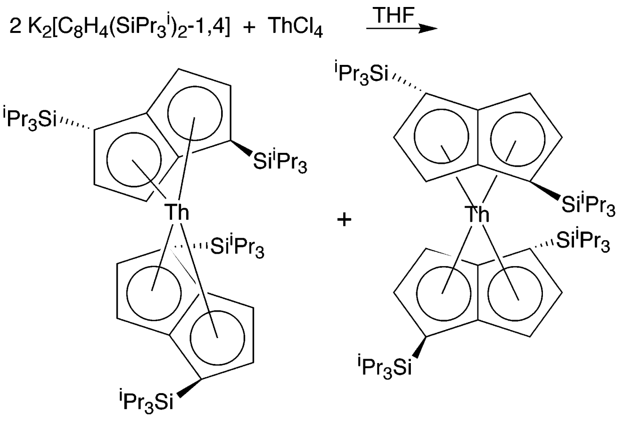
bicyclic analogue of cyclooctatetraene, also can form a 10-π-electron cyclic dianion, $C_8H_6^{2-}$ (**22**). The pentalene dianion was first prepared by Katz and Rosenberger in 1962.[134] The preparation started with the flash pyrolysis of isodicyclopentadiene, which gave dihydropentalene. The latter, on treatment with *n*-butyllithium in THF/heptane, resulted in formation of dilithium pentalenide (**23**), which crystallized on cooling (Scheme 10). The structure of **23** in solution was confirmed by its ^{1}H NMR spectrum. (Katz, as noted earlier, was the first to isolate the dipotassium salt of the cyclooctatetraene dianion and to provide NMR evidence for its planar structure. Thus, his research provided the precursors for both types of the cyclic C_8 uranium complexes.) Later workers crystallographically characterized the pentalene dianion as its $Li_2 \cdot 2DME$ salt.[135]



24

25

(26)

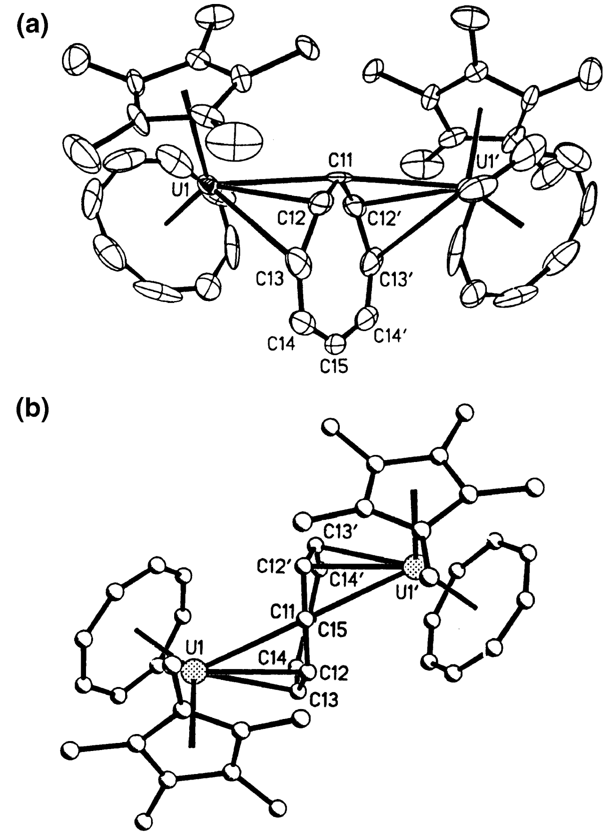
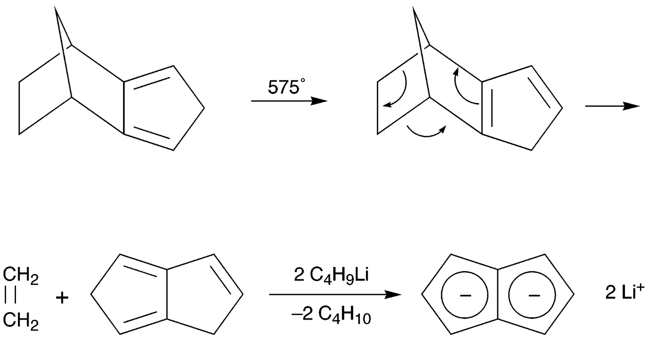


Figure 17. (a) X-ray crystal structure of $(Me_5C_5)(C_8H_8)U(\mu\text{-}\eta^3{:}\eta^3\text{-}C_8H_8)U(C_8H_8)(Me_5C_5)$ (C_{11} is bonded to both uranium atoms). (b) Side view showing the nonplanarity of the bridging C_8H_8 ring (from Evans, W. J.; Nyce, G. W.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 240; reproduced by permission of Wiley/VCH and William J. Evans).

Scheme 10



23

Thirty-five years after Katz's report, the first actinide complex of a substituted pentalene dianion, a mixture of the two isomers **24** and **25**, was prepared by Geoffrey Cloke and structurally characterized by Peter Hitchcock at the University of Sussex (eq 26).[125] Cloke et al. had prepared the required substituted dianion reagent by a route similar to that of Katz: flash vacuum pyrolysis, this time of cyclooctatetraene, which gave a mixture of dihydropentalenes, conversion of these to the dianion salt $[Li(DME)]_2[C_8H_7]$, and treatment of the latter with a trialkylsilyl derivative, followed by deprotonation of the 1,4-disilyl products with *n*-BuLi·DME or KNH_2 to

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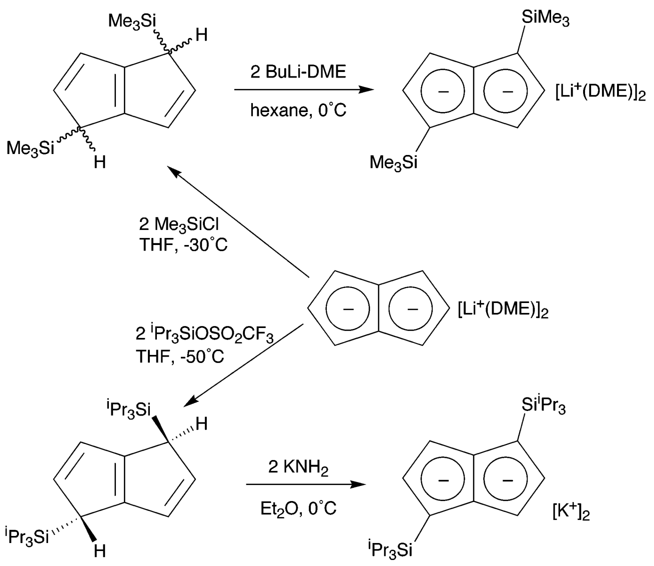
(134) Katz, T. J.; Rosenberger, M. *J. Am. Chem. Soc.* **1962**, *84*, 865.

(135) Stezowski, J. J.; Hoier, H.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1263.

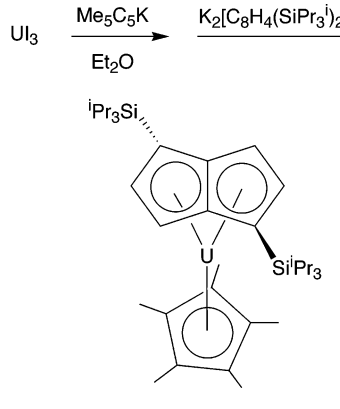
Scheme 11



give the 1,4-disilylpentalene dianion as the dilithium or dipotassium salt, respectively (Scheme 11).[137]

It was the dipotassium 1,4-bis-(triisopropylsilyl)pentalenide that Cloke used in the reaction with $ThCl_4$ to prepare $Th[C_8H_4(SiPr_3^i)_2\text{-}1,4]$. Deep orange crystals were obtained, a mixture of staggered (**24**) and eclipsed (**25**) isomers. These were quite stable thermally, subliming at 260 °C at 5×10^{-6} mbar. The molecular structure, as determined by X-ray crystallography (Figure 18), shows the presence of an almost equal mixture of the two isomers. The pentalene system is not planar; it is folded about the bridgehead bond with a fold angle of 24°. The uranium analogue $U[C_8H_4(SiPr_3^i)_2\text{-}1,4]_2$ was prepared using the same procedure.[138]

A photoelectron and DFT study of the thorium and uranium complexes indicated that the principal binding involves δ bonds between the upper occupied π orbitals of the pentalene dianion and the metal d and f orbitals of appropriate symmetry.[138] Of particular interest is that a uranium(III) pentalene complex, $U(Me_5C_5)(C_8H_4\text{-}(SiPr_3^i)_2\text{-}1,4)$, prepared as shown in eq 27, reversibly



(27)

binds dinitrogen,[139] giving green-black crystals that could be isolated (**26**). An X-ray diffraction study established the structure shown.

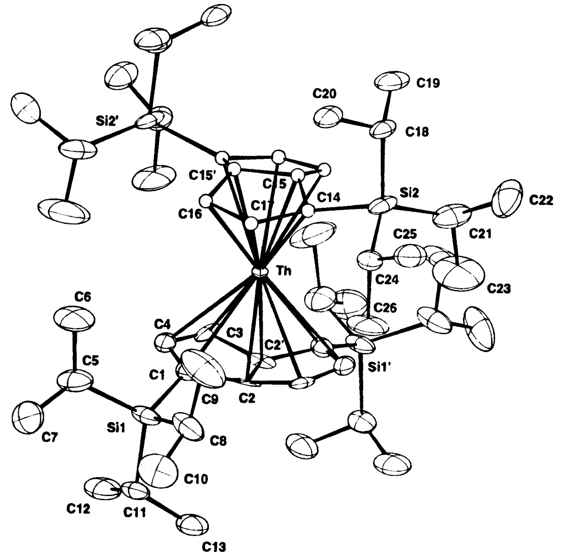
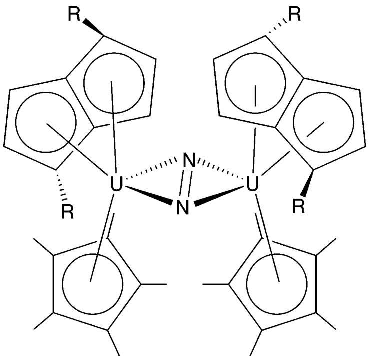


Figure 18. X-ray crystal structure of the silyl-substituted thorium pentalene complex $Th[C_8H_4(SiPr_3^i)_2\text{-}1,4]_2$ (from Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 7899).



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R = Si^iPr_3

VII. Epilogue

The first organoactinide compounds were prepared 105 years after Frankland's discovery of dimethylzinc, the first organometallic compound to be reported in the literature. However, once the first cyclopentadienyluranium compounds had been reported by Reynolds and Wilkinson, the pace of research in this new area of organometallic chemistry was fast and furious. Cyclopentadienyl derivatives of the other actinide elements, thorium, protoactinium, neptunium, plutonium, curium, berkelium, and californium, followed, but organouranium compounds and, to a somewhat lesser extent, those of thorium received most of the attention. Using depleted, i.e., ^{238}U free of ^{235}U, uranium and thorium, actinide chemistry could be investigated in the standard university chemistry laboratory using appropriate precautions, but study of the chemistry of the other actinides required specialized (and expensive) facilities.

The discovery of uranocene in 1968 was a milestone in organouranium chemistry. Uranocene attracted much attention in the general organometallic community,

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(136) (a) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 7899. (b) Cloke, F. G. N.; Hitchcock, P. B.; Kuchta, M. C. *Organometallics* **1998**, *17*, 1934.

(137) Cloke, F. G. N.; Kuchta, M. C.; Harker, R. M.; Hitchcock, P. B.; Parry, J. S. *Organometallics* **2000**, *19*, 5795.

(138) Cloke, F. G. N.; Green, J. C.; Jardine, C. N. *Organometallics* **1999**, *18*, 1080.

(139) (a) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **2002**, *124*, 9352. (b) Cloke, F. G. N.; Green, J. C.; Kaltsoyannis, N. *Organometallics* **2004**, *23*, 832.

since it was the first representative of an entirely new class of π-bonded sandwich complexes. Its structure, as our cover illustration shows, like those of ferrocene and dibenzenechromium, made a visually pleasing picture and provided theoreticians with interesting questions regarding its bonding. It promised new and interesting chemistry and suggested extension to the lanthanide elements (which was realized in subsequent research by Streitwieser and others), but that is beyond the scope of this essay. Andrew Streitwieser, with the help of his pre- and postdoctoral co-workers at Berkeley and of collaborators in other laboratories, did a marvelous job of “rolling up” the field of actinocene chemistry in research that spanned the years 1968−1990s.

In 1984, Michel Ephritikhine initiated research in organouranium chemistry and a few years later began his studies on mono-C_8H_8 uranium chemistry, with great success. He and co-workers developed the field of the uranium-functional chemistry of $C_8H_8UX_2$ complexes, finding it a rich lode of new uranium chemistry.

Organouranium chemistry continues to be a very active area, with many new compounds being prepared, novel structures found, new reactions discovered, and applications in catalysis, for both organic synthesis and polymerization, uncovered. Uranocene played an important role in the development of organometallic chemistry, and it richly deserves to be a highlighted cover molecule of *Organometallics*.

Acknowledgment. I am grateful to Professors Andrew Streitwieser, Ulrich Mueller-Westerhoff, and Christopher Cummins and to Dr. Michel Ephritikhine for reprints, other information, and photographs. My special thanks go to Dr. Carol J. Burns of Los Alamos National Laboratory for a preprint of a relevant chapter of a book, still in press,[38b] that she and Professor Morris Eisen have written. My thanks also go to Professor Arnold L. Rheingold, who provided the cover figure.

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