[Cp$_2$ZrX$_2$(PR$_3$)]$^{-}\cdot$ becomes rather unreasonable; added to this is the fact that such a structure formally implies a 19-electron configuration and a highly crowded metal environment. We therefore formulate them as the monohalide compounds Cp$_2$ZrX(PR$_3$) formed by halogen cleavage following electron addition on the starting dihalides. This structural assignment is further supported by the irreversible character of the cathodic waves which appear in the cyclic voltammetry upon addition of phosphines and the appearance of electroactive species in the anodic region. However, our data with PMePh$_2$ do not agree with earlier reports[20] on compounds obtained by the reactions of alkyl halides with Cp$_2$Zr(PMePh$_2$)$_2$ in pure phosphine and identified by ESR as Cp$_2$ZrX(PMePh$_2$) (X = Cl, Br). The reported spectral parameters do not exhibit any significant halogen dependence (a(P) = 21 G for X = Cl and Br; A(Zr) = 17 G for X = Cl and, surprisingly g = 1.998 for X = Cl, very close to g = 1.995 for X = Br) as is the case with our compounds.

Finally, it may be argued that the species arising from the electrolytic reduction of Cp$_2$ZrMe$_2$ could be due to either metal radicals arising from reaction 2 or 4. ESR signals of the same pattern were obtained with a series of compounds (Cp$_2$MR$_2$) (M = Ti, Zr; R = CH$_2$Ph, CHPh$_2$, CH$_2$SiMe$_3$) by chemical and electrochemical methods for which both types of radicals were postulated.[12,33] On the other hand, electrochemical oxidation of Cp$_2$W(CH$_3$)$_2$ was reported to yield the cation [Cp$_2$W(CH$_3$)$_2$]$^+$ identified by ESR.[34] We believe that the radical anion structure (Cp$_2$ZrMe$_2$)$^{-}\cdot$ is more likely for our electrochemically reduced compound than the highly electron-deficient CpZrMe$_2$ formulation.

Electrolytic reduction of hafnocene compounds along the same lines as above did not generate signals attributable to hafnium(III) paramagnetic species, and the only signals observed were those due to reduction of the accompanying zirconium analogues usually present.

Acknowledgment. We are grateful to Dr. Gourier for computer simulation and discussions on ESR and to Mrs. Hênique for efficient technical assistance.

Registry No. [Cp$_2$ZrCl$_2$]$^{-}\cdot$, 75699-43-3; [Cp$_2$ZrBr$_2$]$^{-}\cdot$, 95765-30-3; Cp$_2$ZrI, 95765-31-4; CpZrCl$_2$, 80042-49-5; [Cp$_2$ZrMe$_2$]$^{-}\cdot$, 95765-32-5; [Cp$_2$ZrCl(PMe$_3$)], 95765-33-6; [Cp$_2$ZrCl(PMePh$_2$)], 80642-23-5; [Cp$_2$ZrBr(PMe$_3$)], 95765-34-7; [Cp$_2$ZrBr(PMePh$_2$)], 80642-24-6; Cp$_2$ZrCl$_2$, 1291-32-3; Cp$_2$ZrBr$_2$, 1294-67-3; Cp$_2$ZrF$_2$, 11090-85-0; Cp$_2$ZrI$_2$, 1298-41-5; Cp$_2$ZrMe$_2$, 12636-72-5; Cp$_2$ZrCl, 86665-14-7; ZrCl$_3$, 10241-03-9; PMe$_3$, 594-09-2; PMePh$_2$, 1486-28-8.

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Paramagnetic Organometallic Molecules. 18.[1] Redox Chemistry of the Flyover Complexes $R_6C_6Co_2(CO)_4$

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The redox chemistry of a series of "flyover" complexes R$_6$C$_6$Co$_2$(CO)$_4$ has been investigated by electrochemical and ESR techniques in a variety of solvents. The compounds all undergo reversible one-electron reduction to a radical anion, the stability of which is dependent on the solvent system. In acetone or dichloromethane, the radical anion (CF$_3$)$_6$C$_6$Co$_2$(CO)$_4$$^{-}\cdot$ decomposes by ring closure of the flyover bridge to give hexakis(trifluoromethyl)benzene, (CF$_3$)$_6$C$_6$, via the radical anion (CF$_3$)$_6$C$_6$$^{-}\cdot$. In contrast the radical anion (CF$_3$)$_6$C$_6$Co$_2$(CO)$_4$$^{-}\cdot$ shows exceptional stability in THF solvent. A second reduction step producing an inherently unstable dianion is also observed in all solvents. Unusual scan rate dependence of this second step under conditions of cyclic voltammetry may be consistent with a homogeneous electron-transfer reaction between the dianion and the neutral "flyover" complex. In acetonitrile, rapid electron-transfer-catalyzed substitution of the radical anions leads to the formation of acetonitrile complexes. The ESR spectra of electrolytically generated radical anions of several of the flyover complexes were observed in THF solutions. The isotropic spectra show coupling to two equivalent cobalt nuclei. Isotropic ESR spectra of (CF$_3$)$_6$C$_6$Co$_2$(CO)$_4$$^{-}\cdot$ in acetone solution again showed coupling to two equivalent cobalt nuclei, but slow decomposition of the radical anion of the flyover complex led to the observation of the radical anion (CF$_3$)$_6$C$_6$$^{-}\cdot$.

Introduction

Complexes of the general formula (alkyne)$_3$Co$_2$(CO)$_4$ in which three acetylenic moieties oligomerize in a "head to tail" fashion to form a "flyover" bridge to the cobalt–cobalt bond are well-characterized,[3] and structural information has been reported for three of them.[4–6] Our interest in the redox chemistry of capped tricobalt[7] and dicobalt[8,9]

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Table I. Electrochemical Data for 1, 4, and 5 in Various Solvents

		dc polarography Hg electrode[a]		dc cyclic voltammetry platinum electrode			
solvent	complex	$E_{1/2}$, V	$E_{1/4} - E_{3/4}$, mV	scan rate, mV s^{-1}	E_p^{red}, V	E_p^{ox}, V	i_p^{red}/i_p^{ox}
acetone	1	0.035 (–0.96)[b]	53 (110)	500	–0.13 (–1.17)	0.10	1.0
				200	–0.09 (–1.13)	0.09	1.0
				50	–0.05 (–1.09)	0.07	1.0
	4	–0.48 (–1.23)	55 (120)	500	–0.58 (–1.53)	–0.37	1.0
				200	–0.54 (–1.43)	–0.40	1.0
				50	–0.52 (–1.41)	–0.41	1.0
	5	–1.46 (–1.69)	57	500	–1.52	–1.40	0.8
CH_2Cl_2	1	0.04 (–0.94)	58 (60)	500	–0.21 (–1.18)	–0.01	1.0
				200	–0.20 (–1.15)	–0.04	1.0
				100	–0.18 (–1.12)	–0.06	1.0
	4	–0.61 (–0.86) (–1.24)	55 (70) (100)	500	–0.78 (–1.58)	–0.51	1.0
				200	–0.74 (–1.58)	–0.53	1.0
				50	–0.70 (–1.58)	–0.56	1.0
THF	1	0.03 (–1.07)	58 (60)	500	–0.17 (–1.35)	0.25	1.0
				200	–0.12 (–1.27)	0.19	1.0
				50	–0.06 (–1.17)	0.13	1.0
THF	4	–0.51 (–1.05) (–1.45) (–1.79)	75 (80) (70) (80)	500	–0.77 (–1.73) (–2.21)	–0.21	1.0
				200	–0.73 (–1.67) (–2.13)	–0.28	1.0
				50	–0.66 (–1.61) (–1.99)	–0.39	1.0
MeCN	1	0.03 (–0.40)[d] (–0.79)	55 (60) (70)	500	–0.02 (–0.46)[d] (–1.12)	0.06	1.0[c]
				200	0.00 (–0.42)[d] (–1.06)	0.06	1.0[c]
				50	0.01 (–0.39)[d] (–1.02)	0.03	1.0[c]
MeCN	4	–0.49 (–1.14)	(60) (120)	500	–0.50 (–1.42)	–0.40	1.0
				200	–0.50 (–1.40)	–0.40	1.0
				50	–0.48 (–1.34)	–0.40	1.0

[a] Drop time = 0.5 s. [b] Figures in parentheses are for electrode processes other than the primary (one-electron reduction) process. [c] Recorded on freshly prepared solutions. [d] This wave grew in intensity with repeated scans and was subsequently found to be due to the reduction of $(CF_3)_6C_6Co_2(CO)_3(NCMe)$.[17]

systems led to a preliminary investigation of the redox behavior of the flyover complex $(CF_3)_6C_6Co_2(CO)_4$[10] which showed a facile one-electron reduction step leading to the formation of a remarkably stable radical anion $(CF_3)_6C_6Co_2(CO)_4^{-}\cdot$. Examination of the paramagnetic species derived from metal cluster systems has shown that the unpaired electron enters a metal-centered LUMO with striking consequences on the strength of the metal–metal bond and subsequent reactivity of the reduced species.[9,11] The ease of production of radical anions from the flyover system coupled with the potential involvement of the parent molecules in the catalytic oligomerization of alkynes[12] prompted us to examine their redox properties more closely. This paper reports detailed electrochemical and ESR studies on the flyover complexes in acetone, dichloromethane, tetrahydrofuran (THF), and acetonitrile solvents.

Experimental Section

The compounds $(CF_3)_{6-n}H_nC_6Co_2(CO)_4$ [$n = 0, 1; n = 1, 2; n = 2, 3; n = 3, 4$] and $t\text{-}Bu_3H_3C_6Co_2(CO)_4$ (5) were prepared by literature methods.[13] Dichloromethane was washed three times with sodium hydroxide and then with distilled water and dried over $CaCl_2$; it was then distilled from CaH_2 and stored over molecular sieves. Acetonitrile was stored over CaH_2 for several days and then fractionally distilled from P_2O_5 under argon onto dry 3-Å molecular sieves. Other solvents were purified and dried by standard methods. A solution of benzophenone ketyl (BPK) was prepared and used as previously described.[11]

Conventional dc polarograms and cyclic voltammograms were recorded on Princeton Applied Research equipment.[7] The reference electrodes used were Ag/AgCl (either saturated LiCl, acetone, or saturated LiCl, CH_2Cl_2) isolated from the solution by Vycor tips, or a Ag/AgCl electrode using saturated LiCl in acetone separated from the solution by a salt bridge containing 0.1 M Et_4NClO_4 in acetone. The reference electrodes were calibrated with the known[7a,b] electrochemically and chemically reversible couple $[PhCCo_3(CO)_9]^{1-,0}$ under dc polarographic conditions in the appropriate solvent. The potential ($E_{1/2}$) of this couple is –0.38 V in acetone, –0.56 V in CH_2Cl_2, –0.36 V in THF, and –0.50 V in MeCN (all vs. Ag/AgCl). All solutions were approximately 10^{-3} M in electroactive species and 0.1 M in supporting electrolyte. Supporting electrolytes used were Et_4NClO_4 in acetone and acetonitrile and $n\text{-}Bu_4NClO_4$ in dichloromethane and tetrahydrofuran. Electrolysis experiments were carried out on a PAR Model 173 potentiostat/galvanostat fitted with a PAR Model 173 coulometer or a home-built potentiostat[14] with a three-electrode system giving a potential stability of 0.01 V in the current range 0–100 mA. A Pt basket was employed as the working electrode in each case with potentials measured against Ag/AgCl as described above.

ESR spectra were obtained either at Otago with a Varian E-4 spectrometer equipped with variable-temperature accessories as previously described[7a] or at Deakin with an X-band reflection type spectrometer employing 100-KHz modulation.[15] Radical anions were produced at Pt electrodes by electrolysis in situ in the ESR cavity, using the appropriate solvent with $n\text{-}Bu_4NClO_4$ or Et_4NClO_4 as the supporting electrolyte.

Results and Discussion

Electrochemistry of 1 in Acetone. Table I summarizes polarographic and voltammetric data in the various

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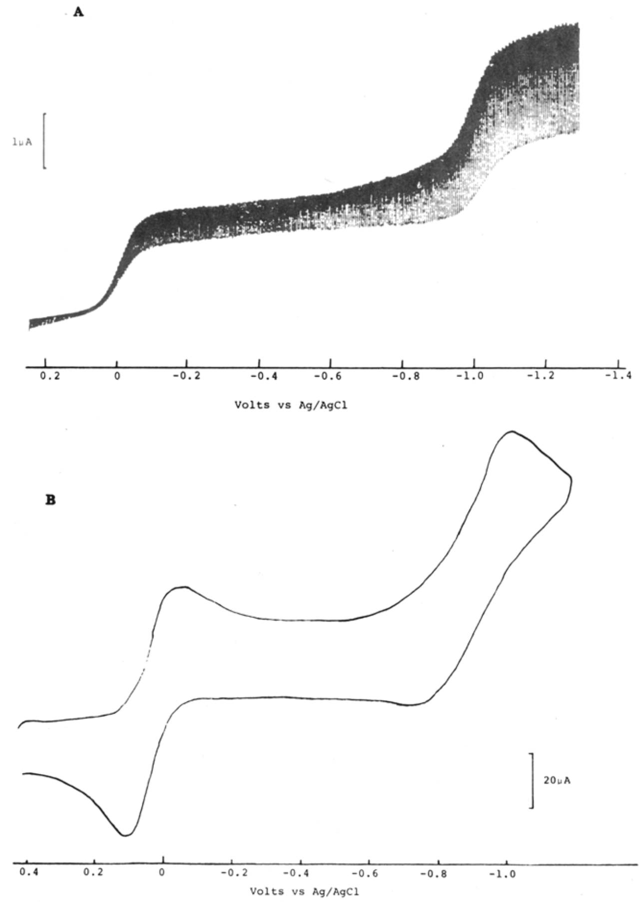
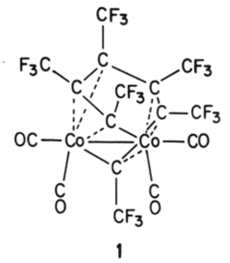


Figure 1. (a) dc polarogram of 1 × 10^{-3} M 1 in acetone [0.1 M Et_4NClO_4] at 293 K (drop time = 0.5 s). (b) Cyclic voltammogram on Pt: scan rate 500 mV s^{-1} of solution from a.



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solvents used in this investigation. Figure 1 shows the two well-defined reduction steps at $E_{1/2}$ = 0.035 and −0.96 V vs. Ag/AgCl for 1 in acetone at room temperature at both Pt and Hg electrodes. The first reduction wave at Hg electrodes under polarographic conditions at 298 K corresponds to an electrochemically and chemically reversible, one-electron process (E vs. log $(i/i_d - i)$ linear and slope −53 ± 2 mV). Cyclic voltammetric data shown in Table I shows this to be a quasi-reversible process at Pt electrodes, $i_p^{ox}/i_p^{red} = 1.0$). These data point to the formation of the flyover radical anion as the product of the primary electrode process (eq 1). The $E_{1/2}$ values at Hg may be

$$(CF_3)_6C_6Co_2(CO)_4 + e^- \leftrightarrow (CF_3)_6C_6Co_2(CO)_4^{-}\cdot \quad (1)$$

assumed to be equal to $E°$, and these are in excellent agreement with the values of $E°$ calculated from data at Pt. $E°$ data at platinum were calculated from digital simulation of cyclic voltammograms using an α value of 0.5 and equal diffusion coefficients (10^{-5} cm^2 s^{-1}) for the reduced and oxidized forms of the compound. Values agree to ±5 mV with $E°$ ($E_{1/2}$) from dc polarography. The electrode response of the second wave leads to an increase in current approximately commensurate with the addition of a second electron. Shape analysis indicates that the process is not a simple, one-electron, charge-transfer process. The process is chemically irreversible at most scan rates although at slow scan rates, perhaps unexpectedly, some degree of chemical reversibility is indicated (vide infra). At fast scan rates small oxidation peaks, clearly unrelated to the formation of a dianion, appear in the reverse scans of the voltammograms. Such peaks were not observed if the potential scan was switched just beyond the primary reduction wave suggesting that these oxidations derive from electroactive products of the decomposition of species produced in the second reduction step. Comparison with the behavior of other di-[7,11] and tricobalt[7] species points to the second electrode process involving the formation of a dianion (eq 2). Support for this assignment

$$(CF_3)_6C_6Co_2(CO)_4^{-}\cdot + e^- \leftrightarrow (CF_3)_6C_6Co_2(CO)_4^{2-} \rightarrow \text{products} \quad (2)$$

of the electrode processes comes from the observation that the electrochemical behavior of both electrode processes is unchanged in the presence of carbon monoxide. The fact that the second reduction step is unaffected by the presence of CO suggests that this process does not derive from the reduction of a fragmentation product of the radical anion. Similar lack of dependence on CO concentration has been observed in other systems in which the second reduction step involves dianion formation.[1,9] It is particularly significant that the separation between the first and second reduction potentials (0.97 V for 1) is similar to those found for the majority of di- and trinuclear clusters.[1,7,9]

Reduction of 1 by sodium metal or sodium amalgam in acetone in a polarographic cell generates a polarogram with a one-electron oxidation process which has an $E_{1/2}$ value identical with that for the process described by eq 1. This step can be assigned to reaction 3 and verifies the chemical

$$(CF_3)_6C_6Co_2(CO)_4^{-}\cdot \leftrightarrow (CF_3)_6C_6Co_2(CO)_4 + e^- \quad (3)$$

reversibility of the primary reduction step. The electrode process described by eq 2 is also observed as required by the proposed mechanism.

In acetone the radical anion is not very stable and undergoes slow decomposition. Controlled potential electrolysis in acetone at −0.2 V requires 0.80 ± 0.05 coulomb/mol of flyover compound. On the longer time scale of controlled potential electrolysis, the radical anion could be detected by ESR spectroscopy, but analysis of the products indicated that breakdown of the flyover complex occurs with time to produce hexakis(trifluoromethyl)benzene $(CF_3)_6C_6$, and other unidentified products.

Electrochemistry of 1 in CH_2Cl_2. The electrochemistry of 1 in CH_2Cl_2 is qualitatively similar to that observed in acetone. Controlled potential electrolysis in CH_2Cl_2 required 0.90 ± 0.05 coulomb/mol of 1, but again the resulting radical anion was not excessively stable. Hexakis(trifluoromethyl)benzene was again identified as a decomposition product by mass spectrometry and comparison with an authentic sample.

Electrochemistry of 1 in THF. Two reduction processes are also observed at both Pt and Hg electrodes in THF. Some iR drop distortion is present in this very high resistance medium. However after allowance for resistance effects, it is clear that as in other solvents the rate of electron transfer at a Hg electrode is greater than at Pt. Interestingly, the second reduction process apparently exhibits a considerable degree of chemically reversible behavior in THF in cyclic voltammograms recorded at slow scan rates (Figure 2). Less pronounced but analogous behavior is observed in other solvents. The scan rate

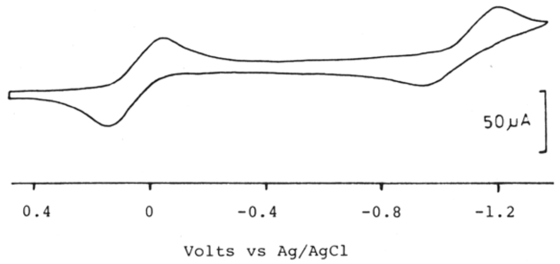
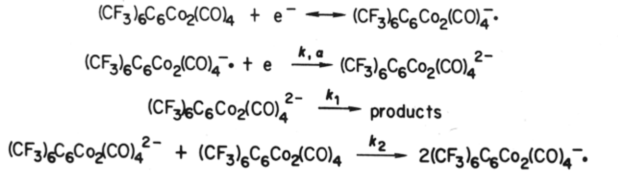


Figure 2. Cyclic voltammogram on Pt of 1 × 10^{-3} M **1** in THF [0.1 M n-Bu_4NClO_4] at a scan rate of 50 mV s^{-1}.

Scheme I



$$(CF_3)_6C_6Co_2(CO)_4 + e^- \rightleftarrows (CF_3)_6C_6Co_2(CO)_4^{-}\cdot$$
$$(CF_3)_6C_6Co_2(CO)_4^{-}\cdot + e \xrightarrow{k,\alpha} (CF_3)_6C_6Co_2(CO)_4^{2-}$$
$$(CF_3)_6C_6Co_2(CO)_4^{2-} \xrightarrow{k_1} \text{products}$$
$$(CF_3)_6C_6Co_2(CO)_4^{2-} + (CF_3)_6C_6Co_2(CO)_4 \xrightarrow{k_2} 2(CF_3)_6C_6Co_2(CO)_4^{-}\cdot$$

dependence is quite unexpected and differs at Hg and Pt electrodes. In addition to the fragmentation of the dianion, a second or higher order process, operating in parallel, may enable regeneration of the anion radical followed by reduction to the dianion, thus providing a competitive pathway to the decomposition of the dianion. One possible mechanism for this is that, on the longer time scales and in a medium in which the radical anion exhibits considerable stability, the conproportionation reaction (4) is

$$(CF_3)_6C_6Co_2(CO)_4 + (CF_3)_6C_6Co_2(CO)_4^{2-} \rightarrow 2(CF_3)_6C_6Co_2(CO)_4^{-}\cdot \quad (4)$$

contributing significantly to the electrochemical response. The overall process would then be of the kind shown in Scheme I. Chemical reduction of **1**, using sodium metal, or controlled potential electrolysis leads to virtually quantitative conversion to the radical anion in THF. Polarographic investigation of solutions of the radical anion thus generated shows that $E_{1/2}$ for the oxidation of the radical anion is 0.03 V (i.e., identical with $E_{1/2}$ for the process described by eq 1). In addition the apparent degree of reversibility of the two electrode processes is different for the two cases. The more negative reduction process, corresponding to dianion formation, shows a greater degree of chemical reversibility when the bulk solution contains $(CF_3)_6C_6Co_2(CO)_4$ rather than the anion radical. Experimental evidence for a restricted range of conproportionation mechanisms and the appropriate theoretical analysis are available in the literature.[16] However, the exact influence of reaction 4 depends on the nature of the irreversibility of the process described by eq 2, and as this is unknown, no quantitative calculations can be made at this stage. It is apparent from the electrochemical response in THF that this solvent provides an excellent medium for studies of reduced species derived from the flyover molecules and that direct evidence for the existence of the dianion can be obtained in this solvent. The small degree of chemical reversibility noted for this process in other solvents at slow scan rates is probably also due to the influence of reaction 4.

Electrochemistry of 1 in MeCN. dc polarography and single scan cyclic voltammetry of **1** in acetonitrile again reveals two well-defined reduction steps corresponding to the chemically reversible formation of a stable radical anion and its reduction to the less stable dianion species respectively (Table I). Figure 3 shows the single scan current–voltage curves obtained in this solvent. As in acetone or CH_2Cl_2, some chemical reversibility of the second process is seen on cyclic voltammograms recorded at slow scan rates. However, repetitive scanning of a solution of **1** in MeCN on Hg reveals a further reduction wave at −0.40 V which grew in intensity at the expense of the primary reduction wave. Cyclic voltammetry at Pt showed this new wave to be chemically irreversible. At the same time the shape of the primary reduction wave is modified. At slow scan rates, the peak current of the wave due to the oxidation of the radical anion of **1** decreases considerably (Figure 4), indicating that this species is probably involved in a reversible substitution reaction (eq 5). In addition to the observed changes in electrochemical

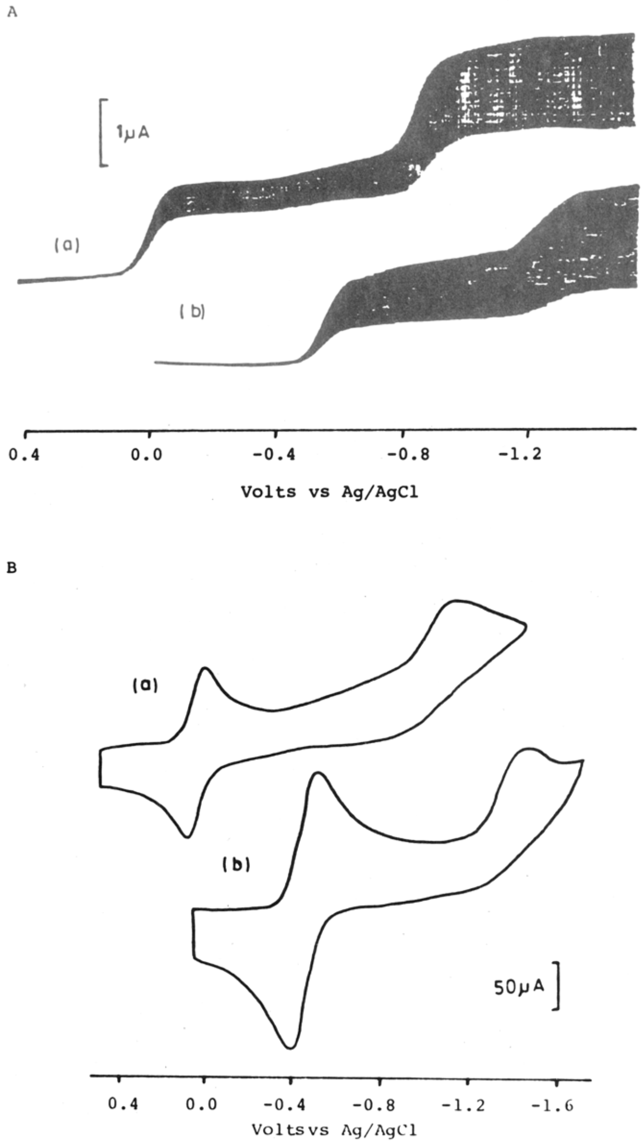


Figure 3. (A) dc polarograms in MeCN (0.1 M Et_4NClO_4) (drop time = 0.5 s): (a) 1 × 10^{-3} M **1**. (b) 1 × 10^{-3} M **4**. (B) Cyclic voltammograms on Pt in MeCN (0.1 M Et_4NClO_4) (scan rate 500 mV s^{-1}): (a) 1 × 10^{-3} M **1**; (b) 1 × 10^{-3} M **4**.

$$(CF_3)_6C_6Co_2(CO)_4^{-}\cdot + MeCN \leftrightarrow (CF_3)_6C_6Co_2(CO)_3(NCMe)^{-}\cdot + CO \quad (5)$$

behavior, the electrochemical solution changed in colour from deep purple to red over a period of several hours following the passage of current. TLC analysis of the

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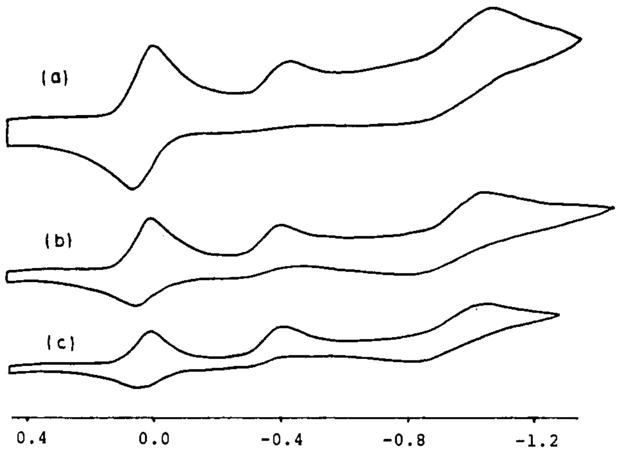
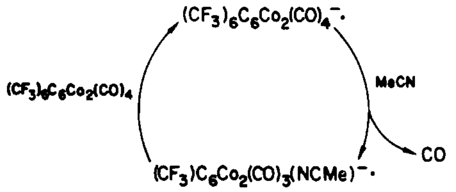


Figure 4. Cyclic voltammograms on Pt of 1×10^{-3} M 1 in MeCN at varying scan rates: (a) 200 mV s^{-1}; (b) 100 mV s^{-1}; (c) 50 mV s^{-1}.

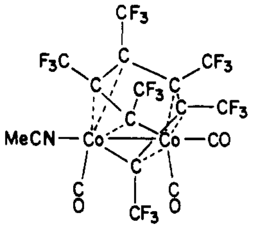
Scheme II



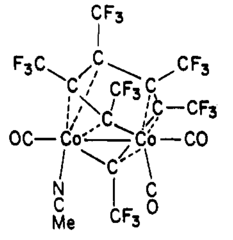
resulting solution indicated presence of two compounds in addition to unreacted 1. Subsequent identification of the principal products as the carbonyl-substituted derivatives $(CF_3)_6C_6Co_2(CO)_3(NCMe)$ (**6A** or **6B**) and $(CF_3)_6C_6Co_2(CO)_2(NCMe)_2$ (**7A** or **7B**)[17] allows the assignment of the additional feature at −0.40 V in the electrochemistry to process 6 followed by further reaction of

$$(CF_3)_6C_6Co_2(CO)_3(NCMe) + e^- \leftrightarrow (CF_3)_6C_6Co_2(CO)_3(NCMe)^{-\cdot} \quad (6)$$

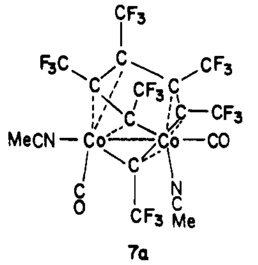
the product. This electrode process is consistent with the occurrence of homogeneous reactions following electron transfer and a subsequent electron-transfer step (Scheme II). The catalytic nature of the substitution process is evidenced by coulometry; 0.07 faraday/mol were required for the complete substitution of 1. Further details of this complex process will be described elsewhere.[17]



6a



6b



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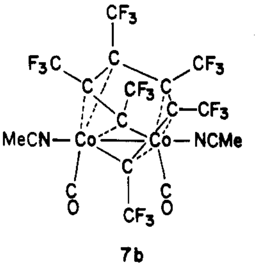

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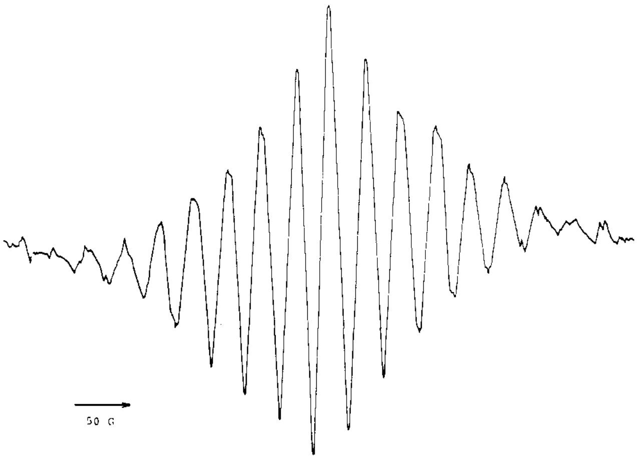

Figure 5. ESR spectrum of 1 in THF [n-Bu_4NClO_4] at 298 K.

Electrochemistry of 4 and 5. In acetone at 298 K, the electrode processes for 4 are identical with those of 1 (Table I), except for a shift to more negative potentials as expected following the replacement of three electronegative CF_3 groups by hydrogen atoms. Modification of the electron acceptor properties of the acetylene will perturb the upper bonding levels of the substrate[18] and also decrease the thermodynamic stability of the radical anion. However sodium reduction of 4 in acetone followed by polarographic monitoring shows that $4^{-\cdot}$, while less stable than $1^{-\cdot}$ in the thermodynamic sense, is reasonably stable kinetically. The lowering of thermodynamic stability of the radical anion (more negative $E_{1/2}$ value) associated with the increased donor ability of the acetylene, is seen even more clearly in the electrode responses of 5 in that $E_{1/2}$-$[5]^{0,1-}$ is very negative (Table I). dc polarograms of 5 at 298 K show the formation of $5^{-\cdot}$ to be chemically irreversible, although chemical reversibility on Pt is approached at 213 K where $5^{-\cdot}$ is seen to be stable on the electrochemical time scale. The nature of the decomposition of $5^{-\cdot}$ is unknown.

Compound 4 was also studied in other solvents (Table I), and, in common with the behavior observed for 1, the radical anion $4^{-\cdot}$ was found to be extremely stable in THF. In acetonitrile, the electrode response is the same as that in acetone and there was no evidence for the electron-transfer chain catalyzed substitution observed with 1 when only cyclic voltammetric or polarographic experiments are performed (Figure 3). The significant kinetic stability of $4^{-\cdot}$ observed in acetone is found also in MeCN. However bulk electrolysis of 4 produces a MeCN complex,[17] suggesting that the different voltammetric behavior is governed solely by the kinetics of the substitution. Compound 4 exhibits an unusual response at Hg electrodes in both CH_2Cl_2 and THF. In addition to the two anticipated reduction processes, an extra feature is observed at −0.8 V vs. Ag/AgCl. This extra wave is not observed at Pt, and it may be concluded that the radical anion $4^{-\cdot}$ is interacting in some way with the Hg electrode.

ESR Spectra of $R_4C_6Co_2(CO)_4$ Complexes. The radical anions were prepared by in situ electrochemical reduction of the parent complex in the ESR cavity, and, in contrast to the results in other solvents but in agreement with the electrochemical data, the resulting radical anions

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Table II. ESR Parameters for Flyover Radical Anions in THF (n-Bu_4NClO_4)

radical anion	$\langle g\rangle^a$	$\langle a\rangle$/G	$g_1{}^b$	a_1/G
$(CF_3)_6C_6Co_2(CO)_4^{-}\cdot$	2.013	-31.1 ± 0.1	2.004	-81.3 ± 0.3
$(CF_3)_5HC_6Co_2(CO)_4^{-}\cdot$		-31.6 ± 0.1	2.008	-83.1 ± 0.2
$(CF_3)_4H_2C_6Co_2(CO)_4^{-}\cdot$	2.017	-32.5 ± 0.1		
$(CF_3)_3H_3C_6Co_2(CO)_4^{-}\cdot$	2.019	-32.9 ± 0.2	2.016	-84.4 ± 0.2

[a] ±0.002. [b] ±0.004.

showed considerable stability in THF over a period of many hours, even at ambient temperatures. The ESR spectrum of $(CF_3)_6C_6Co_2(CO)_4^{-}\cdot$ in THF (Figure 5) typifies those of the radical anions of complexes 1–4. The isotropic spectra show the expected 15 lines due to hyperfine interaction of the unpaired electron with two equivalent cobalt nuclei ($I = {}^7/_2$ for ^{59}Co). Cobalt hyperfine coupling constants and g values are given in Table II. Despite the inequivalence of the cobalt atoms in $2^{-}\cdot$ and $4^{-}\cdot$ there is no evidence for this from the isotropic spectra. However, because of the rather broad lines (typically ~15 G) the assymmetry of the cobalt hyperfine interaction would have to be substantial in order to produce noticeable effects in the spectra. The variation in line width of the isotropic spectra with hyperfine component for radicals containing two or more equivalent nuclei has been shown[19] to derive principally from the incomplete averaging of **g** and hyperfine tensor anisotropies. Line-width variation for these spectra are consistent with the radicals having a reasonably isotropic **g** tensor but with a hyperfine tensor displaying significant anisotropy. There is no evidence of second-order splittings of equivalent nuclei effecting the line shapes in these spectra, but again, the line widths may be too great for this contribution to be resolved.

Frozen THF solutions of the radical anions $1^{-}\cdot$, $2^{-}\cdot$, and $4^{-}\cdot$ show broad and rather poorly resolved spectra which can be analyzed unambiguously to give only one of the **g** and hyperfine tensor components. The wings of the spectra reveal no evidence of a second component, while the resolved features corresponding to a_1 and g_1 begin to deviate markedly from the theoretical ratios in the central 400 G of the spectrum, suggesting that the second hyperfine tensor component is at least as large as 28 G. Assuming that the metal-based LUMO's in the $R_6C_6Co_2(CO)_4$ and $R_2C_2Co_2(CO)_6$ complexes are similar, the larger value of the isotropic cobalt hyperfine coupling constant for the radical anions $R_6C_6Co_2(CO)_4^{-}\cdot$ reflects a smaller delocalization of the unpaired electron onto the ligands.

It is interesting to note that the magnitude of the isotropic hyperfine coupling for the $(CF_3)_{6-n}H_nC_6Co_2(CO)_4$ radical anions decreases as n decreases. This behavior parallels a similar decrease in $|\langle a\rangle|$ with CF_3 substitution in the $R_2C_2Co_2(CO)_6$ complexes.[8] While it is tempting to attribute this effect to increasing delocalization of spin density onto the flyover ligands, the constancy of the dipolar parameter b_1 for the series belies this explanation. Thus the effect is more probably due to a very small increase in the cobalt s character of the LUMO with decreasing n.

In situ electrolysis of 1 in acetone or CH_2Cl_2 also produced well-resolved, 15-line spectra of the radical anion $1^{-}\cdot$. Continued electrolysis in these solvents however led to the growth of further resonances in the central region of the original 15-line spectrum. Ultimately, the 15-line signal collapsed leaving a sharp spectrum of at least 13 lines, which remained for several hours without further electrolysis. This spectrum is identical with that reported[20] for the radical anion of hexakis(trifluoromethyl)benzene, $(CF_3)_6C_6$, and is also observed when the solution is electrolyzed at potentials more negative than the second reduction step. Clearly, ring closure of the flyover bridge to give the substituted benzene represents a major pathway in the decomposition of $1^{-}\cdot$ in acetone and CH_2Cl_2. Additional evidence for ring closure was obtained by the isolation and mass spectrometric characterization of neutral hexakis(trifluoromethyl)benzene from the electrolysis products. It has been shown previously, that flyover complexes can be decomposed chemically or thermally to give good yields of the substituted benzenes,[21] and the intermediacy of flyover derivatives has been proposed for the cobalt-catalyzed, cyclic trimerization of acetylenes.[22] Further investigation of this facile, electron-induced ring closure is currently in progress.

Conclusion

The flyover complexes $R_6C_6Co_2(CO)_4$ are reduced in a chemically reversible, one-electron step to produce radical anions. Electrochemical data shows that the reduction of these molecules occurs more readily with increasing CF_3 substitution on the flyover bridge, to the extent that the radical anion $1^{-}\cdot$ is formed more easily than any of the tricobalt–carbon[1,7] or $R_2C_2Co_2(CO)_6$[9] radical anions that have been investigated previously. This observation can be explained in terms of a significant contribution by the bridging flyover ligand to the HOMO and LUMO orbitals for these molecules. Thus the reduction potential, which is a function of the relative energies of the HOMO and LUMO with respect to that of the electrode,[1] will respond directly to changes in the electron-withdrawing ability of the flyover substituents.

The stability of the radical anion species was found to be extremely solvent dependent, with THF conferring exceptional stability on the primary reduction products. In contrast, electrochemistry in MeCN as solvent revealed that the radical anion species, once formed, undergoes rapid substitution by the donor solvent. The ready formation of reasonably long-lived radical species is an essential prerequisite in electron-transfer chain (ETC) catalysis.[11,23] The result with MeCN indicates that the flyover radical anions should indeed be ideal substrates for ETC substitution reactions and this aspect of the chemistry of the flyover molecules will be reported separately.[17]

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Registry No. 1, 95911-44-7; $1^{-}\cdot$, 71373-22-3; 1^{2-}, 95911-45-8; 2, 95935-28-7; $2^{-}\cdot$, 95935-29-8; 3, 95911-46-9; $3^{-}\cdot$, 95911-47-0; 4, 38999-19-8; $4^{-}\cdot$, 95911-48-1; 5, 95911-49-2; $5^{-}\cdot$, 95911-50-5; 6, 84896-14-0; $6^{-}\cdot$, 95911-52-7; 7, 95911-51-6; $(CF_3)_6C_6$, 2340-93-4; $(CF_3)_6C_6^{-}\cdot$, 35844-19-0.

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