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THE ELECTROCHEMISTRY OF SOME ALKYLIDYNETRICOBALT NONACARBONYL CLUSTER COMPLEXES

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Summary

The electrochemistry of a variety of tetrahedral cobalt cluster compounds of the type $XCCo_3(CO)_9$ (X = halogen, alkyl, aryl, etc.) has been studied in CH_2Cl_2. In general, these clusters undergo a reversible, one-electron reduction in the range of —0.7 to —0.9 V vs. SCE. Cathodic peak potentials (and reversibility of reduction) are somewhat sensitive to the nature of the substituent, clusters having more electronegative substituents being reduced around —0.7 V. ESR spectra of the reduced clusters consist of at least 16 lines, and the hyperfine structure and coupling constant (= 35 ± 1 G) change little with substituent. Irreversible, multielectron oxidation of all clusters occurs around +1.5 V to give unknown, electro-active products.

Introduction

As a part of a general program of study on the electrochemistry of organometallic compounds of the transition metals [1], we have examined the electrochemical properties of some derivatives of the tetrahedral methylidynetricobalt nonacarbonyl cluster, $XCCo_3(CO)_9$ *. There have been two objectives for this study: (*i*) How does the nature of the group X affect the anodic and cathodic behavior of the cluster? (*ii*) What can we learn about the nature of the LUMO by examining the ESR spectrum of the reduced cluster? The electrochemistry of organometallic compounds is as yet only poorly understood, so a knowledge of the influence of substituents on the potentials of oxidation and reduction is an important general objective. In some cases such influences are logical and clear-cut. For example, the potential for oxidation of ferrocene derivatives is clearly related to the electronic properties of a substituent or substituents [3]. The

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* The electrochemical reduction of $ClCCo(CO)_9$ was previously and very briefly reported (see [2]).

second objective of this study was suggested by the publication of the ESR spectrum of $EtCCo_3(CO)_9$; this spectrum (and those of reduced clusters with, inter alia, X = F, $SiMe_3$) showed 22 lines, thereby indicating that the unpaired electron was affected by three equivalent cobalt nuclei ($I_{Co} = 7/2$) [4].

Experimental

Electrochemical techniques

All electrochemical experiments were done using a P.A.R. 174 Polarographic Analyzer equipped with a Houston Model 2000 x-y recorder or an Elscint Model CHP-1 potentiostat. The working electrode was either mercury or platinum while the auxiliary electrode was a platinum wire. The saturated calomel electrode (SCE) was used as the reference electrode.

Approximately 2 m*M* solutions of cobalt clusters were prepared in dichloromethane containing 0.20 *M* tetra-n-butylammonium perchlorate (TBAP) as supporting electrolyte. Solutions were degassed with dry nitrogen before each experiment, and a nitrogen atmosphere was maintained over the solution during all electrochemical experiments.

A sweep rate of 200 mV/sec was generally used for cyclic voltammetry. Sweep rates between 10 mV/sec to 500 mV/sec were examined but no significant differences were observed.

The in situ electrochemical ESR experiments were carried out in a Wilmad Glass Company ESR-electrochemical cell equipped with a platinum working electrode. A Varian E-4 spectrometer was used. A spectrum could generally be obtained within 60 sec of initiating the controlled potential electrolysis at —0.80 V vs. SCE.

Chemicals

Fisher Reagent Grade dichloromethane was distilled from P_2O_5. TBAP was used as obtained from G.F. Smith Chemical Company. The cobalt clusters were used as obtained from Professor D. Seyferth and Miss C.L. Nivert of the Chemistry Department, Massachusetts Institute of Technology.

Results

Twelve cobalt clusters of the type $XCCo_3(CO)_9$ were examined by cyclic voltammetry at a hanging mercury drop or platinum bead electrode. Figure 1 illustrates a typical cyclic voltammogram. The characteristic reduction pattern using either electrode was a reversible, one-electron reduction in the range of —0.7 to —0.9 V vs. SCE followed by an irreversible, multi-electron reduction at about —1.5 to —1.8 V. Cathodic and anodic peak potentials for the reversible process at a hanging mercury drop electrode are shown in Table 1. Peak potentials obtained using a platinum electrode differed very little from those at the mercury electrode. Oxidation of the clusters at a platinum electrode occurred around +1.5 V and was completely irreversible. This oxidation led to a product which was reducible at about —1.0 V, and this latter reduction was also irreversible and led to yet another species oxidizable at about +0.4 V, again irre-

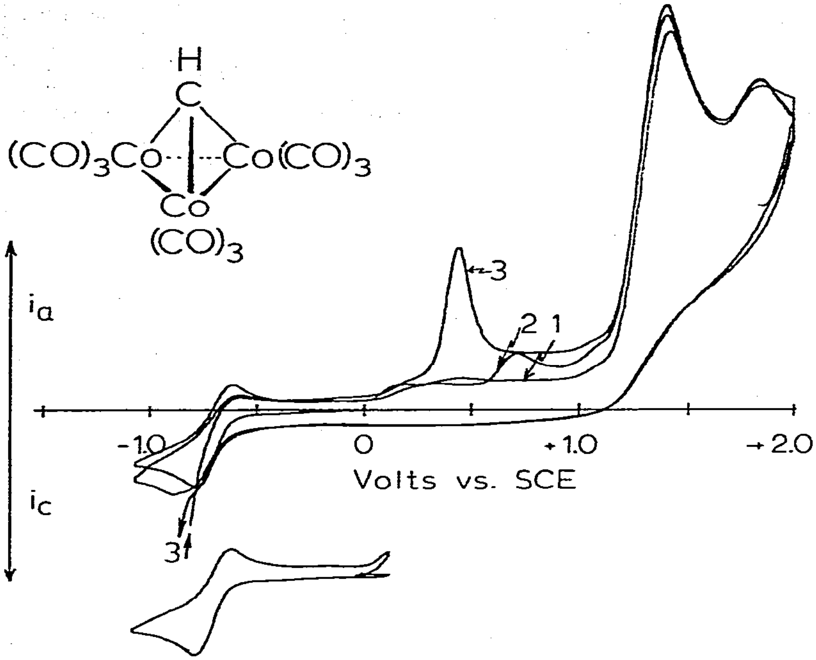

Fig. 1. Cyclic voltammogram of $HCCo_3(CO)_9$, 2 m*M* in CH_2Cl_2 with 0.2 *M* tetra-n-butylammonium perchlorate as supporting electrolyte. Sweep rate was 500 mV/sec. First sweep started at 0.0 V and proceeded in cathodic direction. Sweeps for the first three cycles are marked and a single sweep in the region ca. 0.0 to −1.0 V is at the lower left of the figure.

TABLE 1

CYCLIC VOLTAMMETRIC PEAK POTENTIALS FOR DERIVATIVES OF THE METHYLIDYNE-TRICOBALT NONACARBONYL CLUSTER

X in $XCCo_3(CO)_9$	$E_{\text{peak, cathodic}}$ (V vs. SCE)	$E_{\text{peak, anodic}}$ (V vs. SCE)
H	−0.80	−0.63
Cl [a]	−0.69	−0.52
Br [b]	−0.67	−0.53
I [b,c]	−0.68	−0.51
CH_2CH_3	−0.85	−0.78
$CH{=}CH_2$ [d]	−0.76	−0.68
C_6H_5 [d,e]	−0.79	−0.65
$C(OH)(H)CH_3$	−0.76	−0.64
$C(OH)(H)C_6H_5$	−0.77	−0.66
$C(OH)(CH_3)_2$	−0.78	−0.67
OCH_3	−0.79	−0.66
$C(O)SC(CH_3)_3$ [f]	−0.67	−0.52
$ClCCo_3(CO)_8(PPh_3)$	−0.86	no anodic wave

[a] ESR hyperfine splitting constant = 35.9 G. [b] Although an anodic wave was observed, the anodic current was considerably less than the cathodic current. [c] An attempt was made to observe the ESR spectrum of the reduced species; however, it decayed before the spectrum could be recorded. [d] ESR hyperfine constant = 35.3 G. [e] Based on the rate of decay of the ESR spectrum for the reduced species, its half-life is estimated to be about 30 min. [f] ESR hyperfine constant = 34.2 G.

versible. There was some electrode fouling when using the platinum electrode in either oxidation or reduction.

Controlled potential coulometry at —0.8 V was done for three of the complexes. Reduction of $(H_3C)_3CS(O)CCCo_3(CO)_9$ consumed 1.07 electrons, and the reduced species gave up 0.62 electrons on re-oxidation. The clusters with X = H or Cl consumed 1.6 to 2 electrons upon reduction and could not be reoxidized. Thus, for those clusters where X = H or Cl, reduction by one electron leads to slow decomposition (that is, slower than the time required for the cyclic voltammetry experiment) to give yet another species reducible by 1 electron at —0.8 V.

Controlled potential coulometry at +1.5 V indicated that at least 3 electrons were generally given up by the cobalt clusters, and the resulting product could not be re-reduced.

The ESR spectra of the reduced clusters showed at least 16 lines for each of the complexes examined, and the hyperfine structure and coupling constants changed very little with substituent (see Table 1).

Discussion

In general, all of the compounds investigated undergo a one-electron reduction in the relatively narrow range of potentials, —0.7 to —0.9 V, with the extent of reversibility being somewhat substituent dependent. Clusters having more electronegative substituents are reduced around —0.7 V while substituents normally thought to be electron-donating cause reduction to occur at somewhat more negative potentials (ca. —0.9 V). This range of about 0.2 V is almost identical to that observed for the oxidation of ferrocene with the same substituents [3]. Thus, these substituents have about the same effect on the LUMO of the cobalt cluster as they have on the HOMO of ferrocene.

The ESR spectra of the reduced cobalt clusters are interesting in light of the discussion above. At least 16 of the 22 lines theoretically possible for electron spin coupling with three equivalent cobalt nuclei were observed for each of the complexes examined. The hyperfine structure and coupling constant changed very little with substituent suggesting that the LUMO encompasses three equivalent cobalt atoms of the cluster and that little if any spin density "leaks out" of the cage onto the substituent. This is not an unexpected result for two reasons: (*i*) The methylidynetricobalt non-carbonyl cluster has been found to be strongly electron withdrawing [5]. (*ii*) It is reasonable that the LUMO is closer in energy to the cobalt atoms than the more electronegative carbon atom.

The reduction of $ClCCo_3(CO)_8(PPh_3)$, where a basal CO has been replaced by a phosphine, occurred at a more negative potential than reduction of the twelve substituted methylidynetricobalt nonacarbonyl clusters. In addition, this was the only compound whose reduction was totally irreversible with no anodic current observed even at a sweep rate of 500 mV/sec. Replacement of a basal CO by the poor acceptor ligand Ph_3P apparently reduces severely the ability of the cluster to accommodate a negative charge. Although some decrease in i_{anodic} relative to i_{cathodic} was observed for the nonacarbonyl clusters when the substituent on carbon was changed from Cl to Br to I, replacement of a substituent on carbon had a much less pronounced effect on electrochemical reversibility than did replacement of a substituent on cobalt.

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