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The Chemistry of Electrogenerated Transition Metals Species - The Insertion of Olefins into a Nickel-Carbon Bond

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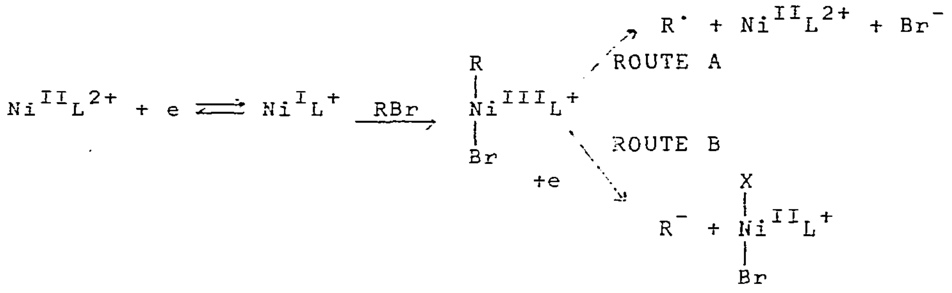
Summary

The nickel(1) complex, $Ni(teta)^+$, formed by cathodic reduction of the corresponding nickel(11) complex, reacts rapidly with alkyl bromides to form an unstable intermediate containing a nickel-carbon bond. When the electrolysis medium also contains an activated olefin an insertion reaction occurs. The new metal-carbon bond is cleaved by further reduction and overall the reduction of $Ni(teta)^{2+}$ in the presence of RBr and CH_2=CHY leads to high yields of RCH_2CH_2Y.

The electrochemical reduction in aprotic solvents of several square planar nickel(11) complexes with macrocyclic quadridentate ligands has been reported and shown to lead to the corresponding nickel(1) species[1,2,3,]. Recently, a study of the reaction between two electrogenerated nickel(1) complexes and a series of alkyl halides in acetonitrile was published[4]. The electrolysis products were all hydrocarbons but there was strong evidence for an unstable organometallic intermediate and the following mechanism was proposed.



SCHEME 1

Whether route A or route B is followed probably depends on the lifetime of the nickel-carbon bond which is determined by both the nature of the ligand, L, and the structure of the alkyl halide. It can be seen that route A leads to the regeneration of the electroactive nickel complex and hence the complex may be used for the catalysis of the cathodic reduction of the alkyl halide to a free radical. Route B again results in the formation of a nickel(ll) complex but it is not the original square planar complex but an electroinactive species. Therefore although the overall reaction leads to the formation of a carbanion from the alkyl halide it is not catalytic with respect of the complex.

This paper discusses the electrochemical reduction of $Ni(teta)^{2+}$ [(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) nickel (ll)] in acetonitrile (AN) containing tetrabutylammonium tetrafluroborate (0.1M), alkyl bromide and an activated olefin.

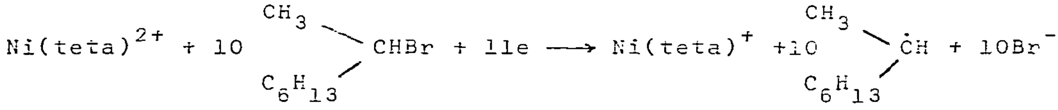
Results and Discussion

A series of electrochemical experiments were carried out with solutions containing various combinations of $Ni(teta)^{2+}$, 2-bromooctane and acrylonitrile in AN/Bu_4NBF_4 and a Pt cathode. The following observations were made (see also table I);

(a) cyclic voltammograms run at potential scan rates in the range 0.03-1.0V s^{-1} for solutions of the complex alone showed a reversible le reduction process at Ep = -1.20V vs SCE and coulometry confirms that the product of the electrode reaction is a stable species $Ni(teta)^{+}$.

(b) the I-E responses are unaffected by the addition to the solution of a large excess of acrylonitrile and hence it must be concluded that on a timescale of 100 s, no chemical reaction occurs between the nickel(1) complex and acrylonitrile. Furthermore, there is no evidence for cathodic reduction of acrylonitrile below -2.0V.

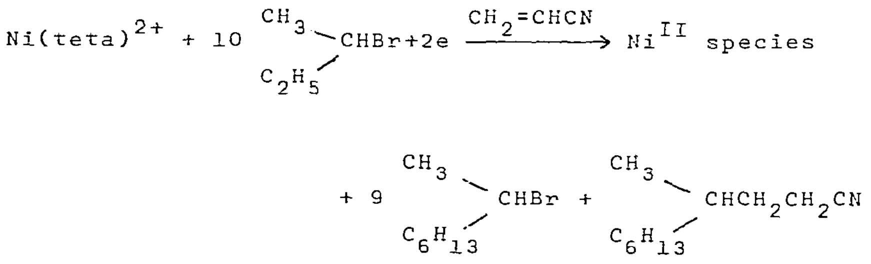
(c) on addition of small quantities of 2-bromooctane to a solution of $\mathrm{Ni(teta)}^{2+}$, the cyclic voltammograms change. The reduction peak for the Ni(11)/Ni(1) couple increases in height while the peak for the reverse process disappears. After adding more alkyl bromide the reduction peak continue to grow and when the ratio of 2-bromooctane to $\mathrm{Ni(teta)}^{2+}$ is 10:1 the peak current density is approximately eight times the height in the absence of alkyl bromide. Therefore it would seem that the $\mathrm{Ni(teta)}^{+}$ and the 2-bromooctane react together rapidly and the reaction regenerates the electroactive species, $\mathrm{Ni(teta)}^{2+}$. The catalytic nature of the electrode reaction is also indicated by the coulometry since the electrolysis continues until the passage of 11F/mol $\mathrm{Ni(teta)}^{2+}$ and all the 2-bromooctane has been consumed. Analysis of the catholyte at the termination of the electrolysis showed the presence of four hydrocarbons all of which are to be expected from a radical intermediate. Hence the overall reaction has the stoichiometry



$$\mathrm{Ni(teta)}^{2+} + 10\,\mathrm{CH_3(C_6H_{13})CHBr} + 11e \longrightarrow \mathrm{Ni(teta)}^{+} + 10\,\mathrm{CH_3(C_6H_{13})\dot{C}H} + 10\mathrm{Br}^{-} \quad (1)$$

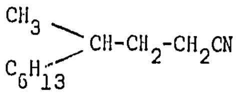
The 2-bromooctane itself is not electroactive before -2.3V.

(d) On monitoring the cyclic voltammetry during the stepwise addition of acrylonitrile to a solution of $\mathrm{Ni(teta)}^{2+}$ and a tenfold excess of 2-bromooctane, one observes a decrease in the peak current density for the catalytic Ni(11)/Ni(1) process until the peak current density is approximately twice the value in the absence of alkyl bromide; no further change occurs on the addition of more acrylonitrile. In these conditions the transfer of 2e/molecule $\mathrm{Ni(teta)}^{2+}$ is indicated and this is confirmed by coulometry. Moreover much of the 2-bromooctane is recovered



$$\mathrm{Ni(teta)}^{2+} + 10\,\mathrm{CH_3(C_2H_5)CHBr} + 2e \xrightarrow{\mathrm{CH_2{=}CHCN}} \mathrm{Ni}^{II}\ \text{species} + 9\,\mathrm{CH_3(C_6H_{13})CHBr} + \mathrm{CH_3(C_6H_{13})CHCH_2CH_2CN} \quad (2)$$

TABLE I

Solution in An/Bu_4NBF_4	Cyclic Voltammetry[a] I_p^{RED} (mA cm^{-2})	Reversible	Coulometry[c] F/mol $Ni(teta)^{2+}$	Products (current yield)
$Ni(teta)^{2+}$ (2mM)	0.56	Yes	1	$Ni(teta)^{+}$ only
$Ni(teta)^{2+}$ (2mM) + CH_2=CHCN (100 mM)	0.56	Yes	-	-
$Ni(teta)^{2+}$ (2mM) + $C_6H_{13}\underset{\underset{Br}{\vert}}{C}HCH_3$ (20 mM)[d]	4.45	No	11	$Ni(teta)^{+}$ + n-C_8H_{18} (33) +$C_{16}H_{34}$ (46)[b] + $C_6H_{13}CH{=}CH_2$ (11)
$Ni(teta)^{2+}$ (2mM)+$C_6H_{13}\underset{\underset{Br}{\vert}}{C}HCH_3$ (20 mM) + CH_2=CHCN (100 mM)	1.17	No	2	 $\begin{array}{l}CH_3\\ C_6H_{13}\end{array}\!>\!CH\text{-}CH_2\text{-}CH_2CN$ (88) + Ni^{II} Species

a. cyclic voltammograms run at 0.1V s^{-1}

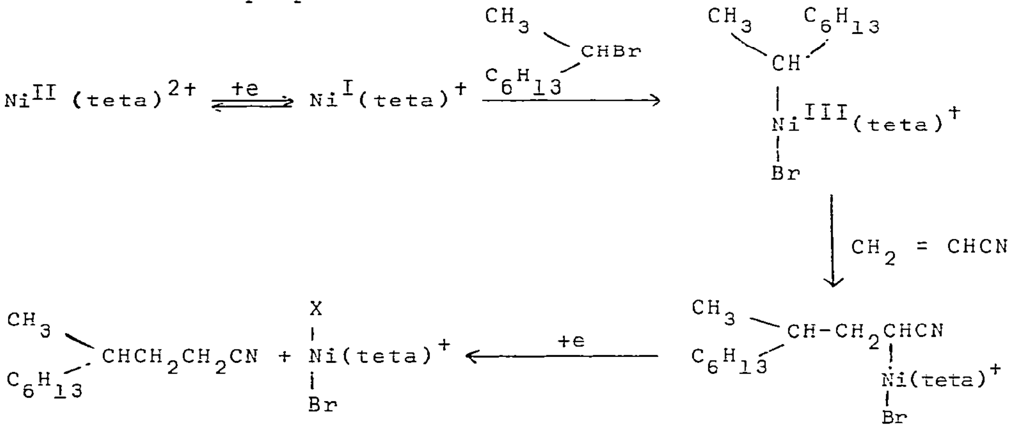
b. branch chain hexadecanes (2 isomers)

c. electrode potential -1.3V vs SCE

d. see ref 4.

unreduced and the only organic product is 4-methyldecanitrile. Indeed the overall reaction appears to have the stoichiometry and the final nickel species is not electroactive since the reaction does not continue further.

The cyclic voltammetry clearly shows that the acrylonitrile reacts not with the Ni(teta)$^+$ but with an intermediate formed during the reaction between Ni(teta)$^+$ and the alkyl bromide. Furthermore this intermediate cannot be the radical of reaction (1) since in the presence of acrylonitrile the reaction does not reform Ni(teta)$^{2+}$. Anyway the reaction of a free radical with acrylonitrile will not lead to single product in such high yield. Hence we would propose the mechanism



SCHEME 2

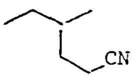
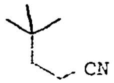
where the final step is analogous to route B of Scheme 1.

A series of experiments were then carried out to establish whether this reaction could be extended to other alkyl halides and to a range of olefins. First the experiments described above were repeated with primary, secondary and tertiary butyl bromide and acrylonitrile as the olefin. The results from the cyclic voltammetry on solutions containing the secondary and tertiary butyl bromide were in essence identical to those with secondary octyl bromide; while the increases in the peak current density for the Ni(11)/Ni(1) reduction on addition of alkyl bromides differed slightly, in both cases the peak current density decreased on the introduction of acrylonitrile to the catholyte and reached a limiting value of twice that for the solution containing only Ni(teta)$^{2+}$. On addition of primary butyl bromide to the solution of Ni(teta)$^{2+}$ the height of the Ni(11)/Ni(1) peak only doubles, however (route B of scheme 1 is followed), and hence the decrease after addition of acrylonitrile cannot be observed.

Controlled potential electrolyses were performed at -1.3V for solutions of each of the butyl bromides under conditions considered likely to give the best yields and conversion to product. The solutions employed contained complex (5mM), an equal concentration of butyl bromide but an excess of acrylonitrile (25 mM). In all electrolyses the coulometry showed that the current dropped to a negligible value after the passage of 2F/mol of Ni(teta)$^{2+}$. The products and their yields are reported in table II. It can be seen that the product is always a single hexyl cyanide and that the yield is good.

A second set of experiments always employed secondary butyl bromide but a range of olefins. Cyclic voltammograms were run during the stepwise addition of the olefins to a solution of the complex (1mM) and the secondary butyl bromide (10 mM) in AN/Bu$_4$NBF$_4$. At the beginning of these experiments a large catalytic peak is observed at the potential of the Ni(11)/Ni(1) couple; during the addition of olefin three types of behaviour were seen

TABLE II

Alkyl halide	Product	Current Yield	Yield based on RBr
1-bromobutane		64[a]	64[a]
		84	69
2-bromobutane		94	94
t-butyl bromide		100	94

Products from the reduction of Ni(teta)$^{2+}$ (5mM) + bromobutane (5mM) + acrylonitrile (25mM) in AN/Bu$_4$NBF$_4$ and at a Pt electrode. Electrode potential -1.3V vs SCE.

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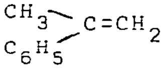
a. only 10 mM acrylonitrile

(i) $CH_2 = CHCN$, $CH_2 = CHCOOC_2H_5$ and $CH_2 = CH - COC_2H_5$. The catalytic peak rapidly becomes smaller and by the time the concentration of olefin is 20 mM, the peak current density has dropped to a value only approximately twice that for the Ni(11)/Ni(1) peak in solutions of the complex alone.

(ii) $CH_3CH = CH_2$, $C_6H_{13}CH = CH_2$,  $(CH_3)(C_6H_5)C{=}CH_2$. No reduction in the peak current density was observed on addition of these compounds. With α-methyl styrene the final concentration of olefin was 50 mM.

(iii) *trans*-$C_6H_5CH = CHCOOC_2H_5$, *trans*-$C_6H_5CH = CHCHO$, *trans*-$CH_3CH = CHCOCH_3$, *trans*-$C_3H_7CH = CHCHO$, and *cis*-$C_2H_5O(CO)CH = CHCOOC_2H_5$. With these olefins the peak current density for the Ni(11)/Ni(1) process gradually decreases during addition of the olefin but the limiting value cannot be reached. The rate of the decrease in peak current density depends on the structure of the olefin.

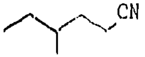
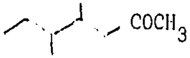
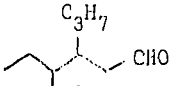
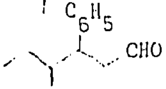
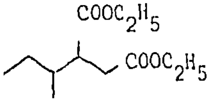
It should be noted that several of the olefins reduced directly at the Pt cathode in this solvent but the potential was always more negative than that for the nickel complex.

Preparative scale electrolyses were carried out with each of the olefins in solutions containing the complex and secondary butyl bromide and at a potential of -1.4V. The coulometric results and the yields of desired products are reported in table III. The yield of product from acrylonitrile, ethyl vinyl ketone and ethyl acrylate was very high. With the other olefins the yields are less good, the coulometry showed that more than 2F/mol Ni(teta)$^{2+}$ passed before the current fell to zero and C_4 and C_8 *hydrocarbons were also formed.*

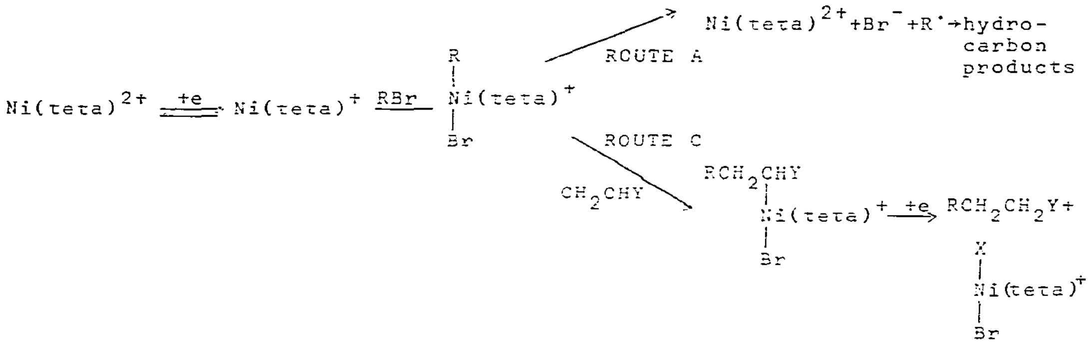
Hence the reaction depicted in Scheme 2 seems to be general for several types of alkyl bromide but to give very high yields of product only with olefins with certain structural features. Firstly, an electron with drawing group attached to the double bond seems essential and the yields are best with terminal olefins. These observations are compatible with a mechanism where the effectiveness of the synthesis is dependent on the rate of insertion of the olefin into the nickel-carbon bond. This must be fast compared with cleavage of the nickel-carbon bond to give radical (route A).

Further studies to elucidate the exact structure of the electroinactive nickel species formed in routes B (Scheme 1) and C and to

TABLE III

Olefin	Concentrations (mM)			Product	Current Yield	Yield based on 2-C_4H_9Br	n-value
	Ni(teta)$^{++}$	2-C_4H_9Br	Olefin				
CH_2=CHCN	5	5	25		94	94	2.0
CH_2=$CHCOOC_2H_5$	5	5	25		82	82	2.0
CH_2=$CHCOC_2H_5$	5	5	25		83	83	2.0
CH_3CH=$CHCOCH_3$	5	5	25		5	5	
	5	10	250		25	20	3.1
C_3H_7CH=CHCHO	2	20	100		19	11	11.4
C_6H_5CH=CHCHO	5	5	15		22	22	2.4
$COOC_2H_5$ $COOC_2H_5$ CH = CH	2	20	40		39	11	5.4
	5	10	250		50	38	3.0

Products from the electrolytic reduction of a solution of Ni(teta)$^{2+}$ + 2-bromobutane + various olefins in AN/Bu_4NBF_4 at a Pt cathode. Electrode potential -1.4V vs SCE.



SCHEME 3

design complexes where such syntheses are catalytic with respect to the metal species are underway.

Experimental

Instrumentation and Cells

The electrochemical experiments were carried out with a modified Chemical Electronics Valve Potentiostat and, where necessary, a Chemical Electronics Waveform Generator (type RB1), a Hewlett Packard X-Y recorder (type 7014A) and a home built current integrator.

All experiments employed three electrode cells. In the two compartment cell for cyclic voltammetry the Pt wire working electrode was surrounded by a Pt spiral counter electrode and the reference electrode (a Radiometer SCE or a Ag wire) was separated from the working electrode by a Luggin capillary and tap. In the cell for coulometry and product determination the working electrode was a Pt gauze, area 3 cm^2, and it was separated from the counter electrode by a fine glass frit. The reference electrode was as in the other cell. The volume of solution in the working electrode compartment was 20 cm^3. All potentials are quoted vs. the SCE. All solutions were degassed with pure N_2 (BOC Ltd) before experiments.

Chemicals

The purification of acetonitrile and the preparation of the complex and base electrolyte have been described elsewhere[4]. The butyl bromides were obtained from BDH Ltd. but the 2-bromooctane was prepared by refluxing octan-2-ol (BDH Ltd) with 48% hydrobromic acid (BDH Ltd). Of the olefins, acrylonitrile, cinnamaldehyde, diethylmaleate, α-methylstyrene and 1-octene were supplied by BDH Ltd and ethyl acrylate, 2-pentene-4-one, 1-pentene-3-one and trans-2-hexenal by Aldrich Chemicals. n-Hexyl cyanide, n-heptyl cyanide and n-octyl cyanide (Koch Light Ltd), 2-nonanone, n-decanal and n-hexanophenone (Aldrich Chemical Co), ethyl cinnamate (BDH Ltd) and ethyl-n-heptanoate and diethyl suberate were used as standards (see below). The latter were prepared from ethanol and n-heptanoic acid (BDH Ltd) and suberic acid (Aldrich Chemical Co) respectively. Cinnamaldehyde was purified by preparative scale g.l.c. on a 9' PEGA column at 150°C.

Procedure and Analysis

At the end of the electrolyses a known weight of a suitable internal standard was added to the catholyte which was then added to water. The resulting solution was saturated with sodium chloride and extracted with ether. This ether extract was subjected to analysis by glc using a Pye 104 gas chromatograph with FID detector and a 9' polyethylene-glycol adidate (PEGA), 2% or 10%, on celite column; the carrier gas was N_2(60 cm^3 min^{-1}) and the temperature in the range 80-150°C. The products were often identified on the basis of their mass spectra obtained on a glc-mass spectrometer (AEI MS 12) but in several cases the products were isolated by preparative scale glc and subjected to a full spectral analysis (see below). IR spectra were run on a Perkin Elmer SP200 spectrometer, proton NMR on a 60 MHz Perkin Elmer R12A or a 100 MHz Varian HA100 spectrometer and ^{13}C NMR Varian XL-100-12 spectrometer operating in the Fourier Transform mode and recorded at 25.15 MHz. The yields of the products were determined by comparison of the area under the glc peak for the product with that for the internal standard. (Where necessary correction was made to allow for the difference in response due to a difference in chain lengt The recovery of internal standard always exceeded 80%.

The spectral data for products from the electrolyses and the internal standards employed were:

2-bromooctane + acrylonitrile

$^m/_e$ 111 (39), 82 (67), 69 (71), 57 (73), 55 (63), 54 (49), 43 (100), 41 (79).

internal standard: n-octylcyanide

1-bromobutane + acrylonitrile

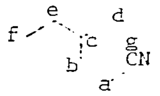
$^m/_e$ 83 (57), 82 (74), 55 (44), 54 (53), 43 (61), 41 (100), 29 (34)

internal standard: n-heptyl cyanide

2-bromobutane + acrylonitrile

$^{m}/_{e}$ 82 (25), 69 (22), 57 (47), 55 (100), 54 (38), 41 (51), 29 (27)

ν_{max}(film) 2300 (C≡N), $\delta(CDCl_3)$ 0.8-0.9 (6H,m), 1.1-1.8 (5H, m), 2.3 (2H,t,J8Hz). ^{13}C (p.p.m. vs TMS, H decoupled) -18.4(1C,s,C_d), -11.1(1C,s,C_f), -15.0(1C, s, C_a), -31.9(1C,s,C_b), -28.8(1C,s,C_e), -120.0(1C,s,C_g), -33.6(1C,s,C_c)



internal standard: n-hexyl cyanide

t-butyl bromide + acrylonitrile

$^{m}/_{e}$ 96 (93), 69 (31), 57 (100), 55 (51), 41 (56), 39 (20), 29 (31)

ν_{max}(film) 2300 (C≡N) $\delta(CDCl_3)$ 0.9(9H,S), 1.6(2H,t,J8Hz), 2.2(2H,t,J8Hz).

internal standard: n-hexyl cyanide.

2-bromobutane + ethyl acrylate

$^{m}/_{e}$ 113 (38), 101 (90), 88 (100), 55 (49), 43 (51), 41 (59), 29 (86), 27 (42).

internal standard: ethyl n-heptanoate.

2-bromobutane + 1-pentene-3-one

$^{m}/_{e}$ 113 (23), 95 (36), 85 (19), 72 (65), 70 (27), 57 (100), 43 (65), 41 (27)

internal standard: nonan-2-one.

2-bromobutane + 2-pentene-4-one

$^{m}/_{e}$ 85 (35), 84 (63), 69 (23), 58 (22), 57 (19), 43 (100), 41 (23), 32 (47).

internal standard: nonan-2-one.

2-bromobutane + 2-hexenal

$^{m}/_{e}$ 112 (66), 83 (100), 70 (26), 57 (44), 56 (22), 55 (68), 43 (29), 41 (56).

internal standard: n-decanal.

2-bromobutane + cinnamaldehyde

$^{m}/_{e}$ 172 (21), 143 (24), 133 (100), 131 (67), 115 (22), 103 (23), 91 (22), 77 (21).

internal standard: n-hexanophenone

2-bromobutane + diethylmaleate

$^m/_e$ 185 (69), 174 (50), 143 (34), 128 (100), 100 (32), 83 (34), 69 (32), 29 (64).

internal standard: diethyl suberate.

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