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# Electronic interactions in diyne $Co_2(CO)_6$ complexes

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## Abstract

Electrochemical criteria are used to evaluate the electronic interaction between redox centres in the  $\pi$ -conjugated diyne complexes  $\{RC \cong C[Co_2(CO)_6]C \equiv C[Co_2(CO)_6]R\}$  and  $\{RC \equiv C[Co_2(CO)_6]-(S)-C \equiv C[Co_2(CO)_6]R\}$  (R = Ph, Fc) where the aromatic spacer S is phenyl, napthalene or anthracene. Voltammetry at microelectrode, differential pulse techniques and low temperature measurements are used to obviate the chemical complications following the primary redox process. A mechanism is proposed which successfully simulates the electrochemical data.

Keywords: Electrochemistry; Cobalt complexes; Carbonyl complexes; Diyne complexes

## 1. Introduction

Organometallic poly-yne compounds may be suitable as precursors for solid state materials of technological interest [1,2] because of their ability to adopt a range of valence states modulated by the electronic characteristics of the ancillary ligands and 'rigid-rod' structures. Effective molecular hyperpolarizability or intra-molecular conductivity demand efficient electronic delocalization through the organic chain [3] and a poly-yne group nicely fulfils the criteria for a delocalized link [4]. A goal in our research programmes [5,6] is to achieve an understanding of the parameters which influence the degree of interaction between organometallic redox centres when they are separated by diyne ligands. The degree of electronic interaction between the redox centres can be determined by electrochemical methods [5,7,8]. There are two extreme cases for (A)-L-L-(A') molecules consisting of two identical redox centres (A, A'). When the bidentate ligand (L-L) is an insulator, and there is no electronic interaction between the two redox cores, the  $E^{\circ}$  values for the redox processes differ by a small statistical factor,  $\sim$  36 mV at 298 K; in polarography/CV there is a single wave/peak having the slope of a one-electron transfer, but the height of a two-electron process. If there is complete charge delocalization over the two centres the  $E^{\circ}$  values for the two redox processes differ by about 600-700 mV giving two well-resolved waves/peaks, each of one electron height. In between these extremes there is not a simple quantitative relationship between  $\Delta E^{\circ}$  and electronic delocalization as structural reorganization, solvation and ion pairing effects play a role. ESR spectra, especially frozen solution spectra, can give useful supporting evidence in all cases [9]. In this paper we report on complexes where the redox centre is the 'Co<sub>2</sub>(CO)<sub>6</sub>' moiety and the bidentate ligand is a dialkyne unit with or without an interpolated aromatic spacer (S) (1-8). The alkyne-Co<sub>2</sub> redox centre was chosen because its electrochemistry is reasonably well understood [10] although it was early recognized that fast ECE processes complicate its behaviour.

### 2. Results and discussion

Complexes for this electrochemical investigation have been synthesized by reaction of  $Co_2(CO)_8$  with the appropriate diyne and most have been reported elsewhere (Fig. 1) [11].

The X-ray structure of 3, obtained serendipitely from the reaction of  $Co_2(CO)_8$  with PhC=CMPPh<sub>3</sub> (M = Ag, Au), has showed that the two 'Co<sub>2</sub>C<sub>2</sub>' cores adopt the usual pseudo-tetrahedral geometry with the alkyne bond lying essentially perpendicular to the Co-Co vector; the original linearity of the diyne is lost [12]. Similar structural arrangement has been found for 6 [13]. The new compounds 2, 4,

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7, 8 have been prepared in good yield and characterized by analysis, NMR and IR spectroscopy.

The electrochemical behaviour of  $Co_2(CO)_6(alkyne)$ derivatives is characterized at room temperature by a oneelectron diffusion-controlled reduction process, followed by fast chemical reactions [10]; i.e., an ECE mechanism (Scheme 1). Chemical reversibility of the primary process is enhanced by eletron-withdrawing (e.g.  $CF_3$ ) or, to a lesser extent, bulky substituents (e.g. t-Bu) on the alkyne. Complexes 1–2 with one  $Co_2(CO)_6$  per diyne unit give electrochemical responses which show that the chemical reactions following reduction to 1<sup>--</sup> and 2<sup>--</sup> are fast even at 213 K; no radical species are detected in frozen solution ESR spectra. For 2 the usual electrochemically-reversible ferrocene (0/ 1+) peak couple is also observed (Table 1).

Table 1 Electrochemical data for 1-9\* At ambient temperature, **3-8** which have two equivalent  ${}^{\circ}Co_2(CO)_6$ ' redox centres undergo an *apparently* single 2*e* reduction followed by fast CE reactions. However, as the temperature is lowered the subsequent voltammetric profile is dependent on the dialkyne. For **3**, the two-electron peak (A') gradually diminishes in height (A) and a new one (C) appears at more negative potentials (Fig. 2); at -80 °C chemical complications are completely quenched, so that full chemical reversibility is achieved as testified by the directly associated peaks B and D, respectively. The  $E^{\circ}$  values for each process can be evaluated as  $(E_{pc}+E_{pa})/2$ :  $E^{\circ}(0,0/0,1-)=-0.94$  V,  $E^{\circ}(0,1-/1-,1-)=-1.16$  V. The resulting  $\Delta E^{\circ}=220$  mV value suggests a true electronic communication between the two bimetallic cores.

There are few measurements of diffusion coefficients (D) for organometallic species in the literature [14] and as we are interested in simulating the electrochemical processes, D is derived from RDE data, measurements of the viscosity and the Levich equation [8]. For 3 the diffusion coefficient is  $2.1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>; as expected this is smaller than the diffusion coefficient for FcC=C-C=CFc (9), of  $2.9 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>. It is larger than the value of  $1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> determined by simply using (in the Stoke-Einstein equation) the cubic root of molecular volume, taken from the X-ray structure of 3 [12]. Electrolysis *in situ* of 3 in an ESR cavity at varying temperatures generates weak eight-line spectra attributable to species with one cobalt atom in the radical species, but no sixteen-line spectra expected [9] for 3<sup>-</sup> has been found even in frozen solutions.

Complex 4 is an interesting molecule as it has two pairs of identical redox centres; a pair which undergoes reduction, i.e.  $^{CO_2(CO)_6}$ , and a pair which undergoes oxidation, i.e. Fc. Ferrocene also acts as an internal reference. At ambient temperature the cathodic scans mirror those for 3 (irreversible 2e wave A' in the scan range 0.10–100 V s<sup>-1</sup>) and while this peaks broadens below -40 °C the resolution into two com-

Complex	<i>E</i> °(0,0/0,1 - )	$E^{\circ}(0,1-/1-,1-)$	$\Delta E^{\circ}(\text{red})$	$E^{\circ}(0,0/0,1+)$	$E^{\circ}(0,1+/1+,1-)$	$\Delta E^{\circ}(\mathrm{ox})$
1	-0.96					
2	- 1.10			0.56	0.63	70
	-1.15					
3	- 0.94 <sup>b</sup>	- 1.16	220			
	0.96 °	- 1.17	210			
	- 0.96 <sup>d</sup>	- 1.19	230			
4	-1.17 °	1.31 °	140	0.54	0.58	40
5	- 1.06 ª	- 1.14	80			
6	-1.10°	- 1.14	60			
7	- 1.13	-1.17	40			
9		,		0.58 <sup>r</sup>	0.68	100

\* Pt electrode,  $CH_2Cl_2$  at 0.200 V s<sup>-1</sup> unless otherwise stated.

<sup>b</sup> CV, -80 °C, 0.050 V s<sup>-1</sup>.

° CV, -20 °C, 5.000 V s<sup>-1</sup>.

<sup>d</sup> SWV, - 20 °C, 200 Hz.

° SWV, - 20 °C, 600 Hz.

<sup>f</sup> From Ref. [15].



Fig. 2. Cyclic voltammogram of 3  $(1 \times 10^{-3} \text{ M})$  in CH<sub>2</sub>Cl<sub>2</sub> at 0.05 V s<sup>-1</sup> at various temperatures. Equimolar ferrocene (Fc) as a reference and Pt electrode.



Fig. 3. Cyclic voltammogram of 4  $(1 \times 10^{-3} \text{ M})$  in CH<sub>2</sub>Cl<sub>2</sub> at 0.20 V s<sup>-1</sup>, 20 °C (top) and -40 °C (bottom).

ponents (A and C) was poor (Fig. 3). Additional peaks on the back scan correspond [10] to the mononuclear fragmentation species derived from the CE processes (Scheme 1). Also the two-electron reversible oxidation peak is poorly resolved at -40 °C into two components (Fig. 3). However, steady-state current-voltage plots (obtained with a microelectrode at slow scan rates) give  $(E_{3/4} - E_{1/4})$  values around 87 mV, which can be resolved into two curves (equivalent plots for Fc and 9 give 58 mV). In contrast, resolution of the 'two-electron' oxidation process for 2 into individual  $E^{\circ}(0,0/0,1+)$  and  $E^{\circ}(0,1+/1+,1+)$  couples is easily seen at -20 °C (Table 1). Noteworthy is the decrease in separation between the two Fc(0/1+) couples from 100  $mV \rightarrow 70 mV \rightarrow 40 mV$  within the series FcC=C-C=CFc (9) [15]  $\rightarrow$  FcC=C-C=C[Co<sub>2</sub>(CO)<sub>6</sub>]Fc<sub>1</sub>(2)  $\rightarrow$  FcC=C- $[Co_2(CO)_6]C \equiv C[Co_2(CO)_6]Fc$  (4), which demonstrates that the  $\sigma/\pi$  coordination of  $Co_2(CO)_6$  moieties progressively decreases the communication between the two ferrocenyl redox centres. The lowering of C-C bond orders and the loss of linearity of the diyne chain can explain this trend.

Species  $4^+$  and  $4^{2+}$  have been generated by the oxidation of 4 by AgPF<sub>6</sub> or exhaustive electrolysis but attempts to obtain frozen solution ESR spectra have been so far unsuccessful.

The ' $Co_2C_2$ ' moieties are directly linked via a C-C bond in 3 and 4 whereas in 5-8 an aromatic spacer (S) is interpolated between them. Compared to 3, the aromatic spacer decreases the electronic communication between the two Co<sub>2</sub> redox centres. Consequently the  $\Delta E^{\circ}$  value cannot be immediately evaluated from the CV response as the peaks are strongly overlapped. For 5 the very fast chemical decomposition can be quenched by lowering the temperature from ambient to -20 °C, and by raising the scan rate up to 5 V  $s^{-1}$  (Fig. 4). Furthermore, a differential technique, such as Square Wave Voltammetry (SWV) [16] has been successfully employed to resolve these partially overlapped peaks, E and F (Fig. 5). A similar electrochemical behaviour is also observed for 6. However, due to the hydrogen substituents, the chemical decomposition of the electrogenerated monoanion, 6<sup>--</sup>, is faster. The chemical reversibility at -20 °C can be achieved at scan rates (CV) and frequencies (SWV) higher than those previously employed for 5. For example,



Fig. 4. Cyclic voltammogram of 5 at a HMDE electrode; scan rate 5 V s<sup>-1</sup>; at 22 °C (solid line) and -20 °C (dashed line). Equimolar Fc as internal reference.



Fig. 5. SWV response of 5 at a HMDE electrode in  $CH_2Cl_2$ , 200 Hz, 20 °C; Fc as internal reference.



Fig. 6. Cyclic voltammogram of 7 ( $1 \times 10^{-3}$  M) in CH<sub>2</sub>Cl<sub>2</sub> at 0.20 V s<sup>-1</sup>, Pt electrode, -78 °C.

at -20 °C the SWV response at 600 Hz clearly indicates two distinct reduction maxima (see Table 1).

Molecules 7 and 8 have an additional reduction centre – the aromatic spacer S itself. The irreversible couple E(0/1-) for the parent diyne of 7 ( $E_{pa}(S) = -1.30$  V at  $0.80 \text{ V s}^{-1}$ ) is close to A' and complicates the interpretation of the CV data at 20 °C. However, at -78 °C there is a clear separation and the 2e redox peak couple for the Co<sub>2</sub> centres has now the appearance of a chemically reversible system (Fig. 6). Resolution of the A and C components within peak A' is still not good, but steady-state plots with a microelectrode give similar results to those for 4 (vide supra) and confirm that  $\Delta E^{\circ}$  is approximately 40 mV.

A small separation is not unexpected as the peak separation for the two Fc(0/1+) couples in the diyne 1,8- $(FcC\equiv C)_2C_{10}H_8$  is only 80 mV. The two reduction processes at  $E_{pc} = -1.20$  and -1.43 V found in 9,10-bis(phenylethynyl)anthracene are within the potential range of the  $Co_2(CO)_6$  reduction processes, therefore no definitive conclusion about the electronic interaction in 8 can be drawn.

### 3. Conclusions

At 20 °C all disubstituted diyne complexes 3–7 undergo an apparently single two-electron irreversible reduction process, suggesting that the (alkyne)Co<sub>2</sub>(CO)<sub>6</sub> redox centres do not 'see' each other. That this is incorrect is shown by the low temperature and fast scan data where competing CE reactions involving the primary radical anions  $3^{-}-7^{-}$  are quenched and two distinct reversible couples,  $E^{\circ}(0,0/0,1-)$ and  $E^{\circ}(0,1-/1-,1-)$  can be discerned, albeit with variable resolution. Communication between the redox centres in an electrochemical sense is maximum for complex 3, with  $\Delta E^{\circ} = 220$  mV. This may be compared with  $\Delta E^{\circ}$  for the isoelectronic and isostructural  $[Ni_2Cp_2]_2[Ph-C=C-C=C-Ph]$ [17] (670 mV), the acetylide complex *trans*-[Pt(PPh\_3)<sub>2</sub>(-C=C-Fc)<sub>2</sub>] [18] (260 mV) and the cluster FcCCo<sub>3</sub>(Cp)<sub>3</sub>CFc [19] (300 mV). The other diyne complexes 4-7 show weakly interacting redox centres. Whether the reduced communication for this group compared to 3 is simply due to interpolation of the aromatic spacer (although 4 does not have a spacer), or to structural effects, is not possible to decide because the small values mean that other factors such as solvation will be significant. It is perhaps surprising that there is any communication at all in 3-7 given the lack of orthogonality in the alkyne backbone in these complexes although there is evidence from optical spectra [20] and in the photoelectron spectra of butadiynyl complexes [21] that the alkyne has the ability to act as a  $\pi$  donor. Through space interaction may have a role but unfortunately frozen solution ESR spectra which may have clarified these possibilities could not be observed because the fast CE reactions led to negligible concentrations of the primary radical anions.

A feasible mechanism (Scheme 2) to simulate the overall electrochemical scenario recognizes that the monosubstituted derivatives { $RC \equiv C[Co_2(CO)_6](S)C \equiv CR$ } undergo their primary reduction process  $E^{\circ}(0/1-)$  at a potential very close to the  $E^{\circ}(0,0/0,1-)$  for the corresponding disubstituted diyne complex { $RC \equiv C[Co_2(CO)_6]-(S)-C \equiv C-[Co_2(CO)_6]R$ } (Table 1). Thus, the key step involves the formation of the monosubstituted radicals from the fast decomposition of the electrogenerated radical anions  $3^{*}-7^{-}$ , which then undergo a further 1*e* reduction at the same  $E^{\circ}(0,0/0,1-)$  potential of the corresponding disubstituted diyne complex. In digital simulations a value of  $2.0 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> has been employed for the diffusion coefficient of the internal standard Fc in CH<sub>2</sub>Cl<sub>2</sub>, and the experimentally determined coefficients for the complexes under study. The



Scheme 2. Proposed mechanism for the reduction of diyne- $Co_2(CO)_6$  complexes.



Fig. 7. Digital simulation according to the mechanism in Scheme 2 with various homogeneous rate constants, k. Fixed parameters: scan rate = 0.050 V s<sup>-1</sup>; heterogeneous rate constant  $(k^{\circ}) = 0.1$  cm s<sup>-1</sup>,  $\alpha = 0.5$ ,  $D(3) = 2.1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>,  $D(Fc) = 2.0 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>;  $E^{\circ}(0,0/0,1-) = E^{\circ}(0/1-) = -0.94$  V;  $E^{\circ}(0,1-/1-,1-) = -1.16$  V.

good fit between the experimental CV responses at different temperatures (Fig. 2), and digital simulations for 3 employing different values of the homogeneous rate constant, k (Fig. 7), supports the proposed mechanism.

To summarize, communication between redox centres, from the electrochemical viewpoint, does occur in diyne complexes with multiple redox centres but the rapid CE reactions of the primary radical anions does not encourage us to believe that networks incorporating these units would be profitable for study. Recent work in our laboratories has indicated that early transition metal organometallic and  $\sigma$ -coordinated acetylide units are more useful.

### 4. Experimental

Alkynes [22] and the complexes, 1, 3, 5 and 6 were synthesized by literature methods [11]. Solvents were dried and distilled by standard procedures, and all reactions and electrochemical scans were performed in an inert atmosphere. IR spectra were recorded on a Digilab FX60 spectrometer and NMR spectra on a Varian VXR300 MHz or a Gemini 200 MHz spectrometer. Microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago. FAB mass spectra were recorded on a Kratos MS80RFA instrument with an Iontech ZN11NF atom gun. Voltammetric responses were recorded in  $CH_2Cl_2(0.1 \text{ M in } [Bu_4N] [PF_6])$ on an EG&G PAR 273 or 173 electrochemical analyser interfaced to a microcomputer using PAR M270 software, with solutions between  $0.5-5 \times 10^{-3}$  M in electroactive material in a three-electrode or BAS RDE-1 cell. Potentials are referred to SCE with the ferrocene/ferrocenium couple taken as 0.460 V versus SCE in CH<sub>2</sub>Cl<sub>2</sub> with a Pt electrode. The steady-state plots were recorded using a 10 or 100  $\mu$ m Pt electrode. Diffusion coefficients were determined from RDE data in  $CH_2Cl_2$  (0.15 M in [Bu<sub>4</sub>N] [ClO<sub>4</sub>]) and 5×10<sup>-4</sup> M in depolarizer, using the Levich equation and the kinematic viscosity of the RDE solution measured with a capillary viscometer (0.37 cm<sup>2</sup> s<sup>-1</sup>) at 20 °C. ESR spectra were recorded as described previously [9] on a Bruker ER 220D-LR spectrometer in toluene, THF or  $CH_2Cl_2/C_2H_4Cl_2$ .

# 4.1. Synthesis of $FcC \equiv C[Co_2(CO)_6]C \equiv CFc$ (2) and $FcC \equiv C[Co_2(CO)_6]C \equiv C[Co_2(CO)_6]Fc$ (4)

FcC=C-C=CFc (9), [23] (0.56 g, 1.3 mmol) was stirred under N<sub>2</sub> at room temperature with an excess of dicobalt octacarbonyl (1.85 g, 5.4 mmol) in 80 ml hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:1) for 30 min. Solvent was removed in vacuo and the product separated using column chromatography (SiO<sub>2</sub>/ hexane). Recrystallization from hexane yielded green-black crystals of 4; 0.57 g (43%). Anal. Found: C, 43.45; H, 1.76. Calc. for C<sub>36</sub>H<sub>18</sub>CO<sub>4</sub>Fe<sub>2</sub>O<sub>12</sub>: C, 43.68; H, 1.83%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.24 (s, 10H, -C<sub>5</sub>H<sub>5</sub>), 4.33 (t, J = 1.9 Hz, 4H), 4.42 (t, J = 1.9 Hz, 4H). IR (hexane)  $\nu_{CO}$ : 2093m, 2074s, 2054vs, 2029s and 2019vs cm<sup>-1</sup>.

A reaction with stoichiometric quantities of FcC=C-C=Fc and Co<sub>2</sub>(CO)<sub>8</sub> produced FcC=C[Co<sub>2</sub>(CO)<sub>6</sub>]C=CFc (2), in addition to 4. Green-black 2 was obtained in 10% yield from the residual hexane solution after 4 had crystallized. (*Anal.* Found: C, 51.16; H, 2.31. Calc. for C<sub>30</sub>H<sub>18</sub>Co<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>: C, 51.18; H, 2.58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.27 (s, 5H, -C<sub>5</sub>H<sub>5</sub>), 4.31 (t, J = 1.7 Hz, 2H), 4.36 (s, 5H, -C<sub>5</sub>H<sub>5</sub>), 4.38 (t, J = 1.7 Hz, 2H), 4.48 (t, J = 1.7 Hz, 2H), 4.58 (t, J = 1.7 Hz, 2H). IR (hexane)  $\nu_{CO}$ : 2087s, 2052 vs, 2030vs, 2022s cm<sup>-1</sup>; (KBr)  $\nu_{C=C}$ : 2168w cm<sup>-1</sup>.

### 4.2. Synthesis of 7

The parent diyne, synthesized from 1,5-diiodonaphthalene and phenylethynylcopper [24], was stirred at room temperature with an excess of dicobalt octacarbonyl in hexane/ CH<sub>2</sub>Cl<sub>2</sub> (1:1) for 60 min, the solvent stripped and the residue separated on silica gel. Hexane eluted unreacted Co<sub>2</sub>(CO)<sub>8</sub> and the green-black product {PhC $\equiv$ C[Co<sub>2</sub>(CO)<sub>6</sub>)]}<sub>2</sub>C<sub>10</sub>H<sub>8</sub> (6), eluted with CH<sub>2</sub>Cl<sub>2</sub>. Anal. Found: C, 49.17; H, 1.82. Calc. for C<sub>38</sub>H<sub>16</sub>Co<sub>4</sub>O<sub>12</sub> · 0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 49.05; H, 1.82%. FAB MS: 900 m/z (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.3 (2H, napth-H), 7.4 (6H, phenyl-H), 7.5-7.6 (4H, phenyl-H), 7.9 (4H, napth-H). <sup>1</sup>IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{CO}$ : 2100w, 2085m, 2053vs and 2024vs cm<sup>-1</sup>.

## 4.3. Synthesis of 8

The diyne, 9,10-bis(phenylethynyl)anthracene (Aldrich), was stirred at room temperature with an excess of dicobalt octacarbonyl in hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:1) for 2 h. Workup as for 7 gave dark-green crystals of 8. Anal. Found: C, 53.21; H, 1.65. Calc. for C<sub>42</sub>H<sub>18</sub>Co<sub>4</sub>O<sub>12</sub>: C, 53.21; H, 1.91%. <sup>1</sup>H NMR (d<sub>6</sub>-acetone):  $\delta$  7.4 (14H), 8.8 (4H). IR (C<sub>6</sub>H<sub>12</sub>)  $\nu_{CO}$ : 2100w, 2081m, 2054vs, 2025vs and 2007m cm<sup>-1</sup>.

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