[1,2-Bis([8]annulenyldimethylsilyl)ethane]uranium, the First Bridged Uranocene

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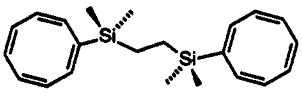
Summary: 1,2-Bis(cyclooctatetraenyldimethylsilyl)ethane (1) was prepared and converted to the corresponding bridged uranocene (η^8:η^8-1,2-bis([8]annulenyldimethylsilyl)ethane)uranium(IV) (2). The temperature-dependent NMR spectrum of 2 indicates a flexible molecule that twists between enantiomeric structures with a barrier of about 13 kcal mol^{-1}.

Bridged ferrocenes, in which the two ligand rings are joined by a tether, were prepared not long after the first preparation of the parent molecule.[2] In contrast, although many uranocenes and related actinide sandwich compounds have been prepared since 1968,[3] no bridged uranocene-type structure has been reported, although chains containing two cyclooctatetraene (COT) rings are known.[4] We report here the synthesis of the di-COT compound 1 and its conversion to the bridged uranocene 2.



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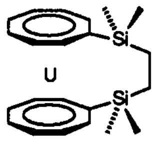

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The preparation of monosubstituted cyclooctatetraenes has been the subject of various studies.[5] The most general methods involve cuprate reactions with bromocyclotetraene,[6] (COT)Br, or alkylation of an organometallic derivative of cyclooctatetraenyl carbanion with a suitable electrophile. The latter method was used for the preparation of 1. Various methods for the generation of the carbanion have been used, but the simplest appears to be that of metal/halogen exchange using (COT)Br and alkyllithium. The reaction of cyclooctatetraenyllithium, generated by Br/Li exchange from the bromide and *n*-butyllithium, with 1,2-bis(chlorodimethylsilyl)ethane gave 45% of 1,2-bis(cyclooctatetraenyldimethylsilyl)ethane (1); however, the use of *tert*-butyllithium for the exchange afforded a cleaner product.

Conversion of the ligand to the corresponding bridged uranocene was accomplished by straightforward analogy to simple uranocenes. Reaction of 1 with metallic potassium occurred readily to give a brown suspension of the tetraanion, which on treatment with 1 equiv of uranium tetrachloride produced a green hexane-soluble solid product whose properties are consistent with 2. This material could be sublimed at relatively low temperatures (130 °C, 10^{-3} mbar) and could be characterized, although X-ray-quality crystals could not be obtained. The mass spectrum shows a molecular ion at *m/z* 588, which is the base peak, and there were no peaks corresponding to dimeric or polymeric structures. The HRMS is consistent with the proposed molecular formula $C_{22}H_{30}Si_2U$.

The NMR spectrum of 2 is typical of uranocenes.[7] In particular, the paramagnetically shifted ring hydrogens are similar to those of 1,1′-bis(trimethylsilyl)uranocene,[8] with the 5-hydrogen furthest upfield. The methyl groups at δ −3 ppm are somewhat downfield from those of the trimethylsilyl substituent, consistent with the average exo-like position of the two methyl groups in 2. The methylene groups in 2, in contrast, are located far upfield at −21 ppm, consistent with their endo-like conformation. The NMR spectrum was also run at low temperatures and showed several features of interest. As shown in Figure 1, the isotropic shifts of several of the protons showed a typical linear dependence on $1/T$ in common with most uranocene protons.[7] Isotropic shifts for a number of uranocenes have been determined using the corresponding thorocenes as diamagnetic analogs.[7] For 2 we used the recently published data for 1,1′,4,4′-tetrakis(trimethylsilyl)thorocene[9] in which the methyl protons have δ 0.58 ppm and the ring protons 6.70 and 6.90 ppm. Accordingly, for 2 we estimated the diamagnetic δ value to be 0.6 for the hydrogens adjacent to the silicon and 6.7, 6.9, 6.9, and 6.9 ppm for the COT ring positions 2, 3, 4, and 5, respectively. Reasonable changes in these numbers do not affect the results. The isotropic shifts for the COT 5-proton show a slight curvature with $1/T$. Except for the COT 5-proton, the NMR spectra show the coalescence behavior at low temperature typical of dynamic NMR systems. The CH_3 and CH_2 protons showed broadening by −68 °C (coalescence) and disappeared into the base line by −79 °C. The COT 2-, 3-, and 4-protons showed coalescence broadening by −40 to −50 °C. A reasonable explanation is given by a structural model of 2, shown as 3 in Figure 2. Using standard bond distances and angles,

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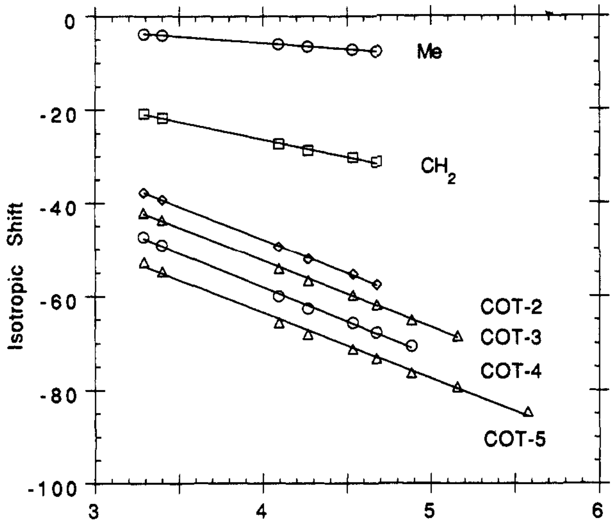

Figure 1. Isotropic shift of protons in **2**. Equations for the linear correlations are as follows: Me, $\delta_{ISO} = 5.078 - 2696.7/T$ ($r = 1.000$); CH_2, $\delta_{ISO} = 3.622 - 7480.2/T$ ($r = 0.998$); COT-2, $\delta_{ISO} = 10.101 - 14524/T$ ($r = 1.000$); COT-3, $\delta_{ISO} = 4.390 - 14195/T$ ($r = 0.999$); COT-4, $\delta_{ISO} = 0.165 - 14566/T$ ($r = 0.999$); COT-5, $\delta_{ISO} = -2.713 - 13950/T$ ($r = 0.998$). Note that the points for COT-5 have been shifted −5 ppm to avoid overlapping the points for COT-4.

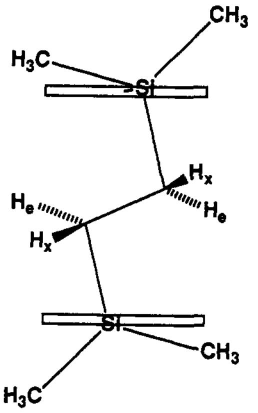

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Figure 2. One conformation of a structural model of **2** shown end-on.

the compound probably has C_2 symmetry; Figure 2 therefore represents one enantiomer and at normal temperatures the compound twists about the methylene groups to interconvert enantiomers at rates fast compared to the NMR time scale. For each enantiomer the two methyls on the silicon, the two methylene hydrogens (shown as H_x (exo) and H_e (endo) in Figure 3), and the pairs of ring protons, 2 and 8, 3 and 7, and 4 and 6, are chemically (and magnetically) different. Unfortunately, we could not get measurements at low enough temperature to see the "frozen" states, but it is possible to get a rough measure of the barrier.

The COT 2- and COT 3-protons coalesce by −52 °C, and the COT 4-proton coalesces by −38 °C. At coalescence the rate constant for interconversion between two states is of the order of magnitude of the chemical shift difference between the corresponding pairs. Considering the total range of chemical shifts of the ring protons, about 10 ppm, the shift differences between pairs such as 2 and 8 and between 3 and 7 are expected to be of the order of magnitude of 1 ppm. Thus, ΔG^* is about 13 kcal mol^{-1}. For the methyl and methylene protons the chemical shift differences are 1 order of magnitude greater and the coalescence temperatures are correspondingly higher. The interconversion of the enantiomers is difficult to accomplish with models and requires substantial spreading apart of the rings; thus, the barrier for interconversion is relatively high but is perhaps lower than might have been judged from mechanical models.

Experimental Section

The handling of air-sensitive compounds, purification of reagents and solvents, and spectroscopic studies have been detailed previously.[10] Analyses, including mass spectra, were obtained at the Analytical Services Laboratory, College of Chemistry, University of California, Berkeley, CA.

1,2-Bis(cyclooctatetraenyldimethylsilyl)ethane (1). To 6.0 g (33 mol) of bromocyclooctatetraene[11] in 50 mL of THF at −75 °C was added 35 mL of *tert*-butyllithium, 1.7 M in pentane (65 mmol), over 1 h. The solution gradually turned orange-brown and finally dark. The solution was stirred at −75 °C for 15 min, and 1,2-bis(chlorodimethylsilyl)ethane (2.54 g, 11.8 mmol) in 15 mL of THF was added over a period of 1 h with vigorous stirring. The reaction mixture was warmed to room temperature overnight. The red reaction mixture was quenched with aqueous NH_4Cl, and the organic layer was separated, poured into water, extracted with ethyl ether, and dried over $MgSO_4$. After the removal of solvent the crude product was chromatographed on silica gel with hexane to give 1.86 g of **1** (45%) as a yellow viscous oil that crystallized slowly over several days. ^{1}H NMR ($CDCl_3$): δ 5.65–5.95 (m, 14 H, COT ring protons), 0.45 (br s, 4H, $-CH_2CH_2-$), 0.04 (s, 12H, $-CH_3$). MS: *m/z* 350 (M^+, 3.37%). Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.71; H, 8.65.

(η^8:η^8-1,2-Bis([8]annulenyldimethylsilyl)ethane)uranium(IV) (2). To 248 mg of **1** (0.708 mmol) in 10 mL of THF was added 300 mg of potassium (7.69 mmol) with vigorous stirring. Stirring was continued for 20 h to give a brown solution. After filtration to remove the excess K, the solution was added slowly (over 25 min) with stirring to 380 mg of UC_4 (1.0 mmol) in 10 mL of THF to give a green solution. After the mixture was stirred for 5 h, the THF was removed in vacuo to give a green solid which was extracted with hexane. Evaporation gave 291 mg (70%) of a green solid that sublimes at 10^{-3} mbar/130 °C. ^{1}H NMR (THF-d_8, 22 °C): δ −3.485 (s, 12H, $-CH_3$), −21.145 (br s, 4H, $-CH_2$-CH_2-), −32.515 (br s, 4H, COT ring protons), −36.769 (br s, 4H, COT ring protons), −42.260 (br s, 4H, COT ring protons), −42.751 (br s, 2H, COT ring protons). MS (EI): *m/z* 588 (M^+, 100%), 589 ($(M + 1)^+$, 33.59%), 590 ($(M + 2)^+$, 1.82%). Simulation for $C_{22}H_{30}Si_2U$: *m/z* 588 (100%), 589 (34.6%), 590 (12.32%). HRMS: *m/z* calcd 588.2393(8), found 588.2384.

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