(i or endo, n) or out (o or exo, x) of the cavity, **12** may exist in *five topological forms* in a way similar to the three forms of macrobicyclic compounds.[4,6] They may be described as i_4, i_3o, i_2o_2, io_3, o_4. The NMR spectrum corresponds either to one highly predominant symmetric form, i_4 or o_4, or to a mixture of all forms in rapid equilibrium since inversion of the nitrogen sites is expected to be very fast.

The i_4 form has a particularly attractive shape. The intramolecular cavity is *spherical* and lined with the ten binding sites in an octahedrotetrahedral arrangement **13:** the four nitrogens are located at the corners of a tetrahedron and the six oxygens are at the corners of an octahedron, the centers of the two polyhedra coincide and the ten corners lie on the same sphere. In addition to its chemical interest, such a ligand is not without aesthetic appeal![7]

Compound **12** should be able to form complexes with metal cations of appropriate size. Indeed, when solid CsBr is added to a $CDCl_3$ solution of **12,** the salt dissolves slowly and the initial NMR spectrum is progressively replaced by a new one (Figure 1) due to the formation of a complex of 1/1 stoichiometry. Complex formation is also observed by NMR in D_2O solution for instance with KBr, CsBr, and $BaBr_2$ as well as with NH_4I in $CDCl_3$.

Since in the slowly exchanging complex in $CDCl_3$ all bridges in the ligand are equivalent, the complex must have a center of symmetry; i.e., the cation is trapped inside the cavity of the ligand. The complexes formed by **12** are thus *macrotricyclic [3]cryptates,*[2] $[Cs^+ \subset \mathbf{12}]Br^-$, analogous to the macrobicyclic [2]cryptates discovered earlier.[2,9] In the complex, the ligand certainly exists in form i_4 which allows optimal interaction of the cation with all four nitrogen sites as well as with the oxygens.

Compound **12** has a cavity radius of about 1.8 Å, larger than that of a given face of the polyhedron (about 1.5 Å) and its high connectivity ensures appreciable rigidity. These two features are expected to influence both stability constants and cation exchange rates of the complexes. Preliminary measurements show that the stability constants for the K^+, Rb^+, and Cs^+ complexes are about 3.4, 4.2, and 3.4, respectively (log K_s in water at 25°). The Cs^+ complex is probably the most stable known to date. The cation exchange rates (determined from ^1H NMR coalescence temperatures) are among the slowest observed,[2] with free energies of activation of 15.5 (at 28°), 16.7 (at 51°) and 16.1 (at 41°) kcal/mol for the K^+, Rb^+, and Cs^+ complexes, respectively.

The properties of ligand **12** and of some derivatives will be described more extensively in future reports.

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(10) Metal cation complexes have also been observed for **10** (work in progress).
(11) ERA No. 265 of the CNRS.

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The Mechanism of Dimer Formation in the Electroreduction of *p*-Fluorobenzonitrile

Sir:

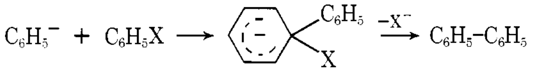
The sodium naphthalenide reduction of several halobenzenes has been shown to result in dehalogenation and to give benzene and biphenyl as the two principal products.[1] The distribution of the principal products for both 1:1 and 2:1 molar ratios of sodium naphthalenide to halobenzene is summarized in eq 1.

$$C_6H_5X + Na^+C_{10}H_8\cdot^- \xrightarrow{THF} C_6H_6 + C_6H_5{-}C_6H_5 + NaX \quad (1)$$

$$\begin{array}{ll} 82\text{–}90\%\ (X = Cl,\ Br,\ I) & 6\text{–}10\%\ (X = Cl,\ Br,\ I) \\ 72\%\ (X = F) & 17\%\ (X = F) \end{array}$$

Although Cheng et al.[1] favored reaction pathways involving phenyl radicals, Sargent[2] disputed this suggestion and proposed instead phenyl anion as the reactive intermediate. The formation of benzene was suggested by Sargent[2] to occur by the abstraction of a proton from the solvent system by the phenyl anion (eq 2), while aromatic nucleophilic substitution was proposed for the formation of biphenyl (eq 3).

$$C_6H_5^- + THF \longrightarrow C_6H_6 + CH_2{=}CHCH_2CHO^- \quad (2)$$



(3)

We have now obtained evidence that dimer formation in the reductive defluorination of *p*-fluorobenzonitrile occurs by neither of these pathways, but occurs, rather, via the apparent dimerization of the halogenated radical anion. The evidence is based upon kinetic studies and substitution experiments.

The electrochemical reduction of *p*-fluorobenzonitrile has been demonstrated in our laboratory to give both monomeric and dimeric products.[3] Although unimolecular decomposition of the intermediate *p*-fluorobenzonitrile radical anion and the formation of benzonitrile was shown to predominate in dilute solution ($<2.5 \times 10^{-4}$ *F*) (eq 4 and 5),

$$p\text{-}FC_6H_4CN + e \rightleftharpoons$$

$$[p\text{-}FC_6H_4CN]\cdot^- \xrightarrow{k=11\ \text{sec}^{-1}} [p\text{-}NCC_6H_4\cdot] + F^- \quad (4)$$

$$[p\text{-}NCC_6H_4\cdot] \xrightarrow{SH} C_6H_5CN + \text{solvent derived products} \quad (5)$$

a significant yield of the dimer, 4,4′-dicyanobiphenyl, was obtained via an undetermined pathway when the concentration of *p*-fluorobenzonitrile radical anion exceeded 10^{-3} *F*. Improved instrumentation has now allowed us to examine the kinetics of dimer formation under conditions which minimize the unimolecular decomposition pathway (eq 4 and 5).

The kinetics of the decomposition of the *p*-fluorobenzonitrile radical anion were studied by the single-potential-step chronoamperometric method.[4-6] In this technique the potential of the planar platinum electrode in a solution containing *p*-fluorobenzonitrile is changed abruptly from a value where no redox process occurs ($E = -2.00$ V vs. SCE) to a value sufficiently negative ($E = -2.70$ V) so as to cause the concurrent reduction of *p*-fluorobenzonitrile ($E_{1/2} = -2.33$ V) and the product of its radical anion decomposition, 4,4′-dicyanobiphenyl.[7] Theory[6] predicts for this sequence of electrochemical and chemical reactions (eq 6-8) that the apparent value of $n(n_{app})$ should vary from a lower limit of 1.0, when the only reaction which occurs is the one-electron reduction of *p*-fluorobenzonitrile to its rad-

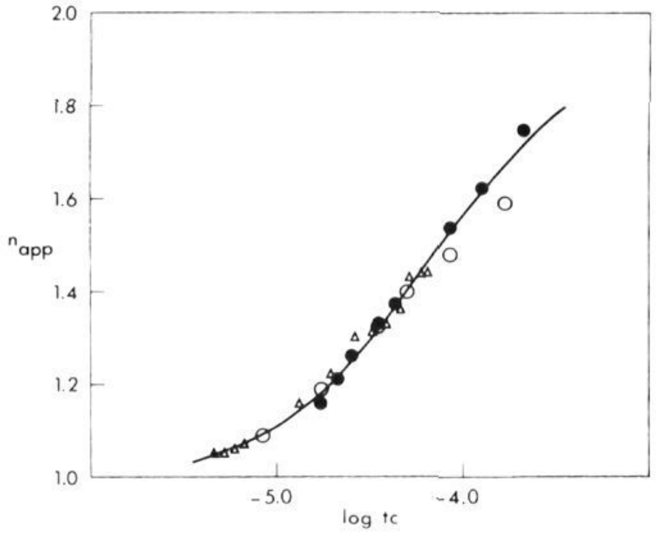


Figure 1. Single-potential-step chronoamperometric data for the formation of 4,4′-dicyanobiphenyl. The solid curve was obtained by the digital simulation[6] of the processes described by eq 6–8 with $k_d = 4.5 \times 10^3\ M^{-1}\ \text{sec}^{-1}$. Since we have defined $d[4,4'\text{-dicyanobiphenyl}]/dt = 2k_d[p\text{-fluorobenzonitrile}]^{\cdot -}$, the rate constants obtained by Nelson and Feldberg[6] were divided by two. Concentrations of *p*-fluorobenzonitrile in 0.1 *F* TEAP-DMF are: (●) 4.2×10^{-3} *F*; (△) 6.5×10^{-3} *F*; and (○) 8.4×10^{-3} *F*. The temperature was 22 ± 1°.

ical anion (eq 6), to an upper limit of 2.0, when reactions 6–8 proceed to completion.

$$p\text{-FC}_6\text{H}_4\text{CN} + e \rightleftharpoons [p\text{-FC}_6\text{H}_4\text{CN}]^{\cdot -} \qquad (6)$$

$$2[p\text{-FC}_6\text{H}_4\text{CN}]^{\cdot -} \xrightarrow{k_d} \text{intermediate(s)} \xrightarrow{\text{fast}} 4,4'\text{-NCC}_6\text{H}_4\text{C}_6\text{H}_4\text{CN} \qquad (7)$$

$$4,4'\text{-NCC}_6\text{H}_4\text{C}_6\text{H}_4\text{CN} \underset{-e}{\overset{e}{\rightleftharpoons}} [4,4'\text{—NCC}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}]^{\cdot -} \underset{-e}{\overset{e}{\rightleftharpoons}} [4,4'\text{-NCC}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}]^{2-} \qquad (8)$$

Although the data were acquired only for $t \leq 20$ msec, the model correctly predicts the observed variation of n_{app} with time and its dependence on the concentration of *p*-fluorobenzonitrile (see Figure 1).[8]

The chronoamperometric data do not allow us to distinguish between kinetically equivalent pathways such as dimerization and disproportionation of *p*-fluorobenzonitrile radical anions. In order to determine if disproportionation and the subsequent aromatic nucleophilic attack of *p*-cyanophenyl anion on the parent compound could be an important reaction pathway in the formation of the dimer, a direct test for this pathway was made. For this experiment, the *p*-cyanophenyl anion is generated in situ, in the presence of *p*-fluorobenzonitrile, by the electroreduction dechlorination of *p*-chlorobenzonitrile. The reduction of *p*-chlorobenzonitrile occurs approximately 0.3 V more easily than the reduction of *p*-fluorobenzonitrile and is facilitated by the rapid rate at which the *p*-chlorobenzonitrile radical anion loses chloride ion.[9] The *p*-cyanophenyl anion is formed during this electroreduction as a short-lived intermediate (eq 9 and 10).[10,11]

$$p\text{-ClC}_6\text{H}_4\text{CN} + e \rightleftharpoons [p\text{-ClC}_6\text{H}_4\text{CN}]^{\cdot -} \xrightarrow{\text{very fast}} [p\text{-NCC}_6\text{H}_4\cdot] + \text{Cl}^- \qquad (9)$$

$$[p\text{-NCC}_6\text{H}_4\cdot] + e \xrightarrow{\text{fast}} [p\text{-NCC}_6\text{H}_4^-] \xrightarrow[\text{SH}]{\text{fast}} \text{C}_6\text{H}_5\text{CN} \qquad (10)$$

The results of the test for aromatic nucleophilic substitution are shown in Figure 2. In the absence of *p*-chlorobenzonitrile, the reversible redox processes due to the stepwise reduction of 4,4′-dicyanobiphenyl (−1.6 and −2.0 V) are seen only after the reduction of *p*-fluorobenzonitrile is first made to occur (Figure 2, top). When *p*-chlorobenzonitrile is also present (Figure 2, bottom), reversal of the potential scan near the cathodic peak for *p*-chlorobenzonitrile but before the onset of the reduction of *p*-fluorobenzonitrile gives neither of the processes attributed to the 4,4′-dicyanobiphenyl system. This result strongly suggests that 4,4′-dicyanobiphenyl formation does not occur by aromatic nucleophilic substitution.

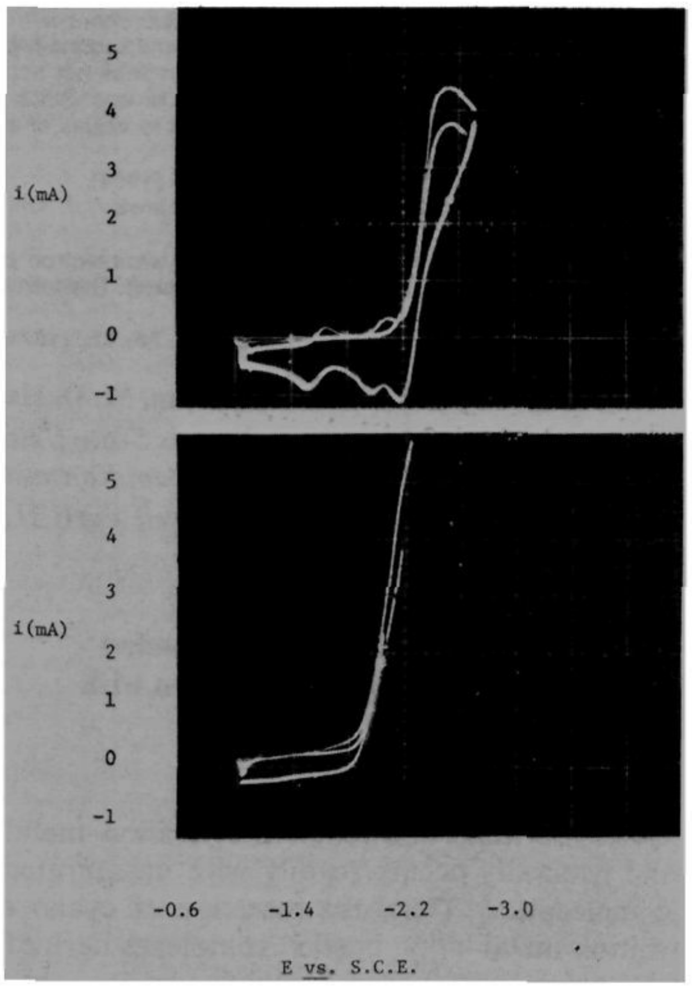


Figure 2. Cyclic voltammograms at a planar platinum electrode (ca. 0.25 cm^2) in 0.1 *F* TEAP–DMF. The initial electrode potential was *−1.0 V vs. SCE*. Two complete cathodic–anodic cycles are shown in each of the cyclic voltammograms. (Top) 5.31×10^{-3} *F p*-fluorobenzonitrile at a scan rate of 30 V/sec. The reversible couples near −1.60 and −2.04 V arise from the stepwise reduction of 4,4′-dicyanobiphenyl. Note the absence of these peaks on the first negative-going sweep. (Bottom) 5.06×10^{-3} *F p*-chlorobenzonitrile in the presence of 5.31×10^{-3} *F p*-fluorobenzonitrile at a scan rate of 30 V/sec.

Although this is the first report of biaryl formation involving the dimerization of halogenated radical anions, evidence consistent with the dimerization of halogenated radical anions has been reported recently for the *p*-nitrobenzyl chloride[12] and *o*-fluorobenzonitrile systems.[3] Since this mechanism also correctly predicts that the largest yield of dimer should be obtained from the halobenzene giving the most stable radical anion (i.e., the fluorobenzonitrile radical anion), the dimerization of radical anions must be considered as a plausible reaction pathway in reductive dehalogenations.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

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(8) It should be noted that the unimolecular decomposition of *p*-fluorobenzonitrile leads to benzonitrile, which is also electroactive ($E_{1/2} = -2.29$ V) at the applied potential. Although reactions 4 and 5 also represent an ECE process (electron transfer, chemical reaction, electron transfer) and would cause n_{app} to vary from a lower limit of 1.0 to an upper limit of 2.0, the variation of n_{app} with time in the first-order ECE process

would be independent of the concentration of *p*-fluorobenzonitrile.[4,5] A comparison of the working curves for these first- and second-order ECE processes shows that unimolecular decomposition does not occur to a significant extent as long as the value of *kt* is 0.2 or less. Since *k* is 11 sec^{-1} at 23°,[3] *t* was restricted in our experiment to values of approximately 20 msec and less.

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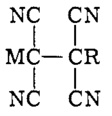
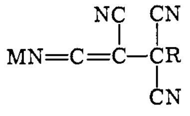
Insertion Reactions of σ-Alkyl-Metal Bonded Complexes. Electron Transfer Mechanism with Tetracyanoethylene

Sir:

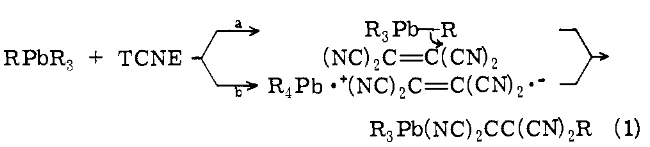
Insertion is an important reaction of σ-alkyl-metal complexes and generally occurs readily with unsaturated electrophilic molecules.[1] Thus, the insertion of cyano olefins into transition metal-alkyl bonded complexes derived from iron, chromium, nickel, and molybdenum has been reported,[2] as well as insertion into alkyl-metals derived from nontransition elements such as mercury and magnesium.[3] Reactions of tetracyanoethylene (TCNE) with alkyl-metals (R-M) can afford isomeric metal cyanoalkyls (I) and metal keteniminates (II), corresponding to 1,2- and 1,4-insertion, respectively. The common mechanism for insertion into an alkyl-metal bond considers TCNE to function as an electrophile, consistent with the well-known susceptibility of alkyl-metals to electrophilic cleavage.[4]


I


II

We wish to demonstrate that insertion of TCNE into alkyl-metals can occur readily by an electron transfer process and to establish criteria based on kinetics and selectivity to distinguish electrophilic from electron-transfer mechanisms. We chose organolead compounds ($PbEt_nMe_{4-n}$, $0 \leq n \leq 4$) as models for study since they are reactive yet substitution stable and, more importantly, they are not commonly considered to participate in electron-transfer processes as are their transition metal counterparts.

TCNE inserts readily and quantitatively into only one R-Pb bond of tetraalkyllead according to eq 1.


$$RPbR_3 + TCNE \begin{cases} \xrightarrow{a} R_3Pb{-}R \cdot (NC)_2C{=}C(CN)_2 \\ \xrightarrow{b} R_4Pb^{\cdot+}(NC)_2C{=}C(CN)_2^{\cdot-} \end{cases} \longrightarrow R_3Pb(NC)_2CC(CN)_2R \quad (1)$$

The mechanism for insertion is represented by either an electrophilic route (1a) or an electron transfer route (1b). ^1H NMR examination of the reaction with tetramethyllead in acetonitrile-d_3/10% acetic-d_3 acid-*d* allows the simultaneous observation of the disappearance of $(CH_3)_4Pb$(δ 0.82 ppm, $J(^{207}Pb-CH_3)$ = 63.5 Hz) and the appearance of $(CH_3)_3Pb^+$ (δ 1.53 ppm, $J(^{207}Pb-CH_3)$ = 78 Hz) as well as the CH_3-TCNE adduct (δ 2.19 ppm). The reaction with tetraethyllead (eq 2a) is much faster than the methyl analog and yields triethyllead 1,1,2,2-tetracyanobutanide (III).

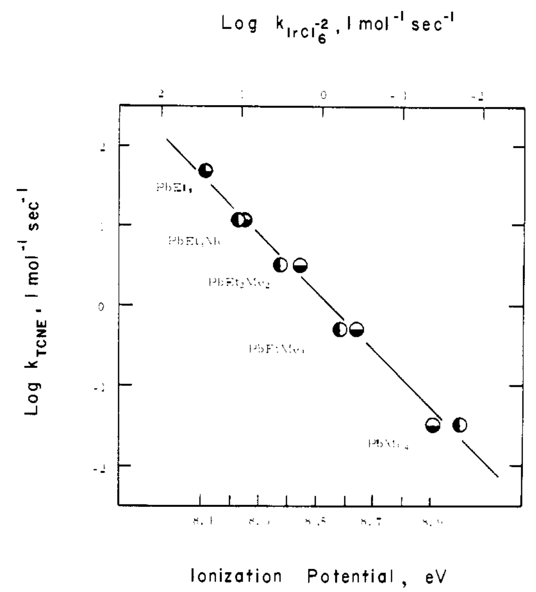
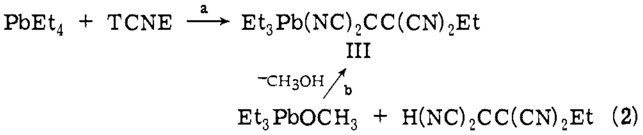


Figure 1. Insertion of TCNE into tetraalkyllead compounds. Correlation of the second-order rate constants with the ionization potentials of R_4Pb denoted by ◒ (lower scale) and the rate constants for the oxidative cleavage of R_4Pb by hexachloroiridate(IV) denoted by ◐ (upper scale).

Table I. Reactivity Parameters for the Reaction between Tetraalkyllead and Tetracyanoethylene

$PbMe_nEt_{4-n}$ ($0 \leq n \leq 4$)	k_{TCNE}[a] (l./(mol sec))	Selectivity[b] k_{Et}/k_{Me}	ν_{CT}[c] (cm^{-1})	IP[c,d] (eV)	$k_{IrCl_6^{2-}}$[c,e] (l./(mol sec))
$PbMe_4$	0.03	–	24,300	8.90	0.02
$PbMe_3Et$	0.52	7	23,300	8.65	0.57
$PbMe_2Et_2$	3.1	9	22,000	8.45	3.3
$PbMeEt_3$	12	⩾12	20,400	8.26	11
$PbEt_4$	48	–	*f*	8.13	26

[a] Second-order rate constant for insertion determined for first 10% in CH_3CN at 25°. [b] From eq 6. [c] References 6 and 7. [d] Ionization potentials from He(I) photoelectron spectra. [e] Second-order rate constant for reaction with $IrCl_6^{2-}$. [f] Complex is highly unstable.


$$PbEt_4 + TCNE \xrightarrow{a} \underset{\text{III}}{Et_3Pb(NC)_2CC(CN)_2Et} \xrightarrow[b]{-CH_3OH} Et_3PbOCH_3 + H(NC)_2CC(CN)_2Et \quad (2)$$

Compound III was isolated as an unstable oil which loses HCN spontaneously. It exhibited the same ^1H NMR and ir spectra as those of an authentic sample prepared by direct metathesis of trimethyllead methoxide and 1,1,2,2-tetracyanobutane according to eq 2b.[5] Further characterization of III was effected by quenching it with trifluoroacetic acid (eq 3), from which triethyllead trifluoroacetate and 1,1,2,2-tetracyanobutane were the only products isolated.

$$III + CF_3CO_2H \longrightarrow Et_3PbO_2CCF_3 + H(NC)_2CC(CN)_2Et \quad (3)$$

The kinetics of insertion of TCNE into various tetraalkyllead compounds listed in Table I were determined spectrophotometrically from the disappearance of TCNE and showed a first-order dependence on each reactant. Significantly, the logarithms of the second-order rate constants follow an excellent linear correlation with the vertical ionization potential of R_4Pb as shown in Figure 1. The latter represents an electron detachment process:

$$R_4Pb \longrightarrow R_4Pb^{\cdot+} + \epsilon$$