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CYCLIC VOLTAMMETRY OF SILYL- AND STANNYL-TRICOBALT CLUSTER COMPOUNDS

ALAN M. BONNY *, THOMAS J. CRANE and NOEL A.P. KANE-MAGUIRE
Department of Chemistry, Furman University, Greenville, South Carolina 29613 (U.S.A.)

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Summary

The electrochemical behavior of the clusters $PhM'Co_3(CO)_n$ ($M' = Si$, $n = 11$ and $M' = Sn$, $n = 12$) has been examined via cyclic voltammetry in CH_2Cl_2 solution. In both cases the radical anions $PhM'Co_3(CO)_n^{\overline{\cdot}}$ are unstable, rearranging to $Co(CO)_4^-$ and other products. However, for the silicon compound, where there is one formal cobalt–cobalt bond, the radical anion is sufficiently stable to allow for detection of anion reoxidation at medium scan speeds. The half-life of $PhSiCo_3(CO)_{11}^{\overline{\cdot}}$ has been calculated as 2.3 s at 25°C.

Introduction

Polynuclear metal clusters have unique potential in reactions which involve scission or activation of strong bonds [1]. Of particular interest are heteropolymetallic systems, where there is the possibility of substrate activation via polycoordination to different metals. Current industrial interest in the cluster area is indicated in several recent reports [2].

One major problem in the application of cluster catalysts in processes such as syngas conversion is that polymetallic clusters will commonly not survive under conditions of greatest interest i.e., elevated temperature and CO pressures [3]. Thus, many metal clusters are overly reactive with respect to processes involving metal–metal scission. Ironically, the coordinative unsaturation resulting from metal–metal scission is one mode of activation for metal cluster catalysts. A principal objective of many groups is thus the design of clusters which activate under forcing conditions without irreversible fragmentation.

Recent experimental studies to probe electronic structures of clusters include reports describing the use of cyclic voltammetry [4]. In one application [5] this

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* Address correspondence to this author; present address: The Standard Oil Company (Ohio), 4440 Warrensville Center Road, Cleveland, Ohio 44128 (U.S.A.).

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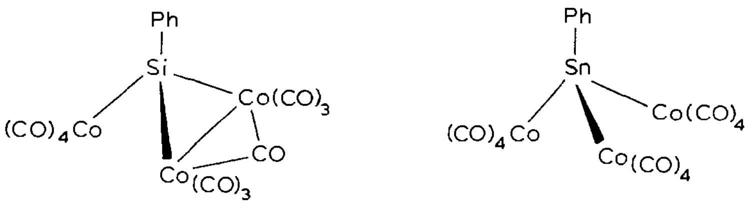

Fig. 1. Structures of $PhSiCo_3(CO)_{11}$ and $PhSnCo_3(CO)_{12}$.

technique was used to estimate the degree of anti- or non-bonding character of low-lying orbitals in clusters of general formulae $RCCo_3(CO)_9$, where (reversible) reduction to a radical anion $RCCo_3(CO)_9^{\dot{-}}$ was found to be sensitive to small variations in the apical substituent R adding support to the concept of delocalized cluster bonding. Reduction to the dianions $RCCo_3(CO)_9^{2-}$ led to rapid disintegration of the cluster unit [5].

We have been interested in the chemistry of Group IV-metal carbonyl clusters [6] since it is evident that the Group IV atom serves to constrain the cluster from fragmentation under forcing conditions. For example, the Ge–Co bonds in the compound $PhGeCo_3(CO)_{11}$ remain intact at over 4000 psi CO pressure and only reversible CO addition to $PhGeCo_3(CO)_{12}$ is observed [7]. This contrasts sharply with the susceptibility of $Co_4(CO)_{12}$ and $Co_4(CO)_{14}^{4-}$ to cluster fragmentation upon reaction with CO [3]. Thus the replacement of the "three electron" [8] $Co(CO)_3$ group by RGe has a significant constraining influence on the cluster framework [9]. More recently other groups have indicated interest in these results from the 1970's.

This report examines the cyclic voltammetry of the clusters $PhM'Co_3(CO)_n$ ($M' = Si$, $n = 11$ and $M' = Sn$, $n = 12$) (Fig. 1) as an extension of work with the alkylidyne analogs [5].

Experimental

Reactions and manipulations were carried out under nitrogen in Schlenk-type glassware, or in glovebox (Vacuum Atmospheres Co.) which maintained oxygen and water at 1–5 ppm levels (monitored by a Teledyne Oxygen Analyzer and Hydrometer). Infrared spectra were recorded on a Perkin–Elmer 283 Spectrometer. Cyclic voltammograms were recorded using a PAR electrochemistry system with a Model 175 Universal Programmer and Model 173 Potentiostat/Galvanostat with Model 176 current to voltage converter, X-Y recorded and Tektronix 5115 storage oscilloscope. Coulometry and preparative scale experiments were carried out in a three-compartment H cell. All cyclic voltammetry and coulometry was carried out in spectroscopic grade methylene chloride purchased from Fisher. 0.05 M Bu_4NPF_6 was used as backing electrolyte (recrystallized twice from ethanol). Peak potentials (E_p) quoted within this paper are versus an Ag wire quasi-reference electrode [10]. For the process $Ru(bipy)_3^{2+} \rightarrow Ru(bipy)_3^{+}$ in the THF under our experimental conditions $E^0 = E_p^c + E_p^a = -0.90$ V versus Ag wire.

The tricobalt clusters $PhSiCo_3(CO)_{11}$ and $PhSnCo_3(CO)_{12}$ were prepared by published procedures [11] and identified by IR [11,12] and ^{13}C NMR [13] spectroscopy.

Results

Representative cyclic voltammograms are shown in Fig. 2 for $PhSiCo_3(CO)_{11}$ in CH_2Cl_2 at room temperature. With the restricted voltage range of Fig. 2a, a single reduction wave is observed at −0.26 V (200 mV/s) attributable to formation of $PhSiCo_3(CO)_{11}^{\cdot-}$. This is consistent with coulometric data at −0.32 V which show that the reduction is a one-electron process. The related reoxidation wave is observed

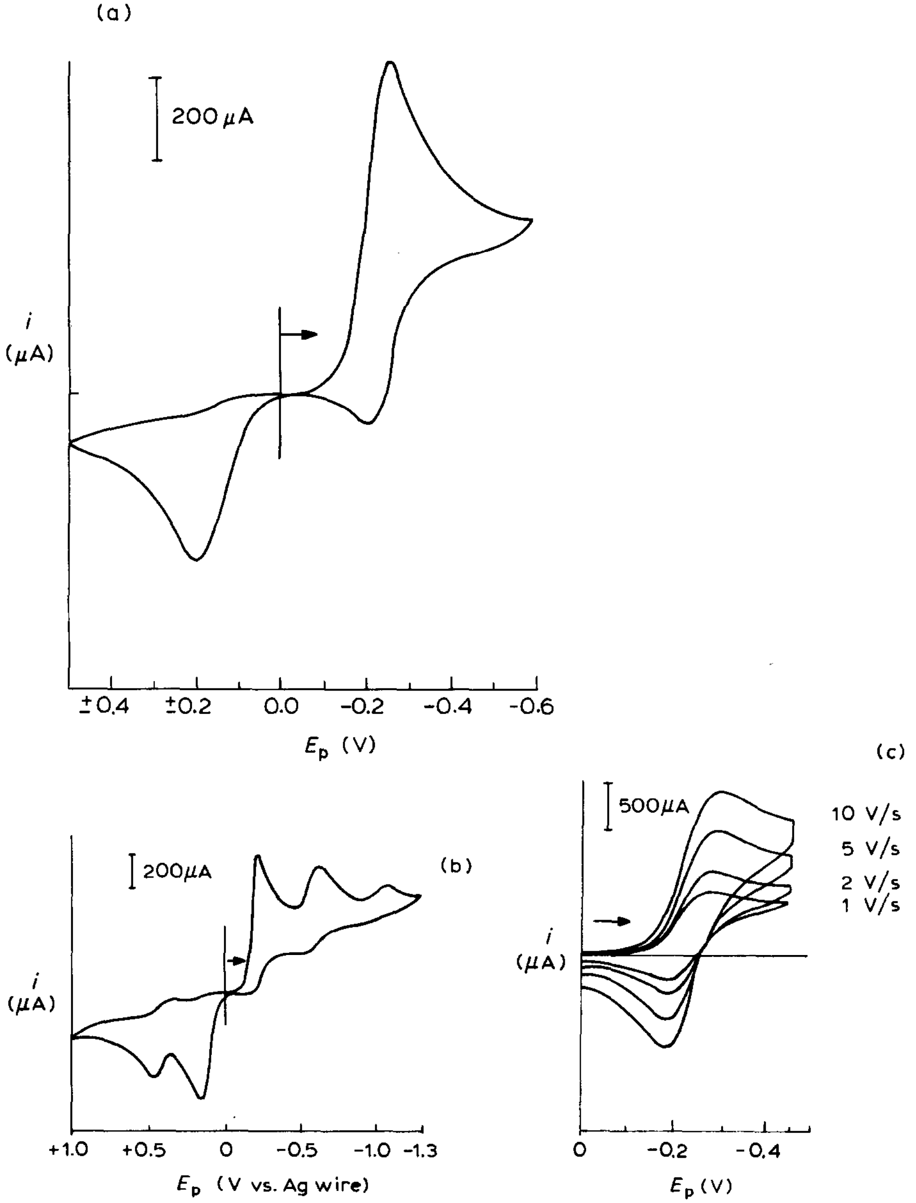

Fig. 2. Cyclic voltammogram of $PhSiCo_3(CO)_{11}$ in CH_2Cl_2 (N_2 atmosphere, room temperature). (a) 200 mV/s (limited range), (b) 200 mV/s (extended range), (c) scan rate dependance.

at −0.20 V; but at the 200 mV/s scan rate i_p^a is significantly less than i_p^c (where i_p^a and i_p^c are the anodic and cathodic peak currents respectively). It therefore appears that the radical anion $\mathrm{PhSiCo_3(CO)_{11}}^{\cdot-}$ is less stable than the corresponding anions derived from alkylidyne clusters [5], and analysis [14] yields a rate constant of 0.3 $\mathrm{s^{-1}}$ for the decomposition of $\mathrm{PhSiCo_3(CO)_{11}}^{\cdot-}$.

Controlled potential reduction of $\mathrm{PhSiCo_3(CO)_{11}}$ at −0.32 V produced a dark brown solution with a single strong CO absorption at 1888 $\mathrm{cm^{-1}}$ characteristic [16] of $\mathrm{Co(CO)_4^-}$. The oxidation wave observed at +0.16 V is attributable [5,17] to $\mathrm{Co(CO)_4^-}$ oxidation. This wave was present to a minor extent on all initial anodic scans.

The above data are consistent with the following equations:

$$\mathrm{PhSiCo_3(CO)_{11}} \xrightarrow{-0.22\ \mathrm{V}} \mathrm{PhSiCo_3(CO)_{11}}^{\cdot-} \tag{1}$$

$$k\ 0.3\ \mathrm{s^{-1}} \downarrow$$

$$\mathrm{Co(CO)_4^-} + \text{other products} \tag{2}$$

In Fig. 2b the electrochemical reversibility of eq. 1 was tested by varying the scan rate from 1 to 10 V/s. The separation between the cathodic and anodic peak potentials ($E_p^a - E_p^c$) increases progressively from a value of approximately 60 mV at 200 mV/s (Fig. 2a) to 80 mV at 1 mV/s and 115 mV at 10 V/s. These results are in accord with a quasi-reversible electrode process [15].

When the cyclic voltammetry scans were carried out over a wider voltage range (Fig. 2b), additional reduction peaks were observed at −0.65 and −1.10 V, together with a further oxidation wave at +0.46 V. No clear assignments are presently possible for these processes, but the cathodic waves are most likely associated with reduction of species generated from the thermal decomposition of the first reduction product, $\mathrm{PhSiCo_3(CO)_{11}}^{\cdot-}$. We observed an additional product in the form of a black precipitate which formed as a gas evolved during the controlled reduction at −0.32 V. Analysis of the black solid yielded 48 wt% Co and a weak broad carbonyl absorption was observed in the infrared at 1900 $\mathrm{cm^{-1}}$ (KBr disc).

During the cyclic voltammetric studies of this compound we observed on occasion broad and irreproducible peaks, especially after the sample had remained in the anaerobic cell for several hours or after repeated scanning. The observations seem most likely related to the high air-sensitivity of the compound, resulting, in these cases, in electrode fouling.

Figure 3 represents the cyclic voltammogram of $\mathrm{PhSnCo_3(CO)_{12}}$ which has a structure without any Co–Co bonds [11]. The first reduction observed at −0.74 V was again established by coulometry (−0.80 V) to be a one-electron process. The reduction occurs at a more negative potential than for $\mathrm{PhSiCo_3(CO)_{11}}$ and no corresponding anodic wave is observed even at high scan speeds (100 V/s).

Tetracarbonylcobaltate anion, $\mathrm{Co(CO)_4^-}$, was again identified by infrared [16] as a coulometric product and is also seen in the CV scans (oxidation at +0.19 V). Infrared spectra of the deep red catholyte solution also showed a new carbonyl absorption at 1947 $\mathrm{cm^{-1}}$ which is not attributable to the parent $\mathrm{PhSnCo_3(CO)_{12}}$ [11]. The ^{13}C NMR spectrum of the catholyte showed two carbonyl resonances at δ 207.1 and 200.2 ppm and a series of phenyl resonances at δ 129.0, 129.2, 129.4, 130.5, 134.3 and 135.9 ppm, consistent with a new $\mathrm{PhSnCo_x(CO)_y}$ species in solution. We have been unable to characterize this species further. (The compound

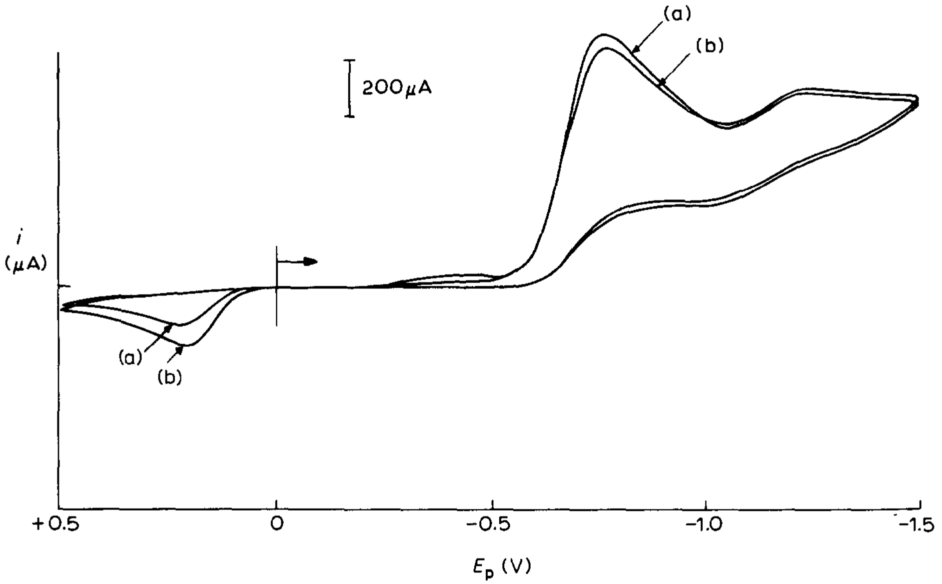

Fig. 3. Cyclic voltammograms of $PhSnCo_3(CO)_{12}$ in CH_2Cl_2 (N_2 atmosphere, room temperature, 200 mV/s), (a) initial scan, (b) repeat scan.

was irreversibly absorbed to silica during TLC experiments inside the glovebox.)

During repeated cyclic voltammogram sweeps with $PhSnCo_3(CO)_{12}$, a reduction peak was observed at -0.4 V (Fig. 3, inset) which we attribute to $Co_2(CO)_8$ arising from recombination of the oxidation product $Co(CO)_4$, as also observed in earlier studies [4,17]. The third reduction wave observed at -1.18 V is attributed to reduction of electrochemically-generated species, since $PhSnCo_3(CO)_{12}^{\overline{\cdot}}$ itself is so unstable. The above data are summarized in eqs. 3 and 4:

$$\begin{array}{l} PhSnCo_3(CO)_{12} \xrightarrow{-0.74\text{ V}} (PhSnCo_3(CO)_{12}^{\overline{\cdot}}) \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad Co(CO)_4^- + \text{other products} \end{array} \tag{3}$$

$$Co(CO)_4^- \xrightarrow{+0.19\text{ V}} Co(CO)_4 \rightarrow 1/2Co_2(CO)_8 \xrightarrow{-0.4\text{ V}} Co(CO)_4^- \tag{4}$$

Discussion

Results from this study parallel earlier work with $YCCo_3(CO)_{9\text{-}x}L_x$ [5] and $PtCo_2(CO)_8PPh_3$ and $PtCo_2(CO)_7(PPh_2CH_2)_2$ [17]. With these compounds, reduction occurred via one-electron steps, and often resulted in the release of one $Co(CO)_4^-$ anion per mole of parent cluster, e.g.

$$\begin{array}{l} YCCo_3(CO)_{9-n}L_n + e^- \rightarrow YCCo_3(CO)_{9-n}L_n^{\overline{\cdot}} \rightarrow \\ \qquad\qquad\qquad Co(CO)_4^- + YCCo_3(CO)_9^- + \text{other products} \end{array} \tag{5}$$

In the case of $PhCCo_3(CO)_9$ a reversible one-electron reduction was observed. This compound has three Co–Co bonds in its structure [18]. The silicon and tin compounds studied here have more open structures and are less rapidly able to accommodate an additional electron. Clearly, the "electron reservoir" concept for metal clusters [17] is dependent upon the cluster system, the types of ligands involved, and the degree of metal–metal bonding within the cluster.

Comparing the silicon and tin clusters more closely it is apparent that $PhSiCo_3(CO)_{11}$, with one formal Co–Co bond is able to accommodate an electron more readily (at a lower potential) than $PhSnCo_3(CO)_{12}$, and that the radical anion product, $PhSiCo_3(CO)_{11}^{\cdot-}$, does have a short but significant lifetime (2.3 s) at room temperature. In comparison, we were not able to directly observe $PhSnCo_3(CO)_{12}^{\cdot-}$, formed from a system with only Sn–Co metallic bonds.

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