for obvious reasons. Chloro coordination in **1** results from a *compelling* steric disposition of the chloro group. Thus a solution of the unsubstituted chelate (*i.e.*, H in place of Cl in **1**) in chlorobenzene shows *no* evidence for population of the triplet state brought about by *intermolecular* chloro coordination.

The bromo compound corresponding to **1** behaves in the same way except that the equilibrium concentration of the octahedral species is *more* in this case. A complete spectral and magnetic (including pmr[12]) characterization of the thermodynamics of such equilibria as shown by **1** and related chelates is in progress.

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(12) The chelates show isotropic proton contact shifts alternating in sign in the aromatic ring.

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

Sir:

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

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

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

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

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

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

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

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Direct Observation of Methyl-Substituted 7-Norbornadienyl and Bicyclo[3.2.0]heptadienyl Cations[1]

Sir:

An interesting facet of the chemistry of nonclassical carbonium ions deals with the rearrangements they can undergo.[2a] In this connection norbornadienyl cations have proved to be very instructive.[2b,c] Two monomethyl-substituted norbornadienyl cations, the 7-methyl ion I and the 2-methyl isomer II, and the rearrangement of I to II were reported recently.[2c] We now report direct observation of the two remaining monomethylnorbornadienyl cations, the 1-methyl species III and the 5-methyl isomer IV, as well as the rearrangement of III to IV. The new data elucidate further the quantitative relationships between the bicyclo[2.2.1]heptadienyl cations and their bicyclo[3.2.0] isomers.[2b]

For the successful generation of the 1- and 5-methyl-7-norbornadienyl cations III and IV we made use of the ring-expanding isomerization of the 2-methylbicyclo[3.2.0]heptadienyl cation VI to its bicyclo-

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(1) Research supported by the National Science Foundation.

(2) (a) S. Winstein, *Experientia Suppl.*, 137 (1955); L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960); (b) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350 (1967); (c) M. Brookhart and R. K. Lustgarten, *ibid.*, **89**, 6352 (1967).