Figure 4. Plot of $k^1_{obsd}{}^{-1}$ vs. $[Ti^{3+}]^{-1}$ for the second reaction in the Ti(III) reduction of $[(NH_3)_5Co(NCacac)]^{2+}$. $T = 25.0$ °C, $I = 1.00$ mol L^{-1} (LiCl); $[H^+] = 0.20$ mol L^{-1} ($\triangle$); $[H^+] = 0.10$ mol L^{-1} (O).

of the rate equation to experimental data is demonstrated in Table III, which contains calculated and experimental observed rate constants for the reduction process.

The rate of electron transfer in the precursor complex, k_{et}, can be estimated by assuming an upper limit of $\sim 10^{-2}$ mol L^{-1} for the acid dissociation constant for coordinated water on titanium-(III)[18] in $[(NH_3)_5Co(NCacac)Ti(H_2O)_4]^{5+}$. This yields a value of at least 6 s^{-1} for the intramolecular electron-transfer rate.

The mechanism proposed, formation of a binuclear intermediate followed by electron transfer within the conjugate base of the intermediate, has been suggested, on the basis of kinetic evidence, for several Co(III)–Ti(III) reactions (in these systems the binuclear intermediate has not been detected).[21,22] In the (fpd)-Ru^{III}–Ti(III) reaction this mechanism yields an intramolecular electron-transfer rate constant of $\geq 10^4$ s^{-1}.[17] The large rate in the latter case has been explained in terms of effective overlap of donor–acceptor orbitals that are of the same symmetry (t_{2g}–t_{2g}). Thus, the relatively slow rate observed in the Co(III)–Ti(III) system under study can be rationalized in part on the basis of the symmetry mismatch (t_{2g}–e_g). Further work will be necessary in order to arrive at a better understanding of the intramolecular electron-transfer between Co(III) and Ti(III). The high affinity of Ti^{3+} for oxygen chelates shown here and elsewhere[7,18] implies that the rapid formation of a relatively stable precursor complex might be observed in related systems presently being developed in our laboratories.

Registry No. $[(NH_3)_5Co(NCacac)]^{2+}$, 87145-53-7; $[(NH_3)_5Co-(NCacac)Ti(OH)(OH_2)_3]^{4+}$, 99798-29-5; Ti, 7440-32-6.

(21) Ali, S. Z.; Chalilpoyil, P.; Earley, J. E. *Inorg. Chim. Acta* **1981,** *48,* 57.
(22) Olubuyide, O.; Earley, J. E. *Inorg. Chem.* **1981,** *20,* 3569.

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Oxidation–Reduction and the Electrocatalytic Ligand Substitution of Tetracobalt Clusters

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The capacity of polynuclear clusters to undergo multiple oxidation and reduction is probed with a series of bicapped tetracobalt carbonyls derived from the phenylphosphinidene-bridged $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ (I). The redox behavior of I and its derivatives $Co_4(CO)_{10-x}(\mu_4\text{-}PPh)_2L_x$, where L is a mono- or diphosphine, is initially examined by a combination of electrochemical methods including cyclic voltammetry, linear sweep microvoltammetry, and polarography. All the techniques reveal a consistent trend for the oxidation of the tetracobalt cluster to be increasingly facilitated upon successive phosphine substitution ($x = 0, 1, 2, 3,$ and 4); but reduction follows the opposite trend. The anion radical derived from the $0/-1$ redox couple of the tetracobalt cluster I is shown to be substitutionally labile. The latter allows a facile ligand substitution to occur under mild conditions when a small cathodic current is passed through a solution of the cluster I containing various phosphorus(III) nucleophiles. The mechanism of the electrocatalytic process is discussed in the light of electron-transfer catalysis applicable to other mononuclear and polynuclear metal carbonyls.

Introduction

Transition-metal clusters are under active investigation as potential catalysts, particularly the utilization of carbon monoxide.[1–5] Their virtue undoubtedly lies in the possibility of multiple coordination sites and the ready access to various oxidation levels that are allowed by the presence of contiguous metal centers. Indeed these two facets of catalytic activity may be coupled. Thus, there is recent evidence that ligand substitution of the coordinated carbon monoxide in diamagnetic bi- and trimetallic complexes of cobalt is induced by electron accession.[6–9] The greatly enhanced

lability of the carbonylmetal anion radicals to substitution has also been observed in various carbonylmetal cation radicals.[10] Such studies suggest that the chemical reactivity of metal clusters may generally be enhanced by deliberate reduction and/or oxidation.

Unfortunately, the relevant data relating to the redox properties of metal carbonyl clusters are limited—certainly in comparison

(1) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 135.
(2) Laine, R. M. *J. Mol. Catal.* **1982,** *14,* 137.
(3) (a) Pittman, C. U., Jr.; Ryan, R. C. *CHEMTECH* **1978,** 170. (b) Ryan, R. C.; Pittman, C. U., Jr.; O'Connor, J. P. *J. Am. Chem. Soc.* **1977,** *99,* 1986. (c) Pittman, C. U., Jr.; Wilemon, G. M.; Wilson, W. D.; Ryan, R. C. *Angew. Chem., Int. Ed. Engl.* **1980,** *19,* 478.
(4) Smith, A. K.; Basset, J. M. *J. Mol. Catal.* **1977,** *2,* 229.
(5) Geoffroy, G. L. *Acc. Chem. Res.* **1980,** *13,* 469.
(6) Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* **1981,** 265.
(7) Arewgoda, M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983,** *105,* 1893.
(8) Darchen, A.; Mahe, C.; Patin, H. *J. Chem. Soc., Chem. Commun.* **1982,** 243.
(9) Jensen, S.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.* **1983,** 1081.
(10) (a) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982,** *104,* 3034. (b) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983,** *105,* 61. (c) Hershberger, J. W.; Amatore, C.; Kochi, J. K. *J. Organomet. Chem.* **1983,** *250,* 345. (d) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984,** *106,* 3771.

with studies of their thermal and photochemical properties. An early example of the oxidation and reduction of the tetranuclear iron carbonyl [CpFe(CO)]$_4$ showed the availability of four electrochemically reversible oxidation states, viz. +2, +1, 0, and −1, with the cluster intact.[11] The redox properties of trinuclear iron, ruthenium, and osmium carbonyl clusters M$_3$(CO)$_{12}$ have been recently examined in detail.[12] A variety of derivatives of the tricobalt alkylidene cluster XCCo$_3$(CO)$_9$ have also been studied.[13] In these systems, the redox chemistry and analysis of the EPR spectra indicated that the LUMO of the cluster was primarily composed of a metal–metal antibonding orbital. This conclusion has received support from theoretical calculations of simple trinuclear clusters,[14] and it may account for the tendency of metal carbonyl clusters to fragment to species of lower nuclearity upon reduction.[15] Accordingly, our primary focus was directed toward metal carbonyl clusters that contain strong bridging ligands. The tetracobalt cluster I reported by Dahl and
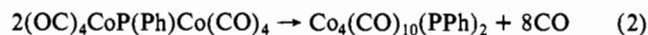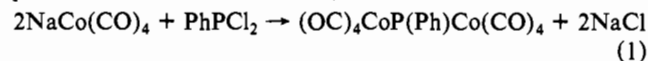

I
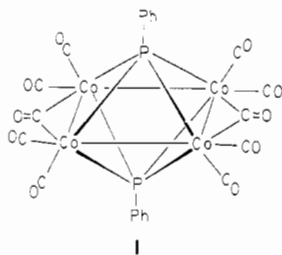
co-workers[16] was of especial interest since it contains a pair of μ_4-phenylphosphinidene ligands binding a planar array of four cobalt atoms as shown. Substitution of some of the carbon monoxide ligands in I is possible.[16,17] Accordingly, we have examined in this paper the redox properties of I and its derivatives Co$_4$(CO)$_9$(PPh)$_2$(NCMe) (II), Co$_4$(CO)$_9$(PPh)$_2$(PPh$_3$) (III), Co$_4$(CO)$_9$(PPh)$_2$[P(OMe)$_3$] (IV), Co$_4$(CO)$_9$(PPh)$_2$(PEt$_3$) (V), Co$_4$(CO)$_8$(PPh)$_2$(PPh$_3$)$_2$ (VI), Co$_4$(CO)$_8$(PPh)$_2$[P(OMe)$_3$]$_2$ (VII), Co$_4$(CO)$_7$(PPh)$_2$[P(OMe)$_3$]$_3$ (VIII), Co$_4$(CO)$_6$(PPh)$_2$[P(OMe)$_3$]$_4$ (IX), and Co$_4$(CO)$_8$(PPh)$_2$(diphos) (X). Of particular interest are the effect of phosphine ligands on the oxidation potential and the redox-promoted substitution processes of the tetranuclear cobalt cluster I and its derivatives.

Results

I. Synthesis of the Tetracobalt Carbonyl Cluster I and Its Ligand-Substitution Derivatives. We found a slight modification of the original procedure to afford relatively reproducible yields

of the tetranuclear Co$_4$(CO)$_{10}$(PPh)$_2$.[18] Thus dicobalt octacarbonyl was first reduced with sodium amalgam in tetrahydrofuran (THF) to sodium tetracarbonyl cobaltate.[19] Addition of 1 equiv of phenyldichlorophosphine followed by stirring at room temperature consistently afforded 15–30% yields of I. By analogy with the formation of the tetranuclear rhodium cluster Rh$_4$-(COD)$_4$(PPh)$_2$ as suggested by Geoffroy and co-workers,[20] it is reasonable to expect that I is formed by the dimerization of the putative binuclear intermediate,[21,22] i.e.

$$2NaCo(CO)_4 + PhPCl_2 \rightarrow (OC)_4CoP(Ph)Co(CO)_4 + 2NaCl \quad (1)$$

$$2(OC)_4CoP(Ph)Co(CO)_4 \rightarrow Co_4(CO)_{10}(PPh)_2 + 8CO \quad (2)$$

The ligand-substitution derivatives of I were prepared by either of two methods. Direct substitution of I could be effected by refluxing it in toluene with triphenylphosphine as described by Dahl and co-workers.[16] This procedure afforded a mixture of the mono- and bis(triphenylphosphine) derivatives, which could be subsequently separated by alumina chromatography. Alternatively, the mono(acetonitrile) derivative II was prepared in good yields by refluxing I in an acetonitrile solution for several hours according to Muetterties et al.[17] Removal of the solvent in vacuo followed by the addition of triphenylphosphine in toluene afforded only the mono(triphenylphosphine) derivative III after several hours. The second procedure was also used to prepare the mono(trimethyl phosphite) and the mono(triethylphosphine) analogues IV and V, respectively.

The product of disubstitution VI was obtained by treating the monosubstitution product III with additional triphenylphosphine, followed by refluxing the mixture for prolonged periods.[16] The bis(trimethyl phosphite) analogue VII was prepared by a similar procedure. Comparison of the infrared spectra suggests that the bis(trimethyl phosphite) and the bis(triphenylphosphine) derivatives have the same basic structure, namely, one in which the ligand substitution occurred on the 1- and 3-cobalt centers.[24]
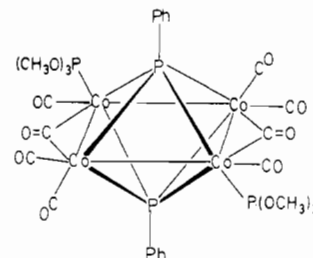

VII

The further substitution of carbon monoxide ligands on VII could be effected by trimethyl phosphite upon prolonged reflux. Only one isomer of Co$_4$(CO)$_7$(PPh)$_2$[P(OCH$_3$)$_3$]$_3$ was isolated in good yield. The location and stereochemistry of the three phosphite ligands on the tetracobalt cluster VIII was established by X-ray crystallography to be[23,24]

(11) Ferguson, J. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 3409.
(12) Bond, A. M.; Dawson, P. A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1977**, *16*, 2199. See also: Cyr, J. C.; DeGray, J. A.; Gosser, D. K.; Lee, E. S.; Rieger, P. H. *Organometallics* **1985**, *4*, 950.
(13) X represents either a heteroatom or a carbon-centered group. (a) Dessey, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112. (b) Kotz, J. C.; Petersen, J. V.; Reed, R. C. *J. Organomet. Chem.* **1976**, *120*, 433. (c) Peake, B. M.; Reiger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1981**, *20*, 2540. (d) Bond, A. M.; Dawson, P. A.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1413. (e) Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 405. (f) Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410. (g) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 943. (h) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 952. (i) Colbran, S. B.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1984**, *265*, 199. (j) Lindsay, P. N.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Honrath, U.; Vahrenkamp, H.; Bond, A. M. *Organometallics* **1984**, *3*, 413. (k) Benoit, A.; Darchen, A.; LeMaroville, J.; Mahe, C.; Patin, H. *Organometallics* **1983**, *2*, 555.
(14) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.
(15) (a) Pittman, C. U., Jr.; Richmond, M. G.; Absi-Halibi, M.; Vahrenkamp, H.; Richter, F.; Beurich, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 786. (b) Richmond, M. G.; Pittman, C. U., Jr.; Absi-Halibi, M. *J. Mol. Catal.* **1984**, *22*, 367.
(16) (a) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. (b) Ryan, R. C.; Pittman, C. U., Jr.; O'Connor, J. P.; Dahl, L. F. *J. Organomet. Chem.* **1980**, *193*, 247.
(17) Kouba, J. K.; Muetterties, E. L.; Thompson, M. R.; Day, V. W. *Organometallics* **1983**, *2*, 1065.

(18) We were able to obtain only low yields (<10%) of I using the zinc reduction described in ref 16.
(19) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. I.
(20) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251.
(21) The dinuclear species (OC)$_4$CoP(Ph)Co(CO)$_4$ has been reported (Burt, J. C.; Schmid, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1385), but no mention was made of the presence of I, which may have escaped detection.
(22) It is noteworthy that the dinuclear (OC)$_4$CoP(Ph)Co(CO)$_4$ is converted to the tetranuclear I under conditions of the hydroformylation reaction. See: (a) Pittman, C. U., Jr.; Ryan, R. C.; Wilson, W. D.; Wilemon, G. M.; Absi-Halibi, M. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1980**, *25*, 714. (b) Wilemon, G. M. Ph.D. Thesis, University of Alabama, 1980.
(23) Ligand substitutions on other tetranuclear clusters are known to occur on three separate metal centers. See: (a) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1980**, *19*, 2585. (b) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1981**, *20*, 1911. (c) Karel, K. J.; Norton, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 6812.
(24) The details of the crystallography will be presented separately.

VIII

IX
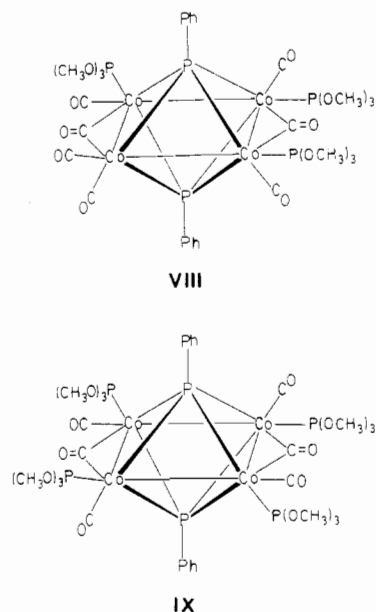
Finally, the treatment of **VIII** with additional trimethyl phosphite yielded the ultimate substitution product **IX**, in which four carbonyl ligands have been replaced.[24]

The direct ligand substitution of **I** by the chelating diphosphine 1,2-diphenylphosphinoethane (diphos) afforded only poor yields (<5%) of $Co_4(CO)_8(PPh_2)_2(diphos)$ (**X**) when the reaction was carried out in either refluxing benzene or refluxing toluene.[25] Examination of the reaction mixture by thin-layer chromatography (TLC) indicated extensive degradation of the tetracobalt cluster as well as the intermolecular ligation of a pair of clusters by the difunctional phosphine. However, we found the rate of ligand substitution to be dramatically increased by the presence of catalytic amounts of potassium benzophenone ketyl.[26] As a result, the ligand substitution could be carried out at room temperature, and the diphos derivative **X** was obtained in almost 50% yield. The structure of **X**, established by X-ray crystallography,[24] is one in which the ligand substitution by diphos has occurred on adjacent cobalt centers:

X
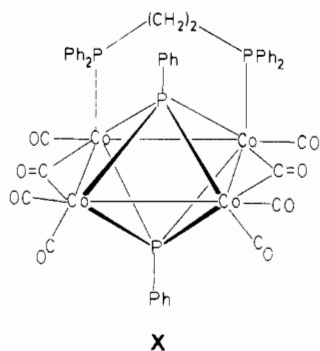
II. Oxidation–Reduction of the Tetracobalt Cluster I and Its Phosphine Derivatives. The redox behavior of the tetracobalt cluster **I** and its phosphine derivatives was examined by a combination of electrochemical methods including cyclic voltammetry, linear sweep microvoltammetry, and polarography.

The *cyclic voltammetry* (CV) of the parent tetracobalt cluster **I** was carried out at a platinum electrode in either a tetrahydrofuran (THF) or a methylene chloride solution containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte. The initial negative scan cyclic voltammogram
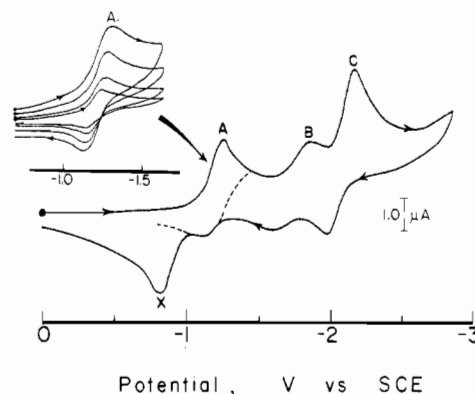

Figure 1. Initial negative-scan cyclic voltammogram of the tetracobalt carbonyl cluster **I** in THF containing 0.1 M TBAP at 200 mV s^{-1} and 25 °C. The inset shows the CV scans of the first (0/−1) redox couple at 1000, 500, 200, and 100 mV s^{-1}.

Table I. Cyclic Voltammetry of the Tetracobalt Cluster **I** and Its Derivatives[a]

cluster	temp, °C	redn[b,c]		oxidn[c]	
		E_p^c, V	$E_{1/2}$, V	E_p^a, V	$E_{1/2}$, V
I	25		−1.19		
	−40		−1.19		
III	25	−1.51		0.67	
	−40		−1.45	0.64	
IV	25		−1.49	0.68	
	−40		−1.45	0.64	
V	25	−1.55		0.59	
	−40		−1.53	0.55	
VI	25	−1.89			0.48
	−40		−1.84		0.43
VII	25	−1.78		0.42	
	−40		−1.80		0.41
VIII	25	−2.04			−0.02
	−40		−2.00		−0.03
IX	25	−2.21			−0.19
	−70		−2.17		−0.14
X	25	−1.83		0.36	
	−40		−1.83		0.26

[a] In ~10^{-3} M THF solutions containing 0.1 M TBAP at a scan rate of 200 mV s^{-1}. Potentials are relative to SCE, calibrated with ferrocene. [b] Refers only to the CV wave A (see text). [c] See ref 27.

of **I** in THF consists of three well-defined cathodic peaks labeled A, B, and C together with their coupled anodic peaks in Figure 1. The first CV wave (A) at $E_{1/2}$ −1.2 V is reversible,[27] as shown by the ratio of the peak current i_p^c/i_p^a, which remains close to unity, and the current function, which varies linearly with the square root of the scan rate v (see the inset of Figure 1). Furthermore, the calibration of the peak current with a ferrocene standard[30] indicates that it represents a one-electron 0/−1 redox couple, i.e.

$$Co_4(CO)_{10}(PPh)_2 \xrightleftharpoons{[e^-]} Co_4(CO)_{10}(PPh)_2^-. \quad (3)$$
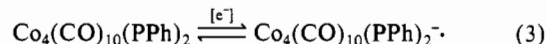
Accordingly, the second wave (B) at −1.73 V and the third wave (C) at −2.08 V are tentatively assigned to the −1/−2 and the −2/−3 redox couples, respectively, on the basis of coulometric analysis. In addition to these three redox couples, an unknown electroactive species **X** is observed as an irreversible anodic wave at E_p^a = −0.82 V.[27a] This species was only found when the negative scan was carried out beyond −1.7 V, as shown by its absence in the inset

(25) Diphos also afforded poor yields of ligand substitution products from $Ru_3(CO)_{12}$ via the thermal route. See: Bruce, M. I.; Hambley, T. W.; Nicholson, B. K.; Snow, M. R. *J. Organomet. Chem.* **1982**, *235*, 83.

(26) Cf.: (a) Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442. (b) Cunninghame, R. G.; Downard, A. J.; Hanton, L. R.; Jensen, S. D.; Robinson, B. H.; Simpson, J. *Organometallics* **1984**, *3*, 180.

(27) (a) E_p^c and E_p^a refer to the cathodic and anodic peak potentials of the CV waves. (b) When both (coupled) waves are observed, the chemically reversible redox couple is given by the half-wave potential $E_{1/2} = (E_p^c + E_p^a)/2$. See ref 28 and 29.

(28) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980.

(29) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(30) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.
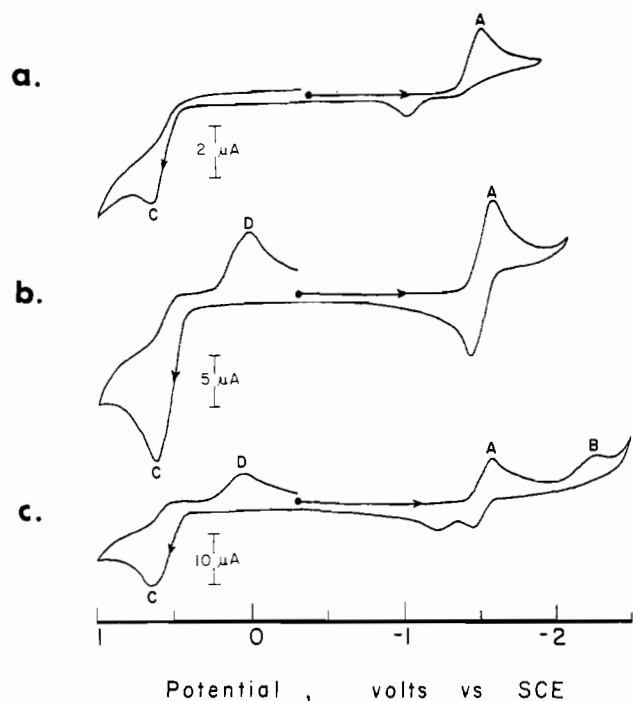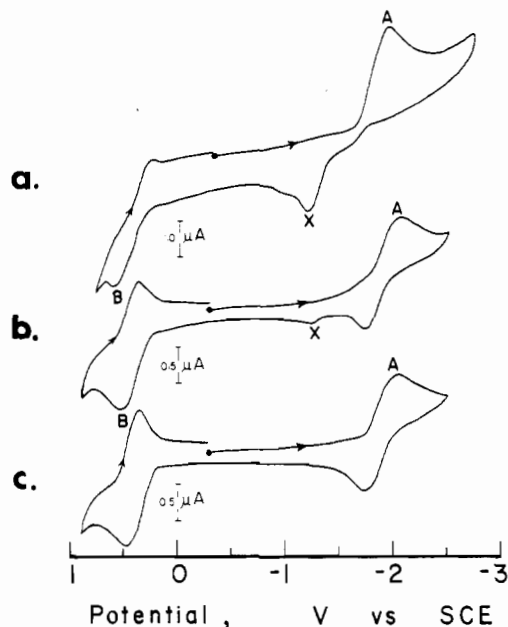
Figure 2. Temperature dependence of the initial negative-scan cyclic voltammogram of the mono(triphenylphosphine) derivative III in THF containing 0.1 M TBAP at 200 mV s^{-1} at (a) 25 and (b) −40 °C. The conditions for (c) are the same as those of (b) except the potential is scanned to −2.5 V.
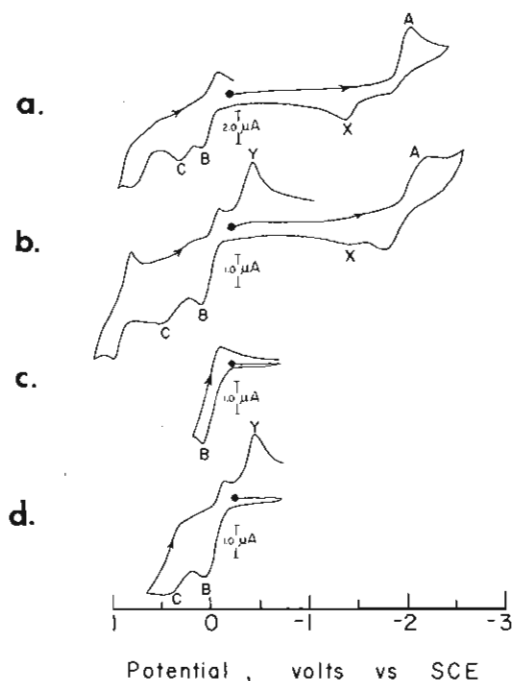

Figure 3. Temperature dependence of the initial negative-scan cyclic voltammogram of the bis(triphenylphosphine) derivative VI at 200 mV s^{-1} in THF containing 0.1 M TBAP at (a) 25, (b) −40, and (c) −65 °C.

of Figure 1. We thus ascribe the anodic peak X to a decomposition product of one of the other redox couples.

The tetracobalt clusters (III–V) that are substituted with monodentate phosphorus-centered ligands all show the first reduction wave A shifted to more negative potentials relative to that of the parent I, as listed in Table I. For example the mono-(triphenylphosphine) derivative III displays an irreversible reduction wave at $E_p{}^c \approx -1.5$ V at room temperature (together with an unknown electroactive species X at $E_p{}^a = -0.98$ V. However, when the solution is cooled to −40 °C, the first CV wave (A) becomes chemically reversible and the second largely disappears. (Compare parts a and b of Figure 2.[31]) Another reduction wave B is observed at $E_p{}^c = -2.20$ V on sweeping beyond −2.5 V in Figure 2c. The new reduction product, presumed to be the dianion, is unstable (judged by the absence of the coupled anodic wave), and it leads to the electroactive species with $E_p{}^a = -1.16$ V on the return anodic sweep. The cluster III can also be oxidized, as shown by the presence of an anodic CV wave C with $E_p{}^a = +0.6$ V on a positive-potential scan in Figure 2a. The appearance at lower temperatures (Figure 2b) of a new cathodic peak D at $E_p{}^c = 0.08$ V can be shown to originate from the oxidation and not from the reduction of cluster III. The cyclic voltammetric behavior of clusters IV and V is similar to that of cluster III, except the initial CV wave (A) of IV is partially reversible even at room temperature.

Clusters VI, VII, and X represent the derivatives of the parent tetracobalt carbonyl I in which a pair of carbon monoxides have been replaced with either mono- or bidentate phosphine ligands. In these clusters, the initial reduction waves (A) are displaced ∼600 mV to more negative potentials relative to that of the parent cluster I and ∼300 mV relative to those of clusters III–V. Similar to the latter, these CV waves become chemically reversible at lower temperatures. On the other hand, the bis(phosphine) derivatives are also more easily oxidized, as shown in Table I by CV peak potentials that are ∼200 mV less positive than those of the

mono(phosphine) analogues. The cyclic voltammetric oxidation for the 0/+1 couple is large irreversible at 25 °C but becomes progressively more reversible as the temperature is lowered. The temperature dependence of the reduction and oxidation is illustrated in Figure 3 by the series of cyclic voltammograms for the bis(triphenylphosphine) derivative VI. In Figure 3a, the transient nature of the radical anion at 25 °C is shown by the irreversible cathodic wave with $E_p{}^c = -1.9$ V, and it readily produces a new electroactive species X ($E_p{}^a = -1.15$ V). Lowering the temperature to −40 °C in Figure 3b leads to an increased reversibility of the 0/−1 CV wave and concomitant diminution of the electroactive species X at $E_p{}^a = -1.15$. Finally at −65 °C in Figure 3c, the reduction is chemically reversible and devoid of decomposition.

The redox behavior of the trisubstituted cluster VIII continues the trend established by the mono- and disubstituted derivatives III–VII. Thus, the first CV wave A for reduction to the radical ion has shifted to $E_p{}^c = -2.0$ V, which is the most negative potential of these derivatives—to accord with the greatest phosphorus content in this cluster polyhedron. In addition, the oxidation occurs at −0.02 V, which is ∼400 mV more negative than that for the bis(phosphine) derivatives, presumably for the same reason that the reduction (wave A) occurs at such a negative potential. The cyclic voltammogram obtained at room temperature is shown in Figure 4a. The first reduction of cluster VIII is irreversible ($E_p{}^c = -2.04$ V), similar to the other substituted clusters, and it produces a new electroactive species X with $E_p{}^a = -1.39$ V. The three anodic waves $E_p{}^a = +0.05$, +0.3, and +0.7 V are shown to represent oxidation of the cluster VIII by reversal of the direction of the initial scan (not shown), temperature-dependence studies, and microvoltammetric analysis (vide infra). The prominent features of the cyclic voltammogram at −40 °C (beside the near-reversible reduction wave of A) are the three distinct anodic waves. The first and third waves are chemically reversible ($E_{1/2} = -0.03$, +0.86 V), and they are assigned to the 0/+1 and +2/+3 oxidation couples, respectively. Although the +1/+2 oxidation couple C is visible, it does not appear to be reversible at this temperature. Furthermore, the unidentified peak Y at $E_p{}^c = -0.45$ V can be shown to originate from this irreversible oxidation in the following way. Figure 4c shows the cyclic voltammogram of cluster VIII when only the 0/+1 oxidation is scanned. However, when it is scanned to a more positive potential that is just short of the +2/+3 couple in Figure 4d, the unidentified electroactive species Y appears at $E_p{}^c = -0.45$ V on the reverse sweep. The cyclic voltammogram of the tetrasubstituted cluster IX is similar to that of VIII, except that the reduction and oxidation waves are

(31) The temperature-dependent (ir)reversibility of the cyclic voltammogram indicates an electrochemical EC process that is modulated by the kinetic stability of the reduced (anionic) species.[32]

(32) For a chemical and electrochemical discussion of CV reversibility, see: Klingler, R. J.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 1731.

Figure 4. Cyclic voltammograms of the trisubstituted cluster VIII $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$ at 200 mV s^{-1} in THF containing 0.1 M TBAP: (a) initial negative scan at 25 °C; (b) initial negative scan at −40 °C; (c) initial positive scan at −40 °C of only the 0/+1 redox couple; (d) initial positive scan at −40 °C of only the 0/+1 and +1/+2 redox couples.
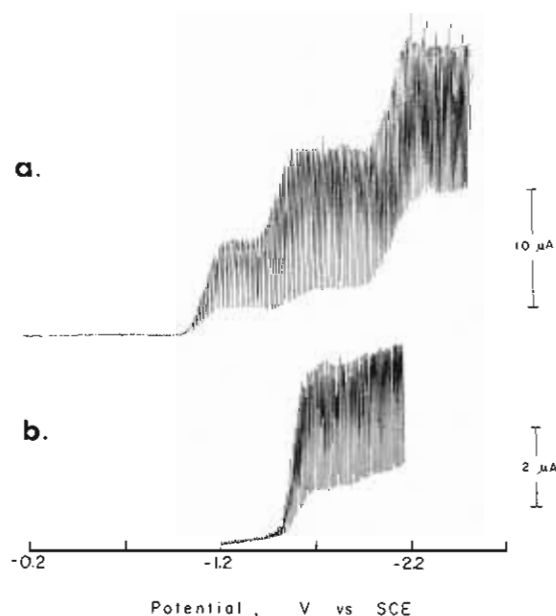
Figure 5. Dc polarogram of (a) the tetracobalt carbonyl cluster I and (b) the bis(triphenylphosphine) derivative VI in THF containing 0.1 M TBAP at 25 °C.

shifted by ~200 mV to more negative and positive potentials, respectively.

The *polarographic reduction* of the tetracobalt clusters I and III–IX was examined in tetrahydrofuran solutions in order to evaluate further their redox properties at a mercury electrode. The dc polarogram of the parent tetracobalt cluster I is shown in Figure 5a. The three reduction couples at $E_{1/2} = -1.20, -1.63,$ and −2.20 V are akin to those obtained at a platinum electrode by cyclic voltammetry (compare Figure 1) for the 0/−1, −1/−2, and −2/−3 redox processes, respectively. The typical shift in the first redox couple with phosphine substitution is illustrated in Figure 5b for the bis(triphenylphosphine) derivative VI. The tabulation of the $E_{1/2}$ values for the series of clusters in Table II

Table II. Polarographic Reduction of the Tetracobalt Cluster I and Its Derivatives[a]

cluster	$E_{1/2}$,[b] V vs. SCE	$E_{3/4} - E_{1/4}$, mV vs. SCE	cluster	$E_{1/2}$,[b] V vs. SCE	$E_{3/4} - E_{1/4}$, mV vs. SCE
I	−1.20[c]	80	VI	−1.63	60
III	−1.30	80	VII	−1.71	80
IV	−1.32	80	VIII	−1.90	90
V	−1.51	75	IX	−2.11	83
			X	−1.71	70

[a] At a dropping mercury electrode of 10^{-3} M tetracobalt cluster in THF containing 0.1 M TBAP at a scan rate of 10 mV s^{-1} and 25 °C. Potentials are calibrated with reference to the Ph$_2$CO/Ph$_2$CO$^-$ couple taken to have $E_{1/2} = -2.06$ V in THF. [b] First wave only. [c] Second and third waves observed at −1.72 and −2.16 V, respectively (with $E_{3/4} - E_{1/4}$ of 90 and 80 mV).

Table III. Microvoltammetric Data for the Tetracobalt Cluster I and Its Phosphine Derivatives[a]

	redn		oxidn	
cluster	$E_{1/2}$, V vs. SCE	$E_{3/4} - E_{1/4}$, mV	$E_{1/2}$, V vs. SCE	$E_{3/4} - E_{1/4}$, mV
I	−1.17[b]	85	...	
III	−1.38	110	0.61	100
IV	−1.37	120	0.65	105
V	−1.32	120	0.66	80
VI	−1.75	140	0.44	60
VII	−1.69	175	0.42	55
VIII	−1.92	185	0.10[c]	50
IX	−2.12	185	−0.20[d]	60
X	−1.62	125	0.38	70

[a] Microvoltammetric analyses performed at a platinum microelectrode with 10^{-3} M tetracobalt cluster in THF containing 0.1 M TBAP at a scan rate of 10 mV s^{-1} and at 25 °C. Potentials are calibrated with Cp$_2$Fe/Cp$_2$Fe$^-$ taken to be $E_{1/2} = 0.31$ V in THF. [b] Second and third reduction waves at −1.72 and −2.16 V, respectively (with $E_{3/4} - E_{1/4} = 150$ and 130 mV). [c] Second and third oxidation waves observed at 0.44 and 0.80 V, respectively (with $E_{3/4} - E_{1/4} = 125$ and 110 mV). [d] Second and third oxidation waves observed at 0.31 and 0.72 V, respectively (with $E_{3/4} - E_{1/4} = 120$ and 100 mV).
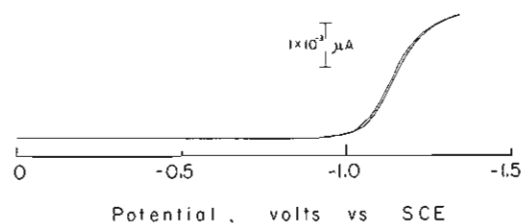
Figure 6. Typical CV wave at a microvoltammetric platinum electrode illustrating the 0/−1 redox couple of the tetracobalt carbonyl cluster I in THF containing 0.1 M TBAP at a sweep rate of 20 mV s^{-1} and 25 °C.

illustrates this trend clearly. The wave shapes given by $E_{3/4} - E_{1/4}$ in Table II are consistent with a one-electron process, but the magnitudes are somewhat greater than that expected for Nernstian behavior.[28] A similar kinetics effect in heterogeneous electron transfer of structurally complex and sterically encumbered systems has been noted previously.[13f]

The *microvoltammetric wave* in Figure 6 for the 0/−1 redox couple of the parent tetracobalt cluster I at a platinum microelectrode occurs at a potential $E_{1/2} = -1.17$ V, which is essentially the same as that observed by conventional cyclic voltammetry.[33,34] The peak shape given by $E_{3/4} - E_{1/4}$ is somewhat larger than that

(33) For a discussion of theory and application using microvoltammetric electrodes, see: Wightman, R. M. *Anal. Chem.* **1981**, *53*, 1125A.
(34) See also: (a) Robinson, R. S.; McCurdy, C. W.; McCreery, R. C. *Anal. Chem.* **1982**, *54*, 2356. (b) Wheeler, J. R.; Cushman, M. R.; Kennedy, S. M.; Anderson, C. W. *Anal. Biochem.* **1982**, *127*, 413. (c) Ewing, A. G.; Dayton, M. A.; Wightman, R. M. *Anal. Chem.* **1981**, *53*, 1842. (d) Gonon, F.; Cespuglio, R.; Ponchon, J. L.; Buda, M.; Jouvet, M.; Adams, R. N.; Pujol, J. F. *C. R. Seances Acad. Sci., Ser. 3* **1981**, *53*, 1842. (e) Cushman, M. R.; Bennett, B. G.; Anderson, C. W. *Anal. Chim. Acta* **1981**, *130*, 323. (f) Ponchon, J. L.; Cespuglio, R.; Gonon, F.; Jouvet, M.; Pujol, J. F. *Anal. Chem.* **1979**, *51*, 1483.

expected for a reversible electron transfer.[35] Similarly, the reduction potentials of the second and third reduction waves at $E_{1/2}$ = -1.72 and -2.16 V are similar to those observed in Figure 1. The values of $E_{1/2}$ for the first reduction and for the oxidation at the platinum electrode are given in Table III for the tetracobalt derivatives III-X. The values of the peak shapes $E_{3/4} - E_{1/4}$ in Table III are consistently larger than those obtained at a mercury electrode—probably reflecting the slower rate of heterogeneous electron transfer from the platinum electrode to the cluster relative to that from mercury.[36] The trend in the microvoltammetric values of $E_{1/2}$ in Table III shows the reduction couples shifting to more negative potentials with increasing phosphine substitution on the tetracobalt cluster. As also noted previously, increasing phosphine substitution leads concomitantly to oxidation potentials that become less positive.

III. Electron Spin Resonance Studies of the Ion Radicals of Tetracobalt Clusters. The reduction of the parent cluster I and its triphenylphosphine derivative III to the corresponding radical anions was examined by both chemical and electrochemical methods in order to probe the nature of the lowest unoccupied orbital (LUMO). However, both clusters failed to give an ESR signal when treated with a sodium mirror in tetrahydrofuran. Bulk electrolysis carried out at -40 °C at the controlled potential E_p^c in Table I required 1.09 and 1.10 electrons for clusters I and III, respectively, indicative of the formation of the corresponding anion radicals. The ESR spectrum of the anion radical of I is centered at $g = 2.077$, but it displayed no resolvable hyperfine splitting from 77 to 195 K. In order to further examine the nature of the anion radical, a dilute solution of I in THF was reduced with 1% sodium amalgam. The ESR spectrum of the anion radical generated under these conditions is the same as that obtained electrochemically. Reduction of the triphenylphosphine derivative III afforded an anion radical whose ESR spectrum is broadened beyond recognition.

Since the bis(triphenylphosphine) derivative VI exhibited a reversible CV oxidation wave (Table I), we also examined the cation radical to obtain information about the highest occupied orbital (HOMO) in the tetracobalt cluster. The chemical oxidation of cluster VI with silver tetrafluoroborate proceeded vigorously, but the resulting solution gave no ESR signal. Unfortunately, the same result was obtained when the cluster VI was electrochemically oxidized at a controlled potential of $E_{1/2} = 0.48$ V required for the 0/+1 redox couple (see Table I) by passage of 0.97 electron through the THF solution.

The failure in these studies to observe any cobalt hyperfine interactions in the tetranuclear planar clusters is in contrast to previous studies of simpler tricobalt alkylidene and mixed alkylidene clusters, which typically afford ESR spectra with resolvable hyperfine structure.[37,38] Thus we are unable to probe the nature of the LUMO in the tetracobalt clusters for the substitution studies described in the next section. In this regard the ESR spectra of the tetracobalt clusters are reminiscent of those of simple mononuclear cobalt(II) systems in which the ESR signal associated with the d^7 electron configuration could only be observed at 20 K or below.[39]

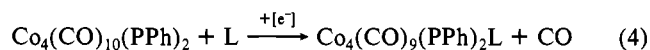**IV. Electrocatalytic Substitution of the Tetracobalt Cluster I.** A solution of the parent tetracobalt cluster I in either tetra-

Table IV. Electrocatalytic Substitution of the Tetracobalt Cluster I by Phosphorus(III) Nucleophiles[a]

nucleophile L (equiv)[b]	solvent	additive	yield, %[c]	current efficiency[d]
PPh₃ (1)	THF		35	5.8
PPh₃ (2)	THF		52	8.7
PPh₃ (10)	THF		54	9.0
PPh₃ (50)	THF		48	8.1
PPh₃ (1)	THF	CO[e]	22	3.7
PPh₃ (1)	THF	DHA[f]	36	6.0
PPh₃ (1)	THF	Bu₃SnH[g]	0	0
PPh₃ (1)	CH₂Cl₂		33	5.6
PPh₃ (2)	CH₂Cl₂		27	4.4
PPh₃ (10)	CH₂Cl₂		34	5.5
PPh₃ (50)	CH₂Cl₂		25	4.2
P(OMe)₃ (1)	THF		48	8.0
P(OMe)₃ (2)	THF		66	11.2
P(OMe)₃ (10)	THF		59	9.1
P(OMe)₃ (50)	THF		46	7.7
P(OMe)₃ (1)	CH₂Cl₂		43	7.2
P(OMe)₃ (2)	CH₂Cl₂		37	6.2
P(OMe)₃ (10)	CH₂Cl₂		30	5.0
P(OMe)₃ (50)	CH₂Cl₂		31	5.1

[a] Bulk electrolysis carried out on 3.5×10^{-5} M cluster I in 5-7-mL solutions containing 0.1 M TBAP at 25 °C and at a constant current until 0.06 faradays of charge passed per mole of reactant. [b] Relative to I. [c] Moles of $Co_4(CO)_9(PPh)_2L$ per mole of I charged, as determined by quantitative IR spectrometry. [d] Moles of $Co_4(CO)_9(PPh)_2L$ per faraday of charge passed. [e] 1 atm. [f] 10 equiv. [g] 5 equiv per mole of I.

hydrofuran or dichloromethane remains unchanged for prolonged periods even in the presence of a large excess of added nucleophile L such as triphenylphosphine. However, when a small cathodic current is passed through the solution (containing 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte), an immediate evolution of carbon monoxide is observed and the phosphine-substitution product can be isolated, i.e.

$$Co_4(CO)_{10}(PPh)_2 + L \xrightarrow{+[e^-]} Co_4(CO)_9(PPh)_2L + CO \quad (4)$$

where L = triphenylphosphine or trimethyl phosphite in this study.

The electrocatalytic nature of the substitution process is readily deduced from the coulometry measured at constant current. The progress of the electrocatalytic process was monitored by following the growth of the characteristic carbonyl stretching band at ~2060 cm⁻¹ in the infrared spectrum of the product (e.g., ν_{CO} = 2060 cm⁻¹ for $Co_4(CO)_9(PPh)_2(PPh_3)$). The turnover numbers reported in Table IV are based on the passage of 0.06 electron (i.e., 6%) through the solution for each mole of tetracarbonyl cluster I charged.

The yields of the substitution product $Co_4(CO)_9(PPh)_2L$ listed in Table IV range from moderate to good, but higher chemical yields can be achieved by the passage of slightly more electrical charge through the solution. Typically, yields of 80-95% were obtained by the passage of 10-20% of the faradays required for complete reduction. Under these conditions, however, the current efficiency as given in column 5 of Table IV is lower, since it is defined as the moles of substitution product obtained per faraday of charge passed through the solution.

The substitution product $Co_4(CO)_9(PPh)_2L$ was readily isolated by column chromatography and compared with authentic samples prepared independently. In each case the unreacted parent tetracobalt cluster I could be recovered in good yields, and thus the amount destroyed by electrolysis under these conditions was negligible.

It is important to emphasize that the thermal substitution of the tetracobalt cluster I by either triphenylphosphine or trimethyl phosphite did not occur in the absence of a cathodic current. Moreover, if the electrocatalysis is carried out at the electrode potentials of the first CV reduction wave of the cluster I, only the monosubstitution product $Co_4(CO)_9(PPh)_2L$ is obtained. Further ligand substitution is effected by increasing the applied

(35) Cf. ref 34c and: Dayton, M. A.; Brown, J. C.; Stutts, K. J.; Wightman, R. M. *Anal. Chem.* **1980**, *52*, 946.

(36) (a) Brockway, D. J.; West, B. O.; Bond, A. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1891. (b) Corrigan, D. A.; Evans, D. H. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *106*, 287.

(37) (a) Beurich, H.; Madach, T.; Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 690. (b) Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1000.

(38) For EPR studies of other types of tetracobalt clusters see: (a) Rimmelin, J.; Lemoine, P.; Gross, M.; de Montauzon, D. *Nouv. J. Chim.* **1983**, *7*, 453. (b) Beringhelli, T.; Gervasini, A.; Morazzoni, S.; Strumolo, D.; Martinengo, S.; Zanderighi, L. *J. Chem. Soc., Faraday Trans. 1* **1984**, *86*, 1479. (c) Huffadine, A. F.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Aust. J. Chem.* **1983**, *36*, 613.

(39) (a) Orton, J. W. "Electron Paramagnetic Resonance"; Iliffe Books Ltd.: London, 1968. (b) Carrington, A.; McLachlan, A. D. "Introduction to Magnetic Resonance"; Wiley: New York, 1979.

potential. For example, the galavanostatic reduction of a solution of the mono(trimethyl phosphite) derivative IV containing added trimethyl phosphite at a starting potential of −1.45 V resulted in a second ligand substitution to afford $Co_4(CO)_8(PPh)_2[P(OMe)_3]_2$ in ∼90% yield. In turn, the treatment of the disubstitution product VII with trimethyl phosphite at −1.75 V led to the third ligand substitution, but the yields were low (∼15%) owing to the extensive reductive degradation of the cluster. Nonetheless, these experiments clearly show that multiple substitution can be selectively carried out a seriatim by tuning the electrode to the potential sufficient to reduce the reactant to the anion radical.

The participation of the anion radical derived from $Co_4(CO)_{10}(PPh)_2$ to electrocatalytically generate the monosubstitution product $Co_4(CO)_9(PPh)_2L$ is also demonstrated by treating a mixture of the tetracobalt cluster I and added nucleophile L with a catalytic amount of potassium benzophenone. For example, when $Co_4(CO)_{10}(PPh)_2$ was treated with 0.025 equiv of $Ph_2CO(K)$ in the presence of either triphenylphosphine or trimethyl phosphite, the substitution products $Co_4(CO)_9(PPh)_2PPh_3$ and $Co_4(CO)_9(PPh)_2P(OMe)_3$ were isolated in 60% and 40% yields, respectively.[40]

There are several characteristics of the ligand substitution carried out under these catalytic conditions that merit special attention. First, the amount of added L beyond 1–2 equiv has little effect on the current efficiency (see Table IV, entries 2–4). Slightly higher yields of substitution product are obtained in THF relative to CH_2Cl_2 under comparable conditions. The presence of 1 atm of carbon monoxide lowers the current efficiency of the electrocatalytic process (see Table IV, entry 5). The addition of 5 equiv of the free radical inhibitor tri-*n*-butyltin hydride completely inhibits the substitution process. Thus no tetracobalt derivative III was obtained even after 0.3 faradays of charge was passed through the solution (entry 7). Inspection of the IR spectrum of the resulting solution showed new bands in the carbonyl region at 1980, 1965, 1950, 1925, and 1825 cm^{-1} in addition to the bands due to the reactant I. The shift to lower frequency is consistent with the formation of an anionic species, which we tentatively assign as $Co_4(CO)_9(PPh)_2H^-$, to be described later.[41] In the absence of a cathodic current there is no reaction between the tetracobalt cluster I and tri-*n*-butyltin hydride (and the new species is not formed). The presence of 10 equiv of the less active hydrogen donor 9,10-dihydroanthracene had little effect on the current efficiency (Table IV, entry 6).

The electrode-mediated ligand substitution can also be observed directly by carrying out the cyclic voltammetry of the tetracobalt cluster I in the presence of added phosphine nucleophile in either THF or CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium perchlorate at a scan rate of 200 mV s^{-1} at 25 °C. When a solution of I containing 2 equiv of triphenylphosphine was scanned to a potential (∼−1.6 V) that is just short of the −1/−2 couple, a new peak was observed at E_p^c = −1.47 V in addition to the main CV wave of I at E_p^c = −1.19 V shown in Figure 1. The new peak is assigned to the mono(triphenylphosphine) derivative III, on the basis of a direct comparison of this cyclic voltammogram with those derived from mixtures of I and various amounts of authentic III. From calibration of the peak currents, we judge that ∼5–10% of III is generated from I and triphenylphosphine. The amount of III formed relative to amount of I charged is *invariant* with the amount of triphenylphosphine (up to 30 equiv) present during reduction. A similar new CV peak was observed when an equivalent experiment was carried out with tricyclohexylphosphine. The analogous phosphine derivative $Co_4(CO)_9(PPh)_2[P(c\text{-}C_6H_{11})_3]$ presumably formed, but it was not isolated and characterized. When the temperature of the CV experiment was lowered to 0 °C, no new CV peak of III was observed. Furthermore, the treatment of the phosphine-substitution product III in the presence of added triphenylphosphine gave no evidence for the formation of a new peak characteristic of the disubstituted cluster Co_4-

$Co_4(CO)_8(PPh)_2(PPh_3)_2$ when the cyclic voltammetry was scanned to a potential (∼−1.8) negative of its reduction to the anion radical. The tetracobalt clusters VI and VIII similarly showed no indication of an electrocatalytic substitution. Finally, the cyclic voltammetric oxidation of the tetracobalt clusters in the presence of added triphenylphosphine at potentials E_p^a positive of the first CV wave produced no evidence for an anodically induced substitution process analogous to those previously observed in mononuclear metal carbonyls.[10]

Discussion

Redox Behavior of Tetracobalt Clusters. The electrochemical examination of the tetracobalt cluster I in either tetrahydrofuran or dichloromethane demonstrates that the parent tetracobalt cluster I undergoes a well-defined one-electron reduction to the anion radical, as given by the 0/−1 redox couple. Furthermore, the two additional reductions, assigned to the −1/−2 and −2/−3 redox couples at more negative potentials, show some degree of chemical reversibility.[42] The latter can be attributed to the stabilizing influence of the pair of bridging μ_4-phenylphosphinidene caps, which serve to maintain the basic cluster polyhedron intact to gross alteration and/or fragmentation.[43]

Substitution of the tetracobalt cluster with one or more phosphorus(III) ligands is accompanied by a shift of the reduction to more negative potentials. For example, the successive substitution of the parent tetracobalt cluster I with one, two, or three $P(OMe)_3$ ligands leads to the gradual shift of $E_{1/2}$ from −1.19 to −1.49, −1.80, and −2.00 V, respectively. The effect appears to be roughly additive—the destabilizing influence being about 6–7 kcal mol^{-1} for each ligand. Phosphine substitution of the tetracobalt cluster also leads to increasing ease of oxidation—the value of $E_{1/2}$ decreasing by about 4 kcal mol^{-1} per $P(OMe)_3$ ligand.

The influence of phosphorus(III) ligands on destabilizing the cluster toward reduction and stabilizing it toward oxidation is also manifested by the temperatures at which the cyclic voltammograms become reversible. For example, the cyclic voltammogram of the parent tetracobalt cluster I shows a reversible wave for the reduction to the anion radical at room temperature. Under the same conditions the cyclic voltammogram of the mono(triphenylphosphine) derivative is irreversible but it becomes chemically reversible as the temperature is lowered to −40 °C. Furthermore, the temperature must be lowered to −65 °C before the cyclic voltammogram of the bis(triphenylphosphine) derivative VI shows signs of chemical reversibility. We associate the temperature dependence of the CV behavior to an electrochemical EC process that is modulated by the kinetic stability of the anion radical (i.e., the magnitude of the rate constant k in eq 5).[32,45]

$$Co_4(CO)_{10-x}(PPh)_2L_x \overset{+[e^-]}{\rightleftharpoons} Co_4(CO)_{10-x}(PPh)_2L_x^- \overset{k}{\longrightarrow} etc.$$ (5)
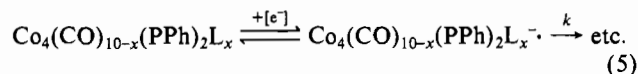
Thus from the temperature-dependent CV behavior, the activation energy for decomposition of the anion radical in eq 5 can be estimated as 13 kcal mol^{-1} for $Co_4(CO)_9(PPh)_2PPh_3^-$ and ∼11 kcal mol^{-1} for the bis analogue $Co_4(CO)_8(PPh)_2(PPh_3)_2^-$. The highly substituted tris derivative $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3^-$ is the least persistent anion radical of the series of tetracobalt clusters examined in this study.

We studied the electrochemical behavior of the tetracobalt derivatives III and VI under an atmosphere of carbon monoxide in an attempt to intercept the decomposition product in eq 5. This possibility is shown by earlier studies of the decomposition of the tricobalt cluster $PhCCo_3(CO)_8PPh_3^-$, which proceeds by tri-

(40) Compare with the method of Bruce et al.[26a]
(41) Studies pertaining to the radical abstraction of a hydrogen atom from Bu_3SnH to generate $Co_4(CO)_9H(PPh)_2$ are currently under way.

(42) As judged by the cyclic voltammetric, microvoltammetric, and polarographic studies.
(43) Such a stabilization has also been noted in simpler systems possessing a μ-PPh$_2$ bridging ligand.[44]
(44) Cf.: (a) Young, D. A. *Inorg. Chem.* **1981**, *20*, 2049. (b) Bender, R.; Braunstein, P.; Metz, B.; Lemoine, P. *Organometallics* **1984**, *3*, 381.
(45) For other organometallic examples of this EC mechanism, see: (a) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790. (b) Tamblyn, W. H.; Klingler, R. J.; Hwang, W. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3161.

phenylphosphine dissociation. The resulting coordinative unsaturated species is trapped by CO to regenerate the parent cluster PhCCo$_3$(CO)$_9$.[6] However, when the bis(triphenylphosphine) derivative VI was electrochemically reduced in the presence of CO, at the potential of the first CV wave ($\sim$1.9 V), we saw no evidence of either the parent cluster I or the mono(triphenylphosphine) derivative III. Similarly, when the cluster III was electrochemically reduced in the presence of CO, none of the parent tetracobalt cluster I could be observed. Additionally we examined the possibility of the tetracarbonylcobaltate fragment Co(CO)$_4^-$ being formed, since it has been observed as a reduction product of many cobalt carbonyl clusters.[13f,46] However, no evidence for the reductive decomposition of the cluster to Co(CO)$_4^-$ was observed, based on the absence of its CV wave at $E_p{}^a = \approx$ 0.3 V in comparison with that of an independently prepared sample.
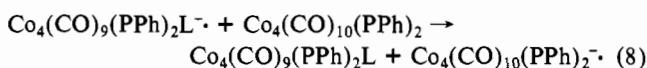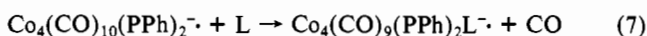
Finally the facile reduction of the tetracobalt clusters at a mercury electrode is noteworthy. Qualitatively the rate of heterogeneous electron transfer is similar for all the clusters as judged by the values of $E_{3/4} - E_{1/4}$ in Table II. By comparison there is a sizable variation of the latter for reductions at a platinum electrode (see Table III), which suggests that the production of the anion radical becomes slower at this electrode as the cluster becomes more highly substituted. A similar observation has been noted by others[36] and has been attributed to an enhanced interaction between the mercury electrode and the cluster. Such a formulation probably relates to the mercury-stabilized salts obtained upon amalgam reduction—such as Hg[YCo$_3$(CO)$_x$]$_2^{2-}$ from PhCCo$_3$(CO)$_9$ and MeCCo$_3$(CO)$_9$.[47]

Electrocatalytic Substitution of Tetracobalt Clusters. The facile, selective substitution of the tetracobalt cluster by phosphorus(III) nucleophiles when it is initiated by either electrolytic methods or electron-transfer agents stands in marked contrast to the strictly thermal process, which is slow, requires elevated temperatures, and is usually not selective. The results in Table IV show that the successful replacement of a single carbonyl ligand in Co$_4$-(CO)$_{10}$(PPh)$_2$ occurs upon the passage of a small cathodic current. Two other examples of similar electrochemically initiated substitutions of clusters have been recently reported. For example, the triiron carbonyl cluster Fe$_3$(CO)$_9$(μ-S)$_2$ was shown by Darchen et al.[8] to lead to stepwise substitution of up to three P(OMe)$_3$ ligands upon electroreduction via a process involving dissociative loss of CO from the anion radicals. The synthetic utility of such an electrocatalytic ligand substitution has been applied by Robinson and co-workers[46] to the production of trinuclear heterometallic alkylidene clusters. These processes represent examples of a general class of substitution reactions that occur by electron-transfer catalysis (ETC).[48,49] As applied to the tetracobalt cluster I, the catalytic sequence is initiated by electron transfer initiation:

$$Co_4(CO)_{10}(PPh)_2 \xrightarrow{[e^-]} Co_4(CO)_{10}(PPh)_2^{-\cdot} \quad (6)$$
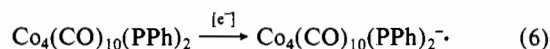
where [e$^-$] refers to either the cathode (heterogeneous) or a reducing agent (homogeneous). The efficacy of the propagation sequence depends on essentially two steps, viz.
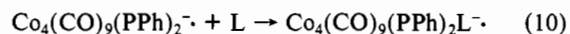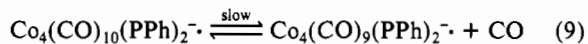
propagation:

$$Co_4(CO)_{10}(PPh)_2^{-\cdot} + L \rightarrow Co_4(CO)_9(PPh)_2L^{-\cdot} + CO \quad (7)$$

$$Co_4(CO)_9(PPh)_2L^{-\cdot} + Co_4(CO)_{10}(PPh)_2 \rightarrow$$
$$Co_4(CO)_9(PPh)_2L + Co_4(CO)_{10}(PPh)_2^{-\cdot} \quad (8)$$

The facile ligand substitution of the anion radical as described

in eq 7 is a consequence of the destabilization of the cluster resulting from electron accession to the antibonding LUMO of the cluster. There is experimental evidence that indicates this process (eq 7) occurs via a prior dissociation of carbon monoxide (Scheme I). Thus, the results in Table IV show that the sub-

Scheme I

$$Co_4(CO)_{10}(PPh)_2^{-\cdot} \underset{\text{slow}}{\overset{}{\rightleftharpoons}} Co_4(CO)_9(PPh)_2^{-\cdot} + CO \quad (9)$$

$$Co_4(CO)_9(PPh)_2^{-\cdot} + L \rightarrow Co_4(CO)_9(PPh)_2L^{-\cdot} \quad (10)$$

stitution is retarded by added carbon monoxide. Moreover, the ligand substitution is insensitive to the concentration and the nature of the entering phosphorus(III) nucleophile. Such a behavior is consistent with ligand incorporation, which occurs in a fast step subsequent to CO loss from the cluster anion radical. Such a dissociative mechanism is also supported by cyclic voltammetric studies of the tetracobalt cluster I in the presence of various amounts of added triphenylphosphine. The appearance of a new peak arising from the formation of the monosubstituted derivative III during the reduction indicates the ligand substitution of the anion radical by triphenylphosphine occurs on the CV time scale of milliseconds.[50] Importantly, the amount of III formed relative to I charged is strikingly invariant with the molar excess of triphenylphosphine. In other words, the electrochemical formation of III is kinetically zero order in the phosphine nucleophile. Such a kinetics situation can only arise if ligand substitution occurs after the rate-limiting step, as depicted in Scheme I.[51]

The basic dissociative mechanism in Scheme I, which involves the prior loss of CO followed by either recapture of CO (i.e., reversible CO loss) or competitive trapping by phosphine nucleophiles, has been observed in other tetranuclear clusters such as the thermal substitution of H$_2$Ru$_4$(CO)$_{13}$ and the photochemical substitution of H$_2$FeRu$_3$(CO)$_{13}$.[5,52] Taken together, we propose the composite mechanism given in Scheme II for the electrocatalytic substitution of the tetracobalt cluster.

According to this mechanism, the initiation of the chain process requires an electrode or chemical potential E_i that is sufficient to reduce some of the tetracobalt cluster to its anion radical. For the parent cluster I, the potential will be reasonably close to the value of its $E_{1/2}$ listed in Table I. The efficiency of ligand substitution depends largely on the dissociative loss of CO to form the coordinatively unsaturated intermediate Co$_4$(CO)$_9$(PPh)$_2^{-\cdot}$ in eq 9, which must effectively compete with other routes for the destruction of Co$_4$(CO)$_9$(PPh)$_2^{-\cdot}$ such as disproportionation, rearrangement, fragmentation, etc. The subsequent ligand coordination of L in the follow-up step (eq 10) is expected to be rapid. Furthermore, the electron-transfer step (eq 8) is also rapid for phosphine substitution since the driving force ΔG is exergonic.[53] (Note the driving force for electron transfer is simply given by the difference ΔE between the reduction potentials of the reactant and the substitution product (i.e. $\Delta G = F(\Delta E)$) as given by the

Scheme II
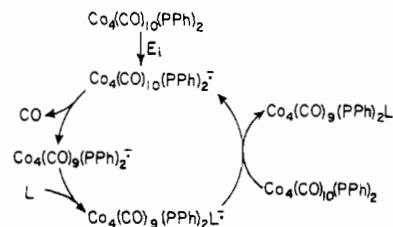
(46) Jensen, S.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1081.

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(48) For a general discussion of the ETC reaction, see: Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1.

(49) For studies of electron-transfer catalysis, see: (a) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (b) Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (c) Amatore, C.; Saveant, J. M.; Thiebault, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *103*, 303.

(50) For a description of the contrasting CV behavior in which the loss of CO is *simultaneous* with phosphine substitution on the ion radical, see ref 10d.

(51) For a discussion of associative and dissociative mechanisms in ligand substitution, see: (a) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965. (b) Tobe, M. L. "Inorganic Reaction Mechanisms"; Nelson: London, 1972.

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(53) See ref 10d and: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 4186. Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3567.

values of $E_{1/2}$ in Table I.) It is this driving force for electron transfer that largely controls the selectivity in multiple ligand substitutions. Thus setting the electrode at the reduction potential of $Co_4(CO)_{10}(PPh)_2$ ensures its selective reduction to the anion radical, since the product $Co_4(CO)_9(PPh)_2L$ will be reduced at more negative potentials when L is a phosphine or a related ligand. (See Table I.) Under these circumstances the driving force will always favor electron transfer in the direction given in eq 11, which is required for electrocatalysis (cf. Scheme II).

$$Co_4(CO)_9(PPh)_2L^- \cdot + Co_4(CO)_{10}(PPh)_2 \rightarrow$$
$$Co_4(CO)_9(PPh)_2L + Co_4(CO)_{10}(PPh)_2^- \cdot \quad (11)$$
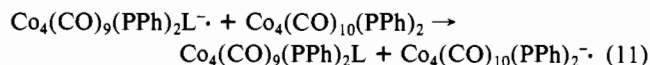
The somewhat limited values of the turnover numbers listed in Table IV are most likely to arise from the extraneous decomposition of the pair of anion radicals involved in the catalytic cycle (see Scheme II), i.e., reactant anion radical prior to CO loss and/or the product anion radical prior to electron transfer. Indeed the cyclic voltammetric studies in Table I indicate the occurrence of such kinetically unstable anion radicals, which are shown (see Table IV) to be scavenged by additives such as dihydroanthracene and tributyltin hydride capable of inhibiting various types of radical-chain reactions.[54] Under these conditions, new species are observed in amounts directly related to the consumption of the reactant cluster. Structural studies to elucidate the identity of the new products are in progress.

The electrocatalytic ligand substitution of the tetracobalt cluster I compares with the earlier studies of tricobalt[6] and triiron clusters. The faster rates of ligand substitution in the latter systems are indicated by the high conversions obtained during a single CV scan. Although no mention was made of a study of phosphine dependence,[6] it is clear that large variations occur in the efficiency of electrocatalysis of ligand substitutions in polynuclear clusters. The delineation of the structural factors involved in such catalytic processes merit further study.

Summary and Conclusions

The utility of electron-transfer catalysis in the ligand substitution of the planar tetracobalt cluster $Co_4(CO)_{10}(PPh)_2$ and its derivatives is limited to low current efficiencies. The catalytic process may be employed to selectively synthesize a variety of monosubstituted derivatives, $Co_4(CO)_9(PPh)_2L$, where L = phosphorus(III) nucleophiles. Further replacement of the carbonyl ligands to afford more highly substituted derivatives is less efficient. Mechanistic investigations including the effects of additives, phosphine dependence studies, and cyclic voltammetric studies support a radical-chain process in which the tetracobalt cluster is reduced to the anion radical that spontaneously loses a carbonyl ligand. The coordinatively unsaturated intermediate is trapped by added nucleophile to form an adduct that affords the substitution product by electron transfer to the reactant and generates the anion radical. We believe that the kinetic stability (i.e. lifetime) of the chain-carrying substituted anion radical plays a critical role in determining the efficiency of the chain process. Our current studies of the myriad pathways by which cluster anion radicals can react, such as hydrogen atom transfer, carbonyl reduction, etc., will provide further facets of electron-transfer catalysis.

Experimental Section

Materials. Dicobalt octacarbonyl (Pressure Chemical) and phenyldichlorophosphine (Strem Chemical) were used as received. Triphenylphosphine (M and T Chemical) and tricyclohexylphosphine and bis(1,2-diphenylphosphino)ethane (Strem Chemical) were reagent grade material. Trimethyl phosphite (Victor Chemical) and triethylphosphine (M and T Chemical) were distilled from sodium and stored under argon. The following tetracobalt clusters were prepared by the procedures described in the literature: $Co_4(CO)_9(PPh)_2PPh_3$ and $Co_4(CO)_8(PPh)_2$-

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$(PPh_3)_2$;[16b] $Co_4(CO)_9(PPh)_2[P(OMe)_3]$ and $Co_4(CO)_8(PPh)_2[P(OMe)_3]_2$.[17] Tetra-*n*-butylammonium perchlorate (G. F. Smith Chemical) was recrystallized twice from a hexane–ethyl acetate mixture and dried in vacuo prior to use. Tetrahydrofuran (Du Pont) was distilled from Na/K benzophenone ketyl under argon and stored in a Schlenk flask. Dichloromethane, benzene, and *n*-hexane were reagent grade commercial solvents that were repurified by stirring them over concentrated sulfuric acid. They were then dried over anhydrous K_2CO_3 and distilled from CaH_2 under argon.

Synthesis of $Co_4(CO)_{10}(PPh)_2$. To 50 mL of a toluene solution containing $NaCo(CO)_4$ (~0.006 mol) at −78 °C was added 0.4 mL (0.003 mol) of $PhPCl_2$. The reaction was stirred for 2.0 h at −78 °C and then allowed to warm to room temperature. The solution was filtered under argon by using Schlenk techniques. The resulting solution was either refluxed for 2.0 h or stirred overnight at room temperature. (The yield of product was essentially the same by either procedure.) Solvent removal, followed by drying in vacuo, afforded a black residue, which was chromatographed on a silica gel column by eluting with hexane. The first band, which was golden yellow, corresponded to $Co_4(CO)_{10}(PPh)_2$. Typical yields of $Co_4(CO)_{10}(PPh)_2$ ranged from 15 to 30%. An analytically pure sample was obtained by crystallization from a 1:10 mixture of toluene and hexane at −20 °C. IR (CH_2Cl_2): ν_{CO} 2040 (vs), 2032 (s), 2016 (s), 1866 (w) cm^{-1}. UV (CH_2Cl_2): λ_{max} 502 (ϵ 335), 428 (5705), 353 (15031), 307 nm (18975). Anal. Calcd for $C_{22}H_{10}Co_4O_{10}P_2$: C, 36.10; H, 1.38. Found: C, 35.60; H, 1.33.

Synthesis of $Co_4(CO)_9(PPh)_2PEt_3$. To 0.5 g (0.68 mmol) of $Co_4(CO)_{10}(PPh)_2$ in 80 mL of degassed toluene was added 0.47 mL (0.0032 mol) of triethylphosphine. The reaction was stirred overnight at ~40 °C. TLC examination of the solution showed the presence of only the monosubstitution produce $Co_4(CO)_9(PPh)_2PEt_3$. The crude product was purified by chromatography on silica gel using 1:1 benzene and hexane. The resulting red material was recrystallized from a 1:1 mixture of toluene and hexane at −20 °C to afford 0.27 g (48.3%) of the red $Co_4(CO)_9(PPh)_2PEt_3$. IR (CH_2Cl_2): ν_{CO} 2055 (w), 2020 (vs), 1998 (s), 1838 (m) cm^{-1}. UV (CH_2Cl_2): λ_{max} 438 (ϵ 7182), 365 (13470), 308 nm (15855). Anal. Calcd for $C_{26}H_{25}Co_4O_9P_3$: C, 39.42; H, 3.04. Found: C, 39.20; H, 3.34.

Synthesis of $Co_4(CO)_8(PPh)_2(diphos)$. To 0.2 g (0.27 mmol) of $Co_4(CO)_{10}(PPh)_2$ and 0.12 g (0.3 mmol) of diphos in 35 mL of THF was added ~0.2 mL of a 0.025 M potassium benzophenone ketyl solution. The initial red color became red-brown immediately, and stirring was continued for 3.0 h at room temperature. TLC examination showed the major product to be the desired cluster, which was isolated and purified by chromatography on Florisil using a 1:1 mixture of benzene and hexane. An analytical sample and crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from a 1:4 mixture of CH_2Cl_2 and hexane at −20 °C. A 0.13-g (44.0%) yield of the red $Co_4(CO)_8(PPh)_2(diphos)$ was obtained. IR (CH_2Cl_2): ν_{CO} 2040 (s), 1985 (vs), 1825 (w) cm^{-1}. UV (CH_2Cl_2): λ_{max} 452 (ϵ 7858), 373 (15064), 321 nm (16864); Anal. Calcd for $C_{46}H_{34}Co_4O_8P_4$: C, 51.42; H, 3.17. Found: C, 50.60; H, 3.34.

Synthesis of $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$. To 1.0 g (0.0014 mol) of $Co_4(CO)_{10}(PPh)_2$ in 50 mL of benzene was added 0.6 mL (0.0048 mol) of $P(OMe)_3$. The reaction mixture was refluxed for 6.0 h and then concentrated in vacuo to afford a red residue. Purification by chromatography with silica gel using benzene gave a red material free of other products, as shown by TLC. An analytically pure sample was recrystallized from a 1:10 mixture of toluene and hexane at −20 °C to yield 0.41 g (28.7% yield) of red $Co_4(CO)_7(PPh)_2[P(OMe)_3]_3$. IR ($CH_2Cl_2$): ν_{CO} 2020 (s), 1970 (vs), 1810 (m) cm^{-1}. UV (CH_2Cl_2): λ_{max} 444 (ϵ 8348), 369 (12648), 318 nm (15529). Anal. Calcd for $C_{28}H_{27}Co_4P_5O_{16}$: C, 32.95; H, 3.63. Found: C, 32.90; H, 3.80.

Synthesis of $Co_4(CO)_6(PPh)_2[P(OMe)_3]_4$. To 0.68 g (0.00092 mol) of $Co_4(CO)_{10}(PPh)_2$ in 40 mL of benzene was added 0.5 mL (0.004 mol) of $P(OMe)_3$, and the solution was refluxed overnight. The tetrasubstituted product was purified by silica gel chromatography using benzene as the eluant. An analytically pure sample was recrystallized from a 1:1 mixture of toluene and hexane at −40 °C to yield 1.00 g (97.0%) of red $Co_4(CO)_6(PPh)_2[P(OMe)_3]_4$. IR ($CH_2Cl_2$): ν_{CO} 1985 (w), 1956 (vs), 1796 (m) cm^{-1}. UV (CH_2Cl_2): λ_{max} 446 (ϵ 9968), 372 (13132), 323 nm (16964). Anal. Calcd for $C_{30}H_{46}Co_4O_{18}P_6$: C, 32.37; H, 4.12. Found: C, 32.16; H, 4.14.

Electrochemical Measurements. Cyclic voltammetry and microvoltammetric analyses were performed at a platinum electrode with an *iR*-compensated potentiostat[55] driven by a Princeton Applied Research Model 175 universal programmer. Polarography at a dropping mercury

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electrode was performed with a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-to-voltage converter. Cyclic voltammetric curves were either displayed on a Tetronix 5115 storage oscilloscope or recorded on a Houston Series 2000 x-y recorder. Polarographic and microvoltammetric results were recorded directly on the x-y recorder. Pollution of the electrodes was not apparent in these studies. Aging of the solution was also undetected under these conditions, since we were able to reproduce the potential/current profiles throughout the course of an experiment. The platinum-disk working electrode was periodically polished with a very fine emery cloth.

The cyclic voltammetric and microvoltammetric cell were of airtight design with high-vacuum Teflon valves (Kontes) and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The adjustable platinum working electrode was imbedded in a cobalt glass seal to allow periodic polishing without significantly changing the surface area. The SCE reference and saturated KCl salt bridge were separated from the solution by a cracked glass tip. The counter electrode, consisting of a platinum gauze was separated from the working electrode by less than 2 mm and was connected to the reference electrode via a $0.1\text{-}\mu\text{F}$ capacitor to aid in the compensation for iR drop.

The standard oxidation and/or reduction potentials for the tetracobalt clusters determined by cyclic voltammetry were evaluated from the anodic (E_p^a) and cathodic (E_p^c) peak potentials (when permitted).[27] The $E_{1/2}$ values from microvoltammetric and polarographic analyses were obtained from the magnitude of the limiting-current and applied-potential curves.

Instrumentation. IR spectra were recorded on either a Perkin-Elmer 467 and 298 spectrometer as liquid solutions in 1.0-mm chloride cells. All IR spectra were calibrated against the 1601-cm^{-1} band of a polystyrene film. UV–vis spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer.

Electrocatalysis of Ligand Substitution. Typical Procedure. To an argon-flushed electrolysis cell was added ~0.03 g (~0.0355 mmol) of $Co_4(CO)_{10}(PPh_3)_2$, followed by 5–7 mL of solvent containing 0.1 M TBAP. The desired amount of the phosphorus(III) nucleophile such as PPh_3 was added to the stirred solution. The electrocatalytic reaction was initiated by passage of ~2.0 mA of cathodic current in the constant-current mode. The initial potential of −1.0 V rose to −1.15 V as the substitution reaction proceeded. The extent of the substitution reaction was monitored by IR spectrophotometry after the passage of 6% of the theoretical charge required for the moles of $Co_4(CO)_{10}(PPh_3)_2$ charged. The yield of $Co_4(CO)_9(PPh_3)_2PPh_3$ was determined by monitoring the absorbance of the 2060-cm^{-1} stretching band of the monosubstituted cluster. In desired cases, the monosubstituted cluster was isolated by column chromatography, and it was shown to be identical with an authentic sample prepared independently. In no case was there any evidence for the disubstituted cluster under these conditions.

Ruthenium(III) Chloride in Aqueous Solution: Electrochemical and Spectral Studies

M. M. Taqui Khan,* G. Ramachandraiah, and A. Prakash Rao

Chloro complexes of ruthenium(III) in 0.1 M KCl at pH 0.4, 1.0, and 2.0 and temperature 25 °C have been investigated with use of electrochemical and spectrophotometric techniques. The species characterized in solution are $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$, and $[RuCl(H_2O)_5]^{2+}$. The equilibrium constants for the formation of these species are reported at 25 °C ($\mu = 0.1$ M KCl). The reduction potentials and the characteristic charge-transfer bands for these ions have also been reported. The electrochemical and spectral behaviors of a solution containing these species were found to change with time, which was explained in terms of the various solution equilibria and stabilities of the species in solution. The species $[RuCl_2(H_2O)_4]^+$ was found to be the most stable present in solution under these experimental conditions. The species $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, and $[RuCl(H_2O)_5]^{2+}$ are converted to the more stable $[RuCl_2(H_2O)_4]^+$ species as evidenced from time-drive absorption spectra. These conversions are found to be fast in solutions heated to temperatures higher than 70 °C at pH 2.0 with the concomitant hydrolysis of the metal ion.

Introduction

Ruthenium and its chloro complexes particularly in the +3 oxidation state have evinced a great deal of interest in recent years because of their use in homogeneous catalysis.[1-10] Ruthenium(III) chloride and its EDTA complexes have recently been successfully employed as catalysts in the oxidation of allyl alcohol, ascorbic acid, and cyclohexanol.[3-6] The spectral behavior and solution stabilities of ruthenium(III) and its chloro complexes, however,

have not yet been studied in detail.

Ruthenium(III) forms a variety of chloro complexes of the type $[MX_mY_n]^{(m-n-3)-}$ (where M = Ru^{3+}, X = Cl^-, Y = H_2O, $m = 1$–6, $n = 0$–5, and $m + n = 6$). The hexa- and pentachloro complexes are isolable[11-13] from concentrated hydrochloric acid (>6 M) solution, but the other species, though known in solution, could not be isolated. The variation of color intensity of ruthenium(III) solution with its concentration[14,15] in hydrochloric acid also supports the existence of several equilibria in solution. Since anionic chloro complexes of ruthenium(III) are substitution labile and equilibrate rapidly in solution,[16] the composition of each complex species under equilibrium in solution is largely affected by hydrochloric acid concentration. Connick et al.[16,17] determined the charge per species of the chloro complexes by ion-exchange elution

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