Electron-induced Nucleophilic Substitution Reactions in Organometallic Systems

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Summary Electrolytically produced anion radicals of several organocobalt and organoiron compounds react rapidly with phosphine or phosphite nucleophiles and are reoxidized to the substitution products at the electrode or by the parent compounds.

IN the course of an investigation of the fate of the anion radicals produced on one-electron reduction of acetylene-bridged dicobalt hexacarbonyls,[1] we have discovered a reaction unprecedented in organometallic chemistry. The d.c. polarogram of $(PhCCPh)Co_2(CO)_6$ in acetone solution (0·1 mol dm^{-3} $Bu^n_4NClO_4$) shows an electrochemically reversible one-electron wave at $-0{\cdot}81$ V (*vs.* Ag/AgCl). Cyclic voltammetry at Hg or Pt electrodes indicates a radical anion lifetime of about 10 ms at room temperature, increasing to about 1 s at -30 °C, and to about 1 min (from direct e.s.r. observation[2]) at -60 °C. In the presence of the ligands PPh_3, PBu^n_3, or $P(OMe)_3$, the d.c. diffusion current is reduced to as little as 1/3rd of the original value depending on the nucleophile concentration, and a second well defined wave is observed at the potential expected for the substitution product $(PhCCPh)Co_2(CO)_5L$, *ca.* $-1{\cdot}1$ V. Cyclic voltammetry indicates the formation of $Co(CO)_4^-$ (anodic peak at *ca.* $+0{\cdot}3$ V on Pt or *ca.* $-0{\cdot}3$ V on Hg) and other decomposition products. These will be discussed in more detail elsewhere.[1]

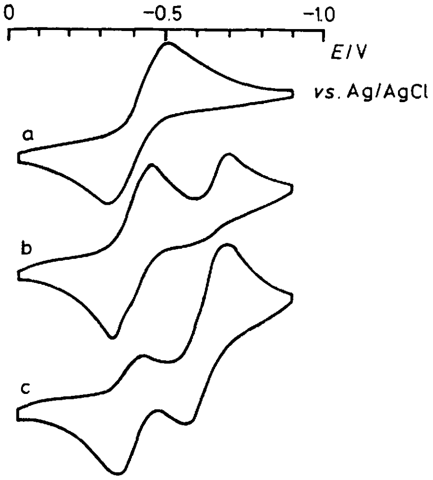


FIGURE 1. Cyclic voltammograms on Pt (1·38 V s^{-1}) of 10^{-3} mol dm^{-3} $PhCCo_3(CO)_9$, 10^{-3} mol dm^{-3} PPh_3, and 0·1 mol dm^{-3} $Bu^n_4NClO_4$ in acetone; (a) -38 °C, (b) -3 °C, (c) $+12$ °C.

The d.c. polarographic current at the first wave of $YCCo_3(CO)_9$ (Y = Ph, Cl)[3] drops nearly to zero in the presence of phosphines or phosphites and a wave appears at the potential expected[4] for the substitution product $YCCo_3(CO)_8L$. Cyclic voltammetry shows that substitution of the anion radical is rapid at room temperature but slows dramatically as the temperature is lowered (Figure 1). Cyclic voltammograms of $PhCCo_3(CO)_8PPh_3$ show some radical anion decomposition and substitution of adventitious CO for phosphine.[4] Under 1 atm CO, virtually complete substitution occurs on the cyclic voltammetry time-scale (Figure 2).

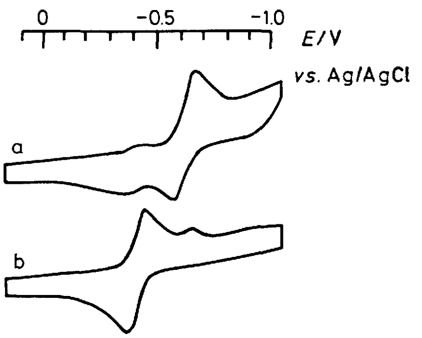
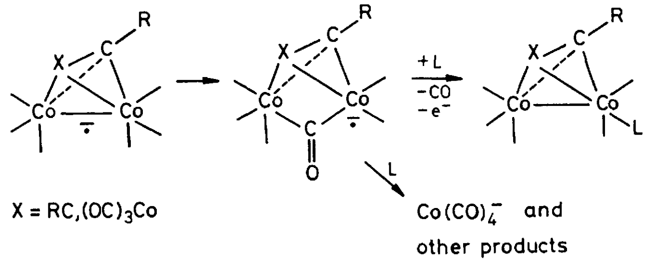


FIGURE 2. Cyclic voltammograms on Pt (1·92 V s^{-1}) of 10^{-3} mol dm^{-3} $PhCCo_3(CO)_8PPh_3$ and 0·1 mol dm^{-3} $Bu^n_4NClO_4$ in acetone at room temperature; (a) 1 atm Ar, (b) 1 atm CO.

The d.c. polarogram of $Fe(CO)_5$ also shows a reduction of current at the first wave in the presence of phosphines or phosphites. The current reduction in this case is only about 10%, but a small wave corresponding to the substitution product $Fe(CO)_4L$ is observed.

In all three cases, nucleophilic substitution occurs rapidly on addition of an electron and the substituted intermediate is rapidly oxidized to the product. Reactions of nucleophiles with the neutral parent molecules are slow[5] under the experimental conditions used.

The extra electrons in $YCCo_3(CO)_9{}^{\bullet-}$ and $(RCCR)Co_2(CO)_6{}^{\bullet-}$ occupy metal–metal anti-bonding orbitals[6] and it is reasonable to suppose that the first step of these reactions is metal–metal bond cleavage. The resulting anion radical intermediate contains a 17-electron metal centre which may be expected to be very labile.[7] Thus the reactions of these species may be rationalized by the Scheme. The final electron transfer may be either to the electrode or to unreduced substrate.



SCHEME

Reduction of $Fe(CO)_5$ is known to produce $Fe_2(CO)_8{}^{2-}$, presumably with $Fe(CO)_5{}^{\bullet-}$ and $Fe(CO)_4{}^{\bullet-}$ as short-lived intermediates.[8] In this case, the action of the nucleophile is to trap $Fe(CO)_4{}^{\bullet-}$. Radical dimerization competes very effectively, however, and only about 10% nucleophilic substitution is obtained.

These reactions correspond to an electrochemical $\overrightarrow{\text{E}}\text{C}\overleftarrow{\text{E}}$ mechanism, first established for the aqueous $Cr(CN)_6{}^{3-}$ system.[9] Reduction of this species leads to the labile Cr^{II} complex which undergoes ligand exchange to produce $Cr(CN)_5OH_2{}^{3-}$ which is rapidly oxidized either at the electrode or by $Cr(CN)_6{}^{3-}$.

The reactions are also analogous to the $S_{RN}1$ mechanism for aromatic nucleophilic substitution investigated by Bunnett and others.[10] Like the latter, we expect that electron-induced nucleophilic substitution will be adaptable to homogeneous reaction conditions.

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