Reaction of Electrogenerated Square-planar Nickel(I) Complexes with Alkyl Halides

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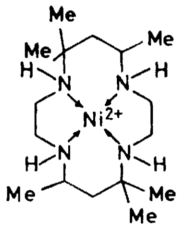
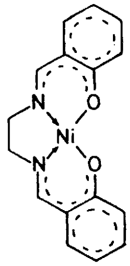
The electrochemical reduction of the complexes, [*NN'*-ethylenebis(salicylideneiminato)]nickel(II), [NiL^2], and (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II), [NiL^1]$^{2+}$, to the corresponding nickel(I) complexes at a platinum cathode in acetonitrile has been studied. The nickel(I) complexes react rapidly with alkyl bromides and alkyl iodides and, with the exception of the [NiL^1]$^{2+}$–primary alkyl bromide systems, the reaction leads to an alkyl radical and regeneration of the nickel(II) complex. Hence in most cases the electrolysis of alkyl halides in the presence of catalytic quantities of the nickel complexes leads to their complete reduction. It is proposed that the chemical reaction involves an organonickel species and that the overall behaviour of the systems is determined by the lifetime of the nickel–carbon bond.

MANY organometallic species are reagents for organic synthesis. Although it is often necessary to prepare the organometallic intermediate in the correct oxidation state, there have been surprisingly few attempts to couple the electrochemical generation of the reactive intermediate with a synthetic reaction.[1] Hence, as a part of a more general study of the role of co-ordination compounds and organometallic species as intermediates in electrosynthetic reactions, this paper reports a study of the cathodic reduction of two square-planar nickel complexes, [NiL^1]$^{2+}$ and [NiL^2], with macrocyclic quadridentate ligands at a platinum electrode in acetonitrile and the reaction of the resulting nickel(I) complex with alkyl bromide and iodides.



[NiL^1]$^{2+}$



[NiL^2]

These systems were chosen for study because such complexes are non-labile and the ligands stabilise the nickel(I) oxidation state while leaving co-ordination sites free for formation of octahedral intermediates during reactions with electrophiles. The chemistry [2-4] and electrochemistry [5,6] of the analogous cobalt complexes have been widely studied and it has been shown that the cobalt(I) complexes have strong nucleophilic properties and that a stable cobalt–carbon bond commonly results from the reactions with electrophiles.[7] The nickel complexes have not received the same attention, although the cathodic reduction of similar macrocyclic square-planar nickel(II) complexes and the spectroscopic characterisation of the nickel(I) products have been reported; [8-10] it is to be expected that the nickel(I) complexes react rapidly with alkyl halides, although without formation of a stable nickel–carbon bond. Hence, provided the NiL entity remains intact throughout the reaction sequence, the complex would have the role of a catalyst in the reduction of alkyl

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halides to radicals and/or carbanions. The direct reduction of alkyl halides is commonly highly irreversible and it will be shown that these reactions only occur at much more negative potentials than the potential of the Ni^{II}–Ni^{I} couples. A platinum cathode was employed in this study to minimise the interaction of the electrode with radical intermediates.

RESULTS

The Reduction of the $[Ni^{II}L]$ *Complexes.*—Cyclic voltammograms run at a series of potential scan rates between 0.03 and 0.3 V s^{-1} at a platinum electrode in MeCN–$[NBu_4][BF_4]$ (0.2 mol dm^{-3}) show that both complexes underwent a reversible one-electron reduction to a stable product and that no further reduction occurred within the potential range of the medium. Data taken from these cyclic voltammograms are reported in Table 1.

TABLE 1

	Cyclic voltammetry				Coulometry [a]	
Complex	$E^{\ominus}$ [b]	ΔE_p/mV	I_p^A/I_p^C	$I_p^C/v^{\frac{1}{2}}CS$ [c]	n	Colour change on reduction
$[NiL^2]$	1.88	60	1.0	0.98	0.93	Yellow to royal blue
$[NiL^1]^{2+}$	1.20	63	1.0	0.91	0.95	Yellow to dark green

[a] Potential 30 mV negative to E_p^C. [b] In V *versus* aqueous s.c.e. [c] In A dm^3 $s^{\frac{1}{2}}$ cm^{-2} $V^{-\frac{1}{2}}$ mol^{-1}.

Controlled-potential coulometry was carried out at potentials just beyond the reduction peak for solutions of each of the complexes. Linear plots of I against Q (charge) were obtained and extrapolation of these lines to $I = 0$ gave n values close to one electron per molecule. Furthermore, cyclic voltammetry carried out before, immediately after completion of the electrolysis, and after a period of 1 h (see Figure 1) showed that even on this time scale the electrode reactions were uncomplicated by chemical reactions and that the nickel(I) complexes were stable. Hence in this medium the electrode reactions are (1) and (2).

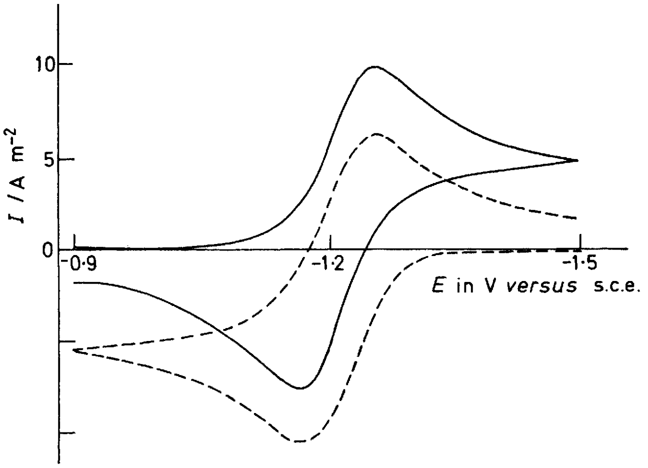


FIGURE 1 Cyclic voltammograms before (——) and 1 h after (— — —) the electrolysis of 5×10^{-3} mol dm^{-3} $[NiL^1]^{2+}$ in MeCN–$[NBu_4][BF_4]$

$$[Ni^{II}L^1]^{2+} + e^- \rightleftharpoons [Ni^{I}L^1]^+ \qquad (1)$$

$$[Ni^{II}L^2] + e^- \rightleftharpoons [Ni^{I}L^2]^- \qquad (2)$$

These reductions are characterised by strong colour changes (Table 1).

The electrochemistry is essentially the same in dimethylformamide (dmf) but the reversible potentials for the Ni^{II}–Ni^{I} couples are affected by ion-pairing phenomena in both solvents. For example, in MeCN–LiBr (0.2 mol dm^{-3}) the reversible potential for $[NiL^2]$–$[NiL^2]^-$ is shifted to -1.46 V.

The Electrochemistry of the Nickel(II) *Complexes in the Presence of Alkyl Halides.*—Cyclic voltammograms were run for a solution of the nickel(II) complexes (10^{-3} mol dm^{-3}) in MeCN–$[NBu_4][BF_4]$ and then following the stepwise addition of one of a series of alkyl halides so that its concentration increased from 10^{-3} to 10^{-1} mol dm^{-3}. None of the alkyl halides reduced directly at potentials less than -2.3 V and the alkyl bromides do not reduce at Pt prior to the negative potential limit.

One mode of behaviour is typified by the system $[NiL^1]^{2+}$–t-octyl bromide. On addition of low concentrations of t-octyl bromide the reduction process for $[NiL^1]^{2+}$ becomes completely irreversible and the reduction peak increases in height. On stepwise addition of t-$C_8H_{17}Br$ up to a concentration of 10^{-1} mol dm^{-3} the peak current for the process $[NiL^1]^{2+}$–$[NiL^1]^+$ continues to increase, and at a single sweep rate the peak current is proportional to the concentration of t-octyl bromide. Furthermore, even with a 100-fold excess of the alkyl halide the peak current is proportional to the square root of the potential scan rate, indicating that the electrode reaction is effectively diffusion-controlled with respect to the alkyl halide. These observations suggest a catalytic electrode process where the regeneration of the electroactive species $[NiL^1]^{2+}$ by a homogeneous chemical sequence is very rapid. No additional reductive process is observed on the addition of t-$C_8H_{17}Br$, but on sweeping to positive potentials peaks are observed for the oxidation of bromide to tribromide and bromine.

The results of such experiments with other alkyl bromides and alkyl iodides and with the complex $[NiL^2]$ are similar except that the increase in the height of the peak for the Ni^{II}–Ni^{I} reduction is less marked and in several cases the peak current is not proportional to the concentration of alkyl halide over the whole range (a plot of I_p against c_{RX} tends to a plateau); the disappearance of the reverse peak for the nickel(I) reoxidation always occurs completely at low concentrations of alkyl halide (Figure 2). Thus, while the reaction of alkyl halide with the nickel(I) complex is always fast (the $Ni^{I} \longrightarrow Ni^{II}$ peak is not observed), the regeneration of the nickel(II) complex by the chemical sequence is dependent on the alkyl halide [the increase in the peak current for the Ni^{II}–Ni^{I} reduction is a measure of the rate at which the nickel(II) complex is regenerated] and hence the reaction between the complex and alkyl halide is not a simple electron transfer. The data from these experiments are summarised in Table 2; the increase in peak current is reported for three concentrations of alkyl halide. There are no overall simple trends. For the $[NiL^1]^{2+}$ systems the peak current decreases in the order tertiary > secondary > primary, and in general the peak currents for this complex are higher than for $[NiL^2]$. For the latter the order is less clear, tertiary > secondary ≈ primary. Only tertiary chlorides reacted significantly with $[NiL^1]^{2+}$ on the time scale of cyclic voltammetry.

Controlled-potential electrolyses were carried out on solutions of both complexes in the presence of each of four octyl halides; the experiments employed several ratios of [RX] : [Ni^{II}L] and in each case I and Q were monitored during the electrolyses and the products were identified and determined after the current had decreased to <5% of its initial value. In general the plots of I against Q were non-linear but the data could be extrapolated to determine the number of electrons transferred per molecule of the nickel(II) complex, and for the ratio [RX] : [Ni^{II}L] = 10 : 1 this n value and the products are reported in Table 3. The current yields are similar to the organic yields reported in the Table.

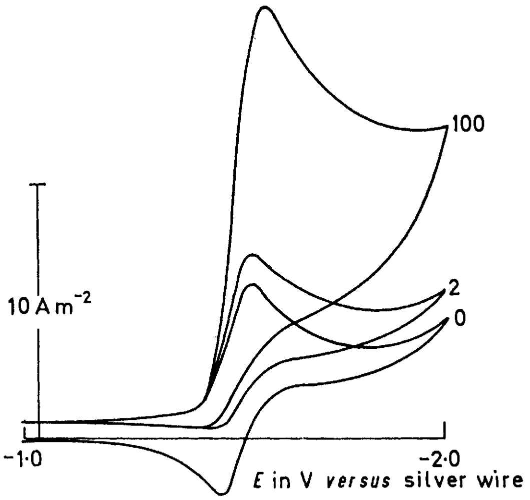


FIGURE 2 Cyclic voltammograms of 10^{-3} mol dm^{-3} [NiL^2] in MeCN–[NBu$_4$][BF$_4$] before and after the addition of n-octyl bromide. Potential sweep rate 0.3 V s^{-1}. The numbers on the curves indicate the concentration of the bromide in 10^{-3} mol dm^{-3}

TABLE 2

Ratios of peak currents after the addition of $x \times 10^{-3}$ mol dm^{-3} RX to peak current for 10^{-3} mol dm^{-3} complex before addition of RX. Potential scan rate 0.1 V s^{-1}, medium MeCN–[NBu$_4$][BF$_4$] (0.2 mol dm^{-3})

	[NiL^2]			[NiL^1]$^{2+}$		
RX	x = 10	50	100	10	50	100
n-$C_8H_{17}I$	4.1	5.6	7.3	3.0	7.0	
n-$C_8H_{17}Br$		2.3	3.9		1.4	2.0
$C_6H_{13}CH(Br)Me$	1.5	1.9	2.9		27	33
t-$C_8H_{17}Br$	4.2	5.2	7.9		50	84
n-C_4H_9Br	1.3	1.9	2.0			
$C_2H_5CH(Br)Me$	1.3	1.7	1.8	9	15	48
t-C_4H_9Br	4.6	8.7	9.4	11	51	87
Cyclohexyl bromide					6.0	8.0
PhBr	1.1	1.4		1.3		
t-C_4H_9Cl	1	1	1	1.13	1.44	1.53

With the exception of the [NiL^1]$^{2+}$–primary alkyl halide systems, the products are consistent with a free-radical intermediate determining the product distribution by reactions (3)—(5). In the case of the primary radical, dimerisation is

$$2R^\bullet \longrightarrow R{-}R \qquad (3)$$

$$2R^\bullet \longrightarrow RH + \text{olefin} \qquad (4)$$

$$R^\bullet + MeCN \longrightarrow RH + \dot{C}H_2CN \qquad (5)$$

the major route while with the tertiary radical disproportionation predominates. For the secondary radical all three reactions are of similar importance. In contrast, the products from the electrolysis of [NiL^1]$^{2+}$ and n-octyl bromide seem to be derived from a carbanion intermediate [equations (6) and (7)], while the products from the octyl iodide electrolysis probably arise from a mixture of radical and carbanion routes.

TABLE 3

Products from the controlled-potential reduction of the nickel(II) complexes in the presence of a 10-fold excess of alkyl halide. Medium MeCN–[NBu$_4$][BF$_4$]

	[NiL^2]		[NiL^1]$^{2+}$	
Substrate	Product (%) [a]	n [b]	Product (%) [a]	n [b]
n-$C_8H_{17}I$	n-$C_{16}H_{34}$ (72) n-C_8H_{18} (5) $C_6H_{13}CH{=}CH_2$ (2)	11	n-$C_{16}H_{34}$ (61) n-C_8H_{18} (29) $C_6H_{13}CH{=}CH_2$ (5) $C_9H_{19}CN$ (6)	5
n-$C_8H_{17}Br$	n-$C_{16}H_{34}$ (77) n-C_8H_{18} (4) $C_6H_{13}CH{=}CH_2$ (2)	12	n-$C_{16}H_{34}$ (8) n-C_8H_{18} (66) n-$C_9H_{19}CN$ (6)	2
$C_6H_{13}CH(Br)Me$	$C_{16}H_{34}$ (27) [c] n-C_8H_{18} (32) $C_6H_{13}CH{=}CH_2$ (7)	11	$C_{16}H_{34}$ (46) [c] n-C_8H_{18} (33) $C_6H_{13}CH{=}CH_2$ (11)	11
t-$C_8H_{17}Br$	$C_{16}H_{34}$ (9) [c] t-C_8H_{18} (28) $C_5H_{11}CMe{=}CH_2$ (20) $C_4H_9CH{=}CMe_2$ (6)	11	$C_{16}H_{34}$ (9) [c] t-C_8H_{18} (31) $C_5H_{11}CMe{=}CH_2$ (32) $C_4H_9CH{=}CMe_2$ (9)	11

[a] Based on octyl halide consumed. [b] In F mol^{-1}; when the current had decreased to 5% of its initial value (1 F ≈ 9.65×10^4 C). [c] Non-straight-chain hexadecanes (two or three isomers).

$$R^- + MeCN \longrightarrow RH + \bar{C}H_2CN \qquad (6)$$

$$\bar{C}H_2CN + RBr \longrightarrow RCH_2CN + Br^- \qquad (7)$$

It should also be noted that the coulometric results indicate two types of system and there is a good correlation with the type of intermediate determining the products. Most systems were totally catalytic, *i.e.* the electrolysis continued until all the alkyl halide was consumed, but with the [NiL^1]$^{2+}$–primary alkyl halide solutions the electrolyses terminated at low n values.

Similar experiments were carried out with [RX] : [Ni^{II}L] = 1 and 100 : 1. The products were completely insensitive to the excess of alkyl halide but the coulometric results were interesting. Although for solutions with equal concentrations of alkyl halide and nickel(II) complex n was always 2, the inorganic product varied. With the systems which gave radical products, the inorganic product was the same as that formed by reduction of the nickel(II) complex in the absence of alkyl halide. Hence the overall reactions are confirmed as (8) and (9), and effectively one electron is

$$[NiL^2] + RX + 2e^- \longrightarrow [Ni^IL^2]^- + R^\bullet + X^- \quad (8)$$

$$[NiL^1]^{2+} + RX + 2e^- \longrightarrow [Ni^IL^1]^+ + R^\bullet + X^- \quad (9)$$

consumed in the reduction of the alkyl halide. For the [NiL^1]$^{2+}$–n-$C_8H_{17}Br$ system the catholyte at the termination of the electrolysis was not the colour of the square-planar nickel(I) complex, and since the formation of a carbanion requires two electrons per mol of alkyl halide the metal must be in the form of a nickel(II) complex. Furthermore, since the electrolysis terminates at this stage this complex is electroinactive.

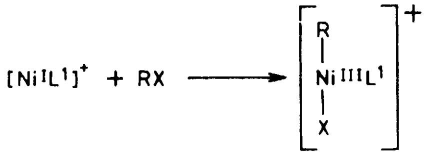
The electrolyses with a 100-fold excess of alkyl halide showed that with the secondary and tertiary alkyl halides and the [NiL^2]–primary alkyl halide systems the electrolyses could still be continued until all the alkyl halide was consumed. The $[NiL^1]^{2+}$–n-$C_8H_{17}Br$ electrolysis terminated at $n = 2$.

DISCUSSION

It can be seen that the presence of these nickel(II) complexes in the electrolysis medium completely modifies the cathodic reduction of alkyl halides. The reductions occur at considerably less negative potentials than in solutions containing the alkyl halide alone and involve nickel(I) intermediates. Alkyl iodides and secondary and tertiary alkyl bromides are completely reduced with only trace quantities of the complexes. This is also the case with the primary bromide with $[NiL^2]$. Furthermore, it is clear from the product distribution and the coulometry that alkyl radicals are being formed selectively, and later papers will discuss attempts to use these intermediates in syntheses by carrying out the electrolyses in the presence of molecules which react with free radicals. With the $[NiL^1]^{2+}$–n-alkyl bromide systems the reduction occurs at the same potential but the electrolyses terminate at low n values, and the peak current for the Ni^{II}–Ni^{I} reduction on a cyclic voltammogram only doubles on addition of the n-alkyl bromide; the products indicate a carbanion intermediate. Hence the reaction mechanisms must be substantially different.

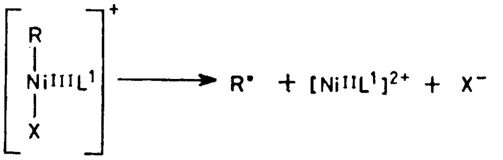
With all the alkyl bromides and iodides, however, a rapid reaction occurs with the nickel(I) complex. In view of the large difference in the reduction potentials between the complexes $[NiL^2]$ (−1.88 V) and $[NiL^1]^{2+}$ (−1.20 V) and those reported for similar alkyl bromides [*e.g.* at Hg: n-C_4H_9Br, −2.23 V; i-C_4H_9Br, −2.32 V; and t-C_4H_9Br, −2.19 V],[11] the reaction is unlikely to be a simple electron transfer; Lund and his co-workers,[12] studying the catalytic reduction of alkyl halides using aromatic hydrocarbon anion radicals as the electron-transfer mediator, have shown that homogeneous electron transfer only occurs at a significant rate when the difference in the reduction potentials of the aromatic hydrocarbon and the alkyl halide is less than 400 mV. Moreover, it should be noted that with secondary and tertiary alkyl bromides the catalytic current is higher for $[NiL^1]^{2+}$ than with $[NiL^2]$ and this is also contrary to expectation for a simple electron-transfer mechanism. Hence it seems that the reaction involves nucleophilic attack by the nickel(I) complex on the alkyl halide with the formation of a nickel–carbon bond.

For $[NiL^1]^{2+}$ this reaction may be written as in (10), and it is proposed that it is the lifetime of the intermediate formed which determines the products.



$$[Ni^{I}L^1]^+ + RX \longrightarrow \left[\begin{matrix}R\\ |\\ Ni^{III}L^1\\ |\\ X\end{matrix}\right]^+ \qquad (10)$$

With the secondary and tertiary alkyl bromides this intermediate is unstable and the nickel–carbon bond cleaves rapidly to give the radical and regenerate the electroactive complex, and hence a catalytic current is observed.

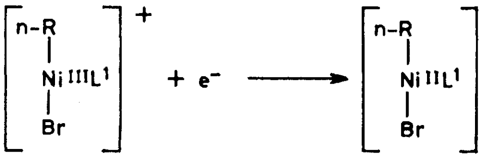


$$\left[\begin{matrix}R\\ |\\ Ni^{III}L^1\\ |\\ X\end{matrix}\right]^+ \longrightarrow R^{\bullet} + [Ni^{II}L^1]^{2+} + X^- \qquad (11)$$

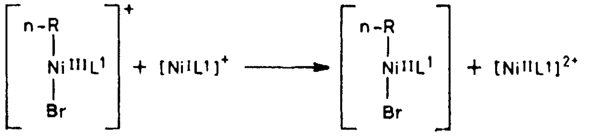
In the presence of a high concentration of halide ion the equilibrium (12) must also be considered, but the electrolyses in the presence of large ratio of

$$[Ni^{II}L^1]^{2+} + 2X^- \rightleftharpoons [Ni^{II}L^1X_2] \qquad (12)$$

[RBr] : $[NiL^1]^{2+}$ indicate that it is of minor importance on the time scale of these electrolyses (30 min). With n-$C_8H_{17}Br$ it is suggested that the Ni–C bonded intermediate has a sufficient lifetime to undergo reduction at the electrode or in solution, *i.e.* as in (13) or (14), before the spontaneous cleavage to a radical can occur.

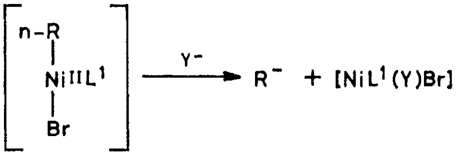


$$\left[\begin{matrix}n\text{-}R\\ |\\ Ni^{III}L^1\\ |\\ Br\end{matrix}\right]^+ + e^- \longrightarrow \left[\begin{matrix}n\text{-}R\\ |\\ Ni^{II}L^1\\ |\\ Br\end{matrix}\right] \qquad (13)$$



$$\left[\begin{matrix}n\text{-}R\\ |\\ Ni^{III}L^1\\ |\\ Br\end{matrix}\right]^+ + [Ni^{I}L^1]^+ \longrightarrow \left[\begin{matrix}n\text{-}R\\ |\\ Ni^{II}L^1\\ |\\ Br\end{matrix}\right] + [Ni^{II}L^1]^{2+} \qquad (14)$$

Since the reaction is not catalytic the decomposition of this reduced organonickel species must lead to a complex which is electroinactive, and although the exact nature of this species was not ascertained it is probably an octahedral nickel(II) complex [equation (15)].



$$\left[\begin{matrix}n\text{-}R\\ |\\ Ni^{II}L^1\\ |\\ Br\end{matrix}\right] \xrightarrow{Y^-} R^- + [NiL^1(Y)Br] \qquad (15)$$

Certainly the cyclic voltammetry has the characteristics for such an e.c.e. process (a reaction where two electron transfers are separated by a homogeneous chemical reaction). The Ni^{I}–Ni^{II} oxidation peak on the reverse sweep disappears on addition of low concentrations of n-$C_8H_{17}Br$, while the peak current for the Ni^{II}–Ni^{I} reduction almost doubles but does not increase further on addition of more n-octyl bromide. The results with n-$C_8H_{17}I$ are different from those with the bromide and seem to represent the intermediate

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situation where both mechanisms, the catalytic and e.c.e. mechanisms, are competing. It is because of the differences between bromide and iodide (there was no evidence of oxidation of the iodide by Ni^{III} to give iodine) that the organonickel(III) species is written as an octahedral complex with the halide in the *trans* position to the alkyl group, rather than as a five-co-ordinate complex as in the analogous cobalt(III) species. The results indicate that the Ni–C bond is weaker in the iodo-complex and hence there is competition between (*a*) spontaneous cleavage to give a radical in a catalytic reaction, and (*b*) reduction to carbanion and the formation of electro-inactive Ni^{II}.

The mechanisms for the reactions with $[NiL^2]$ are similar but the results with the n-octyl halides indicate that $[NiL^2]^-$ is a weaker nucleophile and the Ni–C bond is weaker with this ligand than in the macrocycle L^1. All the alkyl halides which react do so entirely by the catalytic route.

These differences between the two nickel complexes and the clear differences between the nickel and corresponding cobalt complexes indicate the possibilities for designing systems which are both catalytic and lead selectively to radical or carbanion by suitable choice of the metal centre and the ligand(s). Indeed, for these square-planar macrocycles, Lovecchio *et al.*[10] have discussed the effects of changing the structure of the ligand on certain reactions of the nickel(I) complexes. Finally, it should be stressed that the activation of the alkyl halide occurs in homogeneous solution away from the electrode and hence the subsequent reactions of the radical and carbanion intermediates are not complicated by the formation of bonds with the metal of the electrode and which lead to further alternative reaction paths and products (*e.g.* as in the recently discussed reduction of decyl halides at mercury).[13]

EXPERIMENTAL

All the electrochemical experiments were carried out using Chemical Electronics valve or transistorised potentiostats and a type RB1 function generator. Curves of *I* against *E* were recorded on a Bryans series 26000 *x–y* recorder, and the coulometric experiments employed an electronic integrator with a digital display built in these laboratories. The cells for cyclic voltammetry had two compartments: the platinum-wire working electrode was surrounded by a helical platinum-wire counter electrode in the same solution, but the reference electrode was placed in a second compartment separated by a tap and a Luggin capillary mounted on a syringe barrel for easy adjustment of the tip of this capillary with respect to the working electrode. The controlled-potential electrolyses used three compartment cells. The platinum-gauze working electrode (area 1—2 cm^2) was in a compartment which required *ca.* 20 cm^3 of solution and was separated by a no. 3 glass sinter from a platinum-gauze secondary electrode; the reference electrode was mounted in the same way as in the cyclic-voltammetry cell. All the potentials in this paper are quoted *versus* the aqueous saturated calomel electrode (s.c.e.), but in some experiments a silver wire was, in fact, used as the reference electrode. All the solutions were deoxygenated with oxygen-free N_2 prior to experiments, and N_2 was used to stir the electrolysis solutions during coulometry and preparative experiments.

At the end of controlled-potential electrolyses the catholyte was poured into a large excess of salt water and the resulting solution was extracted with diethyl ether. The ether extract was dried and reduced to a small volume. Analysis was carried out on a Pye 104 gas–liquid chromatograph with a 10% silicone oil on Celite column, and using an appropriate temperature programme. The products were analysed by comparison of retention times and mass spectra with authentic samples, the spectra being obtained on an MS 12 mass spectrometer equipped with an inlet from the Pye 104. Nonane was added prior to the start of an electrolysis and was used as an internal standard for the quantitative analysis; recovery was always >70%. A liquid-nitrogen trap was used to recover products escaping from the cell during the electrolysis.

Acetonitrile (Cambrian Chemicals) was purified by successive distillation from NaH, P_4O_{10}, and CaH_2. The electrolyte was prepared from tetrabutylammonium hydrogensulphate (Lab. Kemi AB) and sodium tetrafluoroborate (B.D.H.). The alkyl halides were obtained from B.D.H., except for 1-methylheptyl bromide which was prepared[14] from octan-2-ol (B.D.H.) and t-octyl bromide prepared by stirring the corresponding alcohol (Koch–Light) with 48% HBr and a trace amount of H_2SO_4 for 24 h.

The complex [*NN'*-ethylenebis(salicylideneiminato)]-nickel(II), $[NiL^2]$, was prepared by adding the ligand (Strem Chem. Inc.) in warm ethanol to aqueous nickel(II) acetate (B.D.H.). The red crystals were recrystallised from ethanol (Found: C, 58.85; H, 4.40; N, 8.50. Calc. for $C_{16}H_{14}N_2NiO_2$: C, 59.1; H, 4.35; N, 8.60%). (5,5,7,-12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane)-nickel(II) perchlorate, $[NiL^1][ClO_4]_2$, was prepared by the method of Curtis[15] from nickel(II) perchlorate (B.D.H.), ethylenediamine (May and Baker), and acetone (B.D.H.).

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