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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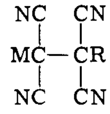
Received April 21, 1975

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

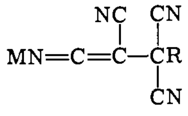
Sir:

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]



$\mathrm{M{-}C(CN)_2{-}C(CN)_2R}$

I

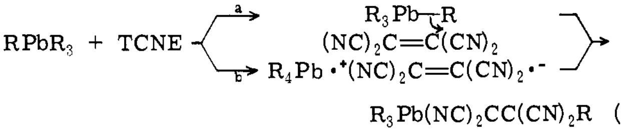


$\mathrm{MN{=}C{=}C(CN){-}C(CN)_2R}$

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.



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

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, $J(^{207}Pb\text{-}CH_3) = 63.5$ Hz) and the appearance of $(CH_3)_3Pb^+$ (δ 1.53 ppm, $J(^{207}Pb\text{-}CH_3) = 78$ 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).

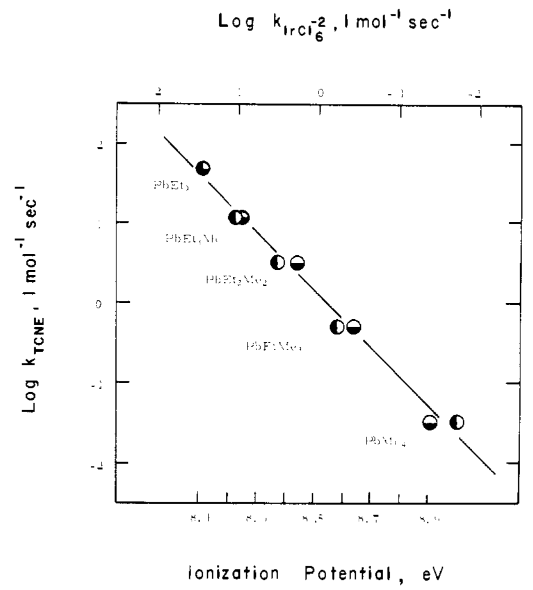


Figure 1. Insertion of TCNE into tetraalkyllead compounds. Correlation of the second-order rate constants with the ionization potentials of R_4Pb denoted by ⊖ (lower scale) and the rate constants for the oxidative cleavage of R_4Pb by hexachloroiridate(IV) denoted by ◐ (upper scale).

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

$PbMe_nEt_{4-n}$ ($0 \leqslant n \leqslant 4$)	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.

$$\begin{array}{l} \mathrm{PbEt_4 + TCNE \xrightarrow{a} Et_3Pb(NC)_2CC(CN)_2Et} \\ \qquad\qquad\qquad\qquad\quad \mathrm{III} \\ \qquad\qquad\qquad\quad {}^{-\mathrm{CH_3OH}} \nearrow_{\mathrm{b}} \\ \qquad\qquad\quad \mathrm{Et_3PbOCH_3 + H(NC)_2CC(CN)_2Et} \end{array} \quad (2)$$

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.

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

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:

$$\mathrm{R_4Pb \longrightarrow R_4Pb^{\bullet +} + \epsilon}$$

and is obtained by He(I) photoelectron spectroscopy.[6] These energetics are also directly related to the electrochemical one-electron oxidation potentials of R_4Pb and the frequencies of the charge-transfer bands of R_4Pb–TCNE complexes are given by ν_{CT}.[6,7]

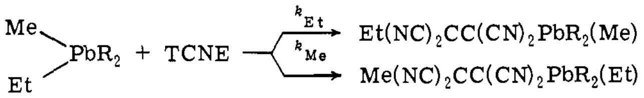
The rates of insertion of TCNE into R_4Pb also show in Figure 1 a striking correlation with the rates of oxidative cleavage of R_4Pb by hexachloroiridate(IV), in which previous studies demonstrated that the process is rate-limited by the electron-transfer step in eq 4.[6]

$$R_4Pb + Ir^{IV}Cl_6^{2-} \longrightarrow Ir^{III}Cl_6^{3-} + R_4Pb\cdot^{+} \qquad (4)$$

For the insertion reaction, a similar rate-limiting process is given by the electron transfer mechanism in eq 1b, in which TCNE functions as an π-electron acceptor. Indeed, the characteristic visible absorption spectrum[8a] of TCNE$\cdot^-$, as well as its electron spin resonance spectrum[8b] can be readily observed during the reaction of tetraethyllead and TCNE (Figures 2a and b).[9] The subsequent fast transfer of the alkyl group from $R_4Pb\cdot^+$ to TCNE$\cdot^-$ is probably a cage process and occurs by transfer of either R· or R^+ as given in eq 5a or 5b, respectively:

$$[TCNE\cdot^{-} R{-}PbR_3\cdot^{+}] \begin{array}{l} \xrightarrow{a} [R{-}TCNE^{-}\ R_3Pb^{+}] \\ \xrightarrow[b]{} [R{-}TCNE\cdot\ R_3Pb\cdot] \end{array} \longrightarrow \text{III} \qquad (5)$$

Selectivity studies with a series of mixed methyl-/ethyllead compounds in Table I show that an ethyl group is preferentially transferred, consistent with a weaker Et–Pb bond compared to a Me–Pb bond in eq 6 (where R = methyl or ethyl).[10,11]



$$\begin{array}{l} Me \\ \quad PbR_2 \\ Et \end{array} + TCNE \begin{array}{l} \xrightarrow{k_{Et}} Et(NC)_2CC(CN)_2PbR_2(Me) \\ \xrightarrow{k_{Me}} Me(NC)_2CC(CN)_2PbR_2(Et) \end{array} \qquad (6)$$

We favor the mechanistic route represented in eq 5a since a similar selectivity (k_{Et}/k_{Me}) was found in the oxidative cleavage of R_4Pb with $Ir^{IV}Cl_6^{2-}$ (compare eq 4, 7 and 8).

$$RPbR_3\cdot^{+} \xrightarrow{fast} R\cdot + R_3Pb^{+} \qquad (7)$$

$$R\cdot + IrCl_6^{2-} \xrightarrow{fast} RCl + IrCl_5^{2-} \qquad (8)$$

The selectivity is associated with the facile fragmentation of the cation-radical in eq 7 subsequent to the slow step in eq 4.[6] The presence of the alkyl radical was shown unequivocally by its interception with hexachloroiridate(IV) as described in eq 8 or spin trapping with nitrosoisobutane.[6] Unfortunately, the nature of the cage process inherent in the insertion reaction described in eq 5 precludes the detection of R·.[12] There are other reports[2a,13] 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. However, none of these by themselves present as compelling an example of an electron transfer mechanism as that provided by the studies with organolead compounds.[14]

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(11) The selectivities were determined from the relative amounts of methyl and ethyl adducts to TCNE[3b] as well as the two trialkyllead cations. The latter were obtained by comparison of the 220-MHz ^{1}H NMR spectra of the trialkyllead chlorides [$Et_3Me_{3-n}PbCl$, $1 \leq n \leq 3$].

(12) Even if some of the ethyl radicals should escape the cage process in reaction 5b, separate experiments show that they add rapidly to TCNE when they are generated independently from the thermal decomposition of dipropionyl peroxide.

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(14) We wish to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial assistance.

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Received April 9, 1975

^{2}H Spin-Lattice Relaxation in the Presence of Paramagnetic Shift Reagents

Sir:

Spin-lattice relaxation times (T_1) for deuterium are generally more readily interpretable than those for carbon.[1] Experimentally, acquisition of T_1 data for ^{2}H is less time consuming than for ^{13}C since relaxation times of ^{2}H are an order of magnitude shorter than those of ^{13}C.[1] These advantages of ^{2}H over ^{13}C are, however, largely offset by intrinsically low deuterium chemical shifts observed at normal field strengths (scaled down by a factor of 6.5 with respect to their proton counterparts). Thus, in perdeuterated molecules overlapping of resonance signals may effectively preclude determination of relaxation times.

We should like to report that some of the problems associated with the small chemical shift disadvantage of ^{2}H relative to ^{13}C can be overcome by application of shift reagents. Because of the overwhelming dominance of quadrupolar vs. dipolar relaxation mechanisms in ^{2}H relaxation,[2] addition of small quantities of paramagnetic shift reagents to readily complexed molecules should produce significant chemical shifts without concomitantly seriously affecting relaxation times. It has been estimated,[2] for example, that the concentration of paramagnetic species large enough to reduce T_1 of ^{1}H in ^1H_2O by a factor of 400 will shorten T_1 of ^{2}H in ^2H_2O by a factor of only 2.[3]

To test the feasibility of the utilization of paramagnetic shift reagents in ^{2}H relaxation time studies, a solution of acetone-d_6 (0.81 M) and acetonitrile-d_3 (0.38 M) in chloroform was employed. The ^{2}H NMR spectrum of this mixture exhibited two partially overlapping resonances ($\Delta\nu < 0.1$