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The Uranocene Half-Sandwich: ([8]Annulene)uranium(IV) Dichloride and Some Derivatives

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A facile synthesis of ([8]annulene)uranium(IV) dichloride (**1**) has been developed via the reduction of cyclooctatetraene (COT) by UCl_3 or through reaction of UCl_4, COT, and NaH. The activation parameters for the coordination of trimethylphosphine (PMe_3) to **1** in THF solution have been measured. The reactivity of **1** with several mono- and bidentate alkylmetal and alkoxymetal reagents is reported. Also reported are the crystal structures of bis(pyridine)([8]annulene)uranium(IV) dichloride, $(C_8H_8)UCl_2(NC_5H_5)_2$ (**3**), and ([8]annulene)uranium(IV) bis(acetylacetonate), $(C_8H_8)U(CH_3COCHCOCH_3)_2$ (**4**). Crystals of **3** are monoclinic $P2_1/c$, with a = 15.431 (3) Å, b = 7.744 (2) Å, c = 15.665 (3) Å, Z = 4, and R_F = 2.8%. Crystals are **4** are monoclinic, $P2_1/n$, with a = 19.166 (4) Å, b = 10.312 (2) Å, c = 9.227 (2), Z = 4, and R_F = 2.7%.

Introduction

Recent years have seen rapid growth in organoactinide chemistry.[1,2] Central to this growth has been the development of thermally stable, coordinatively saturated organometallic systems of the 5f metals, primarily uranium and thorium. Cyclopentadienyl[3] and alkyl-[4a] and silyl-substituted[4b] cyclopentadienyl ligands have been used widely in these systems to provide kinetic stabilization through steric saturation. The use of cyclooctatetraene as a ligand in organoactinide chemistry began over 20 years ago with the synthesis of bis([8]annulene)uranium(IV), or uranocene.[5,6] Bis([8]annulene) complexes of several other tetravalent[7] and trivalent[8] actinides have since been prepared, and their physical properties and reactivity[9] have been thoroughly investigated. Unfortunately, the reactivity of uranocene with respect to ligand displacement has proven to be rather limited. The low reactivity is due at least in part to the inaccessibility of the uranium metal center as a result of the steric constraints imposed by the cyclooctatetraene rings. In order to increase the reactivity of the uranocene system, less coordinatively saturated complexes containing a single cyclooctatetraene ligand would be highly desirable. We have previously reported the syntheses and structures of mono([8]annulene)thorium complexes.[10,11] We have also reported[10] analogous mono([8]annulene) complexes of uranium, but these were never isolated or fully characterized. We now report here the syntheses and X-ray structures of bis(pyridine)([8]annulene)uranium(IV) dichloride and ([8]annulene)uranium(IV) bis(acetylacetonate). Some reaction chemistry of these uranium(IV) half-sandwich complexes is also presented.

Synthetic Approaches to ([8]Annulene)uranium(IV) Complexes

In our efforts to synthesize uranium compounds containing a single cyclooctatetraene ring, $(C_8H_8)UCl_2$ became a synthetic target on the basis of its likelihood as a suitable precursor to more complex and interesting uranium compounds. Initial attempts to synthesize $(C_8H_8)UCl_2(THF)_2$ (**1**) centered on the addition of 1 equiv of cyclooctatetraene dianion to uranium tetrachloride in THF. The reaction appears to be complex and may involve U(III) intermediates, but under various reaction conditions the only product isolated was uranocene (eq 1). This is in contrast to the analogous reaction between cyclooctatetraene dianion and thorium tetrachloride, which cleanly generates[11]

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the ([8]annulene)thorium(IV) dichloride "half-sandwich" 2 in moderate yield (eq 2).

$$\mathrm{UCl_4 + K_2C_8H_8 \xrightarrow{THF} {}^1\!/_2U(C_8H_8)_2 + {}^1\!/_2UCl_4} \quad (1)$$

$$\mathrm{ThCl_4 + K_2C_8H_8 \xrightarrow{THF} \underset{\mathbf{2}}{(C_8H_8)ThCl_2(THF)_2}} \quad (2)$$

Redistribution[11a] of thorocene and thorium tetrachloride in THF at reflux (eq 3) provides an alternative synthesis of 2. However, reaction of uranocene and uranium tetrachloride under analogous conditions generates only small amounts of the uranium half-sandwich 1 (eq 4). The

$$\mathrm{Th(C_8H_8)_2 + ThCl_4 \xrightarrow[reflux]{THF} 2\,\mathbf{2}} \quad (3)$$

$$\mathrm{U(C_8H_8)_2 + UCl_4 \underset{THF\ reflux}{\rightleftharpoons} 2\underset{\mathbf{1}}{(C_8H_8)UCl_2(THF)_2}} \quad (4)$$

product 1 was observed by ^{1}H NMR spectroscopy but never isolated from the reaction mixture. It appears that the accessibility of the U(III) oxidation state complicates this reaction; the products include a purple solid that may contain $\mathrm{UCl_3}$.

Marquet-Ellis[12] reported ^{1}H NMR evidence for the half-sandwich compound $\mathrm{(C_8H_8)U(BH_4)_2}$ in a reaction of $\mathrm{UCl_4}$, $\mathrm{LiBH_4}$, and $\mathrm{K_2C_8H_8}$. Solar and Streitwieser[10] showed that addition of cyclooctatetraene dianion to a THF solution of $\mathrm{U(BH_4)_4}$ yielded uranocene as the only observed product. However, low yields of $\mathrm{(C_8H_8)U(BH_4)_2}$ could be generated from the slow addition of $\mathrm{K_2C_8H_8}$ to a solution of $\mathrm{UCl_2(BH_4)_2}$ generated in situ. The apparent instability of ([8]annulene)uranium(IV) bis(borohydride) under these conditions is in contrast to the case for the analogous ([8]annulene)thorium(IV) bis(borohydride) half-sandwich, which can be synthesized by several methods.[10,11]

Another approach to the synthesis of mono([8]annulene)uranium(IV) half-sandwich complexes involves the reaction of the corresponding bis([8]annulene) metallocene with protic acids (eq 5). The reaction of $\mathrm{(C_8H_8)_2Zr}$[13] or $\mathrm{(C_8H_8)_2Th}$[10] with dry HCl generates the corresponding half-sandwich dichlorides in good yield. In the reaction of uranocene with dry HCl in THF, only moderate yields of the desired product 1 result. The reaction is complicated by the generation of large amounts of $\mathrm{UCl_4}$ (from attack of HCl on 1) and significant amounts of unreacted uranocene in the product mixture. Nevertheless, this reaction remains an important synthetic route to uranium(IV) half-sandwich complexes containing alkyl-substituted cyclooctatetraene rings (vide infra).

$$\mathrm{M(C_8H_8)_2 + 2HCl \xrightarrow{THF} (C_8H_8)MCl_2(THF)_{\mathit{x}}} \quad (5)$$

$$\begin{array}{l} \mathrm{M = Zr\ (79\%)} \\ \mathrm{M = Th\ (70\%)} \\ \mathrm{M = U\ (35\%)} \end{array}$$

The most successful method to data for the synthesis of mono([8]annulene)uranium(IV) complexes involves the reaction of uranium(III) complexes as one-electron reducing agents. Reduction of cyclooctatetraene by $\mathrm{U[N(SiMe_3)_2]_3}$ produces a mono([8]annulene)uranium(IV) complex (eq 6). Although the compound was not isolated, the U(IV)-bound cyclooctatetraene protons were identified in the ^{1}H NMR spectrum. In the related reaction of tris((trimethylsilyl)cyclopentadienyl)uranium(III) with cyclooctatetraene, the products were isolated and characterized (eq 7). The reaction evidently proceeds by electron transfer from U(III) to neutral cyclooctatetraene to form a cyclooctatetraene-bound uranium(IV) compound.

$$\mathrm{U[N(SiMe_3)_2]_3 + C_8H_8 \xrightarrow{hexane} COT\text{-}bound\ U(IV)\ compound\ by\ {}^1H\ NMR} \quad (6)$$

$$\mathrm{2U(C_5H_4SiMe_3)_3 + C_8H_8 \xrightarrow{hexane} (C_8H_8)U(C_5H_4SiMe_3)_2 + U(C_5H_4SiMe_3)_4} \quad (7)$$

Scheme I

$$\begin{array}{l} \mathrm{2UCl_4 + 2NaH \rightarrow 2UCl_3 + 2NaCl + H_2} \\ \mathrm{2UCl_3 + C_8H_8 \rightarrow \mathbf{1} + UCl_4} \\ \hline \mathrm{UCl_4 + C_8H_8 + 2NaH \xrightarrow{THF} \mathbf{1} + 2NaCl + H_2} \end{array}$$

The synthesis of $\mathrm{(C_8H_8)U(C_5H_4SiMe_3)_2}$ in this fashion suggested a new approach to the synthesis of 1. The previous methodology reviewed above focused on approaches such as single addition of cyclooctatetraene dianion to $\mathrm{UCl_4}$ or single removal of a cyclooctatetraene ring from uranocene. However, under these reaction conditions an intermediate such as 1 is apparently susceptible to further reaction; poor yields and complex product mixtures result. This complication particularly limits the use of cyclooctatetraene dianion due to its proclivity to equilibrate rapidly to uranocene. The reaction of $\mathrm{UCl_3}$ with neutral cyclooctatetraene (eq 8) provides a synthetic route to 1 that involves reaction conditions under which 1 may be stable.

$$\mathrm{2UCl_3 + C_8H_8 \xrightarrow{THF} \mathbf{1} + UCl_4} \quad (8)$$

The direct synthesis of 1 (eq 8) is handicapped by the generation of an equivalent amount of $\mathrm{UCl_4}$ as a byproduct. The similar solubility properties of 1 and $\mathrm{UCl_4}$ render them difficult to separate. This problem can be circumvented through utilization of a reducing agent capable of selectively reducing $\mathrm{UCl_4}$ to $\mathrm{UCl_3}$ in the presence of cyclooctatetraene and 1. The $\mathrm{UCl_4}$ generated in the reaction is thus re-reduced to $\mathrm{UCl_3}$ to react with cyclooctatetraene. A convenient reducing agent is NaH (Scheme I). Residual unreacted $\mathrm{UCl_4}$ can be effectively removed through the addition of tetramethylethylenediamine (TMEDA) to the product solution to form the hydrocarbon-soluble[14] $\mathrm{UCl_4(TMEDA)_2}$. Extraction of the product mixture with hexane thus affords $\mathrm{UCl_4}$-free material. The only other significant side product, uranocene, is somewhat hydrocarbon-soluble and is also removed by hexane extraction.

To test the general applicability of this reaction to the synthesis of uranium half-sandwich compounds containing substituted cyclooctatetraenes, the reaction of $\mathrm{UCl_3}$ with *n*-butylcyclooctatetraene was attempted. After a prolonged reaction period, the only product isolated was a trace amount of dibutyluranocene. The electron-donating *n*-butyl substituent raises the reduction potential of *n*-butylcyclooctatetraene relative to that of cyclooctetraene. We propose that this increase in the reduction potential inhibits the electron transfer from U(III) to the neutral alkyl-substituted cyclooctatetraene. This hypothesis is substantiated by the successful preparation of a half-sandwich compound containing a cyclooctatetraene ligand substituted with the electron-withdrawing *m*-fluorophenyl group (eq 9). The electron-withdrawing effect of the *m*-fluorophenyl group lowers the reduction potential of the

$$\mathrm{UCl_4 + (\mathit{m}\text{-}FC_6H_4)C_8H_7 + 2NaH \xrightarrow{THF} [(\mathit{m}\text{-}FC_6H_4)C_8H_7]UCl_2(THF)_2 + 2NaCl + H_2} \quad (9)$$

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cyclooctatetraene moiety and apparently facilitates electron transfer from U(III) to the substituted cyclooctatetraene. As a result of this limitation, half-sandwich complexes bearing electron-donating ring substituents must at this point be synthesized through reaction of the corresponding substituted uranocene with HCl.

Coordination Chemistry of ([8]Annulene)uranium(IV) Dichloride

Because of the tendency of 1 to rapidly desolvate and the concomitant variable THF content in the solid state, more strongly coordinating ligands for the half-sandwich were investigated. It was found that pyridine quantitatively displaces THF from 1 in THF solution. This led to the isolation of a bis(pyridine) adduct of the half-sandwich, 3 (eq 10).

$$1 + C_5H_5N\ (\text{excess}) \xrightarrow[25\ °C]{PhMe} \underset{3}{(C_8H_8)UCl_2(NC_5H_5)_2} \qquad (10)$$

The addition of trimethylphosphine (PMe_3) to 1 in THF similarly led to the displacement of coordinating THF; however, ^1H NMR integration indicates coordination of only one PMe_3 ligand (eq 11). Because the THF-d_8 solvent exchanges rapidly with coordinated THF, the number of THF molecules in the PMe_3-coordinated complex (presumably 0 or 1) cannot be determined.

$$(C_8H_8)UCl_2(THF)_2 + PMe_3 \rightleftharpoons (C_8H_8)UCl_2(PMe_3)(THF)_x + (2-x)THF \qquad (11)$$

$$x = 0, 1$$

Variable-temperature ^1H NMR spectroscopy reveals an exchange behavior for this process. A ^1H NMR spectrum of the product of 1 with excess PMe_3 shows two resonances at room temperature that can be assigned to the ring and PMe_3 protons. When the sample is cooled below room temperature, the peaks assigned to the ring and PMe_3 protons both broaden and disappear into the base line and then reemerge below −10 °C as two signals. Of the resonances associated with PMe_3, the upfield resonance at −5 ppm (−40 °C) follows approximate Curie–Weiss behavior and corresponds to the coordinated PMe_3, while the chemical shift values for the downfield peak (1.25 ppm) remain constant with varying temperature and correspond to free PMe_3. The far-upfield resonances attributed to the ring protons then correspond to the PMe_3-coordinated and uncoordinated half-sandwich complexes. The chemical shift values for the far-upfield peak correspond to those of 1 (within 0.2 ppm) over the temperature range −10 to −60 °C, and the slope of the line from a plot of chemical shift versus inverse temperature is identical with that of 1.

The free energy of activation can be estimated[15a] from the chemical shift values in the fast- and slow-exchange limits and by an estimate of their coalescence temperature. For the PMe_3 resonances with $T_c = +5 \pm 3$ °C and $\Delta\nu = 1016$ Hz, $\Delta G^\ddagger = 11.9 \pm 0.2$ kcal mol^{-1}. From the coalescence temperature of the ring protons of -5 ± 5 °C and $\Delta\nu = 212$ Hz, $\Delta G^\ddagger = 12.3 \pm 0.3$ kcal mol^{-1}. Activation parameters were also determined[15b] by a computer-simulated line-shape analysis of the broadened exchange peaks. When this simulation was applied to the PMe_3 resonances, the following activation parameters were determined: $\Delta H^\ddagger = 12.7 \pm 0.4$ kcal mol^{-1}, $\Delta S^\ddagger = 2.2 \pm 1.3$ eu, $\Delta E^\ddagger = 13.2 \pm 0.4$ kcal mol^{-1}, $A = (4.8 \pm 3.0) \times 10^{13}$ s^{-1}, and $\Delta G^\ddagger = 12.1 \pm 0.5$ kcal mol^{-1}. The value of $\Delta G^\ddagger$ is in excellent agreement with the values estimated above from the coalescence temperature and chemical shift values. The $\Delta S^\ddagger$ value would be consistent with a single PMe_3 group replacing two THF's ($x = 0$ in eq 11) if the methyl motions in the PMe_3 adduct are more restricted than in free PMe_3.

Reaction Chemistry of ([8]Annulene)uranium(IV) Dichloride

Initial reaction studies of 1 showed that there is no inherent instability of 1 in the presence of cyclooctatetraene dianion. Reaction of 1 with $^1/_3$ equiv of $K_2C_8H_8$ resulted in smooth conversion to $^1/_3$ equiv of uranocene (eq 12). In an attempt to synthesize a mixed

$$1 + \tfrac{1}{3}K_2C_8H_8 \rightarrow \tfrac{1}{3}(C_8H_8)_2U + \tfrac{2}{3}1 + \tfrac{2}{3}KCl \qquad (12)$$

$$1 + K_2(t\text{-}BuC_8H_7) \rightarrow \tfrac{1}{4}(C_8H_8)_2U + \tfrac{1}{2}(C_8H_8)(t\text{-}BuC_8H_7)U + \tfrac{1}{4}(t\text{-}BuC_8H_7)_2U \qquad (13)$$

uranocene containing substituted and unsubstituted rings, 1 was treated with 1 equiv of $K_2(t\text{-}BuC_8H_7)$. Rather than quantitative conversion to the desired $(C_8H_8)(t\text{-}BuC_8H_7)U$, the reaction instead produced a statistical distribution of ligand arrangements (eq 13). The equilibration of uranocene with cyclooctatetraene dianion is clearly at least as rapid as the reaction of 1 with cyclooctatetraene dianion.

The replacement of chloride by alkyl or alkoxy ligands in related systems has much precedent in organoactinide chemistry.[16] However, attempted alkylations of 1 with several alkyllithium and Grignard reagents failed to produce any isolable mono- or dialkyl half-sandwich compounds (eq 14).

$$1 + 2RM \xrightarrow[-78\ °C]{THF} \text{no isolated products} \qquad (14)$$

$$M = Li;\ R = CH_3,\ CH_2C_6H_5,\ C_6H_5,\ CH_2C(CH_3)_3,\ CH_2Si(CH_3)_3$$

$$M = MgCl;\ R = CH_3,\ CH_2C_6H_5,\ CH_2Si(CH_3)_3$$

Reaction with sodium or potassium alkoxide reagents also failed to generate any isolable mono([8]annulene)uraniumIV) half-sandwich compounds (eq 15). The mixture of products obtained from the reaction of 1 with alkali-metal alkoxides includes cyclooctatetraene dianion and an array of mixed uranium(IV) chloro alkoxides (e.g. $UCl_2(OR)_2$, $UCl(OR)_3$, $U(OR)_4$).

$$1 + 2MOR \xrightarrow[-78\ °C]{THF} \text{no mono(cyclooctatetraene) U(IV) products} \qquad (15)$$

$$MOR = NaOC(CH_3)_3,\ KOC(CH_3)_3,\ NaOC_6H_5$$

At present, it is unclear whether our lack of success in isolating alkyl or alkoxy derivatives of the half-sandwich is a result of the methods by which we have attempted to synthesize these complexes or of the inherent instability of these complexes. It is conceivable that 1 is unstable in the presence of highly basic anions. Similarly it is possible that the dialkyl or dialkoxy derivatives form at low temperatures but are sterically unsaturated and possess low-energy pathways to decomposition. Sattelberger et al.[17]

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Table I. Positional Parameters with Estimated Standard Deviations

$(C_8H_8)UCl_2(NC_5H_5)_2$ (**3**)				$(C_8H_8)U(CH_3COCHCOCH_3)_2$ (**4**)			
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
U	0.25826 (2)	0.05235 (3)	0.01444 (1)	U	0.11652 (2)		0.20855 (3)
Cl1	0.3853 (1)	0.2449 (3)	−0.0210 (1)	O1	0.0995 (3)	−0.0119 (5)	0.1868 (5)
Cl2	0.2136 (1)	0.2455 (3)	0.1355 (1)	O2	−0.0024 (3)	0.1741 (5)	0.1639 (5)
N1	0.3952 (4)	0.0081 (7)	0.1560 (3)	O3	0.0889 (3)	0.3557 (5)	0.0389 (5)
N2	0.1643 (4)	0.3099 (7)	−0.0765 (3)	O4	0.1894 (3)	0.1702 (5)	0.0533 (5)
C1	0.1540 (8)	−0.069 (1)	−0.1403 (7)	C1	0.0713 (6)	0.201 (2)	0.4939 (9)
C2	0.1011 (7)	−0.076 (1)	−0.082 (1)	C2	0.0629 (6)	0.330 (1)	0.451 (1)
C3	0.1132 (8)	−0.141 (2)	0.004 (1)	C3	0.1059 (7)	0.421 (1)	0.399 (1)
C4	0.183 (1)	−0.229 (1)	0.0631 (8)	C4	0.1760 (8)	0.422 (1)	0.363 (1)
C5	0.269 (1)	−0.285 (1)	0.0606 (7)	C5	0.2302 (6)	0.329 (2)	0.368 (1)
C6	0.3217 (7)	−0.270 (1)	0.0008 (8)	C6	0.2378 (5)	0.200 (2)	0.412 (1)
C7	0.3101 (7)	−0.190 (1)	−0.0830 (8)	C7	0.1938 (8)	0.107 (1)	0.468 (1)
C8	0.2389 (8)	−0.110 (1)	−0.1409 (6)	C8	0.1245 (8)	0.111 (1)	0.5005 (9)
C9	0.4769 (5)	−0.025 (1)	0.1463 (5)	C9	0.0657 (4)	−0.2307 (8)	0.2098 (9)
C10	0.5500 (5)	−0.066 (1)	0.2157 (5)	C10	0.0478 (4)	−0.0879 (7)	0.1938 (7)
C11	0.5384 (6)	−0.069 (1)	0.3003 (5)	C11	−0.0216 (4)	−0.0495 (8)	0.1879 (8)
C12	0.4564 (6)	−0.035 (1)	0.3115 (5)	C12	−0.0437 (4)	0.0783 (8)	0.1715 (7)
C13	0.3871 (5)	0.002 (1)	0.2387 (5)	C13	−0.1208 (4)	0.1099 (9)	0.1608 (9)
C14	0.0858 (5)	0.359 (1)	−0.0628 (5)	C14	0.0801 (5)	0.5070 (9)	−0.1528 (9)
C15	0.0276 (5)	0.474 (1)	−0.1152 (5)	C15	0.1137 (4)	0.3907 (8)	−0.0747 (8)
C16	0.0517 (6)	0.547 (1)	−0.1865 (5)	C16	0.1684 (5)	0.3283 (8)	−0.1290 (8)
C17	0.1302 (6)	0.496 (1)	−0.2026 (5)	C17	0.2050 (4)	0.2224 (9)	−0.0640 (8)
C18	0.1832 (6)	0.381 (1)	−0.1470 (5)	C18	0.2637 (4)	0.1615 (9)	−0.1309 (9)

have also reported that the reactions of 1 and the thorium analogue 2 with alkyllithium and Grignard reagents lead to intractable products. The only σ-bound derivative they report is $(C_8H_8)U[N(SiMe_3)_2]_2$ via the metathesis of 1 with 2 equiv of $NaN(SiMe_3)_2$. In the crystal structre of this compound there is evidence of an agostic interaction between one carbon on each of the $-N(SiMe_3)_2$ ligands and the uranium atom, a property Sattelberger ascribes to a coordination number deficiency in the compound. Given that the $-N(SiMe_3)_2$ ligand is sterically demanding and that a degree of steric unsaturation is observed in its half-sandwich derivative, it is likely that less bulky ligands fail to provide sufficient kinetic stabilization to allow observation of their half-sandwich derivatives, at least at room temperature. Experiments are currently underway to determine whether formation of alkyl or alkoxy derivatives of the half-sandwich is indeed occurring at low temperatures (<−70 °C) with subsequent decomposition upon warming to room temperature.

In addition to the reactions described above with monodentate ligands, the reactions of 1 with several bidentate ligands were attempted. Several examples of stable early-transition-metal and lanthanide complexes containing σ-donor ligands with internal chelating capability have been reported.[17] The reactions of 1 with three such ligands were attempted. These ligands are $o\text{-}LiCH_2C_6H_4N(CH_3)_2$, $o\text{-}LiC_6H_4CH_2N(CH_3)_2$, and sodium 8-quinolinolate. No derivatives of the half-sandwich were isolated; the products were thermally unstable and decomposed rapidly at room temperature both in solution and as solids. However, the acetylacetonate (acac) derivative 4 of 1 was isolated (eq 16). Both lanthanide and actinide complexes[19] involving acac have been reported previously. Complex 4 is thermally stable and soluble in both ethereal and hydrocarbon solvents. In addition, 4 readily sublimes at 80 °C and 10^{-3} Torr.

$$1 + 2Na(CH_3COCHCOCH_3) \xrightarrow[-20\ °C]{THF} \underset{4}{(C_8H_8)U(CH_3COCHCOCH_3)_2} \quad (16)$$

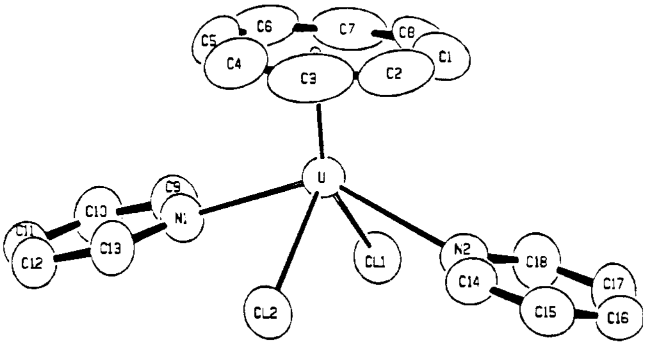

Figure 1. ORTEP diagram of $(C_8H_8)UCl_2(NC_5H_5)_2$ (**3**), with thermal ellipsoids at the 50% probability level.

Table II. Selected Bond Distances (Å) and Angles (deg) for $(C_8H_8)UCl_2(NC_5H_5)_2$ (3)

U-Cl1	2.638 (2)	U-C3	2.658 (9)
U-Cl2	2.649 (2)	U-C4	2.675 (9)
U-N1	2.639 (5)	U-C5	2.703 (9)
U-N2	2.644 (6)	U-C6	2.709 (9)
U-C1	2.689 (8)	U-C7	2.676 (8)
U-C2	2.678 (9)	U-C8	2.683 (7)
Cl1-U-Ct1	127.66	Cl1-U-N1	77.2 (1)
Cl2-U-Ct1	131.75	Cl1-U-N2	77.9 (1)
N1-U-Ct1	111.33	Cl2-U-N1	77.1 (1)
N2-U-Ct1	110.21	Cl2-U-N2	75.5 (1)
Cl1-U-Cl1	100.6 (1)	N1-U-N2	138.5 (2)

Structure and Bonding

Single crystals of 1 were obtained from slow cooling of a THF/toluene solution. However, these crystals were found to desolvate rapidly upon exposure to the glovebox atmosphere, turning into a green powder within seconds. A powder pattern analysis of this green solid shows that it is not isomorphous with $(C_8H_8)ThCl_2(THF)_2$ (**2**). The

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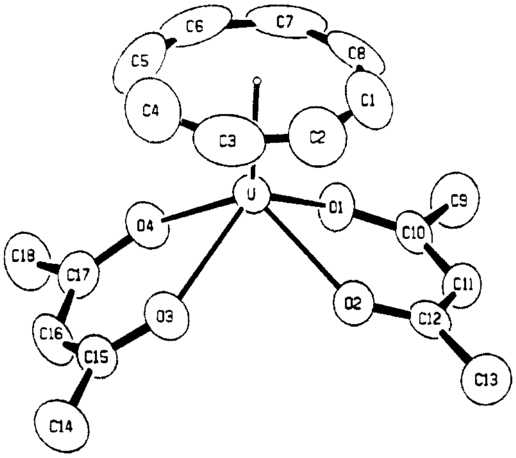

Figure 2. ORTEP diagram of $(C_8H_8)U(CH_3COCHCOCH_3)_2$ (4), with thermal ellipsoids at the 50% probability level.

infrared spectrum of **1** obtained by rapid mull preparation is virtually superimposable on the infrared spectrum of **2**, suggesting that both are isostructural. To avoid desolvation problems, the more strongly coordinating pyridine was chosen as a coordinating ligand (eq 10). Single crystals of **3** were obtained by slow cooling of a toluene solution. The ORTEP plot of the molecular structure of **3** is shown in Figure 1. Positional parameters are listed in Table I with selected bond distances and angles listed in Table II. A comparison of the structural parameters of **3** and the structurally related **2** is outlined in Table V. By the method of Raymond,[20] the average U–C bond distance minus the ionic radius of nine-coordinate U(IV) gives an effective ionic radius for the cyclooctatetraene ligand (r_{COT}) of 1.63 Å. This compares exactly with the r_{COT} value of 1.63 Å for the thorium half-sandwich compound. The effective chloride radii (r_{Cl}) for the uranium and thorium complexes show similar agreement. Thus, despite dissimilar reactivity the two compounds show essentially the same structural characteristics. It is also interesting to compare the average U–C bond distances in 9-coordinate **3** with those of 10-coordinate uranocene.[8c] The U–C bond length would be expected to decrease on going from a 10- to a 9-coordinate species, but in fact it increases from 2.647 Å in uranocene to 2.683 Å in **3**. An X-ray structure analysis was also performed on a single crystal of **4** obtained from slow cooling of a pentane solution to −20 °C. The ORTEP plot is shown in Figure 2, positional parameters are listed in Table I, and selected bond distances and angles are listed in Table III. The molecule assumes the expected C_{2v} symmetry, and the bond lengths and angles within the acetylacetonate moiety compare with those of other bidentate (acetylacetonato)metal complexes.[21] The average U–C bond distance of 2.694 Å is slightly longer than that found in **3** and again longer than the U–C bond distance in uranocene.

^{1}H NMR Spectroscopy

The ^{1}H NMR spectrum of **1** in THF-d_8 at 30 °C shows a single resonance at −31.8 ppm with a line width of 18 Hz corresponding to the [8]annulene ring protons. Replacement of the coordinating THF molecules with pyridine results in a small change in the ring proton resonance. In THF-d_8 at 30 °C, **3** shows a resonance at −31.6 ppm with a line width of 16 Hz. For complex **4**, the ring protons have a resonance at −29.6 ppm at 30 °C with a line width of 13 Hz. The line widths of the [8]annulene ring proton resonances of these half-sandwich complexes are much smaller than that of uranocene (−35.9 ppm, $w_{1/2}$ = 90 Hz). A variable-temperature ^{1}H NMR study of complexes **1** and **4** reveals no dynamic processes operating on the ^{1}H NMR time scale within the temperature range studied for either complex. The plots of chemical shift versus $1/T$ (Figure 3) are linear, exhibiting Curie–Weiss behavior.

Table III. Selected Bond Distances (Å) and Angles (deg) for $(C_8H_8)U(CH_3COCHCOCH_3)_2$ (4)

U–O2	2.313 (5)	O2–C12	1.273 (8)
U–O3	2.339 (5)	C10–C11	1.384 (10)
U–O4	2.310 (5)	C12–C11	1.387 (10)
U–C1	2.682 (8)	C10–C9	1.516 (10)
U–C2	2.699 (9)	C12–C13	1.504 (10)
U–C3	2.712 (9)	O4–C17	1.277 (8)
U–C4	2.703 (8)	O3–C15	1.256 (8)
U–C5	2.686 (9)	C17–C16	1.394 (10)
U–C6	2.697 (8)	C15–C16	1.376 (11)
U–C7	2.700 (8)	C17–C18	1.487 (11)
U–C8	2.675 (8)	C15–C14	1.502 (10)
O1–C10	1.270 (8)		
O2–U–Ct1	122.09	U–O3–C15	138.0 (5)
O3–U–Ct1	115.44	U–O4–C17	138.8 (5)
O4–U–Ct1	120.83	O1–C10–C9	115.9 (7)
O1–U–O2	72.0 (2)	O1–C10–C11	125.0 (7)
O1–U–O3	119.4 (2)	O2–C12–C13	116.1 (7)
O1–U–O4	78.2 (2)	O2–C12–C11	124.0 (7)
O2–U–O3	77.1 (2)	C10–C11–C12	123.7 (7)
O2–U–O4	116.7 (2)	O4–C17–C18	116.3 (7)
O3–U–O4	71.2 (2)	O4–C17–C16	122.4 (7)
U–O1–C10	133.5 (5)	O3–C15–C14	116.5 (8)
U–O2–C12	134.7 (4)	O3–C15–C16	123.6 (7)

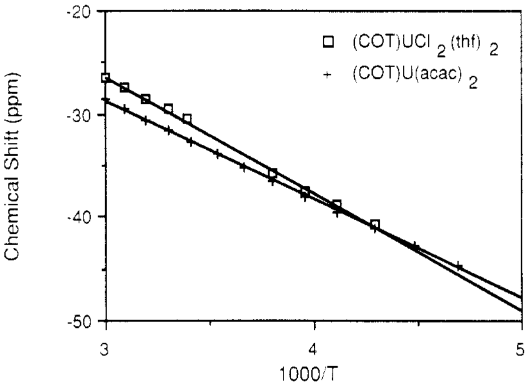

Figure 3. Chemical shift of ring protons vs 1000/T.

Experimental Section

Air- and water-sensitive compounds were handled under argon in a Vacuum Atmospheres glovebox or by use of standard Schlenk-line techniques. ^{1}H NMR spectra were obtained on UC Berkeley 200- and 250-MHz superconducting FT spectrometers equipped with Cryromagnets Inc. magnets and Nicolet Model 1280 data collection systems. For variable-temperature NMR spectra, temperatures were measured with a thermocouple mounted next to the NMR tube. Chemical shift values are reported in ppm with positive shifts reported for peaks downfield of TMS; J values are given in Hz. Peaks are referenced to internal standards. UV-visible spectra were obtained with an IBM Model 9240 ultraviolet–visible spectrophotometer. Values for λ_{max} are reported in nm. Infrared spectra were obtained with a Perkin-Elmer Model 297 infrared spectrophotometer. All values are reported in cm^{-1}. Tetrahydrofuran (THF), toluene, hexane, and diethyl ether were distilled from $LiAlH_4$ (LAH) or CaH_2 and then distilled from sodium benzophenone or potassium benzophenone. Cyclooctatetraene (COT) was obtained from BASF. COT was stirred over activated 4-Å sieves overnight and then vacuum transferred. Tetramethylethylenediamine (TMEDA) and pyridine were dis-

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tilled from CaH_2. All liquids were degassed in three freeze-pump-thaw cycles and stored over 4-Å sieves before use. NaH (60% oil dispersion) was Soxhlet-extracted with hexane overnight to remove oil and ground into a fine powder immediately before use. All other reagents, unless otherwise noted, were obtained from commercial suppliers and used without further purification.

([8]Annulene)bis((trimethylsilyl)cyclopentadienyl)uranium(IV), $(C_8H_8)(C_5H_4SiMe_3)_2U$. To $(Me_3SiC_5H_4)_3U$[22] (1.33 g, 2.05 mmol) dissolved in hexane (10 mL) was added COT (0.22 g, 2.1 mmol) dissolved in hexane (10 mL). The reaction mixture was stirred for 4 h, during which time the solution turned dark red and a dark precipitate formed. Filtering followed by extracting the solid with hexane (15 mL) and cooling the combined filtrates (−20 °C) yielded 0.26 g (41%) of dark green crystals, mp 140–145 °C. ^{1}H NMR (benzene-d_6, 34 °C): −37.18 (s, 8 H), −14.83 (s, 18 H), −11.29 (s, 4 H), 22.97 (s, 4 H). ^{13}C NMR (benzene-d_6, 28 °C): 271.6 (d, J = 168.5), 248.7 (d, J = 165.6), 233.0 (d, J = 159.7), −28.8 (q, J = 119). Mass spectrum: m/e 616 (M^+), 512 ($[M - C_8H_8]^+$), 479 ($[M - C_5H_5]^+$), 138 ($[C_5H_5 + 1]^+$), 104 ($[C_8H_8]^+$), 73 ($[Si(CH_3)_3]^+$). IR (Nujol): 1245 s, 1175 m, 1045 m, 898 w, 885 w, 863 w, 850 w, 830 s, 785 s, 745 w, 722 s, 685 w, 627 m, 620 m, 412 m, 336 m. Anal. Calcd for $C_{24}H_{34}Si_2U$: C, 46.70; H, 5.56. Found: C, 46.50; H, 5.82.

([8]Annulene)uranium(IV) Dichloride, $(C_8H_8)UCl_2$. To a solution of 5.00 g (13.2 mmol) of UCl_4 and 1.37 g (13.2 mmol) of COT in 100 mL of THF was added 1.0 g (42 mmol) of NaH. The mixture was stirred at room temperature for 24 h. To the product solution was added 5 mL of TMEDA, and the solution was stirred for 1 h. The dark red solution was filtered, and the THF and excess TMEDA were removed from the filtrate in vacuo. The resultant red solid was ground into a powder, heated under vacuum for several hours to remove coordinating THF, and then extracted for 18 h with hexane in a Soxhlet extractor and dried for several hours, yielding 3.85 g (70.1%). ^{1}H NMR (THF-d_8, 30 °C): −31.5 (s, 18 Hz). Visible (THF): 454 (ϵ 281), 500 (ϵ 249), 518 (ϵ 227), 570 (ϵ 206), 582 (ϵ 188), 596 (ϵ 174), 742 (ϵ 32). IR (Nujol): 1340 m, 1259 m, 1163 m, 1070 m, 1032 sh, 1008, s, 920 m, 900 m, 840 s, 805 s, 720 s, 660 m.

(*m*-Fluorophenyl)cyclooctatetraene. To 0.80 g (0.033 mol) of magnesium was added 5.25 g (0.03 mol) of *m*-fluorobromobenzene in 60 mL of THF. Maintenance of the reaction over 0.5 h required a total of 0.2 g of dibromoethane, after which the mixture was refluxed for 0.5 h. Titration showed a yield of 80% of Grignard reagent, which was cannulated into a mixture of 0.164 g of (1,3-bis(diphenylphosphino)propyl)nickel(II) dichloride,[23] 40 mL of ether, and 4.58 g (0.025 mol) of bromocyclooctatetraene. An additional 40 mL of THF was added, and the red-brown solution was stirred for 24 h, quenched with 1 M HCl, separated, and extracted with ether. The combined organic portions were washed with water and dried over $MgSO_4$. The solvent was removed, and the residue was distilled to give 2.59 g of yellow oil, bp 69–71 °C (0.2 mm). This material was purified by formation of the silver nitrate complex followed by decomposition of the complex with aqueous ammonia; yield 40%. ^{1}H NMR ($CDCl_3$, 90 MHz): 5.73–6.31 (m, 7 H), 6.87–7.32 (m, 4 H). ^{19}F NMR (δ relative to $CFCl_3$): +114.5 (m). Anal. Calcd for $C_{14}H_{11}F$: C, 84.81; H, 5.60. Found: C, 84.57; H, 5.66.

The ((*m*-Fluorophenyl)[8]annulene)uranium(IV) Dichloride Species $[(m\text{-}FC_6H_4)C_8H_7]UCl_2(THF)_x$. To 0.38 g (1.0 mmol) of UCl_4 and 0.20 g (1.0 mmol) of (*m*-fluorophenyl)cyclooctatetraene in 20 mL of THF was added 0.07 g (2.9 mmol) of NaH. After it was stirred for 12 h, the solution was filtered and THF was removed from the filtrate in vacuo. The resultant red oil was extracted into hexane and the extract cooled to afford 0.44 g (67%) of red crystals. ^{1}H NMR (THF-d_8, 30 °C): −33.9 (t, 2 H), −33.1 (d, 2 H), −30.9 (t, 2 H), −23.9 (t, 1 H), −4.7 (s, 1 H), −2.3 (s, 1 H), 2.6 (s, 1 H), 5.0 (s, 1 H).

Bis(pyridine)([8]annulene)uranium(IV) Dichloride, $(C_8H_8)UCl_2(NC_5H_5)_2$ (3). To a solution of 10 mL of pyridine and 100 mL of toluene was added 1.00 g (2.4 mmol) of $(C_8H_8)UCl_2$. After it was stirred for 24 h, the cherry red solution was filtered and the toluene and excess pyridine were removed from the filtrate in vacuo to yield 1.29 g (98%) of a red solid. ^{1}H NMR (THF-d_8, 30 °C): −31.6 (s, 16.2 Hz, 8 H), 6.4 (broad s, 4 H), 6.6 (m, 4 H), 7.4 (t, 4 H). Visible (toluene): 342, 446. IR (Nujol): 1350 m, 1310 s, 1225, m, 1080 m, 1023 s, 1004 sh, 970 s, 845 m, 800 m, 767 s, 698 m, 633 s, 550 m. Anal. Calcd for $C_{18}H_{18}N_2Cl_2U$: C, 37.85; H, 3.17; N, 4.90. Found: C, 37.48; H, 3.35; N, 5.02.

Table IV. Crystallographic Data and Data Processing Summary

	$(C_8H_8)UCl_2(NC_5H_5)_2$	$(C_8H_8)U(CH_3COCHCOCH_3)_2$
a, Å[a]	15.431 (3)	19.166 (4)
b, Å	7.744 (2)	10.312 (2)
c, Å	15.665 (3)	9.227 (2)
β, deg	105.69 (2)	97.10 (2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
V, Å^3	1802.2	1809.6
d(calcd), g/cm^3	2.105	1.983
Z	4	4
temp, °C	23.0	23.0
empirical formula	$C_{18}H_{18}N_2Cl_2U$	$C_{18}H_{22}O_4U$
F(000)	1064	1016
fw	571.29	540.40
color	red	orange
rfln rules	$h0l$, $l = 2n$; $0k0$, $k = 2n$	$h0l$, $h + l = 2n$; $0k0$, $k = 2n$
cryst size, mm	0.12 × 0.25 × 0.50	0.15 × 0.18 × 0.22
abs coeff, cm^{-1}	88.38	85.18
abs cor range	1.63–6.14	2.67–4.20
cryst decay cor range	0.98–1.02	0.94–1.03
2θ limits, deg	5.4–55.1	6.5–55.1
$(\sin \theta)/\lambda$; min, max	0.066, 0.651	0.080, 0.65
hkl limits	h, ± 20; k, −9 to +10; l, ±20	h, ±24; k, 0–13; l, −12 to +23
scan width (2θ), deg	$1.50 + 0.693 \tan \theta$	$1.30 + 0.693 \tan \theta$
no. of stds	3	3
no. of rflns between stds	250	250
variation of stds, %	1.32, 1.56, 1.11	1.96, 1.84, 2.03
no. of scan data	11614	8351
no. of unique rflns	4106	4184
R_{int}[b]	0.039	0.048
no. of nonzero weighted data	2638 ($F^2 > 2\sigma$)	2442 ($F^2 > 2\theta$)
p[c]	0.035	0.025
extinction k[d]	7.46×10^{-6}	1.22×10^{-4}
max extinction cor, %	11.7	34.1
no. of params	280	208
R (nonzero weighted data)[e]	0.030	0.030
R_w[f]	0.028	0.027
R (all data)	0.068	0.083
goodness of fit[g]	1.02	1.04
max shift/esd in least squares	0.017	0.0002
max, min in diff map, e/Å^3	1.52, −1.35	1.27, −1.24

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 31 reflections ($20 < 2\theta < 30°$) for $(C_8H_8)UCl_2(NC_5H_5)_2$ and 30 reflections ($20 < 2\theta < 29°$) for $(C_8H_8)U(CH_3COCHCOCH_3)$. [b] R_{int} = agreement factor between equivalent or multiply measured reflections = $\sum[I(hkl) - \langle I(hkl)\rangle]/\sum[\langle I(hkl)\rangle]$. [c] In the least squares, the assigned weights to the data are $4F^2[\sigma^2(F^2) + (pF^2)^2]^{-1}$. [d] The simple extinction correction has the form $F_o(\text{cor}) = (Il + kI)F_o$, where I is the uncorrected intensity and F_o is the observed scattering amplitude. [e] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [f] $R_w = \{\sum[w|F_o| - |F_c|]^2/\sum(wF^2)\}^{1/2}$. [g] $\sigma_1 = \{\sum(w[|F_o| - |F_c|]^2)/(\text{no} - \text{nv})\}^{1/2}$, where no is the number of observations and nv is the number of variables.

([8]Annulene)uranium(IV) Bis(acetylacetonate), $(C_8H_8)U(O_2C_5H_7)_2$ (4). To a solution of 1.00 g (2.4 mmol) of $(C_8H_8)UCl_2$ in 50 mL of THF at −78 °C was added via cannula a slurry of 0.62 g (5.08 mmol) of sodium acetylacetonate in 40 mL of THF. The mixture was stirred at −78 °C for 3 h and then warmed to room temperature and stirred an additional 14 h. The

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(23) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.

Table V. Structural Comparison of Uranium and Thorium Half-Sandwiches (Å)

	$(C_8H_8)UCl_2(NC_5H_5)_2$	$(C_8H_8)ThCl_2(OC_4H_8)_2$
M–C	2.684	2.72
M–Cl	2.644	2.686
r_M	1.05	1.09
r_{COT}	1.63	1.63
r_{Cl}	1.59	1.60

THF was removed in vacuo, and the orange solid was dissolved in 150 mL of toluene. The solution was filtered and then concentrated and cooled to afford 1.21 g (92%) of orange crystals. ^{1}H NMR (toluene-d_8, 30 °C): −29.6 (s, 13.1 Hz, 8 H), −10.0 (s, 6.6 Hz, 12 H), 10.2 (s, 3.5 Hz, 2 H). Visible (THF): 382 (sh), 458, 531 (sh), 572 (sh). IR (Nujol): 1355 s, 1288 s, 1201 m, 1145 m, 1075 m, 1010 m, 990 s, 984 sh, 870 m, 850 m, 805 m, 763 s, 710 m, 665 m, 650 s, 600 m, 580 m, 550 w. Anal. Calcd for $C_{18}H_2O_4U$: C, 40.01; H, 4.10. Found: C, 40.33; H, 3.98.

Crystal Structures. The air-sensitive crystals, sealed inside quartz capillaries, were mounted on a modified Picker FACS-1 automated diffractometer equipped with a molybdenum X-ray tube ($\lambda(K\alpha_1)$ = 0.709 30 Å) and an oriented graphite monochromator. A set of θ–2θ scanned intensities were collected and processed. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares. Anisotropic thermal parameters were assigned to all non-hydrogen atoms and isotropic thermal parameters to the hydrogen atoms. In the $(C_8H_8)UCl_2(NC_5H_5)_2$ complex, the hydrogen atomic parameters were all refined in an unrestrained manner. In the $(C_8H_8)UCl_2(CH_3COCHCOCH_3)_2$ complex, the hydrogen atomic parameters were restrained to their estimated values because the data would not support an unrestrained refinement. Atomic scattering factors for all atoms were taken from values in ref 24. The experimental details of the data collection and the least-squares refinements are tabulated in Table IV.

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Registry No. **1**, 117097-69-5; **3**, 127421-19-6; **4**, 127421-20-9; COT, 629-20-9; $(C_8H_8)(C_5H_4SiMe_3)_2U$, 127421-16-3; $(Me_3SiC_5H_4)_3U$, 99708-59-5; UCl_4, 10026-10-5; $(C_8H_8)UCl_2$, 127421-17-4; $[(m\text{-}FC_6H_4)C_8H_7]UCl_2$, 127421-18-5; $(C_8H_8)_2U$, 11079-26-8; $K_2C_8H_8$, 29590-71-4; $U[N(SiMe_3)_2]_3$, 69927-52-2; UCl_3, 10025-93-1; $(C_8H_8)UCl_2(PMe_3)$, 127421-21-0; $K_2(t\text{-}BuC_8H_7)$, 76058-27-0; $(C_8H_8)(t\text{-}BuC_8H_7)U$, 127445-40-3; $(t\text{-}BuC_8H_7)_2U$, 63230-70-6; $o\text{-}LiCH_2C_6H_4N(CN_3)_2$, 96454-49-8; $o\text{-}LiC_6H_4CH_2N(CH_3)_2$, 27171-81-9; (*m*-fluorophenyl)cyclooctatetraene, 127421-15-2; *m*-fluorobromobenzene, 1073-06-9; bromocyclooctatetraene, 7567-22-8; butylcyclooctatetraene, 13402-37-4; 1,1′-dibutyluranocene, 37274-12-7; sodium 8-quinolinolate, 2872-54-0.

Supplementary Material Available: Listings of crystal data, thermal parameters, H atom positional parameters, additional bond distances and angles, and least-squares planes and additional ORTEP views for 3 and 4 (10 pages); listings of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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[24] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2, pp 71–102.

Application of the Fenske–Hall Molecular Orbital Method to the Calculation of ^{13}C NMR Shifts in Organometallic Compounds: Correlation between Calculated σ_p Values and the Observed Chemical Shift, δ

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The nonparameterized Fenske–Hall molecular orbital (MO) approach and the Ramsey sum-over-states approximation are employed to establish that the sign and magnitude of the "paramagnetic" term of the nuclear shielding have excellent correlation with observed ^{13}C NMR shifts in a wide variety of shielding environments in six transition-metal organometallic compounds. In this context it is presumed that changes in the "diamagnetic" or localized charge density term are relatively unimportant in molecules of this type. A detailed analysis of the molecular orbital contributions in the prototype complex $(CO)_5CrC(OCH_3)(CH_3)$—a system in which shift values range over 300 ppm—yields an unambiguous picture of the key contributions to a particular ^{13}C resonance. An examination of individual terms in the sum-over-states expression demonstrates the importance of three factors: the symmetry requirements of the angular momentum operators, the energetic position of ligand MO's in relation to the metal d orbitals, and the energy difference between filled and unfilled MO's containing atomic character of the carbon atom of interest.

Introduction

The nuclear magnetic resonance experiment is unique in its ability to directly provide reaction mechanistic and kinetic data as well as stereochemical and conformational information. Despite the voluminous literature devoted to the experiment and its applications,[1] it has remained difficult to develop a reliable theoretical treatment for calculating shielding factors for large molecular systems of interest. Though the analysis of information such as coupling constants, line widths, and relaxation times is

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[1] For a comprehensive treatment of NMR spectroscopy see: Sohar, P. *Nuclear Magnetic Resonance Spectroscopy*; CRC Press: Boca Raton, FL, 1983; Vols. I–III.

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