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.

Acknowledgment. This research was supported in part by National Science Foundation Grant No. 6125.

(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]

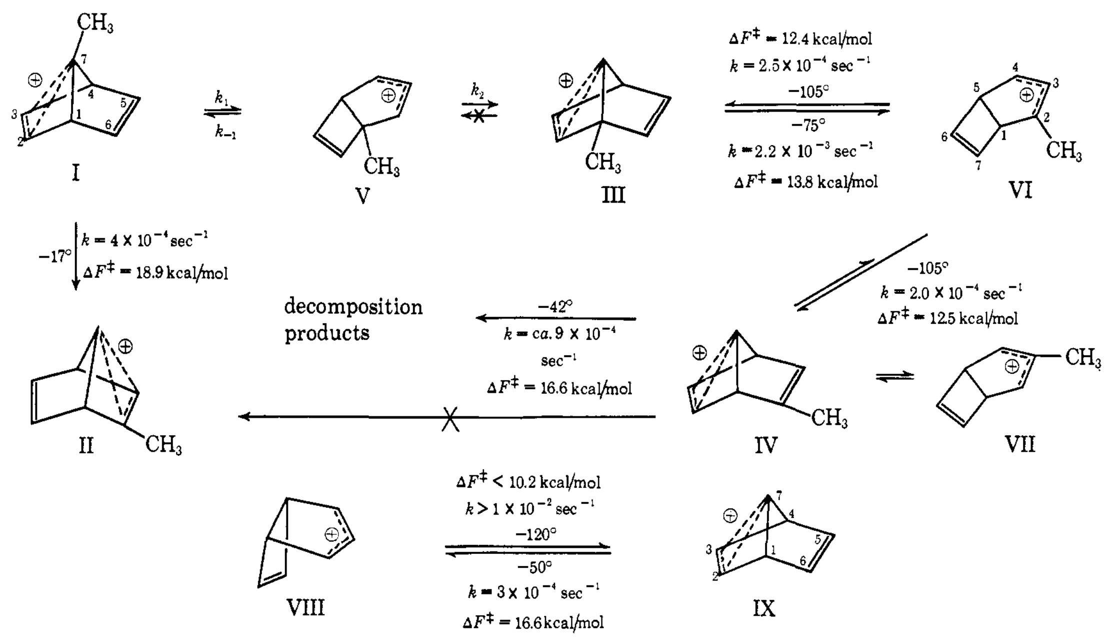
Sir:

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-methyl-bicyclo[3.2.0]heptadienyl cation VI to its bicyclo-

(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).



[2.2.1] isomers. Such ring expansion had already been observed[2b] in the case of the unmethylated parent bicyclo[3.2.0]heptadienyl cation VIII which equilibrates with its bicyclo[2.2.1] isomer IX in the rapid degenerate five-carbon scrambling of C_7, C_1, C_6, C_5, and C_4 encountered with the parent 7-norbornadienyl cation IX. The precursor for ion VI was the tertiary alcohol[3] X, prepared at least 95% epimerically pure (vpc) by addition of methyllithium to bicyclo[3.2.0]heptadienone.[4] Extraction of X from CD_2Cl_2 into FSO_3H-SO_2ClF (1:2, v/v) at −130° cleanly generated ion VI. The nmr spectrum[5] of the 2-methylbicyclo[3.2.0] cation VI, recorded at −105°, displays one-proton doublets (J = 4 cps) at τ −0.20 and 1.90 for H_4 and H_3, respectively, two broad two-proton singlets at τ 4.88 and 3.03, assigned to the bridgehead and vinyl protons, respectively, and a three-proton methyl singlet at τ 6.88. The one-proton resonances at τ −0.20 and 1.90 are very characteristic of protons on the terminal and central allylic carbons, respectively, in cyclopentenyl cations.[6]

At −105°, the [3.2.0] cation VI isomerizes quantitatively to a 55:45 mixture of 1-methyl- and 5-methylnorbornadienyl cations III and IV. The first-order rate constant for disappearance of VI is *ca.* 4.5×10^{-4} sec^{-1}. When the solution was warmed to −75°, cation III rearranged fairly completely to the 5-methyl ion IV with a first-order rate constant equal to 9.8×10^{-4} sec^{-1}. At −42° IV decomposed with a rate constant equal to 9×10^{-4} sec^{-1} with no detectable formation of the 2-methyl ion II or any other cations.

Another precursor was employed for the generation of the 5-methyl ion IV, namely 7-methyl-7-quadricyclanol (XI). Extraction of this alcohol into FSO_3H-SO_2ClF at −120° gives an nmr spectrum identical with that for IV obtained from precursor X. Ion IV is indeed the expected product of a Richey–Story rearrangement[7] of the 7-methyl-7-quadricyclyl cation. This quadricyclic ion was not observed, even when the acid solution was monitored at −100° immediately (2 min) after generation of the ion at −120°.

Structures were easily assigned to the 1- and 5-methylnorbornadienyl ions III and IV on the basis of nmr spectra. The structure of IV was confirmed by quenching in methanol–sodium bicarbonate at −78° to give the *syn*-methyl ether[8] XII whose nmr spectrum is similar to but not identical with that of the *anti*-methyl ether[2c] previously obtained from quenching of II.

Regarding the mechanism of isomerization of the 1-methyl- to the 5-methylnorbornadienyl cation (III → IV), this undoubtedly occurs by sequential ring contraction and ring expansion,[2b] *i.e.*, III $\rightleftharpoons$ VI → IV. The present results allow us to exclude one of the mechanisms previously[2c] considered for the rearrangement of the 7-methyl- to the 2-methylnorbornadienyl ion (I → II). This would involve ring contractions and expansions which convert I successively to V, III, VI, and finally IV, which then might lead to II by "bridge flipping." Since the 5-methyl ion IV has been shown to decompose rather than undergo a bridge flip,[9] this mechanism for rearrangement of I to II can be excluded.[10] Since the I → II transformation[2c, 12] at −17° proceeded in *ca.* 60% yield, *ca.* 40% of I decomposing to give broad, nondescript absorptions, it is possible that 40% of I does proceed to IV by way of V,

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(3) High-resolution mass spectrum: calcd for $C_8H_{10}O$, 122.07316; found, 122.07283.

(4) P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **87**, 1623 (1965).

(5) All chemical shifts relative to internal CH_2Cl_2 at τ 4.70.

(6) (a) T. S. Sorenson, *Can. J. Chem.*, **42**, 2768 (1964); **43**, 2744 (1965); (b) Y. Lin, Ph.D. Thesis, University of California at Los Angeles, 1967, p 377.

(7) (a) H. G. Richey and N. C. Buckley, *J. Am. Chem. Soc.*, **85**, 3057 (1963); (b) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964).

(8) High-resolution mass spectrum: calcd for $C_9H_{12}O$, 136.08881; found, 136.08812.

(9) The decomposition of IV establishes a lower limit to $\Delta F^{\ddagger}$ for bridge flipping of IV to II at 18.0 kcal/mol. (The lower limit to bridge flipping of IX is 19.6 kcal/mol.)[2c]

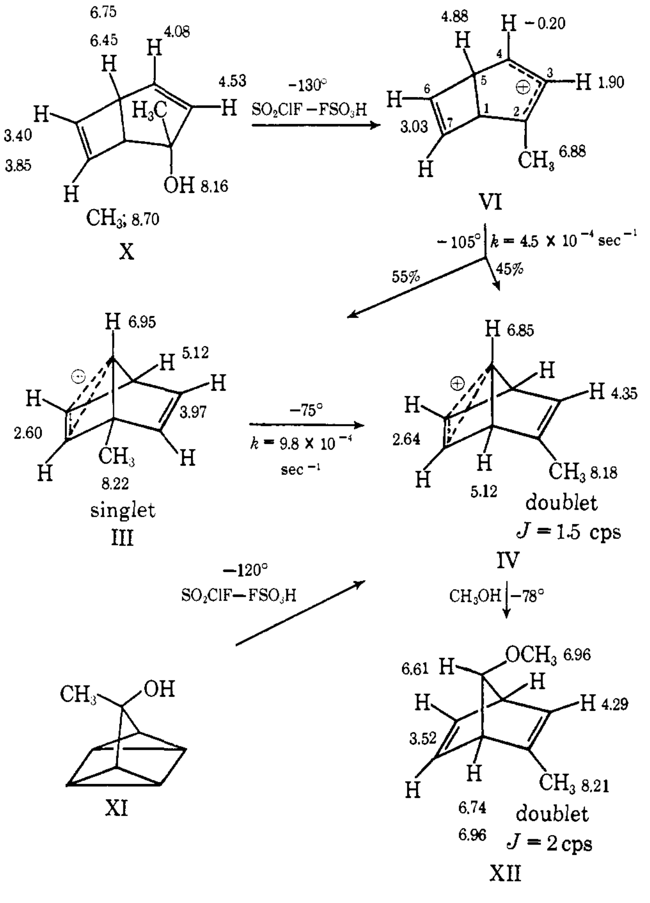
(10) Two other plausible mechanisms remain. One[2c] is the 1,2 shift of C_6 from C_1 to C_2. Another involves a three-carbon scrambling of C_7, C_2, and C_3, akin to the one observed by Hogeveen in a hexamethylbicyclo[2.1.1]hexenyl cation.[11] With suitable labeling, the two mechanisms can be differentiated.

(11) H. Hogeveen and H. C. Volger, *Rec. Trav. Chim.*, **87**, 385 (1968); **87**, in press.

(12) Since the conversion of I to II was originally studied in pure FSO_3H, the experiment was repeated in the FSO_3H-SO_2ClF medium in order to check on possible solvent effects. The nmr spectra of I and II and the rates of bridge flipping of I and rearrangement of I to II were the same in FSO_3H-SO_2ClF as in FSO_3H.

III, and VI, with IV, according to the present results, decomposing rapidly at −17°. Energetically, this is quite plausible.[13]

The present data make available rate constants for interconversion of the 1-methylnorbornadienyl ion III and the 2-methylbicyclo[3.2.0]heptadienyl cation VI, as well as an estimate of the equilibrium constant for VI ⇌ III. The rate constant for the III → VI ring contraction is considerably larger ($\Delta F^{\ddagger}$ = 13.8 kcal/mol) than for the ring contraction of the parent norbornadienyl ion IX ($\Delta F^{\ddagger}$ = 16.6 kcal/mol), while the rate constant for the VI → III ring expansion is considerably smaller than for the VIII → IX ring expansion of the parent [3.2.0] ion. The latter process was too rapid to permit recording of the nmr spectrum of ion VIII at −78° before it isomerized to IX.[2b] We have now made the same observation at −120°, so that $\Delta F^{\ddagger}$ for the VIII → IX ring expansion must be less than 10.2 kcal/mol. These effects of the methyl group in III and VI are obviously associated with the much greater stabilizing effect of the methyl group in the terminal allylic position of VI than in the bridgehead position of III. At −100° the equilibrium constant for VI ⇌ III is *ca.* 60, while it is $>1.2 \times 10^8$ in the parent case VIII ⇌ IX.



The 1-methylnorbornadienyl ion III can be visualized to ring contract to the 1-methylbicyclo[3.2.0] ion V, but this process is apparently not competitive with the III → VI ring contraction.[14] If V were formed, it would be expected to give I at least as rapidly as III; however, I is not observed. Since the methyl group remains on the bridgehead in the III → V ring contraction, the rate of the latter would be expected to resemble that of the parent IX → VIII process ($\Delta F^{\ddagger}$ = 16.6). Thus, it is energetically consistent that III → V, with eventual formation of I, does not compete with III → VI ($\Delta F^{\ddagger}$ = 13.8).

Regarding relative stability of the different methyl-substituted norbornadienyl cations, the equilibrium between the 7-methyl ion I and its 2-methyl isomer II favors II by a factor of at least 50, and that between the 1-methyl ion III and its 5-methyl isomer IV favors IV[15] by a factor of at least 20. Because of the positions of the methyl substituent, II would be expected to be the most stable and III the least stable of the four [2.2.1] ions. However, there remains the interesting, still unanswered, question regarding the relative stability of I with a 7-methyl group and IV with a methyl substituent on the "unbound" olefinic group.

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[13] $\Delta F^{\ddagger}$ for ring contraction in the parent system[2b] IX is 16.6 kcal/mol. If this value is increased by the 7-methyl group in I to *ca.* 19 kcal/mol, ring contraction of I would become only competitive with rearrangement to II ($\Delta F^{\ddagger}$ = 18.9kcal/mol). The value of $\Delta F^{\ddagger}$ for I → IV depends, of course, on the partitioning of V, *i.e.*, on the ratio k_2/k_{-1}. This ratio is not expected to be prohibitively small.

(14) The present results give no information regarding still another ring contraction–ring expansion, namely IV → VII. While such ring contraction would be disclosed by suitable labeling of IV, one would expect IV → VII to be considerably slower than IV → VI or III → VI.

(15) Judging by the τ 3.97 signal in the nmr spectrum of III, *ca.* 4% of the latter ion remains at equilibrium with IV at −75°. This has not yet been confirmed by quenching experiments. On the basis of 4% of III at equilibrium with IV, the rate constant for the IV → VI ring contraction is *ca.* 10^{-4} sec^{-1} at −75°.

(16) (a) National Institutes of Health Postdoctoral Fellow; (b) National Science Foundation Postdoctoral Fellow.

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syn-7-Bromobenzonorbornadiene. Synthesis and Solvolytic Reactivity

Sir:

The chemistry of benzonorbornadiene (**1**) and its derivatives has attracted considerable attention recently.[1] Whereas the solvolytic reactivity of several benzonorbornenyl and benzonorbornadienyl substrates has been reported,[2] that of the interesting *syn*-7-benzonorbornadienyl system has not.[3]

We wish to report the synthesis of the *syn*-7-bromide **6** and its solvolytic reactivity in 80% ethanol. Treatment of **1** in carbon tetrachloride with 1,2-dibromotetrachloroethane using a 275-W sunlamp quantitatively yielded a mixture of *trans*-2,3-dibromide (**2**, 89%), together with the *exo-cis* isomer (11%). The *trans* isomer was converted to *syn*-7-bromo-*exo*-2-acetoxybenzonorbornene (**3**, mp 101–102°) with silver acetate in acetic acid. Hydrolysis of **3** with methyl Grignard reagent to the bromohydrin **4** (mp 126–128°), followed by oxidation with chromium trioxide in pyridine, gave the *syn*-7-bromo ketone **5** (mp 135°). Irradiation of a rotating thin film of the lithium salt of the tosylhydrazone from **5** at 5 mm with a 275-W sunlamp

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(1) For a recent paper with many additional references, *cf.* M. M. Martin and R. A. Koster, *J. Org. Chem.*, **33**, 3428 (1968).

(2) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968), gives a well-documented summary.

(3) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727, 3738 (1967), have mentioned briefly the *syn*-7 chloride and its nmr and mass spectra, with further details promised.