diazomethane gas in a nitrogen stream at room temperature. After the evaporation of the solvent, the residual solid was dissolved in the mixture of diethyl ether–*n*-hexane (3:2). The solution was concentrated to ca. 2 cm^3 and cooled on dry ice to afford orange crystals of **4** (0.15 g, 64%).

Reaction of 1b with $Fe_2(CO)_9$. To a solution of **1b** (0.98 g, 3 mmol) in diethyl ether (20 cm^3) was added $Fe_2(CO)_9$ (1.09 g, 3 mmol), and the solution was stirred for 1.5 h at 35 °C. After the evaporation of the solvent, the residual solid was extracted through a glass filter with 30-cm^3 portions of *n*-hexane. The concentration of the filtrate afforded red crystals of **5** (1.09 g, 78%).

Crystal Structure Determination of 5. Recrystallization under nitrogen from a 1:5 chloroform–petroleum ether solution gave reddish brown single crystals. Specimens used for X-ray diffraction studies were sealed into thin-walled glass capillaries under an argon atmosphere. The crystal system and the space group were obtained from preliminary oscillation and Weissenberg photographs about the *c* axis with Cu Kα radiation. Accurate cell parameters were determined by a least-squares treatment of the 2θ angles of the 47 reflections in the range of 20–35° measured on a computer-controlled four-circle diffractometer with Mo Kα radiation (λ = 0.710 69 Å).

Crystal Data: $C_{14}H_{10}Fe_2O_{11}$, M_r = 465.9, monoclinic, space group $P2_1/n$; a = 15.006 (2) Å, b = 10.896 (1) Å, c = 11.078 (2) Å, β = 100.48 (1)°, V = 1 781.1 (5) Å^3; D_{measd} = 1.72 g cm^{-3} (by flotation method with sodium iodide aqueous solution), Z = 4, D_{calcd} = 1.7376 (5) g cm^{-3}; $F(000)$ = 936, μ = 17.30 cm^{-1}. A specimen of dimensions ca. 0.28 × 0.28 × 0.25 mm was used for X-ray data collection on the diffractometer. Integrated intensities were collected at 21 °C up to 55 °C in 2θ by the θ–2θ continuous scan mode at a θ scan rate of 2° min^{-1} with graphite-monochromated Mo Kα radiation. Stationary background counts of 10-s duration were made on either side of the scan. Intensities of five standard reflections were monitored before every 50 reflections to check the deteriorations of the specimen. No significant variation was observed for these monitoring intensities during the data collection. The intensities were corrected for the Lorentz and polarization effects but not for absorption and extinction. Of the 4080 independent reflections measured, 2850 with $|F_o| > 3\sigma(|F_o|)$ were accepted as "observed" and used in the subsequent calculations.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method. Two Fe atoms were located from a Patterson map and the other nonhydrogen atoms located from subsequent Fourier syntheses. The structure was refined by the diagonal least-squares calculations with isotropic thermal factors for all the atoms. At this stage the residual index, $R = \sum|\Delta F|/\sum|F_o|$, where $\Delta F = |F_o| - |F_c|$, was 0.10. The hydrogen atoms were located from a difference Fourier map. The structure was then refined by the block-diagonal least squares with anisotropic thermal factors for the nonhydrogen atoms and isotropic ones for the hydrogen atoms. In the refinement the function minimized was $\sum w(\Delta F)^2$, where the weight $1/w$ was $\sigma^2(|F_o|) + a|F_o|^2$ for the block-diagonal least-squares. The constant a was chosen to give approximately equal distribution of the mean $w(\Delta F)^2$ for several subgroups of increasing $|F_o|$ and was 0.0001 in the final cycles of the refinement. The final residual indices were R = 0.046 and $R_w = [\sum w(\Delta F)^2/\sum|F_o|^2]^{1/2}$ = 0.037. In the final cycle of least-squares refinement no individual parameter except in the hydrogen atoms shifted by more than one-half of its estimated standard deviation. In the final difference map there were no peaks greater than 0.35 e Å^{-3}. Atomic scatterring factors were taken from ref 31, including corrections for the effects of anomalous dispersion. All computations were performed on a FACOM 230/38 computer and a MELCOM 70/30 computer at Kwansei Gakuin University.

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Registry No. 1a, 6111-92-0; **1b**, 60941-31-3; **3**, 80485-09-2; **4**, 80485-10-5; **5**, 80485-11-6; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of fractional coordinates and temperature factors and structure factors for complex **5** (13 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of Dicyclopentenouranocene, $U[C_8H_6(CH_2)_3]_2$

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The title compound **1** was synthesized by the reaction of dipotassium bicyclo[6.3.0]undeca-2,4,6-triene-1,8-diide, **3**, and UCl_4, and its crystal and molecular structure was determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell with dimensions a = 17.393 (8) Å, b = 22.468 (12) Å, and c = 8.931 (4) Å. The uranium atom is located centrally between the two eight-membered rings with bond distances U–C = 2.64 ± 0.03 Å and C–C = 1.40 ± 0.02 Å. The effects of annulation on the physical properties of uranocene are discussed.

Introduction and Results

As part of a continuing study of annulated derivatives[1,2] of uranocene[3] we report the synthesis and X-ray structure determination of bis[π-(cyclopenteno[8]annulene)]uranium(IV) (dicyclopentenouranocene), **1**.[4] This compound has significance for two reasons. First, it was expected to involve a conformation sufficiently well-defined to assist NMR interpretation. Second, it would be the first X-ray

(1) Zalkin, A.; Templeton, D. H.; Berryhill, S. R.; Luke, W. D. *Inorg. Chem.* **1979**, *18*, 2287.
(2) Luke, W. D.; Berryhill, S. R.; Streitwieser, A., Jr. *Inorg. Chem.* **1981**, *20*, 3086.
(3) Streitwieser, A., Jr.; Muller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8644.
(4) Controversy exists in naming sandwich organometallic actinide compounds of cyclooctatetraene. Other possible names are bis(η^8-bicyclo[6.3.0]undeca-2,4,6-triene-1,8-diide)uranium(IV) and bis(η^8-cyclopentenocyclooctatetraene)uranium(0). The former does not properly describe delocalization of charge in the ligand while the latter fails to convey the proper formal oxidation state of the metal or the delocalized nature of the cyclooctatetraene ligand. Thus, we have chosen to name these compounds organometallic derivatives of [8]annulene or as substituted uranocenes in analogy with ferrocene nomenclature.
(5) Karraker, D.; Stone, J.; Jones, E., Jr.; Edelstein, N. *J. Am. Chem. Soc.* **1970**, *92*, 4841.

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Scheme I

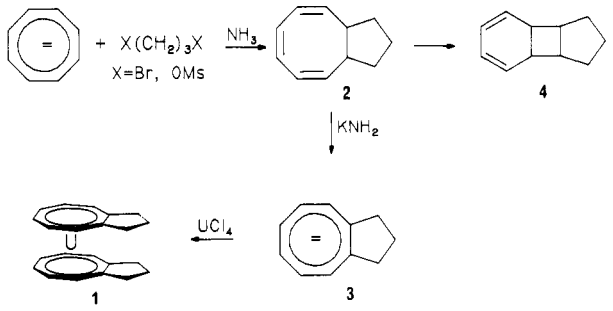

Table I. Infrared Spectrum (cm^{-1}) in Nujol[a]

$(C_8H_8)_2U$[c]	$[C_8H_6(CH_2)_3]_2U$, 1	$(C_8H_8)_2U$[c]	$[C_8H_6(CH_2)_3]_2U$, 1
	1870 (w)	1018 (s)[b]	1020 (m)[b]
1730 (w)	1765 (w)		900 (s)
	1320 (m)	799 (s)	790 (m)
1262 (s)	1260 (m)		745 (s)
1095 (s)[b]	1090 (m)[b]	720 (s)	700 (vs)

[a] w = weak; m = medium; s = strong; vs = very strong. [b] References 11, 12, and 22-25. [c] Very Broad.

structure of an unstrained uranocene in which the ring–U axis is not a C_2 symmetry axis; the position of the uranium was therefore expected to provide a significant indication of the relative roles of covalent and ionic bonding. The title compound was synthesized in a manner similar to dicyclobutenouranocene,[2] shown in Scheme I. The bicyclotriene **2** was prepared by ether addition of 1,3-dibromopropane, or the dimethanesulfonate of 1,3-propanediol, to a solution of dilithium cyclooctatrienediide in liquid ammonia, affording distilled yields of 46.8% and 58.4%, respectively. This compound was contaminated by the tricyclic isomer **4**; on standing, **2** rearranged completely to **4**. Dideprotonation of **2** with potassium amide in THF/liquid ammonia formed a red solution of the dianion **3** which could be isolated as an impure tan solid. Subsequent reaction of **3** with UCl_4 in THF produced the desired uranocene **1** in 15.9% yield. The visible spectrum of this green air-sensitive material exhibited the typical uranocene cascade of four principal absorptions at 632, 656, 663, and 680 nm. The principal IR absorption bands are compared with those of uranocene in Table I.

The ^1H NMR (toluene-d_8) spectrum of **1** at 30 °C showed six sharp well-resolved resonances upfield from Me_4Si, −8.3 (m, 2 H), −18.8 (m, 4 H), −23.1 (s, 4 H), −32.6 (m, 2 H), −34.2 (s, 4 H), −41.2 ppm (s, 4 H), and one resonance downfield from Me_4Si, +24.4 ppm (m, 4 H). The ^{13}C NMR spectrum (dioxane-d_8) at 39 °C showed four broad peaks at 308.0, 296.9, 279.0, and 268.5 ppm downfield from Me_4Si and two sharp peaks at 13.4 and −32.5 ppm.

Magnetic susceptibility measurements on the bulk solid from 2.4 to 95.6 K are shown in Figure 1. Above 20 K the magnetic susceptibility follows the Curie–Weiss Law with $C = 0.743 \pm 0.005$ emu K mol^{-1}, $\mu = 2.4 \pm 0.1$ μ_B, and $\theta = 16.6° \pm 0.5°$. Below 10 K the magnetic moment was independent of temperature with $\chi_m = (2.56 \pm 0.03) \times 10^{-2}$ csu/mol. With use of a diamagnetic correction of -187×10^{-6} emu mol^{-1}, the corrected values are $C = 0.714 \pm 0.005$ emu K mol^{-1}, $\mu = 2.4 \pm 0.1$ μ_B, and $\theta = 16.1° \pm 0.5°$.[5]

The compound crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell with dimensions $a = 17.393$ (8) Å, $b = 22.468$ (12) Å, and $c = 8.931$ (4) Å. With a molecular weight of 526.46 the calculated density is 2.004 g cm^{-3}. The structure was determined by

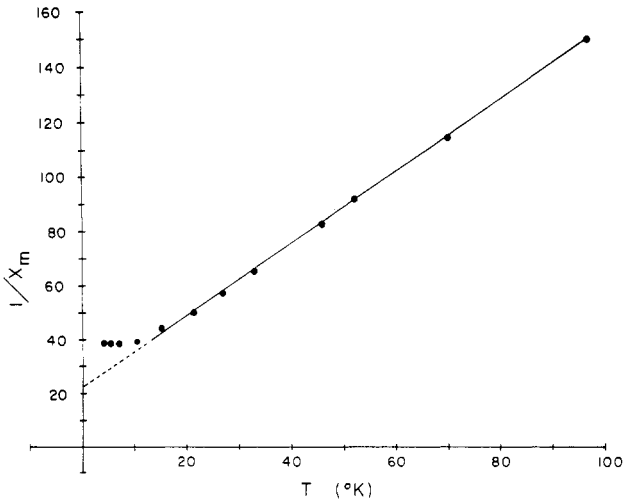

Figure 1. Plot of $1/\chi$ vs. absolute temperature for dicyclopentenouranocene, **1**.

Table II. Positional Parameters[a]

atom	x	y	z
C (1)	0.047 (2)	0.163 (1)	0.159 (3)
C(2)	0.077 (2)	0.122 (1)	0.264 (3)
C(3)	0.147 (2)	0.109 (2)	0.329 (4)
C(4)	0.218 (2)	0.138 (1)	0.309 (3)
C(5)	0.254 (2)	0.182 (2)	0.225 (4)
C(6)	0.228 (2)	0.220 (2)	0.115 (4)
C(7)	0.153 (2)	0.2305 (9)	0.061 (3)
C(8)	0.079 (2)	0.209 (1)	0.074 (3)
C(9)	0.014 (2)	0.230 (1)	−0.032 (3)
C(10)	−0.051 (3)	0.205 (3)	0.029 (6)
C(11)	−0.038 (2)	0.152 (2)	0.122 (6)
C(12)	0.285 (1)	0.098 (1)	−0.160 (3)
C(13)	0.222 (2)	0.116 (1)	−0.245 (3)
C(14)	0.142 (2)	0.111 (2)	−0.258 (4)
C(15)	0.099 (2)	0.067 (2)	−0.184 (4)
C(16)	0.105 (2)	0.022 (1)	−0.078 (4)
C(17)	0.168 (2)	−0.003 (1)	−0.004 (3)
C(18)	0.245 (1)	0.014 (1)	0.016 (2)
C(19)	0.294 (1)	0.054 (1)	−0.052 (2)
C(20)	0.378 (1)	0.058 (2)	0.005 (3)
C(21)	0.407 (2)	0.111 (2)	−0.061 (5)
C(22)	0.361 (2)	0.132 (1)	−0.182 (4)
U	0.17237 (5)	0.11510 (4)	0.0369 (1)

[a] Here and in the following tables the number in parentheses is the estimated standard deviation in the least significant figure. The estimated standard deviations are a result of least-squares refinement on a model in which C-C distances were restrained as described in the text. Hydrogen atoms were included but not refined.

Table III. Uranium-Carbon Distances (Å)

U-C(1)	2.66 (3)	U-C(12)	2.66 (2)
-C(2)	2.63 (3)	-C(13)	2.66 (3)
-C(3)	2.65 (4)	-C(14)	2.68 (4)
-C(4)	2.60 (3)	-C(15)	2.58 (3)
-C(5)	2.66 (3)	-C(16)	2.61 (3)
-C(6)	2.64 (3)	-C(17)	2.67 (2)
-C(7)	2.62 (2)	-C(18)	2.61 (2)
-C(8)	2.68 (2)	-C(19)	2.66 (2)

conventional single-crystal X-ray methods and was refined by full-matrix least squares to an R factor of 0.04 for 1000 data where $F^2 > 3\sigma$. Final positional parameters are given in Table II. Tables of calculated positional parameters for the hydrogen atoms, carbon–carbon distances, thermal parameters, and observed structure factors amplitudes are given in the supplementary material. Uranium–carbon distances are listed in Table III. The atom numbering is seen in Figures 2 and 3.

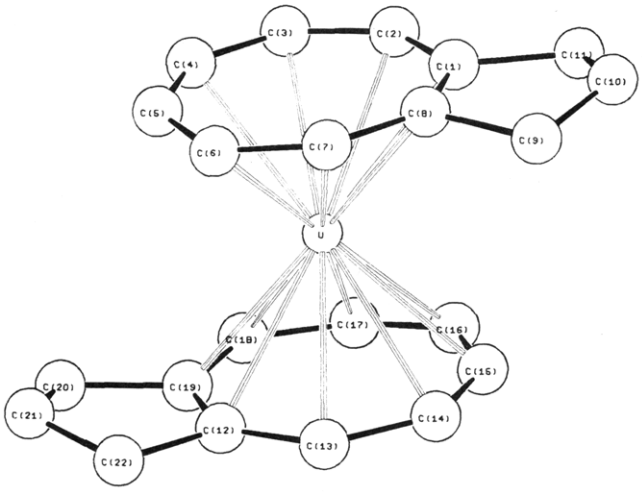

Figure 2. ORTEP ball and spoke view of the molecule. Hydrogen atoms are omitted for clarity.

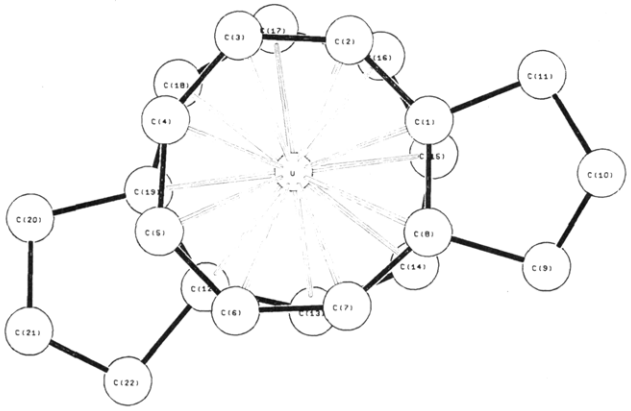

Figure 3. Ball and spoke view of the molecule perpendicular to the cyclooctatetraene rings. Hydrogen atoms omitted.

Discussion

The title compound exists as discrete molecules in the solid state. All atoms are in the general positions, and no symmetry is imposed on the molecule by the space group; however, the molecule does have approximate C_2 symmetry (see Figure 3). The uranium atom is centrally sandwiched between the two eight-membered rings with a U–ring distance of 1.92 Å, in good agreement with other uranocenes.[1,6-8] The COT rings of the molecule are rotated about 8° from a staggered configuration (see Figure 3). In other uranocenes both staggered[11,12] and eclipsed[1,10,11] configurations have been reported. As in ferrocenes, the relative orientation of the rings in uranocene crystals results from crystal packing and not from significant steric interactions between the rings which are 3.85 Å apart. Bond angles and distances for the uranocene part of the molecule are similar to those reported for other uranocenes.[1,6-8] The mean planes of carbons, (C_{11}, C_9, C_1, C_8) and (C_{20}, C_{22}, C_{12}, C_{19}), are bent slightly inward toward the uranium atom from the plane of the 8-membered ring as has been found in dicyclobutenouranocene[1] and in 1,3,5,7,1′,3′,5′,7-octamethyluranocene.[7] Similar convex distortions in the carbocyclic rings have been observed in ferrocenes and chromacene[9] and in a variety of organometallic compounds with planar five-, six- and eight-membered rings.[10]

Unrealistic bond distances (1.38–1.46 Å) and very large and anisotropic thermal parameters in the five-membered rings indicate that we are observing the mean positions of atoms which have disorder up and down from the mean planes, a situation which is commonplace for aliphatic five-membered rings.

The bending appears to be a general feature in sandwich structures where steric interactions between rings is small. Two possible explanations have been offered to account for this bending:[7] (1) bending the substituent toward the metal makes each carbon slightly more pyramidal with the π orbital of the C_nH_n ring bent inward toward the metal and providing greater directionality for overlap between π orbitals and metal orbitals; (2) contraction in volume of the electron density on the side of the ring adjacent to the highly charged metal ion. Nonbonding interaction between the substituted bond and the more diffuse electron density on the uncomplexed side of the ring would result in an inward bend of the substituent. This latter explanation suggests that the inward bending should be independent of ring size. However, it appears that for three- and four-membered rings the substituents bend outward away from the metal.[10] Theoretical calculations on d transition-metal compounds attribute this bending to the former explanation and predict an outward bend for three- and four-membered ring and an inward bend in the substituent for rings larger than five.[10] This bending of the substituent in toward the metal appears to be a general feature in all substituted uranocenes in the absence of steric effects and may reflect the proposed covalency in ligand–metal bonding in these systems.[11]

An especially important point in this regard is the central position with respect to the C_8 rings of uranium in all uranocene structures thus far studied. This result is expected for a model involving important covalent ring–metal bonding. If ionic character dominated we would expect some deviations from C_8 centrosymmetry, particularly in a case such as the present where the overall structure is so lacking in symmetry. This result makes the present structure an especially significant one.

The spectral properties of 1 show no significant differences from those of other uranocenes. In the visible spectrum the shift in λ_{max} from that of uranocene (λ_{max} 616 nm) is between that of 1,1′-dialkyl substituted uranocenes (λ_{max} 610–625 nm) and 1,3,5,7,1′,3′,5′,7′-octamethyluranocene (λ_{max} 650 nm), in accord with the proposed charge-transfer model for the visible spectrum.[12,13]

The paramagnetic shifts of the ^{1}H NMR resonances of 1 are similar to those reported for other substituted uranocenes.[11] Due to the paramagnetic center, the endo and exo protons in the α- and β-positions of the annulated rings are nonequivalent. The three nonequivalent ring proton positions could be assigned to the resonances at −32.1, −34.2, and −41.2 ppm, from the lack of splitting due to J–J coupling and their larger line widths (ca. 30 Hz). The remaining four resonances were partially resolved multiplets and could be easily differentiated into α (+24.4, −18.8 ppm) and (−8.3, −32.6 ppm) sets by integration. Further assignment into endo and exo sets was made in the following manner.

(6) Zalkin, A.; Raymond, K. N. *J. Am. Chem. Soc.* **1969**, *91*, 5667.
(7) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1973**, *12*, 458.
(8) Templeton, L. K.; Templeton, D. H.; Walker, R. *Inorg. Chem.* **1976**, *15*, 3000.
(9) Haaland, A. *Top. Curr. Chem.* **1976**, *53*, 1 and references therein.
(10) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.
(11) Luke, W. D.; Streitwieser, A., Jr. *ACS Symp. Ser.* **1900**, *No. 131*, 93.
(12) Streitwieser, A., Jr.; Harmon, C. A. *Inorg. Chem.* **1973**, *12*, 1102.
(13) Harmon, C. A.; Bauer, D. P.; Berryhill, S. R.; Hagiwara, K.; Streitwieser, A., Jr. *Inorg. Chem.* **1977**, *16*, 2143.

In uranocene[14] and 1,3,5,7,1′,3′,5′,7′-octamethyluranocene[15] the paramagnetic shifts have been factored into contact and pseudocontact components.[11] The contact component affords an upfield shift to ring protons, and an alternating pattern of upfield and downfield shifts to substituent protons such that protons on the β, δ, etc. carbons are shifted upfield and protons on the α, γ, etc. carbons are shifted downfield, with the magnitude of the contact interaction rapidly diminishing to zero along the substituent chain. Variable-temperature studies on uranocene and octamethyluranocene have established that the total paramagnetic shift is linear with $1/T$. Consequently, the pseudocontact contribution can be expressed by eq 1. Where symmetry requires $\chi_x = \chi_y$, the latter term is zero.[16]

$$\Delta_{\text{pseudocontact}} = \frac{(\chi_z - \frac{1}{2}\chi_x - \frac{1}{2}\chi_y)}{3}\frac{(3\cos^2\theta - 1)}{R^3} - \frac{(\chi_x - \chi_y)}{2}\frac{(\sin^2\theta\cos 2\psi)}{R^3} \quad (1)$$

For a number of unsymmetrical uranocenes it appears that $\chi_x = \chi_y$ and that the last term in eq 1 can be generally neglected.[11] With this assumption, the sign of the pseudocontact shift will be controlled by θ. Similar to dicyclobutenouranocene we expect the contact shift of the α_{exo} and α_{endo} protons to be approximately the same; calculation from the observed structure gives $\theta < 54.74°$ for the α_{exo} protons, and thus, the pseudocontact shift is downfield. Hence, the α-proton resonances are assigned as α_{exo} + 24.4 ppm and α_{endo} −18.8 ppm; by analogy, the β-proton resonances are β_{exo} 8.3 ppm and β_{endo} −32.6 ppm.

For ^{13}C NMR the contact shift model for uranocene[15] predicts that the contact shifts for carbons should be just opposite those of the corresponding protons. Ring carbons are shifted to low field and are assigned tentatively to the four resonances at 308.0, 296.9, 297.0, and 268.5 ppm. Correspondingly, the α-carbon is assigned to the upfield resonance (−32.5 ppm) and the β-carbon to the 13.4-ppm resonance.

The similarity of the ^1H and ^{13}C resonances in 1 with those of other substituted uranocenes[12,13] and the parent compound[12] itself suggest that the electronic factors giving rise to the paramagnetic shifts are similar in all uranocenes. Further support for this generalization comes from the magnetic susceptability data which show that the magnetic moment of 1 is equal within experimental error to that of uranocene.[5,17] Further analysis of the NMR spectra of 1 and related annulated uranocenes, their temperature dependences and dissection into contact and pseudocontact components will be detailed in another paper now in preparation.

Experimental Section

All reactions requiring air-free anhydrous conditions were conducted under an Ar atmosphere or in a Vacuum Atmospheres recirculating glovebox. Solvents were distilled from CaH_2 and degassed prior to use. Visible spectra were obtained on a Cary 118 spectrometer, infrared spectra on a Perkin-Elmer 297 spectrometer, ^1H and NMR on Varian T-60 (60 MHz) or the V.C. Berkeley FT-NMR system (180 MHz), and ^{13}C NMR on a Brucker TT-23 spectrometer. Mass spectra and elemental analysis were performed by the Analytical Services Laboratory, University of California, Berkeley, CA. Magnetic susceptability measurements were measured on a vibrating-sample magnetometer previously described in the literature.[17]

X-ray Diffraction. Single crystals suitable for X-ray analysis were grown from hot hexane in an Ar atmosphere glovebox. A crystal fragment approximately 0.10 × 0.15 × 0.35 mm was placed on a Picker FACS-I automated diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å). The setting angles of 12 manually centered reflections (35° < 2θ < 40°) were used to determine the cell parameters by least squares.

Intensity data were collected by using the θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each reflection was scanned from 0.65° before the Kα_1 peak to 0.65° after the Kα_2 peak, and backgrounds were counted for 4 s at each end of the scan range, offset by 0.5°. The temperature during data collection was 22 ± 1 °C. Three standard reflections (6,0,0; 0,0,$\bar{4}$; 0,10,0) were measured after every 200th scan. At the beginning of the data collection ω scans of the 400, 060, and 002 reflections showed half-widths of 0.09°, 0.07°, and 0.09° respectively; at the end of the data collection the values were 0.18, 0.12, and 0.11, indicating significant deterioration of the crystal. Although 6043 scans were collected, only the first 3010 were used; the remaining half of the data, based on the declining intensities of the standards, were rejected. The decay was anisotropic with the largest amount recorded by the 600 standard reflection. An isotropic decay correction varying from 0.91 to 1.06 was applied to the 3010 data used. An absorption correction[18] was estimated, and corrections between 1.5 and 1.8 were applied to the data. Because the crystal had an irregular shape with indistinct faces, a shape and size were estimated, and the dimensions were tailored to fit the intensity variations obtained from three azimuthal scans taken after the data collection was concluded. The 3010 scans resulted in 2312 unique data 1000 of which have $F^2 > 3\sigma$.

A three-dimensional Patterson function calculation revealed the uranium position, and subsequent least-squares calculations and Fourier maps revealed all of the carbon atoms. A series of least squares in which the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ was minimized converged rapidly to the final structure. The expressions that were used in processing the data and estimating the weights are given in the supplementary material; the "ignorance factor", p, was set to 0.06. Scattering factors from Doyle and Turner[19] were used, and anomalous dispersion corrections[20] were applied. The positions of all of the hydrogen atoms were estimated and included in the calculations with isotropic temperature factors but were not refined. Anisotropic thermal parameters were applied to U and all of the carbon atoms.

Because of the low quality of the data, the cyclooctatetraene (COT) ring was not well resolved, and some of the C–C bond distances deviated from the expected values by as much as 0.2 Å. Restraints were imposed on the bond distances in the COT ring and the cyclopenteno group adjacent to the ring in the following manner.[21] Interatomic distances between selected atoms were introduced into the least-squares calculations and treated as observations; estimated standard deviations of these distances were also introduced and used to calculate the weights. The derivatives of these distances with respect to the positional parameters were calculated by a special patch, and these "observations" were not included in the least-squares calculation in the same manner as the observed structure factors. This procedure allows the structure to adjust to the electron density

(14) Edelstein, N.; La Mar, G. N.; Mares, F.; Streitwieser, A., Jr. *Chem. Phys. Lett.* **1971**, *8*, 399.
(15) Streitwieser, A., Jr.; Dempf, D.; LaMar, G. N.; Karraker, D. G.; Edelstein, N. *J. Am. Chem. Soc.* **1971**, *93*, 7343.
(16) The symbols θ, ψ, and R refer to the spherical polar coordinates of the resonating nucleus in a coordinate system whose origin is centered at the metal atom.
(17) Edelstein, N.; Streitwieser, A., Jr.; Morrell, D. G.; Walker, R. *Inorg. Chem.* **1976**, *15*, 1397.
(18) Templeton, L. K.; Templeton, D. H. Abstracts, American Crystallographic Association Proceedings, 1973, Series 2, Vol. 1, p 143.
(19) Doyle, P. A.; Turner, P. S. *Acta Crystallogr.* **1968**, *24*, 390.
(20) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(21) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091.
(22) Goffart, J.; Fuger, J.; Gilbert, B.; Kanellakopulos, B.; Duychaerts, G. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 403.
(23) Streitwieser, A., Jr.; Muller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8644.
(24) Hocks, L.; Goffart, J.; Duychaerts, G.; Teyssie, P. *Spectrochimica Acta, Part A* **1974**, *30A*, 907.
(25) Goffart, J.; Fuger, J.; Brown, D.; Duychaerts, G. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 413.

with a flexibility governed by the weighting. The C–C bond distances within the ring were restrained to 1.40 ± 0.02 Å, and the C–C bonds from the cyclopento carbon to the ring carbons were restrained to 1.54 ± 0.02 Å.

The discrepancy indices for 1000 data where $F^2 > 3\sigma$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.040$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.046$$

R for all 2332 data is 0.14. The error in an observation of unit weight is 1.07. In the last cycle no parameter changed more than 0.13σ. The top three peaks in the final difference Fourier map are 1.0–1.3 e A^{-3} and are all ripples about the uranium atom.

***cis*-Bicyclo[6.3.0]undeca-2,4,6-triene, 2.** Under an Ar atmosphere, 1.4 g (0.2 mol) of lithium wire (1% sodium) was added to 300 mL of anhydrous liquid ammonia in a 500-mL round-bottom flask. To this deep blue solution was added 10.4 g (0.1 mol) of freshly distilled cyclooctatetraene (33 °C (14mmHg)) (BASF), at −40 °C via syringe. The resulting yellow suspension of dianion was stirred for 1.5 h at −40 °C followed by dropwise addition (1 drop every 2 s) of 20.2 g (0.1 mol) of 1,3-dibromopropane (Aldrich) in 20 mL of ether. The reaction mixture was stirred for 4.5 h at ca. −40 °C followed by overnight evaporation of ammonia to afford a red brown solid which was suspended in 200 mL of saturated ammonia chloride and extracted with ether (4 × 100 mL). The ether extracts were washed with water (3 × 100 mL) and dried over $MgSO_4$. Removal of solvent followed by vacuum distillation (25 °C (0.1mmHg)) yielded 6.83 g (46.8%) of a clear yellow liquid: mass spectrum parent m/e 156. The ^1H and ^{13}C NMR ($CDCl_3$) of this material indicated that it was mixture of both the bicyclic (2) and tricyclic (4) valence isomers: bicyclic ^1H NMR δ 5.80 (s, 6 H, vinyl), 2.77 (br m, 1.4 H, bridgehead), and 1.65 (complex m, 5.3 H cyclopentyl); ^{13}C NMR δ 135.4, 127.7, 126.2 (vinyl), 43.5 (bridgehead), 32.3, 19.5 (cyclopentyl); tricyclic ^1H NMR ($CDCl_3$) δ 5.57 (s, 4 H, vinyl), 2.77 and 2.43 (br m, 2 H, bridgehead), 1.67 (complex multiplet, 5.3 H, cyclopentyl); ^{13}C NMR: δ 126.6, 120.3 (vinyl), 51.0, 35.6 (bridgehead), 32.9, 24.7 (cyclopentyl). After standing for 4 days at room temperature, the material had rearranged completely to the tricyclic isomer 4.

Following the same procedure but using 23.2 g (0.1 mol) of 5 in 100 mL of THF instead of 1,3-dibromopropane in 10 mL of ether gave the same product in 58.4% yield.

$AgNO_3$ Adduct of *cis*-Bicyclo[6.3.0]undeca-2,4,6-triene. To a boiling solution of 3.4 g (0.02 mol) of silver nitrate and 15 mL of absolute ethanol was added 2.9 g (0.02 mol) of 2. Most of the silver nitrate dissolved upon addition of the hydrocarbon. Cooling of the solution in a refrigerator for several hours afforded off-white crystals which were recrystallized from absolute ethanol; mp 135–136 °C dec.

Anal. Calcd for $C_{11}H_{14}NO_3Ag$: C, 41.79; H, 4.46; N, 4.43. Found: C, 41.48; H, 4.35; N, 4.29.

1,3-Bis((methylsulfonyl)oxy)propane. To a stirred 0 °C solution of 15.22 g (0.2 mol) of 1,3-propanediol (Aldrich), 70 mL (0.5 mol) of triethylamine, and 1 L of CH_2Cl_2 in a 2-L round-bottom flask was added dropwise 32.5 mL (0.42 mol) of methanesulfonyl chloride (Eastman) over 5 min. The resulting reaction mixture was stirred for 0.5 h during which time a white precipitate formed. After sequential extractions with 200 mL of ice water, 200 mL of cold 10% HCl, 200 mL of saturated sodium bicarbonate, and 200 mL of brine, the organic layer was dried over $MgSO_4$ and stripped of solvent to afford a white solid which was recrystallized from hot methanol: yield 38.4 g (82.7%); mp 40.5–41.5 °C; NMR ($CDCl_3$) δ 4.37 (t, 4 H, OCH_2), 3.07 (s, 6 H, CH_3), 2.19 (p, 2 H, CH_2).

Anal. Calcd for $C_5H_{12}O_6S_2$: C, 25.85; H, 5.21; S, 27.61. Found: C, 26.04, H, 5.26, S, 27.42.

Dipotassium Bicyclo[6.3.0]undeca-2,4,6-triene-1,8-diide, 3. Under Ar a suspension of potassium amide in liquid ammonia was prepared by distilling 300 mL of ammonia from a lithium metal–ammonia solution into a 500-mL round-bottom flask containing several milligrams of anhydrous $FeCl_3$. Subsequent addition of 2.14 g (0.055 mol) of potassium metal at −40 °C afforded a blue solution which was stirred (ca. 5 min) until the blue color disappeared, indicating formation of the amide. A 4.0-g (0.027-mol) aliquot of 2 was added via syringe, and the resulting red brown solution was stirred for 1.5 h at −35 °C. The solution was slowly warmed to room temperature, and the ammonia was swept out with a steady Ar purge overnight, affording 4.66 g of the crude dianion as a highly air-sensitive gray-brown solid: ^1H NMR (THF-d_8) δ 5.67, 1.3, 0.93 (br s); ^{13}C NMR δ 99.9 (quat), 96.9, 89.8, 87.0 (ring), 46.4 (α-CH_2), 27.2 (β-CH_2). No attempt was made to purify this material.

Dicyclopentenouranocene, 1. In an Ar atmosphere glovebox 2.56 g (0.0068 mol) of UCl_4 in 25 mL of THF was added to a solution of 3.0 g (0.0135 mol) of 3 in 100 mL of THF in a 500-mL round-bottom glask, and the resulting green solution was stirred for 18 h. Removal of the solvent by vacuum transfer afforded a green solid which was purified by Soxhlet extraction with hexane: yield 0.57 g (15.9%); mass spectrum, parent peak m/e 526; visible spectrum in hexane, nm ($\epsilon \times 10^3$) 632 (2.1), 656 (0.9), 663 (0.9), 680 (0.7). The IR spectrum is given in Table I, and NMR spectra are discussed in the text.

The NMR spectra showed that the bulk sample was substantially pure (>95%) although a good combustion analysis could not be obtained. The results were always about 1% low in carbon, even with added oxidant. This pattern is not uncommon in attempted combustion analyses of uranocenes, apparently because of the formation of carbides. Anal. Calcd for $C_{22}H_{24}U$: C, 50.2; H, 4.6. Found: C, 48.8; H, 4.8.

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Registry No. 1, 80287-59-8; 2, 64924-30-7; 3, 80263-15-6; 4, 36093-17-1; 1,3-dibromopropane, 109-64-8; 1,3-bis((methylsulfonyl)oxy)propane, 15886-84-7; UCl_4, 10026-10-5.

Supplementary Material Available: Data processing formulas, calculated positional parameters for the hydrogen atoms, anisotropic thermal parameters, carbon–carbon distances, a table of selected angles, and a list of observed structure factors (14 pages). Ordering information is given on any current masthead page.