J. Am. Chem. Soc. **1982**, *104*, 5633–5640

$[Fe_3Co(CO)_{13}]^-$, 72251-84-4; $[Ru_4(CO)_{13}]^{2-}$, 75215-45-1; $[Fe_4(CO)_{13}]^{2-}$, 25767-85-5; $[PPN][V(CO)_6]$, 38856-17-6; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $Mn_2(CO)_{10}$, 10170-69-1; $H_3Mn_3(CO)_{12}$, 51160-01-1; $Re_2(CO)_{10}$, 14285-68-8; $H_3Re_3(CO)_{12}$, 12146-47-3; $Na_2Fe(CO)_4$, 14878-31-0; $Fe(CO)_5$, 13463-40-6; $[PPN]_2[Fe_2(CO)_8]$, 53368-25-5; $Fe_3(CO)_{12}$, 17685-52-8; $[PPN][Ru_3H(CO)_{11}]$, 71936-70-4; $Ru_3(CO)_{12}$, 15243-33-1; $[PPN][Co(CO)_4]$, 53433-12-8; $Co_2(CO)_8$, 10210-68-1; $[PPN][MnFe_2(CO)_{12}]$, 68520-37-6; $W(CO)_3(dien)$, 34630-09-6; $W(CO)_4(diphos)$, 29890-05-9; $W(CO)_4(dppme)$, 41830-14-2; $Mo(CO)_2(PPh_3)_2(CH_3CN)_2$, 23526-71-8; $Mo(CO)_{12}(PPh_3)_2(bipy)$, 15653-24-4; $Mo(CO)_2(PPh_3)(dien)$, 24859-95-8; $Mo(CO)_2(PPh_3)_2(en)$, 24859-94-7; $[PPN][FeCo_3(CO)_{12}]$, 80883-51-8; $[PPN][Fe_3Co(CO)_{13}]$, 72251-83-3; $[PPN]_2[Fe_4(CO)_{13}]$, 69665-30-1; $[PPN][Ru_3Co(CO)_{13}]$, 72152-11-5; $K_2Ru_4(CO)_{13}$, 75215-44-0; $H_2FeOs_3(CO)_{13}$, 12563-74-5; $K_4Ru_4(CO)_{12}$, 75234-73-0; $[PPN]_2[Ru_6(CO)_{18}]$, 62501-17-1; $[PPN]_2[Co_6(CO)_{15}]$, 82891-34-7; $Rh_6(CO)_{16}$, 28407-51-4; methane, 74-82-8.

Paramagnetic Organometallic Molecules. 12.[1] Electrochemical Studies of Reactions with Lewis Bases following Metal–Metal Bond Cleavage in $R_2C_2Co_2(CO)_6$ Radical Anions

Malini Arewgoda,[2a] Philip H. Rieger,*[2b] Brian H. Robinson,*[2a] Jim Simpson,[2a] and Steven J. Visco[2b]

Contribution from the Departments of Chemistry, Brown University,
Providence, Rhode Island 02912, and the University of Otago, Dunedin, New Zealand.

Received November 30, 1981

Abstract: A detailed electrochemical study of the $RC_2R'Co_2(CO)_6{}^{0/-\cdot}$ redox couple is presented [R, R′ = Ph, *t*-Bu, H, CF_3, $Si(CH_3)_3$] utilizing DC polarography and cyclic voltammetry on Hg and Pt electrodes. All acetylene complexes of this type undergo an electrochemically reversible one-electron reduction to the radical anions at potentials ranging from −0.5 to −1.1 V vs. Ag/AgCl in acetone. However, with the exception of the R, R′ = CF_3 compound, the radical anions disintegrate into a variety of monocobalt species including $Co(CO)_4{}^-$ and $RC_2R'Co(CO)_3$. These radical anions also undergo a series of complicated reactions with CO, phosphines, and phosphites that can be analyzed in terms of $\overrightarrow{E}C\overrightarrow{E}$ and $\overrightarrow{E}C\overleftarrow{E}$ mechanisms. Major products include $Co(CO)_4{}^-$, $Co(CO)_3L^-$, $RC_2R'Co(CO)_2L$, and $RC_2R'Co_2(CO)_5L$ [L = PPh_3, $P(OMe)_3$]. The electrochemistry of the R,R′ = CF_3 compound is much cleaner and does not involve fragmentation to monocobalt species. The different redox properties can be correlated with the lifetimes of the radical anions calculated from the electrochemical data. Detailed studies of the redox chemistry of the Lewis base derivatives, $RC_2R'Co_2(CO)_{6-n}L_n$ [L = PPh_3 or $P(OMe)_3$, $n = 1$–4], are also presented. These derivatives also undergo one-electron reductions to radical anions, but the $n = 3$, 4 derivatives undergo reversible one-electron oxidations to radical cations as well. The redox chemistry of all compounds can be rationalized on the basis of reactions involving intermediate radical anions produced by the reversible homolytic cleavage of the metal–metal bond. The synthetic utility of enhanced receptiveness to nucleophilic attack on the metal–metal cleaved intermediate is emphasized.

A number of generalizations and insights into the electronic structure and reactivity of capped trimetal clusters have arisen from work[1,3–6] on paramagnetic species generated from them. In particular, the generality of a nondegenerate antibonding metal-centered a_2 LUMO and the lability of the metal–metal bond in the radical anions have important consequences for the synthetic and catalytic utility of these clusters. Further, it has been demonstrated that the opportunity to add an electron to a cluster may increase the nucleophilicity of the metal atoms or, alternatively, increase the electrophilicity if radical anion formation is accompanied by opening of the capped clusters,[5–7] or enable the species to act in dissociative electron attachment reactions.[8] It is not entirely clear from the work on the trinuclear clusters which factors determine the kinetic stability of radical anions, although carbon- and germanium-capped systems appear to have the longest lifetimes.[6] In order to further elucidate these factors and to widen the scope of possible reaction modes, we have investigated the closely related acetylene complexes, $RC_2R'Co_2(CO)_6$.[9] The acetylene moiety could be regarded as a cap for the Co–Co bond, and it is interesting that acidification of alkyne complexes with an α-hydrogen is a route to the tricobalt carbon clusters.[10] Molecular orbital descriptions[11] of these complexes predict that the LUMO is a nondegenerate antibonding orbital (in this case of b_2 symmetry) that is largely centered on the two cobalt atoms. A detailed picture provided by our recent analysis[12] of the frozen solution ESR spectra of the radical anions supports this description and is also in agreement with the concept[13] of a "bent" Co–Co bond. Preliminary work[14] on this system showed a very wide range of radical anion stability. Therefore it was considered that the redox chemistry of the acetylene complexes would offer a useful comparative extension to the capped cluster system and, moreover, provide a coordinated organic substrate that might show altered reactivity compared to the neutral counterpart. The only previous

---

[1] Part 11: Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1981**, *20*, 2540–2543.

[2] (a) University of Otago. (b) Brown University.

[3] Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 405–410.

[4] Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1000–1005.

[5] Arewgoda, C. M.; Robinson, B. H.; Simpson, J.; manuscript in preparation.

[6] Lindsay, P. N. T.; Robinson, B. H.; Simpson, J.; Vahrenkamp, H. *Inorg. Chem.*, submitted for publication.

[7] Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* **1981**, 265–266.

[8] Kirk, C.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.*, in press.

[9] Dickson, R. S.; Fraser, D. F. *Adv. Organomet. Chem.* **1974**, *12*, 323–377.

[10] Markby, R.; Wender, I.; Fridel, R. A.; Cotton, F. A.; Sternberg, H. W. *J. Am. Chem. Soc.* **1958**, *80*, 6529–6533.

[11] (a) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103–3117. (b) Thorne, D. F.; Hoffmann, R. *Ibid.* **1978**, *17*, 126–140. (c) Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550–6562.

[12] Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1980**, *102*, 156–163.

[13] Braterman, P. S. *Struct. Bonding (Berlin)* **1961**, *10*, 57–86.

[14] Dickson, R. S.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1979**, *172*, C63–C65.

0002-7863/82/1504-5633$01.25/0

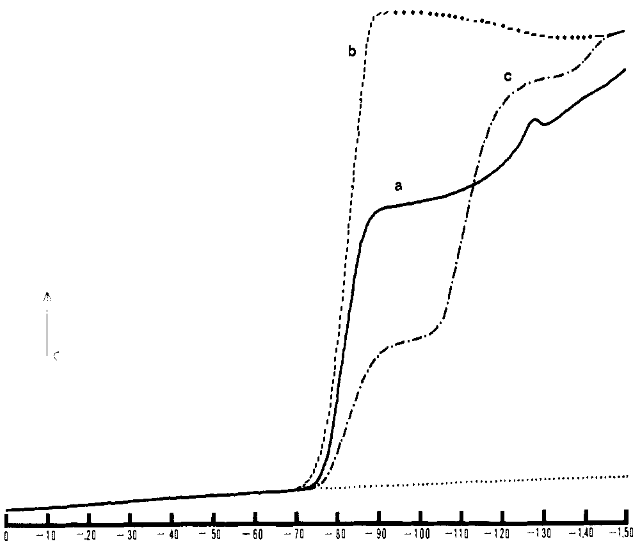


Figure 1. DC polarograms at room temperature: (a) **1**; (b) **1** in the presence of 1 atm CO; (c) **1** in the presence of 10 mM PPh_3.

related work was on $Ph_2C_2Co_2(CO)_6$, for which Dessy[15] reported an irreversible reduction wave at $E_{1/2} = -1.6$ V (vs. Ag/AgCl). In this paper the detailed electrochemistry of $RC_2R'Co_2(CO)_6$ complexes and their phosphine or phosphite derivatives is presented; an analysis of the ESR spectra of mononuclear species derived from the dinuclear radical anions[16] and the synthetic utility of the radical anions[5] will be discussed in subsequent papers.

Experimental Section

Acetylene-bridged dicobalt hexacarbonyls were prepared by literature methods.[9,17] The phosphine- and phosphite-substituted compounds ($Ph_2C_2Co_2(CO)_5L$, L = PPh_3 and $P(OMe)_3$) were prepared according to Chia et al.[18] and purified by thin-layer chromatography; preparations of new Lewis base derivatives will be reported elsewhere.[5,19] Cobalt carbonyl, $Co_2(CO)_8$ (Alfa or Strem), was purified by vacuum sublimation. The salt $(Ph_3P)_2N^+Co(CO)_4^-$ was prepared by the method of Ruff.[20] The dimer $[Co(CO)_3P(OMe)]_2$ was prepared by the method of Manning[21] and purified by thin-layer chromatography. Triphenylphosphine, triphenylarsine, and tri-*n*-butylphosphine (Aldrich), trimethyl phosphite (Alfa), $[Co(CO)_3PPh_3]_2$ (Strem), and hexafluorobut-2-yne (Fluorochem) were used without further purification. Acetone solvent was Fisher Analytical Grade and was also used without purification. Tetrahydrofuran solvent was distilled from benzophenone ketyl. Tetra-*n*-butylammonium perchlorate, obtained from Southwestern Analytical Chemicals as the monohydrate, was recrystallized from ethyl acetate-pentane and dried over P_2O_5 before use; tetramethylammonium perchlorate (Eastman) was used as received.

Electrochemical experiments were performed on a PAR 174 polarographic analyzer equipped with a Hewlett-Packard 202A low-frequency function generator; cyclic voltammograms were recorded on a Hewlett-Packard *x*–*y* recorder or by photographing an oscilloscope trace. Polarograms or cyclic voltammograms at temperatures below ambient were obtained by using a jacketed cell and a Lauda constant-temperature circulator with hexane as the coolant liquid. Solutions used in electrochemical experiments were 10^{-3} M in electroactive material and 0.10 M in supporting electrolyte; acetone, THF, or CH_2Cl_2 was used as the solvent. Solutions were deoxygenated with argon (presaturated with solvent) for several minutes and blanketed with argon for the remainder of the experiment. A three-electrode system coupled with positive-feedback circuitry was employed to minimize *iR* drop.[22] The auxiliary electrode was a platinum wire. The working electrode was either a dropping mercury electrode or a platinum wire. The Pt working electrodes were pretreated before each experiment by anodizing in the electrolyte solution at about +2.0 V for 45 s, or by swirling in chromic acid, washing, and reducing at −0.1 V in 0.1 M perchloric acid, and then scanning through the potential range of interest until a reproducible flat cyclic voltammogram was obtained. These procedures afforded a clean surface that yielded reproducible results from experiment to experiment. Some of the cobalt carbonyl compounds rapidly poisoned the electrode at room temperature so that only a few cyclic scans could be obtained between electrode treatments. Potentials were measured relative to an Ag/AgCl electrode with 0.10 M LiCl in acetone. The stability of the reference electrode was checked periodically by measuring the half-wave potential of benzoquinone, which was taken to be −0.380 V.[23]

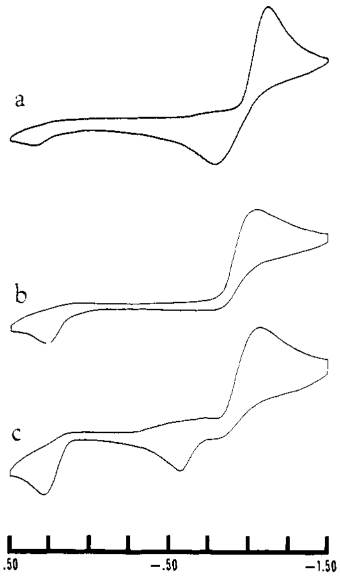


Figure 2. Cyclic voltammograms of **1** on Pt: (a) −30 °C, 160 mV s^{-1}; (b) room temperature, 600 mV s^{-1}; (c) room temperature, 1 atm CO, 600 mV s^{-1}.

Results

Electrochemical Studies of $RC_2R'Co_2(CO)_6$. The DC polarogram of $Ph_2C_2Co_2(CO)_6$ (**1**) in acetone[24] at room temperature (Figure 1a) shows an electrochemically reversible one-electron reduction ($\Delta E = E_{1/4} - E_{3/4} = 50$ mV) at −0.82 V vs. Ag/AgCl. Further ill-defined reduction waves occur between −1.1 and −2.0 V with an increase in current corresponding approximately to an additional electron. A wave at −2.23 V corresponds to the reduction of diphenylacetylene. At −30 °C, the DC polarogram of **1** shows one-electron waves at −0.82 and −1.56 V (ΔE = 47 and 42 mV, respectively). Cyclic voltammograms of **1** on Pt or Hg at −30 °C show a chemically reversible reduction process; the ratio of anodic to cathodic peak currents (i_p^a/i_p^c) is near unity under these conditions (Figure 2a). When the temperature is increased (Figure 2b), the anodic peak current decreases; indicating radical anion decomposition, and further cathodic and anodic peaks are observed. Thus the electrochemical data indicate that the primary electrode process is

$$Ph_2C_2Co_2(CO)_6 + e \rightleftarrows Ph_2C_2Co_2(CO)_6^{-}\cdot$$

The ratio i_p^a/i_p^c was used to estimate the radical anion lifetime as a function of temperature. From room temperature down to about 0 °C, rapid-scan cyclic voltammograms were obtained by using a dropping mercury electrode. At lower temperatures the increased stability of the radical anion necessitated the use of a Pt electrode since the scan rates needed to obtain useful data were slow compared with the rate of Hg-drop growth. The Pt electrode, which was rapidly poisoned at room temperature, performed well

---

[15] Dessy, R. E.; Pohl, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 1995–2001.

[16] Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J., manuscript in preparation.

[17] King, R. B. *Organomet. Synth.* **1965**, *1*, 133–134.

[18] Chia, L. S.; Cullen, W. R.; Franklin, M.; Manning, A. R. *Inorg. Chem.* **1975**, *14*, 2521–2526.

[19] (a) Arewgoda, C. M. Ph.D. Thesis, University of Otago, 1981. (b) Visco, S. J. Ph.D. Thesis, Brown, University, 1982.

[20] Ruff, J. K.; Schlinetz, W. L. *Inorg. Synth.* **1974**, *15*, 84–90.

[21] Manning, A. R. *J. Chem. Soc. A* **1967**, 1135–1137.

[22] Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410–415.

[23] Potential estimated from data given by: Meites, L.; Zuman, P. "Electrochemical Data", Part 1; Wiley: New York, 1974; Vol. A.

[24] Unless otherwise noted, all results refer to acetone solutions. A few electrochemical data were obtained for THF and CH_2Cl_2 solutions with qualitatively similar results.

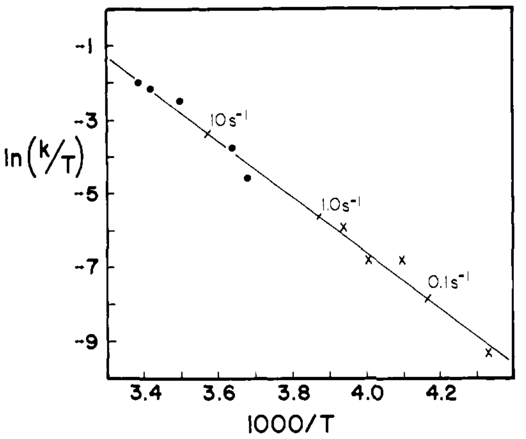


Figure 3. Absolute rate theory plot of first-order rate constants for the decay of $1^{-}\cdot$ derived from cyclic voltammograms; points derived from cyclic voltammograms on Hg are indicated by closed circles, on Pt by crosses. Points corresponding to k = 10, 1, and 0.1 s^{-1} are indicated on the least-squares line.

at lower temperatures. First-order rate constants were derived from these measurements by the methods of Nicholson and Shain.[25] The measurement of the anodic peak current was complicated by the additional poorly defined reduction processes; extrapolation of the cathodic current to the time of the anodic peak was thus subject to considerable error, and the rate constants are probably accurate to no better than ±10%. Nonetheless, an absolute-rate-theory plot of the data (Figure 3) is seen to be remarkably linear over a wide temperature range; activation parameters derived from this plot are $\Delta H^{\ddagger} = 63 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 0 \pm 10$ J mol^{-1} K^{-1}. These activation parameters give a lifetime of 7 min at −60 °C, consistent with the estimate of 1 min obtained from ESR observation of the radical anion in THF solution.[14]

At temperatures above −30 °C, an irreversible oxidation peak appeared at +0.25 V in cyclic voltammograms of **1** on Pt (Figure 2b), which grew in size as the temperature was increased. Cyclic voltammograms on Hg showed an apparently reversible oxidation at −0.07 V that behaved much as the +0.25 V oxidation peak on Pt. $Co(CO)_4^-$, either added to the solution as the $(Ph_3P)_2N^+$ salt or generated by the two-electron reduction of $Co_2(CO)_8$,[26,27] shows an irreversible oxidation peak at +0.25 V on Pt and apparently reversible oxidation at −0.07 V on Hg.[28] It should be noted that cyclic voltammograms in which the potential was scanned just into the primary reduction peak show the $Co(CO)_4^-$ oxidation peak clearly. Thus, $Co(CO)_4^-$ is positively identified as a decomposition product in the decay of $Ph_2C_2Co_2(CO)_6^{-}\cdot$.

The behavior of $(t\text{-}Bu)_2C_2Co_2(CO)_6$ (**2**) is qualitatively very similar to that of **1**. The low-temperature DC polarogram shows an electrochemically reversible one-electron wave at −1.03 V (ΔE = 53 mV), a second one-electron wave at −1.8 V (ΔE = 40 mV), and a third somewhat smaller wave at −1.9 V (ΔE = 71 mV). At room temperature the first wave remains essentially unchanged (ΔE = 48 mV), but a wave is then seen at −1.45 V (ΔE = 58 mV) with a diffusion current corresponding to approximately half an electron; the low-temperature second and third waves are entirely absent. No wave could be assigned to the reduction of $(t\text{-}Bu)_2C_2$; the expected wave was probably obscured by the reduction of supporting electrolyte, which commenced at −2.5 V.

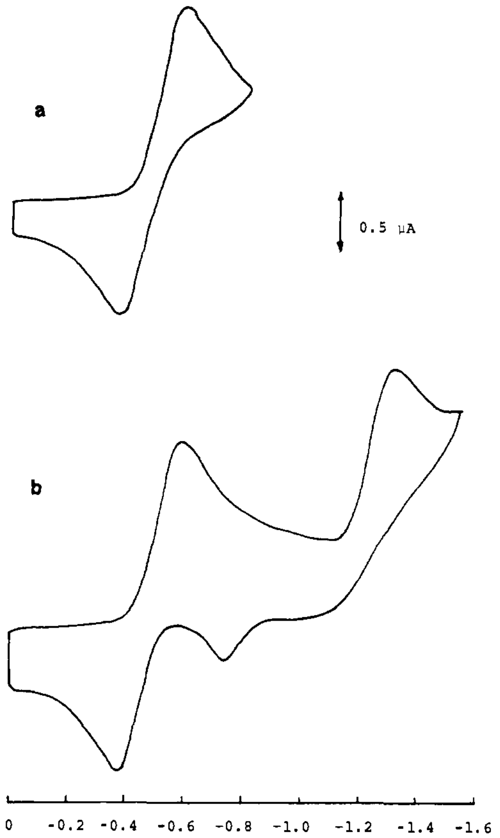


Figure 4. Cyclic voltammograms of **3** on Pt at room temperature, 500 mV s^{-1}.

Cyclic voltammograms of **2** on Hg at room temperature show, at sufficiently high scan rate, a nearly reversible reduction to the radical anion. The ratio i_p^a/i_p^c gives a radical anion lifetime of 70 ms at room temperature. A comparison with the room-temperature lifetime of the radical anion of **1** of about 17 ms is consistent with ESR observations that suggested that $(t\text{-}Bu)_2C_2Co_2(CO)_6^{-}\cdot$ is longer lived than $Ph_2C_2Co_2(CO)_6^{-}\cdot$.[14] A second reduction peak at −1.48 V appears to be completely irreversible but is followed, on the reverse scan, by an oxidation peak at −1.38 V. A small, partially reversible, oxidation peak is also observed at −0.80 V as is the characteristic $Co(CO)_4^-$ oxidation at −0.07 V.

The trifluoromethyl compound $(CF_3)_2C_2Co_2(CO)_6$ (**3**) gives a well-defined DC polarogram at room temperature in acetone. Reduction waves at −0.51 V (ΔE = 60 mV) and −1.28 V (ΔE = 60 mV) have equal diffusion currents, and both are apparently electrochemically reversible one-electron waves. The first wave corresponds to the formation of $(CF_3)_2C_2Co_2(CO)_6^{-}\cdot$. Unlike the alkyl and aryl derivatives, there is no change in the polarographic behavior of **3** at lower temperatures. The "clean" polarographic behavior is a consequence of the stability of the radical anion on the electrochemical time scale; indeed, ESR measurements indicate a room-temperature lifetime of several hours in vacuo.[14,19]

Cyclic voltammograms on **3** on Pt (Figure 4a) show a one-electron reduction with i_p^a/i_p^c near unity and independent of scan rate. In addition, there is an irreversible reduction peak at −1.25 V. When the potential scan is fast (>200 mV s^{-1}) and is switched beyond the second reduction peak, an anodic peak appears at −0.70 V (Figure 4b); this oxidation is not seen at slower scan rates.

The above examples exhibit the extremes of polarographic and voltammetric behavior of $RC_2R'Co_2(CO)_6$ compounds (Table I). In general, the lifetime of the radical anion $RC_2R'Co_2(CO)_6^{-}\cdot$ increases with the electron-withdrawing ability of the substituents and with an increase in lifetime, the polarograms and cyclic voltammograms at room temperature are more like those of **3**.

---

(25) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–723.

(26) Dessy, R. E.; King, R. B.; Waldrop, M. J. *J. Am. Chem. Soc.* **1966**, *88*, 5117–5121.

(27) de Montauzon, D.; Poilblanc, R. J. *J. Organomet. Chem.* 1976, *104*, 99–106.

(28) The nature of this electrode process is unclear. we at first thought that it corresponded to oxidation of mercury to form $Hg[Co(CO)_4]_2$, but reduction of this species is irreversible and much more cathodic[27] than the process observed here. The behavior of the $Co(CO)_4^-$ oxidation at Hg resembles that recently reported by Bond and co-workers[29] for $Fe(CO)_4PPh_3$ and related compounds. Oxidation was found to be completely irreversible on Pt but apparently reversible and shifted cathodically by ca. 400 mV on Hg. A surface species described as a "mercury-stabilized cation" was invoked by these authors.

(29) Blanch, S. W.; Bond, A. M.; Colton, R. *Inorg. Chem.* **1981**, *20*, 755–761.

Table I. Polarographic Data[a]

compound	$E_{1/2}$/V	$E_{1/4} - E_{3/4}$/mV
$Ph_2C_2Co_2(CO)_6$	−0.82	50
$Ph_2C_2Co_2(CO)_5PPh_3$	−1.12	44
$Ph_2C_2Co_2(CO)_5AsPh_3$	−0.93	*b*
$Ph_2C_2Co_2(CO)_5P(OMe)_3$	−1.17	58
$Ph_2C_2Co_2(CO)_4[P(OMe)_3]_2$	−1.52	55
$Ph_2C_2Co_2(CO)_3[P(OMe)_3]_3$	−1.73	88
$Ph_2C_2Co_2(CO)_2[P(OMe)_3]_4$	−1.89	40
$^tBu_2C_2Co_2(CO)_6$	−1.03	48
$(CF_3)_2C_2Co_2(CO)_6$	−0.51	60
$(CF_3)_2C_2Co_2(CO)_5PPh_3$	−0.89	70
$(CF_3)_2C_2Co_2(CO)_5P(OMe)_3$	−0.88	60
$(CF_3)_2C_2Co_2(CO)_4[P(OMe)_3]_2$	−1.17	60
$(CF_3)_2C_2Co_2(CO)_3[P(OMe)_3]_3$	−1.38	58
$(CF_3)_2C_2Co_2(CO)_2[P(OMe)_3]_4$	−1.80	80
$(PhC_2H)Co_2(CO)_6$	−0.90	40
$(t\text{-}BuC_2H)Co_2(CO)_6$	−1.03	38
$(CF_3C_2H)Co_2(CO)_6$	−0.76	58
$[CF_3C_2Si(CH_3)_3]Co_2(CO)_6$	−0.68	58

[a] Half-wave potentials for primary reduction processes at room temperature vs. Ag/AgCl in acetone solution. [b] Wave distorted by polarographic maximum.

The primary electrode process in all cases is the formation of the radical anion. Nonetheless, these radical anions disintegrate into a variety of fragments. The parent acetylene and $Co(CO)_4^-$ are produced in significant yields. Neither $Co(CO)_4^-$ nor the acetylene reacts with other fragments; DC polarograms and cyclic voltammograms of solutions to which $(Ph_3P)_2N^+Co(CO)_4^-$ or RC_2R' were added showed no changes other than the expected larger waves or peaks due to the added species. Several other species are always formed, at least two of which are electroactive. One or more of the decomposition products (including Co metal which was positively identified) is deposited on the electrode, leading to the rapid poisoning of Pt electrodes observed in this work.

In an attempt to gain further understanding of these systems, electrochemical measurements were carried out in the presence of CO and Lewis bases. Evidence was obtained for rapid substitution of Lewis bases for CO in the radical anions, and this led to an investigation of the $R_2C_2Co_2(CO)_{6-n}L_n$ complexes.

Electrochemical Studies in the Presence of CO. The half-wave potentials of the first waves in DC polarograms of **1** (Figure 1b) and **2** are unchanged under 1 atm of CO, but the diffusion current increases in both cases by about 70%. Small waves are observed at −1.7 and −2.23 V (Ph_2C_2) in the polarogram of **1** and at −1.75 V in the case of **2**.

Under 1 atm of CO, cyclic voltammograms of **1** at Pt (Figure 2c) or Hg electrodes show an increase in the anodic peak corresponding to oxidation of $Co(CO)_4^-$ and a new feature, a chemically reversible couple at −0.59 V on Pt (−0.56 V on Hg). No further reduction or oxidation peaks are seen in the potential range 0 to −1.5 V. The behavior of **2** is very similar; the features at −1.48 and −1.38 V are absent, and the small oxidation peak at −0.80 V has developed into a well-defined reversible couple with an average potential of −0.83 V. In either case, the lifetime of the radical anion, determined as above from the ratio i_p^a/i_p^c, *is unaffected by the presence of CO.* It thus appears that CO reacts not with the radical anion initially formed but with the primary decomposition product, thus preventing the formation of the host of apparently secondary products seen in the absence of CO.

In the presence of CO, there appear to be only two major products: $Co(CO)_4^-$ and the species showing the reversible oxidation at −0.56 or −0.83 V (since these oxidation potentials differ, this species must contain the acetylene moiety). Free acetylene is apparently only a minor product in the presence of CO. The oxidized form of the new species is not very long lived. In rapid-scan cyclic voltammograms on Hg, the oxidation product is reduced on the cathodic scan, while in slower scan rate experiments on Pt, this reduction peak is only barely detectable. These results lead us to postulate that the species oxidized at −0.56 or −0.83 V is $R_2C_2Co(CO)_3^-$.

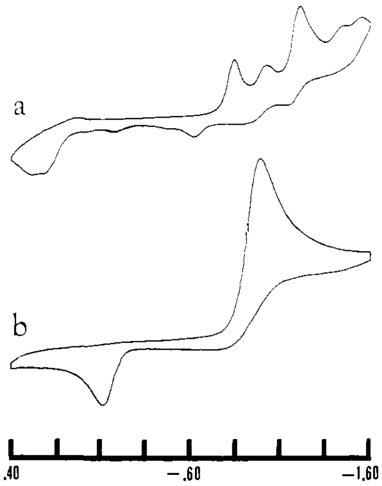


Figure 5. Cyclic voltammograms on Pt at room temperature, 160 mV s^{-1}: (a) **1** in the presence of 10 mM $P(OMe)_3$; (b) $[Co(CO)_3P(OMe)_3]_2$.

In contrast to the behavior of **1** and **2**, the electrochemical behavior of **3** is unaffected by the presence of CO. Fragmentation of the radical anion is not observed; there is no anodic peak corresponding to the oxidation of $Co(CO)_4^-$, and no additional features appear in the cyclic voltammograms. It is interesting that the irreversible electrode process at −1.21 V is unaffected by CO, suggesting that it does not correspond to reduction of a fragmentation product of the radical anion. Rather it would be reasonable to attribute this process to the addition of a second electron to give the very short-lived dianion.

Electrochemical Studies in the Presence of Lewis Bases. Addition of 10 mM PPh_3, $P(OMe)_3$, PEt_3, or $P(OPh)_3$ to solutions of **1** results in a decrease of the diffusion current of the first polarographic wave by 50–70%. Additional waves are observed at more negative potentials (Figure 1c), but the Ph_2C_2 wave was undetectable. The DC polarogram at −30 °C is identical with that observed in the absence of nucleophiles. The DC polarogram of **2** in the presence of $P(OMe)_3$ also shows a 70% reduction of the first-wave diffusion current, but PPh_3 had no discernible effect on the first wave (though small new waves appear at −1.2 and −1.4 V). The DC polarogram of **1** in the presence of $AsPh_3$ consists of overlapping waves with $E_{1/2} \simeq -0.82$ and −0.93 V. The diffusion current plateau for the first wave is not well-defined, but there may be a small decrease from the limiting current observed in the absence of $AsPh_3$.

Cyclic voltammograms on Pt of **1** in the presence of PPh_3 or $P(OMe)_3$ (Figure 5a) exhibit the characteristic oxidation peak at +0.25 V due to $Co(CO)_4^-$ and, in addition, show oxidation peaks at −0.29 or −0.13 V, respectively. Cyclic voltammograms of $[Co(CO)_3L]_2$ show two-electron reduction to $Co(CO)_3L^-$,[27] and, on the reverse scan, irreversible oxidation of the anion at −0.29 V for L = PPh_3 and at −0.13 V for L = $P(OMe)_3$ (Figure 5b).[30] Thus these features may be assigned to $Co(CO)_3PPh_3^-$ and $Co(CO)_3P(OMe)_3^-$, respectively. Cyclic voltammograms on Hg were complicated by Hg oxidation to form phosphine or phosphite complexes[29] but were otherwise consistent with the results obtained with Pt electrodes.

In cyclic voltammograms of **1** in the presence of $P(OMe)_3$ (Figure 6a), the primary reduction peak is much reduced in size, consistent with the current reduction seen in the DC polarogram. A variety of features appear when the scan is extended beyond the primary reduction: reduction peaks at −1.0 and −1.20 V and oxidation at −1.15 and −0.68 V on the reverse scan. The feature of −0.68 V was not seen if the scan switched just beyond the primary reduction peak and apparently corresponds to a product of the −1.20-V electrode process. The reduction peak at −1.20

---

(30) $[Co(CO)_3PPh_3]_2$ is quite insoluble in acetone; cyclic voltammograms were obtained with THF as solvent. The reported potential is corrected to acetone by comparison with other electrode processes observed in both solvents.

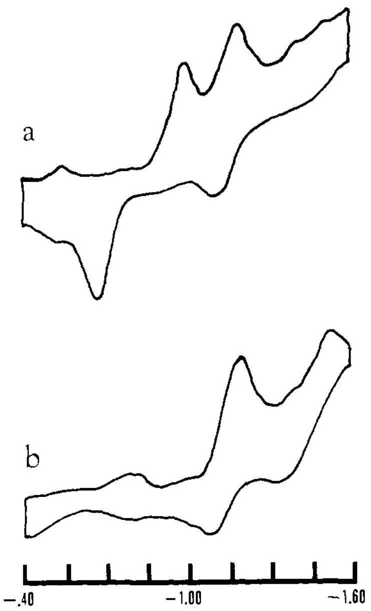


Figure 6. Cyclic voltammograms on Hg at room temperature, 5.06 V s^{-1}: (a) **1** in the presence of 10 mM $P(OMe)_3$; (b) $Ph_2C_2Co_2(CO)_5P(OMe)_3$.

V corresponds, both in potential and in general behavior, to reduction of $Ph_2C_2Co_2(CO)_5P(OMe)_3$ (figure 6b, vide infra) and is therefore assigned to this species. This assignment provides an explanation for the reduction in current for the primary electrode process. The $P(OMe)_3$ derivative must have arisen from substitution on $Ph_2C_2Co_2(CO)_6^{-}\cdot$ followed by oxidation of $Ph_2C_2Co_2(CO)_5P(OMe)_3^{-}\cdot$ at the electrode or by **1**. The process may thus be classified as an electrochemical $\bar{E}C\bar{E}$ mechanism.[31] However, judging by the ratio $i_p{}^a/i_p{}^c$ for the primary electrode process, the radical anion lifetime is unaffected by the presence of Lewis bases, suggesting that, as in the case of CO, the products result from the reaction of Lewis base with a decomposition product closely related to the radical anion but not with the radical anion itself. Cyclic voltammograms of **1** in the presence of $AsPh_3$ are also similar to those with $P(OMe)_3$ except that the cathodic peak at −0.99 V, assignable in this case to $Ph_2C_2Co_2(CO)_5AsPh_3$ (vide infra), is almost entirely irreversible whereas a cleanly reversible couple ($E_p{}^c = -1.16$ V, $E_p{}^a = -1.08$ V) is seen, which can be assigned to $Ph_2C_2Co(CO)_2AsPh_3{}^{\cdot/-}$.

Cyclic voltammograms of **1** in the presence of PPh_3 or $P(n\text{-}Bu)_3$ and of **2** in the presence of $P(OMe)_3$ closely resemble that of **1** with $P(OMe)_3$. An exception is provided by **2** in the presence of PPh_3; no reduction of first-wave current is seen in either the DC polarogram or the cyclic voltammogram. Thus the phosphine-substituted dicobalt compound is not produced in significant amounts in the case. This result is at least somewhat consistent with the behavior of **1**; the DC diffusion current was reduced by about 50% by PPh_3 but by about 70% by $P(OMe)_3$ or $P(n\text{-}Bu)_3$.

Substitution thus accounts for up to 70% of the radical anions. The appearance of $Co(CO)_4^-$ and $Co(CO)_3L^-$ oxidations suggest that fragmentation is the other major reaction pathway. The reversible couple assigned to $(R_2C_2)Co(CO)_3{}^{-/\cdot}$ is just detectable in cyclic voltammograms of **1** and **2** in the presence of PPh_3 or $P(OMe)_3$. The other major fragmentation products are the monocobalt radicals $(R_2C_2)Co(CO)_2L$ (vide infra).

The irreversible reduction at −1.0 V in cyclic voltammograms of **1** in the presence of $P(OMe)_3$ is not presently understood. Analogous reduction peaks are observed in cyclic voltammograms of **1** in the presence of $P(n\text{-}Bu)_3$ and **2** in the presence of PPh_3 but not in voltammograms of **1** with PPh_3 or of **2** with $P(OMe)_3$. It is likely that in these two cases, this reduction peak is superimposed on the larger peak assigned to $(R_2C_2)Co_2(CO)_5L$. Since the potential of this reduction peak depends on both the Lewis base and on the acetylene substituents, it is likely that the species being reduced contains both of these moieties.

The electrochemical behavior of the CF_3 derivative (**3**) in the presence of Lewis bases is significantly different. The DC polarogram of **3** in the presence of excess $P(OMe)_3$ showed waves at −0.88 and −1.20 V; the waves at −0.51 and −1.28 V attributed to the reduction of **3** had dissappeared. Cyclic voltammograms, however, showed the reversible reduction of **3** at −0.51 V followed by chemically reversible couples at −0.88 and −1.20 V. Analysis of the electrochemical solution by thin-layer chromatography showed that the derivatives $(CF_3)_2C_2Co_2(CO)_{6-n}[P(OMe)_3]_n$ (n = 1 or 2) had been produced. The waves at −0.88 and −1.20 V correspond to the one-electron reductions of these derivatives (vide infra). Thus substitution of the radical anion of **3** by Lewis bases is fast and essentially quantitative on the polarographic time scale with negligible fragmentation to $Co(CO)_4^-$ or other products.

Electrochemistry of Lewis Base Substituted Derivatives. In order to validate the assignment of certain cathodic peaks in cyclic voltammograms of **1**, **2**, and **3** in the presence of Lewis bases to reduction of the substituted compounds, $R_2C_2Co_2(CO)_{6-n}L_n$, we investigated the electrochemistry of several of these derivatives in detail.

If our understanding of the electrochemistry of the unsubstituted compounds is correct, then it should be possible to predict the behavior of the substituted derivatives. Thus in the presence of CO, we expect to see an increase in DC polarographic diffusion current and formation of the fragmentation products $Co(CO)_4^-$ and $R_2C_2Co(CO)_3^-$ as well as substitution of L by CO to form the parent radical anion, $R_2C_2Co_2(CO)_6^{-}\cdot$. In the presence of excess Lewis base, both fragmentation to $Co(CO)_3L^-$ and $R_2C_2Co(CO)_2L\cdot$ and further substitution of CO by L are expected; the DC diffusion current is expected to decrease. As we shall demonstrate in the following paragraphs, these expectations were generally realized.

$Ph_2C_2Co_2(CO)_{6-n}[P(OMe)_3]_n$ (n = 1–4) all undergo a primary one-electron reduction to produce the radical anion, with $E_{1/2}$ becoming more negative with increasing n (−1.17 to 1.89 V, Table I). Addition of excess $P(OMe)_3$ to the n = 1 and 2 derivatives (but not n = 3 and 4) decreases the diffusion current of the first wave (by 22% and 25%, respectively), shifts $E_{1/2}$ by about −4 mV, and increases the current due to the secondary electrode processes at more negative potentials (these are due to the reduction of more highly substituted derivatives). Under 1 atm of CO, the first-wave diffusion current increases by up to 60% (depending on n) and $E_{1/2}$ shifts by about +20 mV. Judging from the sizeable shifts of $E_{1/2}$, the lifetimes of the radical anions $Ph_2C_2Co_2(CO)_{6-n}L_n^{-}\cdot$ must be very short. This is consistent with the failure to observe ESR spectra of these radical anions on reduction, even at −60 °C; only mononuclear paramagnetic species were detected.[16,19]

It was therefore surprising to find that cyclic voltammograms of the n = 1 and 2 derivatives show oxidation peaks at about the potential of the primary reduction, suggesting chemically reversible formation of the radical anions (Figure 6b). However, this oxidation peak is absent in cyclic voltammograms of these derivatives in the presence of CO, and the oxidation peak and reversible couple previously assigned to $Co(CO)_4^-$ and $Ph_2C_2Co(CO)_3{}^{-/\cdot}$, respectively, are then observed. Cyclic voltammograms in the absence of CO showed oxidation peaks corresponding to $Co(CO)_4^-$ and $Co(CO)_3P(OMe)_3^-$. Therefore it seems likely that the radical anions of the Lewis base derivatives rapidly fragment into several mononuclear species, one of which (probably $Ph_2C_2Co(CO)_{3-n}L_n^-$) is reversibly oxidized at nearly the reduction potential of the original compound. This interpretation receives convincing support from the results for $Ph_2C_2Co_2(CO)_5AsPh_3$. In that case, cyclic voltammogram peaks assignable to the primary reduction ($E_p{}^c$ = −0.99 V, $E_{1/2}$ = −0.93 V) and the monocobalt radical ($E_p{}^c$ = −1.16 V) are clearly resolved. Reoxidation of $Ph_2C_2Co(CO)_2AsPh_3^-$ ($E_p{}^a$ = −1.08 V) is nearly quantitative, but the primary process is completely irreversible at room temperature. Under 1 atm of CO, the reversible couple disappears and the features assigned to $Ph_2C_2Co(CO)_3{}^{-/\cdot}$ and **1** are prominent in the cyclic voltammogram. Substitution of CO for $AsPh_3$ is apparently

---

(31) Feldberg, S. W.; Jeftic, L. J. *J. Phys. Chem.* **1972**, *76*, 2439–2446.

Table II. Oxidation Electrode Processes[a]

compound	$E_{1/2}$/V[b]	$E_p{}^a$/V[c]	$E_p{}^c$/V[c]
$Ph_2C_2Co_2(CO)_3[P(OMe)_3]_3$	0.28	0.34	0.24
$Ph_2C_2Co_2(CO)_2[P(OMe)_3]_4$	0.01	0.09	−0.03
$(CF_3)C_2Co_2(CO)_3[P(OMe)_3]_3$	0.34	0.42	0.27
$(CF_3)C_2Co_2(CO)_2[P(OMe)_3]_4$	0.25	0.27	0.17

[a] Potentials for primary oxidation processes at room temperature vs. Ag/AgCl in acetone solution. [b] $E_{1/4} - E_{3/4} = 60$ mV for all DC polarographic waves. [c] Peak potentials of cyclic voltammograms on Pt; $i_p{}^c/i_p{}^a = 1.0$ in all cases.

very rapid. Similarly, cyclic voltammograms of $Ph_2C_2Co_2(CO)_5AsPh_3$ in the presence of PPh_3 show mainly features associated with the PPh_3 derivative of **1** and its fragmentation products.

In addition to the primary formation of the radical anion, secondary features are seen at more cathodic potentials in cyclic voltammograms of the $P(OMe)_3$ (n = 1 and 2) derivatives, which correspond to the reduction of the more highly substituted derivatives (n = 2 and 3). The derivative $Ph_2C_2Co_2(CO)_5PPh_3$ behaved similarly to $Ph_2C_2Co_2(CO)_5P(OMe)_3$ except that, as expected, the secondary reduction processes corresponding to more highly substituted species are absent. Also, the current corresponding to electrode processes involving fragmentation products was comparatively much greater, a consequence of the shorter lifetime of phosphine-substituted radical anion.

The derivatives $(CF_3)_2C_2Co_2(CO)_{6-n}L_n$ (n = 1–4) offer an interesting comparison to the diphenylacetylene series. Reversible one-electron reduction to the radical anion is again the primary electrode process for the n = 1 derivative ($E_{1/2}$ = −0.88 V), but a well-defined process with approximately equal current is seen at −1.20 V and a further irreversible wave at −1.40 V (these apparently correspond to reduction of the n = 2 and n = 3 derivatives, respectively). Cyclic voltammograms on Hg or Pt also show two reversible couples with $i_p{}^a/i_p{}^c$ close to unity. If the voltammogram is switched before the second couple, a small oxidation peak appears at −0.38 V on Pt; a corresponding reduction peak is seen on the second and subsequent scans. On the addition of excess $P(OMe)_3$, the wave in the DC polarogram due to reduction of the n = 1 derivative completely disappears and the current of the waves at −1.20 and −1.40 V increases by approximately 50%. The DC polarogram and cyclic voltammograms on Pt and Hg for n = 2 show a reversible one-electron reduction at $E_{1/2}$ = −1.20 V. The peak current ratio $i_p{}^a/i_p{}^c$ on Pt becomes smaller as the scan rate is decreased, and an irreversible peak at −1.38 V and a small oxidation peak at −0.84 V can be identified. In the presence of excess $P(OMe)_3$, the −1.38 V feature is enhanced and a small oxidation peak at −0.12 V appears. A reasonable assignment for the oxidation peaks at −0.38 and −0.84 V would be to the radical anions $(CF_3)_2C_2Co_2(CO)_{6-n}L_n{}^{-}\cdot$ (n = 0 and 1). The oxidation peak at −0.12 V may be $Co(CO)_3P(OMe)_3{}^-$, but it is significant that this is only a minor feature compared with the analogous Ph_2C_2 system. Radical anion formation for the n = 3 and 4 derivatives is irreversible at all temperatures and scan rates and is unaffected by excess ligand.

A reversible one-electron reduction is observed for $(CF_3)_2C_2Co_2(CO)_5PPh_3$ (Table I), but the electrochemistry of $(CF_3)_2C_2Co_2(CO)_4(PPh_3)_2$ is more difficult to interpret. Reduction processes appear in the DC polarogram at −1.14 and −1.28 V, with approximately equal diffusion currents. However, cyclic voltammograms on Pt show an irreversible reduction peak at −1.21 V as well as a reversible couple ($E_p{}^c$ = −1.33 V, $E_p{}^a$ = −1.26 V, $i_p{}^a/i_p{}^c$ = 1).

Primary Oxidation Processes. When three or four carbonyl groups in $R_2C_2Co_2(CO)_6$ are replaced by $P(OMe)_3$, well-defined polarographic oxidation waves are observed. Data for these electrochemically reversible, one-electron processes are given in Table II. Cyclic voltammograms (Figure 7) of $R_2C_2Co_2(CO)_{6-n}[P(OMe)_3]_n$ (R = Ph and CF_3) on Hg (n = 4) or Pt (n = 3 and 4) show chemically reversible oxidations, apparently to form the cation radicals. In marked contrast to the corresponding anion radicals, the cations do not fragment to mononuclear species, and it is possible to isolate the cations for both R = Ph and R = CF_3 as $PF_6{}^-$ or $BF_4{}^-$ salts by chemical oxidation (e.g., with Ag(I) salts).[19]

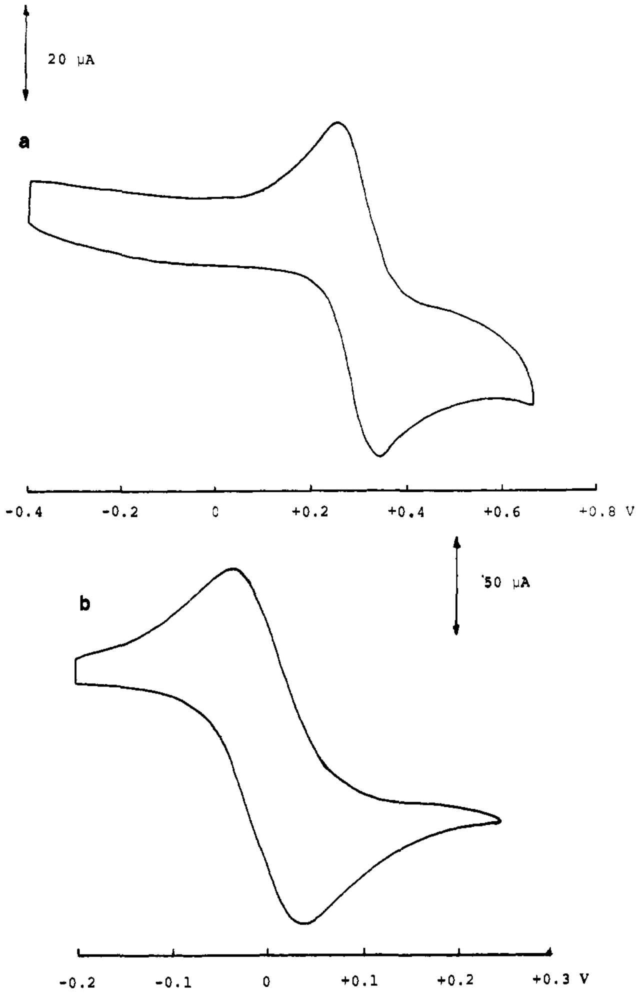


Figure 7. Cyclic voltammograms on Pt, 500 mV s^{-1}, at room temperature: (a) $Ph_2C_2Co_2(CO)_3[P(OMe)_3]_3$; (b) $Ph_2C_2Co_2(CO)_2[P(OMe)_3]_4$.

Discussion

For all $R_2C_2Co_2(CO)_{6-n}L_n$ components, the primary electrode process is one-electron reduction to produce the radical anion:

$$R_2C_2Co_2(CO)_{6-n}L_n + e \rightleftarrows R_2C_2Co_2(CO)_{6-n}L_n{}^{-}\cdot$$

The electrode potential for this process is a function of the acetylene substituents and the number and type of ligand L. Thus a marked cathodic shift in reduction potential occurs as the electron-withdrawing ability of R decreases or when Lewis bases are substituted for CO ligands. While not unexpected since both the HOMO and LUMO have contributions from the acetylene and the ligands,[11] this trend is more pronounced than that observed for the capped tricobalt clusters.[22,32] An explanation for this lies in the respective HOMO and LUMO compositions. Both the $R_2C_2Co_2$ and $RCCo_3$ clusters have an antibonding LUMO predominantly metal in character[11,33] (the metal 3d contributions derived from analysis of ESR parameters are 64% and 75%, respectively[1,12]), but the contribution of the capping group and ligands is signficantly greater in the $R_2C_2Co_2$ system. The HOMO composition probably varies similarly. Thus the reduction potential, a function of the HOMO–LUMO separation,[22] is more sensitive to the nature of the substituent on the capping group and to the ligands with the $R_2C_2Co_2(CO)_{6-n}L_n$ compounds.

---

[32] Bond, A. M.; Dawson, P. A.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1413-1417.

[33] Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456-3467.

Attention should also be drawn to the small difference in *oxidation potential*, 0.06 V, between $Ph_2C_2Co_2(CO)_3[P(OMe)_3]_3$ and $(CF_3)_2C_2Co_2(CO)_3[P(OMe)_3]_3$, compared to 0.31 V for the shift in *reduction potential* from $Ph_2C_2Co_2(CO)_6$ and $(CF_3)_2C_2Co_2(CO)_6$. This is surprising in view of recent SCF X_α scattered-wave calculations[34] and gas-phase UV photoelectron spectra data[35] that favor a C_2Co_2 core orbital (b_1 symmetry) as the HOMO, with an energy dependant on the acetylene substituent. Considering the small difference in oxidation potential between the $n = 3$ and $n = 4$ derivatives—0.27 V for R = Ph and 0.09 V for $R = CF_3$—the lower members of the series (n = 1 and 2) might have been expected to exhibit oxidation processes. In fact, no oxidation electrode processes were observed for these compounds in the potential range 0–+1.0 V, suggesting that there is a change in HOMO composition with progressive phosphite substitution. In appears that the HOMO in the $n = 3$ and 4 derivatives is a metal and carbonyl based orbital with little acetylene character. If this is correct, then the marked perturbation of the M–M interaction should be evident in the X-ray crystal structure of the cation.[36]

The reactions of the acetylene-bridged dicobalt compounds, initiated by one-electron reduction to the radical anions, are extremely complex. In the absence of excess CO or Lewis base, a variety of products are formed, only a few of which have been positively identified. Addition of CO or Lewis bases, however, simplifies the chemistry by channeling the reaction toward a more limited range of products.

In the presence of 1 atm of CO, reduction of **1** and **2** gives $Co(CO)_4^-$ and $R_2C_2Co(CO)_3^-$ in ca. 70% yield. The remaining 30% probably includes acetylene and cobalt metal. Since the radical anion lifetime is independent of the concentration of CO, the first step is apparently first-order conversion of the radical anion to a reactive intermediate X, the identity of which will be discussed below. The results for **1** and **2** may be summarized by Scheme I.

Scheme I

$$R_2C_2Co_2(CO)_6 \overset{e}{\rightleftharpoons} R_2C_2Co_2(CO)_6^{-}\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow[L]{k_2}$$
$$Co(CO)_4^- + R_2C_2Co(CO)_2L \overset{e}{\rightleftharpoons} R_2C_2Co(CO)_2L^-$$

When L = CO, the potential of the second electron transfer of Scheme I is about 200 mV more positive than that of the first. Thus the second electron transfer is fast at the potential of the primary reduction and Scheme I corresponds to an electrochemical ECE mechanism, i.e., to a two-electron polarographic wave.

Scheme I allows an explanation of an otherwise puzzling observation in experiments in which reduction was carried out in situ in the ESR cavity.[16] Electrolysis of **1** or **2** at 213 K resulted in detectable steady-state concentrations of the dicobalt radical anions, but in the temperature range ca. 223–243 K, a weak eight-line spectrum was observed. This spectrum is assigned to the $R_2C_2Co(CO)_3$ radical. In this temperature range, the radical anion lifetime is ca. 10–100 s (Figure 4), long enough to diffuse away from the electrode and sufficiently long that the steady-state concentration should have been ESR detectable. However, decomposition would lead to a CO concentration sufficient to produce the monocobalt radical and the electron transfer process

$$R_2C_2Co(CO)_3 + R_2C_2Co_2(CO)_6^{-}\cdot \rightarrow R_2C_2Co(CO)_3^- + R_2C_2Co_2(CO)_6$$

should be rapid. The monocobalt radicals, once formed, thus tend to scavenge the dicobalt radical anions. The ESR signal seen then represents the extremely small concentration of monocobalt radicals that managed to escape from the electrode without encountering a dicobalt radical anion. Above ca. 223 K, the monocobalt radical lifetime is apparently too short to build up a detectable concentration.

Scheme I also accounts for some of the products observed in reductions of **1** or **2** in the presence of Lewis bases. When L is a phosphine or phosphite, the potential of the second electrode process of Scheme I is more negative than the first, so that the phosphine- and phosphite-substituted monocobalt radicals are not immediately reduced at the electrode. Furthermore, these radicals are substantially more stable than $R_2C_2Co(CO)_3$. It is significant that Klein[37] has recently characterized the fully substituted radical $Ph_2C_2Co(PMe_3)_3$. Monocobalt radicals with one, two, or three phosphorus donors have been detected in ESR spectra following in situ electrolysis of **1** or **2** or Lewis base derivatives of **1**, **2**, or **3** in the presence of excess phosphine, phosphite, or arsine.[16] These spectra were generally much more intense, as expected from the greater stability and nonreducibility of the substituted monocobalt radicals.

In the presence of a Lewis base, an alternative pathway is operative involving substitution of L for CO without fragmentation. An electrochemical ECE mechanism[31,38] (Scheme II) summarizes this behavior.

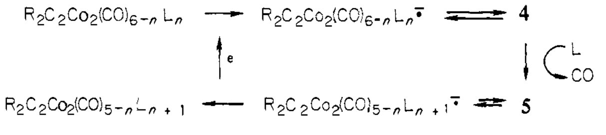
Scheme II

$$R_2C_2Co_2(CO)_{6-n}L_n \overset{e}{\rightleftharpoons} R_2C_2Co_2(CO)_{6-n}L_n^{-}\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow[L]{k_3}$$
$$R_2C_2Co_2(CO)_{5-n}L_{n+1}^{-}\cdot \overset{-e}{\rightleftharpoons} R_2C_2Co_2(CO)_{5-n}L_{n+1}$$

The potential of the second electron transfer of Scheme II is more negative than that of the first, so that reoxidation of the substituted radical anion occurs rapidly at the potential of the primary reduction. Thus a decrease in the polarographic diffusion current is observed to the extent that Scheme II is operative. The relative importance of the fragmentation (Scheme I) and substitution (Scheme II) pathways may be expressed by the rate constant ratio k_2/k_3. Thus when $L = PPh_3$, Schemes I and II are of appproximately equal importance for **1** ($k_2/k_3 \sim 1$), but for **2**, Scheme I dominates ($k_2/k_3 \gg 1$). When $L = P(OMe)_3$, the substitution pathway accounts for about 70% of the total reaction for both **1** and **2** ($k_2/k_3 \sim 0.5$). The same variation in k_2/k_3 is found in the electrochemistry of the $n > 0$ derivatives. The origin of these variations presumably stems from the greater π-acceptor ability of phosphites compared to phosphines, the larger cone angle of PPh_3 compared to $P(OMe)_3$, and the greater steric bulk of *t*-Bu compared with Ph. The electron-withdrawing ability of the acetylene substituent R is obviously very important in determining k_2/k_3 since this ratio is essentially 0 for **3** and its Lewis base derivatives. Only for the tris($P(OMe)_3$) derivative of **3** was evidence found for fragmentation on the electrochemical time scale.

The nature of X, the primary product of radical anion decomposition, may be inferred from its reactions and our knowledge of the electronic structure of the anion radicals $R_2C_2Co_2(CO)_6^{-}\cdot$.[12] The extra electron and a Co–Co antibonding orbital will significantly weaken the bond; the activation enthalpy for radical anion decomposition, 63 kJ mol^{-1} for $1^{-}\cdot$, is consistent with a process in which a weak bond is broken. The capping acetylene might be expected to remain in place in the ring-opening structure, and the activation entropy, 0 ± 10 J mol^{-1} K^{-1}, suggests that frag-

Scheme III



---

(34) Van Dam, H.; Stufkens, D. J.; Oskam, A.; Doran, M.; Hillier, I. H. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *21*, 47–55.

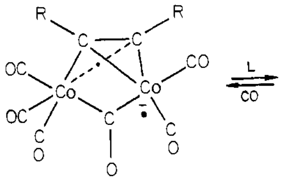
(35) DeKock, R. L.; Lubben, T. V.; Hwang, J.; Fehler, T. P. *Inorg. Chem.* **1981**, *20*, 1627–1628.

(36) Simpson, J., study in progress.

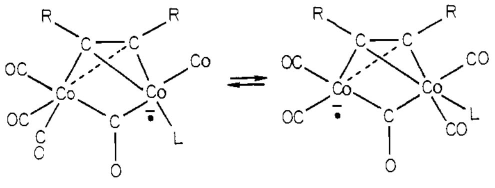
(37) Klein, H. F. *Angew. Chem.* **1980**, *92*, 362–375.

(38) Amatore, C.; Saveant, J. M.; Thiebault, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *103*, 303–320.

mentation does not occur at this step. A reasonable structure for X is **4**.



4



5

Nucleophilic attack on polynuclear metal carbonyl complexes has, in many cases, been shown to be preceded by rupture of the metal–metal bond;[39] in some cases this is reversible.[40] Reversible metal–metal bond cleavage as a reaction mode is more attractive for capped or bridged species for obvious reasons, and evidence for this mode in capped clusters has accumulated in the last few years.[5–8,41] Indeed the lability of metal–metal bonds in polynuclear compounds is probably underestimated.[42] The mechanism of nucleophilic substitution reactions of $Ph_2C_2Co_2(CO)_6$ could well involve a component of this type, where the first-order term[43] could relate as well as to the rapid attack on the metal–metal cleaved species as to a CO dissociative process.

The proposed intermediate in the radical reactions **4** is consistent with the reactions of both Schemes I and II. The two Co atoms are nonequivalent: one is a coordinatively saturated 18-electron center while the other 17-electron center is expected to be labile with respect to ligand exchange.[44] Thus displacement of a terminal CO ligand on the labile center by a nucleophile would result in the sterochemically nonrigid species **5**. If the electrode potential is sufficiently positive, electron transfer can occur with reformation of the Co–Co bond. The net result is nucleophilic substitution of L for CO. On the other hand, displacement of the bridging CO ligand from the labile center in **4** or **5** would lead to loss of $Co(CO)_4^-$ or $Co(CO)_3L^-$, leaving $R_2C_2Co(CO)_2L$ or $R_2C_2Co(CO)_3$, which can accept another electron if the electrode potential is sufficiently negative. Oxidation of **5** to form the nucleophilic substitution product must involve Co–Co bond re-formation; microscopic reversibility would therefore require that **4** be formed reversibly. However, in the presence of excess Lewis base, it appears that $(k_2 + k_3)[L] >> k_{-1}$.

Since $R_2C_2Co_2(CO)_{5-n}L_{n+1}^{-\cdot}$ is capable of electron transfer to $R_2C_2Co_2(CO)_{6-n}L_n$, Scheme II forms the basis for an electron-transfer-chain catalysis mechanism[38,45] (Scheme III). Lewis base derivatives of the acetylene-bridged dicobalt compounds are more easily prepared through application of Scheme III than by the traditional thermal reactions.[18] Thus controlled potential electrolysis of **1** or **3** in the presence of the appropriate ligand affords $R_2C_2Co_2(CO)_{6-n}L_n$ where L = PPh_3 (n = 1 and 2) or $P(OMe)_3$ (n = 1, 2, and 3). The n = 4 derivatives could not be prepared by this method. The reasons for this failure are not entirely understood but are probably related to the instability of the more highly substituted dicobalt radical anions. The details of this synthetic method and other new compounds prepared by this route will be reported elsewhere.[5] The scheme can be adapted easily to other transition-metal cluster systems and to homogeneous reaction conditions in which the reaction is initiated by a chemical reducing agent.[46] Initial investigations have met with startling success.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research both at Brown University and the University of Otago. We thank Professors A. M. Bond and J. O. Edwards for helpful discussions and the University of Kelaniya, Sri Lanka, for leave (M.A.).

Registry No. 1, 14515-69-6; **2**, 59687-97-7; **3**, 37685-63-5; $Ph_2C_2Co_2(CO)_5PPh_3$, 55926-17-5; $Ph_2C_2Co_2(CO)_5AsPh_3$, 12578-19-7; $Ph_2C_2Co_2(CO)_5P(OMe)_3$, 55926-16-4; $Ph_2C_2Co_2(CO)_4[P(OMe)_3]_2$, 55925-86-5; $Ph_2C_2Co_2(CO)_3[P(OMe)_3]_3$, 55925-87-6; $Ph_2C_2Co_2(CO)_2[P(OMe)_3]_4$, 55925-88-7; $(CF_3)_2C_2Co_2(CO)_5PPh_3$, 82963-20-0; $(CF_3)_2C_2Co_2(CO)_5P(OMe)_3$, 82963-21-1; $(CF_3)_2C_2Co_2(CO)_4[P(OMe)_3]_2$, 829-63-22-2; $(CF_3)_2C_2Co_2(CO)_3[P(OMe)_3]_3$, 82963-23-3; $(CF_3)_2C_2Co_2(CO)_2[P(OMe)_3]_4$, 82963-24-4; $(PhC_2H)Co_2(CO)_6$, 12154-91-5; $(t\text{-}BuC_2H)Co_2(CO)_6$, 56792-69-9; $(CF_3C_2H)Co_2(CO)_6$, 15663-90-8; $[CF_3C_2Si(CH_3)_3]Co_2(CO)_6$, 38599-40-5; $Co(CO)_4^-$, 14971-27-8; $Ph_2C_2Co_2(CO)_6^-$, 71251-62-2; $(t\text{-}Bu)_2C_2Co_2(CO)_6^-$, 71251-61-1; $(CF_3)_2C_2Co_2(CO)_6^-$, 71251-63-3; CO, 630-08-0; PPh_3, 603-35-0; $P(OMe)_3$, 121-45-9; PEt_3, 554-70-1; $P(OPh)_3$, 101-02-0; Co, 7440-48-4.

---

(39) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379–392.

(40) (a) Langenback, H.-J.; Vahrenkamp, H. *Chem. Ber.* **1977**, *110*, 1955–1206. (b) Poë, A. *J. Organomet. Chem.* **1981**, *209*, C28–C30.

(41) (a) Beurich, H.; Vahrenkamp, H. *Angew, Chem., Int. Ed. Engl.* **1981**, *20*, 98–99. (b) Huttner, G.; Schneider, J.; Müller, H. D.; Mohr, G.; von Seyerl, J.; Wohlfahrt, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 76–77.

(42) Gansow, O. A.; Gill, D. S.; Bennis, F. J.; Hutchinson, J. R.; Vidal, J. L.; Schoening, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 2449–2450. Gansow, O. A., paper presented at the 181st National Meeting of the American Chemical Society, Atlanta, GA, March 31, 1981.

(43) Cobb, M. A.; Hungate, B.; Pöe, A. *J. Chem. Soc., Dalton Trans.* **1976**, 2226–2229.

(44) (a) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527–2532. (b) Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80–89.

(45) Alder, R. W. *J. Chem. Soc., Chem. Commun.* **1980**, 1184–1186.

(46) Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442–444.