Pathways for Reduction of Nickelocene under CO[1]

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Cyclic voltammetry under CO has been used to show that the short-lived nickelocene anion splits into NiCp and Cp$^-$ (Cp = C$_5$H$_5$) fragments; trapping of the NiCp moiety with CO leads to [Ni(CO)Cp]$^-$, which under high CO pressure loses a further Cp$^-$ to give Ni(CO)$_4$.

The metallocenes [MCp$_2$] (Cp = C$_5$H$_5$) have, since their discovery, attracted attention from electrochemists owing to their ability to accommodate a wide range of valence electrons.[2—4] The known extreme cases are the vanadocene dication [VCp$_2$]$^{2+}$ and the nickelocene anion [NiCp$_2$]$^-$, which formally have 13 and 21 valence electrons respectively.[5] Initial reports of the reduction of nickelocene by Gubin *et al.*[6] were later clarified by Holloway and Geiger[7] who demonstrated the existence of [NiCp$_2$]$^-$ at low temperatures. We now report the use of electrochemical techniques under CO to study the chemistry of the nickelocene anion and to synthesise other Cp–nickel complexes.†

Cyclic voltammetry (c.v.) on C or Pt electrodes in THF showed that nickelocene undergoes one reduction and two oxidation processes at −1.92, +0.10, and +0.98 V *vs.* S.C.E. respectively with all three peaks being of approximately the same size. At room temperature the first oxidation peak was reversible and the second irreversible for scan rates of 0.2 V s^{-1}; it has been shown that at low temperatures both oxidation steps are reversible and involve one electron.[8] The reduction step was irreversible at 0.2 V s^{-1}. Coulometry at −2.1 V under conditions made as anhydrous as possible‡ confirmed that the reduction was monoelectroi (observed values between 1—1.2 F/mol, three trials). After electrolysis, c.v. of the solution showed an anodic wave at −0.25 V, corresponding to oxidation of the cyclopentadienide anion,[9] of approximately the same peak height as the peak due to the original reduction of nickelocene. This indicates the mechanism in equation (1) for the reduction of nickelocene.

$$[NiCp_2] \xrightarrow[-1.92 \text{ V}]{1e^-} [NiCp_2]^- \longrightarrow NiCp + Cp^- \quad (1)$$
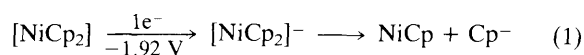
The nickelocene anion rapidly loses a cyclopentadienide anion giving the half-sandwich NiCp fragment probably stabilised by co-ordination of THF molecules. Formation of the NiCp moiety is strongly implicated in the many ligand exchange reactions which are characteristic of nickelocene,[10,11] and indeed nickelocene has been used as a reagent for incorporating the NiCp fragment into metal cluster complexes.[12,13] The cationic [NiCp]$^+$ species has been isolated;[14] an oxidation peak observed by c.v. after electrolysis at +0.56 V may correspond to the process [NiCp] $\rightleftarrows$ [NiCp]$^+$. Similarly, reductions of substituted ferrocenes are known to give the isoleptic [Fe(η-C$_5$H$_4$COMe)] half-sandwich complexes.[15]
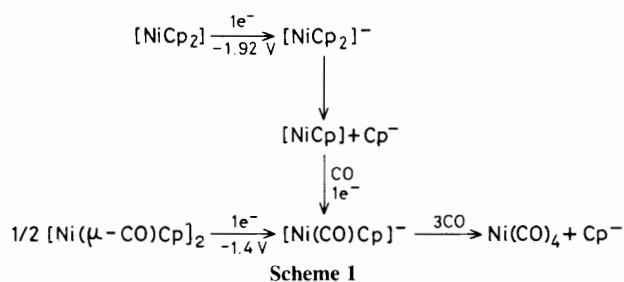
Addition of phenol as a proton source to a THF solution of nickelocene caused the reduction peak to increase in size, becoming equivalent to two electrons, but no anodic peaks were observed in the return scan. Controlled potential electrolysis of nickelocene in the presence of an excess of phenol consumed two electrons per mol and gave a dark red solution of [Ni(η^3-C$_5$H$_7$)Cp] identified by comparison of its i.r. and n.m.r. spectra with reported data.[16] In this case we propose that an ECE mechanism takes place in which H$^+$ attacks the electrogenerated nickelocene anion.

We have observed that decomposition of reduction products does not produce metallic nickel either in the presence or absence of a proton source. In no case in the presence of an excess of buta-1,3-diene was cyclotrimerisation observed indicating that ligand-free nickel(0) species were not formed.[17,18]

In an attempt to trap the transient NiCp fragment, c.v. and controlled potential electrolyses of nickelocene were performed under different pressures of CO gas. Under 1.5 atm CO, the reduction peak of nickelocene increased in height to correspond to two electrons whilst remaining at the same potential, indicating an ECE mechanism. The return scan showed two anodic peaks at −0.60 and −0.25 V. The size of the former peak increased with the CO pressure, reaching a maximum at 1.75 atm CO, and thereafter diminishing. Under

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$$[NiCp_2] \xrightarrow[-1.92\ V]{1e^-} [NiCp_2]^-$$

$$\downarrow$$

$$[NiCp] + Cp^-$$

$$\downarrow \begin{array}{c} CO \\ 1e^- \end{array}$$

$$1/2\ [Ni(\mu-CO)Cp]_2 \xrightarrow[-1.4\ V]{1e^-} [Ni(CO)Cp]^- \xrightarrow{3CO} Ni(CO)_4 + Cp^-$$

Scheme 1

3 atm CO, the only peaks observed were the bielectronic reduction wave of nickelocene and the oxidation peak of the cyclopentadienide anion. The increased size of the peak due to Cp^- suggested that both Cp ligands were now being lost.

C.v. of $[\{Ni(\mu-CO)Cp\}_2]$ showed one bielectronic reduction wave at -1.38 V and re-oxidation to the dimer at -0.60 V, confirming that the anodic peak seen in the cyclic voltammogram of $NiCp_2$ under CO was due to the oxidation of $[Ni(CO)Cp]^-$. Under 3 atm CO, the cyclic voltammogram of $[\{Ni(\mu-CO)Cp\}_2]$ revealed the presence of the cyclopentadienide anion, but the anodic peak due to $[Ni(CO)Cp]^-$ was absent, proving that this species is unstable under moderate CO pressures. Controlled potential electrolysis of nickelocene on a Hg or Pt working electrode under 3 atm CO required 2 electrons per $NiCp_2$ molecule as measured by coulometry. The only product isolated showed a single, strong i.r. absorption at 2040 cm^{-1} in THF solution, identical to that of an authentic sample of $Ni(CO)_4$.

These observations are summarised in Scheme 1. Under low CO pressure, the nickelocene anion loses a Cp^- ligand and co-ordinates a CO molecule to give $[Ni(CO)Cp]$ which is immediately reduced at the electrode. When the CO pressure is increased, the $[Ni(CO)Cp]^-$ anion is unstable, losing a further Cp^- to give $Ni(CO)_4$.

These reactions demonstrate how the use of c.v. and controlled potential electrolysis under gases widens the scope of these techniques both for analytical and synthetic purposes.

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