

Electrochemistry of Transition Metal π -Complexes. IV*. Oxidation of Cyclopentadienyl Diolefine and Cyclobutadiene Cobalt Complexes

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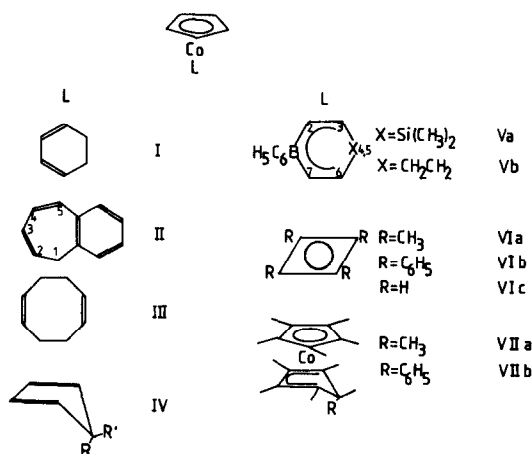
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Electrochemical oxidation of cobalt sandwich complexes CoCpL , where Cp is η^5 -cyclopentadienyl and L an η^4 -diolefine or cyclobutadiene ligand, was investigated by means of cyclic voltammetry and polarography. Oxidation is reversible or nearly so for compounds where L is a cyclic diolefine (I–III) or a cyclobutadiene (VI) and for the methylated complexes $\text{Co}(\text{C}_5\text{Me}_5)(\text{C}_5\text{Me}_5\text{R})$ ($\text{R} = \text{Me}, \text{Ph}$) (VII) and irreversible for $\text{CoCp}(\text{C}_5\text{H}_5\text{Ph})$ (IV) and the complexes V where L is a divinylborane.

Introduction

Cobalt sandwich complexes of the type CoCpL (diolefine) are isoelectronic with ferrocene, whose oxidation has been the most widely studied case in the electrochemistry of transition metal sandwich complexes. In contrast the cobalt analogues have received almost no attention, and so far no cobalt sandwich complex with less than 18 electrons in its valence shell has been reported. A study aimed at the oxidative transformation of (cyclopentadiene)cyclopentadienylcobalt derivatives IV to cobalticenium salts [2] is the only case for which electrochemical oxidation has been investigated.

Our present experiments constitute an effort to assess the stability of the '17-electron' cobalt cations CoCpL^+ and to study their modes of degradation under nucleophilic and non-nucleophilic conditions. A further point of interest is the variations of the redox potential with different η^4 -ligands. The scope of ligands used comprises conjugated and unconjugated cyclic diolefines (I–III), divinylboranes (V) and substituted cyclobutadienes (VI). Cyclopentadienyl(5-*exo*-phenylcyclopentadiene)cobalt, IV, is contrasted to two methylated analogues (VII).



Experimental

Materials

Complexes I[3], III[4], IV[5] and VIb[6] were prepared according to literature procedures and checked for purity by means of $^1\text{H-NMR}$, melting points and tlc. The divinylborane complex Va was previously reported by this laboratory [7]. Its analogue Vb was obtained by a similar complexation (see below). The tetramethylcyclobutadiene derivative VIa was prepared by a modification of the reaction described by Bruce and Maitlis [8] which raises the yield in the final step to 80% and greatly simplifies the workup procedure. The methylated complexes VIIa, b are the products of oxidative addition of CH_3I and $\text{C}_6\text{H}_5\text{I}$ respectively to decamethylcobaltocene [9].

(η^4 -1H-benzo[b]cycloheptane)cyclopentadienylcobalt (III)

A mixture of 1H-benzo[b]cycloheptane (1 g, 7 mmol) and $\text{CoCp}(\text{CO})_2$ (1.3 g, 7.5 mmol) in 300 ml of ether was irradiated for 10 h with a medium pressure mercury lamp (150 W). After evaporation of the solvent the residual oil was chromatographed over

*See ref. 1 for previous communications.

alumina. After unreacted $\text{CoCp}(\text{CO})_2$, complex III was eluted with pentane/ether (100:5) and recrystallized twice from pentane. The yield was 370 mg (20%) dark red crystals of mp. 36–7 °C. *Anal.* Found (calcd.): C, 72.05(72.18); H, 5.65(5.68); Co, 22.34(22.13)%. $^1\text{H-NMR}$ ($[\text{D}_6]$ -benzene, int. TMS, δ): 7.5, m, 4 H, H-6–H-9; 4.77, m, 2 H, H-3, H-4; 4.42, s, 5 H, Cp; 3.55, d, 1 H, H-5; 3.10, m, 1 H, H-2; 2.74, dd, 1 H, H-1_{endo}; $J_{\text{H-1endo}, \text{H-2}} = 7$ Hz; 1.72, d, 1 H, H-1_{exo}, $J_{\text{H-1endo}, \text{H-1exo}} = 18$ Hz.

Cyclopentadienyl(η^5 -1-phenyl-4,5-dihydro-1H-borepine)cobalt (Vb)

1-Phenyl-4,5-dihydro-1H-borepine [7] (2 g, 12 mmol) and $\text{CoCp}(\text{CO})_2$ (2.1 g, 12.2 mmol) dissolved in 400 ml ether was irradiated for 8 h during which time 540 ml CO was evolved. After evaporation of the solvent, the residual oil was chromatographed over alumina as described above for III. The red-brown oil, which remained after evaporation of the second zone, solidified after prolonged standing in a freezer at –30 °C, leaving 2.2 g (63%) of Vb as a red solid with mp. 27 °C. *Anal.* Found (calcd.): C, 69.78(69.90); H, 6.06(6.21)%. $^1\text{H-NMR}$ (CDCl_3 , int. TMS, δ): 8.09 and 7.42, m, 2 H and 3 H, H-arom.; 4.72, s, 5 H, Cp; 4.73, d, 2 H, H-3,6; 4.29, d, 2 H, H-2,7, $J_{\text{H-2}, \text{H-3}} = J_{\text{H-6}, \text{H-7}} = 10$ Hz; 2.2, m, 2 H, H-4,5_{endo}; 1.25, m, 2 H, H-4,5_{exo}.

Cyclopentadienyl(tetramethylcyclobutadiene)cobalt (VIa)

$\text{Co}(\text{C}_4(\text{CH}_3)_4)(\text{CO})_2\text{I}$ [8] (1.5 g, 5.15 mmol) and TiCp (1.5 g, 5.5 mmol) were stirred in 20 ml THF at 60 °C for 6 h. Progress of the reaction was followed by tlc, where the disappearance of the starting carbonyl is readily monitored. After all of the cobalt

carbonyl had reacted, stirring and heating was continued for one additional hour, the mixture was then evaporated to dryness and the residue extracted with three 20 ml portions of pentane. The combined pentane extracts were chromatographed over alumina (4% H_2O) with pentane as the eluent, collecting the first faint yellow band. (No $\text{CoCp}(\text{CO})_2$ was formed under these conditions). Concentration of the pentane eluate to a small volume and crystallization at –80 °C gave 0.95 g (79%) of VIa as orange crystals of mp. 57 °C (lit. 57 °C [8]).

Electrochemical Measurements

Equipment as previously described [10] was used for cyclic voltammetry at Pt and polarography at the dropping mercury electrode (DME). Tetrabutylammonium-hexafluorophosphate was used as supporting electrolyte throughout this study. The concentration of the complexes in dichloromethane was in the range 10^{-4} – 10^{-3} M. Potentials refer to the saturated calomel electrode (SCE), connected to the solution through a luggin capillary and a fritted disc. Positive feedback was applied as appropriate to compensate for ohmic drop in the reference circuit. A storage oscilloscope (Philips PM 3234) was used for monitoring rapid scans.

Low temperature electrolysis was performed in a standard double walled electrolytic cell (Metrohm EA 876) with an inserted electrolysis assembly (Metrohm EA 272).

Cyclic voltammograms were recorded on dichloromethane solutions of each complex using different sweep rates and potential windows. Subsequently 0.1–2% acetonitrile or tetrahydrofuran (THF) was added to the solution and changes in the voltammetric curves noted. Polarography at the DME was

TABLE I. Electrochemical Parameters for the Oxidation of CoCp - and $\text{Co}(\text{C}_5(\text{CH}_3)_5)$ -diolefine and cyclobutadiene Complexes in Dichloromethane.

Complex	$\bar{E}^a$ (V)	E_p^b (mV)	i_p^a/i_p^c	$E_p^{a,c}$	$E_{1/2}^d$	n^e
I	0.32	80	0.71 at $v = 100^f$ 0.94 at $v = 200$	1.15	0.23	0.8
II	0.21	70	0.94	0.9		
III	0.26	90	1.1	1.35	0.24	1.07
IV	0.35 (E_p^a)		irreversible			
Va	0.84 (E_p^a)		irreversible			
Vb	0.82 (E_p^a)		irreversible			
VIa	0.51	75	0.92	1.1	0.58	0.86
VIb	0.91	70	0.97	1.55		
VIIa	–0.21	70	1.05	1.0	–0.16	0.62
VIIb	–0.07	120	1.07			

^aMean value ($E_p^a + E_p^c$)/2 of cyclovoltammetry in V vs. SCE. ^b $E_p^a - E_p^c$. ^cAnodic peak potential of the second, irreversible oxidation. ^dHalf wave potential of polarography at the DME. ^eApparent electronicity ($\alpha \cdot n$) from logarithmic plots of the polarograms. ^fSweep rate in mV/s.

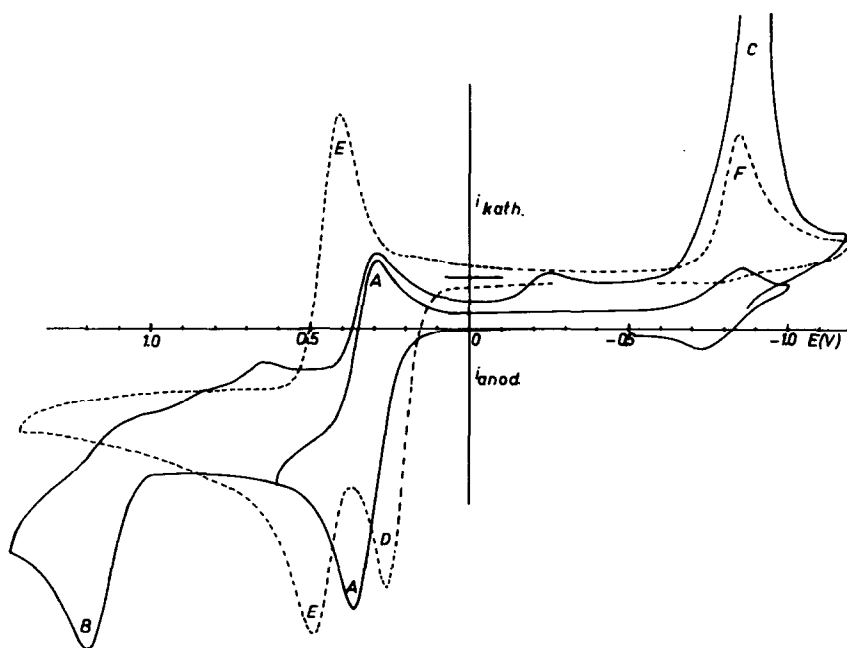


Fig. 1. Cyclovoltammogram of (cyclohexadiene)cyclopentadienylcobalt, I, in dichloromethane (—) and in dichloromethane with 1% acetonitrile (-----). Sweep rate 50 mV/s.

performed on dichloromethane solutions of I, III, VIa and VIIa in order to assess the electronicity of the first oxidation. Further details are given with the results.

Results

Oxidation in Dichloromethane

Electrochemical parameters for the oxidation of complexes I–VII in dichloromethane are collected in Table I. Representative examples of cyclovoltammetric curves are depicted in Figs. 1–3. Complexes II and III show an oxidation peak, reversible as evidenced by the peak current ratios and with loss of one electron as suggested by the apparent n values extracted from logarithmic plots of the polarographic curves. The peak current ratio for the oxidation of I at slower sweep rates deviates from unity, indicating a lower stability for I^+ as compared to II^+ or III^+ . Anodic to the first oxidation (peak A in Fig. 1) a second, irreversible peak (B) was observed for I–III, VIa, b and VIIa (Table I). An ensuing cathodic sweep then gives rise to a new, irreversible peak (C) with an intensity markedly dependent on the duration of the anodic sweep (C grew to many times the intensity of A or B when the potential was held for a length of time anodic of B). Peak C was observed at about the same potential ($E_p^c = -0.95$ V) for all CoCp-complexes irrespective of the olefinic counterligand. Its characteristic shape and the observation that it only slowly decreased if, after sweeping through B, the

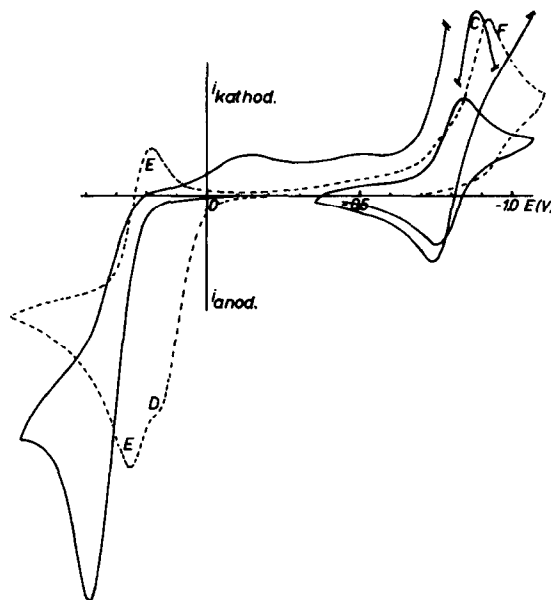


Fig. 2. Cyclovoltammogram of cyclopentadienyl(5-*exo*-phenylcyclopentadiene)cobalt, IV, in dichloromethane (—) and in dichloromethane with 2% acetonitrile (-----). Sweep rate 100 mV/s.

potential was held somewhere between A and C, indicates a nondiffusive behaviour and strongly points towards an adsorbed species, most likely a $CoCp^{2+}$ -fragment. Note also the reversible pair of low intensity at $E = -0.8$ V, present after sweeping through A in the case of I and also concealed under C in the other diolefin complexes.

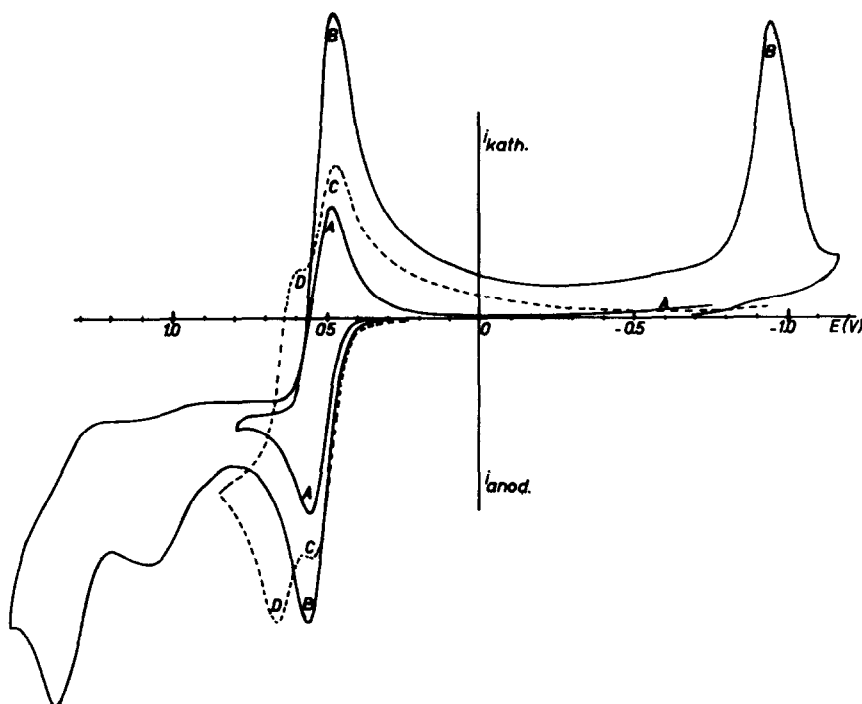


Fig. 3. Cyclovoltammogram of cyclopentadienyl(tetramethylcyclobutadiene)cobalt, VIa, in dichloromethane (—) and in dichloromethane with 2% acetonitrile (-----). Sweep rate 50 mV/s.

In contrast to the foregoing, oxidation of IV proceeded irreversibly* up to sweep rates ≥ 10 V/s (Fig. 2). No second oxidation was observed at more anodic potential and again a reversible pair, along with a peak C, was revealed upon a subsequent cathodic sweep. Likewise oxidation of the divinylborane complexes Va, b was found to be irreversible. Even though only peak potentials can be read from the cyclovoltammograms a marked anodic shift of the order 0.5 V is obvious.

Reversible oxidation occurred for both the cyclobutadiene complexes VIa, b with the potentials again shifted anodic with respect to the simple diolefinic complexes.

The chemical stability of VIa⁺ was further explored in a bulk electrolysis experiment. After an oxidation/reduction cycle of a dichloromethane solution at -10 – -20 °C part of the starting complex was recovered. New peaks in the cyclovoltammogram after reduction (at ± 0 V) indicated the formation of the cobalticenium cation, VIII⁺, and an additional yet unidentified species. Similarly oxidation of VIa with Ag⁺ in dichloromethane yielded VIII⁺ as identified by its ¹H NMR absorption.

Reversible oxidation of the highly methylated cyclopentadienyl(cyclopentadiene)complexes VII

was found at more cathodic potential values, where in particular VIIa⁺ shows a high degree of stability. In this case even the second oxidation appears to be in part chemically reversible.

Oxidation in the Presence of Polar Solvents

Addition of acetonitrile, THF or other polar solvents (0.1–2%) makes most of the foregoing oxidations irreversible. With acetonitrile as the polar medium a particularly clear and conclusive pattern emerged: the oxidation now proceeded in two steps, the first being irreversible and the second exhibiting a reversible pair, whose potential $\bar{E}$ was somewhat dependent on the amount of acetonitrile added, but independent of the olefinic ligand (peaks D and E in Figs. 1 and 2). A diffusive peak (F) was seen upon the subsequent cathodic sweep, whereas peak C was now lacking. It is noteworthy that a similar pattern is also found for IV in the presence of acetonitrile (Fig. 2), whose oxidation in neat dichloromethane was completely irreversible.

Somewhat different behaviour was exhibited by the tetramethylcyclobutadiene complex VIa, where two reversible peaks (C and D) occurred in the anodic region, both of them anodic to the pair E of I–IV and no electroactive species was detected upon the ensuing cathodic sweep (Fig. 3).

The electrochemistry of VIIa remained unaffected by the addition of acetonitrile.

*Chemical irreversibility, that is a rapid follow up chemical reaction subsequent to electron transfer, is designated by the term throughout this discussion.

Discussion

Oxidation Potentials and Stability of the Cations in Dichloromethane

Complexes I–IV with simple conjugated or unconjugated olefinic ligands undergo oxidation in dichloromethane between 0.21 and 0.32 V vs. SCE to give the corresponding monocations. Further oxidation leads to degradation with the characteristic peak C indicative of CoCp^{2+} adsorbed on a Pt surface, which is reduced irreversibly at about -0.95 V. Formation of the cobalticenium cation, VIII^+ , appears as a minor side reaction in this process, as is apparent from the small reversible pair at $\bar{E} = -0.85$ V and can be confirmed by addition of VIII^+ to the solution (note that the $\text{VIII}^{+/0}$ -potential in dichloromethane vs. SCE is more positive than the values reported for more polar solvents, e.g. acetonitrile [11, 12]). An alternative path of degradation would be the deprotonation of the primary cation to form, with concomitant oxidation at the applied electrode potential, in the case of I a cyclohexadienyl(cyclopentadienyl)cobalt cation. Though the latter is reduced at a potential similar to that of VIII^+ [10a] its reduction proceeds irreversibly at slow scan rates and therefore this route is ruled out on the basis of the obvious reversible redox behaviour of the pair in question. Similar argumentation will hold for II and III.

The irreversibility of the oxidation of IV calls for an explanation in terms of a different pathway for the degradation of IV^+ . El Murr and co-workers [2] reported rapid deprotonation of *endo* substituted (cyclopentadiene)cyclopentadienylcobalt derivatives (e.g. IV, $\text{R} = \text{H}$, $\text{R}' = \text{COOR}$) in polar protic media at high pH with formation of the corresponding cobalticenium salts, whereas decomposition was observed on oxidation of the derivative having an *exo* methyl group (IV, $\text{R} = \text{CH}_3$, $\text{R}' = \text{H}$). Nevertheless, deprotonation from the *endo* site to give phenylcobaltocene may occur from IV^+ in a noncoordinating solvent. Assessment of this possibility was achieved in an experiment where IV was oxidized with AgOCCF_3 in dichloromethane. After phase separation dichloromethane/water and precipitation of the cations as hexafluorophosphates, ^1H NMR analysis of the yellow salt mixture indicated VIII^+ and phenylcobalticenium cation in a 1:2 ratio, thus establishing the deprotonation of IV^+ as the major pathway for its degradation. Accordingly the reversible pair at $\bar{E} = -0.8$ V, occurring subsequent to the oxidation of IV and exhibiting a potential slightly more anodic than in the foregoing cases, is much more pronounced than the one observed with I–III.

Most noticeable with the oxidation of the divinylborane complexes V is the strong anodic shift of their (+/o)-potentials as compared to the analogous olefinic compounds. A similar effect, then termed 'borinato shift', was noted by us [10] when first studying the

electrochemistry of borinato complexes, and it is comparable in magnitude to the one observed here. It thus appears to be quite general and one may expect an anodic 'borylene shift' wherever an RB-moiety is 'inserted' into a conjugated double bond system. It originates in the lower electronegativity, and the availability of an empty p_z -orbital of the boron atom amenable to metal back bonding (*cf.* structural results on divinylborane complexes in ref. [7]), making ligands with a borylene group weaker donors and stronger acceptors than their boron free analogues.

Concomitant with the more anodic oxidation is an enhanced electrophilicity of the ensuing cations, which renders all of the oxidations of the cyclopentadienyl(divinylborane)cobalt complexes irreversible. Similar observations were made on borinato-iron compounds [10b].

The enhanced stability towards oxidation when changing a polyolefinic to an aromatic ligand with equal number of complexing sites as is the case when comparing I–III with VIa, b is not without precedence. Pertinent examples are provided by the (+/o)-potentials of $\text{Cr}(\text{CO})_3\text{C}_6\text{H}_6$ (0.72 V) and $\text{Cr}(\text{CO})_3\text{C}_7\text{H}_8$ (0.67 V) [13] or FeCp_2 (0.49 V) and $\text{Fe}(\text{C}_7\text{H}_9)_2$ (0.21 V) [14] (values in dichloromethane vs. SCE). Recent SCF-MO calculations by Clack and Warren [15] on the parent complex, (cyclobutadiene)cyclopentadienylcobalt, VIc, indicate a set of three mainly metal based MO's of a_1 -, b_1 - and b_2 -symmetry as the highest occupied molecular levels. The MO scheme of VIc is reminiscent of that of ferrocene, IX, the two b -type levels of VIc being equivalent to the e_{2g} -orbital of IX and obviously the four methyl groups at the cyclobutadiene ring lower the (+/o)-potential in VIa to a value nearly coincident with that of IX.

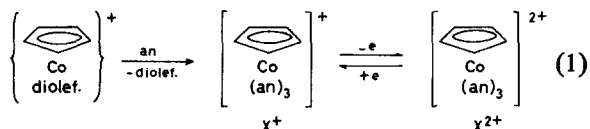
Estimating the potential for the oxidation of VIc as 0.7 V, *i.e.* halfway between VIa and IVb, and applying the linear relationship observed between electrochemical redox potentials and the first ionization energies from PE-spectroscopy for transition metal sandwich complexes [14], an ionization potential of 7.05 eV is calculated for VIc, in fair agreement with the value of 7.84 eV given by the MO calculations.

Complex VIa⁺ nevertheless appears to be of appreciably lower stability than IX⁺ as shown by the bulk oxidation of VIa in dichloromethane at low temperature. This may be accounted for by the fact that, in the cobalt complex as compared to ferrocene, an electron donating Cp-ligand has been replaced by a cyclobutadiene ring with predominantly acceptor properties. Moreover, whereas in IX, and likewise in other metallocenes, bonding of the Cp-ligand is effected by lowering all of the ligand- π -combinations [16], there appears an e -type cyclobutadiene orbital not too far below the above mentioned metal type set in VI. Accordingly loss of a cyclobutadiene ring

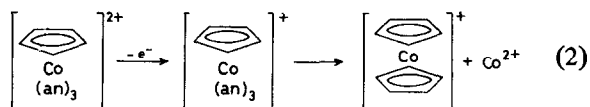
from VIa^+ to yield ultimately VIII^+ is seen to be the principal mode of degradation of this cation.

Oxidation in the Presence of Acetonitrile

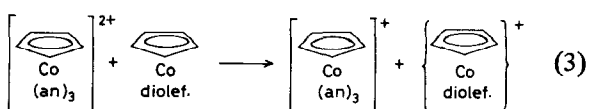
Formation of the reversible pair E in the cyclovoltammograms of I–IV in the presence of acetonitrile (Figs. 1, 2) suggests a reaction pathway common to all diolefine complexes. Substitution of the olefine in the monocations by acetonitrile to yield a cationic cobalt halfsandwich complex X^+ and reversible oxidation/reduction $\text{X}^{+/2+}$ as outlined in eqn. 1 fits best with the observed data.



We have recently prepared [tris(acetonitrile)]cyclopentadienylcobalt-diperchlorate, $\text{X}(\text{ClO}_4)_2$ [17], and found it to undergo reversible reduction in acetonitrile at a potential corresponding to peak E. Although X^+ is stable on the electrochemical time scale it disproportionates to VIII^+ and Co^{2+} on bulk reduction (eqn. 2). The peak F, observed in the cyclovoltammograms of I–IV in the presence of aceto-



nitrile, was also present in the electrochemistry of X^{2+} and indicates the irreversible reduction of X^+ (polarography of X^{2+} was hampered by the fact, that the cation is reduced by elemental mercury in acetonitrile). Bulk oxidation of the diolefine complexes I and IV with AgClO_4 in acetonitrile led to the isolation of only VIII^+ and Co^{2+} along with the free olefinic ligands. Thus cyclohexadiene was extracted with pentane from the acetonitrile reaction mixture after oxidation of I and was identified by means of gc. Likewise was phenylcyclopentadiene isolated as a mixture of Diels-Alderdimers from the oxidation of IV and identified through its ^1H NMR and mass-spectrum. These findings, which contrast to the electrochemical behaviour, are due to the electron transfer outlined in eqn. 3. Two complexes are formed, which have the metal in the formal oxidation state +2 and therefore undergo further transformations according to eqns. 1 and 2 to yield the observed reaction products.



The oxidation pattern of VIa in the presence of acetonitrile (Fig. 3) appears significantly different from the foregoing complexes, in that two reversible steps are now obvious (peaks C and D in Fig. 3), the second at distinctly more anodic potential than the peak E in the above examples and a peak corresponding to F is now absent. It appears thus, that acetonitrile complexes to the monocation VIa^+ to form pseudooctahedral $\text{CoCp}(\text{C}_4(\text{CH}_3)_4)(\text{CH}_3\text{CN})^+$, which in turn is oxidized to a dication at slightly more positive potential. The molybdenum complex $\text{MoCp}(\text{C}_4(\text{CF}_3)_4)(\text{S}_2\text{CN}(\text{CH}_3)_2)$ [18] is cited as an example having a ligand arrangement analogous to that proposed for this cobalt cation. The observation of a two step reversible oxidation of VIa in the presence of acetonitrile further stresses the enhanced stability of cationic cobalt sandwich complexes with a cyclobutadiene compared to a diolefine ligand.

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