Charge Transfer Spectra and the Alkylation of Tetracyanoethylene with the Organometallic Derivatives of Lead, Tin, and Mercury

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Abstract: Charge transfer (CT) bands are observed in the absorption spectra of various tetraalkyllead and -tin as well as dialkylmercury compounds in the presence of tetracyanoethylene. The frequencies of the CT bands and their thermal stabilities vary systematically, occurring at the lowest energies and being the least stable with tetraalkyllead compounds. The energies of the charge transfer bands are correlated with the ionization potentials of the alkylmetals and discussed in relation to their steric properties. The disappearance of the CT bands is shown to be directly related to the insertion of TCNE into an alkyl-metal bond. These 1:1 adducts have been isolated and characterized by their proton NMR spectra. The kinetics and the selectivities observed in a series of methyl/ethyllead compounds afford compelling evidence that the insertion reaction proceeds by a rate-limiting electron transfer mechanism. The relationship between the charge transfer interactions of alkylmetals with TCNE and the occurrence of the thermal insertion reaction is delineated. The highly colored solutions often resulting from a mixture of TCNE and alkylmetals are shown to be due to 3-alkyl-1,1,2,4,5,5-hexacyanopentadienide ions formed from the further reaction of the primary insertion product with an additional molecule of TCNE.

Organometals such as alkyllead, -tin, and -mercury compounds are electron-rich species which are generally subject to cleavage by acids, metal salts, and other electrophiles.[1] The most common pathway by which carbon-metal bonds [R-M] in organometallic complexes are cleaved is the electrophilic process shown schematically in eq 1.[2] However,

$$\mathrm{R{-}M + E^{+}} \begin{cases} \xrightarrow{k_{\mathrm{E}}} \mathrm{R{-}E + M^{+}} & (1) \\ \xrightarrow{k_{\mathrm{et}}} \mathrm{R{-}M^{\cdot +} + E^{\cdot}}, \text{ etc.} & (2) \end{cases}$$

these organometals have relatively low ionization potentials, and an electron transfer mechanism represented in eq 2 is also possible.[3] The rate is limited in the latter process by the ability of the organometal to function as an electron donor and the electrophile to be an electron acceptor.

The electron donating ability of organometals may be examined by various methods including charge transfer spectral techniques found to be useful for other substitution-stable compounds.[4] In the charge transfer (CT) spectrum, the absorption band due to the donor-acceptor complex is a measure of the energetics of electron transfer from the electron donor (D) to the electron acceptor (A). The relative ease of electron transfer among a series of organometallic donors can be determined with a common acceptor.[4]

Tetracyanoethylene (TCNE) has been widely used as an acceptor in charge transfer spectral studies, particularly with arenes, olefins, and other π-donors.[5] Donor-acceptor interactions are generally weak with σ-donors. They have been recently observed between TCNE and organosilicon and -lead compounds, some of which are unstable at room temperature.[6,7] Despite the large number and variety of charge transfer complexes that have been observed with TCNE, little is known about the chemistry which results from such an interaction. Indeed, the transient nature of the CT bands from tetraalkyllead and TCNE suggests that at least one partner of the donor-acceptor pair is undergoing further reaction.

We wish to use this observation to ascertain the type of reactions which occur subsequent to charge transfer in alkylmetal-TCNE complexes. Formally, these reactions may be considered as alkylations of TCNE, although a mixture of products, all formed in low yields, is common.[8,9] In this report we have examined the interaction of TCNE with alkyllead, -tin, and -mercury compounds to determine factors affecting electron transfer and those responsible for further reactions in these systems. Charge transfer bands in the donor-acceptor complexes are examined first, followed by the identification and isolation of the alkylated products as well as the measurement of the kinetics of the reactions between TCNE and alkylmetals. The results have bearing on the mechanism of insertion into alkyl-metal bonds generally, since main group alkyls are not commonly considered to participate in electron-transfer processes as are the transition metal derivatives. Furthermore, unlike the labile organomagnesium and -lithium compounds (which can be considered as carbanionoids[9]), the alkyl derivatives of lead, tin, and mercury are substitution stable and are more like their transition metal counterparts in this regard.

Results

Charge Transfer Spectra of TCNE and Alkylmetals. Charge transfer bands were observed in the absorption spectra of solutions containing TCNE and tetraalkyllead and -tin as well as dialkylmercury compounds as shown in Figure 1. The new absorption bands were examined in solutions of 1,2-dichloropropane or chloroform. The use of relatively high concentration (0.1-0.8 M) of alkylmetals compared to TCNE (0.008 M) was necessitated by the rather low absorbance of the system. It appears, thus, that the equilibrium constant K in eq 3 is generally small.

$$\mathrm{R{-}M + TCNE} \overset{K}{\rightleftharpoons} [\mathrm{RM, TCNE}] \qquad (3)$$

This conclusion is also qualitatively supported by an analysis of the charge transfer spectrum between tetramethyllead or dimethylmercury with TCNE by the Benesi-Hildebrand method.[10,11]

The stability of the CT band depended on the metal and on the alkyl ligand. Generally, the charge transfer bands from alkyllead complexes were much less stable than those observed for the corresponding tin or mercury compounds. For example, only a fleeting blue color was observed immediately after solutions of TCNE and tetraethyllead were mixed. The yellow color due to the tetramethyllead complex persisted for only a few minutes at room temperature. The spectra of solutions of tetraalkyllead and TCNE were examined only at low temperatures since the disappearance of the CT band was too rapid to be followed by conventional

Table I. Charge-Transfer Spectral Data for Alkylmetal σ-Donors and Tetracyanoethylene

Compound	$\lambda_{max}^{CHCl_3}$ (nm)	$\nu_{CT}^{CHCl_3}$ (cm^{-1})	λ_{max}^{DCP} (nm)	ν_{CT}^{DCP} (cm^{-1})	IP (eV)
$PbMe_4$	427[a]	23 400	412[a]	24 300	8.90[a]
$PbMe_3Et$			430[a]	23 300	8.65[a]
$PbMe_2Et_2$			454[a]	22 000	8.45[a]
$PbMeEt_3$			479[a]	20 900	8.26[a]
$PbEt_4$	c, i		e		8.13[a]
$PbBu_4$			e, i		
$SnMe_4$	350[c]	28 600	~330[b]	30 300	9.70[c]
$SnEt_4$	426[c]	23 500	409[b]	24 400	8.93[c]
$SnBu_4$		(21 020)[c,f]			8.83[c]
$SnBu_4$	417[b]	24 000	393[b]	25 400	8.83[c]
$GeBu_4$	377[c]	26 650			
$Me(SiMe_2)_2Me$	417[d]	24 000			8.69[h]
$Me(SiMe_2)_3Me$	480[d]	20 830			8.19[h]
$Me(SiMe_2)_4Me$	520[d]	19 230			7.98[h]
$Me(SiMe_2)_5Me$	543[d]	18 400			
$(SiMe_2)_6$	507[d]	19 700			7.79[h]
$Si(SiMe_3)_4$	458[d]	21 800			8.24[h]
$HgMe_2$	415[c]	24 100	395[b]	25 300	9.33[g,j]
$HgEt_2$	517[b]	19 300	500[b]	20 000	8.45[j]
$HgBu_2$	532[b]	18 800	508[b]	19 700	8.35[j]

[a] From ref 7 at −35 to −50°. [b] This work. [c] From ref 23b. [d] From ref 6a. [e] Unstable. [f] This value is probably incorrect (see text). [g] From ref 23c. [h] From ref 23d. [i] $TCNE\cdot^-$ observed. [j] Unpublished results with J. Ulman and T. P. Fehlner.

techniques at room temperature.[7] For this series of compounds, the stability of the CT band decreased in the order: $Me_4Pb > Me_3EtPb > Me_2Et_2Pb > MeEt_3Pb > Et_4Pb \approx$ *n*-Bu_4Pb. The charge transfer spectra of tetraethyl- and tetra-*n*-butyllead complexes were too transient to measure even at −50°. On the other hand, the CT bands due to TCNE complexes of tetramethyltin and dimethylmercury remained unchanged for hours. Spectra derived from tetraethyl- and tetra-*n*-butyltin as well as diethyl- and di-*n*-butylmercury with TCNE showed intermediate stability, having half-lives of a few hours at room temperature.

The measurement of the absorption maximum for the charge transfer bands in these systems was often complicated by the appearance of other bands in the region of interest. Thus, new absorption bands characteristic of the pentacyanopropenide ion[12] gradually appeared as several alkyllead mixtures were allowed to stand. The change was accompanied by a concomitant decrease in the CT band. The spectrum due to the tetracyanoethylene anion-radical[13] was also observed in mixtures containing tetraethyl- and tetrabutyllead. The formation of highly colored hexacyanopropenide ions is presented later.

The spectral data for the charge transfer complexes derived from various organometallic σ-donors and TCNE are collected in Table I. The ionization potentials of the same organometals taken from the literature are also included in the table. The sensitivity to solvent effects is shown by a comparison of the results obtained in 1,2-dichloropropane with those from chloroform and generally reflects the greater polarity of the latter.[14] The stability of the CT complexes also differed markedly with the solvent, qualitatively decreasing in the order: $CCl_4 > CHCl_3 \approx ClCH_2CHClCH_3 > CH_3CN \approx$ THF. A similar trend with solvent variation has been observed in TCNE complexes with aromatic amines.[14b]

Reaction of TCNE with Tetraalkyllead Compounds. A. Products and Stoichiometry. The transient nature of the charge transfer band in the TCNE-tetraalkyllead complex was scrutinized directly by following the change in the proton NMR spectrum. The reaction of tetramethyllead and TCNE was carried out in a solvent consisting of acetonitrile-d_3-10% acetic-d_3 acid-*d*. The rate was sufficiently slow to allow the simultaneous observation of the disappearance of tetramethyllead (δ 0.82 ppm, $J(^{207}Pb\text{-}CH_3) = 63.5$ Hz) as well as the appearance of the trimethyllead cation (δ 1.53 ppm, $J(^{207}Pb\text{-}CH_3) = 78$ Hz) and the methyl-TCNE adduct (δ 2.19 ppm). TCNE inserts cleanly into only one $Pb\text{-}CH_3$ bond. It is noteworthy that all the lines in the proton NMR spectrum are broadened

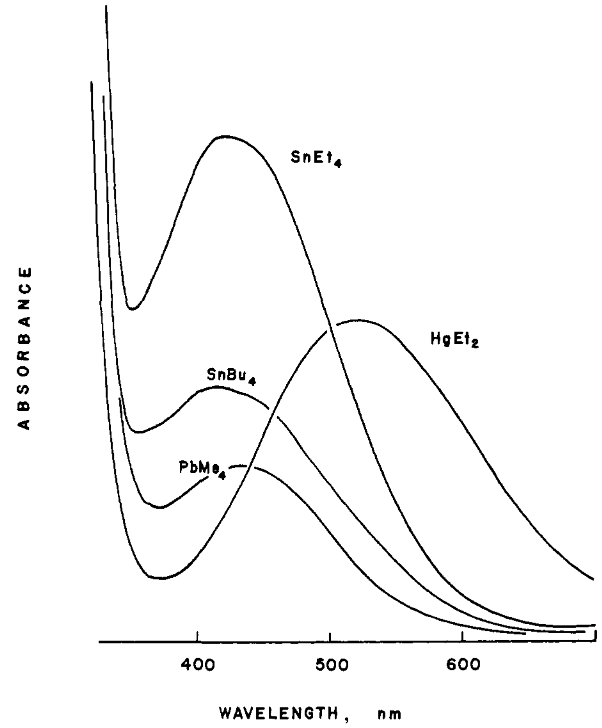


Figure 1. Charge transfer spectra of tetraethyltin (0.60 M), tetra-*n*-butyltin (0.46 M), and diethylmercury (0.41 M) with 0.015 M TCNE in chloroform solutions at room temperature. Spectrum of tetramethyllead (0.30 M) and 0.01 M TCNE in chloroform is at −10°C.

$$\underset{}{(CH_3)_4Pb + TCNE \rightarrow \underset{\textbf{1}}{(CH_3)_3Pb(NC)_2CC(CN)_2CH_3}} \quad (4)$$

if the same reaction is carried out in the absence of acetic acid. Line broadening is attributable to the presence of TCNE anion-radical which is readily quenched by acids.[13]

$$2TCNE\cdot^- + 2H^+ \rightarrow 2HTCNE\cdot \rightarrow TCNE + H_2TCNE \quad (5)$$

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

$PbMe_nEt_{4-n}$ $(0 \leqslant n \leqslant 4)$	k_{TCNE}[a] (l./(mol s))	Selectivity[b] k_{Et}/k_{Me}	ν_{CT}[c] (cm^{-1})	IP[c,d] (eV)	$k_{IrCl_6^{2-}}$[e] (l./(mol s))
$PbMe_4$	0.032	—	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[f]	20 400	8.26	11
$PbEt_4$	48	—		8.13	26

[a] Second-order rate constant for insertion determined spectrophotometrically for first 10% in CH_3CN at 25 °C. [b] From eq 8. [c] Reference 7. [d] Ionization potentials from He(I) photoelectron spectra. [e] Second-order rate constant for reaction with $IrCl_6^{2-}$. [f] The similarity of the ^1H NMR spectra of the alkyllead cations and the lack of a resonance for the CH_3–TCNE adduct make this value a lower limit.

The reaction with tetraethyllead is much faster than the methyl analogue and yields triethyllead 1,1,2,2-tetracyanobutanide (**2**) according to eq 6a.

$$Et_4Pb + TCNE \xrightarrow{a} \underset{\textbf{2}}{Et_3Pb(NC)_2CC(CN)_2Et} \qquad (6)$$

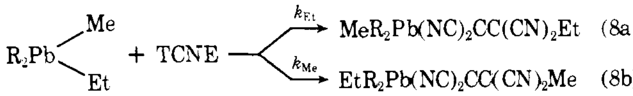
$$Et_3PbOCH_3 + H(NC)_2CC(CN)_2Et \xrightarrow[-CH_3OH]{b} \textbf{2}$$

Compound **2** was isolated as an unstable oil which loses HCN spontaneously. It exhibited the same proton NMR and infrared spectra as those of an authentic sample prepared by direct metathesis of trimethyllead methoxide and 1,1,2,2-tetracyanobutane according to eq 6b.[9a,15] Further characterization of **2** was effected by quenching it with trifluoroacetic acid (eq 7). Triethyllead trifluoroacetate and 1,1,2,2-tetracyanobutane were the only products isolated from the reaction mixture.

$$\textbf{2} + CF_3CO_2H \rightarrow Et_3PbO_2CCF_3 + H(NC)_2CC(CN)_2Et \qquad (7)$$

Adducts **1** and **2** are characterized best as metal tetracyanoalkyls rather than the isomeric metal keteniminates (corresponding to 1,2 and 1,4 addition, respectively), since the characteristic infrared band at ~1300 cm^{-1} for $\nu_{N=C=C}$(asym) is not observed.[8a]

A series of mixed methyl/ethyllead compounds ($Me_{4-n}Et_nPb$, where $3 \geq n \geq 1$) reacts with TCNE in a similar manner to afford a mixture of products corresponding to competitive insertion into a Pb-Me and a Pb-Et bond as shown in eq 8 (R = Me, Et). The intramolecular competition between the two modes of insertion is given by a selectivity factor [k_{Et}/k_{Me}] which is determined by comparing the relative amounts of Me- and Et-TCNE adducts and/or the two trialkyllead moieties (i.e., MeR_2Pb and EtR_2Pb). For the latter species, trialkyllead chlorides ($Me_{3-n}Et_nPbCl$, where $3 \geq n \geq 0$) were used as model compounds for the analysis by proton NMR (see Table VI, experimental section). The results in Table II show the preferential insertion of TCNE into the Pb-Et bond in each of the mixed methyl/ethyllead compounds.



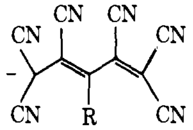
(8a)
(8b)

B. Kinetics. The insertion of TCNE into a particular Pb-alkyl bond is complete within a few seconds to a few minutes, depending on the tetraalkyllead compound. The disappearance of TCNE was followed spectrophotometrically. The kinetics of the reaction were determined by varying the concentrations and showed a first-order dependence on each reactant.

$$-\frac{d[TCNE]}{dt} = k[R_4Pb][TCNE] \qquad (9)$$

The second-order rate constants are listed in Table II for a series of alkyllead compounds. The largest rate constant was observed for tetraethyllead and the smallest for tetramethyllead.

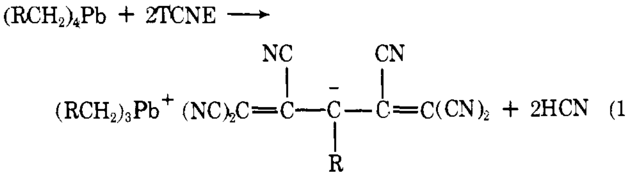
Table III. Formation of Hexacyanopentadienide Ions in the Reaction between Alkylmetals and Tetracyanoethylene[a]



Compound	Solvent	R	$\lambda_{max}^{CH_3CN}$ (nm)	Yield[b] (%)
$PbMe_4$	THF	H	538	41[c]
$PbEt_4$	CH_3CN	CH_3	589	33
$PbBu_4$	CH_3CN	n-C_3H_7	593	47
$PbBu_4$	THF	n-C_3H_7	593	40
$SnMe_4$	CH_3CN	H	538	0
$SnEt_4$	CH_3CN	CH_3	589	17
$SnBu_4$	CH_3CN	n-C_3H_7	593	12

[a] Typical conditions: $[R_4M]_0$ = 0.035 M, $[TCNE]_0$ = 0.07 M, under nitrogen, at room temperature. [b] Determined spectrophotometrically after 8–24 h. [c] Low temperature addition.

C. Formation of 1,1,2,4,5,5-Hexacyanopentadienide Ions. The disappearance of the charge transfer bands is often followed by the formation of highly colored solutions of acetonitrile or tetrahydrofuran. The colors became even more intense when alkylmetals and TCNE were mixed in a 1:2 stoichiometry. Solutions of tetramethyllead and TCNE turned red after 15 min, and the color intensified during the next 8 h. Similarly, mixtures containing tetraethyl- or tetra-*n*-butyllead became dark blue. The products responsible for the intense colors are a series of 3-alkyl-1,1,2,4,5,5-hexacyanopentadienide ions **3**, described in the foregoing study.[9b] The ions formed from tetramethyl-, tetraethyl-, and tetra-*n*-butyllead compounds are 1,1,2,4,5,5-hexacyanopentadienide, **3a**, the 3-methyl derivative **3b**, and the 3-*n*-propyl derivative **3c**, respectively. The anion **3a** was identified by the



$$(RCH_2)_4Pb + 2TCNE \longrightarrow (RCH_2)_3Pb^+ \; (NC)_2C{=}\overset{\overset{\displaystyle NC}{|}}{C}{-}\underset{\underset{\displaystyle R}{|}}{\overset{-}{C}}{-}\overset{\overset{\displaystyle CN}{|}}{C}{=}C(CN)_2 + 2HCN \qquad (10)$$

3a, R = H
3b, R = CH_3
3c, R = n-C_3H_7

isolation of the tetramethylammonium salt, which was compared with an authentic sample.[16] Ions **3b** and **3c** were identified by their characteristic absorption spectra.

The yields of **3** reached nearly 50% (see Table III), when mixtures of tetraalkyllead and TCNE reacted in a nitrogen atmosphere. In the presence of oxygen, however, the yield of **3b** was only 10% from tetraethyllead. Optimum yields of

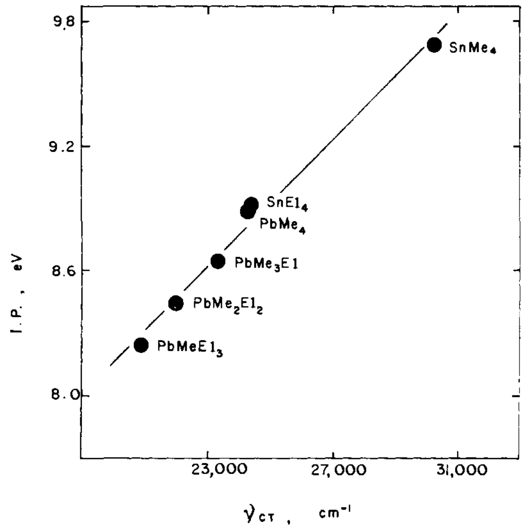


Figure 2. Correlation of the maximum of the charge transfer bands of alkylmetal-TCNE complexes in 1,2-dichloropropane solutions with the vertical ionization potential of the alkylmetal.

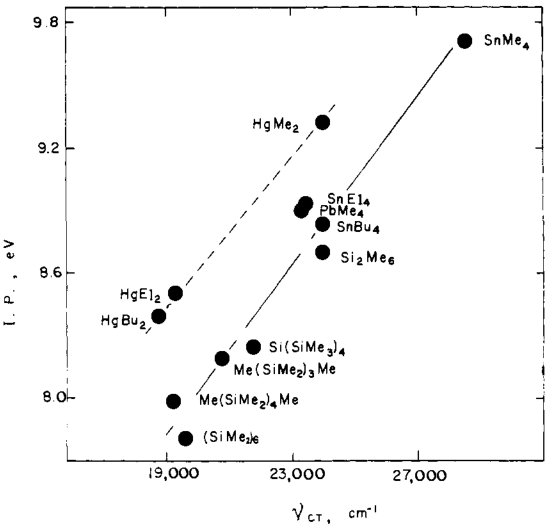


Figure 3. Correlation of the maximum of the TCNE charge transfer bands in chloroform with the vertical ionization potential of the alkylmetal. See text for references.

3 were generally obtained when reactions were carried out in a 1:2 stoichiometry of tetraalkyllead and TCNE. For example, no **3b** was produced in the presence of less TCNE (i.e., a 1:1 mixture). With the less reactive tetramethyllead, the yield of **3a** was not as sensitive to TCNE concentration, being formed in 50% yield even from a 1:1 mixture.

Reaction of TCNE and Tetraalkyltin Compounds. Alkyltin compounds reacted with TCNE more slowly than their organolead counterparts. The stability of the donor-acceptor complex[10] from tetraalkyltin and TCNE is reflected in the rather slow change of the charge transfer spectra when solutions are allowed to stand at room temperature. There is also an accompanying change in the proton NMR spectrum of CH_3CN-HOAc solutions, in which the resonances due to tetraethyltin diminish to about one-half their original intensity in 45 min.

$$Et_4Sn + TCNE \rightarrow Et_3Sn(NC)_2CC(CN)_2Et$$

After 14 h, the insertion product, triethyllead 1,1,2,2-tetracyanobutanide, can be observed in 95% yield.

The formation of hexacyanopentadienide ion **3a** was not apparent in acetonitrile solutions of tetramethyltin and TCNE. Under similar conditions, 17% of the 3-methyl analogue **3b** was observed in the reaction with tetraethyltin and isolated as the tetramethylammonium salt. The reaction between tetra-*n*-butyltin and TCNE formed 3-*n*-propyl-1,1,2,4,5,5-hexacyanopentadienide ion **3c** in 12% yield.

Reaction of TCNE with Dialkylmercury. Organomercurials also reacted rather slowly with TCNE in acetonitrile solutions. The examination of an equimolar mixture of dimethylmercury and TCNE by its proton NMR spectrum indicated that only 14% of the dimethylmercury was consumed during a 24-h period. Diethylmercury reacted more rapidly, affording the product **4** of TCNE insertion into a Hg-Et bond in about an hour.

$$\underset{}{Et_2Hg + TCNE \rightarrow \underset{\mathbf{4}}{EtHg(NC)_2CC(CN)_2Et}} \qquad (11)$$

Neither diethyl- nor di-*n*-butylmercury afforded the corresponding hexacyanopentadienide ions **3b** or **3c**, respectively, despite spectral evidence that the dialkylmercury had been consumed.

Under the same conditions described above, diisopropylmercury reacted with TCNE within 2 min after mixing. The proton NMR spectrum of diisopropylmercury (δ 1.32 ppm singlet, $J(^{199}HgCH_3) = 114$ Hz) was replaced by that of isopropylmercury 1,1,2,2-tetracyano-3-methylbutanide (δ 2.6 (m, 2 H); 1.44 (d, 6 H, $J = 7$ Hz, $J(^{199}HgCH_3) = 287$ Hz); 1.30 (d, 6 H, $J = 7$ Hz)).

$$[(CH_3)_2CH]_2Hg + TCNE \rightarrow \underset{\mathbf{5}}{(CH_3)_2CHHg(NC)_2CC(CN)_2CH(CH_3)_2}$$

Discussion

Charge Transfer Spectra from Alkylmetals and TCNE. Spectral studies indicate that the charge-transfer interaction between TCNE as a π-acceptor and various alkylmetals as σ-donors is a general phenomenon. The frequency of the CT band is correlated well in Figure 2 with the vertical ionization potentials of a selected series of related alkylmetals. The values of the ionization potentials represent a direct measure of the energetics of electron detachment from the organometallic donors in the gas phase. In turn, the correlation of the ionization potentials with the frequencies of the CT bands of the TCNE complexes in solution suggest that the latter also relate in measure to the same relative ease of electron detachment from the organometal.

Extension of this simple correlation to a wider variety of alkylmetals is limited, as shown in Figure 3.[17] Although a general trend exists between charge-transfer frequencies and ionization potentials, there are notable exceptions. However, the scatter in Figure 3 does not appear to be random. Thus, the CT frequency for the tetrabutyltin complex occurs at higher energy than that of the ethyl analogue, despite the similar values of their ionization potentials. Even more strikingly, the charge transfer transitions of all of the dialkylmercury complexes with TCNE occur at much lower energies than expected from the values of their ionization potentials.

These deviations may be related to the interplay of steric factors present during the charge transfer interaction. According to the valence-bond description, the frequency of the CT band corresponds in the simplest form to the energy required to transfer an electron from the donor to the acceptor.[18,19]

$$D, A \xrightarrow{h\nu} D\cdot^{+}, A\cdot^{-} \qquad (12)$$

For weakly associating or contact systems the energy of the

Table IV. Stability Parameters for Alkylmetal–TCNE Charge-Transfer Spectra

Compound	Relative abundance of $P\cdot^{+a}$ (%)	IP^b (eV)	Approx. half-life of charge-transfer band^c
$PbMe_4$	1^d	8.90	>30 min at −10°
$PbEt_4$		8.13	<1 min at −50°
$SnMe_4$	2^e	9.70	>24 h at 20°
$SnEt_4$		8.93	6 h at 20°
$HgMe_2$	40^f	9.33	>24 h at 20°
$HgEt_2$		8.45	6 h at 20°
$Me(SiMe_2)_2Me$	12^g	8.69	>12 h at 20°

^{a}Mass spectral data (70 eV). ^{b}By He(I) PES. ^{c}In $CHCl_3$. ^{d}From ref 22a. ^{e}From ref 22b. ^{f}From ref 22c. ^{g}From ref 22d.

absorption maximum $h\nu_{CT}$ is approximated by eq 13,

$$h\nu_{CT} = I_D - E_A - (G_1 - G_0) \qquad (13)$$

where I_D and E_A refer to the vertical ionization potential of the donor and the electron affinity of the acceptor, respectively. G_0 is the energy of the "no bond" interaction and G_1, the dominant term, involves the coulombic interaction of $D\cdot^+$ and $A\cdot^-$ in the excited state. Since the latter is inversely related to the encounter distance, the frequency of the charge transfer band is expected to shift to lower energies with decreasing degree of steric hindrance in the complex. The negative deviation of the less hindered 2-coordinate organomercurials from the line correlating the other tetrahedral molecules in Figure 2 is in accord with this expectation. It also applies to the positive deviation observed with tetrabutyltin relative to the less hindered ethyl analogue.

The results in Table I also show that the stabilities of the CT bands vary systematically with the metal and the alkyl group. Thus, organolead mixtures are the least stable. Among alkyl groups, ethyl and *n*-butyl decrease the stabilities of organometals more than methyl groups. The reactions accompanying the disappearance of the CT bands are thermal rather than photochemical processes, but all the factors which determine the stabilities of these systems are unknown. However, at least two factors (not necessarily independent) should be considered: (a) the stability of the cation-radical derived from the alkylmetal[20] and (b) the ionization potential of the alkylmetal.

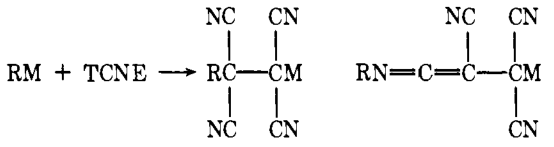
Experimentally, TCNE anion-radical is often the only paramagnetic species observed during ESR studies of donor-acceptor interactions,[6b,21] and the accompanying cation-radical must be short-lived. Estimates of the relative stabilities of cation-radicals may be obtained from mass spectra studies (gas phase). For example, Table IV shows that the parent molecular ions from dimethylmercury and hexamethyldisilane are more stable than those derived from tetramethyllead and tetramethyltin.[22] Photoelectron spectroscopic studies have shown that substitution of ethyl or *n*-butyl groups for methyl leads to lowering of the ionization potential.[23] Replacement of methyl groups in alkylmetals by ethyl or *n*-butyl groups increases their electron donor properties by about 0.2 eV per alkyl group.[7,23] Thus there is a general trend in the alkylmetals toward greater reactivity with TCNE as the ionization potential is lowered and as the stability of the radical-cation is diminished.

The interaction of an electron donor with an electron acceptor may lead to a variety of thermal processes including electron transfer, covalent bond formation, etc. For the weak donor-acceptor interactions pertaining to the alkylmetal-TCNE systems, we use the simplified representation in eq 14, in which all thermal reactions proceed subsequent to electron transfer.

$$\mathrm{RM} + \mathrm{TCNE} \rightleftharpoons [\mathrm{RM}, \mathrm{TCNE}] \rightarrow [\mathrm{RM}\cdot^+, \mathrm{TCNE}\cdot^-], \text{etc.} \qquad (14)$$

The relationship between the *rate* of the thermal process and the *energy* of the charge transfer transition in the donor-acceptor complex is illustrated by the potential energy curves drawn in Figure 4 according to Kosower.[24] It can be seen from this formulation, that the transition energy $h\nu_{CT}$ and the activation energy E_a both depend on the potential energy of the ion pair, although generally not in a direct relationship. Lowering the ionization potential of the donor will usually cause a red shift in the charge transfer band and also lead to an increase in the rate of the thermal reaction. For a more general representation, the scheme in eq 14 must be modified to include other thermal processes which also reflect on the properties relating to the stability of the cation-radical (e.g., simultaneous cleavage of the R–M bond, diffusion of the ion pair, etc.). In the next section, we wish to show how the observation of a charge transfer interaction between TCNE and R_4Pb discussed above can be related directly to an electron transfer mechanism for the insertion reaction.

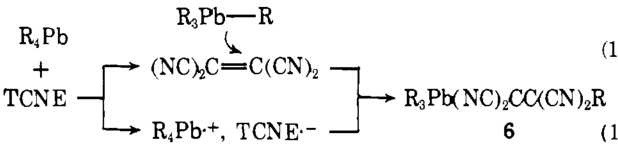
Reactions of Alkylmetals with TCNE. The insertion of alkylmetals into TCNE according to eq 15 occurs quantitatively and at convenient rates to afford adducts, best characterized as metal tetracyanoalkyls **6** rather than the isomeric metal keteniminates **7**.[25]



$$\mathrm{RM} + \mathrm{TCNE} \longrightarrow \underset{\mathrm{NC}\quad\mathrm{CN}}{\overset{\mathrm{NC}\quad\mathrm{CN}}{\mathrm{RC{-}CM}}} \qquad \mathrm{RN{=}C{=}}\overset{\mathrm{NC}}{\mathrm{C}}\mathrm{{-}}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{M} \qquad (15)$$

6 7

Two principal mechanisms for the insertion reaction arise from the consideration of TCNE as an electrophile (eq 16) or as an electron acceptor (eq 17). Electrophilic cleavage is



(16)

(17)

a common mechanistic pathway for alkylmetals and has been proposed for insertion into some transition metal alkyls.[8a] Electron transfer routes have been also demonstrated for cleavages of alkyllead,[7] but they have not been described for insertion reactions.

The results presented in this study indicate that a distinction between electrophilic and electron transfer mechanisms can be made on the basis of the *rates* and the *selectivities* in the reactions of a series of alkyllead compounds. Thus, for a rate-limiting electron-transfer process between TCNE and R_4Pb such as that in eq 17, the second-order rate constant should increase with increasing ease of electron detachment from the alkyllead species. The energetics of electron detachment from R_4Pb represented as,

$$R_4Pb \rightarrow R_4Pb\cdot^+ + \epsilon$$

is measured independently by the ionization potentials in the gas phase, and it is related to the frequencies of the charge transfer interactions in solution.[7] Figure 5 shows the linear correlation between the logarithms of the second-order rate constants for insertion and the ionization potentials of the corresponding tetralkyllead compounds. A similar trend is found with the frequencies of the charge transfer bands in TCNE-R_4Pb complexes listed in Table II.

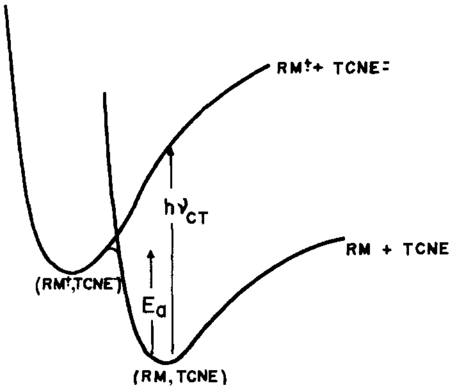


Figure 4. Potential energy diagram for the interaction of alkylmetals with TCNE.

The ability of R_4Pb to participate as a *donor* in electron transfer processes was previously demonstrated in the oxidative cleavage induced by hexachloroiridate(IV) according to Scheme I.[7] Electron transfer as the slow step in eq 18 is

Scheme I

$$R_4Pb + IrCl_6{}^{2-} \longrightarrow R_4Pb\cdot^{+} + IrCl_6{}^{3-} \quad (18)$$

$$R_4Pb\cdot^{+} \xrightarrow{\text{fast}} R_3Pb^{+} + R\cdot \quad (19)$$

$$R\cdot + IrCl_6{}^{2-} \xrightarrow{\text{fast}} RCl + IrCl_5{}^{2-} \quad (20)$$

consistent with the well-known ability of hexachloroiridate(IV) to function as an outer-sphere oxidant (i.e., electron acceptor).[26] The excellent linear correlation shown in Figure 6 between the rates of *oxidative cleavage* by hexachloroiridate(IV) and the rates of *insertion* by TCNE indicate that R_4Pb is subjected to similar perturbations in the transition states of both series of reactions. Indeed, electron transfer to TCNE from R_4Pb in eq 17 is formally akin to the rate-limiting transfer to hexachloroiridate(IV) in eq 18, both depending on the ability of R_4Pb to be an electron donor. The capacity of TCNE as an electron acceptor is measured by the charge transfer interaction $h\nu_{CT}$ described above, and its relationship to the activation energy of the thermal process between TCNE and R_4Pb is presented in Figure 4.

The *intra*molecular competition carried out with the series of mixed methyl/ethyllead compounds in eq 8 and Table II shows that the insertion of TCNE occurs preferentially into an *ethyl*-Pb bond relative to a *methyl*-Pb bond. Similar selectivities were also observed in the cleavage of alkyllead compounds with hexachloroiridate.[7] On the other hand, in electrophilic cleavages a given methyl-lead bond is *more* reactive than the corresponding ethyl-lead bond in tetraalkyllead compounds, in accord with less steric hindrance at a methyl site.[27] This pattern of reactivity is diametrically opposed to the reaction with TCNE and with hexachloroiridate(IV), in which steric factors are largely unimportant.

We have used two principal criteria to distinguish an electrophilic from an electron transfer process in the insertion reaction. Both intermolecular and intramolecular comparisons of reactivities of tetraalkyllead compounds show that the mechanism involving a rate-limiting electron transfer applies to the insertion of TCNE into alkylmetals as described in eq 17. Indeed, the characteristic visible absorption spectrum[28] of the anion-radical of TCNE, as well as its electron spin resonance spectrum[29] can be readily observed during the reaction of tetraethyllead and TCNE.[30] The presence of $TCNE\cdot^-$ is also indicated by the paramagnetic line broadening in the proton NMR spectra obtained during the reactions of TCNE and R_4Pb in acetonitrile.

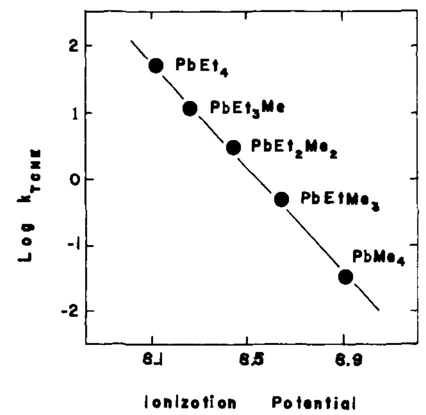


Figure 5. Correlation of the rates of TCNE insertion into tetraalkyllead compounds with their vertical ionization potentials.

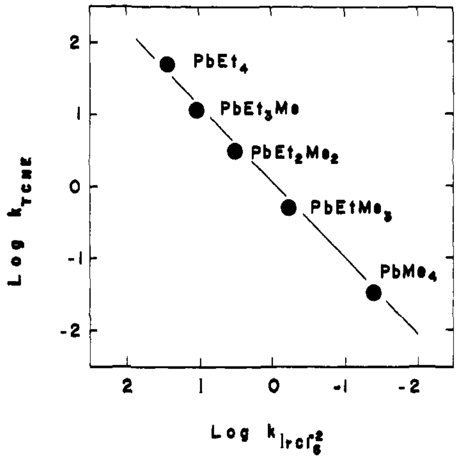
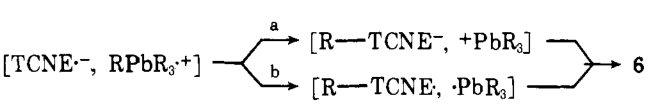


Figure 6. Reactivity of tetraalkyllead compounds. Correlation of the rates of TCNE insertion with the rates of oxidative cleavage by hexachloroiridate(IV).

According to the electron transfer mechanism, actual transfer of an alkyl group from the organolead species to the cyanoolefin occurs subsequent to the rate-limiting step. The alkylation involving the transfer of the alkyl group from $R_4Pb\cdot^+$ to $TCNE\cdot^-$ is probably a cage process. It can occur by transfer of either an alkyl radical ($R\cdot$) or a cation (R^+) as given in eq 21a or 21b, respectively:[31]



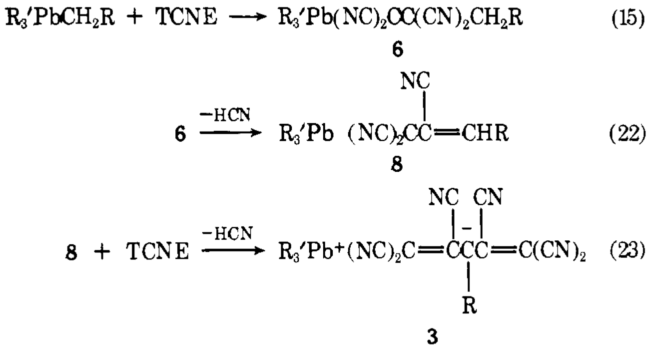
$$[TCNE\cdot^-, RPbR_3\cdot^+] \begin{array}{l} \xrightarrow{a} [R{-}TCNE^-, {}^+PbR_3] \\ \xrightarrow[b]{} [R{-}TCNE\cdot, \cdot PbR_3] \end{array} \longrightarrow 6 \quad (21)$$

The distinction between these processes is not easily made since the selectivity studies are consistent with the transfer of either $R\cdot$ or R^+ from $R_4Pb\cdot^+$ to the anion-radical of TCNE. Furthermore, the nature of the cage process inherent in the insertion reaction described in eq 21 precludes the detection of free radicals. However, we infer from eq 19 (in which an alkyl radical is expelled from $R_4Pb\cdot^+$), that alkyl transfer occurs within the $[R_4Pb\cdot^+ \; TCNE\cdot^-]$ ion pair by an analogous mechanism given in eq 21a. The efficiency of the alkyl transfer is remarkably high, but some leakage of alkyl radicals from the cage is possible. Independent experiments show that such ethyl radicals generated from the thermolysis of dipropionyl peroxide are efficiently trapped by TCNE. Addition of alkyl radicals to $TCNE\cdot^-$ is less certain (see experimental section). Finally, there are other reports based on the observation of alkylmetal charge transfer bands, qualitative rate measurements, and ESR studies, which suggest a homolytic cleavage of alkyl-metal bonds by TCNE.[6,8,32] However, none of these by themselves presents as compelling an example of an electron transfer mechanism as that provided by the studies with organolead compounds.

The reactivity of tetraalkyltin and dialkylmercury compounds qualitatively shows the same dependence on alkyl substitution as those described for lead compounds. Thus, the rates for the ethyl-substituted compounds are always faster than the methyl analogues, and in the case of the mercurials examined, the diisopropyl derivative reacted almost on mixing. It is reasonable to conclude on this basis that TCNE inserts into alkyl-tin and alkyl-mercury bonds by an analogous electron-transfer mechanism. Moreover, many organometal species of other main groups as well as transition metals have relatively low ionization potentials, and the applicability of the electron transfer mechanism to these systems remains to be tested.

Reactions Subsequent to Insertion. The formation of the highly colored 3-alkyl-1,1,2,4,5,5-hexacyanopentadienide ions occurs after the formation of **6** from the insertion reaction. The further reactions of the primary adduct **6** in eq 22 and 23 are closely akin to those of the 1:1 adducts previously derived from Grignard reagents and TCNE.[9b] The formation of **3b** from tetraethyllead suggests that the primary insertion product **6** is sufficiently substitution labile to allow loss of HCN in eq 22 (probably with the aid of TCNE[9]). The decreased yields of **3b** from the tetraethyllead and TCNE in the presence of oxygen suggest that at least one of the intermediates reacts with oxygen. Furthermore, the absence of **3b** from stoichiometric amounts of tetraethyllead and TCNE (i.e., 1:1) suggests that the insertion step 15 is sufficiently fast to deplete TCNE before it can be involved in reactions 22 and 23.[33] Insertion (eq 15) and elimination (eq 21) appear to be competitive with tetramethyllead since varying the amounts of reactants has little effect on the formation of **3a**. Finally, the absence of the hexacyanopentadienide ions **3** from organomercurials suggests that the insertion product, 1-alkyl-1,1,2,2-tetracyanoethylmercury complexes, **4** and **5** are substitution-stable relative to further reaction with TCNE.

Scheme II



$$R_3'PbCH_2R + TCNE \longrightarrow \underset{\mathbf{6}}{R_3'Pb(NC)_2CC(CN)_2CH_2R} \qquad (15)$$

$$\mathbf{6} \xrightarrow{-HCN} \underset{\mathbf{8}}{R_3'Pb\ (NC)_2C\overset{NC}{\overset{|}{C}}{=}CHR} \qquad (22)$$

$$\mathbf{8} + TCNE \xrightarrow{-HCN} \underset{\mathbf{3}}{R_3'Pb^+(NC)_2C{=}\overset{NC}{\overset{|}{C}}\underset{R}{\underset{|}{\overset{-}{C}}}\overset{CN}{\overset{|}{C}}{=}C(CN)_2} \qquad (23)$$

Experimental Section

Materials. The alkyllead compounds $PbMe_nEt_{4-n}$ ($0 \leq n \leq 4$) were prepared as described previously.[27,34] The following compounds were used as received: Me_2Hg (Columbia Organic Chemicals), $Pb(n\text{-}Bu)_4$ (Organisch Chem. Inst. T.N.O., Utrecht), $SnMe_4$ (Alfa Inorganics). $SnEt_4$ (Alfa), $Sn(n\text{-}Bu)_4$ (M and T Chemicals), $HgEt_2$ (Alfa), and $Hg(n\text{-}Bu)_2$ (Eastman) were distilled under reduced pressure before use. TCNE was generously supplied by Dr. O. W. Webster of E. I. duPont (Wilmington, Del.) and was sublimed before use. The extinction coefficient of the sublimed sample was determined to be 15 500 M cm^{-1} at 270.5 nm. Reagent grade CH_3CN was distilled from P_2O_5 under nitrogen. Tetrahydrofuran was transferred under vacuum from a solution containing benzophenone ketyl. 1,2-Dichloropropane was purified by successive washing with concentrated H_2SO_4, 5% Na_2CO_3, and distilled water followed by drying over $CaSO_4$ and distillation from CaH_2.

Trimethyllead chloride was a gift from the Ethyl Corporation. Triethyllead chloride was prepared by the method of Calingaert et al.[35] Ethyldimethyllead chloride and methyldiethyllead chloride were prepared by the method of Calingaert et al.[35a,b] The products were recrystallized twice at −33° from room temperature $CHCl_3$-hexane mixtures to give constant melting points (ethyldimethyllead chloride, mp 98° dec; methyldiethyllead chloride, mp 118° dec) and were used immediately after recrystallization. Triethyllead trifluoroacetate was prepared by the method of Huber.[36]

1,1,2,2-Tetracyanobutane was prepared as described previously.[9b] Sodium *N,N*-dimethyldithiocarbamate dihydrate was prepared by stirring an aqueous solution of equimolar amounts of NaOH, CS_2, and dimethylamine for 3 h at 40°. Solvent removal under vacuum gave the product in quantitative yield.

General. The following instruments were used to record the appropriate data: a Perkin-Elmer Model 621 grating infrared spectrometer, Varian Models EM-360 and HR-220 nuclear magnetic resonance spectrometers, and a Beckman Model DB-G ultraviolet-visible recording spectrophotometer. Infrared spectra of solids were recorded of KBr pellets. Dichloromethane (δ 5.49 ppm) was used as a secondary reference and an internal standard for NMR experiments in CD_3CN–10% HOAc-d_4. Melting points are uncorrected. Charge-transfer spectra with alkyltin and -mercury compounds were examined at room temperature.

Kinetics of the Reaction between Tetraalkyllead Compounds and TCNE. A solution of TCNE in CH_3CN in a quartz cuvette was placed in the cell compartment of a Beckman DB-G spectrophotometer. The cell compartment was maintained at 25 ± 0.2° by means of a Neslab RT-E thermostated bath. A solution of tetraalkyllead compound was then added by syringe to the cell. The progress of the reaction was followed by monitoring the decrease in the absorbance band for TCNE at 270.5 nm (ϵ 15 500). Only the initial rates were measured. With $PbEt_4$, the rates in air and under a nitrogen atmosphere were the same: ($k_{air} = 48 \pm 3$, $k_{N_2} = 46$ l. mol^{-1} sec^{-1}). The absorbance for each tetraalkyllead compound at 270.5 nm was negligible (ϵ <800). The uv data for the tetraalkyllead compounds appear in Table V.

Preparation of Triethyllead Methoxide. Methanol, 5 ml, was added to 0.39 g (17 mg-atoms) of sodium under a nitrogen atmosphere in a 250-ml round-bottomed flask cooled in an ice-water bath. After all of the sodium had reacted, a suspension of 5.3 g (16 mmol) of triethyllead chloride in 80 ml of anhydrous ether was added in one portion. The mixture was stirred for 20 min at room temperature and then filtered under a nitrogen atmosphere. The solvent was removed under reduced pressure from the filtrate, leaving a hygroscopic oil. Sublimation (60–80° at 0.01 mm) of the oil yielded 3.6 g of hygroscopic white needles, triethyllead methoxide (69%): mp 77–78° (sealed capillary) (lit.[15] 81–83°).

Reaction of Triethyllead Methoxide and 1,1,2,2-Tetracyanobutane. Triethyllead methoxide, 0.24 g (0.65 mmol), was dissolved in 6 ml of anhydrous ether under a nitrogen atmosphere in a 50-ml round-bottomed flask sealed with a serum cap. The flask was placed in an ice-water bath and a solution of 0.105 g (0.65 mmol) of 1,1,2,2-tetracyanobutane in 10 ml of ether was added in one portion. The solvent was immediately removed under reduced pressure leaving a pale yellow oil (0.32 g). The infrared spectrum of this oil was obtained immediately. The ^1H NMR spectrum was also obtained: ir (cm^{-1}) 2962 (w), 2937 (m), 2854 (m), 2175 (s), 2092 (s), 1454 (m), 1375 (w), 1306 (w), 1153 (s), 1020 (w), 961 (w), 883 (w), 682 (m); NMR (CD_3CN–10% HOAc-d_4) for Et_3Pb^+ δ ~2.16 (q, 6, J = 7.5 Hz), 1.82 (t, 9, J = 7.5 Hz); for 1,1,2,2-tetracyanobutanide δ 2.30 (q, 2, J = 7 Hz), 1.30 (t, 3, J = 7 Hz).

Characterization of the Tetraethyllead–TCNE Reaction Product. Tetraethyllead, 80.6 μl (0.41 mmol), was added by hypodermic syringe to a solution of 52.4 mg (0.41 mmol) of TCNE in 3 ml of CH_3CN under a nitrogen atmosphere at 0°. The blue charge-transfer band faded to pale yellow in 30 s. The solvent was immediately removed on a vacuum line, leaving a yellow oil. The ir spectrum of the oil was recorded immediately: ir (cm^{-1}) 2981 (m),

Table V. ^{1}H NMR and Uv Spectral Parameters for Tetraalkyllead Compounds $Me_nEt_{4-n}Pb$ ($0 \leqslant n \leqslant 4$)[a]

	^{1}H NMR					Uv	
Compound	δ[b] (ppm)	Multiplicity	$J(^{207}PbCH_3)$ (Hz)	$J(^{207}PbCCH_3)$ (Hz)	Relative area	λ_{max} (nm)	(ϵ)[c] (M^{-1} cm^{-1})
$PbMe_4$	0.73	s	63.5			206	(8 900)
$PbMe_3Et$	0.64	s	59		9 H	208	(11 100)
	1.45	s		144	5 H		
$PbMe_2Et_2$	0.59	s	52		6 H	209	(10 100)
	1.47	s		145	10 H		
$PbMeEt_3$	0.53	s	46.5		3 H	210	(10 600)
	1.43	s		134	15 H		
$PbEt_4$	1.43	s	~50	125.5		209	(17 500)

[a] In CD_3CN–10% HOAc-*d* at 26°. [b] Relative to dichloromethane (5.49 ppm). [c] In CH_3CN.

Table VI. ^{1}H NMR Parameters for Trialkyllead Chlorides

	$Me_{3-n}Et_nPbCl$ ($0 \leqslant n \leqslant 3$)					
Compound	δ[a] (ppm)	Multiplicity	J (Hz)	$J(^{207}PbCH_3)$ (Hz)	$J(^{207}PbCCH_3)$ (Hz)	Relative area (%)[b]
Me_3PbCl	1.52	s		69		78
$Me_2EtPbCl$	2.24	q	7.5			21
	1.74	t	7.5		215	23
	1.44	s		56		36
$MeEt_2PbCl$	2.19	q	7.5			35
	1.77	t	7.5		198	36
	1.44	s				9
	1.32	s				16
Et_3PbCl	2.20	q	7.5			48
	1.80	t	7.5		175	47

[a] In $CDCl_3$ relative to Me_4Si. [b] Approximate percent of the total signal represented by this resonance (excluding ^{207}Pb splittings).

2963 (m), 2845 (m), 2175 (s), 2091 (s), 1454 (m), 1373 (w), 1307 (w), 1152 (s), 1020 (w), 961 (w), 884 (w), 681 (m). The NMR spectrum is given in Table VII.

Isolation of Triethyllead Trifluoroacetate and 1,1,2,2-Tetracyanobutane from the Tetraethyllead-TCNE Reaction Mixture. Tetraethyllead, 200 μl (1.02 mmol), was added by syringe to a solution of 0.130 g (1.02 mmol) of TCNE in 3 ml of anhydrous CH_3CN at 0° under an atmosphere of nitrogen. The initial blue solution faded to pale yellow in about 30 s. Then 76 μl (1.02 mmol) of trifluoroacetic acid was added by syringe. The solution was transferred to a vacuum line, where the volatile components were removed. The oily residue was extracted with 10 ml of water to remove most of the triethyllead trifluoroacetate. The remaining material was dissolved in 10 ml of $CHCl_3$, washed with two 10-ml portions of 1 M HCl, dried over $MgSO_4$, and concentrated on a rotary evaporator to yield an off-white solid, 0.57 mg (37%), which was shown to be 1,1,2,2-tetracyanobutane by comparison of the ir and NMR spectra with those of an authentic sample: ir (cm^{-1}) 2985 (vw), 2905 (s), 1465 (s), 1459 (s), 1440 (w), 1392 (w), 1336 (vw), 1308 (w), 1285 (vw), 1244 (vw), 1120 (m), 1035 (vw), 1015 (vw), 979 (m), 943 (s), 916 (vw), 883 (m), 792 (w), 739 (s); NMR ($CDCl_3$) δ 4.48 (s, 1), 2.38 (q, 2, J = 7 Hz), 1.45 (t, 3, J = 7 Hz). The aqueous layer containing triethyllead trifluoroacetate was placed on a rotary evaporator. The tan solid remaining after removal of the water was recrystallized from toluene with the aid of activated charcoal to yield 0.26 g (62%) of an off-white solid. This solid was identified as triethyllead trifluoroacetate by comparison of its ir and NMR spectra with those of an authentic sample: ir (cm^{-1}) 2965 (m), 2930 (m), 2850 (m), 1658 (s, br), 1433 (m), 1372 (w), 1200 (s, br), 1133 (s, br), 1020 (w), 960 (w), 940 (w), 836 (s), 805 (s), 724 (s), 679 (s); NMR ($CDCl_3$) δ 2.08 (q, 6, J = 7.5 Hz); 1.75 (t, 9, J = 7.5 Hz, $J(^{207}PbCCH_3)$ = 179 Hz).

Determination of the Selectivity of Insertion of TCNE. A sample of tetraalkyllead compound Me_nPbEt_{4-n} ($1 \leq n \leq 3$) was added by syringe to an NMR tube containing 0.50 ml of CD_3CN, 50 μl of HOAc-d_4, and 20 μl of CH_2Cl_2. The NMR spectrum of the solution was recorded at 60 MHz (Table V). A weighed sample of TCNE was added, and the tube was shaken for 5–10 s. Then, the NMR spectra of the reaction products were obtained at 60 and 200 MHz. The selectivities were determined by comparing the relative areas of (a) certain peaks for the trialkyllead cations and/or (b) the methylene group of 1,1,2,2-tetracyanobutanide and the methyl group of 1,1,2,2-tetracyanopropanide. The relative areas of the resonances for the trialkyllead cations were obtained by examination of the 220-MHz spectra of the trialkyllead chlorides $Me_nEt_{3-n}PbCl$ ($1 \leq n \leq 3$). These data are listed in Table VI.[37]

Table VII lists the resonances appearing in PbR_4–TCNE reaction mixtures. Because 1,1,2,2-tetracyanoalkyl anions are unstable,[9] selectivity values based on the relative amounts of these products were obtained within 1 h after mixing. The selectivity values are unaffected by reversing the order of addition of reactants.

Yields of Hexacyanopentadienide Products. Typically, a sample of alkylmetal (0.1 mmol) was added by syringe to a magnetically stirred solution of 0.2 mmol of TCNE in 3 ml of CH_3CN under a nitrogen atmosphere. Samples of the solution were removed periodically to monitor the yield of hexacyanopentadienide products by spectrophotometric analysis of absorbance bands in the region of 540–595 nm, where there was little interference from absorbance bands from other reaction products. The yields of hexacyanopentadienide products were computed with the use of the extinction coefficients of corresponding tetramethylammonium salts.[9b] Others have shown that the ϵ values for cyanocarbon anions are independent of the cation.[12]

For alkyllead and -tin reactions, the yield of 3-substituted hexacyanopentadienide ions reached a maximum after 8–24 h. 4-Alkyl-2,3,5,6-tetracyanoanilines[9b] formed in low yield from decomposition of the hexacyanopentadienide ions.

For tetraalkyllead reactions, the effect of stoichiometry on the yield of hexacyanopentadienide products was examined under the following conditions: 1:1 stoichiometry, $[PbMe_4]_0 = [TCNE]_0$ = 0.07 M in THF; $[PbEt_4]_0 = [TCNE]_0$ = 0.07 M CH_3CN. For the 1:2 stoichiometry, $[PbR_4]_0$ = 0.035 M.

Isolation of 1,1,2,4,5,5-Hexacyanopentadienide Ion from the Reaction between Tetramethyllead and TCNE. Tetramethyllead, 0.69 ml (5.1 mmol), was added by syringe to a magnetically stirred suspension of 1.30 g (10.2 mmol) of TCNE in 60 ml of THF at −78° under a nitrogen atmosphere. Stirring was continued for 1 h at −78° and then for 8 h at room temperature. The solvent was removed under vacuum to yield a red oil, which was dissolved in 300 ml of H_2O. The addition of 1.0 g of sodium *N*,*N*-dimethyldithiocarbamate caused the precipitation of a gray solid, 0.8 g, which was filtered and identified as crude trimethyllead *N*,*N*-dimethyldithiocarbamate by comparison of ir spectra with that of an authentic sample.[38] To the red filtrate was added 1.5 g of tetramethylam-

Table VII. ^{1}H NMR Parameters for the Products from the Reaction between Tetraalkyllead Compounds and Tetracyanoethylene[a, b]

	Reactants				
Products	Me_4Pb	Me_3PbEt	Me_2PbEt_2	$MePbEt_3$	$PbEt_4$
Me_3Pb^+	1.53, s, $J(^{207}Pb-CH_3)$ = 78 Hz	1.44, s, $J(^{207}Pb-CH_3)$ = 78 Hz (*)			
$EtPbMe_2^+$		2.22, q, J = 7.5 Hz 1.78, t, J = 7.5 Hz 1.44, s 1.35, s (*)			
Et_2PbMe^+			2.19, q, J = 7.5 Hz 1.81, t, J = 7.5 Hz, $J(^{207}PbCCH_3)$ = 199 Hz 1.35, s 1.25, s (*)		
Et_3Pb^+				2.15, q, J = 7.5 Hz 1.80, t, J = 7.5 Hz, $J(^{207}PbCCH_3)$ = 175 Hz	
1,1,2,2-Tetracyano-butanide		2.34, q, J = 7.5 Hz (*) 1.35, t, J = 7.5 Hz	2.35, q, J = 7.5 Hz (*) 1.35, q, J = 7.5 Hz	2.31, q, J = 7 Hz (*) 1.33, q, J = 7 Hz	2.28, q, J = 7 Hz 1.32, t, J = 7 Hz
1,1,2,2-Tetracyano-propanide	2.19, s	2.11, s (*)	2.17, s (*)	c (*)	

[a] In CD_3CN–10% HOAc-d_4 at 26°. Chemical shifts relative to dichloromethane (δ 5.49 ppm). [b] The asterisk indicates that this peak was used to determine selectivity. [c] Not observed. Addition of 1,1,2,2-tetracyanopropane results in a new resonance at 2.09 ppm.

monium chloride. Filtration of the chilled mixture yielded 0.66 g (42%) of tetramethylammonium 1,1,2,4,5,5-hexacyanopentadienide, which was identified by comparison of ir and uv-visible spectra with those of an authentic sample.[9b] ν_{CN} 2183 cm^{-1}, $\lambda_{max}^{CH_3CN}$ 538 nm.

Isolation of the 3-Methyl-1,1,2,4,5,5-hexacyanopentadienide Ion from the Reaction between Tetraethyltin and TCNE. Tetraethyltin, 1.0 ml (5.05 mmol), was added by syringe to a solution of 1.29 g (10.1 mmol) of TCNE in 60 ml of CH_3CN under a nitrogen atmosphere. The reaction was stirred for 36 h. The solvent was removed under vacuum, yielding a purple oil which was extracted with three 150-ml portions of $CHCl_3$. The extracts were concentrated and chromatographed on alumina with CH_3CN. The dark blue band for 3-methyl-1,1,2,4,5-hexacyanopentadienide ion was the second band to elute. Removal of the solvent left a red solid (0.21 g) which was dissolved in 50 ml of 2:1 acetone:H_2O. Sodium *N,N*-dimethyldithiocarbamate (0.09 g) was added, and the major part of the organic solvent removed under vacuum. The chilled mixture was filtered and 0.2 g of tetramethylammonium chloride was added. Filtration of the chilled solution yielded 70 mg (4.5%) of tetramethylammonium 3-methyl-1,1,2,4,5,5-hexacyanopentadienide which was identified by comparison of ir and uv-visible spectra with those of an authentic sample:[9b] $\nu_{C\equiv N}$ 2185 cm^{-1}, $\lambda_{max}^{CH_3CN}$ 589 nm.

Reaction of Dimethylmercury and TCNE. Dimethylmercury, 13.3 μl (0.18 mmol), and 26.7 mg (0.18 mmol) of TCNE were added to an NMR tube containing 360 μl of CD_3CN, 40 μl of HOAc-d_4, and 20 μl of CH_2Cl_2. The reaction mixture was examined over a 25-h period. The only change noted was a gradual decrease in the resonance for dimethylmercury (14% loss after 25 h): δ 0.13 (s, $J(^{199}Hg-CH_3)$ = 107 Hz).[39]

Reaction of Diethylmercury and TCNE. Diethylmercury, 19.1 μl (0.18 mmol), and 28.0 mg (0.22 mmol) of TCNE were added to an NMR tube containing 360 μl of CD_3DN, 40 μl of HOAc-d_4, and 20 μl of CH_2Cl_2. The reaction was examined over a 25-h period. The 60-MHz spectrum of diethylmercury was complex, and was not analyzed completely.[39] However, the principal resonance (δ 1.27 (t, 6, J = 7 Hz, $J(^{199}HgCCH_3)$ = 131 Hz)) decreased to about half of its original intensity in about 1 h as new peaks appeared: δ 2.30 (q, J = 7 Hz, -CH_2 of $(NC)_2\bar{C}C(CN)_2Et$). Because of the number of resonances in the regions of δ 1.5–1.8 ppm (from $EtHg^+$ and -CH_3 of $(NC)_2\bar{C}C(CN)_2Et$) a complete analysis of the products was not attempted.

Reaction of Diisopropylmercury and TCNE. Diisopropylmercury was prepared by the method of Gilman and Brown,[40] and distilled under reduced pressure immediately before use. The proton NMR spectrum of diisopropylmercury consists of a single line in CD_3CN-10% HOAc-d_4 (δ 1.32 s, $J(^{199}HgCCH_3)$ = 114 Hz). TCNE, 25.6 mg (0.20 mmol), was added to a solution of 25 μl (0.175 mmol) of diisopropylmercury in 360 μl of CD_3CN, 40 μl of HOAc-d_4, and 20 μl of CH_2Cl_2. An immediate reaction occurred. The spectrum of the mixture was assigned to isopropylmercury 1,1,2,2-tetracyano-3-methylbutanide: NMR δ 2.6 (m, 2), 1.44 (d, 6, J = 7 Hz, $J(^{199}HgCCH_3)$ = 287 Hz), 1.30 (d, 6, J = 7 Hz). The multiplet at 2.6 results from superposition of the methine protons in the product. The spectrum slowly changes over a 3-h period. The resonances at 1.44 and 1.30 ppm are replaced by resonances at 1.39 (d, 6, J = 7 Hz, $J(^{199}HgCCH_3)$ = 216 Hz) and 1.27 (d, 6, J = 7 Hz). The new product may result from rearrangement to the keteniminato anion or from the loss of HCN from the anion. The infrared spectrum of an equimolar mixture of diisopropylmercury and TCNE was recorded by the procedure described previously for tetraethyllead-TCNE mixtures: ir (cm^{-1}) 2951 (s), 2840 (s), 2181 (sh, s), 2095 (br, s), 1619 (m), 1581 (m), 1495 (m), 1380 (w), 1332 (w), 1197 (s), 1149 (s), 1022 (w), 1010 (w), 904 (w). The shape and intensity of the bands centered at 2181 and 2095 cm^{-1} were very similar to those observed in the $PbEt_4$–TCNE mixtures.

Reaction of Tetraethyltin and TCNE. Tetraethyltin, 30 μl (0.15 mmol), and 22.8 mg (0.18 mmol) of TCNE were added to an NMR tube containing 360 μl of CD_3CN, 40 μl of HOAc-d_4, and 20 μl of CH_2Cl_2. The reaction was examined over a 14-h period. The ^{1}H NMR spectrum of $SnEt_4$ is complex,[41] with all resonances appearing in the region of δ 1.9–0.3 ppm. With TCNE, the resonances for $SnEt_4$ decreased to one-half their original intensity in about 45 min. New resonances appeared at δ 2.42 (q, 2, J = 7 Hz), 1.35 (t, 3, J = 7 Hz), and 1.31 (s, 15). The first two resonances were assigned to the 1,1,2,2-tetracyanobutanide ion, and the last to the triethyltin cation.[42] After 14 h, the presence of 0.14 mmol of the insertion product was determined by comparison with the CH_2Cl_2 internal standard.

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Thin Layer Spectroelectrochemical Study of Vitamin B_{12} and Related Cobalamin Compounds in Aqueous Media

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Abstract: The oxidation-reduction behavior of vitamin B_{12} and related cobalamins in aqueous media has been studied by a spectroelectrochemical technique using an optically transparent thin layer electrode cell (OTTLE). It was found, contrary to previous reports, that all of the cobalamins are reduced via two distinct one-electron steps. The rate of the electron transfer in the first one-electron step is unusually slow in all cases except for aquocob(III)alamin, B_{12a}, and no wave is observed even at the slow voltage scan rates used in polarography. It is also shown that aquocob(III)alamin, previously assumed to be a single compound, is a nonequilibrium mixture of two compounds which have an approximately 500 mV difference in the one-electron reduction potential. It is suggested that the two species may be a "base on" and "base off" form with respect to the corrin ring side chain benzimidazole in the *y*-axial position.

The electrochemical behavior of vitamin B_{12} (cyanocob(III)alamin) and related cobalamin compounds in aqueous media is of importance for elucidating the biomechanistic reaction sequences which involve cobalamin species.[1] There has been considerable study of the redox processes of cobalamins using the conventional electroanalytical techniques of polarography,[2-14] coulometry,[9,15,16] and cyclic voltammetry,[17-20] and diverse working electrode materials such as mercury[2-20] and platinum.[12,20] However, the interpretation of the electrochemical data to unambiguously determine even the most fundamental parameters such as the thermodynamic redox potentials, the number of electrons (n values) involved in the electron transfer steps, and the sequence of steps in the mechanism has not been possible because of numerous complicating conditions. The complications encompass strong adsorption of both reactant and

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