Actinide Organometallic Chemistry

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The actinides are the elements occupying the final row of the periodic table—that in which the 5f shell is filled. The name actinide is derived from the Greek aktinos, meaning beam or ray. The actinide elements play an essential role in nuclear energy production. In addition, a large number of other technical applications exists, including catalysis.[1]

Interest in the organometallic chemistry of the actinide elements dates back to the Manhattan project and to the search for volatile compounds to be agents for uranium isotope separation. Unsuccessful attempts to synthesize species such as tetramethyluranium characterize the early history of organoactinide chemistry.[2] Though the groups of Wilkinson[3] and Fischer[4] reported π-bonded cyclopentadienyluranium and -thorium complexes some years ago, it was not until the last half decade that activity and excitement in this field began to quicken.[5] The report of the novel complex "uranocene", $(\eta^8\text{-}C_8H_8)_2U$, is likely an important reason.[6]

The purpose of this Account is to review some of the recent organoactinide chemistry done at Northwestern University. Interest in this Laboratory grew out of some properties of actinide ions which we considered to be unique. First, these ions exhibit high coordination numbers and novel coordination geometries, unknown or unusual for d transition metals. Second, these metals have available 5f valence orbitals which may in some cases possess the appropriate energy and spatial extension to be of chemical significance. These characteristics suggested that organoactinides might display interesting properties both as reagents and as catalysts. In addition, we were dismayed by how little was known about actinide organometallic chemistry and were curious as to whether the reaction patterns would most resemble those of transition elements or main group elements. For these reasons we set out to explore the chemical and physicochemical properties of new molecular systems involving the coordination of organic ligands to actinide ions. An essential part of this program was to attempt to explore new ligand systems and to relate chemical reactivity to coordination pattern and electronic configuration.

σ-Bonded Organometallics

The findings of earlier workers regarding uranium tetraalkyls apparently led to the assumption that there was something intrinsically unstable about actinide-to-carbon σ-bonded organometallics. It seemed to us (and to others as we later discovered) that this might not be so, and that proper choice of supporting ligands might stabilize such a two-electron linkage, which is a fundamental unit of organometallic chemistry. Thus, the reaction of $(\eta^5\text{-}C_5H_5)_3UCl$ with Grignard and lithium reagents yields a large series of compounds (eq 1).[7-9]

$$(C_5H_5)_3UCl \xrightarrow{\text{RMgX or RLi}} (C_5H_5)_3U\text{–}R \qquad (1)$$

R = CH_3, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9, neopentyl, allyl, 2-methylallyl, vinyl, C_6H_5, C_6F_5, ferrocenyl, $C_2C_6H_5$, p-tolyl, benzyl, 2-*cis*-2-butenyl, 2-*trans*-2-butenyl

The molecular structure of one complex is shown in Figure 1.[10] Though highly sensitive to air, these compounds possess rather surprising thermal stability. For example, the half-life in toluene solution of the R = n-butyl compound is over 1000 h at 97 °C.[7b] The U(IV) series is a $5f^2$ valence system; it was also of interest to explore the comparable chemistry of actinides with other electronic configurations. Thorium(IV) ($5f^0$) also yields a series of alkyl and alkenyl complexes (eq 2).[11] These compounds possess even higher thermal stability than the $(C_5H_5)_3U$–R analogues. The R = n-butyl complex has a half-life in toluene solution of ca. 100 h at 167 °C!

$$(C_5H_5)_3ThCl \xrightarrow{\text{RMgX or RLi}} (C_5H_5)_3Th\text{–}R \qquad (2)$$

R = n-C_3H_7, i-C_3H_7, n-C_4H_9, neopentyl, cyclohexyl, allyl, 2-*cis*-2-butenyl, 2-*trans*-2-butenyl

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(1) See, for example: (a) M. Bruzzone, A. Mazzei, and G. Giuliani, *Rubber Chem. Technol.*, **47**, 1175 (1974); (b) G. Lugli, A. Mazzei, and S. Poggio, *Makromol. Chem.*, **175**, 2021 (1974); (c) SNAM Progetti, Belgian Patent 791 709 (1972); (d) K. Ziegler, H. Breil, E. Holzkamp, and H. Martin, U.S. Patent 3 257 332 (1966); (e) K. Ziegler and H. Breil, German Patent 1 008 916 (1957).

(2) (a) H. Gilman, R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. F. Nobis, J. R. Thirtle, H. L. Yale, and F. A. Yoeman, *J. Am. Chem. Soc.*, **78**, 2890 (1956); (b) J. J. Katz, private communication.

(3) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956).

(4) (a) E. O. Fischer and Y. Hristidu, *Z. Naturforsch.*, **176**, 275 (1962); (b) E. O. Fischer and A. Triebner, *ibid.*, **176**, 276 (1962).

(5) For review articles see: (a) E. Cernia and A. Mazzei, *Inorg. Chim. Acta*, **10**, 239 (1974); (b) B. Kanellakopulos and K. W. Bagnall, *MTP Int. Rev. Sci., Inorg. Chem., Ser. One*, **7**, 299 (1972); (c) R. G. Hayes and J. L. Thomas, *Organomet. Chem. Rev., Sect. A*, **7**, 1 (1971); (d) H. Gysling and M. Tsutsui, *Adv. Organomet. Chem.*, **9**, 361 (1970); (e) E. C. Baker, G. W. Halstead, and K. N. Raymond, *Struct. Bonding (Berlin)*, **25**, 23 (1976).

(6) U. Müller-Westerhoff and A. D. Streitwieser, *J. Am. Chem. Soc.*, **90**, 7364 (1968).

(7) (a) T. J. Marks and A. M. Seyam, *J. Am. Chem. Soc.*, **94**, 6545 (1972); (b) T. J. Marks, A. M. Seyam, and J. R. Kolb, *ibid.*, **95**, 5529 (1973).

(8) (a) A. E. Gebala and M. Tsutsui, *Chem. Lett.*, 775 (1972); (b) A. E. Gebala and M. Tsutsui, *J. Am. Chem. Soc.*, **95**, 91 (1973); (c) M. Tsutsui, N. Ely, and A. Gebala, *Inorg. Chem.*, **14**, 78 (1975).

(9) G. Brandi, M. Brunelli, G. Lugli, and A. Mazzei, *Inorg. Chim. Acta.*, **7**, 319 (1973).

(10) (a) G. W. Halstead, E. C. Baker, and K. N. Raymond, *J. Am. Chem. Soc.*, **97**, 3049 (1975). (b) $(C_5H_5)_3UC_2C_6H_5$: J. L. Atwood, C. F. Hains, Jr., M. Tsutsui, and A. E. Gebala, *J. Chem. Soc., Chem. Commun.*, 452 (1973).

(11) T. J. Marks and W. A. Wachter, *J. Am. Chem. Soc.*, **98**, 703 (1976).

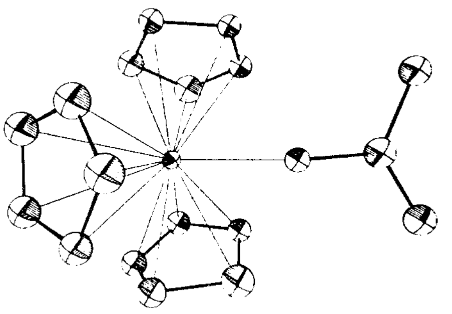


Figure 1. The molecular structure of (η^5-$C_5H_5)_3U$(2-methylallyl) (from ref 10a).

Variable-temperature magnetic susceptibility studies of the $(C_5H_5)_3UR$ compounds indicate appreciable distortion of the 5f shell from a tetrahedral environment.[7b] Solution nuclear magnetic resonance studies have provided additional information on electronic structure as well as molecular configuration and dynamics. The NMR spectra of paramagnetic U(IV) compounds generally exhibit large displacements of resonances from diamagnetic positions due to contact and dipolar interactions.[7b,12] The former quantity is an electron–nuclear hyperfine term reflecting the distribution of unpaired 5f electron spin density through the molecule,[13] while the latter interaction arises from anisotropy in the magnetic susceptibility of the molecule.[14] An exempletive spectrum is shown in Figure 2. The sharpness of the lines reflects extremely rapid electron spin relaxation and is reminiscent of lanthanide shift reagents. It has proven possible to separate the contact and dipolar contributions to the various experimentally observed shifts.[7b] The former quantities are surprisingly large in magnitude and indicate an appreciable hyperfine interaction; the signs indicate the shift arises either from donation of ligand electron density into empty or partially filled actinide orbitals or from polarization of the ligand orbitals by the unpaired 5f electrons.[15] The distribution of unpaired spin density in the ligands parallels that in alkyl radicals, and it is possible to roughly predict contact shifts via SCF INDO/2 molecular orbital calculations.[7b] We find no evidence in these or other U(IV) systems (vide infra) of appreciable back-donation of 5f electron density into empty ligand orbitals. It should be emphasized that, besides providing a clearer physical insight into bonding in organoactinides, the above considerations are extremely useful in guiding synthetic research since they aid in unraveling the complex NMR spectra exhibited by some reaction mixtures.

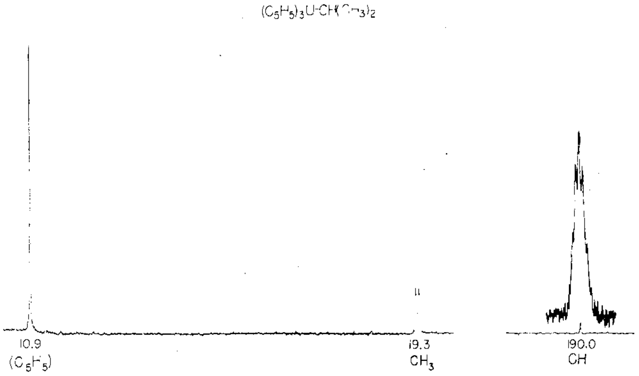
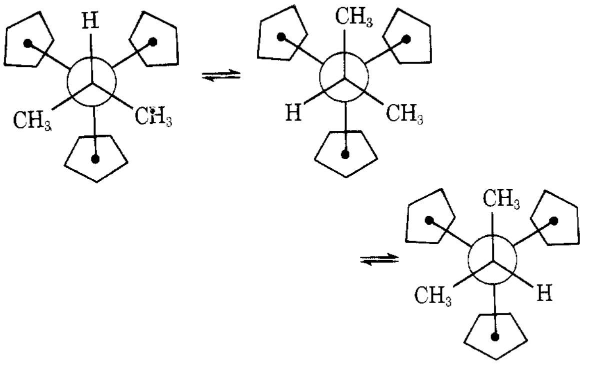


Figure 2. Proton NMR spectrum of (η^5-$C_5H_5)_3U$(i-Pr) at 90 MHz. The calibration is in parts per million upfield of the solvent, benzene. The methine resonance was recorded in the field-sweep mode, hence the x and y scales are different from the low-field portion.

Nuclear magnetic resonance spectra also provide information on molecular structure and the shape of potential energy surfaces which describe excursions from the ground-state configuration. For example, variable-temperature ^1H NMR spectra of $(C_5H_5)_3U(i\text{-Pr})$ in the C_5H_5 region (Figure 3) provide evidence that considerable steric congestion occurs about the uranium ion. This will later be seen to be of chemical significance. The barrier to rotation (eq 3) about the uranium-to-carbon σ bond is on the order of 10 kcal/mol. Variable-temperature ^1H NMR studies of $(C_5H_5)_3U$(allyl) and $(C_5H_5)_3Th$(allyl) reveal that both have η^1-allyl instantaneous structures and that both undergo rapid sigmatropic rearrangement[16] (eq 4) at room temperature. Surprisingly, within experimental error both uranium and thorium complexes have identical activation energies for this process, ca. 8 kcal/mol. These results contrast with the tetraallyls of thorium and uranium which have η^3-allyl ground-state geometries.[5]



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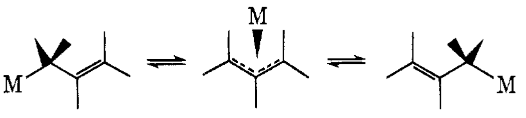

(4)

Both η^5 and η^3 linkages suffer alcoholysis in the $(C_5H_5)_3MR$ series. The rates are several orders of magnitude higher for M = Th, presumably indicating greater ionic character in the bonding. There is no evidence that the actinide–alkyl bond in these complexes is appreciably nucleophilic. No addition to ke-

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[12] R. D. Fischer in "Chemical Applications of NMR in Paramagnetic Molecules", G. N. La Mar, W. D. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N.Y., 1973, Chapter 13.

[13] The pragmatic approximation that J is a valid quantum number leads to:[7b,12]

$$\frac{\Delta H_i^{\text{con}}}{H} = -\frac{A_i(g_J - 1)\chi}{N g_J \beta g_N \beta_N}$$

where A_i is the electron-nuclear hyperfine coupling constant for nucleus i, χ is the magnetic susceptibility, and the other terms are as usual.[12]

[14] (a) W. D. Horrocks, Jr., ref 12, Chapter 4. (b) For axial symmetry,

$$\frac{\Delta H_i^{\text{dip}}}{H} = -\frac{1}{3N}[\chi^{\parallel} - \chi^{\perp}] \left\langle \frac{3\cos^2\theta_i - 1}{r_i^3} \right\rangle$$

where θ_i and r_i define the geometric factor for nucleus i.

[15] (a) G. N. La Mar in ref 12, Chapter 3; (b) A. Streitwieser, Jr., D. Dempf, G. N. La Mar, D. G. Karraker, and N. Edelstein, *J. Am. Chem. Soc.*, **93,** 7343 (1971); (c) J. Owen and J. H. M. Thornley, *Rep. Prog. Phys.*, **29,** 675 (1966).

[16] K. Vrieze in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, Chapter 11.

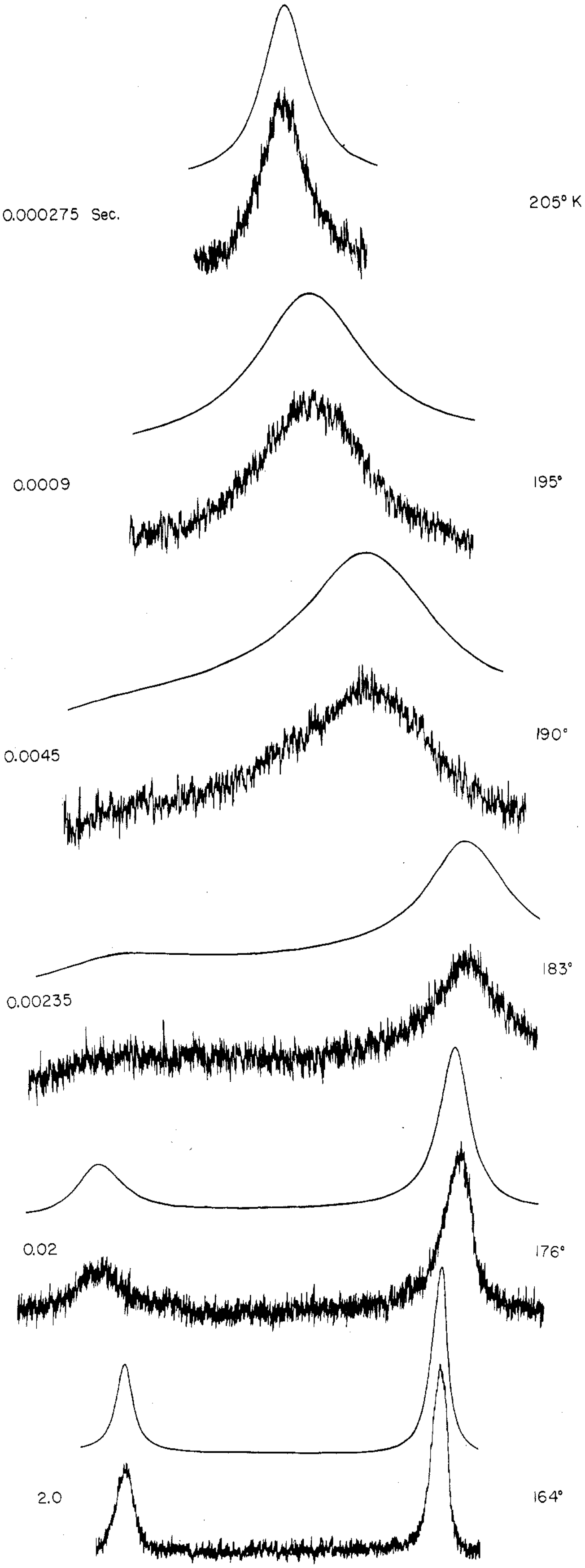


Figure 3. Variable-temperature 90-MHz ^{1}H NMR spectra of (η^5-$C_5H_5)_3U(i$-Pr) in the C_5H_5 region. Computer-generated spectra are for the mean preexchange lifetimes indicated (from ref 7b).

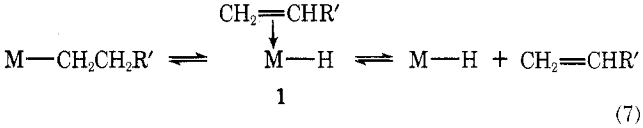
tones or to carbon dioxide is observed in the course of several hours.

$$(C_5H_5)_3MR \xrightarrow{R'OH} (C_5H_5)_3MOR' + RH \quad (5)$$

$$(C_5H_5)_3MR \xrightarrow{R'OH} (C_5H_5)_2M(R)OR' + C_5H_6 \quad (6)$$

$$M = Th, U$$

The remarkable thermal stability of the (C_5H_5)$_3$MR compounds in comparison with what had been reported for the corresponding tetraalkyls prompted us to undertake a mechanistic investigation of those factors which stabilize actinide-to-carbon σ bonds. One surprising result of this study was that the commonly observed β-hydrogen elimination pathway[17] (eq 7, sometimes followed by eq 8) was not important in $(C_5H_5)_3$MR thermolysis.



$$\mathrm{M{-}CH_2CH_2R'} \rightleftharpoons \underset{\mathbf{1}}{\overset{\mathrm{CH_2{=}CHR'}}{\overset{\downarrow}{\mathrm{M{-}H}}}} \rightleftharpoons \mathrm{M{-}H} + \mathrm{CH_2{=}CHR'} \quad (7)$$

$$\mathrm{M{-}H} + \mathrm{M{-}CH_2CH_2R'} \longrightarrow 2\mathrm{M} + \mathrm{CH_3CH_2R'} \quad (8)$$

Rather, elimination of RH was observed for both M = Th[11] and U.[7b] The principal source of the H was shown to be the cyclopentadienyl ring; the elimination was found by a variety of kinetic and labelling experiments to occur intramolecularly and with retention of configuration at the carbon originally bound to M[18]. There is no evidence that this pathway involves free R· radicals.

The above observations are in marked contrast to those for the thermally unstable products of eq 9[19] which, based upon analogous reactions,[5] are presumed to be actinide tetraalkyls.

$$MCl_4 + 4RLi \rightarrow [R_4M] \rightarrow \text{products} \quad (9)$$

$$M = Th, U$$

When a β hydrogen is present in the alkyl group, comparable quantities of alkane and alkene result from thermolysis, consistent with the sequence of eq 7 and 8. The difference in behavior of the $(C_5H_5)_3$MR and R_4M series is explicable in terms of saturation (and immobilization) of the coordination sphere by the bulky η^5-cyclopentadienyl ligands. This crowding was evident in the above-mentioned structural and spectral studies and is expected to destabilize intermediates such as **1** and to stabilize the complex with respect to β elimination. In d transition-metal chemistry, there is considerable evidence that β elimination requires a vacant coordination site on the metal or prior dissociation of a ligand.[17,20] The actinide tetraalkyls are coordinatively unsaturated, and it is not surprising that β elimination is facile. Since the tetraalkyls without β hydrogens are also less thermal-

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(17) (a) G. Wilkinson, *Science*, **185**, 109 (1974); (b) P. J. Davidson, M. F. Lappert, and R. Pearce, *Acc. Chem. Res.*, **7**, 209 (1974); (c) P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 171 (1973); (d) M. C. Baird, *J. Organometal. Chem.*, **64**, 289 (1974); (e) sometimes eq 8 is intramolecular.

(18) For the 2-*cis*-2-butenyl and 2-*trans*-2-butenyl derivatives.

(19) (a) T. J. Marks and A. M. Seyam, *J. Organometal. Chem.*, **67**, 61 (1974); (b) T. J. Marks, A. M. Seyam, and W. A. Wachter, unpublished results; (c) see also: R. Andersen, E. Carmona-Guzman, K. Mertis, E. Sigurdson, and G. Wilkinson, *J. Organometal. Chem.*, **99**, C19 (1975), for work on uranium(IV) hexaalkyl dianions.

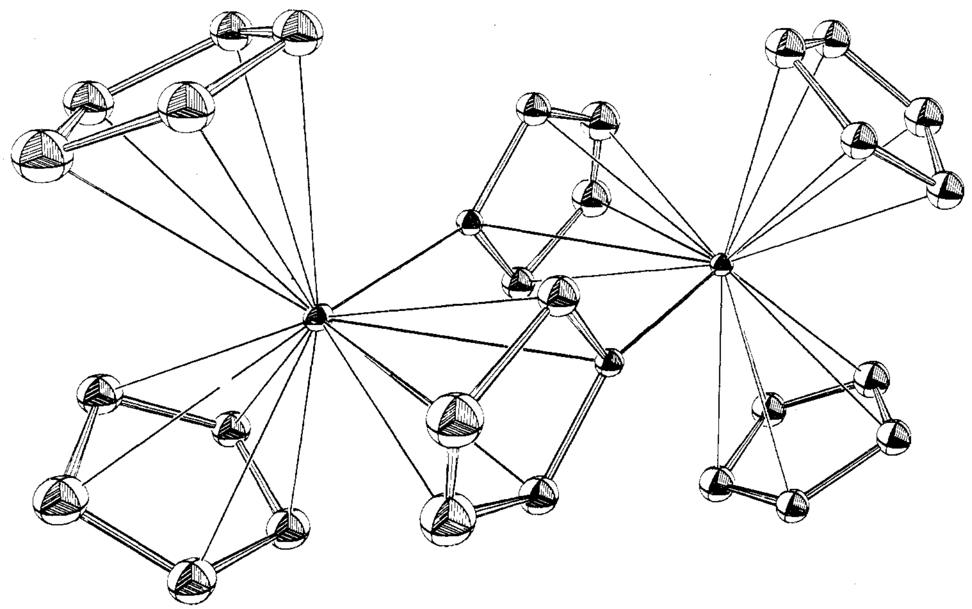
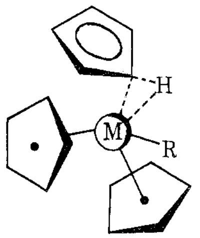


Figure 4. The molecular structure of the $(\eta^5\text{-}C_5H_5)_3ThR$ thermolysis product $[(\eta^5\text{-}C_5H_5)_2Th(\eta^5{:}\eta^1\text{-}C_5H_4)]_2$ (from ref 22).

ly stable than the corresponding triscyclopentadienyls, it appears that coordinative congestion hinders other thermolysis pathways as well. Interestingly, these latter tetraalkyls thermolyze, as do the triscyclopentadienyls, by forming RH in a predominantly nonradical reaction. Such a process has also been observed for homoleptic d transition metal alkyls.[21]

The metal-containing products of $(C_5H_5)_3MR$ thermal decomposition are of obvious mechanistic interest and importance. In the case of thorium, a colorless crystalline product precipitates from solution (at +167 °C). This product was shown by spectroscopic (infrared and mass) and chemical analysis to have the composition $[(C_5H_5)_2Th(C_5H_4)]_2$; Figure 4 presents the x-ray structural results.[22] Operationally, the molecule is derived from $(C_5H_5)_3ThR$ by extrusion of RH and dimerization of the resulting species. Chemically, metalation of the $\eta^5\text{-}C_5H_5$ rings has occurred, yielding a μ-di($\eta^5{:}\eta^1$-cyclopentadienyl) configuration reminiscent of "niobocene".[23] The uranium analogue has not yet been obtained in crystalline form; however, spectral and chemical analyses suggest that it too is a polymetallic $\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5H_4$ complex.[19b]

The experimental observations on $(C_5H_5)_3MR$ thermal decomposition evoke two questions: (a) how does RH formation take place and (b) how is the final organometallic product formed? The first question, in view of our data, can best be answered either by transfer of a hydrogen to the actinide (**2**), forming a metal hydride which subsequently undergoes reductive elimination of RH, or by direct transfer of a hydrogen (presumably a proton) to the R group (**3**). The first pathway is electronically analogous to the metalation of arenes by low-valent d transition-metal complexes, which is believed to proceed via an initial multihapto arene complex.[24] The intramolecular reductive elimination of alkane is likely to be stereospecific.[17,25] The second pathway is an intramolecular interligand proton transfer, analogous to the protonation of the M–R bond in eq 5. The latter kinds of reactions are generally stereospecific.[26] That $(C_5H_5)(C_5D_5)_2U(n\text{-Bu})$ exhibits $k_H/k_D \approx 8 \pm 1$[27] indicates considerable H–D discrimination at some step along the reaction coordinate, but does not differentiate between the two pathways.



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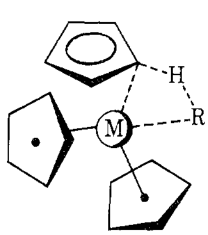

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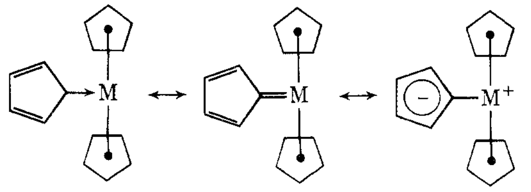
The product resulting from RH elimination can most reasonably be represented as the carbene complex–ylide species **4a**–**4c**. Similar cyclopentadienylide



4a **4b** **4c**

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(20) (a) H. C. Clark and C. S. Wong, *J. Am. Chem. Soc.*, **96,** 7213 (1974); (b) H. C. Clark and C. R. Jablonski, *Inorg. Chem.*, **13,** 2213 (1974); (c) A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Am. Chem. Soc.*, **96,** 6140 (1974); (d) J. Schwartz and J. B. Cannon, *ibid.*, **96,** 2276 (1974); (e) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *ibid.*, **92,** 1426 (1970).

(21) (a) R. R. Schrock, *J. Am. Chem. Soc.*, **96,** 6796 (1974); (b) P. J. Davidson, M. F. Lappert, and R. Pearce, *J. Organometal. Chem.*, **57,** 269 (1973).

(22) E. C. Baker, K. N. Raymond, T. J. Marks, and W. A. Wachter, *J. Am. Chem. Soc.*, **96,** 7586 (1974).

(23) L. J. Guggenberger, *Inorg. Chem.*, **12,** 294 (1973).

(24) (a) G. W. Parshall, *Acc. Chem. Res.*, **8,** 113 (1975); (b) I. S. Kolomnikov, V. P. Kukolev, and M. E. Vol'pin, *Russ. Chem. Rev.*, **43,** 399 (1974).

(25) The best evidence concerning the stereochemistry of elimination in metal alkyl hydrides is derived from studies of catalytic hydrogenation: (a) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974, Chapter IVA; (b) G. Dolcetti and N. W. Hoffman, *Inorg. Chim. Acta,* **9,** 269 (1974); (c) J. D. Morrison, W. F. Masler, and M. K. Neuberg, *Adv. Catal.*, **25,** in press.

(26) M. H. Abraham in "Comprehensive Chemical Kinetics", Vol. 12, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1973, Chapter 7.

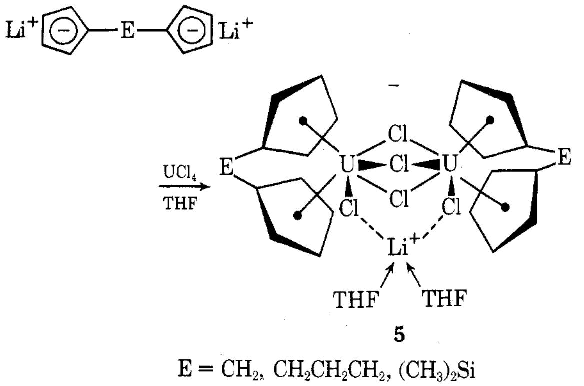
(27) T. J. Marks and A. M. Seyam, unpublished results.

compounds are well known in phosphorane chemistry,[28] and may be involved in a number of organo-transition-metal reactions where η^5-cyclopentadienyl hydrogens are activated.[29] In the case of M = Th, 4 apparently persists until dimerization can occur. Efforts to trap this intermediate and to better define the uranium system are in progress.

Thus, for the organoactinide alkyls examined to date, coordinative saturation plays a major role in directing the course of chemical transformations. The effects of 5f electron configuration should also be significant, judging from redox potentials. Uranium(IV) can be oxidized or reduced with relative ease, whereas thorium(IV) is essentially impossible to oxidize and very difficult to reduce.[30] These factors may explain some of the mechanistic differences between the thorium and uranium reactions. They should exert a strong influence on the possibility of homolytic bond scission reactions, and, on a more general level, on catalytic cycles which require the metal to shuttle between formal oxidations states. The dominance of the 3+ oxidation state in the heavier actinides is evident in organoneptunium chemistry—reaction 1 yields only $(C_5H_5)_3Np$.[31]

Modified Cyclopentadienyl Systems

The observations on $(C_5H_5)_3MR$ and MR_4 chemistry suggest that it would be of interest to achieve some intermediate degree of coordinative saturation. Since $(C_5H_5)_2MX_2$ systems form the basis of much Ti, Zr, and Hf organometallic chemistry, the compound $(C_5H_5)_2UCl_2$ would seem to be an ideal precursor. However, it now appears that in solution this species is actually a mixture involving $(C_5H_5)_3UCl$ and solvated $(C_5H_5)UCl_3$.[32] We sought to circumvent such ligand redistribution by joining the cyclopentadienyl rings (eq 10).[33] These complexes are isolated as tetrahydrofuran adducts; NMR and x-ray studies indicate structure 5[34] and suggest that in solution coordinated THF rapidly exchanges with excess free THF. These complexes can serve as precursors to a wide variety of species;[34] it should also be possible, to some degree, to "tune" the congestion about the uranium by controlling the size of the bridge.



(10)

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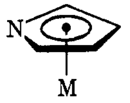
E = CH_2, $CH_2CH_2CH_2$, $(CH_3)_2Si$

Another device by which to modify the properties of a cyclopentadienyl ligand is by introducing a heteroatom. The pyrrolyl ligand C_4H_4N offers the possibility of acting either as a η^5 π-bonding ligand, 6, as in $(C_4H_4N)Mn(CO)_3$,[35] or as a η^1 amido ligand[36], 7, as in $U[N(C_2H_5)_2]_4$.[2a] We have synthesized a series of uranium pyrrolyl complexes via reactions 11 and 12.



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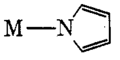

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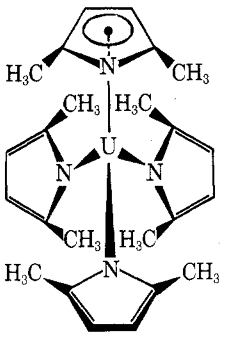
$$3Pyr^-K^+ + UCl_4 \xrightarrow[0\ °C]{THF} (Pyr)_3UCl \qquad (11)$$

$$4Pyr^-K^+ + UCl_4 \xrightarrow[0\ °C]{THF} (Pyr)_4U \qquad (12)$$

PyrH = pyrrole, 2,5-dimethylpyrrole, 2,4-dimethyl-3-ethylpyrrole, indole

All of the new complexes are highly oxygen and moisture sensitive. In several cases it has been possible to obtain structural information in solution by NMR. One interesting example is tetrakis(2,5-dimethylpyrrolyl)uranium(IV); the low-temperature (−122 °C) ^1H NMR spectrum is in best agreement with a structure possessing three η^1 rings (in two nonequivalent sets) and one η^5 ring, as in 8. As the temperature is raised, the σ-bonded rings first equilibrate by rotation about the U–N bonds. At higher temperatures ($\gtrsim$60 °C), interchange of η^1 and η^5 rings becomes fast on the NMR time scale.[37] Interestingly, tris(2,5-dimethylpyrrolyl)uranium(IV) chloride appears, from ^1H NMR studies, to have three η^1 rings; again, restricted rotation about the U–N bonds is observed.[38] Further chemical as well as crystallographic studies are under way.



8

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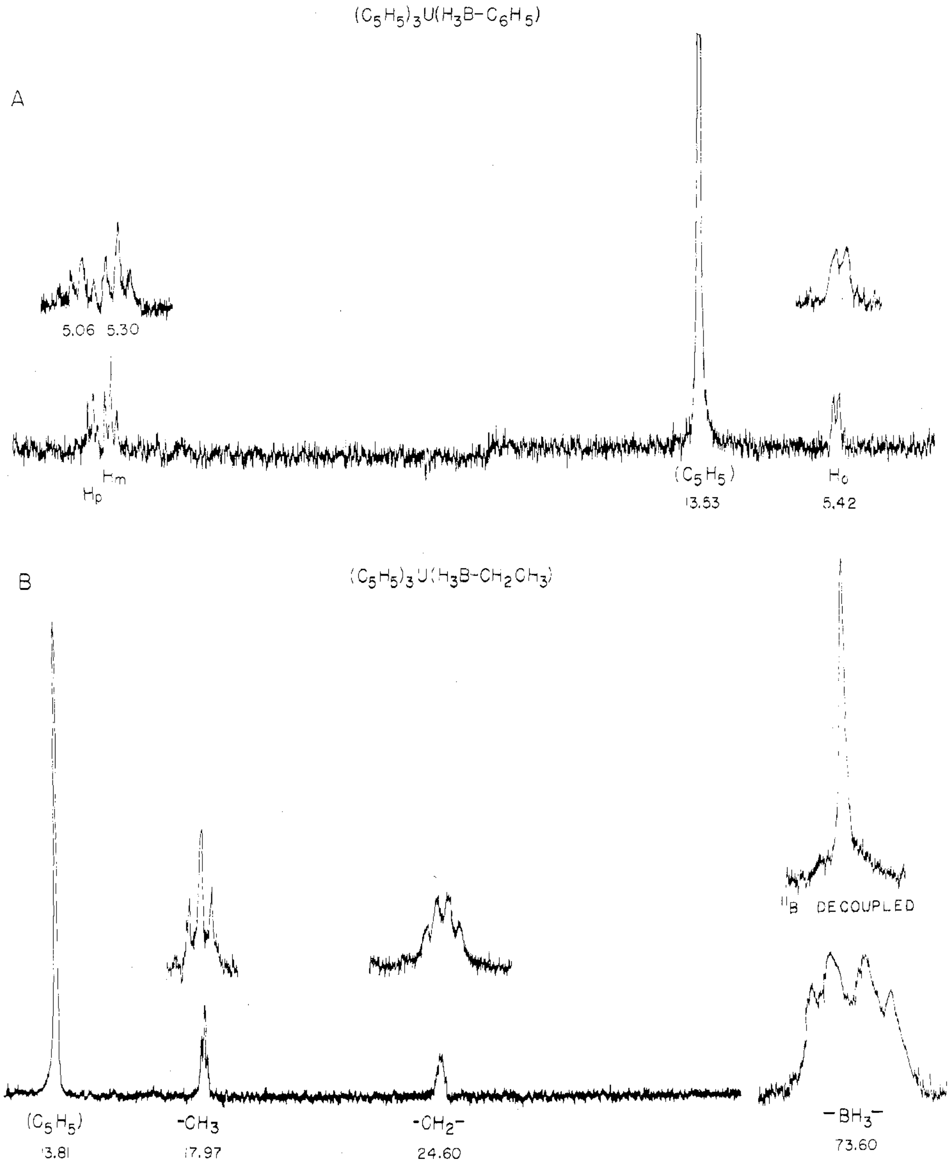
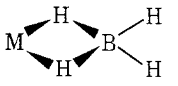


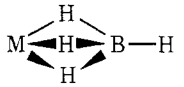
Figure 5. Proton NMR spectra (90 MHz) of (A) (η^5-C_5H_5)$_3$$UH_3BC_6H_5$ and (B) (η^5-C_5H_5)$_3$$UH_3BC_2H_5$. Chemical shifts are in parts per million from internal benzene (from ref 45).

Tetrahydroborate Complexes

The tetrahydroborate (also known as borohydride) ligand, BH_4^-, forms covalent complexes with a number of actinides and d transition metals.[39] All compounds characterized to date possess either bidentate or tridentate ligation geometry. The chemical and



bidentate



tridentate

spectroscopic properties of such complexes may lead to a better understanding of hydrogen-transfer reactions between metals and substrates. Since BH_4^- and CH_4 are isoelectronic, model structures for saturated hydrocarbon activation are also provided.

One of the earliest tetrahydroborate complexes to be synthesized was $U(BH_4)_4$, which was sufficiently volatile to be tested for gaseous diffusion.[40] Since a number of analogies exist between η^3-allyl and BH_4 complexes,[41,42] we explored the BH_4 ligand system as a means to elaborate and functionalize organoactinides. Reactions 13 through 16 provide examples of species accessible by simple halide ion displacement using $LiBH_4$ or $NaBH_4$.

$$(C_5H_5)_3UCl + BH_4^- \rightarrow (C_5H_5)_3UBH_4 + Cl^{-\,43} \qquad (13)$$

$$(C_5H_5)_3ThCl + BH_4^- \rightarrow (C_5H_5)_3ThBH_4 + Cl^{-\,41} \qquad (14)$$

$$(C_4H_4N)_3UCl + BH_4^- \rightarrow (C_4H_4N)_3UBH_4 + Cl^{-\,44} \qquad (15)$$

$$[CH_2(C_5H_4)_2]_2U_2Cl_5^-Li^+ + 4BH_4^- \rightarrow 2CH_2(C_5H_4)_2U(BH_4)_2 + 4Cl^- + LiCl^{34} \qquad (16)$$

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It is possible to prepare boron-substituted complexes either by starting with substituted borohydrides[45] (eq 17 and 18) or by operating on the BH_4 complex (eq 19).[45]

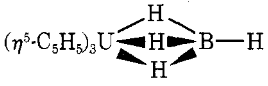
$$(C_5H_5)_3UCl + H_3BCN^- \rightarrow (C_5H_5)_3UH_3BCN + Cl^- \quad (17)$$

$$(C_5H_5)_3UCl + (C_6H_5)_3BCN^- \rightarrow (C_5H_5)_3U(C_6H_5)_3BCN + Cl^- \quad (18)$$

$$(C_5H_5)_3UBH_4 + R_3B \rightarrow (C_5H_5)_3H_3BR + R_2BH \quad (19)$$

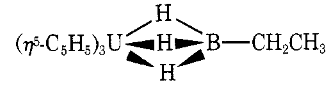
$$R = C_2H_5,\ C_6H_5$$

The mode of metal–ligand attachment in most tetrahydroborate complexes can be assigned using vibrational spectroscopy.[41] Infrared and laser Raman spectra indicate that, with the exception of the cyanoborohydrides, all of the above complexes have tridentate ligation,[45] as in **9** and **10**. For the cyano compounds, complexation appears to involve the CN group, as in **11**.



$(\eta^5\text{-}C_5H_5)_3U\begin{smallmatrix}H\\H\\H\end{smallmatrix}B-H$

9



$(\eta^5\text{-}C_5H_5)_3U\begin{smallmatrix}H\\H\\H\end{smallmatrix}B-CH_2CH_3$

10

$$(\eta^5\text{-}C_5H_5)_3\overset{+}{U}\leftarrow N\equiv C-\bar{B}<$$

11

The NMR spectra of the uranium(IV) tetrahydroborates exhibit large isotropic shifts.[45] Typical proton spectra are shown in Figure 5. For the $(C_5H_5)_3UH_3BC_6H_5$ derivative it was possible to separate the contact and dipolar contributions. The mechanism of unpaired spin distribution is the same as that in the $(C_5H_5)_3UR$ series,[7b] involving ligand donation to, or polarization by, metal orbitals.

The ambient-temperature NMR spectrum of $(C_5H_5)_3UBH_4$ shows, as do spectra of nearly all[46c] covalent tetrahydroborates examined to date, the bridge and terminal BH_4 hydrogens to be magnetically equivalent. It has been thought for some time that this anomaly was due to rapid intramolecular hydrogen interchange, but proof was lacking.[46] The large isotropic shifts in $(C_5H_5)_3UBH_4$ effectively expand the time resolution of the dynamic NMR experiment,[45] as can be most easily seen in the Gutowsky–Holm formula[47] for spectral coalescence, involving exchange between two equally populated sites:

$$1/\tau = \pi\delta\omega/\sqrt{2} \quad (20)$$

Here τ is the mean preexchange lifetime and $\delta\omega$ is the frequency separation between sites. The contact and dipolar shifts in $(C_5H_5)_3UBH_4$ vastly expand $\delta\omega$ to 15 000–36 000 Hz, allowing the approach to spectral coalescence to be observed at ca. −120 °C with broad-band decoupling of ^{11}B. In contrast, the spectrum of $(C_5H_5)_3UH_3BC_2H_5$ does not appreciably broaden. A plausible mechanism for the hydrogen permutation is shown in eq 21, suggesting that the potential-energy surface connecting the two structures is rather flat. We find $\Delta G^{\ddagger} \approx 5$ kcal/mol.[45]

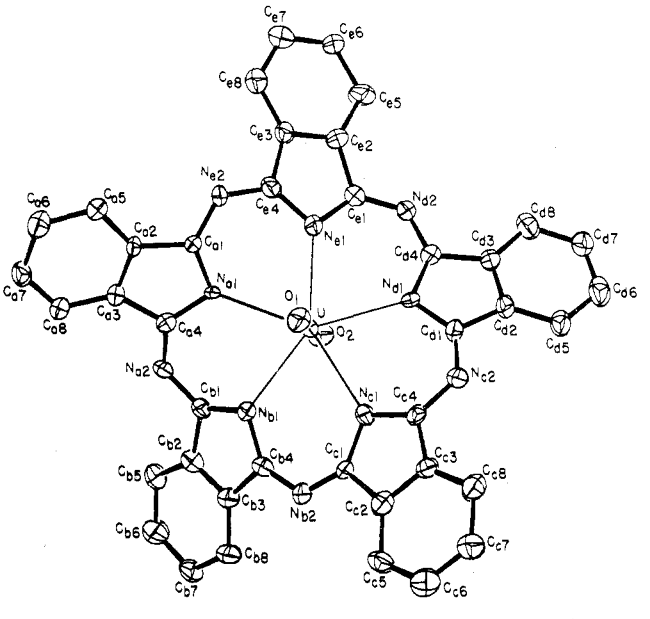
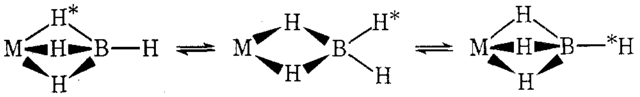


Figure 6. The molecular structure of uranyl "superphthalocyanin"; the view is approximately perpendicular to the uranyl pentagonal plane (from ref 50a).

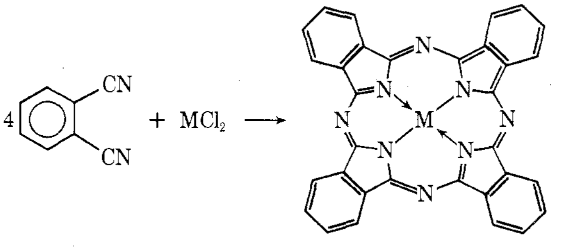


$M\begin{smallmatrix}H^*\\H\\H\end{smallmatrix}B-H \rightleftharpoons M\begin{smallmatrix}H\\H\end{smallmatrix}B\begin{smallmatrix}H^*\\H\end{smallmatrix} \rightleftharpoons M\begin{smallmatrix}H\\H\\H\end{smallmatrix}B-{}^*H$

(21)

Prospects

Organoactinide chemistry is a relatively new area, and at this stage it is premature to draw any sweeping generalizations. However, it does appear that coordinative properties and 5f electron configuration exert significant control over the direction of many chemical transformations. Such features may allow the subtle design of reagents and catalysts tailored for very specific purposes. The goal for us should not be to duplicate and mimic d transition-metal organometallic chemistry but to develop a chemistry unique to actinides. One very intriguing example, and hopefully a preview of future chemistry, is the possibility of creating new expanded macrocycles by performing oligomerization reactions in the presence of large, coordinatively specific actinide templates.[48] Thus, while eq 22 leads to a normal phthalocyanin in the presence of transition metal ions,[49] a uranyl ion tem-



(22)

M = Fe, Co, Ni, Zn

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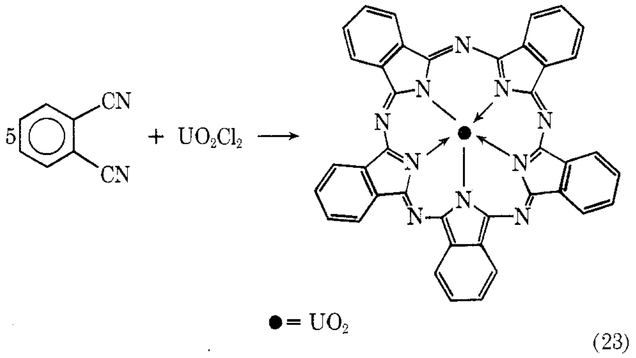
plate leads to an expanded "superphthalocyanin", eq 23.[50] The molecular structure of this remarkable complex is shown in Figure 6.[50a] The strong preference of the uranyl ion to achieve a pentagonal-bipyramidal or hexagonal-bipyramidal coordination geometry has doubtless altered the normal course of the cyclization. The new ligand has a high specificity for the uranyl ion.[51] The scope of this type of transformation is under investigation. Surely a wealth of new compounds, reactions, and useful applications awaits the explorer of actinide organometallic chemistry.



(23)

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Silver-Assisted Reactions of Chloroformates: A New Route to Reactive Carbocations

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Of the many different ways of effecting substitution, elimination, and rearrangement at carbon, reactions of amines with nitrosating agents generally produce the greatest variety of products and therefore are considered to involve the least discriminating and most reactive intermediates.[1] Although interpretations differ as to how the reaction mechanism should account for the product diversity, there seems to be agreement that reactive carbocations are involved and that the essence of the contrast between deaminations and more conventional substitutions, eliminations, and rearrangements lies in the unusually large driving force for the loss of nitrogen from a diazonium ion or its formal equivalent.[1,2] On that basis, it might be expected that other reactions in which a stable nonnucleophilic leaving group can be formed would also provide reactive carbocations. Analogies have, in fact, been suggested between the loss of nitrogen in deaminations and losses of carbon monoxide,[3] carbon dioxide,[4] nitrous oxide,[5] sulfur dioxide,[4a,6] sulfur trioxide,[7] sulfoxides,[8] or metals[9] from a variety of carbocation precursors.

$$\begin{tikzcd}
 & RG^+X^- \arrow[d] \arrow[dr] & \\
RGX \arrow[ur] \arrow[dr] & & \text{products of substitution, elimination, and rearrangement} \\
 & R^+GX^- \arrow[ur] &
\end{tikzcd}$$

$G = N_2, CO, CO_2, N_2O, SO_2, SO_3, SOR_2$, metal

Peter Beak was born in Syracuse, N.Y., did undergraduate work at Harvard and graduate work at Iowa State, and is presently a professor at the University of Illinois at Urbana-Champaign. His current research interests include structure-stability relationships, reaction mechanisms, enzyme models, and the discovery and use of novel reactions.

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(2) Current interpretations consider the crucial steps in deamination to be either: (a) formation of a "hot" or "unencumbered" carbocation: R. Huisgen and C. H. Rüchardt, *Justus Liebigs Ann. Chem.*, **601,** 1 (1956); D. Y. Curtin and M. C. Crew, *J. Am. Chem. Soc.*, **76,** 3719 (1954); J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **76,** 4501 (1954); M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta*, **40,** 2129 (1957); D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79,** 2866 (1957); J. T. Keating and P. S. Skell, "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 573; (b) partitioning between ionization and direct reaction of the diazonium ion: A. Streitwieser, *J. Org. Chem.*, **22,** 861 (1957); L. Friedman, "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 655; or (c) formation of a separated ion pair: E. H. White and D. J. Woodcock, "The Chemistry of the Amino Group", S. Patai, Ed., Interscience, New York, N.Y., 1968, p 440; C. J. Collins, *Acc. Chem. Res.*, **4,** 315 (1971); R. A. More O'Ferrall, *Adv. Phys. Org. Chem.*, **5,** 331 (1967); J. A. Berson, *Angew. Chem., Int. Ed. Engl.*, **1,** 779 (1968).

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