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ELECTROCHEMICAL AND ALKALI METAL REDUCTION STUDIES OF SILICON, GERMANIUM, AND TIN DERIVATIVES OF CYCLOOCTATETRAENE

PROPERTIES CONFERRED TO CYCLOOCTATETRAENIDE DIANIONS BY GROUP IV SUBSTITUENTS

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Abstract—The electrochemical behavior of trimethylsilyl-, trimethylgermyl-, trimethylstannyl- and t-butylcyclooctatetraenes has been examined by the techniques of polarography and cyclic voltammetry in THF and hexamethylphosphoramide (vastly preferred) solutions. Chemical reduction by means of potassium in ND_3 has also been studied. Evidence is presented that all four compounds undergo reduction to their respective dianions. However, the energetics of $(Me_3)MCOT^{\dot{-}}$ and $(Me_3)MCOT^{2}$ formation vary widely, as do the rates and mechanism of dianion disappearance under the conditions of electrochemical measurement. The available kinetic data suggest, for example, that destruction of the t-Bu and trimethylgermyl substituted dianions proceeds via protonation and/or disproportionation pathways. In contrast, the silyl and stannyl examples experience metal-ring carbon cleavage reactions at yet faster rates. Interestingly, the $E^1_{1/2}$ values give evidence of being quite well correlated by σ_p. Furthermore, when the magnitudes of the $E^1_{1/2}$–$E^2_{1/2}$ gap are plotted vs the covalent radii of the M atoms, a straight line is obtained for the Si, Ge and Sn examples; C deviates widely. This effect is believed to have its origin in resonance of the $M \leftarrow C_\pi$ type involving the d orbitals of M which, of course, is not possible in the carbon case. The significance of these results as well as the other observations made in the course of this work is discussed.

During reduction of cyclooctatetraene to its dianion, a pair of electrons are introduced into each of two singly occupied non-bonding orbitals. As concerns introduction of the first electron, electron-donating substituents can be expected to render reduction relatively more difficult while electron-withdrawing groups should exert the opposite effect. The extent to which the electron affinity is affected can be determined by measurement of the half-wave potential of the first reduction wave, provided that the process is electrochemically reversible.[2] On this basis, the $E_{1/2}$ value for wave A of methylcyclooctatetraene (−2.125 V in THF solution) which is shifted 0.15 V to more negative potential than the parent hydrocarbon[3] should be correlatable to the degree of electron release by the alkyl group as it affects the LUMO of the polyolefin.[4] Other factors such as steric effects on the ring flattening process, solvastion, and outer sphere solvent reorganization energies also control the potential at which the initial electron is introduced. Within a regular series of compounds, however, differences from these latter influences are optimistically minimal, with the result that electronic contributions of the substituent become evident on a somewhat quantitative basis.

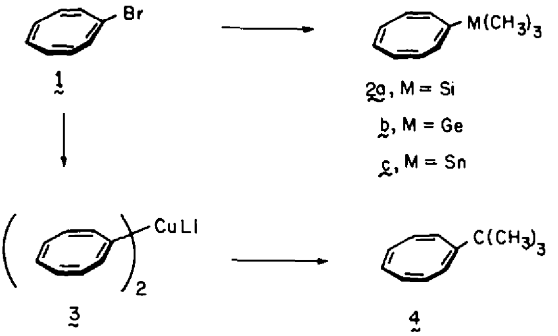
The purpose of the present work was to assess the relative effects of t-Bu, trimethylsilyl, trimethylgermyl and trimethylstannyl groups on the electrochemical behavior of the cyclooctatetraene ring system. Also detailed is an examination of the independent chemical generation of the corresponding dianions. Such an extension to the congeners of carbon has been made in an effort to gain added information concerning the fascinating irregular variability in the intrinsic chemical behavior of C, Si, Ge and Sn[5]. Also, because ESR studies of radical anions of silyl and germyl substituted aromatics abound,[6] the possibility existed that the substituent perturbations on the LUMO's of cyclooctatetraene might be correlated with these earlier data. The electron spin resonance spectra of the radical anions of trimethylsilyl and trimethylgermyl derivatives of benzene[7] and biphenyl,[8] for example, provide a picture consistent with appreciably more effective π-electron withdrawal by these substituents relative to the t-Bu group. In fact, Sipe and West noted in the radical anions of Me_3Si- and Me_3Ge-substituted alkyl benzenes that the organometallic substituent completely dominated the spin distribution by accepting electron density more efficiently than the alkyl groups release it.[9] Silicon appears to be more effective in π-electron withdrawal than gemanium, presumably as a consequence of more effective dative π-bonding.[10] In line with these findings, Bock and Seidl observed that silyl substituted olefins and butadienes are more readily reduced than their t-Bu counterparts where electron repulsion seemingly operates.[11]

RESULTS

Synthesis. Preparation of the organometallic cyclooctatetraenes **2a–c** was readily accomplished by reaction of lithioCOT with the appropriate Me_3MX as previously described by Stone *et al.*[12] Access to the unknown t-Bu derivative required utilization of an indirect method.

Whereas the attempted coupling of **1** with lithium di(t-Bu)cuprate[13] proved unsatisfactory, the reverse procedure involving prior generation of **3** and its reaction with t-BuBr afforded **4** in 13% isolated (VPC) yield. This pale yellow hydrocarbon exhibited a ^1H NMR spectrum consisting of the expected downfield multiplet (δ 5.42–5.88, 7H) and sharp upfield singlet (δ 1.04, 9H).

Electrochemical behavior. The reducibility of **2a–c** and **4** was first examined polarographically in anhydrous hexamethylphosphoramide (HMPA) solutions containing



tetra-n-butylammonium perchlorate (TBAP) as supporting electrolyte with strict exclusion of moisture and oxygen. The entire series of measurements was conducted on the specially designed vacuum line apparatus developed by Anderson.[14] Relative to COT, MR_3 substitution is seen to raise the potential of the first reduction wave significantly (Table 1). The ordering is such that progression from silicon to germanium to tin generates increased resistance toward introduction of the first electron. Significantly, the t-Bu derivative commands the position of most difficulty reducible. Since its $E^1_{1/2}$ appears 0.15 V more cathodic than that of methylCOT, the phenomenon cannot be attributed merely to generalized alkyl substitution.

The present findings agree in direction with the reduction potentials of 4-substituted biphenyls as determined by Curtis and Allred in dimethylformamide solution.[8a] Although the spread in $E_{1/2}$ values for the four COT's (0.242 V, HMPA) is much greater than for the biphenyl series (0.07 V, DMF), it is not known to what extent the solvent changeover affects this parameter. In Fig. 1, the first half-wave potentials (standardized to COT) have been plotted vs the Hammett σ_p constants; data for several additional monosubstituted COT's have been included for completeness.[15] When all 8 points are taken collectively, the equation for the resulting least-squares line is $\Delta E^1_{1/2} = 0.628\ \sigma_p + 0.013$. The discrepancy of the fluoro substituent can be attributed to enhanced levels of resonance interaction with the radical anion core. Such complications are at best of marginal significance with the organometallic derivatives, thereby implying that d orbital participation, if present, produces negligible effects.

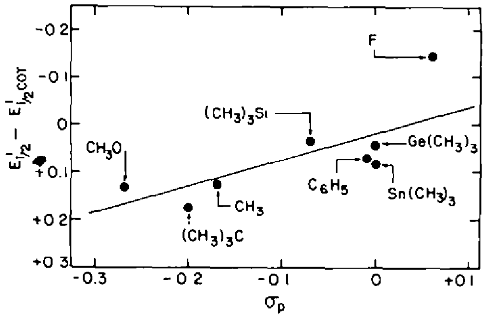


Fig. 1. Plot of σ_p vs $E^1_{1/2} - E^1_{(1/2)COT}$. The σ_p constants are based on the ionization constants of *p*-substituted benzoic acids and are taken from the compilation of D. H. McDaniel and H. C. Brown [*J. Org. Chem.* **23**, 420 (1958)]. The methoxyl example was determined in acetonitrile solution [L. B. Anderson, J. F. Hansen, T. Kakihana and L. A. Paquette, *J. Am. Chem. Soc.* **93**, 161 (1971)].

Cyclic voltammetric response. Cyclic voltammetric studies of the title compounds in anhydrous HMPA revealed dramatic differences in dianion reactivity. Figures 2–5 illustrate their typical behavior under conditions of the most efficacious scan rate in each instance. (Me_3)GeCOT, the most well behaved member of the series, is characterized by two reduction waves at −1.651 and −1.795 V. The peak current constant for the first electron transfer is 0.44 A/cm^{2}V$^{1/2}$M, a value essentially identical to that observed for COT (Table 1). The ratio of the second anodic to the first cathodic peak height, I_{pa_2}/I_{pc_1}, at 200 mV/sec is 0.97 (Fig. 2) again similar to that of COT (0.89 at 100 mV/sec) in HMPA. The anodic half cycle shows clearly the oxidation peaks for Me_3GeCOT^{2-} and $Me_3GeCOT^{\dot{-}}$. The dianion is seen to have a finite existence in this medium. Its lifetime varies with scan rate, is consequently time dependent, and therefore is not governed by kinetically first-order decomposition. Expressed as a pseudo first-order rate constant, the rate of disappearance of $(CH_3)_3GeCOT^{2-}$ lies in the range of 0.01–0.02 sec^{-1} at scan rates of 20–200 mV/sec.[16] Since this value compares closely to that

Table 1. Electrochemical results in HMPA solution (linear sweep voltammetry)[a]

COT	R	$E^1_{\frac{1}{2}}$ [b]	$E^2_{\frac{1}{2}}$ [b]	$\Delta E_{\frac{1}{2}}$, mV	I_p [c]	Slope[d]	$\underline{n}_{overall}$
2a	$-Si(CH_3)_3$	-1.640	-1.804	164	0.40	0.0173	2
2b	$-Ge(CH_3)_3$	-1.651	-1.795	144	0.44	0.018	2
2c	$-Sn(CH_3)_3$	-1.69	-1.77	80	0.53-0.74	0.0132	e
4	$-C(CH_3)_3$	-1.882	-1.996	114	0.65-0.85		2
--	$-CH_3$	-1.730	-1.955	225	0.40		2
--	-H	-1.606	-1.921	315	0.42		2

[a] All measurements were performed in the 0.5-1.5 m$\underline{M}$ concentration range and at two different concentrations. In each run, an excess of cyclooctatetraene was injected into the cell for the purpose of internal standardization. [b] The $E_{\frac{1}{2}}$ values were obtained vs $AgClO_4/Ag$ and are corrected to sce by adding 0.36 V: K. Izutsu, S. Sakura, and T. Fujinaga, Bull. Chem. Soc. Japan, **45**, 445 (1972). [c] Peak current constant for the first reduction wave in A/cm^2 V$^{\frac{1}{2}}$ $\underline{M}$. [d] Slope of graph of E vs ln(i/i$_d$-i). [e] Decomposition of dianion too rapid to permit accurate measurement of electron uptake.

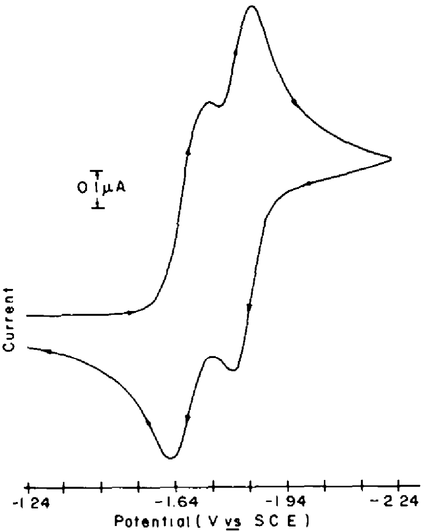


Fig. 2. Single sweep voltammogram of **2b** (1.70×10^{-3} M solution) in HMPA solvent, $v = 20$ mV/sec.

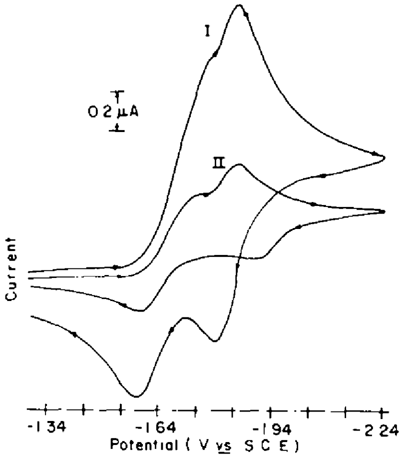


Fig. 3. Single sweep voltammograms of **2a** (1.53×10^{-3} M solution) in HMPA solvent, $v = 100$ mV/sec for cycle I and 20 mV/sec for cycle II.

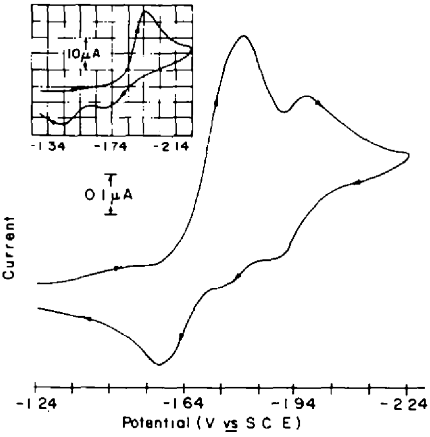


Fig. 4. Single sweep voltammogram of **2c** (0.66×10^{-3} M solution) in HMPA solvent, $v = 100$ mV/sec. Inset shows oscilloscopic determination of CV at 15 V/sec (6.6×10^{-3} M, HMPA).

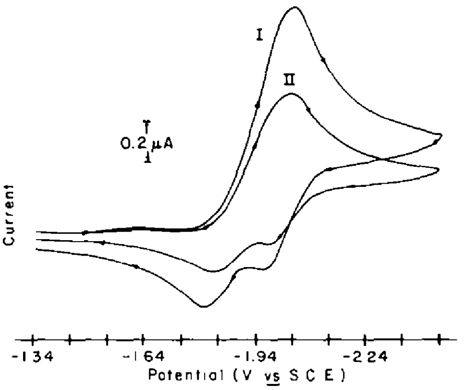


Fig. 5. Single sweep voltammograms of **4** (0.90×10^{-3} M solution) in HMPA solvent, $v = 150$ mV/sec for cycle I and 50 mV/sec for cycle II.

for COT^{2-} ($k = 0.022\ sec^{-1}$ at 100 mV/sec, HMPA) and because such destruction of the parent dianion is known to be the result of protonation and disproportionation reactions,[3,17] this analogy serves as our basis for believing that $(CH_3)_3GeCOT^{2-}$ is removed from solution by similar pathways.

In the case of $(CH_3)_3SiCOT$, the initial cathodic scan at 20 mV/sec again consists of two separate waves corresponding to two 1ϵ reduction steps. At scan speeds in excess of 100 mV/sec, the two peaks become increasingly superimposed as illustrated by the two sweep cycles in Fig. 3. Of greater significance, the anodic segment of the scans provides direct evidence for the marginal stability of Me_3SiCOT^{2-} in this medium. At 20 mV/sec, for instance, no evidence for reoxidation of the silyl dianion is present although the anodic peak for Me_3SiCOT^{-} remains suitably prominent (COT^{-} is also oxidized at this potential). Instead, there appears a peak representing reoxidation of COT^{2-} (Fig. 3). At increased scan speeds, the anodic half cycle is typified by two nicely defined electrooxidation steps quite similar to those witnessed for the germanium derivative. Evidently, the elapsed time span between generation and oxidation of Me_3SiCOT^{2-} at the 100 mV/sec sweep rate is sufficiently short that decomposition of the dianion has not reached measurable levels. On the basis of the Nicholson-Shain model,[16] the pseudo first-order rate constant for the disappearance of the silyl anion at this scan rate is computed to be $0.079\ sec^{-1}$. The value of k determined for sweep rates varying between 50–250 mV/sec increase in an approximately linear relationship with the sweep rate according to the relationship $k = 0.23\ (V\ sec^{-1}) + 0.058\ sec^{-1}$.

Because a general treatment of the ECE mechanism for stationary electrode processes is also available,[18] it becomes possible to calculate the rate of appearance of COT^{2-}, although such computations are perforce somewhat more approximative than the above. This is because the formation of COT^{2-} does not manifest itself on cathodic scans (except for some alteration of line shape), but is seen only on anodic scans in sufficient intensity for peak height measurements. Analysis of cyclic voltammograms recorded at a relatively slow 20 mV/sec established the peak current constant for oxidation of the COT^{2-} formed *in situ* to be $0.155\ A/cm^2\ V^{1/2}\ M$. Since the I_p value for one-electron transfer in COT is 0.42, the level of parent dianion generated under these conditions is approximately 37%. The data denote the rate of appearance of COT^{2-} to be somewhat in excess of $0.023\ sec^{-1}$.[19]

The rate constant associated with the destruction of Me_3SiCOT^{2-} is considerably larger in magnitude than that observed for COT^{2-} and the trimethylgermyl substituted dianion. It is therefore unlikely that the mechanism associated with disappearance of the silyl species is akin to the protonation or disproportionation reactions discussed earlier. Rather, the appearance of COT^{2-} supports the contention that C–Si bond cleavage gains kinetic importance as the rate-determining step in Me_3SiCOT^{2-} decomposition. In view of the well established greater ease of cleavage of C–Sn bonds,[5] it remained to demonstrate for confirmatory purposes a still greater rate of dianion appearance in the case of **2c**. As discussed below, such added proof has been acquired. On the basis of the available data, however, it has not proven possible to distinguish between the generalized eqns (1) and (2).

$$(CH_3)_3MCOT^{2-} \rightarrow \begin{cases} C_8H_7^{\dot{-}} + (CH_3)_3M^{\cdot} \\ \quad\quad \text{or} \\ C_8H_7^{-} + (CH_3)_3M^{-} \end{cases} \tag{1}$$

$$(CH_3)_3MCOT^{2-} \rightarrow [?] \rightarrow COT. \tag{2}$$

The cyclic voltammetric data for Me_3SnCOT reveal an even greater instability of the dianion species. Thus, the cathodic portion of the cycle at normal sweep rates shows two unresolved waves followed at more negative potential by the wave arising from reduction of $COT^{\dot{-}}$ to COT^{2-} (Fig. 4). The electrode product must therefore be highly unstable and give rise to the parent cyclooctatetraene ring during its rapid disintegration. As a direct consequence of the short lifetime of Me_3SnCOT^{2-}, the anodic wave for its conversion to the radical anion is not in evidence at scan speeds below 100 mV/sec. Because the wave for oxidation of $(CH_3)_3SnCOT^{\dot{-}}$ is almost coincident with that of $COT^{\dot{-}}$, the chart-recorded voltammograms ($\leqslant$ 300 mV/sec) exhibit a second anodic wave which is disproportionately large relative to the first anodic wave. Only at sweep rates in excess of 10–15 V/sec (oscilloscopic measurements, see inset of Fig. 4) is the absence of COT (as $COT^{2-} \rightarrow COT^{\dot{-}}$) noted. Again, the rate of disappearance of Me_3SnCOT^{2-} is seen to increase with increasing scan rates and is consequently not first-order. The average pseudo first-order rate constant for decomposition of the stannyl dianion at 100 mV/sec was assessed to be 1.3 sec^{-1}. Determination of the rate of appearance of COT^{2-} under these conditions gave the value 0.6 sec^{-1}.

In contrast to the exceedingly reactive nature of the tin derivative, the t-Bu compound gave evidence of a return to normal stability. The average peak current constant for the broad wave observed in the 50–200 mV/sec range is 0.74 $A/cm^2\ V^{1/2}\ M$ (Fig. 5). This value is lower than that anticipated for a simultaneous two-electron reduction (1.2), but is significantly greater than that for single electron reduction of COT (0.42). This apparent discrepancy can be rationalized in terms of Polcyn and Shain's calculations[20] which predict a diminution in the magnitude of the peak current constant with concomitant broadening of the reduction wave when the successive one-electron transfers are separated by approximately 100 mV. In the present example $E_c^1 - E_c^2 = 76$ mV.

Slow scan rates (2.5–20 mV/sec) are necessary to sufficiently resolve the two reduction waves in order that their half-wave potentials can be determined. However, the peak current constant calculations derived from these experiments generate artificially large values for each wave ($I_p = 0.65$–$0.845\ A/cm^2\ V^{1/2}\ M$) because the period of the scan is not sufficiently rapid to overcome convection. Notwithstanding, it is possible to estimate the pseudo first-order rate constant for disappearance of $(CH_3)_3CCOT^{2-}$ as 0.154 sec^{-1} at 100 mV/sec. The conclusion to be derived from the magnitude of this k is that protonation and/or disproportionation return as the likely operative mechanisms (*vide supra*).

Alkali metal reduction. When solutions of **2a–2c** and **4** in freshly distilled (vacuum line techniques) anhydrous ND_3 were treated with 2 g-atom equiv of potassium metal, rapid reduction occurred as determined by PMR spectroscopy at −55°. In Table 2 are summarized the chemical shift data of the neutral molecules and their dianions generated under the above conditions. The notable exception to respectable dianion stability is that derived from **2c** which was found to undergo rapid C–Sn bond cleavage even at such low temperatures. Direct observation of this dianion was consequently complicated by its limited stability.

Table 2. Summary of chemical shift data for several $(CH_3)_3MCOT$'s (CCl_4, 35°) and their dianions (ND_3, −55°) (δ, 60 MHz)[a]

	Neutral species		Dianion	
M	Methyls	Olefinics[b]	Methyls	Olefinics[b]
Si	0.1 (s)	5.73 (br m)	0.25 (s)	5.8 (br m)
Ge	0.2 (s)	5.7 (br m)	0.33 (s)	5.8 (br m)
Sn	0.15 (s)	5.7 (br m)	0.15 (s)	5.75 (br m)
C	1.04 (s)	5.7 (br m)	1.50 (s)	5.7 (br m)

[a] Shifts in ND_3 solvent have been assigned relative to trimethylamine ($\delta^{NH_3}_{TMS}$ 2.135) as internal standard: S. W. Staley and N. J. Pearl, J. Amer. Chem. Soc., 95, 3437 (1973). [b] The approximate weighted center of the multiplet is given.

All of the NMR changes attending reduction are congruent with the anticipated diatropic character[21] of the resulting dianions. The combined influence of charge density, planarity, and electronic delocalization is reflected in the small downfield shifting of the ring protons. In the absence of a ring current, shielding of the protons by approximately 2.5 ppm can be anticipated.[22] Consequently, the aromatic nature of such species exerts a substantial deshielding effect which counteracts the above phenomenon. In methyl substituted COT dianions, the alkyl groups experience downfield shifting of *ca.* 1 ppm as compared to their neutral precursors.[3] In the present series, the methyl substituents are not directly bonded to the ring but rather to an insulating atom. The magnitude of the effect is consequently diminished, the larger atoms being more effective in this regard than carbon.

DISCUSSION

Briefly stated, the first reduction wave of an aromatic hydrocarbon is electrochemically reversible because electron transfer to the LUMO occurs without bond breaking or a significant change in molecular geometry, and hence requires little activation energy.[2,23] In contrast, the response of COT and several of its derivatives to introduction of the first electron is electrochemically irreversible. This dichotomy arises because electron transfer now involves a change in molecular geometry from an initially tub-shaped neutral species to a planar or nearly planar radical anion and is demanding of a significant increase in the activation energy.[3,17,24,25] This reasoning implies that the conversion of $COT^{\dot{-}}$ to COT^{2-}

should be reversible or nearly so since minimal conformational perturbation is now involved. The earlier experimental findings fully support this interpretation.

The need to provide considerable energy to flatten or nearly flatten the COT ring upon introduction of the first electron manifests itself in a small heterogeneous electron transfer rate constant and in a charge transfer coefficient (α) considerably less than 0.5.[17b,24,26] Assuming that the mechanisms of initial electron transfer to **2a**–**2c** and **4** are comparable, then the similarities of the slopes of their first polarographic waves can be taken as an indication that the values of α correspond closely. This being the case, the energy changes accompanying each of the four electrode processes become directly relatable to the differences in $E^1_{1/2}$ according to eqn (3).[3] Substitution of the thermodynamic interpretation of $\Delta\Delta G^{\neq}$ by the Taft treatment of homogeneous reactions[27] leads to eqn (4) which covers most substituent effect contributions to the half-wave potentials.[15,28] Combination of eqns (3) and (4) generates eqn (5), a form convenient for polarography, where the independent variables P, M_π and S comprise the polar, resonance, and steric contributions to the activation energy of electron transfer.

$$\Delta E^1_{1/2} = \Delta\left(E^{\circ\prime} - \frac{RT}{\alpha n F}\ln\left(\frac{i_0}{k_s n F}\right)\right) \approx \Delta\Delta G^{\neq} \qquad (3)$$

$$\Delta\Delta G^{\neq} = \Delta\Delta E^{\neq}_{\sigma} + \Delta\Delta E^{\neq}_{M} + \Delta\Delta E^{\neq}_{S} \qquad (4)$$

$$\Delta E^1_{1/2} = P + M_\pi + S. \qquad (5)$$

Thus, we see that insofar as kinetic complications are responsive to the same factors which determine the free energy of the primary charge transfer and the compounds compared are all subject to the same complications, empirical correlation of half-wave potentials with structural parameters should provide useful results. Because of the similar tertiary nature of the substituents in **2a**–**2c** and **4**, the differences in steric contributions for this series are likely to have less impact on $\Delta E^1_{1/2}$ than polar and resonance contributions. Therefore, the substituent influence might well reside in the P and M_π terms. The linearity of the plot in Fig. 1 lends credence to the present treatment and suggests furthermore that first reduction potentials for any given monosubstituent may well be influenced chiefly by electronic factors.

Because of incipient electron repulsion, the second electron transfer step for aromatic and nonbenzenoid systems alike occurs with greater difficulty.[29] In either case, effects due to conformational alteration of structure are negligible and the ability of a substituent to assist in charge delocalization should accordingly have marked impact on the magnitude of the $E^1_{1/2} - E^2_{1/2}$ gap. We have addressed this point by simply plotting the extent of this peak separation *vs* the covalent radius (r) of the Group IV atom (Fig. 6). Interestingly, the Si, Ge, and Sn examples comprise a straight line from which the t-Bu derivative deviates significantly. On this basis, the trio of metallic compounds is seen to be capable of facilitating second electron transfer by mechanism(s) not available to the carbon analog.

Such behavior has been anticipated by Craig *et al.*, who on the basis of high C–M overlap integrals (M = Si, Ge, Sn, Pb) predicted that π-bonding should be important in the chemistry of unsaturated derivatives of these elements.[30] Whether the interaction is that of vacant d orbitals or of rehydrbidized dp orbitals, each containing one electron as in the Longuet-Higgins treatment,[31] is not known with certainty. In either event, such resonance predicts withdrawal of electron density from the COT^{2-} nucleus. These conclusions are supported by the observations of Bedford[7a] and Bock[32] who demonstrated that Me_3M-substituents on phenyl radical anions are electron attracting for Si and Ge (i.e. $Si \leftarrow C_\pi$), but electron releasing for C. Simple Hückel MO calculations on monosubstituted biphenyls indicate further a π-bond order of 0.18 for the Si–C bond and 0.13 for the Ge–C bond, pointing to stronger d_π–p_π electron withdrawal by silicon relative to germanium.[8a,33] The present data suggest further that the actual magnitude of resonance delocalization through the d orbitals of the substituent (excluding carbon) is related directly (and linearly) to the covalent radius of the given atom.

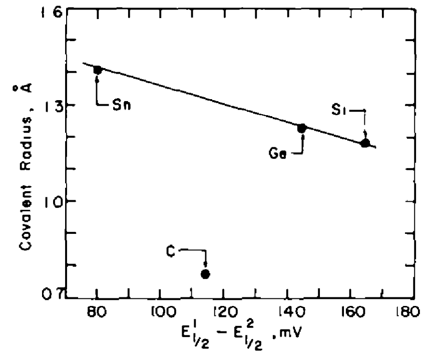


Fig. 6. Plot of $E^1_{1/2} - E^2_{1/2}$ vs the covalent radius of the atom.

The proclivity of Me_3SiCOT^{2-} for Si–C bond cleavage under conditions of electrochemical generation was not entirely expected. Birch[34a] and Benkeser reduction[34b] of aryltrimethylsilanes results in C–Si bond cleavage only when an allylic or benzylic bond is involved and not otherwise. The enhanced stability of the silyl dianion obtained by K/NH_3 reduction likely arises because of the favorable consequences of counterion and solvation influences.

On the other hand, the fragile nature of Me_3SnCOT^{2-} was predeterminable. Thus, reaction of tetravinyltin with excess lithium in ether at room temperature proceeds under the catalytic action of benzophenone and results in cleavage of the organic group and formation of pure vinyllithium.[35] *cis*- and *trans*-Propenyltrimethyltins are merely isomerized by lithium in ether, but in THF solution destruction occurs with formation of propenyllithium and methyllithium.[36] Brief treatment of 4,4′-bistrimethylstannylbiphenyl with Na–K alloy in THF at −50° leads to formation of an anion radical of limited stability.[33] Given such analogy, the likelihood that Me_3SnCOT^{2-} could escape the inevitability of reductive sidechain cleavage was viewed as remote. With the electrochemical behavior of **2c** as a guide, the chemical reduction of the trimethyltin derivative is viewed as proceeding to the dianion stage prior to Sn–C bond cleavage. This conclusion receives added support from our observation that the methyl signal of Me_3SnCOT^{2-} (δ 0.15) is replaced by a singlet at higher field (−0.45) upon warming of the ND_3 solution to room temperature. This change is not reversible.

Undoubtedly the most satisfying aspect of this work has been our ability to derive the pseudo first-order rate constants for disappearance of the several dianions. From the varying magnitudes of these k's as determined from the cyclic voltammetric responses of the Me_3MCOT's, it proved possible to attribute their subsequent chemistry either to the customary protonation-disproportionation reaction channel or to the heretofore unprecedented ejection of the ring substituent.

EXPERIMENTAL

The NMR spectra were determined with a Varian A-60A spectrometer and mass spectra were recorded with an AEI MS-9 instrument at an ionizing energy of 70 eV. Microanalytical data were acquired by the Scandinavian Microanalytical Laboratories, Herlev, Denmark.

t-Butylcyclooctatetraene (**4**). A stirred soln of **1** (2.0 g, 11 mmol) in 25 ml of dry ether cooled to −78° under N_2 was treated slowly via syringe with 33 ml of a 0.96 M soln of t-BuLi in pentane (32 mmol) and the mixture was stirred for 1.5 hr at −78°. Then 2.65 g (16 mmol) of cuprous iodide in 25 ml of dry ether was added and the resulting mixture stirred for 30 min. By means of an addition funnel, 15.1 g (110 mmol) of t-BuBr in 25 ml of ether was introduced and the resulting dark green soln was stirred for 1.5 hr at −78°, then allowed to warm slowly to 0°. The mixture was hydrolyzed with NH_4Cl aq, filtered to remove insoluble solid, and the aqueous phase removed for reextraction. The combined organic layers were dried and evaporated to leave 13.6 g of an orange-yellow oil. Distillation of this oil afforded 100 mg of **4**, bp 32° (0.28 mm), which was further purified by preparative VPC techniques on a 6 ft × 0.25 in. 10% SF-96 column (78°). (Found: C, 89.69; H, 10.18. Calc. for $C_{12}H_{16}$: C, 89.94; H, 10.06%).

Electrochemical measurements. The polarographic studies in anhyd THF were carried out by the procedure previously described[3] with the exception that a PARC 173D potentiostat was used. Cyclic voltammetry experiments were executed in a similar manner with HMPA as solvent. A planar platinum electrode ($A = 5.2 \times 10^{-3}\ cm^2$) was employed as the working electrode. Samples were introduced into the cell by injection via syringe of aliquots (25–75 μl) of the anhyd THF stock solution prepared for the polarographic studies. Neat COT (2 μl) was injected into the cell at the end of the experiments to provide an internal reference. In all cases, the cyclic voltammetric measurements were conducted at two different substrate concentrations.

Purification of the HMPA (MC/B reagent grade) was effected by double fractional distillation from calcium hydride followed by crystallization by cooling. The remaining supernatant was decanted. Clean sodium metal was added to the crystalline HMPA and the solvent allowed to warm to room temperature *in vacuo*. Once purified, the HMPA was stored under the vapor pressure of the solvent and was distilled directly into ampoules containing the requisite quantities of solid electrolyte.

Method for obtaining PMR spectra of dianions in ND_3. The earlier procdure[3] was followed in every detail.

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