

Electron Transfer in Organometallic Clusters. 9.¹ Redox Chemistry of $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ and $\text{RCCo}_3(\text{CO})_{9-n}(\text{L-L})_n$ ($\text{L-L} \equiv$ Polydentate Ligands)

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Electrochemical studies of $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$, $[\text{RCCo}_3(\text{CO})_8]_2(\mu\text{-dppe})$, $\text{RCCo}_3(\text{CO})_7(\mu\text{-dppe})$ (or dppm), $\text{RCCo}_3(\text{CO})_5(\text{dppm})_2$, and $\text{RCCo}_3(\text{CO})_6(\text{tpme})$ ($\text{R} = \text{Ph}, \text{CH}_3$) are described. Although the primary reduction step is one-electron for all derivatives, a fast ECE process gives rise to an overall two-electron diffusion currents for the primary wave unless the Co-Co bond is spanned by a chelate ligand. The $i\text{-E}$ responses for $[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$ and $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ are also complicated by ECE and EC reactions and are solvent dependent. An explanation is offered on the basis of fast ligand dissociations with the radical anions $\text{RCCo}_3(\text{CO})_8\text{L}^-$ and $\text{RCCo}_3(\text{CO})_8(\text{L-L})^-$ ($\text{L} \equiv \text{PR}_3$; $\text{L-L} \equiv$ "dangling" polydentate ligand) coupled with ligand and solvent-dependent chemical and homogeneous electron-transfer rates. Reversible oxidation was recognized in the series $[\text{RCCo}_3(\text{CO})_5(\text{dppm})_2]^{2/1/0/1-}$ and $[\text{RCCo}_3(\text{CO})_6\text{tpme}]^{1/0/1-}$. $\text{RCCo}_3(\text{CO})_7(\text{PPh}_3)_2$ was obtained by an ETC reaction.

The preparation and characterization¹ of a series of complexes containing polydentate ligands $[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$, $\text{RCCo}_3(\text{CO})_7\text{dppm}$, $\text{RCCo}_3(\text{CO})_7\text{dppe}$, $\text{RCCo}_3(\text{CO})_5(\text{dppm})_2$, and $\text{RCCo}_3(\text{CO})_6\text{tpme}^1$ provided an opportunity to study the influence of ligational parameters on current-voltage responses for capped cluster derivatives and to provide the background information required for a kinetic investigation of electron transfer chain catalyzed reactions with cluster substrates.

Previous redox studies of Lewis base substituted tricobalt carbon clusters $\text{RCCo}_3(\text{CO})_{9-n}\text{L}_n$ have been restricted to $\text{L} = \text{PR}_3$ or $\text{P}(\text{OR})_3$ with $n = 1-3$.²⁻⁴ Substituent parameters can be calculated from trends in the reduction potentials, and, in general, chemical reversibility for the reduction process decreases as the extent of substitution increases. With increasing electron density on the cluster oxidation becomes viable, and at $n = 3$ and $\text{L} = \text{P}(\text{OR})_3$, oxidation was shown to be chemically reversible. Bidentate and tridentate ligands offer ligational properties which could modify these trends noted with monodentate ligands. First, the clamping effect of a chelating ligand may lead to an increase in chemical reversibility. Second, processes at or near the electrode surface may include structural reorganization (which may be catalytic) as well as electron transfer and the observed electrochemical responses may arise from a different isomer to the neutral reactant.

These expectations were indeed central to the electrochemistry of the molecules described herein. The redox chemistry of the derivatives provides a framework for an interpretation of the transient and bulk electrochemical behavior on the addition of a particular ligand to $\text{RCCo}_3(\text{CO})_9$ in the presence of an electrode and the elucidation of the ETC mechanism which is described in the following paper. Included in this paper is a reinvestigation

Table I. Polarographic Data for Derivatives of $\text{RCCo}_3(\text{CO})_9^a$

cluster	reduction (oxidation)			
	$E_{1/2}^b$ V	slope ^c of log plot	$w_{1/2}^d$	i_d/i_d^e (FCH) ^e
$\text{PhCCo}_3(\text{CO})_8\text{PPh}_3$	-0.56	54	94	1.8 ± 0.2
$\text{CH}_3\text{CCo}_3(\text{CO})_8\text{PPh}_3$	-0.58	53	89	1.8 ± 0.2
$[\text{PhCCo}_3(\text{CO})_8]_2\text{dppe}$	-0.69	63		3.6 ± 0.2
$[\text{CH}_3\text{CCo}_3(\text{CO})_8]_2\text{dppe}$	-0.75	60		3.8 ± 0.2
$\text{PhCCo}_3(\text{CO})_7\text{dppe}$	-1.09	60	98	1.0
$\text{CH}_3\text{CCo}_3(\text{CO})_7\text{dppe}$	-1.09	55	96	1.0
$\text{PhCCo}_3(\text{CO})_7\text{dppm}$	-0.99	60	98	1.0
$\text{CH}_3\text{CCo}_3(\text{CO})_7\text{dppm}$	-1.03	60	94	1.0
$\text{PhCCo}_3(\text{CO})_5(\text{dppm})_2$	-1.46	90		1.0
	(0.35)	45		1.0
	(0.63)	50		
$\text{CH}_3\text{CCo}_3(\text{CO})_5(\text{dppm})_2$	-1.50	110		1.0
	(0.30)	60		1.0
	(0.64)			
$\text{PhCCo}_3(\text{CO})_6\text{tpme}$	-1.48	85		1.0
	0.72	60		1.0

^a In CH_2Cl_2 at 295 K; 0.1 mol dm^{-3} Bu_4NClO_4 ; 5×10^{-4} mol dm^{-3} cluster except $[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$ at 2.5×10^{-4} mol dm^{-3} ; drop time, 0.5 s; potential vs. Ag/AgCl (LiCl -acetone). ^b Scan rate, 10 mV s^{-1} . ^c Plot E vs. $\log [(i_d - i)/i]$. ^d Peak width at half-height in differential pulse polarograms; scan rate, 5 mV s^{-1} . ^e Ratio of limiting current for cluster derivative to that of $\text{PhCCo}_3(\text{CO})_9$ under identical conditions.

of the archetypal derivatives $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ as it became clear that their redox behavior was not as simple as previously described.²

Results

In general the electrochemical response is independent of the alkyl or aryl substituent R on the apical carbon atom, and the data in this paper will refer to $\text{R} = \text{Ph}$ and CH_3 . Although isomers have been isolated for most of the dppe and dppm derivatives,¹ experiments in the absence of an electrode showed that interconversion of the isomers did not take place in bulk solution during the time scale of the transient electrochemistry. Polarographic and voltammetric data are given in Tables I and II.

$\text{RCCo}_3(\text{CO})_8\text{PPh}_3$. Provided clean electrodes were used, a single reduction wave was observed for $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ in a number of solvents (THF, acetone, CH_2Cl_2 , CH_3CN) with all techniques used, pulse and differential pulse

(1) (a) Part 8. Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics*, first of three papers in this issue. (b) $\text{dppm} \equiv$ bis(diphenylphosphino)methane; $\text{dppe} \equiv$ bis(diphenylphosphino)ethane; $\text{tpme} \equiv$ 1,1,1-tris((diphenylphosphino)methyl) ethane.

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

(3) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* 1983, 2, 943.

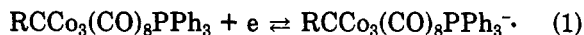
(4) Bezems, G. J.; Reiger, P. H.; Visco, S. J. *J. Chem. Soc., Chem. Commun.* 1981, 265.

Table II. Cyclic Voltammetry Data at Pt for Derivatives of $RCCO_3(CO)_3$

cluster	reduction			oxidation			
	$[(E_p^a + E_p^c)/2], V$	i_p^a/i_p^c	$\Delta E_p, mV$	i_p^c/i_p^c (PhCCO ₃)	E_p^a, V	E_p^c, V	i_p^c/i_p^a
PhCCO ₃ (CO) ₈ PPh ₃		1.0		
CH ₃ CCO ₃ (CO) ₈ PPh ₃		1.0		
[PhCCO ₃ (CO) ₈] ₂ dppe	-0.66	0.9	210 ^b	3.1
[CH ₃ CCO ₃ (CO) ₈] ₂ dppe	-0.69	0.9	150 ^b	3.3
PhCCO ₃ (CO) ₇ dppe	-1.08	1.0	80	1.0	0.88	0.84	0.2
CH ₃ CCO ₃ (CO) ₇ dppe	-1.09	1.0	80	0.9	0.90	0.82	0.5
PhCCO ₃ (CO) ₇ dppm	-0.98	1.0	60	1.0	1.00		
CH ₃ CCO ₃ (CO) ₇ dppm	-1.03	1.0	60	0.8	0.97		
PhCCO ₃ (CO) ₅ (dppm) ₂	-1.44	1.0	60	0.6	0.39	0.33	1.0
					0.70	0.64	0.5
CH ₃ CCO ₃ (CO) ₅ (dppm) ₂	-1.52	1.0	60	0.5	0.36	0.29	1.0
					0.48	0.41	0.1
PhCCO ₃ (CO) ₆ tmpe	-1.43	1.0	140	1.0	0.76	0.67	1.0

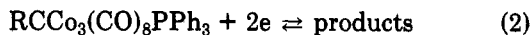
^a In CH₂Cl₂ at 295 K; 0.1 mol dm⁻³ Bu₄NClO₄; 5 × 10⁻⁴ mol dm⁻³ cluster except for [RCCO₃(CO)₈]₂dppe at 2.5 × 10⁻⁴ mol dm⁻³; potential vs. Ag/AgCl (LiCl-acetone). Results independent of scan rate (0.05–5 V s⁻¹) unless noted otherwise). ^b Scan rate, 50 mV s⁻¹. ^c Scan rate, 800 mV s⁻¹.

voltammetry and linear sweep voltammetry. Cyclic voltammetry showed (Figure 1) that the charge transfer was chemically reversible, $i_{pa}/i_{pc} \approx 1$, and the extra oxidation waves noted previously^{2,4} were absent if clean electrodes were used. Diagnostic data⁵ such as constant functions $i_{pc}/V^{1/2}$ and i_{pa}/i_{pc} over a range of scan rates were consistent with fast diffusion-controlled charge-transfer reaction. Other criteria such as the slope of the E vs. $\log [(i_d - i/i)]$ from the pulse polarograms, peak width at half-height in the differential pulse polarograms, and the ΔE_p values from the cyclic voltammograms pointed (Tables I and II) to a reversible one-electron process (eq 1).



Despite these data the cyclic voltammograms could only be approximately simulated, assuming (1), by the use of a much larger diffusion coefficient and smaller heterogeneous rate constant compared to $RCCO_3(CO)_9$ which did not seem physically reasonable (these observations have been made with other monodentate complexes $RCCO_3(CO)_8L$ as well⁶).

A separate estimate of n was obtained by comparison of the diffusion currents for the reduction wave in the various techniques with equal concentrations of known one-electron substrates, such as PhCCO₃(CO)₉ and Fe₃(C-O)₁₂, which are assumed to have similar diffusion coefficients (see Experimental Section). In all solvents, and over a range of scan rates, the diffusion currents for the reduction process were greater than expected for a one-electron transfer and values of n between 1.6 and 2 were obtained. Further, the cyclic voltammograms could be satisfactorily simulated with reasonable diffusion coefficients and heterogeneous rate constants on the assumption that two electrons are transferred (eq 2).



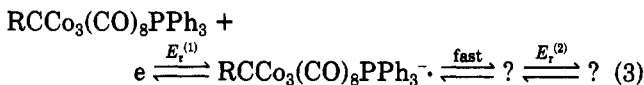
Enhanced currents (i.e., over one-electron transfer) could arise from an $\bar{E}_r\bar{C}\bar{E}_r$, $\bar{E}_r\bar{E}_r$,⁵ or catalytic process. Constant potential coulometry at -0.7 V in CH₂Cl₂ gave values of n between 1.7 and 1.95 (Table III) at 3% of the initial current which argue against the catalytic mechanism and confirms the overall two-electron step (2). Given that there is a variation in the enhanced diffusion currents with scan rate, we conclude that an $\bar{E}\bar{C}\bar{E}$ mechanism operated when

Table III. Coulometric Data^a

complex	potential ^b	electron/molecule ^c
PhCCO ₃ (CO) ₈ PPh ₃	-0.80	1.8 ± 0.2
PhCCO ₃ (CO) ₇ dppe	-1.00	0.95 ± 0.05
PhCCO ₃ (CO) ₇ dppm	-1.00	1.00 ± 0.05
PhCCO ₃ (CO) ₆ tmpe	-1.43	0.98 ± 0.05
[PhCCO ₃ (CO) ₈] ₂ dppe	-0.82	3.4 ± 0.3
CH ₃ CCO ₃ (CO) ₈ PPh ₃	-0.80	1.7 ± 0.2
CH ₃ CCO ₃ (CO) ₇ dppe	-1.00	1.00 ± 0.05
CH ₃ CCO ₃ (CO) ₇ dppm	-1.00	1.00 ± 0.05
[CH ₃ CCO ₃ (CO) ₈] ₂ dppe	-0.98	3.2 ± 0.4

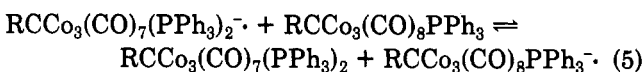
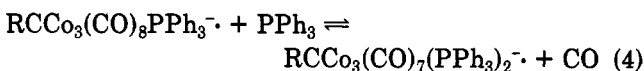
^a In CH₂Cl₂/TBAP at 293 K. ^b Volts vs. Ag/AgCl. ^c Values at 3–5% of initial current.

a monodentate ligand is coordinated to be Co₃C unit (eq 3). Possibilities for this mechanism will be discussed



below; a detailed theoretical interpretation including data from a variety of $RCCO_3(CO)_8L$ complexes will be considered elsewhere.⁶

Another reduction wave ~0.2 V negative of E_{pc} - [RCCO₃(CO)₈PPh₃] appeared at high concentrations of PPh₃. This wave is assigned to the reduction of $RCCO_3(CO)_7(PPh_3)_2$ formed via an ETC reaction (eq 4 and 5).



$RCCO_3(CO)_7(PPh_3)_2$ complexes had not been obtained from thermal reactions,⁷ contrary to the general observation that the highly substituted complexes are best prepared by thermal reactions. Substitution of a second PPh₃ was achieved electrochemically by reducing [RCCO₃(CO)₈PPh₃] at -0.7 V in CH₂Cl₂ in the presence of a 20-mol excess of PPh₃. For this step the current efficiency is ~0.6 electron/molecule $RCCO_3(CO)_8PPh_3$ and the current decreased linearly with time. The new $RCCO_3(CO)_7(PPh_3)_2$ complexes were characterized by analysis (for R = Ph) and IR spectroscopy. The $\nu(CO)$ profiles are similar to those of other $RCCO_3(CO)_7L_2$ complexes in which there is no CO bridging of a Co-Co bond and an axial/equatorial con-

(5) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods Fundamentals and Application"; Wiley: New York, 1980.

(6) Unpublished work at University of Otago and Deakin University (A. M. Bond).

(7) Matheson, T. W.; Robinson, B. H.; Tham, W. S. *J. Chem. Soc.* 1971, 1457.

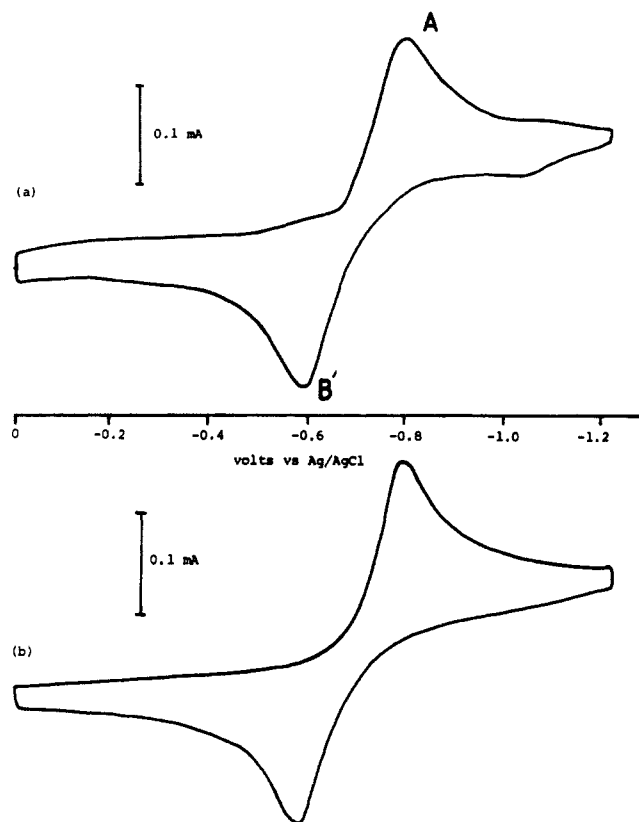
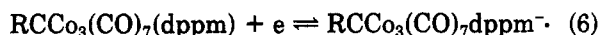


Figure 1. (a) Cyclic voltammogram of $\text{CH}_3\text{CCO}_3(\text{CO})_8\text{PPh}_3$ in CH_2Cl_2 at Au (500 mV s^{-1} , 295 K) under Ar. (b) Cyclic voltammogram of $[\text{CH}_3\text{CCO}_3(\text{CO})_8]_2\text{dppe}$ in CH_2Cl_2 at Au (500 mV s^{-1} , 295 K) under Ar.

formation of the PPh_3 groups is predicted.⁷ They decompose rapidly in solution and instantly revert to $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ in the presence of CO.

$\text{RCCo}_3(\text{CO})_7\text{dppm}$. The complexes $\text{RCCo}_3(\text{CO})_7\text{dppm}$ were the only products isolated from ETC reactions between $\text{RCCo}_3(\text{CO})_9$ and dppm; two isomers, A (major) and B, were identified, and a configuration in which dppm spanned a Co-Co bond was established for A.¹

The i - E responses for both isomers in CH_2Cl_2 or acetone at 293 or 213 K, under Ar or CO, show an electrochemically and chemically reversible reduction step and a multielectron irreversible oxidation (Tables I and II). A comparison of i_{pc} or i_d with those of equimolar $\text{PhCCo}_3(\text{CO})_9$, and the electrochemical and coulometric data (Table I-III) establish the primary reduction step as a diffusion-controlled one-electron transfer (eq 6). This result focuses



on the important distinction between those complexes where there is one phosphorus donor atom per cluster unit when an ECE mechanism gives rise to greater than one-electron transfer and $\text{RCCo}_3(\text{CO})_9$ and $\text{RCCo}_3(\text{CO})_7(\text{L-L})$ where diffusion-controlled one-electron reduction is the norm. Despite the evidence for chemical reversibility, reduction of $\text{PhCCo}_3(\text{CO})_7\text{dppm}$ in situ in the ESR cavity did not give detectable paramagnetic species.

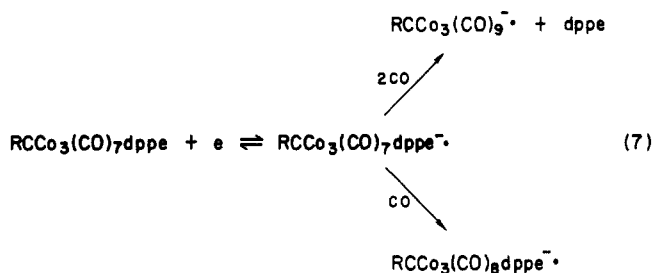
There were no apparent differences in the i - E responses for isomers A and B in CH_2Cl_2 , so it is possible that, on reduction, only one isomer exists on the electrode surface. If we assume that A is the isomer, then, providing $E_{pc}(\text{A}) < E_{pc}(\text{B})$, a fast "cross reaction"⁸ would give only one wave for B on the electrochemical time scale. Electrolysis of B

at -0.70 V in CH_2Cl_2 gave A, but since this was within the time scale of thermal interconversion, the electroactive isomer cannot be further defined. $\text{RCCo}_3(\text{CO})_5(\text{dppm})_2$ or $\text{RCCo}_3(\text{CO})_6(\text{dppm})_2$ were not formed by any electrocatalytic reaction chemistry of $\text{RCCo}_3(\text{CO})_7\text{dppm}$ in the presence of dppm.

$\text{RCCo}_3(\text{CO})_7\text{dppe}$. While the general picture for $\text{RCCo}_3(\text{CO})_7\text{dppe}$ derivatives was the same as that for $\text{RCCo}_3(\text{CO})_7\text{dppm}$ (chemically reversible one-electron couples), the responses on Hg tended to be erratic and those on Pt less electrochemically well-behaved. Under CO, in CH_2Cl_2 , a minor reduction wave was seen at $E_{pc} \approx -0.5 \text{ V}$ attributable to the reduction of $\text{RCCo}_3(\text{CO})_9$, whereas, under Ar, a small reduction wave $\sim 0.2 \text{ V}$ positive of E_{pc} [$\text{RCCo}_3(\text{CO})_7\text{dppe}$] was observed at slow scan rates; this disappeared at low temperatures. The potential of this latter wave is consistent with the reduction of the species $\text{RCCo}_3(\text{CO})_8\text{dppe}$. No paramagnetic species were observed when $\text{RCCo}_3(\text{CO})_7\text{dppe}$ was reduced at E_{pc} in CH_2Cl_2 in the ESR cavity.

In acetone, under Ar, the primary reduction wave is followed by a second wave for which i_{pc} decreases with increasing scan rate; a companion oxidation wave also appears. This is consistent with the formation by an ETC reaction of a more highly substituted derivative from $\text{RCCo}_3(\text{CO})_7\text{dppe}$ and extraneous dppe, but this could not be confirmed by bulk electrolysis experiments.

All these observations point to a slow quasi-reversible one-electron transfer with minor decomposition of the primary radical anion $\text{RCCo}_3(\text{CO})_7\text{dppe}^-$ to $\text{RCCo}_3(\text{CO})_9$ and $\text{RCCo}_3(\text{CO})_8\text{dppe}$ under CO or in $\text{CH}_2\text{Cl}_2/\text{Ar}$, respectively (eq 7).



$[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$. Not unexpectedly in view of the complexities of the i - E responses for $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ and $\text{RCCo}_3(\text{CO})_7\text{dppe}$, i - E responses for $[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$ (the isomer characterized by X-ray crystallography)¹ were complicated and solvent dependent. Data for two solvents, CH_2Cl_2 and acetone, will be described.

In CH_2Cl_2 under Ar at 293 K the data for the primary reduction process are consistent with an electrochemically quasi-reversible charge transfer which is apparently chemically reversible (Figure 1). Thus ΔE_p increased from ~ 130 at 20 mV s^{-1} to 240 mV at 500 mV s^{-1} but $i_{pa}/i_{pc} \approx 1$, and $(E_{pc} + E_{pa})/2$ remains constant at -0.69 V (a potential consistent with a complex with one donor atom per RCCo_3 unit). The quasi-reversible behavior is confirmed by the nonsuperposition of the forward and backward convoluted⁹ CV, particularly at low scan rates. A second couple with small peak currents appears $\sim 0.4 \text{ V}$ negative of the primary process for which i_{pc} increases with decreasing scan rate (Figure 1). This can be assigned to $[\text{RCCo}_3(\text{CO})_7\text{dppe}]^{0/-}$.

Measurement of the polarographic diffusion currents for the primary reduction process (dme, pulse, and differential pulse) relative to those of known one-electron couples gave values of $2 < n < 4$. These enhanced currents were also

(8) Bond, A. M.; Darensbourg, D. J.; Mocellin, E.; Stewart, B. J. *J. Am. Chem. Soc.* 1981, 103, 6827.

(9) Reference 5, p 238.

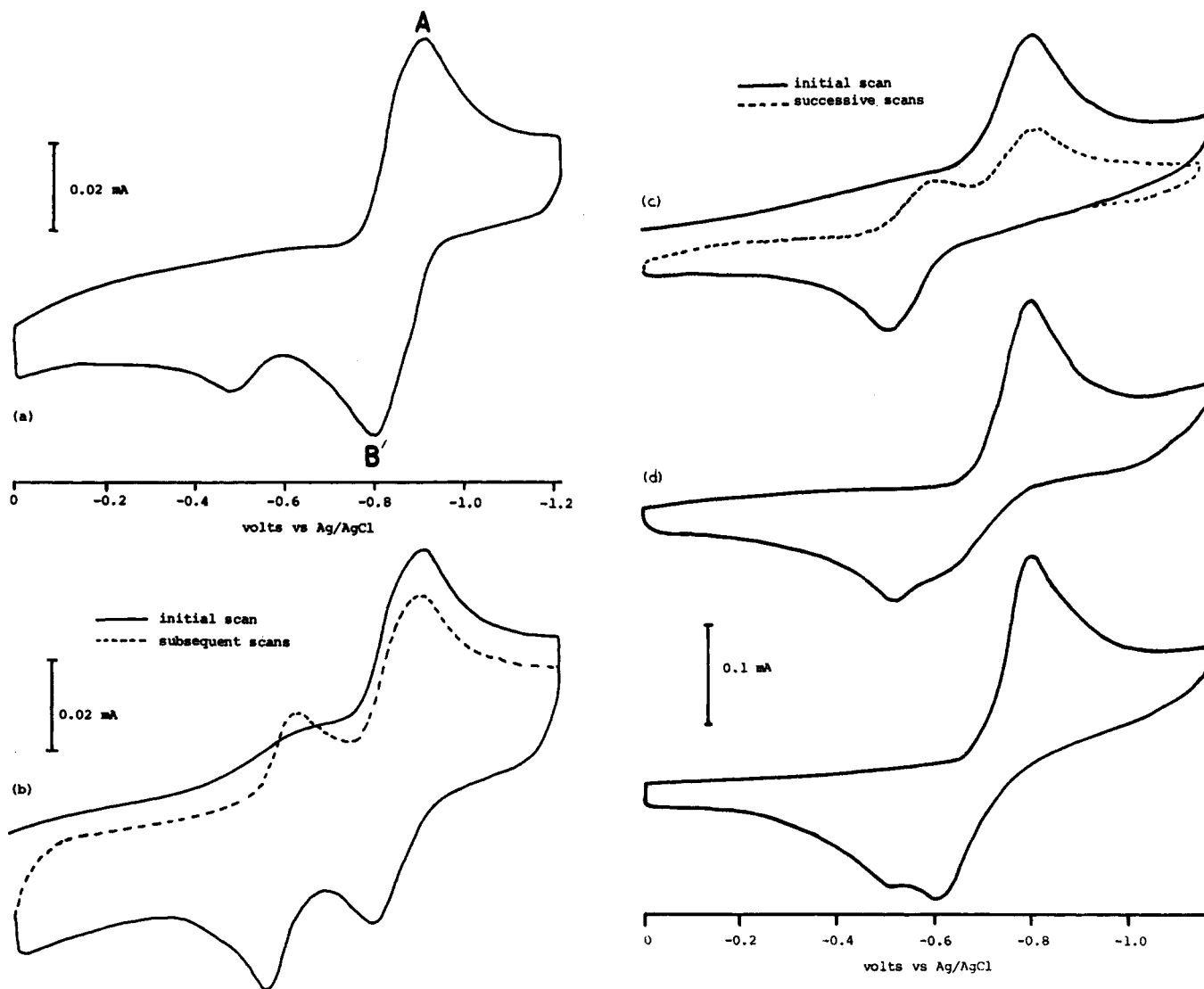


Figure 2. Cyclic voltammograms of $[\text{CH}_3\text{CCo}_3(\text{CO})_8]_2\text{dppe}$ in CH_2Cl_2 : (a) 207 K under Ar at Au, 500 mV s^{-1} ; (b) 217 K under CO at Au, 500 mV s^{-1} ; (c) 295 K under CO (1 atm) at Pt, 500 mV s^{-1} ; (d) 295 K decreasing CO concentration at Pt, 500 mV s^{-1} .

found in the cyclic voltammograms of $[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$ with values of $2 < n < 3.5$ and can be ascribed to the same type of $\bar{E}_r\text{C}\bar{E}_r$ behavior described for $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ (vide supra). As the temperature of the electrolyte solution is lowered, the relative peak currents for the primary reduction process decrease and below 207 K are approximately twice those for one-electron couples (eq 8). There

$[\text{RCCo}_3(\text{CO})_8]_2\text{dppe} + 2e \rightleftharpoons \{[\text{RCCo}_3(\text{CO})_8]_2\}^{2-}\text{dppe}$ (8)

is also a change in profile with the reduction peak becoming grossly asymmetric and two oxidation waves resolved (Figure 2). The peak separation $E_p(\text{A}) - E_p(\text{B})'$ at 207 K is $\sim 140 \text{ mV}$ which was the same as ΔE_p for the reference one-electron couples under the same conditions. From the progressive shift in the oxidation waves with temperature, $E_{pa}(\text{B})'$ at 207 K can be equated with $E_p(\text{B})$ (Figure 1) at 295 K. At low temperatures there is no evidence for the couple seen at 295 K negative of $E_{pc}([\text{RCCo}_3(\text{CO})_8]_2\text{dppe})$.

At 295 K under CO in CH_2Cl_2 wave B disappears to be replaced, on repeat scans, by a wave at $E_{pa} \approx -0.5 \text{ V}$ (Figure 2c); a companion reduction wave $E_{pc} \approx -0.6 \text{ V}$ also appears on repeat scans. The currents $i_p(\text{A})$ are lower than those for A under Ar but still higher than expected for a two-electron charge transfer. Below 217 K, under CO, the cyclic voltammograms (Figure 2b) resemble those at the same temperature under Ar, with smaller peak currents for the primary process, but there is a reduction wave due

to $\text{RCCo}_3(\text{CO})_9$ on repeat scans. It is important to note the distortion of the primary reduction peak which suggests two closely spaced reduction waves.

Figure 3 shows cyclic voltammograms of $[\text{PhCCo}_3(\text{CO})_8]_2\text{dppe}$ in acetone. At 295 K under Ar steady-state $i-E$ responses are obtained after four to eight cycles which show three apparent couples at $E_{1/2}$ (V) = -0.38 , -0.63 , and -0.94 . The relative peak currents of these couples vary with scan rate and switching potential; an increase in scan rate leads to a decrease in current due to couple $E_{1/2} = -0.94 \text{ V}$ while that at $E_{1/2} \approx -0.38 \text{ V}$ increases. These changes are consistent with the assignments $E_{1/2} = -0.38 \text{ V}$ $[\text{RCCo}_3(\text{CO})_9]^{0/-}$ and $E_{1/2} = -0.94 \text{ V}$ $[\text{RCCo}_3(\text{CO})_7\text{dppe}]^{0/-}$. The $\bar{E}\text{C}\bar{E}$ reaction giving rise to $\text{RCCo}_3(\text{CO})_7\text{dppe}$ is faster in acetone than CH_2Cl_2 , and this is reflected in the sharper primary reduction wave in acetone, this peak shape being characteristic of fast ETC reactions. At scan rates of $> 200 \text{ mV s}^{-1}$ i_{pc} for the primary wave at $E_{pc} \approx -0.63 \text{ V}$ rapidly decreases with repeat scans to reach the steady-state response shown in Figure 3. The initial i_{pc} values are again larger than expected for two-electron transfer, and the polarographic currents gave values of $n \approx 2.6$, that is, lower than in CH_2Cl_2 . The $i-E$ response is simplified between 258 and 248 K with only one chemically reversible couple with $n = 2$, but below 248 K the oxidation profile consists of two merged waves with $\Delta E_p \approx 0.1 \text{ V}$ (Figure 3). Two closely spaced reduction waves are in-

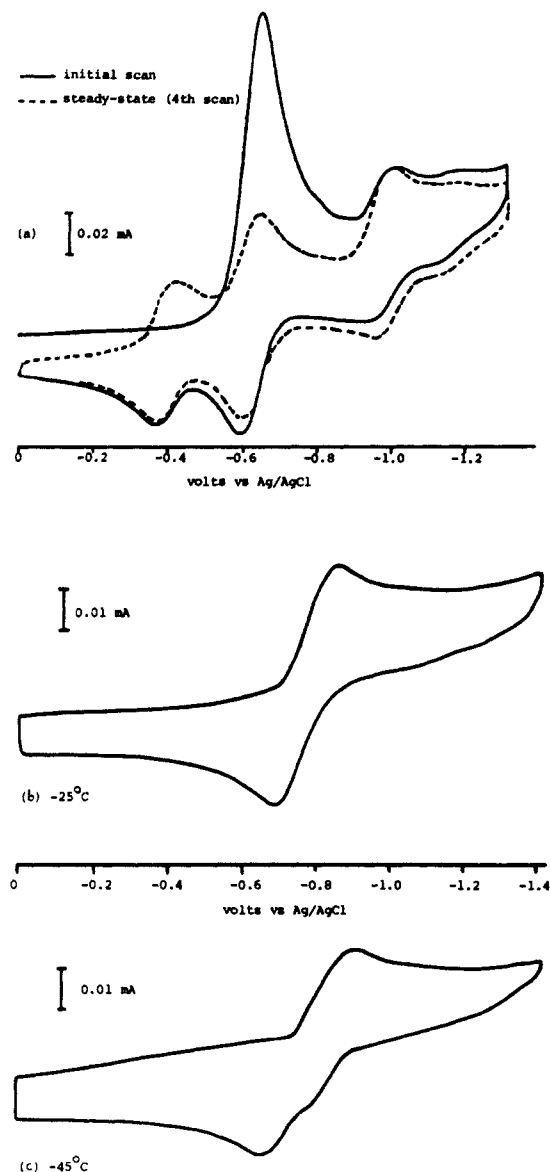


Figure 3. Cyclic voltammograms of $[\text{PhCCo}_3(\text{CO})_8]_2\text{dppe}$ in acetone at Pt: (a) under Ar, 295 K, 200 mV s^{-1} , initial and steady-state scan; (b) under Ar, 100 mV s^{-1} , 248 K; (c) under Ar, 100 mV s^{-1} , 228 K.

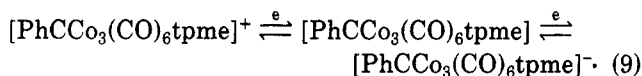
indicated by a distortion of the reduction wave at 228 K. Under CO the i - E responses are similar to those in CH_2Cl_2 under CO but with increased currents for the couples $(\text{RCCo}_3(\text{CO})_9)^{0/-}$ after the initial reduction scan.

In summary, the electrochemistry of $[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$ is characterized by a primary two-electron reduction process which gives rise to radical anions in which one phosphorus atom of dppe is coordinated per RCCo_3 unit, but these undergo subsequent CE_r , CE , and chemical reactions.

Redox Chemistry of $\text{PhCCo}_3(\text{CO})_6\text{tpme}$. Triaxial coordination of the tpme in $\text{PhCCo}_3(\text{CO})_6\text{tpme}$ provided an opportunity to evaluate the effect on the redox behavior when all three Co-Co bonds are clamped by a polydentate ligand. This derivative is not strictly analogous to $\text{RCCo}_3(\text{CO})_6\text{L}_3$ [$\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, $\text{R} = \text{Ph}$, CH_3] complexes studied previously in this laboratory² as the latter do not adopt a bridging CO configuration.

The obvious difference in the electrochemical properties of $\text{PhCCo}_3(\text{CO})_6\text{tpme}$ compared to other cluster derivatives is the existence of both a stable (on the electrochemical timescale) radical anion and cation (Figure 4). The one-electron reduction is electrochemically quasi-reversible

($\Delta E_p = 140 \text{ mV}$, cf. 80 mV for ferrocene) but chemically reversible ($i_{pa}/i_{pc} = 1$) in CH_2Cl_2 , and the $E_{1/2}$ value of -1.43 V shows that the three phosphorus donor atoms are still coordinated. Electrochemical and chemical reversibility is shown by the one-electron oxidation response ($\Delta E_p = 80 \text{ mV}$, $i_{pc}/i_{pa} = 1$). The full redox series for this complex is therefore



and the unexpected chemical reversibility can be directly attributed to the clamping effect of the ligand. This chemical reversibility encouraged us to attempt an isolation of the cation and anion but without success.

Redox Chemistry of $\text{RCCo}_3(\text{CO})_5(\text{dppm})_2$. Previous studies^{2,3} and the behavior of $\text{RCCo}_3(\text{CO})_6\text{tpme}$ has shown that an oxidizable center is generated on the Co_3C cluster by replacing three carbonyl groups. Consequently, in the complexes $\text{RCCo}_3(\text{CO})_5(\text{dppm})_2$ where four have been replaced facile oxidation of the cluster would be predicted.

Indeed, both clusters ($\text{R} = \text{CH}_3$, Ph) exhibit three electron-transfer processes in the CV's on Pt in CH_2Cl_2 , two oxidation and one reduction, with equal peak currents corresponding to the transfer of one electron. The first oxidation ($E_p \approx 0.35 \text{ V}$) and reduction process are chemically reversible ($i_{pa}/i_{pc} \approx 1$) while the second oxidation step is partially reversible, the degree of reversibility depending on R (Figure 4; Table II). Chemical reversibility for the reduction process is surprising as there is an inverse relationship between the chemical reversibility of oxidation and reduction steps in this type of cluster derivative; certainly, reduction of $\text{RCCo}_3(\text{CO})_6[\text{P}(\text{OR})_3]_3$ is chemically irreversible.^{2,3}

These primary responses are unaffected by temperature or CO. If the anodic scan is reversed, under Ar, after the second oxidation step, a new reduction wave appears at $E_{pc} \approx 0.0 \text{ V}$; this is not observed if the oxidation scan is reversed before the second oxidation wave. These complexes were oxidized by Ag^+ , but the resulting cations were too unstable to characterize; likewise, controlled reduction gave no detectable paramagnetic species.

Discussion

When interpreting the i - E responses for the systems studied, we were conscious of the slow electron transfer and ohmic losses in CH_2Cl_2 and acetone which result in large peak-peak separations and which could lead to erroneous conclusions about the charge-transfer processes. The use of an in situ one-electron couple as a reference overcame this problem to some extent, but extensive digital and convolution calculations demonstrated that, even with an applied correction for uncompensated iR losses of $R \approx 10 \Omega$, ΔE_p was still larger than expected for one-electron transfer with $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ and $[\text{RCCo}_3(\text{CO})_2]_2\text{dppe}$. Consequently, other criteria were used to evaluate the number of electrons transfer in the primary reduction process.¹⁰

Redox Potentials. To a first approximation the redox potentials are only determined by the number of phosphorus donor atoms per RCCo_3 unit, and so structure/ $E_{1/2}$ correlations can be discussed in isolation from the details of the charge-transfer sequence. Substituent parameters for various ligands coordinated to RCCo_3 clusters have

(10) Van de Linden, J. G. M.; Paulissen, M. L. H.; Schmitz, J. E. J. *J. Am. Chem. Soc.* **1983**, *105*, 1903, discuss other examples where diagnostic criteria are not a reliable guide to n .

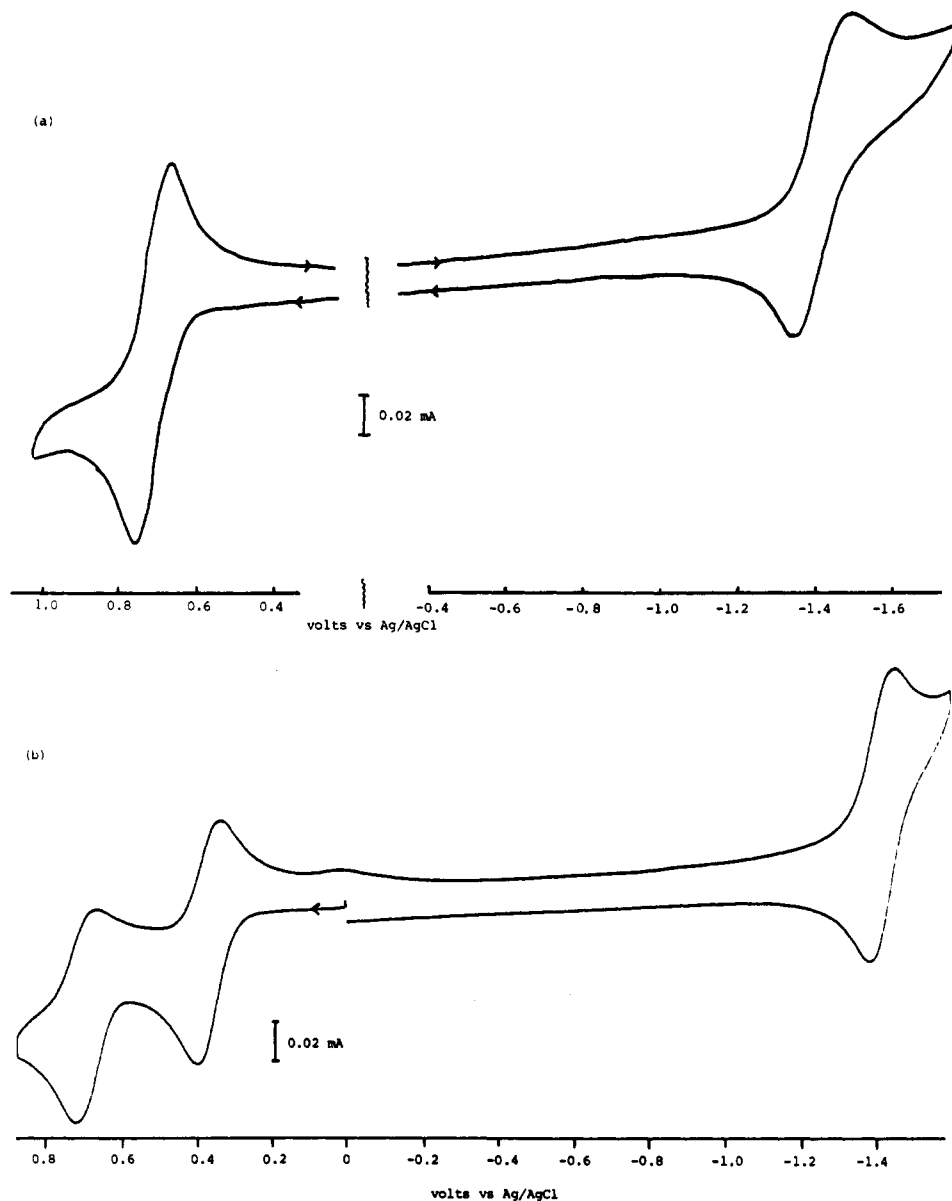


Figure 4. Cyclic voltammogram in CH_2Cl_2 under Ar (295 K) at Pt (200 mV s^{-1}): (a) $\text{PhCCo}_3(\text{CO})_6\text{tpme}$; (b) $\text{PhCCo}_3(\text{CO})_5(\text{dppm})_2$.

been derived,^{3,11} and these have been useful for structural assignment.

Assuming that a Ph_2P group can be equated with Ph_3P for which the substituent parameter is $\delta_{\text{Ph}_3\text{P}} = -0.23 \text{ V}$, then $E_{1/2}$ is predicted to be -0.61 and -0.84 V in acetone for monodentate or chelate coordination, respectively, of dppm and dppe to PhCCo_3 (the comparable values for coordination to MeCCo_3 are respectively -0.60 and -0.87 V). These values can be compared with those for $[\text{PhCCo}_3(\text{CO})_8]_2\text{dppe}$ (-0.63 V), $\text{PhCCo}_3(\text{CO})_7\text{dppe}$ (-0.94 V), $\text{PhCCo}_3(\text{CO})_7\text{dppm}$ (-0.90 V), and $\text{PhCCo}_3(\text{CO})_8\text{dppm}$ (-0.65 V) estimated from digital simulation of the cyclic voltammograms. The correlation is good for coordination of one phosphorus but *not* for chelate formation. Formation of a radical anion requires a lengthening of the Co–Co bond as the electron enters an a_2^* antibonding orbital. Consequently, in molecules where a Co–Co bond is “clamped” by a bidentate ligand, formation of the radical anion will be thermodynamically unfavorable relative to a $\text{RCCo}_3(\text{CO})_7\text{L}_2$ complex—the reduction potential is therefore more negative than predicted. Support for this explanation comes from a comparison with the estimated

$E_{1/2}[\text{PhCCo}_3(\text{CO})_7(\text{PPh}_3)_2]$ of -0.85 V and a similar observation for the molecule $\text{Co}_4(\text{CO})_6(\text{dppm})_2$.¹²

Data for $\text{RCCo}_3(\text{CO})_5(\text{dppm})_2$ are not available in acetone, but $E_{1/2}$ values for these complexes in CH_2Cl_2 are accommodated by the relationship

$$E_{1/2}[\text{PhCCo}_3(\text{CO})_5(\text{dppm})_2] = 2\Delta E_{1/2}[\text{PhCCo}_3(\text{CO})_7\text{dppm} - \text{PhCCo}_3(\text{CO})_9] + E_{1/2}[\text{PhCCo}_3(\text{CO})_9] \quad (10)$$

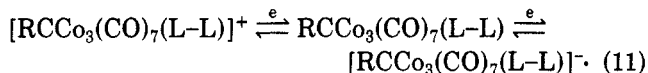
The inference from this additivity relationship is that the electronic structure is not grossly perturbed by the coordination of *two* chelating dppm and that the electron enters a Co_3 -based antibonding orbital. The chemically reversible formation of $[\text{RCCo}_3(\text{CO})_5(\text{dppm})_2]^-$ is contrary to the decrease in stability through the series $[\text{RCCo}_3(\text{CO})_{9-n}\text{L}_n]^-$ ($n = 0-3$), but this kinetic stability can be attributed to the clamping effect of the chelate ring described above. The chemically reversible formation of $[\text{RCCo}_3(\text{CO})_5(\text{dppm})_2]^+$ is reasonable for an electron-rich Co_3C core, but the formation of a dication and the small ΔE_p ($200-300 \text{ mV}$) between the first and second oxidation steps are unusual. The second oxidation step may rep-

(11) Robinson, B. H.; Simpson, J., submitted for publication in *J. Organomet. Chem.*

(12) Rimmelin, J.; Lemoine, P.; Gross, M. *Nouv. J. Chim.* 1983, 7, 453.

resent an oxidation of coordinated dpmm.¹³

Electron-Transfer Steps in $RCCo_3(CO)_8PPh_3$, $[RCCo_3(CO)_8]_2dppe$, and $RCCo_3(CO)_7(L-L)$. Straight-forward reversible one-electron transfers characterize the electrochemistry of $RCCo_3(CO)_9$ and $RCCo_3(CO)_7(L-L)$ ($L-L \equiv dpmm, dppe$) (eq 11).



This sequence was believed² to hold for $RCCo_3(CO)_8L$ derivatives, but this must be revised as diffusion-controlled multielectron transfers are established by the data in this paper and elsewhere⁶ for $RCCo_3(CO)_8L$ and $[RCCo_3(CO)_8]_2dppe$. Related examples were recognized in the complexes $FcCCo_3(CO)_9-xL_x$ ($L = P(OR)_3, PPh_3; x = 1-3$), where the ferrocene couple provided a reliable estimate of n divorced from problems of slow electron transfer and adsorption.³ It is important to note that the diagnostic electrochemical parameters in these molecules may obey the polarographic criteria for one-electron transfer¹⁰ although there is a wide variation in the slopes of E vs. $\log(i_d - i)/i$ plots within the $RCCo_3(CO)_8L$ series. Other examples of multielectron transfers include $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and derivatives where the apparent two-electron transfer arises from an $\bar{E}C\bar{E}$ mechanism.^{14,15}

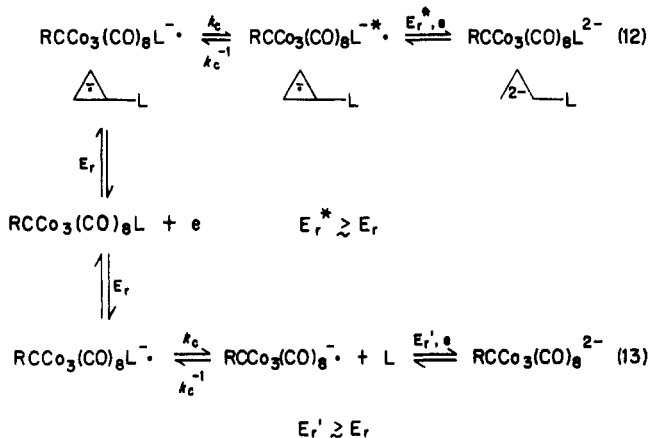
The archetypal $RCCo_3(CO)_8PPh_3$ will be considered first because of the added problems associated with two redox centers in the bridged species $[RCCo_3(CO)_8]_2dppe$.

$RCCo_3(CO)_8PPh_3$. Diffusion currents indicative of charge transfer up to two electrons are found in the transient electrochemistry of $RCCo_3(CO)_8PPh_3$ (and indeed other $RCCo_3(CO)_8PR_3$ derivatives) in CH_2Cl_2 and acetone, on Pt and Au, and over a temperature range—the relative currents decrease slightly with temperature. Satisfactory digital simulation was achieved by using a two-electron transfer, and coulometry gives values of n between 1.6 and 2.

Simultaneous two-electron transfer seems unlikely in view of the known electrochemistry of $RCCo_3$ compounds and because the spectroscopic data⁷ for $RCCo_3(CO)_8PPh_3$ do not indicate a gross change in electronic energy levels compared to $RCCo_3(CO)_9$. The enhanced reduction currents could arise from an E_rE_r process, but analysis by convolution techniques gave no credence to this mechanism. Further, at fast scan rates a minor reduction wave is seen at more negative potentials than the primary wave, and this is assigned to the irreversible reduction of $RCCo_3(CO)_8PPh_3^-$ to $RCCo_3(CO)_8PPh_3^{2-}$ —it is related by an appropriate shift in potential (~ -0.8 V) to the reduction wave of $PhCCo_3(CO)_9^-$.¹⁶ We therefore suggest that the enhanced currents arise from an $\bar{E}C\bar{E}$ mechanism¹⁷ where a fast chemical reaction follows the formation of $RCCo_3(CO)_8PPh_3^-$; an analysis of the CV's by convolution techniques suggested that this was an appropriate mechanism. Three possibilities for this fast step are isomerization, ligand dissociation, or Co-Co bond cleavage.¹⁷

Electron-induced isomer interconversion with virtually nil current flow is known¹⁸ to be fast for some cluster derivatives, and the existence of isomers *in solution* has been demonstrated⁷ for neutral $RCCo_3(CO)_8PPh_3$. Nernstian behavior does not imply structural integrity of reactant and product; the counter argument that slow electron-transfer correlates with structural change is also not necessarily true.^{8,19} Nonetheless, under no circumstance would enhanced reduction currents be expected.

Providing the product of ligand dissociation is not reduced further at or near the potential of the primary wave, then enhanced currents would only occur if the ligand itself is reduced, but this is not the case for phosphines.¹³ Two scenarios which could give rise to the observed electrochemistry are shown in (12) and (13) ($L = PPh_3$). To get



enhanced reduction currents a species must be formed by a rapid chemical reaction which is more easily reduced than $RCCo_3(CO)_8PPh_3$. In (12) a formal 17e species is created by Co-Co bond cleavage of the "clos" cluster radical anion to give a "bond-opened" radical anion whereas in (13) the 17e species is produced by ligand dissociation. Both schemes imply the existence of diamagnetic 18e dianions, and this is consistent with the ESR data. No paramagnetic species have been observed in reduced solutions of $RCCo_3(CO)_8PPh_3$ in the temperature range 293–213 K where maximum concentration of the diamagnetic anions is expected, but electrolysis at low temperatures followed by rapid freezing to 73 K gives a weak anisotropic ESR spectra consistent with a "clos" $RCCo_3(CO)_8PPh_3^-$ anion (the anisotropic parameters showing coupling to three equivalent cobalt atoms are the same as those for $RCCo_3(CO)_9^-$ at 73 K with slight changes in line shape and line width²⁰).

The alternatives, (12) and (13), are not mutually exclusive, and we have no definitive evidence for one or the other. Option (13) is attractive as it rationalizes diverse qualitative observations— $RCCo_3(CO)_8PPh_3$ complexes readily undergo ligand exchange reactions on the addition of BPK to the reactant solutions,⁶ the decreased reduction currents at low temperatures, rapid isomerization reactions of $[(CF_3)_6C_6]Co_2(CO)_2L_2$ complexes,¹⁸ the one-electron transfer of $RCCo_3(CO)_7[\mu-(L-L)]$ complexes (a "chelate" effect), and the wide variation in electrochemical parameters and behavior within the $RCCo_3(CO)_8L$ series of complexes.²

A theoretical interpretation of the $i-E$ response will therefore need to consider the relative rates of all elec-

(13) In CH_2Cl_2 dpmm is irreversibly oxidized at 1.08 V, dppe at 1.16 V, and PPh_3 at 0.94 V vs. Ag/AgCl; the ligands are not reduced in the potential range under consideration.

(14) Cyr, J. E.; De Gray, J. A.; Gosser, D. K.; Lee, E. S.; Rieger, P. H. *Organometallics* 1985, 4, 950.

(15) Downard, A. J. Ph.D. Thesis, University of Otago, 1984. Robinson, B. H. Pacific Basin Chemical Congress, Honolulu, 1984.

(16) Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* 1979, 16, 405.

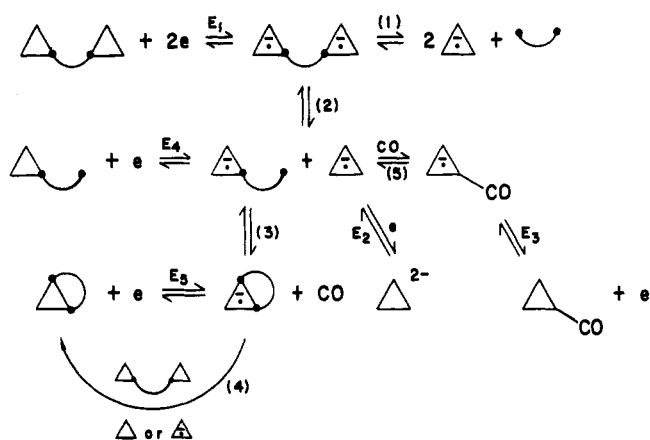
(17) The influence of dis- and conproportionation reactions has been considered (see: Ruzic, I.; Smith, D. E. *J. Electroanal. Chem. Interfacial Electrochem.* 1975, 78, 145), but there are no data which support these as the major effects on electrochemical responses.

(18) Arewogoda, C. M.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.*, 1982, 284.

(19) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* 1981, 103, 4779.

(20) Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* 1979, 18, 1000.

Scheme I



tron-transfer processes and the chemical step; the fact that simulation with $n = 2$ gives a satisfactory fit for $L = \text{PPh}_3$ indicates that the chemical step is not rate-determining. Another factor which influences the i - E response is the nature of the electrode surface. Unless suitably prepared electrodes are used, oxidation waves at potentials positive of the wave shown in Figure 1 are observed, with a concomitant decrease in i_{pa} of the primary wave, and ΔE_p for the primary couple can increase to 200–300 mV; enhanced reduction currents are still observed. Not all electrochemical processes are equally activated by an electrode surface,²¹ and while the additional oxidation waves can be ascribed to $\text{RCCo}_3(\text{CO})_9^-$, it is possible that they are due to the oxidation of $\text{RCCo}_3(\text{CO})_8^-$ or $\text{RCCo}_3(\text{CO})_8\text{L}^*$ having moved out from under the primary oxidation wave because of the slower electrode kinetics at a nonactivated electrode surface.

$[\text{RCCo}_3(\text{CO})_8]_2(\mu\text{-dppe})$. The primary i - E responses at 295 K in CH_2Cl_2 for these complexes are essentially a superposition of i - E responses for two $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$ complexes. Diffusion-controlled currents corresponding to $3 < n < 4$ for the reduction wave at 295 K reduce to currents of $n \approx 2$ at 213 K. Consequently, we conclude that each redox center (a $\text{RCCo}_3(\text{CO})_8\text{P}$ unit) is undergoing the $\bar{E}_1\bar{C}\bar{E}_1$ process described above (eq 13) and, furthermore, that there is no interaction in the electrochemical sense between the two redox centers.²²

The data in CH_2Cl_2 and acetone show that other reactions besides the $\bar{E}_1\bar{C}\bar{E}_1$ process occur resulting in complicated solvent-dependent i - E responses—these are encompassed in Scheme I ($E_5 < E_4 \approx E_1 < E_3 < E_2$).

An $\bar{E}\bar{C}\bar{E}$ chain (2)–(4) produces $\text{RCCo}_3(\text{CO})_7(\mu\text{-dppe})$ to a minor extent in CH_2Cl_2 but with greater efficiency in acetone, and hence the “dangling” species must be an important intermediate. All scans recorded at low temperatures, under both Ar and CO, show a shoulder on the rising slope of the primary reduction wave. Since the number of donor atoms per RCCo_3 unit does not change on formation of this dangling complex, $E_{pc}(4) \approx E_{pc}(1)$, and the following chemical reactions 3 and 5 are slower at these temperatures, we ascribe the two reduction waves to $E_{pc}(1)$ and $E_{pc}(4)$. The i - E responses from the dangling

complex $\text{RCCo}_3(\text{CO})_8\text{dppe}$ were the same as $[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$, but, unfortunately, its lability and low yield synthesis precluded quantitative studies.

Step 2 is clearly faster in acetone, and the different i - E responses and lower i_{pc} for the primary reduction wave to those in CH_2Cl_2 can be explained on this basis. The increased CO concentration in the diffusion layer arising from the $\bar{E}\bar{C}\bar{E}$ reaction makes the couple E_3 more dominant on repeat scans at 293 K in acetone (Figure 3). As the temperature is lowered, the $\bar{E}\bar{C}\bar{E}$ contribution decreases and at 248 and 228 K the i - E responses are analogous to those in CH_2Cl_2 (the different electrode kinetics in acetone giving different peak separations).

In the presence of CO the coordinatively unsaturated $\text{RCCo}_3(\text{CO})_8^-$ is trapped and the couple E_3 dominates (Figure 2). This also explains the lower primary reduction currents under CO; that is, the chemical step competes with the heterogeneous electron transfer associated with E_2 .

Conclusion

Substitution by a bidentate ligand has two major effects on the redox behavior of Lewis base derivatives of $\text{RCCo}_3(\text{CO})_9$. First, for complexes with chelating ligands successive replacement of carbonyl groups makes reduction thermodynamically more difficult but the resulting radical anion becomes kinetically more stable. Second, chelated derivatives undergo CO-displacement reactions in contrast to derivatives of monodentate phosphines which tend to undergo phosphine-displacement reactions.

The observation of an overall two-electron $\bar{E}\bar{C}\bar{E}$ step involving facile ligand dissociation for complexes of monodentate or “dangling” phosphines may be peculiar to tricarbonyl carbon derivatives. Certainly, derivatives of $(\text{CF}_3)_2\text{C}_2\text{Co}_2(\text{CO})_6$, whose redox behavior is similar to Co_3C complexes, have a one-electron charge transfer.²³ An explanation for the kinetic instability could reside in the extreme steric congestion in Co_3C molecules which is manifested in many aspects of their chemistry.^{24,25}

Experimental Section

$\text{RCCo}_3(\text{CO})_9$ ($R = \text{Ph}, \text{CH}_3$),²⁶ $\text{RCCo}_3(\text{CO})_8\text{PPh}_3$,⁷ $[\text{RCCo}_3(\text{CO})_8]_2\text{dppe}$, and $\text{RCCo}_3(\text{CO})_7(\text{L-L})$ were prepared by literature methods.¹ Dichloromethane was stored over CaCl_2 and distilled under Ar from P_2O_5 immediately prior to use. Analytical grade acetone was dried over 3-Å molecular sieves and filtered prior to use; otherwise the acetone was refluxed with successive small quantities of KMnO_4 until the violet color remained, fractionated, and distilled prior to use. Acetonitrile was stirred for several days in contact with CaH_2 after which it was decanted and fractionally distilled from P_2O_5 ; this product was refluxed over CaH_2 and fractionally distilled prior to use. THF was purified as previously described.¹ TBAP (Fluka) was recrystallized several times from EtOAc and dried in vacuo at 253 K. TEAP (Fluka) was recrystallized from methanol and dried in vacuo at 243 K.

Electrochemical Techniques. Polarographic and voltammetric measurements were made with a PAR 174 Analyzer equipped with a PAR 175 universal programmer. Responses were recorded on an X-Y recorder ($<1 \text{ V s}^{-1}$), Tectronix Storage oscilloscope ($>1 \text{ V s}^{-1}$), or an interfaced Apple microcomputer. Controlled potential experiments were performed as described in the preceding paper.¹ A standard three-electrode cell designed to allow the tip of the Ag/AgCl reference electrode to approach within 2 mm of the working electrode was used for the transient

(21) Cabaniss, G. E.; Diamantis, A. A.; Murphy, W. R.; Linton, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* 1985, 107, 1845.

(22) If these centers were interacting in the electrochemical sense, then more than one diffusion-controlled reduction wave would be expected. If the two centers were not interacting, then $E_2^0 - E_1^0 = -35.6 \text{ mV}$ at 298 K (for one-electron Nernstian waves) and the observed wave would have the characteristics of a one-electron transfer with a current twice that of the analogous single-centered molecule. For a discussion see: Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* 1978, 100, 4248.

(23) Arewogoda, C. M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* 1983, 105, 1893. Jensen, S. D. M.Sc. Thesis, University of Otago, 1984.

(24) Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* 1973, 6, 73.

(25) Seyferth, D. *Adv. Organomet. Chem.* 1976, 14, 97.

(26) Dent, W. T.; Duncanson, L. A.; Guy, R. G.; Reed, H. W. B.; Shaw, B. L. *Proc. Chem. Soc.* 1961, 169.

electrochemistry. All measurements were carried out under Ar, and TBAP was used as electrolyte with CH_2Cl_2 or THF and TEAP with acetone and CH_3CN , all at a concentration of 0.1 mol dm^{-3} . The cluster concentration was normally $5.0 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^{-3}$.

In common with many metal carbonyl systems there was rapid deterioration in the electrode surface over a short time interval (ca. 10 scans). The condition of the electrode surface was critical to the reproducibility of the i - E responses and, in particular, to the number and type of oxidation waves on the reverse scans of the cyclic voltammograms. It is not known why this problem is so severe with these substrates, but it occurs on Pt, Au, and glassy carbon electrodes, in all solvents, and only when reduction of the substrate takes place. Surface studies are underway to determine the nature of the surface film. The following procedure gave reproducible Pt surfaces. The electrodes were swirled in concentrated chromic acid followed by thorough washing with distilled water. After being dried, the working electrode was oxidized at $\sim 1.0 \text{ V}$ vs. SCE in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ for 5 min, then reduced at $\sim -0.6 \text{ V}$ vs. SCE in the same solution for 10 minutes, washed with distilled water, and dried.

Potential data were collected by reference to (normally in situ) ferrocene or $\text{PhCCO}_3(\text{CO})_9$ using the following values (vs. Ag/AgCl).

	[ferrocene] ⁺⁰	[$\text{PhCCO}_3(\text{CO})_9$] ^{0/-}
CHCl_2	0.68 V	-0.56 V
acetone	0.63 V	-0.38 V
THF	0.77 V	-0.36 V
CH_2Cl_2	0.49 V	-0.54 V

Under most conditions ΔE_p was $\approx 60 \text{ mV}$ for the oxidation of ferrocene provided the electrodes were carefully positioned. A deviation from this value was taken as an indication of electrode passivation and/or uncompensated IR drop—where ΔE_p was $> 60 \text{ mV}$, the electrochemical reversibility (diffusion control) of the electrode process was determined by a comparison with the ferrocene value. In some cases the potential was checked by reference to ferrocene in another cell to ensure that ferrocene was not interfering with the electrode process. The controlled potential electrolyses were carried out as described in the preceding paper.¹

Treatment of the Electrochemical Data. The diffusion coefficients of ferrocene and $\text{PhCCO}_3(\text{CO})_9$ in CH_2Cl_2 , the influence of resistance effects, and heterogeneous rate constants were obtained from digital simulation of the cyclic voltammograms. Background currents were simulated as linear potential ramps. Fortran programs for the simulation were based on the relevant

statements given by Feldberg²⁷ and run on a Digital VAX 11/780 computer. Convolution analyses were applied to the cyclic voltammograms using a program based on the algorithm for the convolution integral $I(t)$ given in ref 5. Other work (see following paper²⁸) had shown that the diffusion coefficient for $\text{PhCCO}_3(\text{CO})_9$ is $9.8 (5) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in CH_3CN . It was assumed that the diffusion coefficients for the derivatives would be approximately the same as $\text{PhCCO}_3(\text{CO})_9$ —this seemed to correlate with an independent value of $9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $\text{PhCCO}_3(\text{CO})_7\text{dppm}$ obtained by standard polarographic techniques. From this data the number of electrons transferred in a particular redox process can be determined by comparison of the dc limiting currents or cyclic voltammetric peak currents with those of the couples [ferrocene]⁺⁰ or [$\text{PhCCO}_3(\text{CO})_9$]^{0/-} providing the charge transfer for the process is diffusion-controlled.

The Controlled Potential Electrolysis of $\text{PhCCO}_3(\text{CO})_8\text{PPh}_3$ with PPh_3 . The electrolyte, solution volume, concentration, and general procedure were the same as that outlined previously.¹ Electrolyses to produce $\text{PhCCO}_3(\text{CO})_8\text{PPh}_3$ were performed in acetone at -0.5 V . The product of the electrolysis was not isolated, a further equimolar amount of PPh_3 was added, and the potential was incremented to -0.7 V . This led to the slow formation of $\text{PhCCO}_3(\text{CO})_7(\text{PPh}_3)_2$ with the consumption of ~ 0.6 electron/molecule of $\text{PhCCO}_3(\text{CO})_9$. The labile product was isolated as a red-brown powder which rapidly decomposed in air and in all solvents. Anal. Calcd: C, 60.87; H, 3.58. Found: C, 58.87; H, 3.94. IR (CH_2Cl_2): $\nu(\text{CO})$ 2047 (m), 2010 (m), 1985 (s), 1950 (m) cm^{-1} .

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Registry No. $\text{PhCCO}_3(\text{CO})_8\text{PPh}_3$, 13681-99-7; $\text{CH}_3\text{CCO}_3(\text{CO})_8\text{PPh}_3$, 15633-24-6; [$\text{PhCCO}_3(\text{CO})_8$]₂dpppe, 87828-99-7; [$\text{CH}_3\text{CCO}_3(\text{CO})_8$]₂dpppe, 101031-40-7; $\text{PhCCO}_3(\text{CO})_7\text{dpppe}$, 101312-98-5; $\text{CH}_3\text{CCO}_3(\text{CO})_7\text{dpppe}$, 101312-99-6; $\text{PhCCO}_3(\text{CO})_7\text{dppm}$, 84896-18-4; $\text{CH}_3\text{CCO}_3(\text{CO})_7\text{dppm}$, 96919-62-9; $\text{PhCCO}_3(\text{CO})_5(\text{dppm})_2$, 101011-59-0; $\text{CH}_3\text{CCO}_3(\text{CO})_5(\text{dppm})_2$, 101011-60-3; $\text{PhCCO}_3(\text{CO})_6\text{tpme}$, 101011-55-6; $\text{PhCCO}_3(\text{CO})_7(\text{PPh}_3)_2$, 101011-57-8; Co, 7440-48-4.

(27) Feldberg, S. W. *Electroanal. Chem.* 1969, 3, 199.

(28) Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics*, third of three papers in this issue.

Electron Transfer in Organometallic Clusters. 10.¹ Mechanism and Solvent Effects in ETC Reactions of $\text{PhCCO}_3(\text{CO})_9$ with Phosphine Ligands

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The mechanism of the electron-transfer chain catalyzed (ETC) reactions of $\text{PhCCO}_3(\text{CO})_9$ with PPh_3 , dppm, dppe, and tpme was elucidated by using coulometric and transient electrochemical techniques. The catalytic efficiency for the attachment of one phosphorus atom to the cluster is independent of the ligand ($\sim 0.01 \text{ F mol}^{-1}$ in CH_2Cl_2), but the rate of reaction is solvent-dependent. The subsequent step to $\text{PhCCO}_3(\text{CO})_7\text{L}_2$ or $\text{PhCCO}_3(\text{CO})_7(\text{L-L})$ is much slower and of short chain length. Evidence is presented to show that "dangling" complexes $\text{PhCCO}_3(\text{CO})_8(\text{L-L})$ are the initial ETC products but that a rapid EC reaction takes place to give [$\text{PhCCO}_3(\text{CO})_8$]₂(L-L) or $\text{PhCCO}_3(\text{CO})_7(\text{L-L})$ depending on the "bite" of the ligand. A simplified kinetic scheme is used to evaluate a first-order rate constant for the primary dissociative step for $\text{PhCCO}_3(\text{CO})_9$ as $k_1 = 3.2 \text{ mol}^{-1} \text{ s}^{-1}$ in CH_2Cl_2 . The behavior of $\text{RCCO}_3(\text{CO})_9$ (R = Ph, Me) under ETC conditions is also described; in CH_3CN the derivatives $\text{RCCO}_3(\text{CO})_8\text{NCCH}_3$ are produced, and in CH_2Cl_2 carbyne coupling occurs to give $\text{R}_2\text{C}_2\text{CO}_4(\text{CO})_{10}$.

The previous two papers¹ provide a framework for the interpretation of the electron-catalyzed reactions between

tricobalt carbon clusters and phosphine ligands. A number of electron transfer chain catalyzed (ETC) reactions with