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 5.0×10^{-4} mol^{-1} 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 ~1.0 V vs. SCE in 0.1 mol dm^{-3} $NaClO_4$ for 5 min, then reduced at ~–0.6 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 $PhCCo_3(CO)_9$ using the following values (vs. Ag/AgCl).

	$[\text{ferrocene}]^{+/0}$	$[PhCCo_3(CO)_9]^{0/-}$
$CHCl_2$	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 ≃60 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 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 $PhCCo_3(CO)_9$ 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 Feldberg[27] 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 paper[28]) had shown that the diffusion coefficient for $PhCCo_3(CO)_9$ is 9.8 (5) $\times 10^{-6}$ cm^2 s^{-1} in CH_3CN. It was assumed that the diffusion coefficients for the derivatives would be approximately the same as $PhCCo_3(CO)_9$—this seemed to correlate with an independent value of 9×10^{-6} cm^2 s^{-1} for $PhCCo_3(CO)_7dppm$ obtained by standard polaragraphic 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 $[\text{ferrocene}]^{+/0}$ or $[PhCCo_3(CO)_9]^{0/-}$ providing the charge transfer for the process is diffusion-controlled.

The Controlled Potential Electrolysis of $PhCCo_3(CO)_8PPh_3$ with PPh_3. The electrolyte, solution volume, concentration, and general procedure were the same as that outlined previously.[1] Electrolyses to produce $PhCCo_3(CO)_8PPh_3$ 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 $PhCCo_3(CO)_7(PPh_3)_2$ with the consumption of ~0.6 electron/molecule of $PhCCo_3(CO)_9$. 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): ν(CO) 2047 (m), 2010 (m), 1985 (s), 1950 (m) cm^{-1}.

Acknowledgment. The award of a post-graduate research scholarship by the University Grants Committee to A.J.D. is acknowledged. We thank Professor A. Bond for helpful discussions.

Registry No. $PhCCo_3(CO)_8PPh_3$, 13681-99-7; $CH_3CCo_3(CO)_8PPh_3$, 15633-24-6; $[PhCCo_3(CO)_8]_2dppe$, 87828-99-7; $[CH_3CCo_3(CO)_8]_2dppe$, 101031-40-7; $PhCCo_3(CO)_7dppe$, 101312-98-5; $CH_3CCo_3(CO)_7dppe$, 101312-99-6; $PhCCo_3(CO)_7dppm$, 84896-18-4; $CH_3CCo_3(CO)_7dppm$, 96919-62-9; $PhCCo_3(CO)_5(dppm)_2$, 101011-59-0; $CH_3CCo_3(CO)_5(dppm)_2$, 101011-60-3; $PhCCo_3(CO)_6tpme$, 101011-55-6; $PhCCo_3(CO)_7(PPh_3)_2$, 101011-57-8; Co, 7440-48-4.

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[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 $PhCCo_3(CO)_9$ with Phosphine Ligands

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Received July 18, 1985

The mechanism of the electron-transfer chain catalyzed (ETC) reactions of $PhCCo_3(CO)_9$ 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 (~0.01 F mol^{-1} in CH_2Cl_2), but the rate of reaction is solvent-dependent. The subsequent step to $PhCCo_3(CO)_7L_2$ or $PhCCo_3(CO)_7(L\text{–}L)$ is much slower and of short chain length. Evidence is presented to show that "dangling" complexes $PhCCo_3(CO)_8(L\text{–}L)$ are the initial ETC products but that a rapid EC reaction takes place to give $[PhCCo_3(CO)_8]_2(L\text{–}L)$ or $PhCCo_3(CO)_7(L\text{–}L)$ 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 $PhCCo_3(CO)_9$ as $k_1 = 3.2$ mol^{-1} s^{-1} in CH_2Cl_2. The behavior of $RCCo_3(CO)_9$ (R = Ph, Me) under ETC conditions is also described; in CH_3CN the derivatives $RCCo_3(CO)_8NCCH_3$ are produced, and in CH_2Cl_2 carbyne coupling occurs to give $R_2C_2Co_4(CO)_{10}$.

The previous two papers[1] 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

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Table I. Data for Bulk Electrolysis Reactions of $PhCCo_3(CO)_9$ with Added Ligand[a]

solvt	potential/V	max current/mA	reactn time/min	charge/C	electron/molecule[b]	major product
L = dppm						
CH_3CN	−0.45	2.0	1.5	0.12	0.01	$PhCCo_3(CO)_7dppm$
acetone	−0.45	4.5	2.0	0.20	0.01	$PhCCo_3(CO)_7dppm$
THF	−0.50	1.5	2.8	0.20	0.01	$PhCCo_3(CO)_7dppm$
CH_2Cl_2	−0.65	1.3	4.0	0.24	0.01	$PhCCo_3(CO)_7dppm$
L = dppe						
CH_3CN	−0.45	2.4	1.5	0.17	0.01	$[PhCCo_3(CO)_8]_ndppe$
	−0.66	1.5	4.5	0.20	0.01	$PhCCo_3(CO)_7dppe$
acetone	−0.50	2.7	1.5	0.18	0.01	$[PhCCo_3(CO)_8]_ndppe$
	−0.74	2.0	13	0.50	0.03	$PhCCo_3(CO)_7dppe$
THF	−0.45	1.6	5.3	0.17	0.01	$[PhCCo_3(CO)_8]_ndppe$
	−0.70	0.7	40	0.80	0.04	$PhCCo_3(CO)_7dppe$
CH_2Cl_2	−0.65	1.1	9.0	0.21	0.01	$[PhCCo_3(CO)_8]_ndppe$
	−0.85	1.1		0.57	0.03	$PhCCo_3(CO)_7dppe$
L = tpme						
CH_3CN	−0.41		14	0.58	0.02	$[PhCCo_3(CO)_8]_ntpme$
	−0.60		180			$PhCCo_3(CO)_7tpme$
acetone	−0.45	4.5	23.5	2.7	0.14	$PhCCo_3(CO)_7tpme$
CH_2Cl_2	−0.55	2.2	25			$PhCCo_3(CO)_7tpme$
L = PPh_3						
CH_2Cl_2	−0.52	1.5	22		0.01	$PhCCo_3(CO)_8PPh_3$
THF	−0.40	2.6	8		0.02	$PhCCo_3(CO)_8PPh_3$
acetone	−0.35	3.5	5		0.01	$PhCCo_3(CO)_8PPh_3$
CH_3CN	−0.40	5.0	6		0.01	$PhCCo_3(CO)_8PPh_3$
$PhCCo_3(CO)_8PPh_3/PPh_3$						
acetone	−0.60	3.2	30		0.6	$PhCCo_3(CO)_7(PPh_3)_2$
$[PhCCo_3(CO)_8]_2dppe/dppe$						
CH_2Cl_2	−0.85	1.7			0.03	$PhCCo_3(CO)_7dppe$

[a] Similar results were obtained with $CH_3CCo_3(CO)_9$; vs. Ag/AgCl (LiCl–acetone). [b] Molecule of starting cluster, values at 3–5% of initial current. [c] Reactions were performed in two steps without isolation of the initial products.

metal carbonyl substrates have been studied electrochemically but these have generally involved monodentate ligands.[2,4]

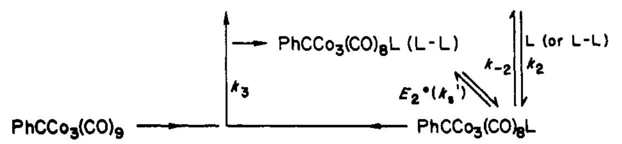
This paper describes the reactions of electrochemically generated cluster anions $PhCCo_3(CO)_9^{-}\cdot$ with Lewis base ligands. It was anticipated that a study of these reactions by bulk electrolysis and transient electrochemical techniques would allow clarification of aspects of the ETC mechanism.[5] Four questions were addressed. First, the role of the solvent was examined since stabilization of a reactive intermediate by coordination of a solvent molecule seemed feasible, at least in CH_3CN and THF. Second, the relative importance of homogeneous and heterogeneous electron transfer following electrochemical initiation was investigated since other workers either have not attempted to make the distinction[2] or have assumed that homogeneous electron transfer is very rapid.[2,3] Elucidation of the sequence of electron transfer and coordination steps for reactions involving the bidentate ligands dppm and dppe was a third objective, and finally, the determination of rate constants for a proposed mechanistic scheme was attempted.

Results and Discussion

Controlled Potential Electrolysis Reactions of $PhCCo_3(CO)_9$ with Added Ligand. Controlled potential electrolysis of $PhCCo_3(CO)_9$ was studied in CH_3CN, acetone, THF, and CH_2Cl_2 in the presence of PPh_3, dppm, dppe, and tpme (Table I) in order to elucidate the chain length of the ETC reaction.

Examination of the data in Table I reveals that no significant differences in efficiency (i.e., chain length) of the reactions are apparent as the solvent and/or ligand is varied; ~0.01 electron/molecule of parent cluster was consumed during the substitution of one carbonyl group by dppe and PPh_3 or two carbonyl groups by dppm. In each case the charge consumed was measured to the time when solution analysis showed >90% conversion to the product; no thermal reaction took place within the time scale of the primary ETC reactions.

These data substantiate the conclusion from the preparative work[1a] that catalyzed nucleophilic substitution involving $PhCCo_3(CO)_9$ is extremely efficient. There is no doubt that the initiating step is reduction to the radical anion $PhCCo_3(CO)_9^{-}\cdot$. Specific molecular pathways for the ETC reactions have been given in a preceding paper,[1] and a general kinetic scheme for cathode-induced reactions of $PhCCo_3(CO)_9$ is shown in (1) ($PhCCo_3(CO)_9$* activated cluster). The equilibrium constant K_3 for the primary



(1)

homogeneous electron-transfer reaction is related by the

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(1) (a) Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics*, first of three papers in this issue. (b) Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics*, second of three papers in this issue.

(2) (a) Arewgoda, C. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 5633. (b) Bezems, G. J.; Rieger, P. H.; Visco, S. J. *J. Chem. Soc., Chem. Commun.* 1981, 265. (c) Arewgoda, C. M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983**, *105*, 1893.

(3) (a) Darchen, A.; Mahe, C.; Patin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 243. (b) Darchen, A.; Mahe, C.; patin, H. *Nouv. J. Chim.* **1982**, *6*, 539.

(4) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61.

(5) Alder, R. W. *J. Chem. Soc., Chem. Commun.* **1980**, 1184.

Nernst equation to $E_1°$ and $E_2°$, and since $K_3 > 5 \times 10^3$ (at 293 K), it can be replaced by the unidirectional rate constant k_3. For a particular substrate k_s is constant and k_s', the heterogeneous electron-transfer rate constant for the product, is also unlikely to vary significantly with L as the steric requirements and general molecular configuration of the ligand are maintained throughout. Similarly, k_2 should be constant given that phosphorus is the common donor atom. Consequently, provided the chain termination pathways for $PhCCo_3(CO)_9^{-}\cdot$ are slow relative to k_3, the catalytic efficiency should be independent of L. The inference from the data is that homogeneous electron transfer is very fast.

The secondary $\bar{E}C\bar{E}$ reaction to substitute a second phosphorus atom is less efficient and is essentially noncatalytic, oxidation of the precursor radical anions occurring by heterogeneous rather than homogeneous electron transfer. The overall electron-induced pathway for dppe is given by eq 2. The chain-terminating step in this

$$PhCCo_3(CO)_9 + dppe \xrightarrow[\text{fast}]{0.01\ \text{F mol}^{-1}} PhCCo_3(CO)_8dppe + (CO) \xrightarrow[\text{slow}]{\sim 0.6\ \text{F mol}^{-1}} PhCCo_3(CO)_7dppe + CO \quad (2)$$

case could be the fast ligand-dissociative $\bar{E}C\bar{E}$ mechanism (see ref 1b) which will be in competition with the $\bar{E}C\bar{E}$ process (1). Moreover, the increased electron density on the cluster, once one CO group has been replaced by a phosphine ligand, will make nucleophilic substitution more difficult in the thermodynamic sense. This trend has also been found with other tricobalt carbon clusters and the substrates $(CF_3)_2C_2Co_2(CO)_6$[2c,6] and $Ru_3(CO)_{12}$.[7]

Reaction with dppm could be regarded as an exception to this trend as $PhCCo_3(CO)_7(\mu\text{-dppm})$ is the only kinetically stable product of ETC reactions. A "dangling" complex, $PhCCo_3(CO)_8dppm$, must be an intermediate species in these reactions, and this is supported by other evidence (vide infra). Spectroscopic data[1a] show that the partially ligated complexes $[RCCo(CO)_3]_m dppm$ (m = 1, 2) are kinetically labile and the fast ring closure to give $RCCo_3(CO)_7(\mu\text{-dppm})$ is thermal rather than electron-induced. The tighter "bite" of dppm compared to dppe may well explain the fast ring closure.

The shapes of the current–time curves observed during these reactions are interesting. Figure 1 shows typical curves obtained for electrolyses of $PhCCo_3(CO)_9$ in the presence of dppm. The current decreases at an increasing rate with time, resulting in a convex curve. In all solvents the current fell sharply to the background level, and TLC analysis of the solution at this point showed essentially complete conversion to $PhCCo_3(CO)_7dppm$. For reactions with dppe and PPh_3, a different current–time profile is observed in that, after an initial convex curve, a concave current–time curve was observed. In general, analysis of the solution by IR or TLC showed >80% conversion to the products $[PhCCo_3(CO)_8]_nL$ (L = dppe, PPh_3) after the initial rapid decrease in current. Since the electrolysis current is proportional to the concentration of electroactive material, a convex current–time curve indicates that the concentration of $PhCCo_3(CO)_9$ decreases at an increasing rate during electrolysis. This is consistent with an ETC reaction in which homogeneous electron transfer rapidly effects the overall conversion of $PhCCo_3(CO)_9$ to substituted product.

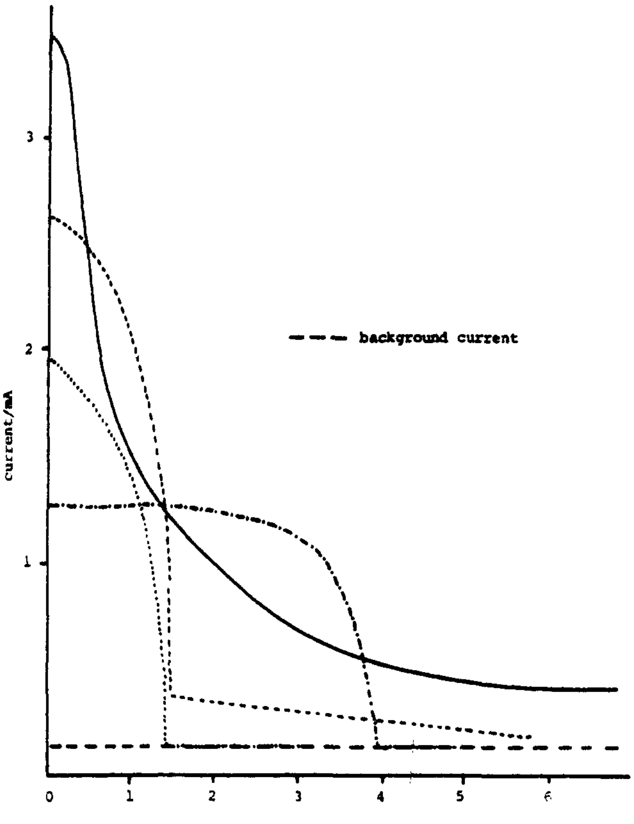

Figure 1. Current-time curves for the controlled electrolysis of $PhCCo_3(CO)_9$ with (—)PPh_3 in acetone, (- - -) dppm in CH_3CN, (···) dppe in acetone, and (- · -) dppm in CH_2Cl_2.

The observation of a further slow decrease in the current following the almost complete reaction of $PhCCo_3(CO)_9$ is probably indicative of the reduction of a product of the electrolysis. As the efficiency and completeness of ETC reactions is not dependent on the electrolysing potential (providing some reduction of the substrate occurs), no attempt was made to accurately control the potential of the working electrode and hence it is likely that some reduction of $[PhCCo_3(CO)_8]_nL$ (L = PPh_3, dppe) occurred. Electrolyses in the presence of dppm produced $PhCCo_3(CO)_7dppm$, and as the reduction potential of this species is ~0.4 V negative of that of $PhCCo_3(CO)_9$, reduction of this product would probably be negligibly small under the experimental conditions used. (The fraction (x) of a species reduced by electrolysis at the potential E is given by $x = \{1 + 10^{[(E-E^0)n/0.059]^{-1}}\}$ (at 25 °C, assuming Nerstian behavior), and for $E - E^0 = 0.3$ V, $x = 8 \times 10^{-6}$).

In discussing the overall efficiency of the bulk ETC reactions, we have not considered the *rate* of product formation. Data in Table I show that the rate is solvent-dependent, being faster in the polar solvents than in CH_2Cl_2. Furthermore, the formation of $PhCCo_3(CO)_7(PPh_3)_2$ is slower than the formation of $PhCCo_3(CO)_7(\mu\text{-dppe})$ from $[PhCCo_3(CO)_8]_2dppe$ even though the overall efficiency is the same. Changes in solvation arising from the disparate structures of the participating species in (1) and differing heterogeneous rate constants could cause the solvent dependence. Alternatively, the solvent itself may be involved in a cycle like (1) (L = solvent), and this prompted an investigation of the decomposition routes of $PhCCo_3(CO)_9^{-}\cdot$ in different solvents.

Electrochemical Reduction of $PhCCo_3(CO)_9$ in the Absence of Ligand. In acetone only $Co(CO)_4^-$ and a green non-carbonyl-containing precipitate were isolated from the electrolyte solution. By contrast, reduction of $PhCCo_3(CO)_9$ in CH_2Cl_2 led to the slow formation of acetylene

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[6] Cunninghame, R. G.; Downard, A. J.; Hanton, L. R.; Jensen, S. D.; Robinson, B. H.; Simpson, J. *Organometallics* **1984**, *3*, 180.

[7] Downard, A. J. Ph.D. Thesis, University of Otago, 1984.

[8] Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73.

products $Ph_2C_2Co_2(CO)_6$ and $Ph_2C_2Co_4(CO)_{10}$; the latter compound was isolated in 50% yield assuming a reaction stoichiometry shown in eq 3.

$$2PhCCo_3(CO)_9^{-}\cdot \rightarrow Ph_2C_2Co_4(CO)_{10} + 2[Co(CO)_4]^{-} \quad (3)$$

Several high-temperature reactions of $PhCCo_3(CO)_9$ have been found[9] to give similar alkyne complexes as does the reaction of BBr_3 with $RC(O)CCo_3(CO)_9$,[10] whereas clusters with Co_3C units linked by C—C or C≡C bonds are produced from reactions with $XCCo_3(CO)_9$ (X = Cl, Br).[9] Since the source of the acetylene fragment was shown to be the carbyne carbon in the thermal reactions, we presume the same holds for the electrolysis reactions. A mechanism involving Co–Co bond cleavage is necessary, and the weakened Co–Co bond in the radical anion would encourage the carbyne coupling reactions.

A mauve-colored product was formed in low yield in CH_2Cl_2, and a similar colored compound was isolated as the major product from electrolysis in THF. It is very sensitive to oxygen, aerial oxidation giving $PhCCo_3(CO)_9$ and decomposition. The band at 2047 cm^{-1} is consistent with the $\nu(CO)_{t\text{-sym}}$ mode of either a substituted cluster, $PhCCo_3(CO)_9^{-}\cdot$, or a decomposition product. However, the spectroscopic data are different to those of green Na^+-[2,2,2-kryptand][$PhCCo_3(CO)_9^{-}\cdot$],[10] and no esr signal was observed; the addition of a phosphine ligand did not give Co_3C products.

In CH_3CN, electrolysis of $RCCo_3(CO)_9$ (R = Ph, Me) afforded the first CH_3CN derivatives of the Co_3C cluster $RCCo_3(CO)_8(NCCH_3)$ as labile compounds in both solid and solution (eq 4). Addition of a monodentate phosphine

$$RCCo_3(CO)_9 + NCCH_3 \xrightarrow[\sim 1\ F\ mol^{-1}]{0.5\ V} RCCo_3(CO)_8NCCH_3 + CO \quad (4)$$

$$R = Ph, CH_3$$

ligand to these complexes gave $RCCo_3(CO)_8L$ in 100% yield; the addition of dppm gave $RCCo_3(CO)_7$dppm. The profile of the $\nu(CO)$ spectra of $RCCo_3(CO)_8(NCCH_3)$ is unlike those of other monosubstituted clusters being identical with $RCCo_3(CO)_9$ but with an appropriate shift in energy of ~15 cm^{-1}. Structural analyses of $(CF_3)_2C_2Co_2(CO)_5(NCCH_3)$[2c] and $[(CF_3)_6C_6]Co_2(CO)_2(NCCH_3)_2$[11] revealed that coordination was to the normally less favorable coordination site because of the reduced steric demand of the CH_3CN ligand. Thus in $RCCo_3(CO)_8(NCCH_3)$ the CH_3CN group may substitute axially rather than to the normal[12] equatorial site. Cyclic voltammograms at Pt of $CH_3CCo_3(CO)_8(NCCH_3)$ in CH_3CN under Ar show a one reduction process, $E_{p,c} \approx -0.9$ V, and oxidation waves at $E_{p,a} \approx -0.5$ and 0.3 V; the latter wave is assigned to $Co(CO)_4^-$. If the solution is saturated with CO, the peak at $E_{p,c} = -0.9$ V disappears to be replaced by the one at $E_{p,c} = -0.50$ V (i.e., $RCCo_3(CO)_9$). Thus the original wave at −0.90 V is assigned to the reduction of $CH_3CCo_3(CO)_8(NCCH_3)$. The transient electrochemistry of $RCCo_3(CO)_9$ in CH_3CN, and the coulometry which gives $n = 1$ show that the acetonitrile complexes are not produced by a catalytic process; their formation in bulk electrolysis reactions is simply electron-induced nucleophilic substitution.

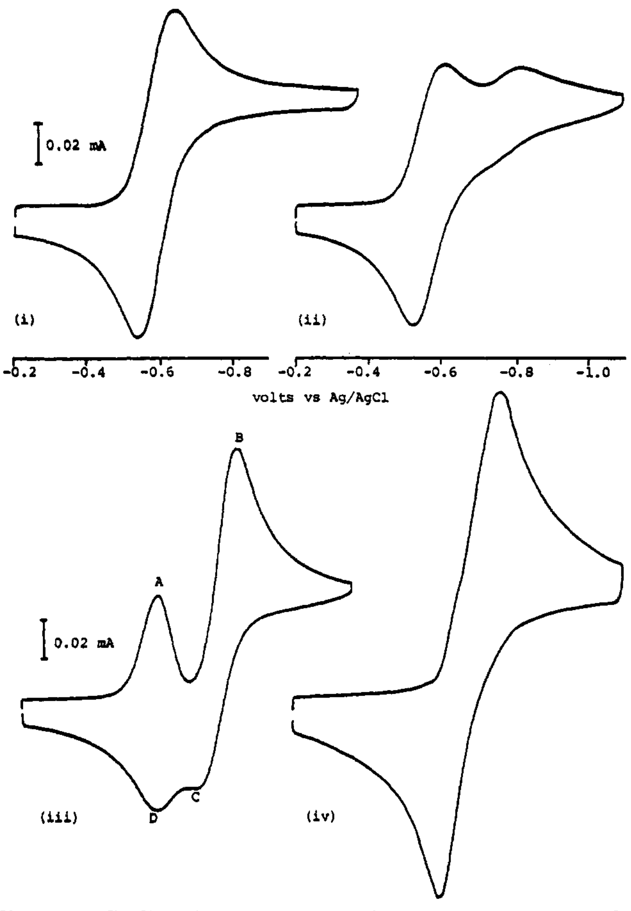

Figure 2. Cyclic voltammograms in CH_2Cl_2 at Pt (100 mV s^{-1}) of (i) $PhCCo_3(CO)_9$ (0.5 mM), (ii) $PhCCo_3(CO)_9$ (0.5 mM) + PPh_3 (0.1 mM), (iii) $PhCCo_3(CO)_9$ (0.5 mM) + PPh_3 (1.75 mM), and (iv) $PhCCo_3(CO)_8PPh_3$ (0.5 mM).

These experiments demonstrate that the reactivity of $PhCCo_3(CO)_9^{-}\cdot$ in the absence of a nucleophile is solvent-dependent, but significantly, the reactions are slow compared to the reactions with nucleophiles like phosphines. Consequently, solvated complexes $PhCCo_3(CO)_8(solv)^{-}\cdot$ are not intermediates in the ETC reactions described for the polydentate ligands although the rate-determining step is solvent-dependent. Further basis for this assertion comes from the similar efficiency for the ETC reactions in all solvents and the observation that the decomposition products do not appear during these reactions.

Electrochemistry of $PhCCo_3(CO)_9$/Ligand Solutions. Cyclic voltammetry can be used to follow an $\bar{E}C\bar{E}$ process such as (1) as the magnitude of the peak current of a reduction wave due to the product is indicative of the relative rates of nucleophilic substitution and homogeneous electron transfer.[2-4] Since the electrode processes for the products are not straightforward,[1b] we will consider each ligand in turn.

(a) PPh_3.[13] The electrochemistry of $PhCCo_3(CO)_9$ in the presence of PPh_3 in CH_2Cl_2 was studied initially as this was expected to be a relatively simple system. Typical cyclic voltammograms are shown in Figure 2 where scan (iii) shows the limiting behavior at high concentration of PPh_3. As the concentration of added PPh_3 increases, the current due to reduction of $PhCCo_3(CO)_9$ decreases and a new reduction process is seen at more cathodic potentials; behavior indicative of an $\bar{E}C\bar{E}$ mechanism.

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[9] Robinson, B. H.; Spencer, J. *J. Organomet. Chem.* **1971**, *30*, 267. Acetylene complexes derived from μ_3-CR groups have also been found with Fe_3 clusters. De Montauson, D.; Mathieu, R. *J. Organomet. Chem.* **1983**, *328*, C83.

[10] Trounson, M. E.; Lindsay, P. N. T. Ph.D. Theses, University of Otago, 1984 and 1983, respectively.

[11] Arewgoda, C. M.; Ditzel, E. J., unpublished work, University of Otago.

[12] Matheson, T. W.; Penfold, B. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr.* **1977**, *B33*, 1980.

[13] Rieger and co-workers[2b] have briefly considered the electrochemistry of $PhCCo_3(CO)_9/PPh_3$ solutions.

Closer inspection of the scans however reveals some interesting features. Considering scan (iii), peak A can be assigned to the reduction of $PhCCo_3(CO)_9$ which has been shifted to more positive potentials by the following chemical reaction. Peaks B, C, and D all arise from the product(s), but none of these corresponds in position to those observed in CV's of $PhCCo_3(CO)_8PPh_3$ recorded separately (scan (iv)). The peak potential of D, $E_p(D)$, becomes cathodic of $E_p(A)$ at slow scan rates (<100 mV s^{-1}), indicating that D does not correspond to oxidation of $PhCCo_3(CO)_9^{-}\cdot$. However, $[E_p(B) + E_p(D)]/2$ equals $(E_p^{red.} + E_p^{ox.})/2$ for $PhCCo_3(CO)_8PPh_3$, suggesting a common assignment.

$$PhCCo_3(CO)_8PPh_3 + e \underset{D}{\overset{B}{\rightleftharpoons}} PhCCo_3(CO)_8PPh_3^{-}\cdot \quad (5)$$

Peak C (scan (iii)) is not a feature of the electrochemistry of $PhCCo_3(CO)_8PPh_3$ in the presence of PPh_3 alone.[1b]

An explanation for peak C is provided by the ligand dissociative $\bar{E}C\bar{E}$ mechanism outlined in the preceding paper.[1b] This mechanism involves rapid PPh_3 dissociation from the $PhCCo_3(CO)_8PPh_3^{-}\cdot$ to give a species, $PhCCo_3(CO)_8^{-}\cdot$ (or $PhCCo_3(CO)_8solv^{-}\cdot$) which is more difficult to reduce than $PhCCo_3(CO)_9^{-}\cdot$. Thus, under the condition of scan (iii) (Figure 2), further reaction of $PhCCo_3(CO)_8L^{-}$ can occur via path 6 or 7. If the electron transfer step (7)

$$PhCCo_3(CO)_8PPh_3^{-}\cdot \xrightarrow{-PPh_3} [PhCCo_3(CO)_8^{-}\cdot] \xrightarrow{C} [PhCCo_3(CO)_8] \quad (6)$$

$$PhCCo_3(CO)_8PPh_3^{-}\cdot + PhCCo_3(CO)_9 \rightarrow PhCCo_3(CO)_8PPh_3 + PhCCo_3(CO)_9^{-}\cdot \quad (7)$$

competes successfully with chemical step C (path 6), then oxidation of $PhCCo_3(CO)_8PPh_3^{-}\cdot$ will be observed. This corresponds to peak C while the final product of path 6 is oxidized at D. This result is important since it indicates that homogeneous electron transfer plays an important role in this reaction. Formation of the bissubstituted product $PhCCo_3(CO)_7(PPh_3)_2$ was not observed.

Addition of PPh_3 to a solution of $PhCCo_3(CO)_9$ in CH_3CN results in an electrochemical response which is qualitatively similar to that observed in CH_2Cl_2. However, under the same concentration and scan rate conditions, the decrease in current due to reduction of $PhCCo_3(CO)_9$ is greater in CH_3CN, indicating a more rapid reaction in this solvent. Formation of $PhCCo_3(CO)_7(PPh_3)_2$ is not observed under these conditions, indicating that the electron transfer step (7) is faster than the alternative reaction (8). This again demonstrates the involvement

$$PhCCo_3(CO)_8PPh_3^{-}\cdot + PPh_3 \rightleftharpoons PhCCo_3(CO)_7(PPh_3)_2^{-}\cdot + CO \quad (8)$$

of the homogeneous electron-transfer step. Consistent with this is the observation of an oxidation process analogous to that assigned to $PhCCo_3(CO)_8PPh_3^{-}\cdot$ in CH_2Cl_2. Its relative oxidation current is similar to that in CH_2Cl_2, suggesting that the increased reaction rate in CH_3CN is not due to a faster homogeneous electron-transfer step and hence that this step is not rate-controlling.

(b) dppm. Figure 3 shows CV's of $PhCCo_3(CO)_9$ recorded in CH_2Cl_2 in the presence of dppm; scans (iii) and (iv) show the limiting behavior at high concentrations of ligand. Two new reduction processes appear; the more cathodic couple can be assigned to $[PhCCo_3(CO)_7dppm]^{0/-}$ by comparison with its known electrochemistry.[1b] A reduction wave, intermediate between $E_{p,c}[PhCCo_3(CO)_9]$ and $E_{p,c}[PhCCo_3(CO)_7dppm]$, is found in all the polarographic and cyclic voltammetric responses, and a reasonable assignment is to the reduction of $PhCCo_3(CO)_8dppm$ (eq 9), where dppm is coordinating via one phosphorus

$$PhCCo_3(CO)_8dppm + e \overset{E_p^{r}}{\rightleftharpoons} PhCCo_3(CO)_8dppm^{-}\cdot \xrightarrow{fast} products \quad (9)$$

atom (E_p^{r} at -0.65 V is also similar to that for E_p^{r}-$[PhCCo_3(CO)_8]_2dppe$ at -0.66). This species was not observed during bulk electrolysis or chemically induced reactions but has a significant lifetime on the cyclic voltammetric time scale. Figure 3 illustrates that at 100 mV s^{-1}, the current due to reduction of $PhCCo_3(CO)_8dppm$ is small compared to that due to $PhCCo_3(CO)_7dppm$, while at 500 mV s^{-1}, the opposite relation is observed. This is consistent with a very rapid reaction, eq 10.

$$PhCCo_3(CO)_8dppm \rightleftharpoons PhCCo_3(CO)_7dppm + CO \quad (10)$$

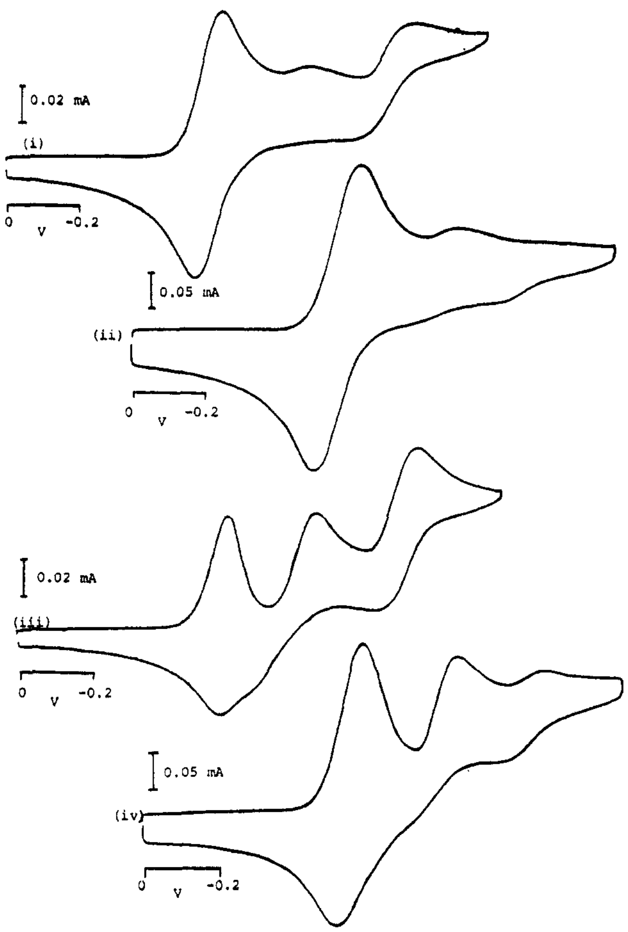

Figure 3. Cyclic voltammograms of 0.5 mM $PhCCo_3(CO)_9$ in CH_2Cl_2 at Pt (295 K) with added dppm: (i) 0.15 mM dppm, 100 mV s^{-1}; (ii) 0.15 mM dppm, 500 mV s^{-1}; (iii) 3.0 mM dppm, 100 mV s^{-1}; (iv) 3.0 mM dppm, 500 mV s^{-1}.

The detection of the neutral species $PhCCo_3(CO)_8dppm$ indicates that under these conditions, electron transfer occurs to an appreciable extent prior to further substitution. This raises the question as to whether ring closure (eq 10) is an electron-catalyzed process.

The electrode response of $PhCCo_3(CO)_7dppm$ under ETC conditions is well-behaved, while scans (iii) and (iv) suggest that the electrochemistry of $PhCCo_3(CO)_8dppm$ is similar to that of $PhCCo_3(CO)_8PPh_3$ discussed above. Comparison of the reduction peaks due to $PhCCo_3(CO)_9$ and $PhCCo_3(CO)_8dppm$ in Figure 3, scans (iii) and (iv), is informative. As observed for scans in the presence of PPh_3, the reduction peak of $PhCCo_3(CO)_9$ is very sharp. This is the expected result of depletion of $PhCCo_3(CO)_9$ at faster than the diffusion-controlled rate or of electron transfer

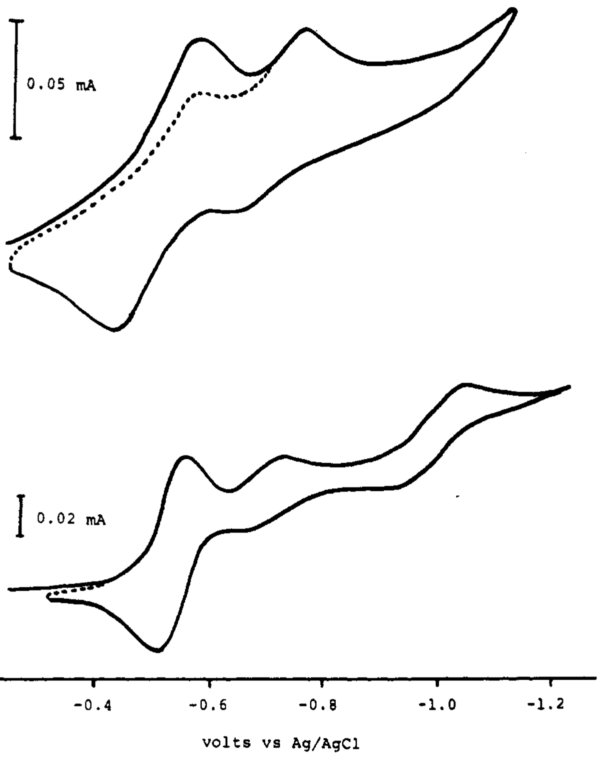

Figure 4. Cyclic voltammograms of $PhCCo_3(CO)_9$ with equimolar dppe in CH_2Cl_2 at Pt under Ar (295 K): upper scan, 5 V s^{-1}; lower scan, 20 mV s^{-1}.

back to the electrode occurring during an $\vec{E}C\bar{E}$ process. The reduction peak due to $PhCCo_3(CO)_8dppm$ on the other hand has the appearance of a normal diffusion-controlled wave. This indicates that a rapid $\vec{E}C\bar{E}$ process does not occur with this species. Either reaction to form $PhCCo_3(CO)_7dppm^{-}\cdot$ does occur on reduction of $PhCCo_3(CO)_8dppm$, but subsequent electron transfer is slow, or alternatively, $PhCCo_3(CO)_8dppm^{-}\cdot$ is stable on the cyclic voltammetric time scale (and coordination of the second phosphorus atom occurs largely in the neutral compound). Clearly a complex mechanistic scheme is necessary to accommodate all these possibilities.

(c) dppe. Current-voltage responses in CH_2Cl_2 or acetone for the reduction of $PhCCo_3(CO)_9$ in the presence of equimolar dppe (Figure 4) are consistent with the formation of neutral $[RCCo_3(CO)_8]_n$dppe ($n = 1$ or 2) and $PhCCo_3(CO)_7$dppe by ETC reactions. Formation of $PhCCo_3(CO)_7$dppe is slow on the electrochemical time scale in CH_2Cl_2 (but faster than the formation of $PhCCo_3(CO)_7(PPh_3)_2$) so that the minor wave at $E_{p,c} \simeq -1.15$ V is only significant at scan rates <100 mV s^{-1}; its formation is faster in acetone.

The product with $E_{p,c} \simeq -0.8$ V in CH_2Cl_2 is an octacarbonyl derivative, but the question is whether $[PhCCo_3(CO)_8]_2$dppe is the initial ETC product or, as seems more likely, $PhCCo_3(CO)_8$dppe with a "dangling" ligand the initial ETC product. In CH_2Cl_2 there are *two* oxidation waves ($E_{p,a} \approx -0.68$ and -0.53 V at 100 mV s^{-1}), apart from the oxidation wave associated with $PhCCo_3(CO)_7dppe^{-}\cdot$. The most positive oxidation wave moves ~40 mV negative of $E_{p,c}$, $[PhCCo_3(CO)_9]$ at 50 mV s^{-1}, showing that it is not due to the oxidation of $PhCCo_3(CO)_9^{-}\cdot$. While $i_{p,c}$ for the reduction of $PhCCo_3(CO)_9$ decreases on repeat scans, $i_{p,c}$ for the reduction of $[PhCCo_3(CO)_8]_n$dppe and the peak currents for the oxidation waves remain constant even at slow scan rates where $PhCCo_3(CO)_7$dppe formation is insignificant. Thus an ECE reaction depletes $PhCCo_3(CO)_9$ at the electrode surface, but the total amount of oxidizable material remains constant.

Consideration of the ligand dissociative $\vec{E}C\bar{E}$ mechanism[1b] provides an explanation for the two extra oxidation waves on the reverse scan. The wave at $E_{p,a} = -0.53$ V is at similar potential to that attributed to the oxidation of $PhCCo_3(CO)_8^{-}$; the other wave at $E_{p,a} = -0.68$ V is assigned to the oxidation of the dangling species $PhCCo_3(CO)_8dppe^{-}\cdot$ (eq 11 and 12).

$$\mathrm{PhCCo_3(CO)_9}^{-\cdot} + \mathrm{dppe} \rightleftharpoons \mathrm{PhCCo_3(CO)_8dppe}^{-\cdot} + \mathrm{CO} \quad (11)$$

$$\begin{tikzcd}
\mathrm{PhCCo_3(CO)_8dppe}^{-\cdot} \arrow[r, shift left] \arrow[d, shift left, "-0.68\ \mathrm{V}"] & \mathrm{PhCCo_3(CO)_8}^{-\cdot} + \mathrm{dppe} \arrow[l, shift left] \arrow[d, shift left, "-0.53\ \mathrm{V}"] & \\
\mathrm{e} + \mathrm{PhCCo_3(CO)_8dppe} \arrow[u, shift left] \arrow[d] & + \ \mathrm{PhCCo_3(CO)_8} \arrow[u, shift left, "\mathrm{e}"] \arrow[d, "\mathrm{CO}"] \arrow[r] & {[\mathrm{PhCCo_3(CO)_8}]_2\mathrm{dppe}} \\
\mathrm{PhCCo_3(CO)_7dppe} & \mathrm{PhCCo_3(CO)_9} & (12)
\end{tikzcd}$$

(d) tpme. The *i–E* responses of $PhCCo_3(CO)_9$ in the presence of tpme were obtained in CH_3CN. Formation of substituted products was slow relative to dppm and dppe, but the appearance of a new reduction wave ~0.2 V negative of that due to $PhCCo_3(CO)_9$ is compatible with an ETC reaction to form the monosubstituted $[PhCCo_3(CO)_8]_m$tpme ($m = 1$ or 2). There was no evidence in the transient electrochemistry for further catalyzed substitution which supports the thesis that only the substitution of one CO group in the $RCCo_3(CO)_9$ clusters is efficiently catalyzed. This observation is also consistent with the preparative work.[1a]

Kinetics of Ligand Substitution Reactions of $PhCCo_3(CO)_9$. Evaluation of the rate data for the various steps in the ETC reactions is methodologically and computationally a difficult goal because of the interwoven electron-transfer steps and structural rearrangement.[4,14] A rigorous treatment will be described elsewhere,[15] but in this paper we will take a realistic approach of simulating the electrochemical behavior of the reactant only, in one solvent—$PhCCo_3(CO)_9$ in CH_2Cl_2 is used as the model substrate.

Figures 5 and 6 show a series of initial scan cyclic voltammograms of $PhCCo_3(CO)_9$ in the presence of PPh_3 and dppm which were utilized in the quantitative interpretation of the *i–E* response. For all ligands the current i_p^0 due to the reduction of $PhCCo_3(CO)_9$ becomes independent of ligand concentration at high concentrations, suggesting a rate-determining dissociative step. Given that the charge transfer is electrochemically and chemically reversible,[16] the first-order dissociation step of $PhCCo_3(CO)_9^{-}\cdot$ is reversible (eq 13).

$$\begin{tikzcd}
\mathrm{C{-}CO} \arrow[r, shift left, "\mathrm{e}"] & \mathrm{C{-}CO}^{-\cdot} \arrow[l, shift left] \arrow[r, shift left, "k_1"] & {[\mathrm{C{-}CO}^{-\cdot}]^*} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left, "k_2"] \\
\mathrm{C{-}L} & \arrow[u] & \mathrm{C{-}L}^{-\cdot} \arrow[u, shift left, "k_{-2}"] \arrow[ll, "\mathrm{C{-}CO}", "k_3"']
\end{tikzcd} \quad (13)$$

In eq 13 $[C \equiv PhCCo_3(CO)_8]$ the activated complex is written for convenience with the Co–CO bond intact. This coordinatively unsaturated complex could be formed by Co–CO bond cleavage[2] or CO dissociation,[3] and it is easily shown that the steady-state rate laws do not allow an experimental distinction between these two mechanisms

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(14) See: Zizelman, D. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771, for application of simulation techniques to catalyzed reactions of mononuclear carbonyls.

(15) Unpublished work at University of Otago and Deakin University (A.M.B.).

(16) Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1979**, *16*, 410.

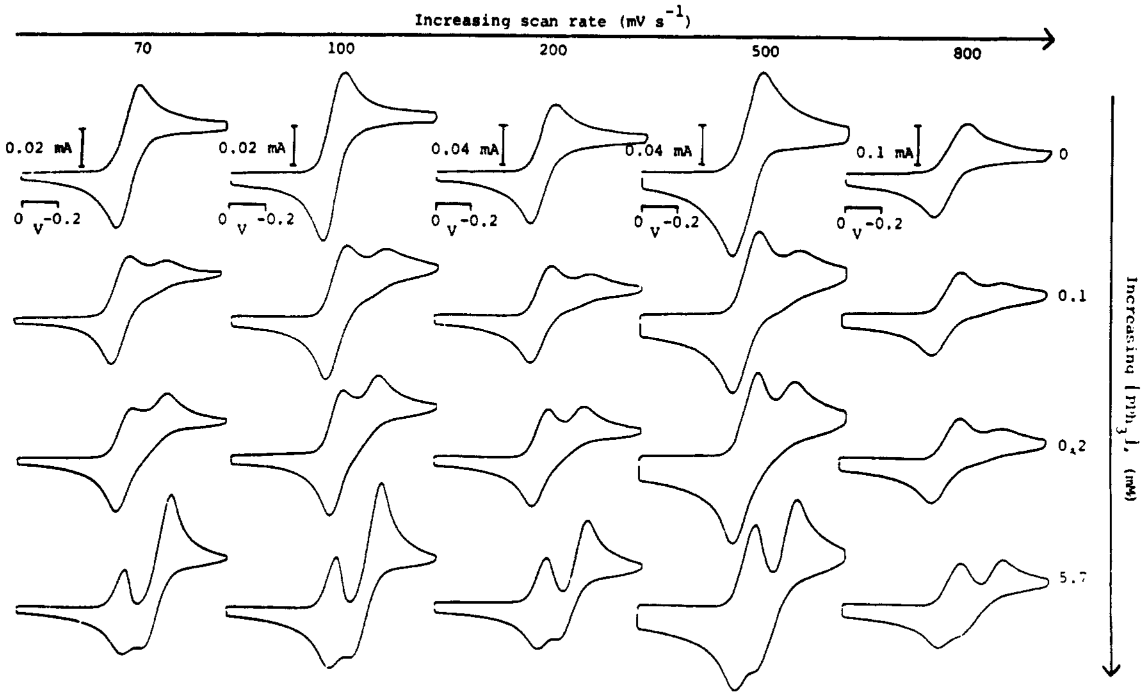


Figure 5. Initial scan cyclic voltammograms of 0.5 mM $PhCCo_3(CO)_9$ in CH_2Cl_2 at scan rates of 70–800 mV s^{-1} and PPh_3 concentrations of 0–5.7 mM (at Pt; V vs. Ag/AgCl; 295 K).

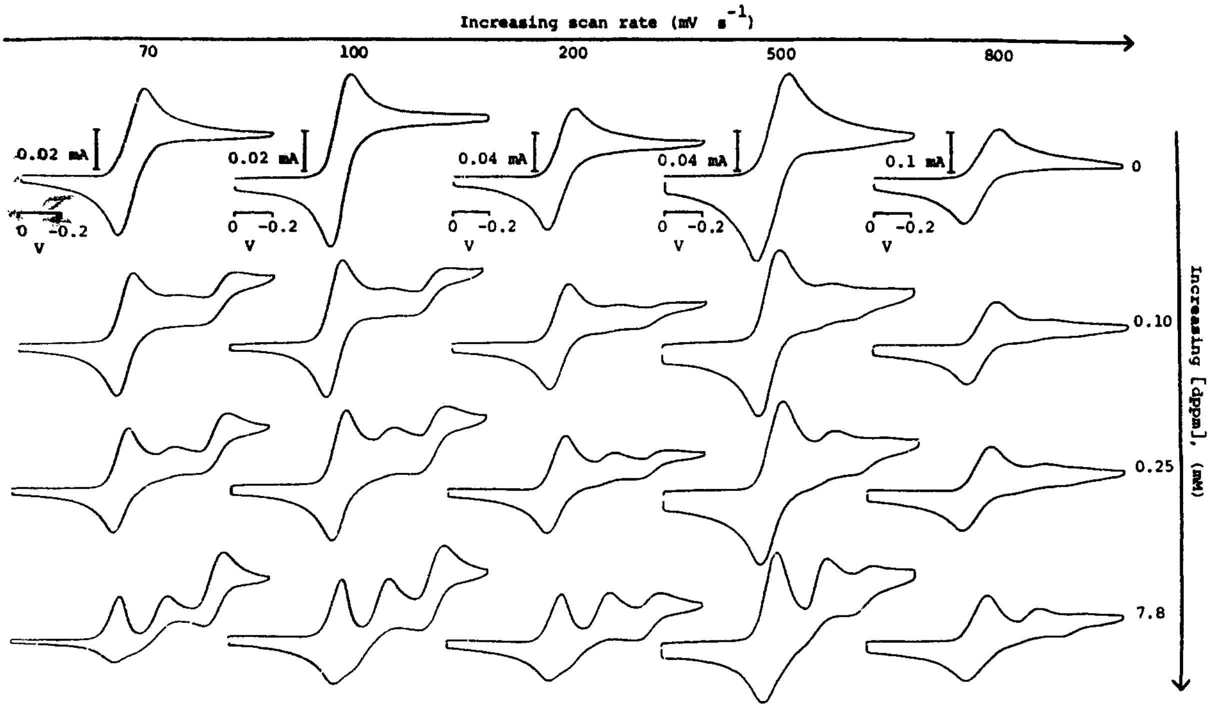


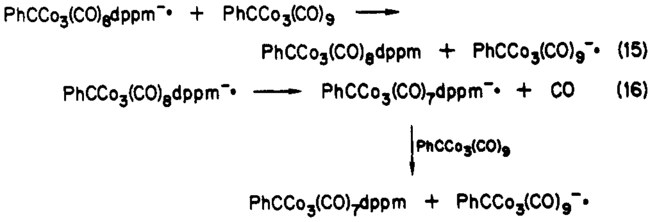
Figure 6. Initial cathodic scan cyclic voltammograms of 0.5 mM $PhCCo_3(CO)_9$ in CH_2Cl_2 at scan rates of 70–800 mV s^{-1} and dppm concentrations of 0–7.8 mM (at Pt; V vs. Ag/AgCl; 295 K).

(i.e., from the dependence on ligand or CO). For simplicity we will write the dissociative step as CO loss and assume that, in the potential range under discussion (where heterogeneous reduction of $PhCCo_3(CO)_9$ occurs), the rate of consumption of $PhCCo_3(CO)_8L^{-}\cdot$ (or L–L) by homogeneous reaction equals the rate of formation (i.e., k_3[C–CO] >> k_{-2}). The results of the bulk electrolysis experiments and transient electrochemistry provide clear justification for this assumption. The steady-state rate law is then[7] (14).

$$\text{rate} = k_1[\text{C–CO}^{-}\cdot]/[1 + (k_{-1}[\text{CO}]/k_2[\text{L}])] \quad (14)$$

When k_2[L] >> k_{-1}[C–CO], the rate depends only on k_1[C–CO$^{-}\cdot$]; hence, k_1 can be determined from the response at high ligand concentrations. The experimental parameter from the cyclic voltammograms which measures the rate of disappearance of $PhCCo_3(CO)_9$ is the cathodic peak current ratio i_p/i_p^0 which represents the cathodic peak currents of $PhCCo_3(CO)_9$ with and without added ligand. Since the kinetic expression does not include the product, its electrochemical and chemical behavior is unimportant. For example, in the reactions with dppm it is irrelevant whether homogeneous electron transfer occurs by path 15 or 16.

Table II compares the results of simulations by using k_1 = 3.2 s^{-1} with the experimental results obtained from CV's of $PhCCo_3(CO)_9$ in the presence of dppm; a similar value was obtained with PPh_3 and dppe. This value obtained for k_1 has an estimated error of ±0.2 s^{-1}, the un-



$$\mathrm{PhCCo_3(CO)_8dppm^{-\bullet} + PhCCo_3(CO)_9 \longrightarrow PhCCo_3(CO)_8dppm + PhCCo_3(CO)_9^{-\bullet}} \quad (15)$$

$$\mathrm{PhCCo_3(CO)_8dppm^{-\bullet} \longrightarrow PhCCo_3(CO)_7dppm^{-\bullet} + CO} \quad (16)$$

$$\mathrm{PhCCo_3(CO)_7dppm^{-\bullet} \xrightarrow{PhCCo_3(CO)_9} PhCCo_3(CO)_7dppm + PhCCo_3(CO)_9^{-\bullet}}$$

certainty being an estimate of the sensitivity of the simulated i_p/i_p^0 values to changes in k_1 as other parameters used in the simulations could be calculated independently.

The value of 3.2 s^{-1} for k_1 at 293 K in CH_2Cl_2 can be compared with k_{obsd} = 3.6 × 10^{-5} s^{-1} at 308 K for the thermal substitution reaction (17) in hexane.[17] Thus there is at least 5 orders of magnitude increase in rate of nucleophilic substitution by PPh_3 upon the addition of an electron to $PhCCo_3(CO)_9$.

$$\mathrm{PhCCo_3(CO)_9 + PPh_3 \rightarrow PhCCo_3(CO)_8PPh_3 + CO} \quad (17)$$

A comparison of the k_{-1}/k_2 ratio would give an indication of the differing rates of nucleophilic attack, but evaluation of this ratio by simulation techniques is subject to greater uncertainty as it depends on the diffusion coefficients chosen for the ligand and CO. Qualitatively, the cathodic peak currents at low ligand concentrations for the primary products should reflect the rate of nucleophilic attack by the ligand, relative to attack by CO, and this assessment gives the order PPh_3 > dppe ≈ dppm. The respective k_{-1}/k_2 ratios were ~2, ~6, and ~8 (error ±2), but to some extent, this agreement in trend is expected given the simulation procedure, and a more complete treatment is necessary to evaluate k_2.

The reasonable agreement of theoretical and experimental values of i_p/i_p^0 achieved for the cyclic voltammetry of $PhCCo_3(CO)_9$ in the presence of phosphine ligands suggests that under these conditions (of scan rate and concentration), the kinetic scheme (13) is a good approximation of the real system. This does not provide support for a carbonyl-dissocation mechanism for the rate-determining step since k_1 can only be described as the rate constant of a dissociative step (or the overall rate constant of several dissociative steps) while k_{-1}/k_2 corresponds to the ratio of rate constants for two associative steps.

The coulometric data show that the rate-determining step is strongly influenced by the solvent. Unfortunately, the, albeit slow, ECE process in CH_3CN and the possibility of a similar process in THF to give $PhCCo_3(CO)_8THF$ precluded a detailed kinetic analysis in these solvents. Preliminary results gave values of k_1 of ~7 s^{-1} for both THF and acetone.

Conclusion

For electron-induced substitution reactions of $RCCo_3(CO)_9$[18] with PPh_3, dppm, and dppe we conclude first that homogeneous electron transfer from the Lewis base substituted cluster radical anions is very rapid (i.e., is not rate-controlling). Second, the efficiency and specificity of the primary ETC reaction vary little with solvent and a long chain length catalytic reaction is implied by the consumption of ~0.01 electron/molecule of substituted cluster product. Third, coordination of solvent molecules at any stage of the reaction is not detected but the rate-determining dissociative step is solvent dependent. Finally, the addition of an electron to $PhCCo_3(CO)_9$ leads to a substantial increase in its rate of substitution by monodentate or polydentate ligand.

Table II. Experimental and Theoretical Cathodic Peak Current Ratios (i_p/i_p^0) for the Substitution of $PhCCo_3(CO)_9$ by dppm in CH_2Cl_2[a]

10^4 [dppm], mol dm^{-3}	scan rate, V s^{-1}	i_p/i_p^0 exptl	i_p/i_p^0 theor
2.5	0.07	0.66	0.71
2.5	0.10	0.72	0.76
2.5	0.20	0.76	0.83
2.5	0.50	0.85	0.89
2.5	0.80	0.89	0.92
17.5	0.07	0.53	0.53
17.5	0.10	0.61	0.60
17.5	0.20	0.73	0.73
17.5	0.50	0.85	0.85
17.5	0.80	0.88	0.89
77.5	0.07	0.48	0.46
77.5	0.10	0.56	0.54
77.5	0.20	0.69	0.69
77.5	0.50	0.84	0.83
77.5	0.80	0.88	0.88

[a] $[PhCCo_3(CO)_9]$ = 5 × 10^{-4} mol dm^{-3}; k_1 = 3.2 s^{-1}; k_{-1}/k_2 = 8.

Electrochemical synthesis of polydentate complexes of tricobalt carbon clusters is only chain-catalyzed for the coordination of one donor atom; subsequent ring closure or polymer formation is either thermal or the result of an EC mechanism.

While the species $RCCo_3(CO)_8L$ is well-established, the isolated products from the primary ETC reaction with dppe and dppm are respectively $[RCCo_3(CO)_8]_2$dppe and $RCCo_3(CO)_7$dppm. However, there is no doubt from the transient electrochemistry of $RCCo_3(CO)_9$/L–L systems or $[RCCo_3(CO)_8]_2$dppe that "dangling" complexes are formed in the initial ETC reaction with polydentate ligands. With dppm homogeneous and heterogeneous electron transfer successfully compete with ring closure at the electrode surface so that there is sufficient neutral $RCCo_3(CO)_8$dppm to be reduced on the voltammetric time scale. In bulk solution thermal ring closure is obviously very fast. By comparison, for dppe, dimer formation is faster than ring closure; subsequent electron-induced or thermal reactions to give the chelate complexes are also slow. These rate factors combine to allow the ETC reaction to be controlled to give specific polydentate complexes.[1]

The principles established in this study form a basis for a detailed kinetic description of ETC reactions with $RCCo_3(CO)_9$ clusters, as well as other cluster substrates which will be reported in subsequent papers.

Experimental Section

Preparative methods, solvent purification, and techniques for transient electrochemistry and controlled potential electrolyses have been described in the preceding papers.[1]

Treatment of Electrochemical Data. Fortran programs for the simulations were based on the relevant statements given by Feldberg[19] and run on a Digital Vax 11/780 computer. Instead of the normalized potential calculated by Feldberg's method, most programs output the potential in volts to enable a direct comparison of experimental and theoretical cyclic voltammograms. In the absence of chemical kinetics there was no requirement for a large number of iterations and simulations from 2000 iterations before reversal were not significantly different to those of 200. However, where homogeneous electron transfer took place and

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(17) Cartner, A.; Cunninghame, R. G.; Robinson, B. H. *J. Organomet. Chem.* **1975**, *92*, 49.

(18) Results for $CH_3CCo_3(CO)_9$ reactions were virtually identical with those for $PhCCo_3(CO)_9$ and have not been reproduced here. The general concepts apply to all $YCCo_3(CO)_9$ clusters where Y is aryl or alkyl or F. The instability of the radical anions when Y = Cl, Br, or H means that their reactions with nucleophiles are not open to systematic study.

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

the concentration of added nucleophile was small compared to $RCCo_3(CO)_9$, more than 5000 iterations were required for accurate simulation and this was prohibitively time-consuming. Other methods are being used to overcome this problem.

The area of the electrode used (if nonplanar) was calculated from cyclic voltammograms in CH_3CN using the published value for the diffusion coefficient of ferrocene,[20] and use of this result gave values for the diffusion coefficients in CH_2Cl_2 of 2.0 (5) × 10^{-5} $cm^2\ s^{-1}$ for ferrocene and 9.8 (5) × 10^{-6} $cm^2\ s^{-1}$ for $PhCCo_3(CO)_9$. The latter figure is in reasonable agreement with 5.7 × 10^{-6} $cm^2\ s^{-1}$ for $PhCCo_3(CO)_9$ obtained from polarography at the dme and is similar to that reported for $Au_9(PPh_3)_8^{3+}$ in acetone (6.4 × 10^{-6} $cm^2\ s^{-1}$).[21] There is little variation in D with the nature of the alkyl or aryl group R in $RCCo(CO)_9$, and the simulated diffusion coefficients for $RCCo_3(CO)_7$(L–L) derivatives were also similar.

Convolution analyses were applied to the cyclic voltammograms using a program based on the algorithm for the convolution integral $I(t)$ given in ref 22.

Determination of the Experimental Cathodic Peak Current Ratio. The peak current due to the reduction of $PhCCo_3(CO)_9$ (5.0 × 10^{-4} mol dm^{-3}) in the absence of phosphine ligand was initially measured as a function of the scan rate ν. For a reversible fast electron transfer occurring at a planar electrode, a linear dependence on $\nu^{1/2}$ is expected, but since the rate of electron transfer for $PhCCo_3(CO)_9$ is not very fast and a cylindrical electrode was sometimes used, a curved function may result. A standard solution of phosphine ligand was made up in a 10 cm^3 volumetric flask. The concentration of this solution was chosen so that a 0.5 or 1 cm^3 aliquot added the required minimum molar equivalent of phosphine to the reaction solution. An aliquot (typically 0.5 cm^3) of this solution was added to the electrochemical solution by using a 1 cm^3 graduated syringe. Argon was briefly bubbled through the solution to ensure homogeneity. CV's were recorded at each scan rate; argon was bubbled through the solution after each scan. Addition of the phosphine dilutes the electrochemical solution but also increases the electrode area, and it was assumed that the combination of these two effects, which are both very small, would lead to a negligible error. Addition of further aliquots was by the same procedure. IR analysis confirmed that reaction of cluster and ligand in the bulk solution was negligible in the absence of electrochemical initiation.

The experimental cathodic peak current function $i_p/i_p{}^0$ was calculated from this data by dividing the peak current due to reduction of $PhCCo_3(CO)_9$ obtained in the presence of a given amount of phosphine, by the peak current for the same process at the same scan rate in the absence of added phosphine.

Determination of the Theoretical Cathodic Peak Current Ratio. The electrochemistry of $PhCCo_3(CO)_9$ in CH_2Cl_2 in the absence of phosphine was simulated and the peak currents were recorded at each scan rate. The parameters determined by this procedure were used in subsequent simulation (D = 9.8 × 10^{-6} $cm^2\ s^{-1}$, k_s = 9.8 × 10^{-3} cm s^{-1}, and α = 0.5). Setting $k_{-1}/k_2 = 0$ in the program enabled k_1 to be determined by trial and error. Thus a value for k_1 was chosen and simulation enabled $i_p/i_p{}^0$ to be calculated as described above. The procedure was repeated, varying k_1, until satisfactory agreement between experimental and theoretical values of $i_p/i_p{}^0$ was achieved. Since only the peak current was required, simulation over 0.3 V was sufficient.

The following data demonstrate the sensitivity of peak current to k_1 for the reaction of dppm with $PhCCo_3(CO)_9$.

10^4[ligand], mol dm^{-3}	scan rate, V s^{-1}	$i_p/i_p{}^0$	
		k_1 = 2.9 s^{-1}	k_1 = 3.2 s^{-1}
77.5	0.07	0.50	0.46
77.5	0.10	0.58	0.54
77.5	0.20	0.72	0.69
77.5	0.50	0.86	0.83
77.5	0.80	0.90	0.88

Using the value of k_1 of 3.2 s^{-1}, the ratio k_{-1}/k_2 was varied and the match with the $i_p/i_p{}^0$ data obtained in the presence of 2.5 × 10^{-4} and 17.5 × 10^{-4} mol dm^{-3} of phosphine was used to judge the suitability of the rate constant ratio. A value of D = 2.5 × 10^{-5} $cm^2\ s^{-1}$ has been derived by other workers[23] for monodentate phosphine ligands in CH_2Cl_2, and this value was used for dppm and dppe. Small changes in D caused large changes in $i_p/i_p{}^0$; e.g., when D = 2.0 x 10^{-5} $cm^2\ s^{-1}$, $k_{-1}/k_2 = 4 \pm 2$. It was found that the electrochemistry of $PhCCo_3(CO)_9$ in the presence of [L] < 1.5 × 10^{-4} mol dm^{-3} could not be simulated by using a reasonable amount of computer time. This is because with a low initial ligand concentration, the concentration of ligand in certain parts of the solution (for example near the electrode surface) will become very small during the reaction, and to prevent a negative concentration being produced during simulation, a very small volume element size (and hence a very large number of elements) is required.

Controlled Potential Electrolysis of $RCCo_3(CO)_9$ without Added Ligand. In THF. $PhCCo_3(CO)_9$ (0.1029 g, 0.2 mmol) was dissolved in 20 cm^3 of degassed and preelectrolyzed THF (0.1 mol dm^{-3} Bu_4NClO_4). Electrolysis at –0.5 V for ~2 h resulted in a mauve solution. The 1-mA current remained approximately constant throughout this period. All attempts to isolate the mauve compound (ν(CO) = 2047 (ms), 1995 (s), 1960 (sh) cm^{-1}; λ_{max} 520, 830 nm) resulted in decomposition to $Co(CO)_4{}^-$ and Co(II) compounds.

In CH_2Cl_2. Electrolysis of $CH_3CCo_3(CO)_9$ afforded the best yield of $R_2C_2Co_4(CO)_{10}$. $CH_3CCo_3(CO)_9$ (0.0906 g, 0.2 mmol) was dissolved in 20 cm^3 of degassed and preelectrolyzed CH_2Cl_2 (0.1 mol dm^{-3} Bu_4NClO_4). Electrolysis at –0.65 V for 4 h was accompanied by a decrease in the current from 2.5 to 0.3 mA and the production of blue-black and yellow-orange products. The solvent was removed in vacuo and the residue extracted with hexane/ether. Chromatography (silica gel) gave a 50% yield of $(CH_3)_2C_2Co_4(CO)_{10}$[24] (assuming a reaction stoichiometry $2RCCo_3(CO)_9{}^{-}\cdot \rightarrow R_2C_2Co_4(CO)_{10} + 2[Co(CO)_4]^-$) while the yellow product decomposed during workup. IR of this species suggested that it was a dicobalt acetylene complex $(CH_3)_2C_2Co_2(CO)_6$.[24] Electrolysis of $PhCCo_3(CO)_9$ in the same way gave a 30% yield of $Ph_2C_2Co_4(CO)_{10}$ and 10% yield of $Ph_2C_2Co_2(CO)_6$.

In Acetone. Electrolysis of $PhCCo_3(CO)_9$ in acetone at –0.5 V for several hours resulted in formation of a green precipitate and $[Co(CO)_4]^-$. The precipitate was soluble in methanol and water, and IR spectra showed that no carbonyl groups were present.

Preparation of $PhCCo_3(CO)_8NCCH_3$. Bulk Electrolysis. $PhCCo_3(CO)_9$ (0.10 g, 0.2 mmol) was dissolved in 20 cm^3 of dry, degassed CH_3CN (0.1 mol dm^{-3} Et_4NClO_4). The solution was electrolyzed at –0.45 V for 1.75 h during which time the current fell from 5 to 0.85 mA. TLC of the reaction mixture showed the formation of a brown product with R_f of ~0.47 in hexane, while IR spectra indicated the formation of a new cluster derivative and $[Co(CO)_4]^-$.

The solvent was removed at 0 °C and the residue chromatographed on silica gel plates. Development in hexane separated two bands from insoluble decomposition material. The first band (R_f ~0.87) yielded unreacted $PhCCo_3(CO)_9$ (0.05 g, 0.1 mmol, 50%). The second band (R_f ~0.47) was washed off the gel with CH_3CN (it was essential to use this solvent) and gave $PhCCo_3(CO)_8NCCH_3$ (0.04 g, 0.07 mol, 35% yield). Anal. Calcd for $C_{17}H_8Co_3NO_8$: C, 38.45; H, 1.52; N, 2.64. Found: C, 43.71; H, 2.86; N, 1.84. IR (CH_3CN): ν(CO) 2079 (w), 2031 (s), 2014 (s), 1990 (sh) cm^{-1}. Approximately 12 C of charge was consumed during the reaction which corresponds to ~1.2 electrons/molecule of $PhCCo_3(CO)_9$ reacted.

CH_3CN solutions of the complex and the dry solid both slowly reverted to an ~50:50 mixture of $PhCCo_3(CO)_9$ and $PhCCo_3(CO)_8NCCH_3$ at 0 °C while in other solvents or under a CO atmosphere, the reversion was more rapid and complete. After several unsuccessful attempts, brown crystals were obtained from a concentrated CH_3CN solution of the complex and a preliminary X-ray study by precession methods indicated that the crystals were not those of $PhCCo_3(CO)_9$. However, the crystals were found to be intimately twinned and the investigation was not continued.

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[20] Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969.

[21] Van de Linden, J. G. M.; Paulissen, M. L. H.; Schmitz, J. E. J. *J. Am. Chem. Soc.* **1983**, *105*, 1903.

[22] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980.

[23] Watson, D. J. Ph.D. Thesis, University of Otago, 1975.

[24] Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

Preparation of $CH_3CCo_3(CO)_8NCCH_3$. Bulk Electrolysis. $CH_3CCo_3(CO)_9$ (0.10 g, 0.35 mmol) was electrolyzed in 30 cm^3 of dry, degassed CH_3CN (0.1 mol dm^{-3} Bu_4NClO_4) at −0.50 V until TLC and IR showed no increase in the amount of purple-gray product. Workup as described for the phenyl cluster derivative gave $CH_3CCo_3(CO)_8NCCH_3$ as a gray solid (0.05 g, 0.11 mmol, 31% yield). Attempts to crystallize $CH_3CCo_3(CO)_8NCCH_3$ from a concentrated CH_3CN solution were unsuccessful, and the solution and solid both slowly reverted to $CH_3CCo_3(CO)_9$ at 0 °C (~50% over 12 h). This complex does not give rise to a molecular ion peak in its mass spectrum; the highest mass peak observed is at *m/e* 456 ($[CH_3CCo_3(CO)_9]^+$). Anal. Calcd for $C_{12}H_6Co_3N$: C, 30.73; H, 1.29; N, 2.98. Found: C, 28.89; H, 2.15; N, 2.39. IR (CH_3CN): ν(CO) 2078 (w), 2030 (vs), 2010 (s), 1990 (sh) cm^{-1}.

Thermal Reaction. $CH_3CCo_3(CO)_9$ (0.14 g, 0.3 mmol) was refluxed in 25 cm^3 of dry, degassed CH_3CN for ~10 min. This appeared to maximize the yield of the desired product, and further heating led to increasing amounts of an insoluble black material. Chromatography on silica gel plates eluted in hexane allowed recovery of $CH_3CCo_3(CO)_8NCCH_3$ (0.06 g, 0.12 mmol, 40% yield). In an attempt to improve the yield the reaction was stirred at 60–75 °C for ~2 h but no significant difference in yield of the desired product was achieved.

BPK Reaction. BPK was added dropwise to an ~10^{-2} mol dm^{-3} solution of $CH_3CCo_3(CO)_9$ in CH_3CN. Monitoring of the reaction by TLC showed that the formation of the desired product was <30% and so this preparative route was not favored.

Registry No. $CH_3CCo_3(CO)_9$, 13682-04-7; $(CH_3)_2C_2Co_4(CO)_{10}$, 12564-37-3; $(CH_3)_2C_2Co_2(CO)_6$, 12264-15-2; $PhCCo_3(CO)_9$, 13682-03-6; $Ph_2C_2Co_4(CO)_{10}$, 11057-43-5; $Ph_2C_2Co_2(CO)_6$, 14515-69-6; $PhCCo_3(CO)_8NCCH_3$, 84896-16-2; $CH_3CCo_3(CO)_8NCCH_3$, 101011-53-4; $PhCCo_3(CO)_7$dppm, 101141-55-3; $[PhCCo_3(CO)_8]_2$dppe, 101141-59-7; $PhCCo_3(CO)_4$dppe, 101011-54-5; $[PhCCo_3(CO)_8]$tpme, 101011-55-6; $PhCCo_3(CO)_4$tpme, 101011-56-7; $PhCCo_3(CO)_8PPh_3$, 13681-99-7; $PhCCo_3(CO)_7(PPh_3)_2$, 101011-57-8.

Mono- and Dimeric Phosphine Complexes of Cyclopentadienylvanadium(II) Halides

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Received August 28, 1985

Reduction of $CpVX_2(PR_3)_2$ (X = Cl, R = Me, Et; X = Br, R = Et) with Al or Zn in THF gives dimeric vanadium(II) complexes $[CpVX(PR_3)]_2$. Methylcyclopentadienyl compounds are accessible by the same method. Treating the dimers with an excess of PR_3 gives $CpVX(PR_3)_2$, and treating the dimers with bidentate phosphines, CpVCl(DMPE) and CpVCl(DPPE) are obtained. All compounds are paramagnetic with, *in principle*, three unpaired electrons on the metal atom. ^1H NMR spectra of the complexes show large downfield shifts of the cyclopentadienyl protons (range of 64–250 ppm). The phosphine ligands show smaller shifts, varying between −3.0 and 4.60 ppm for the dimers $[CpVX(PR_3)]_2$ and between −25.5 and −17.0 ppm for CpVCl(DMPE). The complexes are very reactive and their reactions with a variety of substrates, e.g., dioxygen, cyclohexene oxide, alkynes, and carbon monoxide, proceed easily. With α-olefins no reaction (hydrogenation, isomerization, or oligomerization) was observed.

Introduction

In contrast to well-investigated low-valent titanium and chromium species, relatively little is known about vanadium(II) compounds. There are a few reports on the reduction of dinitrogen- and nitrogen-containing molecules by inorganic vanadium(II) complexes.[1] Vanadium(II) compounds also seem to be active in the reduction of epoxides[2] and reductive coupling of allylic or benzylic halides.[3]

Several metals can reduce vanadium(III). Thus $VX_3(THF)_3$ (X = Cl, Br) in THF reacts with various metals (e.g., Al, Zn, Fe, Mn) to form a dinuclear vanadium(II) cation, $[V_2X_3(THF)_6]^{1+}$.[4]

In this paper we report the preparation and reactivity of two series of well-defined vanadium(II) compounds containing one cyclopentadienyl and one halide ligand per vanadium atom using cyclopentadienyl vanadium(III) dihalide complexes $CpVX_2(PR_3)_2$ as starting compounds.[5]

Experimental Section

General Remarks. All reactions were performed under purified nitrogen using Schlenk and glovebox techniques. Solvents were distilled under nitrogen from sodium (toluene) or sodium–potassium melts (THF, ether, pentane) before use. $CpVX_2(PR_3)_2$ and $Cp'VX_2(PR_3)_2$ ($Cp = \eta^5$-C_5H_5; $Cp' = \eta^5$-C_5H_4Me; X = Cl, Br; R = Me, Et), PMe_3,[6] PEt_3,[7] and DMPE[8] were prepared according to published procedures. Zinc powder (UCB), aluminium powder (Fluka), and DPPE (Strem) were used as purchased.

IR spectra (Nujol/KBr) were recorded on a JASCO-IRA-2 spectrophotometer. EPR spectra were recorded with a Varian E-4 EPR spectrometer. ^1H NMR spectra were recorded by Dr. R. J. Bouma in toluene-d_8 or benzene-d_6 with a Nicolet NT 200 spectrometer equipped with a Nicolet Model 1180 data system. Chemical shifts are given relative to Me_4Si (internal standard, δ 0, downfield shifts positive). Molecular weights were determined by cryoscopy in benzene. Melting points were determined by DTA (heating rate 2 °C/min). Gas chromatography was performed

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[1] Olah, G. A.; Chao, Y. L.; Arvanaghi, M.; Prakash, G. K. S. *Synthesis* **1981**, *476*.

[2] Hayashi, H.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 3473–3481.

[3] Ho, T.-L.; Olah, G. A. *Synthesis* **1977**, 170–171.

[4] Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715–1718.

[5] Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193–204.

[6] Markham, R. T.; Dietz, E. A.; Matin, D. R. *Inorg. Synth.* **1976**, *16*, 153–155.

[7] Houben-Weyl, "Methoden der Organischer Chemie"; Georg Thieme Verlag; Stuttgart, 1963; Band XII/1.

[8] Butter, S. A.; Chatt, J. *Inorg. Synth.* **1974**, *15*, 185–191.

0276-7333/86/2305-1149$01.50/0