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THE ELECTROCHEMICAL REDUCTION OF SOME SUBSTITUTED π-CYCLOPENTADIENYLNICKEL(II) COMPLEXES

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Summary

The electrochemical reduction of the complexes $[CpNi(PR_3)_2]^+$, where R = C_2H_5, C_3H_7, C_4H_9 or C_6H_5, $[CpNi(diphos)]^+$ and $[CpNi(diars)]^+$ in acetonitrile is described and the data are compared with those for the complexes Cp_2Ni, $[Ni(PR_3)_4]^{2+}$ and $Ni(diphos)_2^{2+}$.

In recent years there has been an increasing interest in the chemistry of nickel(I), for example its role as a catalyst in organic reactions (for review see ref. 1). In particular, it has been shown that, in aprotic media, a wide variety of ligands are able to stabilise (in both a thermodynamic and kinetic sense) this lower oxidation state of nickel. This paper describes the reductive electrochemistry of the complexes $[CpNi(PR_3)_2]^+$, where R = C_2H_5, C_3H_7, C_4H_9 and C_6H_5, $[CpNi(diphos)]^+$ and $[CpNi(diars)]^+$ in acetonitrile and compares the data with that for nickelocene [2,3] and the nickel phosphine complexes $[Ni(PR_3)_4]^{2+}$ and $Ni(diphos)_2]^{2+}$ [4,5].

Experimental

The acetonitrile (Fisons Ltd. HPLC grade), methylene dichloride (Koch Light Ltd) and dimethylformamide (Hopkin and Williams Ltd) were each purified by distillation from calcium hydride. The base electrolyte was prepared by double decomposition from concentrated hot aqueous solutions of tetrabutylammonium bisulphate (Labkemi AB) and sodium tetrafluoroborate and recrystallised from ethanol/water. The complexes were either prepared in the laboratory or were gifts from Dr. W. Levason of our Department; in any case the corresponding bromide was made using a literature procedure [6] and the tetrafluoroborate

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or hexafluorophosphate salts were prepared by adding a saturated aqueous solution of sodium tetrafluoroborate or hexafluorophosphate to a saturated ethanolic solution of the bromide; the electrochemistry of tetrafluoroborate and hexafluorophosphate salts were identical. The structures of the complexes were checked by NMR and IR spectroscopy. Prior to electrochemical experiments, the electrolyte solutions were deaerated with a stream of O_2-free nitrogen (BOC Ltd).

The electrochemical measurements were taken with a Hi-Tek Instruments potentiostat DT 2101 and function generator PPR1 and recorded with a Hewlett Packard 7015 X-Y recorder. Charges were measured with a laboratory built integrator. Cyclic voltammetry was carried out using a three-electrode, two-compartment cell; the Pt wire working electrode and Pt helix counter electrode were in the same compartment but the Ag/10^{-2} *M* $AgNO_3$ reference electrode was separated from the working electrode by a Luggin capillary and glass sinter. The coulometry used a three-compartment tube cell. The working and counter electrodes were 2.6 cm diameter Pt gauzes separated by a glass sinter, 3.5 cm diameter. The reference electrode was again separated from the working electrode by a Luggin capillary and glass sinter. The catholyte volume was 20 cm^3.

Results and discussion

Cyclic voltammograms were run for each of the six nickel(II) complexes (concentration 1—2 m*M*) at a Pt electrode in acetonitrile containing tetrabutylammonium tetrafluoroborate (0.1 *M*) and at potential scan rates between 0.02

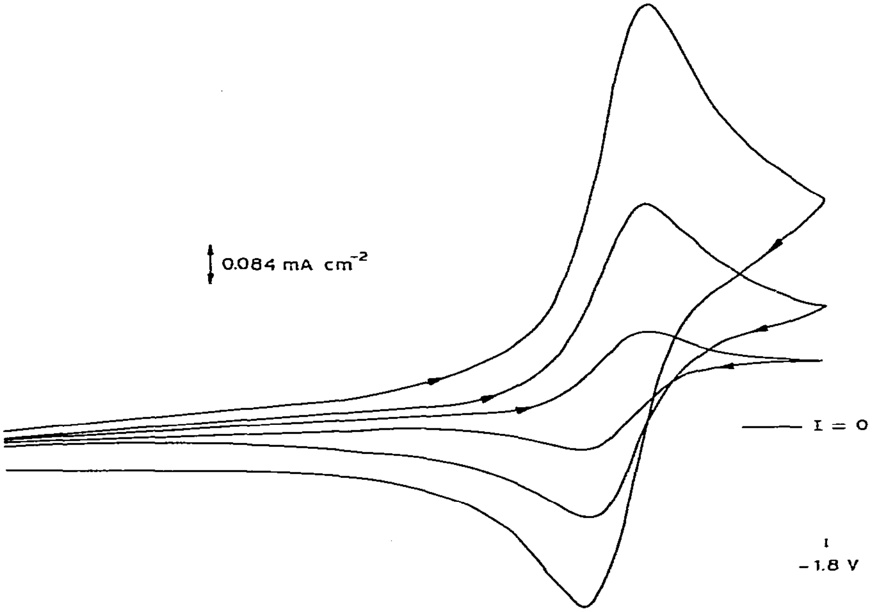

Fig. 1. Cyclic voltammograms of $[CpNi(P(C_3H_7)_3)_2]^+$ in acetonitrile containing tetrabutylammonium tetrafluoroborate. Pt electrode: complex concentration 1.43 m*M*, potential scan rates: 0.02; 0.12 and 0.45 V s^{-1}.

TABLE 1

CYCLIC VOLTAMMETRIC DATA FOR THE NICKEL(II) COMPLEXES IN CH_3CN CONTAINING $(C_4H_9)_4NBF_4$ (0.1 *M*). Pt ELECTRODE.

Complex	$-E^{\ominus}$(V vs. Ag/Ag$^+$)	ΔE_p (mV)	I_p^A/I_p^C	10^5 D (cm^2 s^{-1})
$[CpNi(P(C_2H_5)_3)_2]^+$	1.73	60	1.0	1.7
$[CpNi(P(C_3H_7)_3)_2]^+$	1.74	65	1.0	1.1
$[CpNi(P(C_4H_9)_3)_2]^+$	1.76	65	1.0	1.2
$[CpNi(P(C_6H_5)_3)_2]^+$	1.37	60	0.57 [a]	1.2
$[CpNi((C_6H_5)_2PCH_2)_2]^+$	1.61	70	1.0	1.6
$[CpNi((C_6H_5)_2AsCH_2)_2]^+$	1.60	70	1.0	1.3

[a] Measured at 0.24 V s^{-1}.

and 0.45 V s^{-1}. In every case a single reduction process was observed and Fig. 1 shows a typical set of voltammograms; quantitative data taken from the current-potential curves are reported in Table 1. With the exception of the triphenylphosphine complex, the characteristics of the voltammograms are those for a fast, single electron transfer process leading to a nickel(I) species stable on the timescale of the experiments (1—100 s), i.e. the electrode processes are reversible. Hence the formal electrode potentials may be taken directly from the curves and the current functions, $I_p/v^{1/2}$, which are independent of the potential scan rate, may be used to estimate the diffusion coefficients [7]. The voltammograms for the triphenylphosphine complex differ slightly in that the peak current ratio I_p^A/I_p^C is less than one and is a function of the potential scan rate; it must be concluded that the species $[CpNi(P(C_6H_5)_3)_2]$ undergoes a chemical reaction and its half life may be calculated to be 2.5 s^{-1} using the dimensionless plots of Nicholson and Shain [7]. The reasons why this nickel(I) species is less stable than the other phosphine analogues is not yet clear.

The reactions were also studied by controlled potential electrolysis. During several reductions of the tributylphosphine complex (concentration 1—10 m*M*) in acetonitrile at —1.95 V, the current was monitored as a function of charge passed and the data was extrapolated to zero current to show that 1.1 ± 0.1 F/mol of complex is consumed in the complete reduction. Cyclic voltammograms were also run periodically during the electrolysis; the reduction peak at —1.79 V and its coupled anodic peak at —1.73 V both decrease linearly with charge passed and no other peaks could be detected in the potential range 0 to —2.0 V. It is therefore clear that on the timescale of the electrolyses (30 min) the nickel(I) species, $[CpNi(P(C_4H_9)_3)_2]$, is not stable and decomposes to an electroinactive product. The electrolysis is also accompanied by a colour change, initially from colourless to green, but by the end of the electrolysis the catholyte is brown. The coulometry for the diphos complex also confirmed that the electrode reaction involved a single electron, $n = 1.0 \pm 0.1$ F/mol, but the cyclic voltammograms during the electrolysis showed that the nickel(I) species, $[CpNi((C_6H_5)_2PCH_2)_2]$, has some stability. Hence the stabilities of the nickel(I) species would appear to be

$$(C_6H_5)_3P < (C_4H_9)_3P < (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$$

At the low concentrations used in these electrolyses, it is not possible to determine the final products and the only study [8] in the literature of a related process is that of the reduction of the complexes [$Ni(PR_3)_2(CN)_2$]. The product there was reported to be the dimeric species [$Ni(PR_3)_2CN$]$_2$.

Cyclic voltammograms were also run for the complexes [$CpNi(P(C_4H_9)_3)_2$]$^+$ and [$CpNi((C_6H_5)_2PCH_2)_2$]$^+$ in two other aprotic solvents, dimethylformamide and methylene dichloride. In dimethylformamide the behaviour of the complexes is essentially similar to that in acetonitrile but in methylene dichloride the current-potential responses showed the nickel(I) intermediates to be very much less stable. Indeed, the reduction of the tributylphosphine complex was completely irreversible even at 0.45 V s^{-1} while the voltammogram for the diphos complex only showed the anodic peak for the $Ni^I \rightarrow Ni^{II}$ process at the faster scan rates. It was considered likely that the cyclopentadienyl ring is protonated by the methylene dichloride, a solvent which is likely to be a stronger proton donor than either acetonitrile or dimethylformamide.

A comparison of the reduction of these nickel(II) complexes with that of the nickel(II) complexes of cyclopentadiene and the phosphine ligands alone was also of interest. It is well known [2,3,9] that nickelocene is readily oxidised to the nickelocinium ion and, indeed, a reversible oxidation was observed, $E^0 = -0.35$ V vs the Ag/10^{-2} M Ag^+ reference electrode; of more interest to this study was a reduction peak at −2.23 V. This reduction is, however, totally irreversible and it appears that unlike the cobalt analogue [10,11], the nickelocene anion has no stability; by analogy with the chemical reduction with sodium amalgam, the product is likely to be $CpNiC_5H_7$ [12,13]. The cyclic voltammograms for the phosphine complexes show that reduction occurs in two, reversible, one-electron steps. For the complex, $Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2^{2+}$ the formed potentials of the Ni^{II}/Ni^I and Ni^I/Ni^0 couples are −0.65 V and −0.85 V vs the Ag/10^{-2} M Ag^+ electrode, respectively. The corresponding values for the complex $Ni(P(C_4H_9)_3)_4^{2+}$ are −0.90 V and −1.48 V. The data for both complexes compare well with that reported by Bontempelli et al. [5].

Hence it may be seen that the stability of the various oxidation states of nickel is quite different in the three types of complex. With two cyclopentadienyl ligands, the nickel(II) is reduced only with great difficulty, i.e. at very negative potentials, and neither the Ni^I or Ni^0 oxidation states have any stability. On the other hand, with only phosphine ligands, Ni^{II}, Ni^I and Ni^0 can all be stable and the lower oxidation states are formed at quite low negative potentials; nickel(I) is, however, only stable in a narrow potential range and, in solution, will have some tendency to disproportionation ($\log K = -3.33$ for the diphos complex). The complexes [$CpNiP_2$]$^+$ are more difficult to reduce but the resulting nickel(I) complexes have some chemical stability and appear not to be reduced further even at very negative potentials. Thus their behaviour is akin to that of the complexes of nickel(II) with macrocyclic, tetradentate ligands [14—17].

The relative values for the formal potentials reported in Table 1 would suggest that delocalisation of the extra electron into the phosphine ligands is an important mechanism for stabilising the nickel(I) oxidation state in the complexes [$CpNiP_2$]. The Ni^{II}/Ni^I potential is most positive with the triphenylphosphine ligands having empty π^* orbitals and most negative with the aliphatic phosphenes where delocalisation can only occur to the empty d-orbitals on the phosphorus atoms.

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