

Figure 4. Unit cell of complex 7,  $[\text{Cu}_2(\text{ClCH}_2\text{-COO})_3\text{EtSal}(\text{C}_2\text{H}_5\text{OH})]_\infty$ , showing the packing of the polymeric chains in the lattice.

HSal·ROH represent the Schiff base condensates of salicylaldehyde derivatives with amino alcohols. When the reagents are mixed and heated, the final (brown) product is obtained after an initial immediate color change to green. Careful removal of the solvent without strong heating preserves the initial green color and deposits green crystals of type 5 complexes. These can be redissolved and heated to give the final product. This demonstrates that acetates and other bridging groups are readily interchanged, although the bridging is not necessarily in the conventional form as in 1. Of the new complexes reported here, 5 is unique in exhibiting ferromagnetic exchange interactions. The others are all antiferromagnetic.

Complex 6,  $[\text{Cu}_3(\text{OH})(\text{EtSal})_3(\text{F}_3\text{C.COO})_2]_2^0$  ( $R = 5.9\%$ , refinement continuing),<sup>5</sup> is a hexanuclear copper(II) complex consisting of two independent oxygen-bridged  $\text{Cu}_3(\text{OH})$  units with Cu atoms labeled A, B, C and D, E, F (Figure 3). The complex is a unique combination of hydroxyl, carboxylate, and salicylaldimine ligands. Each  $\text{Cu}_3(\text{OH})$  fragment contains three independent and structurally different copper atoms. Despite the elaborate structure, the complex is quite stable, and can be dissolved and recrystallized in organic solvents without disproportionation into component ligands. The distances bridged in this case are 3.111 (1), 3.229 (1), and 3.398 (1) Å within the  $\text{Cu}_3(\text{OH})$  unit A, B, C and 3.130 (1), 3.194 (1), and 3.471 (1) Å in D, E, F. The nearest metal-to-metal distances between the two  $\text{Cu}_3(\text{OH})$  units is 3.359 (1) Å (C-F).

Complex 7,  $[\text{Cu}_2(\text{ClCH}_2\text{-COO})_3\text{EtSal}(\text{C}_2\text{H}_5\text{OH})]_\infty$  ( $R = 4.9\%$ , refinement continuing) (Figure 4),<sup>5</sup> consists of two types of dimeric unit,  $[\text{Cu}_2(\text{ClCH}_2\text{-COO})_4]$  with the standard structure 1 and  $\text{Cu}_2\text{Sal}_2\text{X}_2$  with standard structure 2 (but containing a coordinated solvent molecule,  $\text{C}_2\text{H}_5\text{OH}$ ), where X is  $\text{ClCH}_2\text{-COO}^-$  and is attached via one of its carboxylate oxygen atoms. This leaves the other carboxylate oxygen, which is relatively electronegative, pointing away from the body of the  $\text{Cu}_2\text{Sal}_2\text{X}_2$  dimeric unit to attach to the  $[\text{Cu}_2(\text{ClCH}_2\text{-COO})_4]$  dimer. This linkage repeats to form an infinite chain  $-\text{O}-\text{C}-\text{O}-[\text{Cu}_2\text{EtSal}_2(\text{C}_2\text{H}_5\text{OH})_2]-\text{O}-\text{C}-\text{O}-[\text{Cu}_2(\text{ClCH}_2\text{-COO})_4]-\text{O}-\text{C}-\text{O}-$ . This mode of acetate bridging is also new, and unique to this kind of complex. The distances spanned

are 2.629 (1), 3.062 (1), and 5.476 (1) Å within the  $[\text{Cu}_2(\text{ClCH}_2\text{-COO})_4]$  dimer, within the  $[\text{Cu}_2\text{EtSal}_2(\text{C}_2\text{H}_5\text{OH})_2]$  dimer, and between the two dimers, respectively.

The series of complexes 4, 5, 6, and 7 demonstrates the versatility of salicylaldimine and acetate-type ligands in the chemically very closely related, yet structurally very different, complexes. The formate ion has been an apparent exception among carboxylates in its ready ability to form a variety of different bridges between metal atoms,<sup>1,13</sup> but evidently formate is not unique in this regard.

The single-crystal X-ray crystallographic work was carried out by counter methods as described previously.<sup>14</sup>

**Acknowledgment.** Support received under NSF Grant CHE77-01372 is gratefully acknowledged.

**Supplementary Material Available:** Positional and thermal parameters for complexes 4, 5, 6, and 7 (8 pages). Ordering information is given on any current masthead page.

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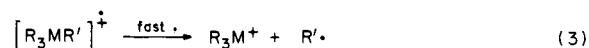
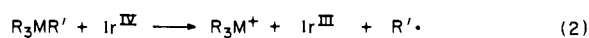
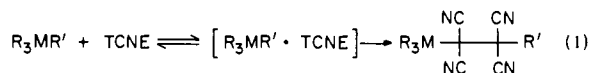
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Received August 20, 1979

## One-Electron Oxidation of Benzyltrialkylstannanes. 1. Cation Radical Fragmentation by Dual Modes

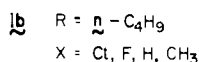
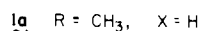
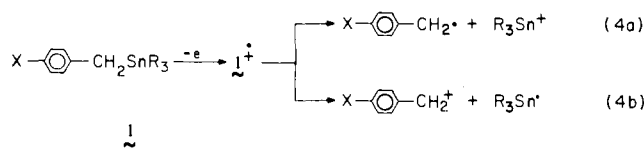
Sir:

Reactions of group 4a organometallics ( $\text{R}_3\text{MR}'$ ,  $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ;  $\text{R}, \text{R}' = \text{alkyl}$ ) with tetracyanoethylene (TCNE; charge transfer, eq 1) or iridium(IV) complexes (one-electron transfer, eq 2) have been shown by Kochi and co-workers<sup>1</sup> to involve the intermediacy and fragmentation of cation radicals (eq 3). In all cases examined, the rate-determining step was

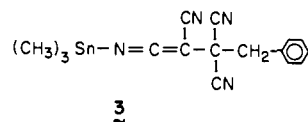
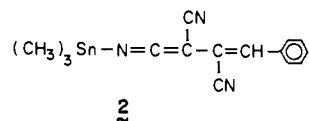


conclusively shown to be electron transfer. Subsequent cation radical fragmentation was rapid and presumably occurred within the initial contact cage.

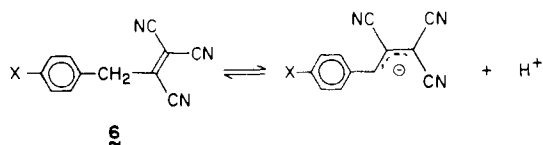
In the present paper we describe the reactions of benzyltrialkylstannanes **1** with TCNE and silver ion ( $Ag^+$ ). We present evidence for the unusual formal partitioning of the fragmentation of intermediate cation radicals  $1^+$  into two separate channels (eq 4). The partition ratio (4a:4b) depends on the substituent X in a systematic fashion and reaction products derive from both in-cage and cage-free processes.



TCNE and benzyltrimethylstannane (**1a**)<sup>2</sup> give a violet CT complex<sup>3</sup> when solutions in CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>CN are mixed, but the color rapidly fades. On standing overnight the ketenimine derivative **2**<sup>4</sup> precipitated as a yellow powder. Removal of solvent immediately after dissipation of the CT color afforded another compound believed to be **3**.<sup>5</sup> Colorless **3** is moderately



unstable. Loss of HCN gave **2**. Contrary to the behavior of **1a**, tri(*n*-butyl)benzylstannanes **1b** do not afford adducts comparable with **2** or **3** when added to TCNE in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN mixtures. Instead, products isolated<sup>6</sup> in all cases were tri(*n*-butyl)tin cyanide (**4**), tri(*n*-butyl)tin chloride (**5**), and the highly colored cyanocarbons (**6**). Relative yields of **4** and



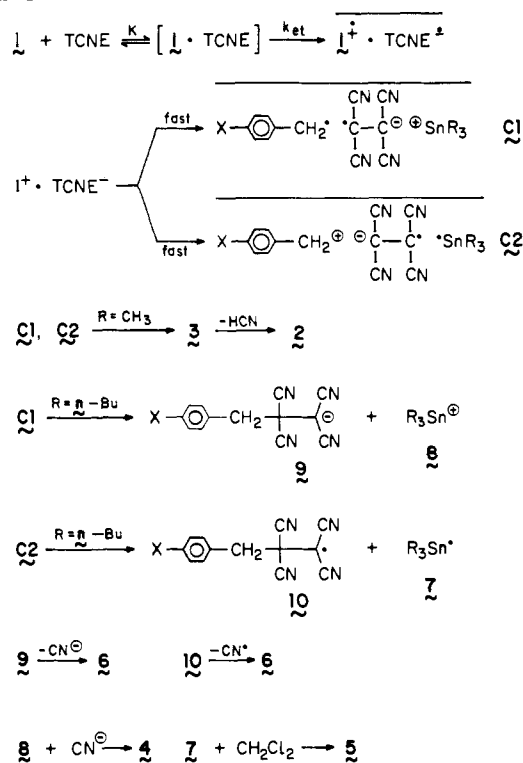
**5** and the mass balance for tin-containing products<sup>6b</sup> are shown in Table I. The formation of chloride **5** appears to require the intermediacy of tri(*n*-butyl)tin radical (**7**), while **4** can result from combination of tri(*n*-butyl)tin cation with cyanide anion. We view the reactions of benzyl tin compounds **1** with TCNE as proceeding as outlined in Scheme 1.<sup>7</sup> Rapid CT complex

**Table I.** Relative Yields of Tin-Containing Products from Reactions of **1b** with TCNE

X <sup>a</sup>	[CT color] <sup>b</sup>	rel yield, %		mass balance, % <sup>c</sup>
		<b>4</b>	<b>5</b>	
CH <sub>3</sub>	blue-black	13	87	95
F	violet	17	83	75
H	royal blue	30	70	97
Cl	red	44	56	89

<sup>a</sup> Substituent (para) in **1b**. <sup>b</sup> Color of transient CT complex of **1b** and TCNE. <sup>c</sup> Based on isolated yields of **4** and **5**.

**Scheme 1**

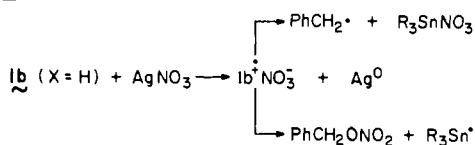


formation followed by rate-determining electron transfer gives the ion pair  $1^{\cdot+} \cdot TCNE^{\cdot-}$ , which suffers rapid, in-cage cation radical fragmentation in one of two formal<sup>8</sup> senses to produce either C-1 or C-2. In the case of reaction involving **1a**, the tight triple cage (C-1 or C-2) collapses to the observed product **3**. For the reactions of the sterically bulky **1b** series, we propose that cage escape (or internal displacement) occurs to afford reactive precursors (**7** or **8**) to the observed tin containing products (**4** and **5**) as cage-free intermediates.

Support for the proposed scheme is found in the product ratios (**4**:**5**) obtained in the reactions of **1b** with TCNE. When X is electron donating, which would stabilize a benzylic cation, the yield of **5** is high and thus the relative amount of **7** produced by fragmentation of  $1b^{\cdot+}$  is high. Conversely, the yield of **5** is systematically lowered as X becomes increasingly electronegative. A plot of  $\log \{[\%5/\%4]^X / [\%5/\%4]^H\}$  vs.  $\sigma_p^+$  is linear (correlation 0.92) with a slope of  $\rho = -1.6 (\pm 0.3)$  indicating that there is moderate electron demand at the benzylic center in the product forming step.

Additional evidence for dual fragmentation modes is provided by the reaction of **1b** (X = H) with  $Ag^+$ . Addition of **1b** to 1.0 equiv of  $AgNO_3$  in CH<sub>3</sub>CN-CHCl<sub>3</sub> mixtures afforded silver metal ( $71 \pm 3\%$ ) within the time of mixing. Organic products isolated were bibenzyl (40%),<sup>9</sup> 1-phenyl-2,2-dichloroethane (4%), benzyl nitrate (39%), tri(*n*-butyl)tin chloride

## Scheme II



(**5**, 36%), and tri(*n*-butyl)tin nitrate (**11**, 36%).<sup>10</sup> Analysis of the product mixture according to Scheme II indicates that the partition ratio of 4a:4b (cf. eq 4) is 52:48. Kinetically free benzyl and (*n*-Bu)<sub>3</sub>Sn radicals are implicated since bibenzyl and **5** are isolated.<sup>11</sup> However, products derived from formal cationic intermediates appear to be formed via in-cage processes: when the **1b**-Ag<sup>+</sup> reaction is carried out in CH<sub>3</sub>CN-CHCl<sub>3</sub>-CH<sub>3</sub>OH, benzylmethyl ether is *not* present (GC analysis) at early stages after reaction, but appears only after methanolysis of the primary product benzyl nitrate.

We conclude that charge transfer induced radical ion formation in the systems **1**-TCNE or **1**-Ag<sup>+</sup> proceeds via tight radical ion-ion caged partners, and that in-cage ion recombination at either a benzyl or a tin center displaces a tin-centered radical or a benzyl radical, respectively. The initial ion recombination site appears to be determined by both the nucleophilicity of the counterion (or ion radical in the case of TCNE<sup>-</sup>) and the relative electrophilic character of the benzylic and tin centers in **1**<sup>+</sup> as modulated by substituents.

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- Yields 78% (CH<sub>2</sub>Cl<sub>2</sub>), 59% (CH<sub>3</sub>CN); mp 190–200 °C dec; NMR (DMSO-*d*<sub>6</sub>-Me<sub>4</sub>Si) δ 7.6–7.1 (m, 5 H), 6.20 (s, 1 H), 0.55 (s, 9 H); IR (KBr) 2207 (conj CN), 2145 (C=C=N), 1190 (Sn—C), 690 cm<sup>-1</sup>; UV (acetone), λ<sub>max</sub> (ε), 408 (22 100 M<sup>-1</sup> cm<sup>-1</sup>). Anal. (C, H, N, Sn) and high resolution MS (calcd M<sup>+</sup>, 357.0288; found, 357.0246). Raman spectrum showed no unconjugated nitrile.
- NMR (CDCl<sub>3</sub>-2% CH<sub>2</sub>Cl<sub>2</sub>) δ 7.4 (m, 5 H), 3.33 (s, 2 H), 0.41 (s, 9 H). During the preparation of this manuscript, Reutov and co-workers (Reutov, O. A.; Rozenberg, V. I.; Gavrilova, G. V.; Nikanorov, V. A. *J. Orgmet. Chem.* **1979**, *177*, 101) reported the **1a**-TCNE reaction to afford a product whose properties closely match those of **3**. These workers concluded that the adduct would have the structure resulting from 1,2-oxidative addition rather than that of the 1,4-addition product that we propose for **3**. We prefer the structure shown for **3** based on its conversion into **2** but cannot rule out the 1,2-addition structure conclusively.
- (a) Products were isolated by silica gel chromatography and compared with authentic samples (**4** and **5**); compounds **6** were characterized by UV/vis and NMR spectroscopy. (b) Isolated yields of **6** were 10–28%.
- Reutov<sup>5</sup> obtained **6** (X = H) and Me<sub>3</sub>SnCN as the ultimate products from reaction of **1a** and TCNE, and proposed a thermal elimination of Me<sub>3</sub>SnCN from **3** as an explanation for the formation of **6** (X = H). We have not observed decomposition of **3** to **6** (X = H). Reutov further showed facile HCl cleavage of **3** to Me<sub>3</sub>SnCl and 1,1,2,2-tetracyanopropylbenzene (**12**). We have eliminated an acid cleavage route to **5** in the present work based on our failure to observe **12** and on the systematic change in the **5**:**4** ratio obtained as a function of substituent.
- We do not imply that true bipartite fragmentation of **1**<sup>+</sup> occurs. The triple cage species C-1 and C-2 are valence-bond representations of intermediates which we believe to be required to rationalize the nature of the products and the substituent dependence of their ratio.
- Yields are expressed in terms of total benzyl fragment or tin fragment yield. All compounds were isolated, except the tin nitrate (cf. note 10), by chromatography and compared with authentic samples. Silver metal was identified by atomic absorption spectroscopy.
- Not isolated. An authentic sample was prepared from **5** and AgNO<sub>3</sub> and its presence in the reaction mixture proved by IR. Analysis was performed by determining **5** by GC and then adding fluoride ion to precipitate all ionic tin (**5** and **11**), which was weighed; **11** was determined by difference.
- Alternate mechanisms involving PhCH<sub>2</sub>Ag or Bu<sub>3</sub>SnAg species cannot be eliminated at this time.

David F. Eaton

Contribution No. 2752

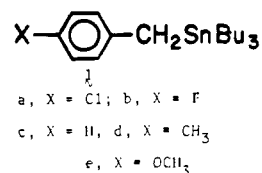
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Received January 2, 1980

## One-Electron Oxidation of Benzyltrialkylstannanes. 2. Excited-State Quenching of 9,10-Dicyanoanthracene

Sir:

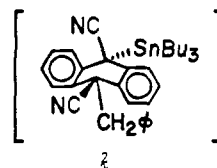
Group 4a organometallics containing M-C σ bonds situated β to a neighboring π system are exceedingly electron rich as indicated by photoelectron spectroscopy,<sup>1</sup> facile formation of charge transfer (CT) complexes with electron-poor acceptors,<sup>2</sup> and reactivity toward electrophiles.<sup>3</sup> The one-electron oxidation of organotin compounds by electron acceptors is well established.<sup>4</sup> We now report that benzyltrialkylstannanes (**1**)



are efficient quenchers of the electron-deficient singlet excited state of 9,10-dicyanoanthracene (DCA). Steady-state analysis of fluorescence quenching and photochemical product formation as a function of quencher concentration allows nearly complete dissection of the exciplex-mediated decay kinetics of the (**1**-DCA)\* system and reveals several unusual facets of the processes which occur.

Observed rate constants for fluorescence quenching of singlet DCA\* in benzene solutions ([DCA] ~ 10<sup>-4</sup> M; [**1**] ~ 10<sup>-3</sup>–10<sup>-1</sup> M) are listed in Table I. Stern-Volmer rate constants *k*<sub>q</sub><sup>f</sup>, were derived from both lifetime and intensity measurements using τ<sub>f</sub><sup>0</sup>(DCA) = 15.3 ns.<sup>5</sup> No new emission features (exciplex emission) were observed. A plot of log (*k*<sub>q</sub><sup>X</sup>/*k*<sub>q</sub><sup>H</sup>) vs. σ was linear with slope ρ = -1.4 which implicates a degree of electron transfer, in the direction (**1**<sup>+</sup>—DCA<sup>-</sup>), during the quenching act.

Photobleaching of DCA was observed on irradiation<sup>6</sup> of **1**-DCA solutions in degassed benzene. In a preparative experiment (Pyrex filter) with the pair **1c**-DCA, products isolated were bibenzyl (3%), hexa(*n*-butyl)ditin (48%, 96% based on tin), 9-benzyl-10-cyanoanthracene (28%<sup>7</sup>), and a material tentatively identified as 9-cyano-10-(tri-*n*-butyl stannyl)anthracene (1–2%<sup>8</sup>). We propose that the observed products result from secondary photolysis of an initial 9,10 adduct (**2**<sup>9</sup>)



via preferential benzyltin homolysis. Under analytical conditions<sup>6</sup> (uranium glass filter), the progress of DCA photobleaching in the presence of various concentrations of **1a–e** can be cleanly followed spectrophotometrically to ~80% conversion of DCA. Isosbestic points in the visible spectra of DCA are retained throughout the experiments indicating that only one photoreaction occurs. Plots of the inverse of the quantum yields for DCA disappearance (φ<sub>p</sub><sup>-1</sup>) vs. inverse quencher concentration<sup>10</sup> yield a family of straight lines (Figure 1).

We adopt the kinetic scheme delineated in eq 1 in which initial, reversible, exciplex (E\*) formation is followed by either

