Electron Transfer Catalysed Synthesis of Metal Carbonyl Clusters

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Electron transfer catalysed reactions between metal carbonyl clusters and metal-centred nucleophiles offer a facile new method of cluster synthesis; the syntheses of the clusters $\mathrm{RCCo_2M(cp)(CO)_8}$ (R = Me, Ph, H, M = Cr, Mo, W) and $\mathrm{RCCo_2Fe(cp)(CO)_7}$ (cp = η^5-cyclopentadienyl) are given as examples.

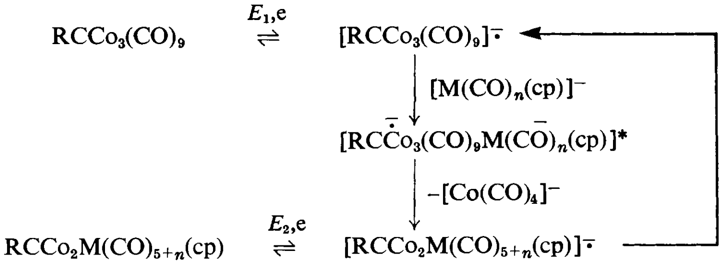
Electron transfer catalysed (ETC) reactions offer a convenient, rapid, and high yield synthesis of Lewis base derivatives of transition metal carbonyl clusters.[1,2] These reactions involve the intermediacy of the respective radical anions and the rapidity of the ETC reaction is believed[1] to be due to 'stretching' or breaking of the metal–metal bond in the transition state which creates a formal 17e centre. Electron transfer from the substituted radical anion to the neutral parent cluster closes the catalytic cycle. It seemed to us that metal carbonyl anions, or other electron-rich, metal-centred species, could also act as nucleophiles in ETC reactions with concomitant formation of new metal–metal bonds, an expectation which is the basis for the syntheses reported in this note.

A typical scheme for an ETC reaction of a carbonyl cluster, *e.g.* $\mathrm{RCCo_3(CO)_9}$, with a metal carbonylate nucleophile, *e.g.* $[\mathrm{M(CO)_{\mathit{n}}(cp)}]^-$, is shown in Scheme 1. The catalytic cycle will be efficient providing that $E_1 > E_2$; this should hold true for most substrates as heteronuclear clusters and clusters of higher nuclearity are more difficult to reduce than their homonuclear or low nuclearity counterparts.[3] The species $[\mathrm{RC\dot{C}o_3^{-}(CO)_9M(C\bar{O})_{\mathit{n}}(cp)}]^*$, arising from direct nucleophilic attack of $[\mathrm{M(CO)_{\mathit{n}}(cp)}]^-$ on the 17e centre of the activated cluster radical anion, has two choices. Expulsion of an anionic fragment can produce a heteronuclear cluster of the same nuclearity, as shown in Scheme 1, or aggregation will take place to give a cluster of higher nuclearity. The presence of a good leaving group, *e.g.* $[\mathrm{Co(CO)_4}]^-$, or a capped metal cluster framework will favour the option shown in Scheme 1; synthesis involving substrates of the heavier elements may proceed *via* the aggregation route.

On the addition of 0.1 cm^3 of purple benzophenone ketyl (BPK) in tetrahydrofuran (THF) to a vigorously stirred solution of $\mathrm{PhCCo_3(CO)_9}$ (0.50 mmol) and $[\mathrm{(cp)Mo(CO)_3}]_2$ (0.50 mmol) in THF (*ca.* 10^{-2} M) at 298 K under argon there was a colour change from brown to black–green. This dark colour was fully developed after 2 min at which point t.l.c. analysis indicated the formation of a new green compound as well as unchanged material. Removal of the solvent and chromatographic purification of the resultant solid gave dark green crystals, shown by comparison with an authentic sample[4] to be $\mathrm{PhCCo_2Mo(cp)(CO)_8}$ (>50% yield) [equation (1)].

$$2\mathrm{PhCCo_3(CO)_9} + [\mathrm{(cp)Mo(CO)_3}]_2 \xrightarrow[<2\ \mathrm{min}]{2\mathrm{e}} 2\mathrm{PhCCo_2Mo(cp)(CO)_8} + 2\,[\mathrm{Co(CO)_4}]^- \quad (1)$$

The above procedure utilizes the *in situ* production of the nucleophile $[\mathrm{(cp)Mo(CO)_3}]^-$ from the dimer since the potential



Scheme 1. cp = η^5-$\mathrm{C_5H_5}$.

for the 2e chemically irreversible reduction of $[(cp)Mo(CO)_3]_2$ is −0.92 V (in PhCN *vs.* Ag–AgCl).[5] A control demonstrated that there was no reaction under similar conditions between $[(cp)Mo(CO)_3]^-$ and $PhCCo_3(CO)_9$ in THF over a period of 30 min. That is, the anion is not initiating the electron-induced reaction and indeed, from the potential, $E_{\frac{1}{2}}[(cp)Mo(CO)_3]^{-1,0}$ = 0.00 V (PhCN *vs.* Ag–AgCl),[5] would not be expected to do so. Nonetheless, the direct reaction between $PhCCo_3(CO)_9$ and $K^+[(cp)Mo(CO)_3]^-$ can be initiated by controlled potential electrolysis at the potential[6] for the couple $[PhCCo_3(CO)_9]^{0,-1}$ [equation (2)].

$$PhCCo_3(CO)_9 + [(cp)Mo(CO)_3]^- \xrightarrow[\text{THF}]{-0.40\text{ V}} PhCCo_2Mo(cp)(CO)_8 + [Co(CO)_4]^- \quad (2)$$

The reaction is again rapid and proceeds in good yield. Transient electrochemistry on this system is consistent with an ETC reaction of a relatively long chain length. $[Co(CO)_4]^-$ is a good leaving group, a major contributing factor to the efficiency of this system; the other requirement for ETC that $E_2 < E_1$ is also met as $E_{\frac{1}{2}}[PhCCo_2Mo(cp)(CO)_8]^{0,-1}$ is 0.5 V more negative than $E_{\frac{1}{2}}[PhCCo_3(CO)_9]^{0,-1}$.

The compound $PhCCo_2Mo(cp)(CO)_8$ is a member of a series of heterometal capped clusters first synthesised by Vahrenkamp's group.[4,7] A comparison of reaction (1) with the original synthesis [equation (3)] illustrates the convenience of the ETC route.

$$PhCCo_3(CO)_9 + \tfrac{1}{2}[(cp)Mo(CO)_3]_2 \xrightarrow[\text{heat, benzene}]{\text{3 days}} PhCCo_2Mo(cp)(CO)_8 + \text{`}Co(CO)_4\text{'} \quad (3)$$

ca. 20%

The mechanism of the thermal reaction (3) is similar to that outlined in Scheme 1 for ETC synthesis as both involve a labilization of metal–metal bonds; labilization by electron addition to a cluster antibonding orbital is however considerably more efficient than thermal activation. This synthetic strategy has been extended to the high yield synthesis of other capped heteronuclear clusters in the series [equations (4) and (5)].†

These reactions emphasise the advantages of the ETC method as they allow the isolation of thermally unstable

$$YCCo_3(CO)_9 + [(cp)M(CO)_3]^- \xrightarrow{\text{BPK}} YCCo_2M(cp)(CO)_8 + [Co(CO)_4]^- \quad (4)$$

$$Y = Me,Ph,H \qquad M = Cr,Mo,W$$

$$YCCo_3(CO)_9 + [(cp)Fe(CO)_2]^- \xrightarrow{\text{BPK}} YCCo_2Fe(cp)(CO)_7 + [Co(CO)_4]^- \quad (5)$$

clusters (*e.g.* when Y = H) and the incorporation of hetero-fragments [*e.g.* $(cp)Fe(CO)_2$] which could not be achieved in significant yields by thermal activation. We have found that the appropriate mercury salts of the metallate anions provide a good *in situ* source of the anion. Thus, only traces of $PhCCo_2Fe(cp)(CO)_7$ were isolated using $[(cp)Fe(CO)_2]_2$ compared to 40% yields starting from $Hg[(cp)Fe(CO)_2]_2$.

Electron-induced synthesis of transition metal carbonyl clusters is not restricted to the carbon-capped substrates used as examples in this note. We have achieved controlled syntheses with a variety of capped and non-capped metal frameworks. Capped substrates follow the pathway outlined in Scheme 1 but non-capped substrates normally follow an aggregation pathway. These syntheses will be reported in detail elsewhere.

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† Satisfactory analyses and spectral data were obtained for the new compounds.