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(9) The carbinol **2** was prepared from bullvalone.[10] Satisfactory elemental analyses were obtained for all new compounds in this report. **2**: ν_{max}^{KBr} 3350, 2950, 1410, 1210, 1150 cm^{-1}; λ_{max} (in cyclohexane), 230 nm (sh, ϵ 3450); ^{1}H NMR (δ, ppm, CDCl$_3$) 5.93 (1 H, dd, J = 17.0, 10.0 Hz), 5.19 (1 H, dd, J = 17.0, 2.0 Hz), 4.91 (1 H, dd, J = 10.0, 2.0 Hz), 5.85 (2 H, m), 2.1–2.7 (6 H, m).

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(11) ν_{max}^{KBr} 3350, 1650, 1400 cm^{-1}; *m/e* 174 (M$^+$), 159, 145, 132, 117, 103, 91, 89 (100%); ^{1}H NMR (δ, ppm, CDCl$_3$) 2.97 (C$_1$, d of t, J = 9.0, 9.0, 10.0 Hz), 6.01 (C$_2$, dd, J = 9.0, 11.0 Hz), 5.59 (C$_3$, dd, J = 1.5, 11.0 Hz), 1.40–2.40 (C$_5$, C$_6$, m), 2.80 (C$_7$, C$_8$, m), 5.76 (C$_9$, ddd, J = 1.5, 8.0, 9.0 Hz), 6.46 (C$_{10}$, dd, J = 9.0, 10.0 Hz), 5.88 (C$_{11}$, dd, J = 9.0, 12.0 Hz), 5.52 (C$_{12}$, dd, J = 5.0, 9.0 Hz) (by the simultaneous irradiation of three methine hydrogens at the C$_1$, C$_7$, and C$_8$ positions, all of the olefinic hydrogens become doublets at the designated positions); ^{13}C NMR (δ, ppm, CDCl$_3$), 127.2 (d), 129.3 (d), 132.8 (d), 136.2 (d), 136.5 (d), 142.7 (d) (C$_2$, C$_3$, C$_9$, C$_{10}$, C$_{11}$, C$_{12}$), 79.0 (s) (C$_4$), 36.1 (d), 39.0 (d), 50.0 (d) (C$_1$, C$_7$, C$_8$), 31.7 (t), 42.4 (t) (C$_5$, C$_6$).

(12) **9** was obtained in low yield by the lithium–ethylamine reduction[13] of **8**: ^{1}H NMR (δ, ppm, CDCl$_3$) 3.00 (C$_1$, dd, J = 8.0, 9.0 Hz), 5.90 (C$_2$, C$_{11}$, dd, J = 8.0, 11.0 Hz), 5.59 (C$_3$, C$_{12}$, dd, J = 5.0, 11.0 Hz), 2.65 (C$_4$, C$_7$, m), 1.5–2.0 (C$_5$, C$_6$, m), 2.65 (C$_8$, m), 5.78 (C$_9$, dd, J = 8.5, 10.0 Hz), 6.40 (C$_{10}$, dd, J = 9.0, 10.0 Hz).

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(16) The mechanistic interpretation of a formal [1,3]-sigmatropic rearrangement of an oxy-Cope related system often differs. For instance, in thermal rearrangement of 7-propenyl-7-methoxynorbornenes to 4-*endo*-methyl-2-methoxybicyclo[3.2.0]nona-2,6-diene, Berson[17] proposed a sequence of [1,3]- and [3,3]-sigmatropic rearrangements to account for high stereospecificity of the rearrangement, whereas Fukui's proposal, a multicyclic interaction effect,[18] rather suggests a direct concerted [1,3]-sigmatropic rearrangement which does not require any intermediate. Similarly, the [1,3]-sigmatropic rearrangement[4] reported by Thies and Seitz can also be explained by two intrinsically different mechanisms, i.e., a direct [1,3]-sigmatropic pathway and a sequential [1,3]- and [3,3]-sigmatropic rearrangement which are not discussed about in their report.

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(19) $\nu_{max}^{CCl_4}$ 3520 cm^{-1}; ^{1}H NMR (δ, ppm, CDCl$_3$), 1.4–1.8 (C$_1$, C$_2$, C$_{10}$, m), 6.0–6.2 (C$_3$, C$_4$, C$_5$, m), 3.03 (C$_7$, dddd, J = 1.5, 1.5, 6.0, 9.0 Hz), 1.19 (endo C$_9$, dd, J = 3.0, 13.5 Hz), 2.16 (exo C$_9$, ddd, J = 1.5, 6.5, 13.5 Hz), 6.18 (C$_\alpha$, dd, J = 11.0, 17.0 Hz), 4.97 (C$_\beta$, dd, J = 2.0, 11.0 Hz), 5.25 (C$_\beta$,dd, J = 2.0, 17.0 Hz).

Effect of Eu(fod)$_3$ on the ^{1}H NMR Spectrum of **3** (M = H)

Mol ratio of Eu(fod)$_3$/**3**	$\Delta\delta$, Hz			
	C$_\alpha$ H	endo C$_9$ H	exo C$_9$ H	C$_7$ H
0	0	0	0	0
0.038	37	33	28	27
0.079	82	68	58	59
0.173	172	141	114	121
0.377	387	313	244	273
0.565	552	446	364	387

(20) Tricyclo[5.3.0.0^{2,10}]deca-3,5-dien-8-one was prepared by irradiation of bicyclo[4.2.2]deca-2,4,7-trien-9-one in benzene: T. Hagiwara, Ph.D. thesis, Tohoku University, Sendai, Japan, 1974.

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(22) The ^{1}H NMR spectrum (100 MHz) of the product 7-*d* from **3**-*d*$_3$ is complex, unlike **7**, but the simultaneous irradiation of three methine hydrogens at the C$_1$, C$_7$, and C$_8$ positions can simplify the complicated splittings in the olefinic region as follows: C$_2$ (d + s), C$_3$ H (d), C$_9$ H (d), C$_{10}$ H (d + s), C$_{11}$ H (d), C$_{12}$ H (d + s). However, integration of the magnetic resonance signals in this spectrum does not provide accurate hydrogen intensities since signals locate closely. Integration of all the hydrogens was conducted by pseudo-contact ^{1}H NMR spectra using Eu(fod)$_3$ which were measured in six different mole ratios (Eu(fod)$_3$/**7**-*d*) from 0.121 to 0.975. Similarly, the C$_2$ and C$_{10}$ hydrogens and the C$_{11}$ and C$_{12}$ hydrogens shift in pairs, respectively. In each spectrum, the magnetic resonance signals were integrated and then hydrogen intensities were corrected as described in this report based on the exo C$_6$ (1 H) and endo C$_8$ (1H) hydrogens which do not shift so much, but separate clearly.

(23) The bicyclo[5.1.0]pentadienyl anion derivative **13** could be also considered

13

as a possible intermediate for the rearrangement of **2** to **3**, but could be ruled out since the bicyclo[5.1.0]pentadienyl anion[24] is reported to be unstable and readily isomerizes to the 1,6-methanoheptatrienyl anion at 0 °C.

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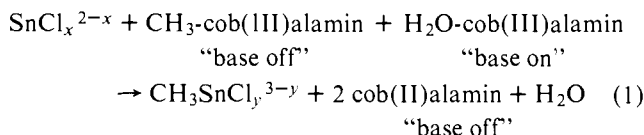*Tohoku University, Sendai 980, Japan*

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A Mechanism for the Biomethylation of Tin by Reductive Co–C Bond Cleavage of Alkylcobalamins

Sir:

The alkylation of various metals and metalloids by methylcobalamin is a reaction of both mechanistic interest and considerable environmental importance.[1] When the demethylating agent is an electrophile such as Hg^{II}, Tl^{III}, or Pd^{II}, the cleavage has been found to occur by carbanion transfer from cobalt to the attacking metal center.[2-4] More recently the reaction of thiols,[5] or Cr^{II},[6] with alkylcobalamins has been found to occur by reductive homolytic cleavage of the cobalt–carbon bond with alkyl radical transfer. As part of our continuing interest in the bioalkylation of heavy metals, we now present evidence for the alkylation of tin through reductive cobalt–carbon bond cleavage by a species which is generated by one equivalent oxidation of Sn^{II}.

The reaction of methylcobalamin ($\sim$5 $\times$ 10^{-4} M) with equimolar aquocobalamin plus a half-fold deficiency of Sn^{II} under N$_2$ at pH 1.0, in 1.0 M NaCl, was allowed to proceed for 24 h at 20 °C. This reaction was found to follow

$$\text{SnCl}_x^{2-x} + \text{CH}_3\text{-cob(III)alamin} + \text{H}_2\text{O-cob(III)alamin}$$
$$\text{"base off"} \qquad \text{"base on"}$$
$$\rightarrow \text{CH}_3\text{SnCl}_y^{3-y} + 2 \text{ cob(II)alamin} + \text{H}_2\text{O} \qquad (1)$$
$$\text{"base off"}$$

The product cob(II)alamin was found in 92% yield based on tin. Methyltin was identified by 270-MHz NMR. The CH$_3$–Sn resonance appeared at 1.01 ppm relative to TSP with detectable satellites for ^{1}H coupling with ^{117}Sn and ^{119}Sn.[7] Unreacted methylcobalamin and aquocobalamin were found in the ratio 1.3:1. A similar cleavage reaction was found when FeCl$_3$ was substituted for aquocobalamin in the above reaction; however, excesses of Sn^{II} and Fe^{III} over methylcobalamin were necessary to achieve significant cleavage of the cobalt–carbon bond. No reaction was observed between Sn^{II} and methylcobalamin in the absence of an oxidizing agent such as aquocobalamin or Fe^{III}. Catalytic amounts of aquocobalamin, under strictly anaerobic conditions produced no appreciable cleavage.[8] Experiments using ^{14}C-labeled methylcobalamin showed no ^{14}CH$_4$, ^{14}CH$_3$OH, or ^{14}HCHO formation resulting from Sn^{II} cleavage of the cobalt–carbon bond.

The kinetics of the reactions of methyl and ethylcobalamin (2 $\times$ 10^{-5} to 2 $\times$ 10^{-4} M) were investigated at 20 °C in aqueous solutions of hydrochloric acid–sodium chloride with a 10- to 100-fold excess of Sn^{II}. Fe^{III} was added to the reaction mixtures either equimolar or in excess of Sn^{II}. Reactions were followed for 2 to 3 half-lives, when possible, by monitoring the decrease in absorbance at 460 nm for the alkylcobalamin and the concomitant increase in absorbance at 530 nm for the aquocobalamin product.[9] Because of the slow reaction for ethylcobalamin, initial rates were used in this kinetic study. Reactions were found to obey the rate expression

$$-\text{d}[\text{B}_{12,\text{alkyl}}]/\text{d}t = k_{\text{obsd}}[\text{B}_{12,\text{alkyl}}] \qquad (2)$$

giving good linear plots of $-\ln(A - A_\infty)$ vs. time.[10] Pseudo-first-order rate constants are plotted vs. [Sn^{II}] in Figure 1. In

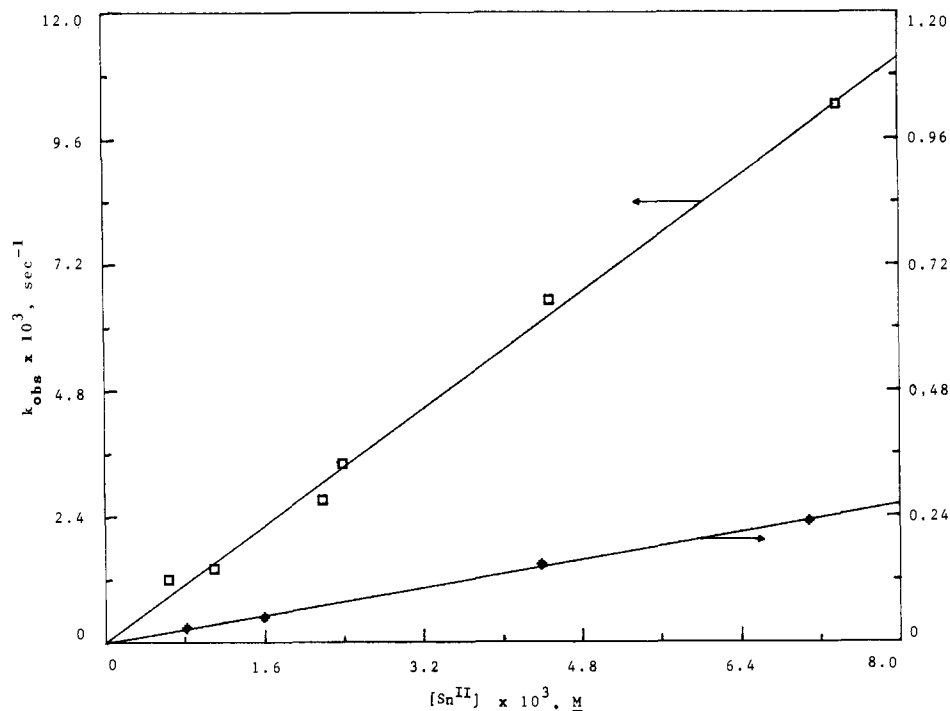**Figure 1.** Plots of k_{obsd} vs. [Sn^{II}] for the reactions of methylcobalamin (open square) and ethylcobalamin (diamond) with $\sim$10 to 100-fold excess of Sn^{II} and Fe^{III} in aqueous, pH 1.0 NaCl–HCl at 20 °C.
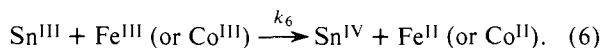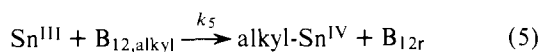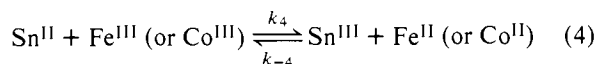
Figure 1 the linearity and zero intercept are consistent with the rate law

$$-d[B_{12,alkyl}]/dt = k_{alkyl}[Sn^{II}][B_{12,alkyl}] \qquad (3)$$

with $k_{methyl} = 1.4 \pm 0.1$ M^{-1} s^{-1}; $k_{ethyl} = 3.3 \pm 0.4 \times 10^{-2}$ M^{-1} s^{-1}; $2 \times 10^{-3} < [Fe^{III}] < 1 \times 10^{-2}$, $\mu = 1.0$–1.2 M, [H^+] = 0.1 M. The reactions were found to be zero-order in the excess Fe^{III}.[11] Addition of Sn^{IV} equimolar with Sn^{II} yielded no rate enchancement. No cleavage reaction occurred when Sn^{IV} was substituted for Sn^{II}. No dealkylation of methylcobalamin was observed under either anaerobic or aerobic conditions with Fe^{II} in the absence of Sn^{II}.

The kinetics for these cleavage reactions proved to be sensitive to added nitroso salt and slightly sensitive to changes in pH. For example, the addition of the disodium salt of 1-nitroso-2-OH-naphthalene-3,6-disulfonic acid [$HO–C_{10}H_4(NO)(SO_3Na)_2$], in threefold excess of methylcobalamin and in $^1/_{10}$ of the Sn^{II} concentration used, completely inhibited cobalt–carbon bond cleavage.[12] Over the pH range of 0–2.0 k_{methyl} was found to increase by a factor of 2.

A dramatic effect on the reaction rate was observed upon changing the anion in the reaction mixtures. In aqueous Na_2SO_4–H_2SO_4, or $NaClO_4$–$HClO_4$, at pH 1.0, Sn^{II} was found not to react with methyl- or ethylcobalamin in the presence of Fe^{III}, even though the Sn^{II} was oxidized by Fe^{III} to Sn^{IV}. At higher pHs it was possible to run cleavage reactions by using appropriate complexing anions. For example, at pH 3.0–5.0 in aqueous sodium tartrate–tartaric acid, methylcobalamin was found to undergo cobalt–carbon bond cleavage by Sn^{II} with added Fe^{III}. A reasonable mechanism for these reactions is presented in eq 4–6.

$$Sn^{II} + Fe^{III} \text{ (or } Co^{III}) \overset{k_4}{\underset{k_{-4}}{\rightleftharpoons}} Sn^{III} + Fe^{II} \text{ (or } Co^{II}) \quad (4)$$

$$Sn^{III} + B_{12,alkyl} \overset{k_5}{\longrightarrow} alkyl\text{-}Sn^{IV} + B_{12r} \quad (5)$$

$$Sn^{III} + Fe^{III} \text{ (or } Co^{III}) \overset{k_6}{\longrightarrow} Sn^{IV} + Fe^{II} \text{ (or } Co^{II}). \quad (6)$$

In this mechanism the initial step is one equivalent oxidation of Sn^{II} to Sn^{III} by either Fe^{III} or Co^{III} (aquocobalamin). Such

an oxidation of Sn^{II} by Fe^{III} has previously been reported by Wetton and Higginson.[13] When the Sn^{III} is stabilized to decomposition by the k_{-4} and k_6 paths, as the coordinating anions Cl^- and tartrate appear to do, cobalt–carbon bond cleavage occurs by eq 5. If a steady-state concentration of Sn^{III} is assumed and if $k_6[Fe^{III}] \gg k_{-4}[Fe^{II}]$ or $k_5[B_{12,alkyl}]$, then the observed kinetics result.[14] Cleavage by eq 5 appears to be a bimolecular reaction between complexed Sn^{III} and the cobalt–carbon bond where either the greater bulkiness of the ethyl group or the ease of reduction of methylcobalamin relative to ethylcobalamin may account for the rate differences found. Such a reaction by a complexed Sn^{III} species, as $SnCl_2^+$ or $SnCl_3$,[15] is analogous to but slower than the cleavage of methyl and ethylcobalamin by Cr^{II}, $k_{Me} = 3.57 \pm 0.30 \times 10^2$ and $k_{Et} = 4.40 \pm 0.35$ M^{-1} s^{-1}.[6] The mode of cleavage similarly appears to be either an S_H2 displacement of the saturated carbon atom or a site-specific reduction of the alkylcobalamin at the alkyl group with concurrent carbanion transfer to tin. The high yield of methyltin from the reaction of methylcobalamin with a deficiency of Sn^{II}, and with added aquocobalamin, indicates that the oxidation of Sn^{III} by Co^{III} is not a very facile process. This may be a consequence of the protection afforded the cobalt atom by the corrin macrocycle.

Recently, Huey and coworkers[16] have reported the microbial methylation of tin by a *Pseudomonas* species isolated from Chesapeake Bay. Our discovery that methylcobalamin alkylates tin merits serious consideration as a possible metabolic pathway for this microbial process.

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(5) T. Frick, M. D. Francia, and J. M. Wood, *Biochim. Biophys. Acta*, **428**, 808 (1976).

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(7) By comparison with the spectrum of an authentic sample recorded by the authors in pH 1.0 DCl–D_2O and 1.0 M NaCl.

(8) In the presence of O_2, Sn^{II} will slowly dealkylate $B_{12,Me}$ without added B_{12a} or Fe^{III}. An induction period observed preceeding this cleavage implicates a catalytic cycle where the slight B_{12a} impurity, always present in alkyl-cobalamins, is reduced by Sn^{II}, reoxidized by O_2, and reduced by more Sn^{II}, etc.

(9) The excess Fe^{III} very rapidly oxidizes the product B_{12r} to B_{12a}.

(10) Linear plots for reactions of both methyl- and ethylcobalamin could be obtained only for 7 to 10 min after mixing. A sudden dramatic decrease in the rate of cleavage after this time indicates complete or nearly complete depletion of one of the reactants, Sn^{II} or Fe^{III}, by competing side reactions (eq 4–6).

(11) The Fe^{III} was found to dealkylate $B_{12,Me}$ but at a rate too slow to interfere in the kinetic determinations.

(12) The HO–$C_{10}H_4(NO)(SO_3Na)_2$ salt has been used as a complexing reagent for a number of metal ions: E. B. Sandell, "Chemical Analysis", Vol. III, Interscience, New York, N.Y., 1959, p 208. Also the nitroso salts have been found to be effective scavengers for both organic and inorganic free radicals: E. G. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971); P. T. Krusic, P. T. Fagan, and T. San Filippo. Jr., *J. Am. Chem. Soc.*, **99**, 250 (1977).

(13) E. A. M. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 5890 (1965).

(14) The rate expression for eq 5 is

$$-d[B_{12,alkyl}]/dt = k_5[Sn^{III}][B_{12,alkyl}]$$

$$-d[Sn^{III}]/dt = k_{-4}[Sn^{III}][Fe^{II}] + k_5[Sn^{III}][B_{12,alkyl}] + k_6[Sn^{III}][Fe^{III}] - k_4[Sn^{II}][Fe^{III}] = 0$$

$$[Sn^{III}] = \frac{k_4[Sn^{II}][Fe^{III}]}{k_{-4}[Fe^{II}] + k_5[B_{12,alkyl}] + k_6[Fe^{III}]}$$

so

$$-d[B_{12,alkyl}]/dt = k_5k_4/k_6[Sn^{II}][B_{12,alkyl}]$$

(15) With 1 M NaCl, Sn^{II} in solution exists largely as $SnCl_3^-$ and $SnCl_2$: K. G. Moodley and M. J. Nicol, *J. Chem. Soc., Dalton Trans.*, 239 (1977).

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1   2

Anodic Oxidation of Uranocene. Evidence for New Organouranium Cations in Solution

Sir:

The synthesis of uranocene (di-π-cyclooctatetraenyluranium(IV)) (1) by Streitwieser and Müller-Westerhoff in 1968[1] opened an exciting new era in organoactinide and lanthanide chemistry. We have extended this area by investigating the existence and properties of the uranocene mono- and possibly dication, and present evidence for formation of a diuranium cluster complex.

In spite of the fact that numerous related actinide and lanthanide complexes have been prepared,[2] uranocene is the most interesting. It, for example, has remarkable thermal stability and is resistant to attack by water and weak acids.[3] Streitwieser has proposed an ingeneous bonding scheme for uranocene[3] in which 5f orbitals on the metal and molecular orbitals (MOs) on the ligand, both having the proper energy and symmetry, interact to form a covalent bond.[4] The model also predicts that 1 should have two unpaired electrons in nonbonding orbitals which are largely 5f in character.

Many laboratories have conducted experiments on 1 designed to test the Streitwieser model.[5] One interesting approach has been to study the photoelectron spectrum of 1.[6] Although these spectra are largely in agreement with the bonding model, much information is lost because little is learned about the ions, particularly the ground-state ion, formed by photoejection.[7] However, problems with the model remain. Is the covalency ascribed to 1, which is based on its stability to water, due to the 5f electrons on the uranium, or
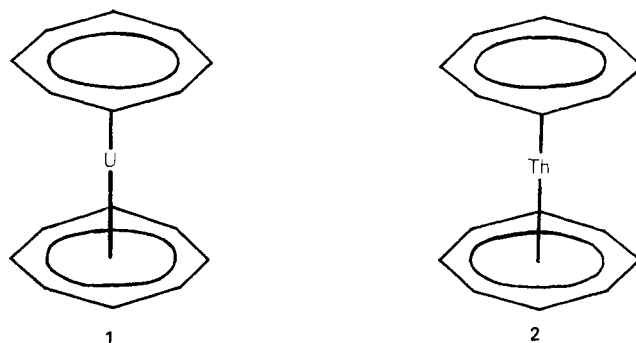
are they truly nonbonding as the model suggests? Loss of these electrons would form the uranocene dication, a species which is isoelectronic with thoracene (2), the latter being largely ionic in nature[8] and highly sensitive to water. Thus we anticipated that solution oxidation of uranocene would lead to simple cation species, making further tests of the uranocene bonding scheme possible via comparison to the known properties of 2.

Because chemical oxidants proved unsatisfactory in the controlled oxidation of uranocene,[9] anodic oxidation was investigated. Owing to the extreme air sensitivity of 1, cyclic voltammograms were obtained under argon in an inert atmosphere box using a Pt disk working electrode with (n-Bu)$_4$-$N^+PF_6^-$ as the supporting electrolyte.[10] Figure 1 shows cyclic voltammograms of 1 in benzonitrile, a solvent which showed good electrochemical characteristics and in which 1 was reasonably soluble.[11] Simple reversible faradaic processes are not observed at sweep rates up to 20 V/s, and only at subambient temperatures is a quasi-reversible ($E_p^a - E_p^c = 200$ mV) one-electron oxidation wave obtained at 0.06 V vs. SCE.[12] Added cyclooctatetraene (COT) in THF at room temperature had no effect on the general appearance of the voltammogram and the position of the uranocene oxidation wave. This result implies that COT is not lost reversibly by the uranocene cation formed in the initial electron-transfer process. Based on the known ionization potential of uranocene,[13] an $E_{1/2}$ value may be calculated by Miller's formula[14a] which corresponds very closely to the experimental value.[14b] It would appear that a uranocene cation is being generated but that it is unstable under our reaction conditions.

$$U(COT)_2 \underset{}{\overset{-e^-}{\rightleftharpoons}} U(COT)_2^+ \xrightarrow{U(COT)_2} \longrightarrow products$$
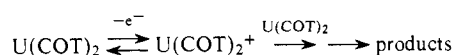
If the potential is swept past the first wave, a broad poorly defined oxidation process is observed which consists of at least two waves (+0.445 and +0.679 V). The best resolution of these two waves was observed when the voltammograms were obtained in the presence of suspended alumina.[15,16] The position of the third wave corresponds very closely to that observed in cyclic voltammograms of exhaustive electrolysis solutions.

Coulometric electrolyses were carried out on ~25-mg samples of uranocene in THF/(n-Bu)$_4N^+PF_6^-$ using a reticulated vitreous carbon working electrode (100 pores per inch, Chemitronics).[17] The oxidation proceeded smoothly at potentials up to 0.85 V vs. SCE with continuous argon flushing of the working electrode compartment.[18] After all of the uranocene had reacted (20–35 min), an *air-stable,* yellow-green solution was produced.

Although the separation of this green material from the supporting electrolyte defied our best efforts,[19a] the evidence below leaves little doubt that it is an organouranium cation possessing two or more uranium atoms. An n value of 1.42 ± 0.08 was obtained from 12 coulometry experiments indicating $3e^-$ were lost per 2 molecules of uranocene. Cyclic voltammograms of the oxidized solution demonstrated that COT was liberated during the electrolysis. By FT NMR it could be