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Substituted Uranocenes with Alkoxy and Amino Groups

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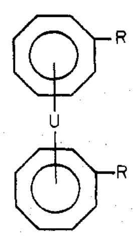
The following derivatives of uranocene, di-η^8-cyclooctatetraeneuranium, $U(C_8H_7R)_2$, R = H (**1**), are described: R = OCH_3 (**2**), OCH_2CH_3 (**3**), $OC(CH_3)_3$ (**4**), $OCH_2CH{=}CH_2$ (**5**), $N(CH_3)_2$ (**6**), $CH_2N(CH_3)_2$ (**7**), $(CH_2)_3N(CH_3)_2$ (**8**), $N^+(CH_3)_3I^-$ (**9**), $CH_2N^+(CH_3)_3I^-$ (**10**). Thermal Claisen rearrangement of the allyloxy compound **5** has not been observed. The ether **2** and ammonium salt **9** react with alkyllithium reagents to give the corresponding dialkyluranocene apparently by a metalation chain reaction involving a cyclooctatrienyneuranium intermediate. Internal coordination of uranium by nitrogen in **7** and **8** is not significant.

Di-η^8-cyclooctatetraeneuranium, "uranocene" (**1**), was first prepared as a possible metallocene-like sandwich organometallic compound having ring–metal covalency with significant involvement of metal f orbitals.[1,2] To establish the degree and character of the bonding in this compound we have studied a broad area of the chemistry of **1** and related derivatives,[3] with further motivation derived from the novel and potential significance of such organoactinide materials. We have previously reported on some uranocenes with hydrocarbon substituents.[4] In this paper we report the preparation and chemical and physical properties of substituted uranocenes containing alkoxy and amino groups.[5] These compounds further emphasize the generality of the uranocene structure and provide a broad expansion of this organometallic chemistry. The structures to be discussed are given in Chart I.

Preparation of Substituted Uranocenes. The necessary monosubstituted cyclooctatetraenes (COT) were synthesized according to literature methods[6-8] with the exception of the previously unreported allyloxycyclooctatetraene whose preparation is described in the Experimental Section.

The reduction of these substituted COT's to the corresponding dianions was accomplished with either potassium metal or potassium naphthalide[9] in THF at −70 °C. Other investigations in this laboratory have demonstrated that for less stable substituted COT dianions the long reaction times required for generation with potassium metal can produce intractable tars. Reaction of COT's with potassium naphthalide in solution is virtually instantaneous and can be followed rapidly by addition of uranium tetrachloride.[10] A significantly higher yield of disubstituted uranocene **7** resulted when *N*,*N*-dimethylaminomethylcyclooctatetraene was reduced with potassium naphthalide than when it was treated with potassium metal (see Table III). After reaction of the substituted COT dianions with UCl_4 the crude products were extracted with hydrocarbon solvents to give 60–80% yields (Table III) of crystalline 1,1′-disubstituted uranocenes. The compounds could generally be further purified by sublimation under high vacuum.

Chart I



1, R = -H
2, R = $-OCH_3$
3, R = $-OCH_2CH_3$
4, R = $-OC(CH_3)_3$
5, R = $-OCH_2CH{=}CH_2$
6, R = $-N(CH_3)_2$
7, R = $-CH_2N(CH_3)_2$
8, R = $-(CH_2)_3N(CH_3)_2$
9, R = $-N^+(CH_3)_3I^-$
10, R = $-CH_2N^+(CH_3)_3I^-$
11, R = $-CH_2CH_3$
12, R = $-(CH_2)_3CH_3$
13, R = $-C(CH_3)_3$
14, R = $-(CH_2)_4CH_3$

During the preparation and handling of the *N*,*N*-dimethylamino compounds **6** and **7** an enhanced stability toward atmospheric oxygen was noted. A consideration of molecular models indicated the possibility of an interaction between the nitrogen lone pairs and the uranium atom (Figure 1). The existence of such coordination could lead to reduced reactivity of the uranium. This concept was tested by the preparation of the di-γ-(*N*,*N*-dimethylamino)propyl compound **8**. The flexibility of the side chain in **8** should allow close approach of the nitrogen atom to the uranium and should confer on **8** still greater air stability. Unfortunately, careful study of the spectral properties of **8** gives no evidence of such intramolecular coordination. This point is considered in greater detail below in the discussion of spectral properties. This result suggests, for example, that the uranium in uranocenes is coordinatively saturated. Another corollary of this result is that the remarkable air stability of di-η^8-(1,3,5,7-tetraphenylcyclooctatetraene)uranium, recently reported[11] from this laboratory, is indeed due to steric blocking of the uranium by the phenyl substituents. A study of uranocenes with various bulky groups is in progress and will be published separately.

Characterization of Substituted Uranocenes. A variety of physical and chemical studies have clearly demonstrated the similarities between these heteroatom-containing complexes and the parent and alkyl-substituted uranocenes. There are, however, some important differences which will be stressed

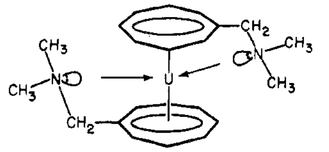


Figure 1. Possible internal coordination in aminoalkyluranocenes.

Table I. Visible Spectral Data on Substituted Uranocenes

Compd	Visible spectrum, nm ($\epsilon \times 10^{-3}$), THF
1	616 (1.8), 643 (0.72), 661 (0.41), 671 (0.12)
2	634 (0.86), 657 (0.54), 686 (0.46), 698 (0.10)
3	632 (0.93), 653 (0.64), 684 (0.46), 693 (0.14)
4	632 (0.83), 654 (0.45), 680 (0.40), 692 (0.28)
5	638 (0.79), 655 (0.59), 683 (0.57), 694 (0.47)
6	635 (1.1), 657 (0.51), 674 (0.41), 688 (0.37)
7	619 (1.4), 643 (0.48), 668 (0.28), 678 (0.11)
8	620.5 (1.23), 648 (0.55), 667 (0.40), 679 (0.32)

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

Compd	*m/e* of major identifiable peaks
1	446 $(C_8H_8)_2U^+$, 342 $(C_8H_8)U^+$, 104 $(C_8H_8)^+$
2	506 $(C_9H_{10}O)_2U^+$, 372 $(C_9H_{10}O)U^+$, 134 $(C_9H_{10}O)^+$
3	534 $(C_{10}H_{12}O)U^+$, 386 $(C_{10}H_{12}O)U^+$, 148 $(C_{10}H_{12}O)^+$
4	590 $(C_{12}H_{16}O)_2U^+$, 478 $(C_8H_8O)_2U^+$, 399 $(C_{11}H_{13}O)U^+$, 357 $(C_8H_7O)U^+$, 356 $(C_8H_6O)U^+$, 176 $(C_{12}H_{16}O)^+$, 120 $(C_8H_8O)^+$
5	558 $(C_{11}H_{12}O)_2U^+$, 491 $(C_8H_8O)(C_9H_9O)U^+$, 398 $(C_{11}H_{12}O)U^+$, 356 $(C_8H_6O)U^+$, 160 $(C_{11}H_{12}O)^+$, 119 $(C_8H_7O)^+$
6	532 $(C_{10}H_{13}N)_2U^+$, 385 $(C_{10}H_{13}N)U^+$, 147 $(C_{10}H_{13}N)^+$
7	560 $(C_{11}H_{15}N)_2U^+$, 399 $(C_{11}H_{15}N)U^+$, 161 $(C_{11}H_{15}N)^+$
8	616 $(C_{13}H_{19}N)_2U^+$, 427 $(C_{13}H_{19}N)U^+$, 356 $(C_9H_{10})U^+$, 189 $(C_{13}H_{19}N)^+$, 115 $(C_9H_7)^+$

in the present paper. All of these compounds are easily oxidized and, therefore, must be prepared and handled under vigorously oxygen-free conditions. Controlled oxidation leads to quantitative recovery of the COT ligands. In common with the alkyl-substituted uranocenes,[4] the heteroatom-containing complexes all show markedly increased solubility over that of the parent molecule in nonpolar solvents.

Compounds **2**–**8** all dissolve readily in THF giving green solutions which show cascades of four absorptions in the 600–700-nm region characteristic of the uranocene structure[2,4] (Table I). The significance of these spectra will be considered in the section on spectral properties.

The mass spectra of these compounds (Table II) are very distinctive, indicating clearly their sandwich-type structure. The most important *m/e* peaks are P (parent), P – L (ligand), and L. All of the compounds show this pattern except di-*tert*-butoxyuranocene, **4**, which gives a peak corresponding to P – L – methyl instead of one for P – L. In addition, several of the compounds show other uranium-containing peaks which are consistent with the assigned structures. For example, the di-*tert*-butoxy compound **4** gives a peak larger than the parent at *m/e* 478 and assigned to $U(C_8H_7OH)_2{}^+$. Both **4** and **5** give a peak at *m/e* 356 which corresponds to an epoxy fragment $(C_8H_6O)U^+$, whereas **5** also gives a peak at *m/e* 491, $(C_8H_7O)U(C_8H_7OCH_2)^+$. The di-$\gamma$-*N*,*N*-dimethylaminopropyl compound **8** gives a peak at *m/e* 356 assigned in this case to the methyl substituted fragment $(C_8H_7CH_3)U^+$.

Spectroscopic Properties. Substituted uranocenes generally have visible spectra in the 600–700-nm range consisting of four absorptions of decreasing intensity going toward longer wavelength. The positions of the absorptions along with their extinction coefficients are given in Table I. It should be noted that the λ_{max} for each of these compounds is shifted to longer wavelength than that of uranocene itself. Similar bathochromic shifts have been reported for various dialkyluranocenes.[4] These visible spectra have been interpreted as ligand-to-metal charge-transfer transitions, probably from the π-ligand orbital derived from e_{2g} of uranocene to metal f orbitals with $l_z = \pm 1$ (or ± 3).[4] Electron-donating groups, such as those in Table I, raise the ligand π orbitals to give lower energy transitions.

The visible spectrum of **8** is especially important in determining whether there is coordination of the nitrogen lone pairs with the uranium atom. The spectrum of a THF solution of **8** shows absorptions at 620.5, 648, 667, and 679 nm. The visible spectrum of a THF solution of 1,1′-di-*n*-butyluranocene, **12**, the nearest hydrocarbon equivalent to **8** for which data are available, shows absorptions at 620, 647, 666, and 678 nm.[12] In addition, the spectrum of **8** in *n*-hexane solution shows absorptions at 622.5, 650, 670, and 679 nm. The similarity of the spectra of **8** and **12** as well as the absence of an appreciable solvent effect on the spectrum of **8** argues convincingly against significant intramolecular coordination.

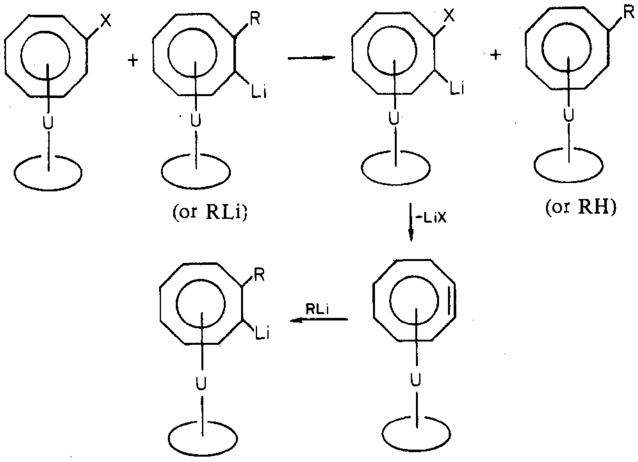
The proton NMR spectra of the heteroatom-containing uranocenes (run at 40 ± 1 °C) are consistent with those already reported for uranocene,[13] 1,3,5,7,1′,3′,5′,7′-octamethyluranocene,[14] and various dialkyl-substituted uranocenes.[4] These spectra are summarized in the Experimental Section. The interpretations of these spectra are based on pseudocontact shifts from uranium 5f electrons and contact shifts derived from spin density in the π systems of the ligands. The chemical shifts for the substituent protons are clearly consistent with the assigned structures in all cases. The protons on the methyl group α to the ligand ring in **8** show a large upfield shift similar to that reported for the α-methylene protons in **11** and **12**.[4] Protons on carbons β to the ligand rings show much smaller upfield shifts, whereas those farther away show little, if any, shifts. The dipolar shifts are sensitive to the conformation of the ring substituents and detailed studies are in progress for some of these and other uranocenes. Preliminary results suggest that preferred conformations are those with substituent chains directed toward the side of the ligand rings *away* from the uranium. We also note in this connection that the NMR spectrum of **8** also provides no evidence for significant coordination of the amino group with uranium.

The chemical shifts for the ligand ring protons of compounds **2**, **4**, **5**, and **8** have also been determined. These ring protons give broad signals that fall in the range from 27 to 46 ppm upfield from Me_4Si. All of these compounds show four signals of area 2:1:2:2 moving from lower to higher field. The four resonances for the ring protons of the uranocenes with alkoxy substituents are spread over a wider range than those of **8**.

Carbon-13 NMR spectra have also been obtained for **2**, **4**, **5**, and **8** at 36 ± 1 °C, and the chemical shifts are consistent with the assigned structures in all cases. All of the compounds give five signals for the ring carbons in the range from 265 to 342 ppm downfield from Me_4Si. The resonance farthest upfield has been assigned, using off-resonance proton-decoupling techniques, to the carbon bearing the substituent in all cases.

Both the ^{13}C and proton NMR spectra of these compounds are highly temperature dependent. This temperature dependence and several other aspects of both the ^{13}C and proton NMR spectra of various substituted uranocenes are the subject of current investigations in this laboratory because of their

Chart II



significance in terms of electronic structure. For example, for octagonal rings with centrosymmetric uraniums, the dipolar shift of all ring carbons and protons should be identical and observed differences should be contact shift differences resulting from changes in spin density at different positions. The *downfield* shift of ring carbons compared with the *upfield* contact shift of ring protons is consistent with a spin polarization mechanism for relaying ligand π-spin density to ring protons.[14] Details will be reported subsequently.

Reactions of Substituted Uranocenes. Although uranocene itself has not been metalated,[2] uranocenes with alkoxy or ammonium groups do react with organolithium reagents.[5] For example, 1,1′-dimethoxyuranocene (**2**) reacts with *n*-butyllithium or *tert*-butyllithium in cyclohexane at room temperature to give **12** or **13** in 70 and 64% yields, respectively. 1,1′-Bis(uranocyl)trimethylammonium iodide (**9**) was prepared from **6** and methyl iodide, and its reactions with a variety of organolithium compounds have been studied. The net reaction was replacement of the trimethylammonium group by the organolithium substituent in yields summarized in Table IV.

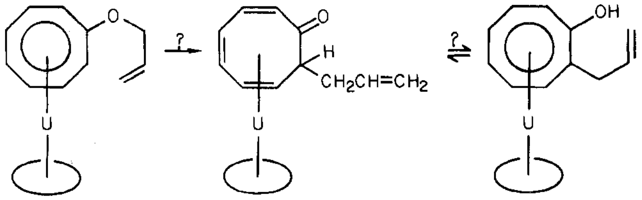
The proposed reaction mechanism[5] involves a carbanion chain sequence initiated by metalation of the substituted uranocene at a position adjacent to the heteroatom substituent. Subsequent elimination of trimethylamine with formation of lithium iodide liberates an intermediate uranium complex of cyclooctatrienyne,[15] as shown in Chart II. An organolithium reagent next adds to the reactive "triple" bond to give a new organolithium reagent which can now metalate another ring and continue the chain. The result is almost 1:1 stoichiometry between organolithium reagent and groups displaced.

An important confirmation of this mechanism derives from the following experiment. Dimethoxyuranocene **2** reacts readily with *n*-butyllithium but not with methyllithium. The latter compound is apparently too weak a metalating agent to initiate metalation of **2**. When **2** was treated with *n*-butyllithium in the presence of excess methyllithium a mixture of uranocenes was obtained, which, on air oxidation liberated both methyl- and *n*-butylcyclooctatetraene. This experiment demonstrates the formation of an intermediate that can react with alkyllithium reagents including methyllithium. Finally, we point to an analogy to the proposed "yne" mechanism in reaction of chloroferrocene with bases.[16]

Compound **7** is quaternarized with methyl iodide to give 1,1′-bis(uranocylmethyl)trimethylammonium methyl iodide, **10**. Compound **10** reacts with methyllithium to give 59% of **11** and with *n*-butyllithium to give 51% of 1,1′-di-*n*-pentyluranocene (**14**). These reactions probably involve substitutions of the direct displacement type at the α-carbon center.

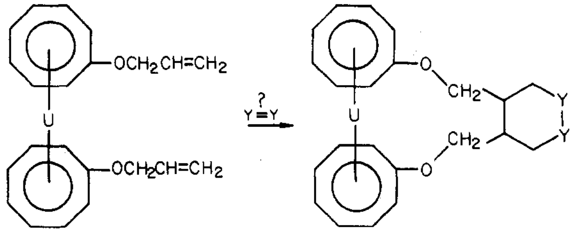
Di-*tert*-butoxyuranocene (**4**) also reacts with *n*-butyllithium, but the reaction product is not **12**. The characterization of the product of this reaction is in progress, and the results will be reported later.

1,1′-Diallyloxyuranocene (**5**) was synthesized in order to study the applicability of the Claisen rearrangement[17] to the uranocene system. Such a rearrangement could provide a route to hydroxyuranocenes. The ligand itself, allyloxycyclooctatetraene, rearranges on heating to the corresponding allylcyclooctatrienone; however, heating **5** at temperatures ranging from 35 to 160 °C in a variety of solvents (benzene, diglyme, *N*,*N*-dimethylaniline, and glyme–sodium acetate[18]) gave only decomposition at about 160 °C. Some substituted uranocenes decompose slowly in refluxing diglyme;[20] hence, the present results do not permit distinction between a direct thermal decomposition of **5**, perhaps by loss of a ligand, from rearrangement followed by decomposition of an intermediate cyclooctatrienone complex.



The Claisen rearrangement of **5** was also attempted photolytically by irradiating a benzene solution with a medium-pressure mercury lamp. Examination of the reaction mixture after 1 week showed only starting material with no observable amount of rearranged sandwich complex. These attempted Claisen rearrangement reactions emphasize the covalent nature and substantial magnitude of ring–metal bonding in uranocenes.

Several cycloaddition reagents were used with **5** in an attempt to prepare a bridged uranocene of the type **15**.



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However, treatment of **5** with dimethyl acetylenedicarboxylate, maleic anhydride, or *N*-phenylmaleimide in benzene solution gave only dark brown polymer-like material. Controlled air oxidation liberated 70–85% yields of allyloxycyclooctatetraene and left an unidentified brown gum.

Experimental Section

Materials and Methods. *N*,*N*-Dimethylaminocyclooctatetraene,[21] (*N*,*N*-dimethylaminomethyl)cyclooctatetraene, and 3-(*N*,*N*-dimethylaminopropyl)cyclooctatetraene[7] were prepared by the literature methods. Methoxy-,[8] ethoxy-,[8] and *tert*-butoxycyclooctatetraenes[8] were synthesized by the reaction of bromocyclooctatetraene with the respective alkoxide in Me_2SO. All reagents and solvents were commercially obtained unless otherwise noted. All solvents used in the preparation of the organometallic compounds were dried and degassed before use. Reactions involving organometallic compounds were carried out under argon using standard techniques for handling air-sensitive materials.[22]

Instruments used in this study were the following: visible, Cary Model 118;[23] IR, Perkin-Elmer 337 (spectra calibrated with polystyrene); proton NMR, Varian T-60 and NV-14 (+δ in parts per million downfield from Me_4Si);[24] ^{13}C NMR, Bruker WH-90 FT (+δ in ppm downfield from Me_4Si);[24] mass spectra, CEC-103.

Analyses were performed by Chemalytics, Inc., Tempe, Ariz., the Analytical Laboratory, University of California, Berkeley, or by A. Bernhardt, Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany.

Table III. Preparation of Alkoxy- and Aminouranocenes

Compd	Method of synthesis[a]	% yield	Solvent used	Sublimation temp, °C (Torr)
2	A	80	Hexane	130 (10^{-2})
3	A	75	Hexane	130 (10^{-2})
4	B	77	Benzene	160 (10^{-7})
5	B	65	Pentane	125 (10^{-7})
6	A	72	Pentane	140 (10^{-2})
7	A	58	Pentane	160 (10^{-2})
	B	80		
8	A	70	Hexane	140 (10^{-3})

[a] See Experimental Section.

Allyloxycyclooctatetraene. Into a 500-mL round-bottom flask were placed 4.64 g (80 mmol) of freshly distilled 2-propen-1-ol and 75 mL of dry Me_2SO under argon. The flask was cooled in an ice bath and 3.84 g (80 mmol) of 50% sodium hydride was added portionwise over a 0.5-h period. After stirring for 0.5 h the mixture was cooled in an ice bath and 14.64 g (80 mmol) of bromocyclooctatetraene[21] in 75 mL of dry Me_2SO was added dropwise during 1 h. The reaction mixture was stirred overnight and quenched with 200 mL of ice cold saturated brine. After extracting the aqueous solution with ether, the combined organic solutions were washed with water, dried ($MgSO_4$), filtered through 200 g of aluminium oxide, and concentrated in vacuo. The yellow oily residue was chromatographed on silica gel using petroleum ether:benzene (97:3) as eluent. After removal of the solvent in vacuo, the allyloxycyclooctatetraene was isolated in 85% yield as a bright yellow oil: R_f (petroleum ether) 0.16; ^{1}H NMR ($CDCl_3$) δ 6.30–4.80 (m, 10 H), 4.20 (m, 2 H); ^{13}C NMR ($CDCl_3$) 158.9, 133.3, 132.6, 131.1, 130.5, 130.0, 129.5, 129.3, 117.0, 101.3, 68.5; IR (neat) 3068, 2996, 1664, 1639 cm^{-1}; mass spectrum *m/e* (relative abundance) 160 (M^+, 14.7), 119 (43.9), 91 (100).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.54. Found: C, 82.19; H, 7.45.

Preparation of Substituted Uranocenes. Method A. Conversion of the cyclooctatetraene derivatives to the substituted uranocenes was achieved by reduction with potassium as previously reported.[2,4]

Method B. To 0.46 g (12.0 mmol) of potassium dispersion in 75 mL of THF at 0 °C in the usual reaction vessel[1] was added 3.07 g (24.0 mmol) of naphthalene. The mixture instantaneously turned green and was allowed to stir for 6 h. After cooling the dark green solution to −70 °C, 6.0 mmol of cyclooctatetraene derivative was added all at once. The solution rapidly changed from dark green to reddish brown indicating the formation of the corresponding cyclooctatetraene dianion. Uranium tetrachloride[25] (1.14 g, 3.0 mmol) in 75 mL of THF was immediately added and the resulting thick green slurry was stirred at −70 °C for 3 h. The reaction mixture was allowed to warm to room temperature and the solvent was removed by vacuum transfer. The residual solid was warmed to ~45–50 °C under a high vacuum (10^{-3} mm) for 24 h to sublime all the naphthalene from the residue. The remaining green solid was extracted and isolated as previously described.[2] Physical and spectroscopic data for these compounds are summarized below and in Tables I and II.

2: ^{1}H NMR (C_6D_6) δ −3.73 (s, 6 H), −27.5 (s, 4 H), −30.2 (s, 2 H), −35.6 (s, 4 H), −43.7 (s, 4 H); ^{13}C NMR (C_6D_6) δ 309.1, 289.7, 288.1, 275.6, 267.8, 100.5; IR (Nujol) 1453 (w), 1340 (w), 1279 (m), 763 (s) cm^{-1}.

4: ^{1}H NMR (C_6D_6) δ 2.07 (s, 18 H), −28.1 (s, 4 H), −28.7 (s, 2 H), −36.2 (s, 4 H), −45.7 (s, 4 H); ^{13}C NMR (C_6D_6) δ 330.0, 299.0, 296.1, 283.0, 259.6, 33.8, 1.2.

Anal. Calcd for $C_{24}H_{32}O_2U$: C, 48.81; H, 5.46; U, 40.31. Found: C, 48.90; H, 5.56; U, 40.09.

5: ^{1}H NMR (C_6D_6) δ 2.60 (d, *J* = 10.5 Hz, 2 H), 1.75 (m, 2 H), 0.70 (d, *J* = 17.5 Hz, 2 H), −0.33 (d, *J* = 5.0 Hz, 4 H), −27.9 (s, 4 H), −30.5 (s, 2 H), −35.5 (s, 4 H), −43.5 (s, 4 H); ^{13}C NMR (dioxane-d_8) δ 341.2, 307.9, 289.2, 275.5, 268.5, 132.7, 115.0, 112.6; IR (Nujol; fluorolube) 3030 (w), 2998 (w), 1640 (w), 1175 (m) cm^{-1}.

Anal. Calcd for $C_{22}H_{24}O_2U$: C, 47.32; H, 4.33. Found: C, 49.39; H, 4.30.

6: IR (Nujol) 1470 (w), 1351 (w), 1303 (m), 769 (s) cm^{-1}.

8: ^{1}H NMR (C_6D_6), δ 2.80 (t, *J* = 7.0 Hz, 4 H), 1.13 (s, 6 H), 0.63 (m, 4 H), −18.3 (t, *J* = 7.5 Hz, 4 H), −31.5 (s, 4 H), −32.9 (s, 2 H), −34.9 (s, 4 H), −38.1 (s, 4 H); ^{13}C NMR (C_6D_6) δ 312.1, 301.5, 298.3, 286.3, 281.9, 76.9, 63.7, 45.2, −33.0.

Table IV. Reaction of Organolithium Reagents with 9

Organolithium reagent, RLi	% yield of $(RC_8H_7)_2U$	Sublimation temp, °C (Torr)
tert-Butyllithium	67	130 (10^{-5})
n-Butyllithium	59	120 (10^{-2})
Methyllithium	52	100 (10^{-2})
Phenyllithium	45	160 (10^{-2})
Vinyllithium	57	120 (10^{-2})
Allyllithium	62	120 (10^{-2})

Quarternization of 6 and 7 with Methyl Iodide. To a solution of **6** (2.65 g, 5.0 mmol) in 75 mL of THF was added 5 mL of methyl iodide via syringe. The mixture was stirred for 48 h at room temperature during which time a green precipitate formed. The volatile materials were removed by vacuum transfer and the remaining green solid was collected in the glovebox to give 3.7 g (91%) of 1,1′-bis(uranocyl)trimethylammonium iodide **9**.

Anal. Calcd for $C_{22}H_{32}N_2I_2U$: C, 32.35; H, 3.95; I, 31.10. Found: C, 32.21; H, 4.17; I, 30.85.

1,1′-Bis(uranocyl)trimethylammonium methyl iodide (**10**) was isolated in 96% yield using the above procedure with **7**.

Anal. Calcd for $C_{24}H_{36}N_2I_2U$: C, 34.12; H, 4.27; I, 30.07. Found: C, 34.73; H, 4.49; I, 29.74.

Reactions of Organolithium Reagents with Substituted Uranocenes. A. Reaction of *tert*-Butyllithium with 9. To a stirred suspension of **9** (0.82 g, 1.0 mmol) in 100 mL of hexane at 0 °C was added 3.0 mmol of commercial *tert*-butyllithium in hexane. After stirring of the suspension for 24 h, acetic acid (0.3 mL) was added to destroy the excess organolithium; then the solvent was removed under vacuum. Degassed water (25 mL) was introduced to dissolve the inorganic salts and the mixture was filtered to isolate a green solid. Upon sublimation (10^{-5} mm, 130 °C), a 0.37-g (67%) sample of 1,1′-di-*tert*-butyluranocene, **13**, was isolated: ^{1}H NMR (toluene-d_8), δ −11.18 (s, 18 H), −33.7 (s, 4 H), −34.1 (s, 4 H), −39.8 (s, 4 H); −43.1 (s, 2 H); ^{13}C NMR (C_6D_6) δ 308.0, 291.8, 288.8, 275.6, 42.6, −24.7; mass spectrum, *m/e* 558 (M^+), 398, 160; visible (THF), 624 (1.42), 652 (0.38), 671 (0.26), 684 nm (0.12).

Other organolithium reagents were allowed to react with **9** with results summarized in Table IV. The physical and spectral data for these uranocenes have been previously published.[4]

B. Reaction of Methyllithium with 10. To a stirred suspension of **10** (0.84 g, 1.0 mmol) in 50 mL of benzene was added 8.0 mmol of commercial methyllithium. After stirring at room temperature for 2 days, the reaction mixture was hydrolyzed with acetic acid (0.3 mL) and the solvent was removed under vacuum leaving a green residue. The residue was triturated with THF to yield 0.29 g (59%) of **11**. The physical and spectral data of the product were identical with an authentic sample.[4]

Similar results were obtained with *n*-butyllithium to give **14** in 51% yield; mass spectrum *m/e* 586 (M^+).

C. Reaction of *tert*-Butyllithium with 2. To a suspension of **2** (0.5 g, 1.0 mmol) in 75 mL of hexane at 0 °C was added 6.0 mmol of commercial *tert*-butyllithium. After stirring for 3 days, the reaction mixture was quenched with 0.5 mL of methanol. The solvent was removed under vacuum and the remaining green residue was sublimed to give 0.36 g (64%) of **13**.

D. Preparation of Methyluranocenes from 2. Into a standard uranocene reactor[2] was placed 16.0 mmol of methyllithium in ether. The solvent was removed under vacuum and replaced with approximately 100 mL of benzene to which were added 2.0 mmol of *n*-butyllithium and 1.0 mmol of **2**. The resulting uranocene derivatives were stirred for 4 days and air-oxidized and hydrolyzed (acetic acid) in the usual manner.[2,4] GC analysis (SE-30, 5 ft, 130 °C) showed a 2.1:1.0 mixture of methyl- and *n*-butylcyclooctatetraene.

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Registry No. **1**, 11079-26-8; **2**, 63230-73-9; **3**, 63230-74-0; **4**, 63230-75-1; **5**, 63230-76-2; **6**, 63230-77-3; **7**, 63269-83-0; **8**, 63230-67-1; **9**, 63230-68-2; **10**, 63230-69-3; **11**, 37274-10-5; **12**, 37274-12-7; **13**, 63230-70-6; **14**, 63230-71-7; ((phenyl)C_8H_7)$_2$U, 37274-13-8; ((vinyl)C_8H_7)$_2$U, 37274-09-2; ((allyl)C_8H_7)$_2$U, 63230-72-8; allyloxycyclooctatetraene, 63197-34-2; 2-propen-1-ol, 107-18-6; bromocyclooctatetraene, 7567-22-8; methyl iodide, 74-88-4; *tert*-butyllithium, 594-19-4; *n*-butyllithium, 109-72-8; methyllithium, 917-54-4; phenyllithium, 591-51-5; vinyllithium, 917-57-7; allyllithium, 3052-45-7.

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Preparative and Kinetic Study on the Mechanisms of Isomerization of Square-Planar Complexes. Kinetic Evidence for Pseudorotation of a Five-Coordinate Intermediate

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It was found that, on addition of a stoichiometric or excess amount of L to PtX_2L_2, $PtXL_3^+$ is formed in polar solvents and PtX_2L_3 (X = Cl, Br, I; L = PMe_2Ph, PEt_3) in nonpolar solvents. In conjunction with this, either no or a very slow isomerization occurs in polar solvents, while a very fast isomerization proceeds in nonpolar solvents. A kinetic study of the iodide-catalyzed cis to trans isomerization of $PtI_2(PEt_3)_2$ showed that pseudorotation of a five-coordinate intermediate is most probably the isomerization pathway. Some further arguments are presented in support of this mechanism for the phosphine-catalyzed as well as uncatalyzed MX_2L_2, MR_2L_2, and $AuR_2R'L$ (R = alkyl or aryl) isomerizations. However, the consecutive displacement mechanism most probably operates for $MXRL_2$ and $MX_2X'_2$ (X' = halide, amine, or water) systems.

Introduction

Catalyzed isomerization of platinum(II) and palladium(II) phosphine–, arsine–, stibine–, and amine–halo complexes (MX_2L_2) is well-known. Two of the previously proposed mechanisms can accommodate all of the observations to date. Basolo and Pearson[1] postulated a consecutive displacement mechanism that does not contradict the stereospecific nature of substitution in square-planar complexes:

$$cis\text{-}MX_2L_2 \overset{L'}{\rightleftharpoons} MXL'L_2 + X^- \overset{-L}{\rightleftharpoons} trans\text{-}MX_2L'L \qquad (1)$$

Haake et al.[2] presented some data from which they concluded that the phosphines L and L′ do not mix during isomerization. They therefore postulated "a distorted penta-coordinate state in which L′ occupies a unique position. This distorted state must be able to undergo fluxional change which interconverts the positions of L and X and, therefore enables isomerization" to occur:

$$cis\text{-}MX_2L_2 \overset{L'}{\rightleftharpoons} MX_2L_2L' \overset{-L'}{\rightleftharpoons} trans\text{-}MX_2L_2 \qquad (2)$$

However, Cooper and Powell[3] later did some NMR studies from which they concluded that Haake's conclusion was erroneous, though a pseudorotation mechanism could not be discounted from their observations. The latter experiments were repeated and different results were found which will be discussed in the section on NMR studies.

Recently Redfield and Nelson[4] showed that MX_2LL' can be isolated in certain cases and is formed from mixtures of MX_2L_2 and MX_2L_2'. Their data implied that there can be phosphine mixing, and therefore no unique M–L′ bond need exist. They suggested that both mechanisms 1 and 2 operate, depending on choice of solvent and ligand. A third mechanism was also suggested,[4] namely, consecutive displacement of a neutral ligand by a neutral ligand:

$$cis\text{-}MX_2L_2 + L' \rightleftharpoons MX_2L_2L' \rightleftharpoons MX_2LL' + L \rightleftharpoons MX_2L_2L' \rightleftharpoons trans\text{-}MX_2L_2 + L' \qquad (3)$$

Because of the very stereospecific nature of the square-planar substitution reactions it is however very doubtful whether isomerization will be achieved by this mechanism.

Two further mechanisms can be proposed for *cis–trans* isomerization. First, one can conceive that an equilibrium between the tetrahedral and square-planar structures can result in isomerization, but this mechanism has been found to be symmetry forbidden.[5] Second, isomerization can be effected by an equilibrium between a square-planar and trigonal structure, but such a dissociative step is violating Tolman's 16–18 electron rule[29] and has never been found in Pt(II) and Pd(II) square-planar substitutions to date.[1] Nevertheless, this mechanism has been postulated for some uncatalyzed isomerizations[24] and will be discussed later.