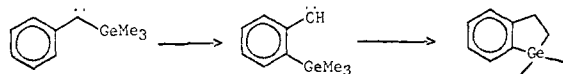Germaindan **6** is doubtless the product of a carbene-to-carbene rearrangement just as is the analogous silaindan **3**.[2,4]

We suggest that styrene owes its appearance to the formation of germirane **7** which extrudes dimethylgermylene,[5] again in analogy to the silicon case.[2] Stable germiranes are not known,[6] although reactions in which they are permissible intermediates have been reported.[4,7] Nevertheless, it is fair to say that no reaction yet described *demands* the intermediacy of a compound containing germanium in a three-membered ring. We believe that the isolation of styrene provides strong evidence for the transient existence of a germirane. Germaindan **6** is a source of neither styrene nor α-methylstyrene, although higher molecular weight products are formed on pyrolysis of **6**.[8]
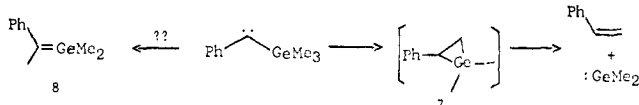
We have been unable to detect the germene **8** that would be produced by carbon–germanium insertion.[9] Although we have attempted several trapping experiments, the caution warranted by all negative results is most appropriate here.[10]

References and Notes

(1) Support for this work by the National Science Foundation through Grant MPS 74-05690 is gratefully acknowledged. Portions of this work are taken from the A.B. thesis of E.B.N., Princeton University, 1977.

(2) W. Ando, A. Sekiguchi, A. J. Rothschild, R. R. Gallucci, M. Jones, Jr., T. J. Barton, and J. A. Kilgour, *J. Am. Chem. Soc.*, **99**, 7707 (1977).

(3) A. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957); K. Yates and F. Agolini, *Can. J. Chem.*, **44**, 2229 (1966); A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957).

(4) Anal. Calcd for $C_{10}H_{14}Ge$: C, 58.08; H, 6.82. Found: C, 58.26; H, 6.78. ^1H NMR (δ, CCl_4): 7.37 (m, 4 H), 3.33 (t, 2 H), 1.35 (t, 2 H), 0.02 (s, 6 H). See ref 2 for a comparison with the analogous silicon-containing compound.

(5) For a review of germylenes see J. Satge, M. Massol, and P. Riviere, *J. Organomet. Chem.*, **56**, 1 (1973).

(6) See, however, the last sentence of R. L. Lambert and D. Seyferth, *J. Am. Chem. Soc.*, **94**, 9246 (1972).

(7) D. P. Paquin, R. J. O'Connor, and M. A. Ring, *J. Organomet. Chem.*, **80**, 341 (1974). For a dissenting view see S. P. Kolesnikov, A. I. Ioffe, and O. M. Nefedov, *Bull. Acad. Soc. USSR Chem. Sci.*, **24**, 896 (1975); A. I. Ioffe, L. I. Korzhenevich, S. P. Kolesnikov, and O. M. Nefedov, *ibid.*, **25**, 323 (1976).

(8) Neither photolysis of **5** in a neopentane matrix at −196 °C, followed by quenching with methanol at −30 °C, nor irradiation of benzene/methanol solutions of **5** at room temperature yielded evidence of **7**. In the latter experiment reaction of the carbene with methanol yielded the major product. It is scarcely surprising that in solution intermolecular reaction should be preferred to formation of a germirane.

(9) For a successful trapping of a germene see T. J. Barton, E. A. Kline, and P. M. Garvey, *J. Am. Chem. Soc.*, **95**, 3078 (1973).

(10) We prefer not to comment at this time upon the formation of α-methylstyrene, but it is possible that its appearance and the absence of **8** are connected.

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Hypovalent Radicals. 2.[1] Fluorenylidene Anion Radical—Possible Redox Potentials for the Fluorenylidene/Fluorenylidene Anion Radical Couple

Sir:

The electronic structure of $H_2C^-\cdot$ has been examined by ab initio[2] and MINDO/3[3,4] calculations and is in excellent agreement with the estimated experimental structure derived from its photoelectron spectrum;[2a] in the present context, $H_2C^-\cdot$ is a σ-anion p radical.[5] MINDO/3 calculations of cy-
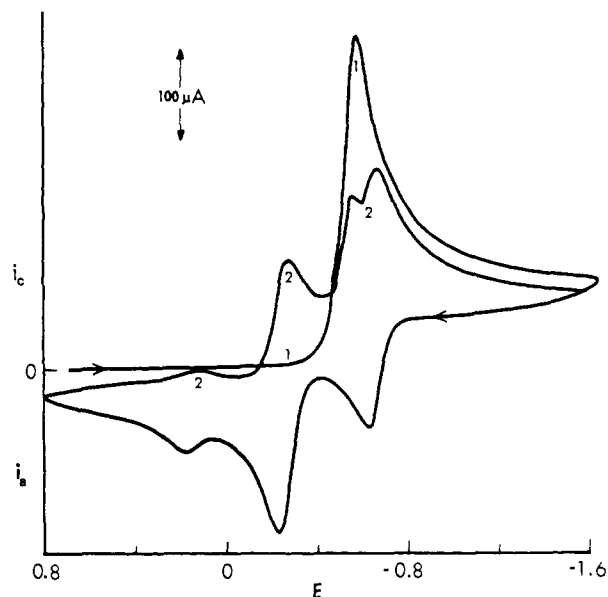

Figure 1. Cyclic voltammogram of 5×10^{-3} M FlN_2 in DMF-$(n\text{-}Bu)_4$-$N^+ClO_4^-$ at a scan rate of 0.2 V/s: working electrode, 0.25-cm^2 planar Pt button; reference electrode, $Cd(Hg)/CdCl_2$, KCl (saturated) in DMF (−0.75 V vs. SCE). The numbers 1 and 2 denote first and second cycles, respectively.

clopentadienylidene anion radical show that the doublet ground state is a carbene π-anion σ radical.[6,7] It was felt that this electronic structure should also apply to the fluorenylidene anion radical ($Fl^-\cdot$). Thus, the reactions of and products from $Fl^-\cdot$ might then serve as a "standard" to which other carbene anion radicals, e.g., diphenylcarbene anion radical ($Ph_2C^-\cdot$),[1] could be compared to gain some structure/reactivity information from their reactions.

The cyclic voltammetric reduction of 9-diazofluorene (FlN_2) at a platinum electrode in DMF-$(n\text{-}Bu)_4N^+ClO_4^-$ shows a cathodic wave near −0.60 V vs. $Cd(Hg)/CdCl_2$ (Figure 1). Although the 9-diazofluorene anion radical ($FlN_2^-\cdot$) is too short-lived to give an anodic wave on the reverse, positive-going sweep, three reversible couples do arise which are seen on this and all subsequent cycles near +0.16, −0.24, and −0.64 V. The normalized peak heights for the most positive couple are kinetically controlled and decrease in magnitude with either an increase in the concentration of FlN_2 or a decrease in the cyclic voltammetric scan rate. The two remaining processes are also kinetically controlled and were ascertained from product studies of exhaustively electrolyzed solutions and by comparison with an authentic sample to arise from the stepwise reduction of fluorenone azine [(Fl=N+)$_2$] to its dianion. Exhaustive, controlled-potential electrolysis of FlN_2 at any potential in the range from −0.8 to −2.0 V afforded (Fl=N+)$_2$ in high yield (91 ± 7%).[8] Fluorenone was observed as a minor product when electrolysis was effected in the presence of adventitious amounts of oxygen; neither fluorene nor any dimeric product was detected by gas chromatography in other than trace amount (<0.5%).
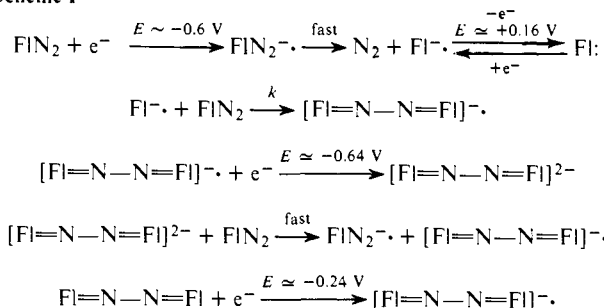
The identities of the transient species which give rise to the most positive redox couple in Figure 1 and the observed kinetic behavior are even more interesting. The possibility that a solvent- or electrolyte-derived intermediate was the unidentified electroactive component was eliminated when similar cyclic voltammetric behavior was observed for FlN_2 in solvent-electrolyte systems of CH_3CN-$(n\text{-}Bu)_4N^+ClO_4^-$, DMF-$LiClO_4$, and $(CH_3)_4N^+PF_6^-$ in DMF and CH_3CN. In addition, cyclic voltammetric examination of (Fl=N+)$_2$ and other plausible products (fluorene, fluorenone, 9-aminofluorene, 9,9'-bifluorenyl, and 9,9'-bifluorenylidene) showed that none of these compounds gave a reversible redox couple near 0.16

V. Since the results of separate single- and double-potential-step chronoamperometric experiments require that the reduction of FlN_2 to product be an overall one-electron process and that all intermediates and products be reoxidized reversibly in a one-electron step per molecule of FlN_2 reduced,[9] we conclude that the electroactive species of the couple is in the product-forming reaction channel.

The 9-fluorenyl anion (FlH^-) was at first considered to be this intermediate since it could be formed by $Fl^-\cdot$ abstracting a hydrogen atom from a component of the solvent–electrolyte system.[11,13] However, FlH^- was rejected as being the electroactive intermediate when its oxidation was determined to occur slightly more readily ($E_{p,a} = 0.08$ V) than that of the species in Figure 1 ($E_{p,a} = 0.16$ V) and to be irreversible at all scan rates up to 100 V/s.[14]

In view of these considerations and our expectation that $Fl^-\cdot$ should be oxidized at a similar potential to that of FlH^-, we tentatively assign this redox couple to that of the carbene, fluorenylidene, and its anion radical, $Fl{:}/Fl^-\cdot$ (Scheme I). If the assignment of this redox couple is correct, this requires a significantly longer lifetime of the carbene $Fl{:}$ compared with that of the 9-fluorenyl radical ($FlH\cdot$) under these reaction conditions since the $FlH^-/FlH\cdot$ couple was not shown to be reversible in this solvent–electrolyte system.

Scheme I

$$FlN_2 + e^- \xrightarrow{E \sim -0.6\ V} FlN_2^-\cdot \xrightarrow{fast} N_2 + Fl^-\cdot \underset{+e^-}{\overset{-e^-}{\underset{\xrightarrow{\hspace{1cm}}}{\xleftarrow{E \simeq +0.16\ V}}}} Fl{:}$$

$$Fl^-\cdot + FlN_2 \xrightarrow{k} [Fl{=}N{-}N{=}Fl]^-\cdot$$

$$[Fl{=}N{-}N{=}Fl]^-\cdot + e^- \xrightarrow{E \simeq -0.64\ V} [Fl{=}N{-}N{=}Fl]^{2-}$$

$$[Fl{=}N{-}N{=}Fl]^{2-} + FlN_2 \xrightarrow{fast} FlN_2^-\cdot + [Fl{=}N{-}N{=}Fl]^-\cdot$$

$$Fl{=}N{-}N{=}Fl + e^- \xrightarrow{E \simeq -0.24\ V} [Fl{=}N{-}N{=}Fl]^-\cdot$$

Two features of these results should be stressed. The first, of course, is the possibility that we now have a method for measuring carbene/carbene anion radical redox potentials. Such data are important for understanding the structures and chemistry of these classes of reactive intermediates. The second feature is the increased production of the corresponding azine and concomitant decrease in the amount of hydrocarbon products from $Fl^-\cdot$ compared with $Ph_2C^-\cdot$.[1a] We believe that this may be related to the structures and, therefore, the relative reactivities of the two carbene anion radicals. Efforts are presently underway to elaborate further on these and other features in a number of hypovalent radical systems both in solution and in the gas phase.

References and Notes

(1) (a) R. N. McDonald, J. R. January, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, **99**, 1268 (1977). (b) A minor product of electroreduction of Ph_2CN_2, benzophenone, was mistakenly identified as diphenylmethylamine.[1a]

(2) (a) P. F. Zittel, G. B. Ellison, S. V. ONeil, E. Herbst, W. C. Lineberger, and W. R. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3732 (1976). (b) R. B. Davidson and M. L. Hudak, *ibid.*, **99**, 3918 (1977): $\theta_{HCH} = 99°$, $r_{CH} = 1.145$ Å.

(3) This work: $\theta_{HCH} = 99.9°$, $r_{CH} = 1.144$ Å, $\Delta H_f = 100.6$ kcal/mol.

(4) (a) We wish to thank Professor S. D. Worley, Auburn University, for making this program written for an IBM-370 computer available to us, and Professor Keith Purcell for his efforts to get it running on our machine. (b) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975).

(5) MINDO/3 calculations of the electronic ground state of the ($^2A_1$) cation radical $H_2C^+\cdot$ give $\theta_{HCH} = 138.7°$ and $r_{CH} = 1.093$ Å (see also W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377

(1971)). Structurally $H_2C^-\cdot$ is that of singlet ($^1A_1$) methylene with an electron added to the out-of-plane p orbital while $H_2C^+\cdot$ is triplet ($^3B_1$) methylene with the electron ionized from that p orbital.

(6) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968), using EHT calculations reported that the p_y (in-plane) orbital of cyclopentadienylidene is "0.13 eV below the delocalized p_x" orbital.

(7) O. W. Webster, *J. Am. Chem. Soc.*, **88**, 4055 (1966), considered the structure of the tetracyanocyclopentadienylidene anion radical to be a π-anion σ radical.

(8) The yield of ($Fl{=}N{+}_2$ was not affected by the addition of either 1% water or 90% tetrahydrofuran to solutions of a FlN_2 in DMF. Typical n values were 0.25–0.50.

(9) The sequence of reactions described by Scheme I (vide infra) was digitally simulated for the single- and double-potential-step chronoamperometric methods by procedures developed by Feldberg.[10] The model correctly predicts the ~10% decrease which is seen in the single-potential-step chronoamperometric $it^{1/2}c$ values in the 10-ms to 10-s time range ($E_c = -1.20$ V) and the current–time behavior for the double-potential-step chronoamperometric experiment when all three anodic processes are made to occur ($E_c = -1.20$ V and $E_a = 0.40$ V). The deficiency in the model when only the $[(Fl{=}N{+}_2]^{2-}$ and the $[(Fl{=}N{+}_2]^-\cdot$ are reoxidized in the double-potential-step chronoamperometric experiment may be due to other reactions which occur at nearly the same rate as the coupling of $Fl^-\cdot$ with FlN_2 (e.g., electron transfer from $[(Fl{=}N{+}_2]^{2-}$ to FlN_2, and disproportionation of $[(Fl{=}N{+}_2]^-\cdot$). Since these additional reactions would greatly increase the complexity of the simulations, and since the rates of these reactions are not known, additional attempts to model the system do not appear justified.

(10) S. W. Feldberg in "Electroanalytical Chemistry", Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1969, pp 199–296.

(11) The anion FlH^- was prepared electrochemically by exhaustive controlled potential electrolysis of fluorene[12] and chemically by reaction of fluorene with sodium hydride and n-butyllithium. The method of FlH^- preparation had no effect upon its redox behavior. Although the products of FlH^- oxidation were not examined in detail, a cyclic voltammetric peak was observed for the reduction of 9,9'-bifluorenyl near −1.9 V on the reverse, negative-going sweep.

(12) (a) J. R. Jezorek, A. Lagu, T. M. Seigel, and H. B. Mark, *J. Org. Chem.*, **38**, 788 (1973); (b) A. Lagu and H. B. Mark, *ibid.*, **42**, 1063 (1977).

(13) FlH^- was considered since this anion was shown in separate experiments to react with FlN_2 to give azine dianion and fluorene.

(14) The lack of reversibility of the $FlH^-/FlH\cdot$ couple also precludes $FlH\cdot$, the assumed oxidation product of FlH^-, as being the electroactive species in this most positive redox couple.

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Transition Metal Initiated Cationic Photopolymerization

Sir:

Photochemical activation of electron transfer within organic donor–acceptor complexes is a useful method for initiating a variety of ionic polymerization reactions.[1,2] Such a concept has not been applied to complexes of transition metal ion acceptors with organic donors. The intrinsic coordinative preferences of the metal ion might be expected to impart reaction selectivity both in terms of organic substrate binding (type, number, and relative orientation of ligands) and the photochemical behavior of the complex.[3] We wish to report that efficient cationic photopolymerization of tetrahydrofuran (THF) can be initiated by small quantities of copper and silver salts.[4] This report constitutes the first example of a transition metal ion mediated cationic photopolymerization[5] and also the first report of THF photopolymerization.

Solutions of the silver salts $AgBF_4$, $AgPF_6$, $AgSbF_6$, and $AgOTf^6$ in anhydrous[7] THF are stable indefinitely in the dark. However, upon irradiation with 254-nm light at 25 °C, degassed solutions of any of these silver salts in THF become increasingly viscous. Also formed is a black precipitate, shown by analysis to be silver metal.[8] Addition of water to the irradiated solutions produces a white precipitate, characterized as polytetrahydrofuran[9] by the infrared spectrum,[10] elemental analysis,[11a] and molecular weight.[11b] In a typical preparative reaction, irradiation of 0.24 g of $AgPF_6$ in 8.9 g of THF for 13.5 h followed by 11.5 h in the dark yielded 4.5 g (50%) of