**Registry No.** 1, 37685-63-5; 2, 108151-11-7; 3, 84896-13-9; 3′, 108151-17-3; 4, 108151-12-8; 5, 108151-13-9; 5′, 108151-14-0; 6, 87828-96-4; 7, 87828-97-5; 8, 87828-98-6; BPK, 16592-08-8; dppm, 2071-20-7; dppe, 1663-45-2; ttas, 2774-08-5.

**Supplementary Material Available:** Thermal parameters of non-hydrogen atoms (Tables S3 and S4), positional parameters for calculated hydrogen atoms (Tables S5 and S6), additional bond length and angle data (Tables S7 and S8), and selected least-squares planes (Tables S9 and S10), and selected intra- and intermolecular nonbonded contacts (Table S11) for 5 and 7 (12 pages); listings of structure factors for 5 and 7 (Tables S1 and S2) (31 pages). Ordering information is given on any current masthead page.

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# Electron Transfer in Organometallic Clusters. 13. Catalytic Sequential Ligation of $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ by Polydentate Ligands and Electrochemistry of Derivatives

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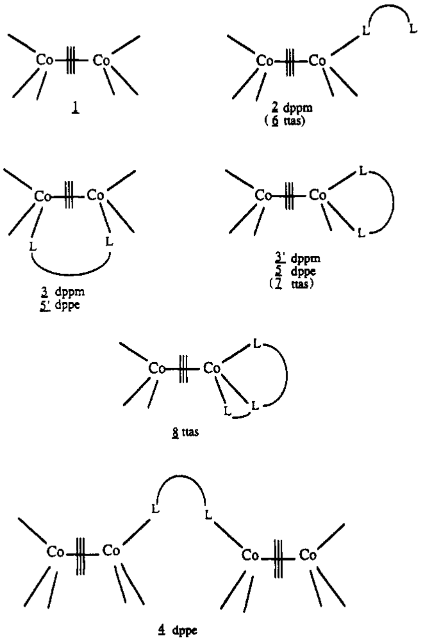
Analysis of *i–E* responses for $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_{6-n}(L\text{-}L)$ (L-L = dppm, dppe, ttas), $\{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5\}_2(dppe)$, and $[\mu\text{-}Ph_2C_2]Co_2(CO)_4(L\text{-}L)$ (L-L = dppm, dppe) provides an understanding of the electron transfer catalyzed sequential substitution of $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ by polydentate ligands. All derivatives undergo a primary one-electron reduction step at the cluster center which is electrochemically and chemically reversible when $n = 2$ but chemically irreversible for $n = 1$ due to subsequent ETC reactions and rapid structural rearrangements. Electron transfer to the $\mu\text{-}\eta^1$-dppe complex cleaves the dppe bridge to give a $\eta^1$-radical anion and $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5^{\bullet -}$ while an axial–equatorial rearrangement occurs when the $\eta^1$-dppm complex is reduced. The ttas derivatives, $n = 2$ and 3, undergo reversible one-electron oxidation at the ligand, and oxidation of the cluster also occurs for $n = 3$. Homogeneous electron transfer chain (ETC) catalyzed sequential substitution occurs with decreasing catalytic efficiency as $n$ increases; for L-L = ttas the transformation $n = 2 \rightarrow n = 3$ is not catalyzed. Fast structural rearrangements are observed during catalysis, and the primary substitution rate is in the order ttas > dppe > dppm, but the ring closure rate is in the order ttas > dppm > dppe.

Scheme I[a]



[a] ≡ corresponds to the acetylene ligand $(CF_3)_2C_2$.

An understanding of how a metal carbonyl cluster responds structurally in an electron transfer reaction is important to the design of electrocatalytic cluster systems and to stereospecific syntheses involving electron transfer. Questions such as whether structural change occurs before or after the homogeneous electron transfer step are central to a determination of rates of heterogeneous and homogeneous transfer and to the rate of nucleophilic or electrophilic attack at the reduced or oxidized center.[2] If we restrict discussion to a reductive electron transfer, the dominant redox behavior with carbonyl cluster compounds,[3] the structural changes which can occur range from changes in molecular parameters like metal–metal bond lengths (in which case electron transfer is usually fast[2,4]), through isomerization,[5,6] to completely different bond connectivities[7] and/or ligand dissociation.[5,8] From an electrochemical view these structural changes influence the height of the activation barrier between reactant and product and, consequently, the electrochemical reversibility.

A variety of ligational modes are often possible for carbonyl cluster polydentate Lewis base derivatives, and this can make the quantitative interpretation of the

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electrochemistry difficult. In a study of the $RCCo_3(CO)_9$/L-L (L-L ≡ polydentate ligand) system an overall two-electron reduction process was brought about by a combination of $\vec{E}C\vec{E}$ (ligand dissociation) and $\vec{E}C\overleftarrow{E}$ (catalytic nucleophilic substitution) as well as isomerization unless the ligand was firmly "anchored" in a chelate conformation.[5] Preparative studies described in the preceding paper[1] provided a series of complexes $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_{6-n}$(L-L) with well-defined stereochemistries in solution. Selective ETC nucleophilic substitutions were utilized in these syntheses, and, since it transpired that diffusion-controlled one-electron transfer was involved, the μ-alkyne complexes offered a system in which the structural rearrangements incumbent upon electron transfer could be studied in some detail. Electron transfer processes for a number of $(\mu\text{-alkyne})Co_2(CO)_{6-n}L_n$ derivatives have been reported,[9] but there are no comparable studies for polydentate complexes. Scheme I details the compounds examined here.

## Experimental Section

The complexes $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_{6-n}$(L-L) (L-L = dppm, dppe, ttas; $n$ = 1, 2, or 3) were prepared as described in the previous paper.[1] $[\mu\text{-}(Ph_2C_2)Co_2(CO)_4(\mu\text{-}\eta^2\text{-dppm})$ was prepared by the method of Cullen et al.[10] Purification procedures for the solvents have been given in previous papers.[8]

Polarography and cyclic voltammetry studies were carried out with a PAR Model 174 analyzer driven by a PAR Model 175 programmer. Current–voltage curves were recorded on a Tektronix Model 5103 oscilloscope or an X-Y recorder. A conventional three-electrode cell was used in all polarographic and CV experiments, and coulometry was carried out in a cell with a basket Pt working electrode. The reference electrode was a Ag/AgCl (saturated LiCl, water, or acetone) electrode isolated from the solution by a Vycor tip of a solid Ag/AgCl electrode immersed directly in the solution. These reference electrodes were calibrated before each run with the known[11,12] electrochemically and chemically reversible couples $[PhCCo_3(CO)_9]^{0,1-}$ or $[\text{ferrocene}]^{1,0}$ by dc polarography in the same solvent and under the same conditions as the test solution. In some cases the reference was cross-checked by using ferrocene in situ in the test solution. Scan rates were 10 or 20 mV $s^{-1}$ for polarographic and 50 mV $s^{-1}$ to 5 V $s^{-1}$ for voltammetric measurements. Solutions were $\sim 10^{-3}$ M in electroactive material and 0.10 (TEAP) or 0.08 M (TBAP) in supporting electrolyte.

Severe poisoning of the electrodes was experienced in this work such that reproducible repeat scans with reasonable dc slopes or peak–peak separations were difficult to achieve. The cause is unclear, but there was no satisfactory remedy except to clean the electrodes after each scan. Pt electrodes were prepared by anodizing at 2 V for 3 min in 0.1 M perchloric acid and polishing and glassy carbon electrodes by washing thoroughly with $CH_2Cl_2$, then acetone, and water and finally polishing the surface. "Ideal" diffusion-controlled parameters for one-electron electrode processes were derived from measurements of $PhCCo_3(CO)_9$ or ferrocene under the same conditions. It should be emphasized that the electrochemical response of the $(CF_3)_2C_2Co_2(CO)_{6-n}$(L-L) derivatives can be altered quite drastically by the condition of the electrode, especially in the anodic region of CV's. The data discussed in this paper are the result of several runs and refer to those attained at clean electrodes.

ESR spectra were recorded by the methods described previously.[13]

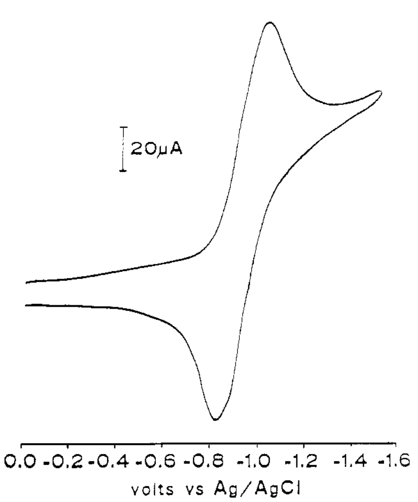

**Figure 1.** Cyclic voltammogram of **3** in $CH_2Cl_2$ on Pt at 293 K (scan rate 200 mV $s^{-1}$, 0.10 mol $dm^{-3}$ TBAP).

**Oxidation of ttas Complexes.** Oxidation of the green ($n$ = 2) or purple ($n$ = 3) ttas complexes was carried out either by passing 1 F $mol^{-1}$ through a $CH_2Cl_2$ solution of the complex by using a conventional Pt-basket working electrode setup or by stoichiometric oxidation with $AgPF_6$ in $CH_2Cl_2$. Both methods gave identical results—greenish brown ($n$ = 2) and green ($n$ = 3) solutions—but the resulting solids isolated by stripping the solvent were too unstable for characterization. Infrared spectra are shown in Figure 5 and the electronic spectra in the text.

## Results and Discussion

**Electrochemistry of 3, 3′, 5, and 5′.** Complexes in which the bidentate ligand either spans the Co–Co bond (**3**, **5′**) or chelates to one cobalt atom (**3′**, **5**) display well-defined $i$–$E$ responses (Figure 1). For both complexes **3** and **5** primary reduction processes in $CH_2Cl_2$ or acetone are diffusion-controlled and chemically reversible at Hg, Pt, or glassy carbon electrodes and in all solvents (slopes V vs. log $[(i_d - i)/i]$ = 60 mV, $i_{pa}/i_{pc}$ = 1, and $i_{pc} \propto v^{1/2}$). Diffusion coefficients for these derivatives, obtained by standard polarographic techniques or by digital simulation of the cyclic voltammograms,[12] are smaller than those for ferrocene[14] in the same solvent, and, when allowance is made for this difference, the limiting currents for the polarographic waves are consistent with the transfer of one electron. The reduction step therefore involves the formation of the radical anion (eq 1). However we were

$$[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\text{L-L}) + e \rightarrow [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\text{L-L})^{\bullet-} \quad (1)$$

unable to detect the any paramagnetic species following in situ electrolytic reduction of the complexes in an ESR cavity. Similar observations have been made for other mono-[19] and bidentate[12] cluster complexes and attributed to the lability of the phosphine ligands.

Both CO and temperature have no effect on the electrochemical behavior, and this fact, together with well-behaved reversible $i$–$E$ responses, could be interpreted as a retention of stereochemistry in the radical anions $3^{\bullet-}$ and $5^{\bullet-}$. However, the $i$–$E$ responses for the isomers **3′** and **5′** were identical with those of **3** and **5**, respectively, in $CH_2Cl_2$. Clearly, a rapid interconversion between isomers occurs with nil current flow.

The electrochemistry of the analogous $\mu\text{-}Ph_2C_2$ derivatives $[\mu\text{-}Ph_2C_2]Co_2(CO)_4(\mu\text{-}\eta^2\text{-L-L})$ (L-L ≡ dppm, dppe) is strictly comparable to the isostructural **3** and **5′** (Table I). This is an interesting result as complexes with mon-

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[9] (a) Arewgoda, C. M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983**, *105*, 1893. (b) Arewgoda, C. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 5633.

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[11] Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410.

[12] Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1132.

[13] Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. *Inorg. Chem.* **1977**, *16*, 405.

[14] $D(\text{ferrocene})^{15} = 2.0 \times 10^{-5}$ $cm^2$ $s^{-1}$, $D(3) = 7 \times 10^{-6}$ $cm^2$ $s^{-1}$.

**Table I**[a]

| complex | $E_{pc}^1$ | $E_{pc}^2$ | $E_{pa}^1$ | $E_{pa}^2$ | $E_{pa}^3$ | $i_{pa}/i_{pc}$ | $E_{1/2}^{r\,b}$ |
|---|---|---|---|---|---|---|---|
| **2** | −0.73 | −1.02 | (*−0.53*) | −0.90 | −0.33 | | −0.66 |
| **3** | −1.04 | | −0.93 | | | 1.0 | −1.06 |
| **4** | −0.72 | −1.05 | −0.69 | −0.95 | −0.43 | | −0.62 |
| | −0.71 | −1.05 | −0.61 | −0.95 | −0.33 | | *c* |
| **5** | −1.04 | | −0.95 | | | 1.0 | −1.01 |
| **6** | −0.77 | −1.08 | −0.59 | −0.90 | | 0.2 | −0.71 |
| | | 0.75 | | 0.52 | | 1.3 | 0.60 |
| **7** | −1.09 | | −0.90 | | | 1.0 | −0.99 |
| | | 0.73 | | 0.54 | | 1.0 | 0.61 |
| **8** | −1.35 | | | | | | −1.26 |
| | | 0.78 | | 0.53 | | 1.2 | 0.62 (0.80) |
| **9**[d] | −1.26 | | −1.18 | | | 1.0 | −1.22 |

[a] In $CH_2Cl_2$ under Ar at 293 K and 200 mV $s^{-1}$ unless stated otherwise. Volts vs. Ag/AgCl referenced against $[\text{ferrocene}]^{+/0}$ couple. Pt electrode. $E_{pc}^1$ and $E_{pa}^1$ refer to the potentials for the primary redox process. $E_{pc}^2$ and $E_{pa}^2$ refer to the potentials for the secondary redox process which for **2**, **4**, and **6** is formation of the bidentate derivative. $E_{pa}^3$ refers to the oxidation of $1^{\bullet-}$ or $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5{}^{\bullet-}$. Note that the potentials for **2** and **4**, particularly $E_{pa}$ values, will vary considerably with scan rate and electrode preparation. [b] From polarographic measurements. [c] Under CO. [d] Compound **9** ≡ $[\mu\text{-}Ph_2C_2]Co_2(CO)_4(\mu\text{-}\eta^2\text{ dppm})$.

odentate ligands, $[\mu\text{-}Ph_2C_2]Co_2(CO)_nL_{6-n}$, rapidly fragment upon reduction to give mononuclear species $[\mu\text{-}Ph_2C_2]\text{-}Co(CO)_2L$.[9] The increased stability can be attributed to "clamping" of the Co–Co bond by the bidentate ligand.

**Electrochemistry of 2.** DC polarograms of the $\eta^1$-dppm complex **2** in $CH_2Cl_2$ or acetone are characterized by two reduction waves, $E_{1/2} = -0.66$ and $-1.07$ V. At ambient temperatures the first wave shows an increase in currents normally attributed to a catalytic process[15] and of the type noted with other $[\mu\text{-}(CF_3)_2C_2]Co_2$ compounds.[9a] This may be attributed to the lability of the phosphine ligand and possible involvement of the electrode in the redox process. At 273 K a "normal" polarographic wave is seen with parameters indicative of an electrochemically reversible one-electron reduction process. These data support an assignment of the first wave at −0.66 V to the formation of $2^{\bullet-}$ (eq 2).

$$2 + e = 2^{\bullet-} \tag{2}$$

The second polarographic wave has the potential of the couple $[3]^{0/-}$ showing that an $\bar{E}C\bar{E}$ reaction is occurring to give neutral **3** (eq 3 and 4). The limiting current for

$$[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppm})^{\bullet-} = [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\mu\text{-}\eta^2\text{-dppm})^{\bullet-} + CO \tag{3}$$

$$[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\mu\text{-}\eta^2\text{-dppm})^{\bullet-} + [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppm}) = [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\mu\text{-}\eta^2\text{-dppm}) + [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppm})^{\bullet-} \tag{4}$$

the first polarographic wave is a resultant of the current due to the reduction of **2**, the rate at which $2^{\bullet-}$ changes to $3^{\bullet-}$ and the heterogeneous oxidation of $2^{\bullet-}$. If the conversion to $3^{\bullet-}$ is slow, then, on the polarographic time scale, the limiting current should be that expected for a one-electron reversible reduction; if it is fast, this limiting current will be substantially reduced. The large reduction ($i_d$ is ~40% compared to ferrocene, adjusted for the different diffusion coefficient) is consistent with a fast ring closure reaction.

In order to interpret the voltammetric data we must recognise that the $\bar{E}C\bar{E}$ process (3) involves a rearrangement of the phosphorus donor from a pseudoaxial to pseudoequatorial configuration[1] if the product of (3) has the same conformation as the $\mu\text{-}\eta^2$ complex **3**. From the efficiency and rate of the transformation $2 \rightarrow 3$ (0.1 F $mol^{-1}$ from coulometry) there seems to be no structural impediment and two pathways, (5) and (6), for this transformation can be envisaged ($2_A \equiv 2$ axial conformation, $2_E \equiv 2$ equatorial).

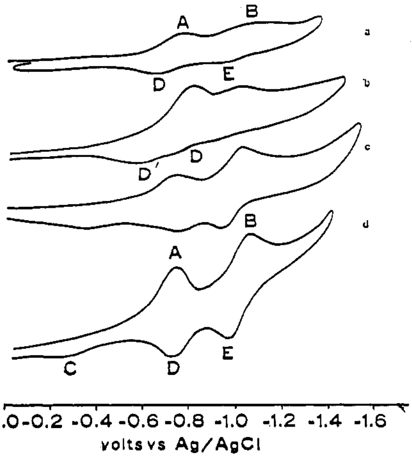

**Figure 2.** Cyclic voltammograms of **2** in $CH_2Cl_2$ on Pt (0.10 mol $dm^{-3}$ TBAP): (a) 50 mV $s^{-1}$, 233 K; (b) 500 mV $s^{-1}$, 233 K; (c) 50 mV $s^{-1}$, 293 K; (d) 500 mV $s^{-1}$, 293 K.

$$2_A\text{-}[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppm})^{\bullet-} = 2_E\text{-}[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppm})^{\bullet-}$$

$$2_E\text{-}[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppm})^{\bullet-} = [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\mu\text{-}\eta^2\text{-dppm})^{\bullet-} + CO \tag{5}$$

$$2_A\text{-}[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppm})^{\bullet-} = [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\eta^2\text{-dppm})^{\bullet-} + CO$$

$$[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\eta^2\text{-dppm}) = [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\mu\text{-}\eta^2\text{-dppm}) \tag{6}$$

An analysis of the voltammetric data (Figure 2) supports option (5). The primary reduction wave A does not have a $v^{1/2}$ profile at 293 K, confirming that a chemical reaction follows reduction of **2** to $2^{\bullet-}$, at 233 K and scan rates <200 mV $s^{-1}$ it does have a $v^{1/2}$ profile. Reduction wave B and oxidation wave E form a reversible couple $3^{0/-}$ at all temperatures (Figure 2). Additional oxidation waves are seen on the reverse scan following the formation of $2^{\bullet-}$. Wave C is only seen at fast scan rates or when there is nearly quantitative conversion to **3**, or if the solution is maintained in a CO atmosphere; it can be assigned to the oxidation of $1^{\bullet-}$. A companion oxidation wave to A, wave D, is only significant at 293 K at scan rates >500 mV $s^{-1}$ and

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[15] Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Application*; Wiley: New York, 1980.

is at a *negative* potential relative to A. On cooling, this wave becomes more significant as the current due to the couple $3^{0/-}$ decreases and progressively shifts to more positive potentials. Eventually, when A has a $v^{1/2}$ profile and at scan rates <200 mV $s^{-1}$, D forms an apparently chemically reversible couple with A (Figure 2a). Under the same conditions (~233 K) at scan rates >200 mV $s^{-1}$ another wave D′ appears at ~0.1 V positive of D (Figure 2b).

These complex data can be interpreted on the basis of reaction 5. Upon reduction to $\mathbf{2}_{\mathrm{A}}^{\bullet-}$ there is a fast conversion to $\mathbf{2}_{\mathrm{E}}^{\bullet-}$, the formation of the sterically unfavorable isomer being encouraged by the "opening" of the cluster framework through the electron entering an $a_2$* LUMO. The $\eta^1$ species now has the correct conformation for transformation to an $\eta^2$-complex and very fast ring closure (eq 3) and homogeneous electron transfer (eq 4) take place at 293 K to the extent that wave D, due to oxidation of a $\eta^1$-species, has significant peak current only at scan rates >500 mV $s^{-1}$. If the reduction potential of $\mathbf{2}_{\mathrm{E}} < \mathbf{2}_{\mathrm{A}}$, then the cross redox reaction (7) can occur, the thermodynamic

$$\begin{tikzcd}
2_A + e \arrow[r, leftrightarrow] \arrow[dr, leftrightarrow] & 2_A^{\bullet-} \arrow[d] \arrow[dl, leftrightarrow] \\
2_E + e \arrow[r, leftrightarrow] \arrow[u] & 2_E^{\bullet-}
\end{tikzcd} \qquad (7)$$

constraint being the small difference in potential between the isomers (<0.1 V). At ambient temperatures wave D can be attributed to the oxidation of $\mathbf{2}_{\mathrm{E}}^{\bullet-}$ while, at low temperatures, oxidation of both $\mathbf{2}_{\mathrm{A}}^{\bullet-}$ and $\mathbf{2}_{\mathrm{E}}^{\bullet-}$ is observed. The lifetime of the neutral $\mathbf{2}_{\mathrm{E}}$ isomer is very short on the electrochemical time scale as the repeat scans virtually mirror the initial scan.

These fast isomeric conversions with nil current flow upon oxidation or reduction of the substrate are similar to those noted with other dppm (and dppe) mono-[16] and polynuclear[5] metal carbonyl complexes and are seen in the catalytic reactions discussed below.

**Electrochemistry of 4.** In the dc polarograms and cyclic voltammograms of 4 in acetone and $CH_2Cl_2$ the primary *two*-electron reduction wave is followed by a wave at potential corresponding to the reduction of the $\eta^2$-dppe derivative 5. The Nernstian characteristics and two-electron transfer for the primary reduction of 4 are compatible with a molecule in which the two redox centers $[\mu\text{-}(CF_3)_2C_2]Co_2$ are noninteracting in the electrochemical sense.[17]

The ratio of the diffusion-controlled polarographic reduction currents and the voltammetric currents, $i_{pc}$, for 4 and 5 are dependent on the extraneous CO concentration, temperature, scan rate, and dppe concentration in a manner consistent with an ECE process (eq 8).

$$\begin{tikzcd}
\{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5\}_2(\eta^1\text{-dppe}) + 2e \arrow[d] \\
\{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5\}_2(\eta^1\text{-dppe})^{2-} \arrow[d, "\overleftrightarrow{ECE} / \text{dppe}"] \\
[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\eta^2\text{-dppe}) + 2CO
\end{tikzcd} \qquad (8)$$

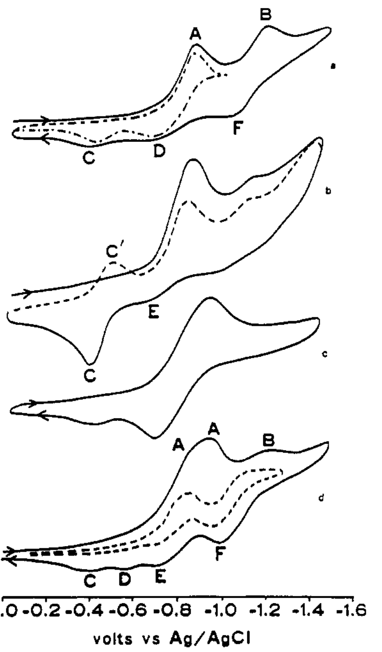

**Figure 3.** Cyclic voltammograms of 4 in $CH_2Cl_2$ on Pt (0.10 mol $dm^{-3}$ TBAP; scan rate 500 mV $s^{-1}$): (a) 293 K (---, repeat scan); (b) 293 K under CO (---, repeat scan); (c) 233 K under CO; (d) 233 K Ar with 1 mol equiv excess of dppe (---, scan rate 50 mV $s^{-1}$).

Coulometry shows that the catalytic chain is short (efficiency is ~0.2 F $mol^{-1}$) and that the products of a bulk two-electron charge transfer are 5 and 1 plus decomposition (eq 9).

$$\begin{tikzcd}
\{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5\}_2(\eta^1\text{-dppe}) \arrow[d] \\
\{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_4(\eta^2\text{-dppe})\} + \{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6\}
\end{tikzcd} \qquad (9)$$

Reaction sequences 8 and 9 are simplistic for what must be a series of structural rearrangements concomitant with, or following, electron transfer. This was borne out by an examination of the cyclic voltammograms (Figure 3).

(a) Two reduction and three oxidation waves are observed at scan rates > 100 mV $s^{-1}$ at 293 K. Only oxidation wave F is significant at scan rates < 100 mV $s^{-1}$, and this forms a reversible couple with B—the couple $5^{0/-}$.

(b) In the presence of CO another reduction wave C′ due to the reduction of $\mu\text{-}(CF_3)_2C_2Co_2(CO)_6$[9] is seen on repeat scans (Figure 3).

(c) At temperatures below 243 K under Ar the primary reduction wave A becomes asymmetric with partial resolution of a new wave, A′, ~0.07 V positive of A at scan rates where the couple $5^{0/-}$ is insignificant. (This asymmetry was reproducible on different electrodes and is unlikely to be due to electrode kinetic effects.)

(d) In $CH_2Cl_2$ at 293 K the oxidation wave in the potential range corresponding to A is at ~−0.68 V at (D) but at <243 K shifts in the presence of CO or dppe to ~−0.75 V (E) despite the increased *iR* drop; at 233 K under CO it is asymmetric with the principal component at −0.68 V and the minor component at ~−0.77 V, while in the presence of dppe at 233 K there are two distinct waves (D and E).

(e) At scan rates >1 V $s^{-1}$ under Ar at 293 K C moves *negative* of C′.

(f) Waves C–E arise from reactions after electron transfer at A.

An interpretation of these electron transfer processes is given in Scheme II in which the main chemical reaction following a two-electron transfer is assumed to be cleavage of one end of the dppe link as the presence of excess dppe

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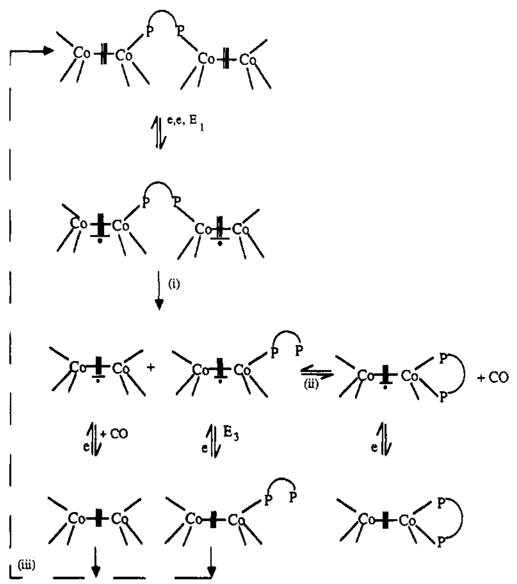
[16] (a) Bond, A. M.; Darensbourg, D. J.; Mocellin, E.; Stewart, B. J. *J. Am. Chem. Soc.* 1981, *103*, 6827. (b) Blagg, A.; Carr, S. W.; Cooper, G. R.; Dobson, I. D.; Gill, J. B.; Goodall, D. C.; Shaw, B. L.; Taylor, N.; Buddington, T. *J. Chem. Soc., Dalton Trans.* 1985, 1213.

[17] Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C.; *J. Am. Chem. Soc.* 1978, *100*, 4248.

**Scheme II**



had no marked effect on the electrochemical parameters for the primary reduction wave A. Dissociation (i) gives a $\eta^1$-dppe complex and a coordinatively unsaturated complex $\mu$-$(CF_3)_2C_2Co_2(CO)_5^{\bullet-}$; this can react with extraneous CO to give $1^{\bullet-}$ or dppe (to give initially the $\eta^1$-dppe complex).

Wave C is therefore attributed to oxidation of either $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5^{\bullet-}$ or $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6^{\bullet-}$. The primary oxidation wave is due to the oxidation of either $4^{\bullet-}$ or $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppe})^{\bullet-}$ depending on the temperature and scan rate. At 293 K or at scan rates <2 V $s^{-1}$ wave D represents the oxidation of the $\eta^1$-dppe species. This is consistent with the increased current of D under CO at 233 K as ring closure (ii) becomes insignificant. When the chemical reaction (i) is slower (low temperatures, fast scan rates), wave E, due to the oxidation of $4^{\bullet-}$, dominates. Once radical anions produced by the dissociation (i) are oxidized, recombination by way of (iii) can occur to regenerate 4. This leaves the question of why A is asymmetric at low temperatures. There will be little difference in the reduction potentials of 4 and the $\eta^1$-dppe species as the reduction potentials of Lewis base derivatives are a function of the number of donor atoms—in fact $E_3$ could be less than $E_1$. If this is so, a homogeneous electron transfer step (eq 10) could take place, the thermodynamic constraint being the small difference in reduction potentials.

$$4 + [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppe})^{\bullet-} = 4^{\bullet-} + [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5(\eta^1\text{-dppe}) \quad (10)$$

Consequently, at ambient temperatures, most of the peak current for A could correspond to the reduction of the $\eta^1$-dppe. At lower temperatures, where the production of the $\eta^1$-dppe species is slower, current due to the reduction of 4 gives rise to the asymmetric wave. This correlates with the behavior of the oxidation waves on the reverse scan.

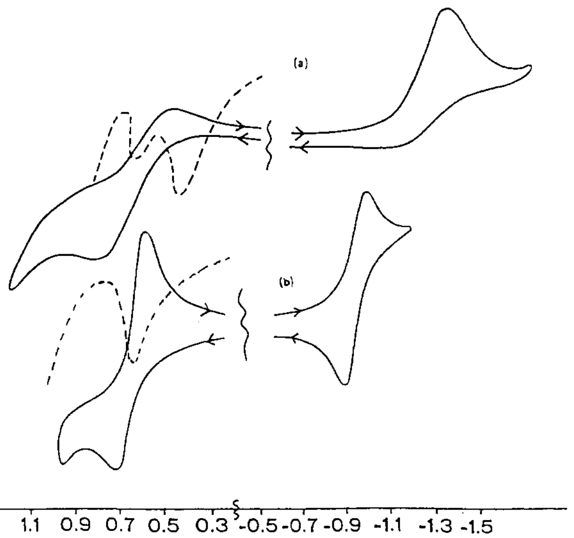


**Figure 4.** Cyclic voltammograms in $CH_2Cl_2$ on Pt at 293 K (0.10 mol $dm^{-3}$ TBAP; scan rate 200 mV $s^{-1}$ - - -, differential pulse polarogram on Hg at 293 K; drop time 0.1 $s^{-1}$): (a) 8 and (b) 7.

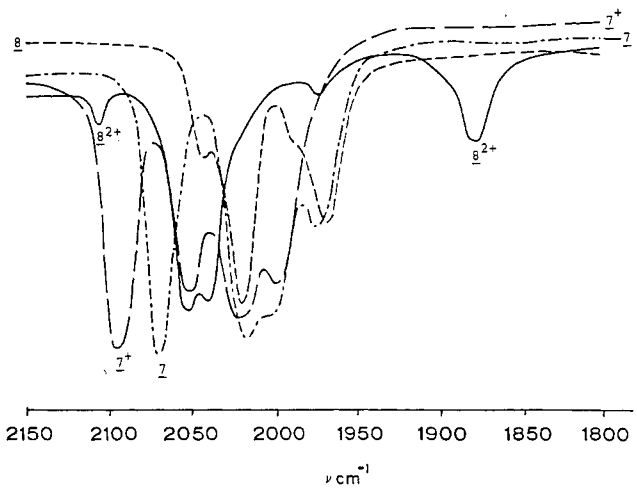


**Figure 5.** Infrared spectra in $CH_2Cl_2$ of ttas complexes, 2150–1800 $cm^{-1}$; 7 (– –), $7^+$ (– - –), 8 (- - -), and $8^+$ (—).

**Redox Chemistry of ttas Derivatives.** All ttas derivatives 6–8 undergo a one-electron reduction step[18] (eq 11), but electrochemical and chemical reversibility is variable.

$$[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_{6-n}(ttas) + e = \{[\mu\text{-}(CF_3)_2Co_2(CO)_{6-n}(ttas)]\}^{\bullet-} \quad (n = 1\text{–}3) \quad (11)$$

Thus it is quasi-reversible and chemically irreversible for 6, electrochemically and chemically reversible for 7, and quasi-reversible and reversible at low temperatures for 8. The chemical reaction following electron transfer to 8 is dissociation of an $Me_2As$ group to give 7, evidenced by the appropriate waves for the couple $7^{0/-}$ on the repeat scans. Rapid ECE reaction occurs on the formation of $6^{\bullet-}$, and 7 is the only neutral product at the electrode surface after two scans.

An interesting feature of their electrochemistry was a reversible one-electron oxidation couple (eq 12) at ~0.6 V on Hg and Pt (Figure 4) (with 8 this wave is obscured on Pt by a subsequent oxidation process, vide infra) which is chemically reversible at low temperatures.

$$\{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_{6-n}(ttas)\}^+ + e \overset{E_{1/2}}{=} [\mu\text{-}(CF_3)_2C_2]Co_2(CO)_{6-n}(ttas) \quad (12)$$

$$E_{1/2}(6) = 0.6;\ E_{1/2}(7) = 0.61\ V;\ E_{1/2}(8) = 0.62\ V$$

Oxidation of the $[\mu\text{-}(CF_3)_2C_2]Co_2L_n$ moiety has been observed with other derivatives where at least three Lewis bases are coordinated,[5,19] but in the ttas system the very small difference in $E_{1/2}$ values above suggests that the *ligand* rather

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(18) Cunninghame, R. G.; Downard, A. J.; Hanton, L. R.; Jensen, S. D.; Robinson, B. H.; Simpson, J. *Organometallics* **1984**, *3*, 180.

(19) Bond, A. M.; Dawson, P. A.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1413.

than the cluster unit is being oxidized ttas is irreversibly oxidized at $E_{pa} = 0.3$ V vs. Ag/AgCl, and, as coordination of the ttas to the metal ion should make it more difficult to oxidize, it is probable that oxidation takes place at a $Me_2As$ group. Stoichiometric oxidation of **7** produced the unstable brown/green $\mathbf{7}^+$ which has a $\nu(CO)$ profile similar to **6** but shifted to higher energy by ~20 cm$^{-1}$ (Figure 5). Two explanations for this shift are that either the structure has remained intact and the shift is the result of the positive charge on the cluster or oxidation of the ligand has weakened coordination of a $Me_2As$ group. The energy levels with Co–Co character are not greatly perturbed as shown by a similar electronic transition at ~595 nm in both **7** and $\mathbf{7}^+$. A detailed assignment of the electronic spectra of ($\mu$-alkyne)$Co_2(CO)_6$ is not possible because of the limited photoelectron data, but bands between 1000 and 350 nm are unlikely to be associated with the ligand—for example, only metal-based d–d transitions are found in the spectra of Co(III), Ni(II), Pt(II), and Rh(III) ttas complexes[20] —and it is reasonable to assign the lowest energy band to transitions from the upper bonding levels. There is a red shift in the charge transfer band of **7** at 392 nm (a band which is likely to have considerable Co–CO character) on oxidation.

The oxidation behavior of **8** is more difficult to interpret as two waves are resolved on Hg—the response on Pt corresponds to a two-electron transfer. The second electron transfer will be from the cluster (eq 13) as other

$$\{[\mu\text{-}(CF_3)_2C_2]^+Co_2(CO)_3(ttas^+) + e = \{[\mu\text{-}CF_3)_2C_2]Co_2(CO)_3(ttas^+)\} \quad (13)$$

$[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_3L_3$ derivatives have a similar oxidation process. However, the diffusion currents for the two processes are not equal, do not individually correspond to a one-electron transfer on Hg, and vary with drop time and temperature. This suggests that Hg is not an "innocent" electrode or, more likely, that the disproportionation reaction (14) is important.

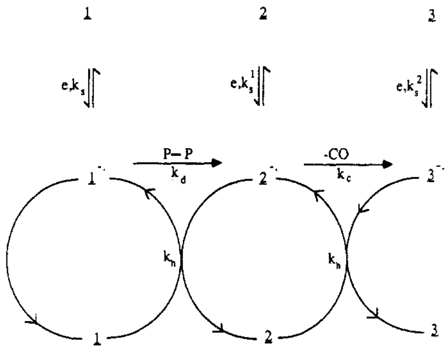
$$2(\mathbf{8}^{\bullet+}) = \mathbf{8} + \mathbf{8}^{2+} \quad (14)$$

Stoichiometric one-electron oxidation could not be achieved electrochemically or chemically. Unstable green solutions due to $\mathbf{8}^{2+}$ were produced, and the $\nu(CO)$ profile was unlike **8**, being characterized by a band at relatively high energy, 2105 cm$^{-1}$, and a bridging $\nu(CO)$ band at 1879 cm$^{-1}$. Support for a notional structure change came from the electronic spectra where the bands at 620 and 502 nm in **8** disappear and a more intense band arises at 427 nm; a charge transfer band is seen at 350 nm in $\mathbf{8}^{2+}$.

**Electrode-Induced Reactions between [$\mu$-$(CF_3)_2C_2$]$Co_2(CO)_6$ and L-L.** The electrochemical responses of $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ in the presence of L-L (L-L = dppm, dppe, ttas) were recorded in $CH_2Cl_2$, acetone, and THF at Hg and Pt electrodes. Infrared and TLC analyses demonstrated that no thermal reactions took place in $CH_2Cl_2$ within the polarographic and CV time scale used. In THF and acetone this was not necessarily the case, especially for the ttas reactions, so the results given below refer to $CH_2Cl_2$.[21]

**dppm and dppe.** Cyclic voltammograms at Pt when L-L = dppm or dppe conform to the recognized electron transfer chain (ETC) catalyzed behavior for metal carbonyl clusters.[8,22] The product/reactant distribution being a function of the scan rate, temperature, and relative amount of nucleophile. Incremental addition of the ligand leads to a rapid increase in the current of a wave at $E_{pc} \approx -0.90$ V. This is undoubtedly due to an ETC reaction to give a product with only one CO-substituted per cluster unit—that is, **2** and either **4** or a $\eta^1$-dppe complex.

Scheme III



An additional wave is seen at more negative potentials $E_{pc} \approx -1.2$ V, and while this could be assigned to the chemically reversible couples $[\mathbf{3}]^{0/-}$ or $[\mathbf{5}]^{0/-}$, the wave is close to the potential for the irreversible reduction of $\mathbf{1}^{\bullet-}$.[9] From an analysis of the companion oxidation current which must be due to the product couple, it is possible to deduce the amount of $\mathbf{3}^{\bullet-}$ or $\mathbf{5}^{\bullet-}$ at a given nucleophile concentration and hence the extent of the ring closure ETC reaction ((3) and (4)).

The *i–E* responses can be interpreted by using Scheme III (a similar scheme can be written for dppe). Simulation[23] suggests that rate constants for heterogeneous electron transfer are in the order $k_s > k_s^1 > k_s^2$, and these are all smaller than those for homogeneous electron transfer ($k_h$). The latter should not change significantly with ligand as the reacting molecules have a common skeletal framework. Consequently, the $i_d$(or $i_{pc}$)(product)/$i_d(i_{pc})$(reactant) ($\equiv i^P/i^R$) ratio should be determined by the rates of intermolecular nucleophilic attack $k_d$ and intramolecular ring closure $k_c$ (ignoring concomitant stereochemical changes). Since $i_d^P/i_d^R$ and $i_{pc}^P/i_{pc}^R$ are smaller for dppm for a given nucleophile concentration, the first ETC cycle is *faster for dppe*. This was bourne out by the coulometry (in $CH_2Cl_2$ the turnover was >3000 for dppe and >1500 for dppm) and preparative observations.[1] The solvent has little influence on the voltammetric responses.

The converse is true for the ring closure $k_c$ which is considerably *faster for dppm* probably as a consequence of the tighter "bite" of a dppm ligand. Ring closure is also faster in polar solvents such as THF, but as this is also the case for thermal conversion of **2** → **3**, or **4** → **5**, it may not be an electrochemical effect. Ring closure for both dppm and dppe is however *slower* than the initial nucleophilic attack $k_d$. Decreasing rates of nucleophilic attack with increasing ligand coordination is the norm for the ETC reaction with monodentate ligands as well, a trend related to the stability of the coordinatively unsaturated 17e center in the activated complex.[8]

Stereochemical changes, taking place on reduction, have been ignored in Scheme III. Peak potentials for the primary and secondary reduction processes correlate with those of **2** and **3** (dppm) and **4** and **5** (dppe), but this could be deceptive as the stereochemistry at the electrode surface

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[20] Cunninghame, R. G.; Hanton, L., unpublished work, University of Otago.

[21] The results in acetone were similar to those in $CH_2Cl_2$ apart from the expected shift in potential.

[22] Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* 1981, 265.

[23] Bond, A. M.; Robinson, B. H., work in progress at Deakin and Otago Universities.

may be different to those of the isolated products. Indeed, it is unlikely that **4** is formed by a simultaneous nucleophilic attack on *two* $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6{}^{\bullet-}$—the initial $\eta^1$-dppe configuration, assumed in Scheme III, is more reasonable.

At >1.5 mol equiv of either dppm or dppe the CV's at Pt closely resemble those described for **2** and **4** respectively. Of particular note is that $E_{pc} > E_{pa}$ ($E_{pa}$ is a function of scan rate but independent of dppm concentration) for the first product wave in the dppm system, confirming the analysis given for **2** that a stereochemical change from axial-$\eta^1$ to equatorial-$\eta^1$ with nil current flow takes place on radical anion formation. Similarly, analysis of the oxidation waves on scan reversal for the dppe system reaches the same conclusions outlined in the interpretation of the electrochemistry of **4**. Dissociation of the $\mu$-$\eta^1$ species occurs on two-electron transfer, and the oxidation waves can be attributed to a $\eta^1$-dppe radical anion (probably of equatorial conformation) and $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5{}^{\bullet-}$ (or $1^{\bullet-}$). Given this overall scenario one can readily give a qualitative interpretation of the scans at various scan rates and lower concentrations of ligand.

This discussion demonstrates the complexity of ETC catalyzed reactions with polydentate Lewis bases. Because of the large number of variables required for digital simulation or convolution analysis, the large amount of computer time required for iterative optimization, and the fact that the voltammetric data were affected by adsorption ($i_p$ was not necessarily $\propto v^{1/2}$), we have not given a quantitative description of these systems; this will be given elsewhere.[23]

**ttas.** The essential features of the catalytic reaction of **1** with ttas have already been described.[18] The conversion **7** → **8** is not an ETC process shown by the absence of appropriate waves in the polarographic and voltammetric data and the coulometry which gives an efficiency of ~1 F mol$^{-1}$. It is significant that this conversion to a $\eta^3$ species requires a substantial structural reorganization.[1] There is no evidence in the electrochemical data for stereochemical configurations other than **7** and **8**, and indeed none would be expected as the substitution of CO group on *one* cobalt atom of the cluster should be the most efficient process. From the $i^P/i^R$ ratios it is clear that the rate of nucleophilic attack by ttas to give the $\eta^1$-species is slower for ttas than dppm or dppe. This is attributed to the lower basicity of ttas.

## Conclusion

Polydentate derivatives of $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ all undergo a primary one-electron reduction step to the respective radical anions. Subsequent to reduction the $\eta^1$-dppm (**2**) and $\mu$-$\eta^1$-dppe (**4**) complexes change their stereochemistry as well as participate in $\bar{E}C\bar{E}$ reactions to give the disubstituted products. Only the $\eta^1$-ttas derivative **6** participates in an $\bar{E}C\bar{E}$ reaction.

Utilizing these radical anions, it is possible to carry out selective electron transfer chain catalyzed sequential substitution of $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ by polydentate ligands. Catalytic efficiencies decrease with increasing ligation and are virtually zero for a $\eta^2 \rightarrow \eta^3$ conversion. The degree of selectivity for a particular ligand depends on solvent, reaction temperature, and reductant as well as the relative rates of the primary and secondary ligation steps. Low-temperatures and nonpolar solvents accentuate the selectivity. Electrode initiation of an ETC reaction gives greater control compared to the "sledgehammer" approach using BPK. There are three reasons for this. First, the reduction potential of BPK is sufficient to reduce the radical anions to dianions which rapidly fragment. Second, heterogeneous as well as homogeneous oxidation of the primary radical anion will occur with electrode initiation at the reduction potential of the reactant, thus preventing further substitution. Third, the concentration of the radical anions is lower through electrochemical generation which in turn slows the rate of formation of other products.

Irrespective of the thermodynamically preferred stereochemistry of the neutral complex the ETC reactions proceed via a common pathway in which the ETC process assembles the ligand on one cobalt atom. We consider that this supports activation by Co–Co bond stretching or breaking in the radical anion, which creates a 17e center rather than a CO-dissociative mechanism. A 17e center is stabilized by coordination of the Lewis base, and hence further nucleophilic attack is encouraged at that metal atom. Moreover, the extra flexibility achieved in the activated, bond-opened radical anion would account for the fast stereochemical changes that are observed.

**Registry No.** **1**, 37685-63-5; **2**, 108151-11-7; **3**, 84896-13-9; **3′**, 87828-97-5; **4**, 108151-12-8; **5**, 108151-13-9; **5′**, 108151-14-0; **6**, 87828-96-4; **7**, 87828-97-5; $7^{+}\cdot ClO_4{}^{-}$, 108151-15-1; **8**, 87828-98-6; $8^{2+}\cdot(ClO_4)_2$, 108151-16-2; dppm, 2071-20-7; ttas, 2774-08-5; dppe, 1663-45-2; $[\mu\text{-}Ph_2C_2]Co_2(CO)_4(\mu\text{-}2^2\text{-dppm})$, 52659-27-5; $[\mu\text{-}Ph_2C_2]Co_2(CO)_4(\mu\text{-}\eta^2\text{-dppe})$, 55925-96-7.