Sulfur–Nitrogen Bonded Metal Chelates. Part 17.[1] Reactions of Alcohols with the Co-ordinated Nitrile in Nickel(II) Complexes $[NiL(NCR)][ClO_4]$ (L = a *S,N,N*-tridentate anion; R = Me, Et, or Ph) under Different Conditions

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The reactions of the nitrile complexes $[NiL(NCR)][ClO_4]$ {HL^1 = methyl 2-[(2′-aminoethyl)amino]-cyclopent-1-enedithiocarboxylate, HL^2 = methyl 2-[(2′-dimethylaminoethyl)amino]cyclopent-1-enedithiocarboxylate, HL^3 = methyl 2-[(2′-diethylaminoethyl)amino]cyclopent-1-enedithiocarboxylate; R = Me, Et, or Ph} with methanol and ethanol under different experimental conditions have been investigated. Rate constants for these reactions have been measured spectrophotometrically at 25 °C. Dry methanol reacts with the nitrile complexes, in absence of free nitrile, to produce dinuclear μ-methoxo complexes $[Ni_2L_2(\mu\text{-}OMe)][ClO_4]$ and the same reaction with wet methanol gives $[Ni_2L_2(\mu\text{-}OH)][ClO_4]$. Both methoxo- and hydroxo-bridged compounds react with imidazole to form μ-imidazolato dinuclear complexes. All the complexes have been isolated and characterized. Dry methanol adds to the co-ordinated nitrile in complexes $[NiL(NCR)][ClO_4]$ in the presence of excess of free RCN, to produce imino-ether complexes $[NiL\{NH{=}C(OMe)R\}][ClO_4]$. The rate data show the following decreasing order of reactivity of the nitrile complexes: $[NiL^1(NCMe)]^+ > [NiL^1(NCEt)]^+ > [NiL^2(NCMe)]^+ > [NiL^3(NCMe)]^+$. The reaction rate with ethanol is much slower than that with methanol. The rates of formation of imino-ether complexes increase by more than four orders of magnitude when sodium alkoxide is used as a catalyst.

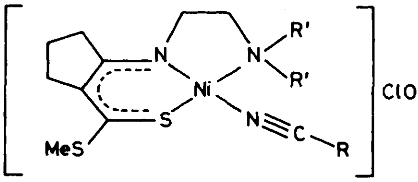
Over the past 20 years considerable attention has been paid to reactions involving addition of alcohols, amines, and hydroxide ion to co-ordinated nitriles in metal complexes.[1] From a reaction mechanism point of view, base hydrolysis of robust penta-amine nitrile complexes of cobalt(III),[2–9] ruthenium(II),[10] ruthenium(III),[11] rhodium(III),[12] and iridium(III)[12] have received detailed consideration. The reaction (1) (R = substituted aryl group) mostly shows first-order dependence on OH^- concentration, indicating its direct attack on the nitrile carbon atom.

$$[M(NH_3)_5(NCR)]^{3+} + OH^- \longrightarrow [M(NH_3)_5(NHCOR)]^{2+} \quad (1)$$

Similar direct attack of nucleophiles also takes place during the hydrolysis of $[Co(NH_3)_5(NCCH{=}CH_2)]^{3+}$ in carbonate buffer medium[9] ($k_{obs.} = k^1[OH^-] + k^2[CO_3^{2-}]$). However, deviation from a first-order rate equation has been reported[12] for the base hydrolysis of $[Ir(NH_3)_5(NCMe)]^{3+}$; the second-order term in the rate equation, $k_{obs.} = k_1[OH^-] + k_2[OH^-]^2$, arises due to the partial formation of $[Ir(NH_3)_4(NH_2)(NCMe)]^{2+}$. Significant departure from expected rates have also been reported[4,6,7] to occur for a number of penta-amine functionalized-nitrile complexes of cobalt(III). These deviations are consequences of side reactions, such as hydration of the formyl group of *m*- and *p*-formylbenzonitrile,[4] cyclization following the hydrolysis of phthalonitrile,[6,7] and *ortho*-group participation of 2-carboxamidobenzonitrile.[7] The rate constants for the base hydrolysis of $[M(NH_3)_5(NCPh)]^{3+}$ (M^{III} = Co, Rh, or Ir)[10,11] follow the trend Co > Rh > Ir, which is expected on the basis of decreasing charge density of the metal ions. It has been observed that aromatic nitriles co-ordinated to metal ions are more prone to hydrolysis[4] and for a number of such systems a Hammett linear free-energy relation has been obtained.[8]

In contrast to the robust d^6 systems, the mechanism of nucleophilic attack on a nitrile carbon atom in d^8 systems has received scant attention.[13] Concerning the addition of alcohols and amines to co-ordinated nitriles, most of the studies involve palladium(II) and platinum(II) complexes.[14–19] Prior to our work,[1] only a few studies have been made with nickel(II) systems.[20,21] However, one can expect that nickel(II) complexes will be the most reactive among the divalent d^8 triads because of the greater charge density of the Ni^{2+} ion, provided substitution of the nitrile(s) in such labile systems can be prevented.

In a recent paper[1] we reported that facile addition of alcohols (R′OH) and amines (NHR'_2) takes place to the nitrile carbon atom of the nickel(II) complexes $[NiL(NCR)][ClO_4]$ (L = L^1—L^3) in the presence of excess free RCN leading to the formation of the imino-ether $[NiL\{NH{=}C(OR')R\}][ClO_4]$ and amidine $[NiL\{NH{=}C(NR'_2)R\}][ClO_4]$ complexes, respectively. We have now found that the imino-ether complexes form more readily when sodium alkoxide is used as a catalyst, and reaction of the nitrile complexes with an alcohol in the absence of free RCN leads to the formation of the alkoxo-bridged dinuclear complexes $[Ni_2L_2(\mu\text{-}OR')][ClO_4]$. The present study is concerned with the kinetics and mechanistic aspects of these reactions.



$[NiL(NCR)][ClO_4]$

L^1; R′ = H
L^2; R′ = Me
L^3; R′ = Et

Table 1. Analytical, i.r. and electronic spectral data for the dinuclear complexes

	Analysis (%)[a]					
Compound	C	H	N	Ni	I.r. (ν/cm^{-1})[b]	λ/nm (ε/dm^3 mol^{-1} cm^{-1})[c]
$[Ni_2L^1{}_2(\mu\text{-OH})][ClO_4]$	32.5 (32.4)	4.65 (4.8)	8.4 (8.45)	17.8 (17.7)	3 500 (OH); 3 300, 3 240 (NH); 1 100, 625 (ClO_4^-)	585 (sh), 400 (8 900), 310 (17 250)
$[Ni_2L^1{}_2(\mu\text{-OMe})][ClO_4]$	33.3 (33.65)	5.0 (4.85)	8.2 (8.25)	17.2 (17.3)	3 300, 3 250 (NH); 1 100, 625 (ClO_4^-)	585 (sh), 420 (5 950), 360 (7 200), 310 (19 800)
$[Ni_2L^1{}_2(\mu\text{-OEt})][ClO_4]$	34.2 (34.7)	4.95 (5.05)	8.4 (8.1)	17.2 (16.95)	3 300, 3 240 (NH); 1 090, 625 (ClO_4^-)	590 (sh), 400 (6 980), 310 (18 800)
$[Ni_2L^1{}_2(\mu\text{-im})][ClO_4]$	35.6 (35.3)	4.75 (4.6)	12.0 (11.75)	16.3 (16.45)	3 300, 3 250 (NH); 1 090, 625 (ClO_4^-); 755, 670 (ring)	540 (250), 410 (12 350), 310 (9 600)
$[Ni_2L^2{}_2(\mu\text{-OMe})][ClO_4]$	37.9 (37.6)	5.75 (5.6)	7.9 (7.65)	15.8 (16.0)	1 100, 630 (ClO_4^-)	590 (sh), 425 (10 850), 355 (12 400), 315 (32 500)
$[Ni_2L^2{}_2(\mu\text{-OEt})][ClO_4]$	38.85 (38.5)	5.85 (5.75)	7.8 (7.5)	15.5 (15.7)	1 100, 630 (ClO_4^-)	

[a] Calculated values are given in parentheses. [b] In KBr disc. [c] In *N,N*-dimethylformamide.

Experimental

Materials.—Unless otherwise stated, reagents were those available commercially and were used as received. MeOH and EtOH were made 'superdry' by standard methods.[22] MeCN, EtCN, and PhCN were successively dried over CaH_2 and P_4O_{10} and stored over molecular sieves. Complexes [NiLCl] (L = L^1—L^3), $[NiL(NCR)][ClO_4]$ (L = L^1—L^3; R = Me, Et, or Ph), and $[NiL\{NH{=}C(OR')R\}][ClO_4]$ (L = L^1—L^3; R = Me, Et, or Ph; R′ = Me or Et) were prepared as described earlier.[1]

$[Ni_2L_2(\mu\text{-OR})][ClO_4]$ (L = L^1 *or* L^2, R = Me *or* Et).—*Method* (*a*). $[NiL(NCMe)][ClO_4]$ (*ca.* 1 g) in *dry* MeOH or EtOH (100 cm^3) was refluxed for 8 h. The dark brown solution obtained was concentrated to *ca.* 40 cm^3 (L = L^1) or 20 cm^3 (L = L^2) and filtered. The filtrate, on standing over $CaCl_2$ for 12—24 h, deposited shiny dark brown crystals; yield 70%.

Method (*b*). To a stirred suspension of [NiLCl] (2 mmol) in *dry* MeOH or EtOH (100 cm^3) was added the corresponding alcoholic solution (5 cm^3) of $AgClO_4$ (2 mmol). After stirring for 10 h at room temperature the mixture was filtered. On concentration in a rotary evaporator, followed by standing over $CaCl_2$, the filtrate afforded the desired complex in *ca.* 60% yield.

$[Ni_2L_2(\mu\text{-OH})][ClO_4]$ (L = L^1 *or* L^2).—These complexes were obtained when alcohols which were not *dry* were used in the above preparations.

$[Ni_2L^1{}_2(\mu\text{-im})][ClO_4]$ (im = imidazolate).—To a stirred suspension of $[Ni_2L^1{}_2(\mu\text{-OMe})][ClO_4]$ or $[Ni_2L^1{}_2(\mu\text{-OH})][ClO_4]$ (1 mmol) in CH_2Cl_2 (50 cm^3) were successively added imidazole (0.068 g, 1 mmol) and triethylamine (0.15 cm^3). A clear brown solution obtained after stirring for 6 h was filtered, concentrated to 10 cm^3, and kept in an ice-chest. The brown crystals deposited were recrystallized from CH_2Cl_2; yield 80%.

CAUTION! Perchlorate salts of the complexes under consideration are potentially explosive at elevated temperatures.

Physical Measurements.—Electronic spectra were recorded with a Pye-Unicam SP8-150 spectrophotometer and i.r. with a Perkin-Elmer 783 spectrophotometer. Magnetic susceptibilities were obtained at room temperature with a PAR 155 vibrating sample magnetometer. A Philips PR-9500 bridge was used for conductivity measurements. C, H, and N analyses were performed on a Perkin-Elmer 240C elemental analyzer. Analytical and some characterizing data for the newly prepared complexes are given in Table 1.

Kinetic Measurements.—The reaction kinetics were followed spectrophotometrically in a Pye-Unicam SP8-150 spectrophotometer equipped with thermostatted cell holders, at 25 ± 0.1 °C. The change in absorbance of the solution was measured in a 1-cm path length stoppered quartz cell against a matched cell containing appropriate solvent as a blank. The rate of formation of $[Ni_2L^1{}_2(\mu\text{-OMe})][ClO_4]$ from $[NiL^1(NCMe)][ClO_4]$ (whose concentration was varied between 5×10^{-4} and 4×10^{-3} mol dm^{-3}) in *dry* MeOH was monitored at 560 nm. The kinetics of imino-ether complex formation from $[NiL(NCR)][ClO_4]$ (L = L^1—L^3, R = Me or Et) solutions (4×10^{-3} mol dm^{-3}) in varying amounts of MeCN or EtCN and MeOH were monitored concurrently at 620 and 525 nm. In these experiments the total volume of the solutions (RCN + MeOH) was kept constant to 10 cm^3, while the volume of MeOH was varied between 5 and 8 cm^3. For alkoxide-catalyzed reactions, the nitrile to alcohol ratio was kept constant, but the concentration of the alkoxide was varied in the range 4—25 mol% (1.6×10^{-4}—1×10^{-3} mol dm^{-3}) of the concentration of the nitrile complex (4×10^{-3} mol dm^{-3}). In all cases absorbance *vs.* time data were subjected to pseudo-first-order plots to obtain the observed rate constants ($k_{obs.}$).

Results and Discussion

Synthesis and Characterization of μ-*Alkoxo,* μ-*Hydroxo, and* μ-*Imidazolato Complexes.*—The acetonitrile co-ordinated complexes $[NiL(NCMe)][ClO_4]$ on boiling with *dry* MeOH or EtOH form the corresponding μ-alkoxo complexes $[Ni_2L_2(\mu\text{-OR})][ClO_4]$ (L = L^1 or L^2, R = Me or Et). These compounds are also obtained when [NiLCl] are treated with a stoicheiometric amount of $AgClO_4$ in *dry* alcohol. The alkoxo-bridged compounds are very sensitive to moisture present in solvents and hydrolyse to the hydroxo-bridged derivatives. Thus, complexes $[Ni_2L_2(\mu\text{-OH})][ClO_4]$ (L = L^1 or L^2) were obtained on attempting to prepare $[Ni_2L_2(\mu\text{-OR})][ClO_4]$ with 'undried' alcohols. The hydroxo or alkoxo bridge can be replaced by other suitable bridging units, for example, by imidazolate to form $[Ni_2L^1{}_2(\mu\text{-im})][ClO_4]$. All the compounds behave as 1:1 electrolytes (Λ_M *ca.* 70—80 Ω^{-1} cm^2 mol^{-1} in *N,N*-dimethylformamide) and are diamagnetic. A few characteristic i.r. and electronic spectral data of these complexes

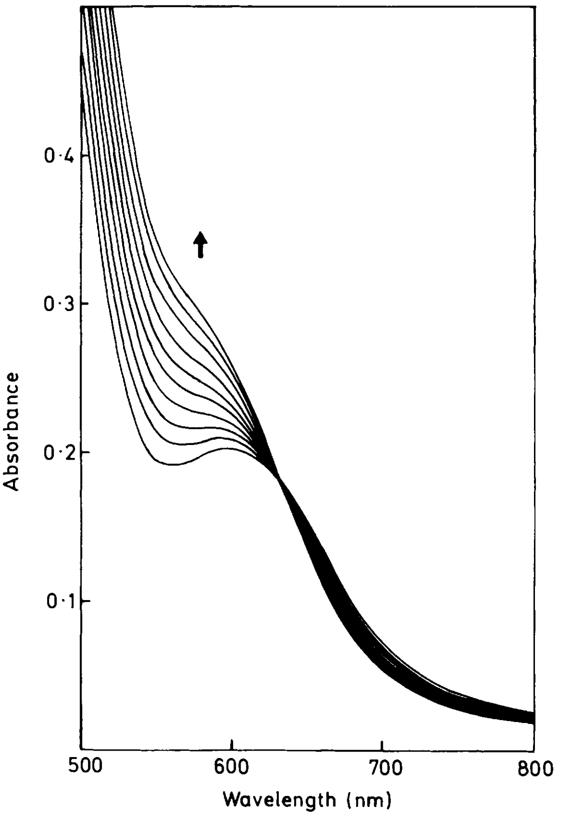


Figure 1. Kinetic spectra of the conversion of $[NiL^1(NCMe)]^+$ (3 mmol dm^{-3}) to $[Ni_2L^1_2(\mu\text{-}OMe)]^+$ in MeOH over a period of 3.5 h

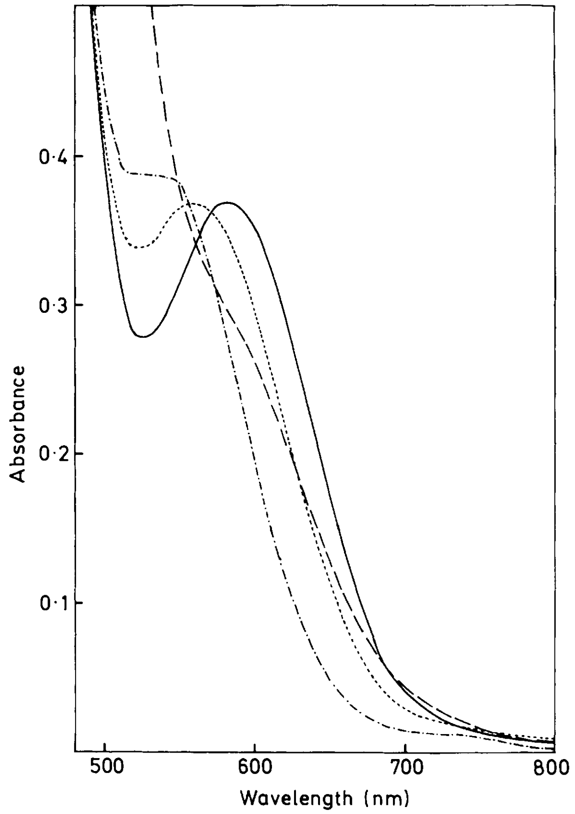


Figure 2. Electronic spectra of some nickel(II) complexes in the visible range: $[NiL^1(NCMe)][ClO_4]$ (———), 4 mmol dm^{-3} in MeCN; $[NiL^1(NCMe)][ClO_4]$ (• • •), 4 mmol dm^{-3} in $MeNO_2$; $[NiL^1\{NH{=}C(OMe)Me\}][ClO_4]$ (–•–•–•–), 3.62 mmol dm^{-3} in MeCN–MeOH; and $[Ni_2L^1_2(\mu\text{-}OMe)][ClO_4]$ (– – –), 0.9 mmol dm^{-3} in MeOH

Table 2. Kinetic data for the reaction: $2[NiL^1(NCMe)]^+ + MeOH \longrightarrow [Ni_2L^1_2(\mu\text{-}OMe)]^+ + H^+ + 2MeCN$, at 25 ± 0.1 °C

Concentration of $[NiL^1(NCMe)][ClO_4]$/mmol dm^{-3}	$10^5k_{obs.}$/s^{-1}
0.5	3.25 ± 0.05
1.0	3.60 ± 0.05
2.0	4.30 ± 0.02
3.0	5.11 ± 0.01
4.0	5.80 ± 0.05

are given in Table 1. It is noteworthy that the literature abounds with di-μ-hydroxo, di-μ-alkoxo, or μ-alkoxo-μ-phenoxo complexes, especially those of copper(II). However, the formation of 'naked' μ-alkoxo complexes, as reported here is quite uncommon to our knowledge.

Kinetics of Formation of $[Ni_2L^1_2(\mu\text{-}OMe)][ClO_4]$.—The spectral changes observed during the conversion of $[NiL^1(NCMe)][ClO_4]$ to $[Ni_2L^1_2(\mu\text{-}OMe)][ClO_4]$ in dry MeOH at 25 °C is shown in Figure 1. The successive absorption curves pass through a sharp isosbestic point at 630 nm. The final spectrum of Figure 1 coincides with that of an authentic specimen of $[Ni_2L^1_2(\mu\text{-}OMe)][ClO_4]$ shown in Figure 2, and gives a clear indication of the absence of any side reaction. The absorbance *vs.* time data [$\ln(A_t - A_\infty)$ *vs.* t, where A_t and A_∞ are the absorbances at time t and infinity, respectively] gave good linear plots from which $k_{obs.}$ values were obtained. The rate of formation of $[Ni_2L^1_2(\mu\text{-}OMe)][ClO_4]$ was found to depend upon the concentration of the nitrile complex used and the $k_{obs.}$ values obtained for various concentrations of $[NiL^1(NCMe)][ClO_4]$ are given in Table 2. The rate data obtained for reaction (2) when plotted against the concentration of $[NiL^1(NCMe)][ClO_4]$, gave a straight line with a positive intercept.

$$2[NiL^1(NCMe)]^+ + MeOH \longrightarrow [Ni_2L^1_2(\mu\text{-}OMe)]^+ + H^+ + 2MeCN \quad (2)$$

From preliminary studies it was observed that compared to the formation of the methoxo-bridged complex, formation of the ethoxo-bridged complex takes place at a much slower rate. This may be related to the relative acid strengths of the two alcohols:[23,24] MeOH, $pK_a = 15.5$; EtOH, $pK_a = 16$.

Kinetics of Formation of Imino-ether Complexes. $[NiL\{NH{=}C(OMe)R\}][ClO_4]$ ($L = L^1$—L^3, R = Me; $L = L^1$, R = Et).—In the presence of excess RCN reaction (2) is totally inhibited, and instead reaction (3) takes place.

$$[NiL(NCR)]^+ + MeOH \longrightarrow [NiL\{NH{=}C(OMe)R\}]^+ \quad (3)$$

In order to investigate the kinetics of this reaction the concentration of RCN was varied in the range 3.8—9.5 mol dm^{-3} (for MeCN) or 2.8—5.7 mol dm^{-3} (for EtCN) and the concentration of MeOH varied between 19.8 and 12.3 mol dm^{-3}. It may be noted that the concentration of RCN and MeOH of the reaction medium varied simultaneously. The experimental conditions are such that to keep the concentration of one of the

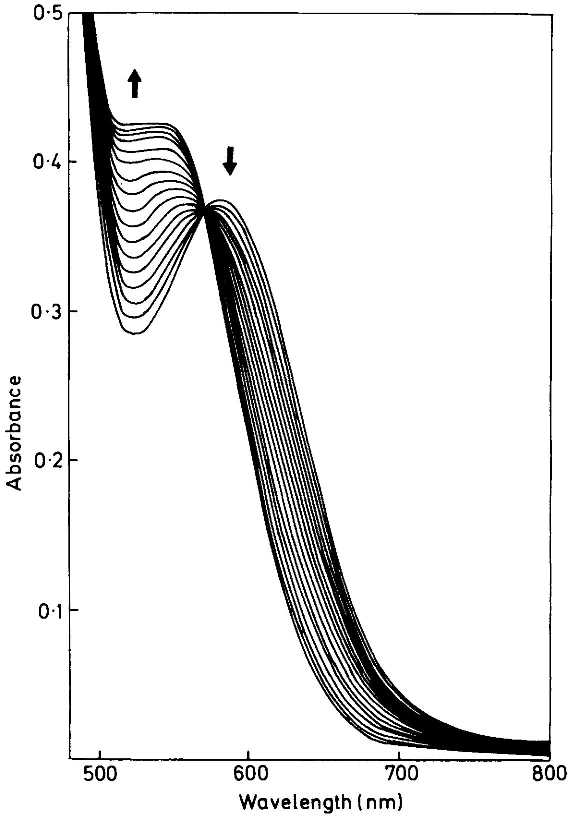


Figure 3. Kinetic spectra of the conversion of $[NiL^1(NCMe)]^+$ (4 mmol dm^{-3}) to $[NiL^1\{NH{=}C(OMe)Me\}]^+$ in a mixture of MeCN (6.66 mol dm^{-3}) and MeOH (16.05 mol dm^{-3}). Spectral recordings were made at the following time intervals: 0, 20, 40, 65, 90, 120, 150, 185, 220, 260, 300, 350, 400, 480, 600, 800 min, and 24 h

components fixed, the introduction of a third solvent becomes necessary. However, since a third solvent could affect the reaction rate in an unpredictable manner, a binary solvent mixture was used.

Figure 3, which is typical for all the systems investigated, shows time-dependent spectral changes for $[NiL^1(NCMe)][ClO_4]$ in a mixture of MeCN (6.66 mol dm^{-3}) and MeOH (16.05 mol dm^{-3}) at 25 °C. The sharp isosbestic point at 570 nm indicates the absence of any side reaction. Here also the final spectrum of Figure 3 matches exactly with the spectrum of a pure specimen of $[NiL^1\{NH{=}C(OMe)Me\}][ClO_4]$ shown in Figure 2. The variation of solvent composition shows a negligible effect on the spectral profile.

We have reported[1] earlier that the imino-ether complexes are stable in dry solvents, do not undergo dissociation, and the imino-ether is not substituted by weak nucleophiles. However, they are readily hydrolysed to the corresponding amido complexes, $[NiL(NH_2COR)][ClO_4]$. ^1H N.m.r. spectral studies[1] show that due to the restricted rotation of the C=N bond of the imino-ether moiety, a temperature dependent equilibrium exists in solution between the *E* and *Z* conformers of the complex species $[NiL\{NH{=}C(OR')R\}]^+$.

The change in absorbance of $[NiL(NCR)][ClO_4]$ (R = Me or Et) in various MeCN–MeOH and EtCN–MeOH mixtures measured concurrently at 620 and 525 nm with time gave identical pseudo-first-order rate constants ($k_{obs.}$). The $k_{obs.}$ values for all the systems in different solvent compositions are given in Table 3. The results show that for any particular complex, the $k_{obs.}$ values increase with increasing [MeOH].

Table 3. Kinetic data for the reaction: $[NiL(NCR)]^+ + MeOH \longrightarrow [NiL\{NH{=}C(OMe)R\}]^+$ at different concentrations of RCN and MeOH at 25 ± 0.1 °C

Complex	[RCN]/mol dm^{-3}	[MeOH]/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$
$[NiL^1(NCMe)]^+$	3.81	19.75	3.51 ± 0.06
	4.76	18.52	2.99 ± 0.03
	5.71	17.28	2.69 ± 0.02
	6.66	16.05	2.28 ± 0.02
	9.51	12.34	1.50 ± 0.03
$[NiL^2(NCMe)]^+$	3.81	19.75	1.50 ± 0.02
	4.76	18.52	1.38 ± 0.01
	6.66	16.05	1.13 ± 0.02
	7.61	14.81	0.91 ± 0.01
	9.51	12.34	0.71 ± 0.01
$[NiL^3(NCMe)]^+$	3.81	19.75	1.33 ± 0.05
	4.76	18.52	1.24 ± 0.04
	5.71	17.28	1.12 ± 0.03
	6.66	16.05	0.97 ± 0.03
	7.61	14.81	0.90 ± 0.03
	9.51	12.34	0.65 ± 0.01
$[NiL^1(NCEt)]^+$	2.84	19.75	2.00 ± 0.04
	3.54	18.52	1.74 ± 0.04
	4.25	17.28	1.57 ± 0.06
	4.96	16.05	1.39 ± 0.06
	5.67	14.8	1.20 ± 0.05

However, satisfactory linear plots could not be obtained either for $k_{obs.}$ *vs.* [MeOH] or $k_{obs.}^{-1}$[MeOH] *vs.* $[MeOH]^{-1}$.

These observations have led us to consider a general stepwise mechanism[25] (Scheme) which involves direct nucleophilic attack of MeOH on the nitrile carbon atom producing a labile intermediate which may either revert to reactants (k_{-1}) or yield the imino-ether complex through transfer of a proton to the nitrogen atom of RCN. The proton transfer may take place either intramolecularly (k_2) *via* a four-membered cyclic transition state, or intermolecularly (k_3) through the participation of another MeOH molecule which functions as a proton acceptor–donor bifunctional catalyst in a six-membered activation state. If both the intra- and inter-molecular proton-transfer reactions are considered to take place in parallel then under pseudo-first-order conditions the rate equation can be expressed as (i). Equation (i), however, becomes much simpler when only the intramolecular proton transfer process is operative, thus, giving equation (ii). For an intermolecular step alone, equation (iii) rearranges to (iv).

$$k_{obs.} = k_1[MeOH]\frac{k_2 + k_3[MeOH]}{k_{-1} + k_2 + k_3[MeOH]} \qquad \text{(i)}$$

$$k_{obs.} = \frac{k_1k_2[MeOH]}{k_{-1} + k_2} \qquad \text{(ii)}$$

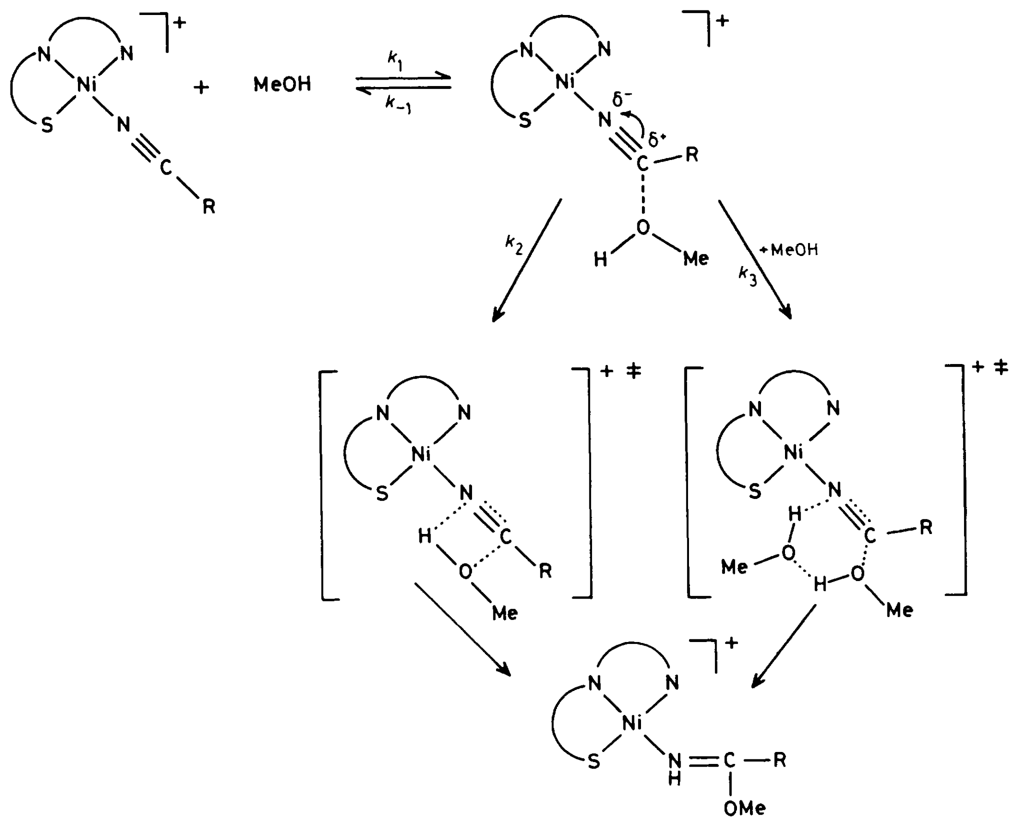
$$k_{obs.} = \frac{k_1k_3[MeOH]^2}{k_{-1} + k_3[MeOH]} \qquad \text{(iii)}$$

$$\frac{[MeOH]}{k_{obs.}} = \frac{k_{-1}}{k_1k_3}\cdot\frac{1}{[MeOH]} + \frac{1}{k_1} \qquad \text{(iv)}$$

On the other hand, if a pre-equilibrium is not considered the rate equation becomes (v).

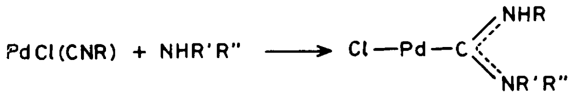
$$k_{obs.} = k_2[MeOH] + k_3[MeOH]^2 \qquad \text{(v)}$$

We have already noted that the kinetic data presented in



Scheme.

Table 3 cannot be satisfactorily treated using simplified equations (ii), (iv), or (v). It may be pointed out that the kinetic data were collected in solvent media of varying polarities due to the varying ratio of [MeOH]–[RCN]. Such changing medium effects can adversely affect the reaction rate. Although rate parameters have not been extracted using equation (i) by non-linear regression analysis, due to the limited number of data points available and also due to the uncertainty imbibed in changing medium effects, we believe that equation (i) gives a realistic expression for the reaction (3). It may be mentioned that a similar mechanism[25] satisfactorily explained the formation of palladium(II) carbene complexes from palladium isocyanide complexes and amines [reaction (4); PdCl(CNR) is part of a binuclear chloride-bridged species[25]].



$$\mathrm{PdCl(CNR)} + \mathrm{NHR'R''} \longrightarrow \mathrm{Cl{-}Pd{-}C}\begin{smallmatrix}\mathrm{NHR} \\ \mathrm{NR'R''}\end{smallmatrix} \qquad (4)$$

From the gross rate parameters given in Table 3 it is possible to recognize the influences of electronic and steric effects on the reaction rates. It may be noted that for any particular concentration of MeOH, $k_{obs.}$ decreases in the order $[NiL^1(NCMe)]^+ > [NiL^2(NCMe)]^+ > [NiL^3(NCMe)]^+$. From the Scheme it is evident that the nucleophilic attack of MeOH will depend upon the extent of polarization of the co-ordinated nitrile by the metal ion. The polarizing ability of the metal ion, in turn, will be affected by the electronic influence of the other donor groups present. A ligand containing electron-releasing groups will render the metal ion electron-rich in character and hence reduce its polarizing ability. In the series under consideration, ligands L^1—L^3 differ only by the groups attached to the terminal nitrogen atom whose electron-releasing power decreases in the order Et (L^3) > Me (L^2) > H (L^1). Moreover, the steric hindrance to the incoming alcohol molecule(s) by these peripheral groups also decreases in the same order. A comparison of the rate data for $[NiL^1(NCMe)]^+$ and $[NiL^1(NCEt)]^+$ with MeOH shows the greater reactivity of the former. This can again be related to the lesser polarizing ability of EtCN. A preliminary kinetic study of the reaction of $[NiL^1(NCMe)]^+$ with EtOH showed that the reaction rate is too slow for precise measurements. The proposed mechanism indicates that the rate of reaction will depend upon the ease with which the proton from the alcohol is transferred to the nitrile nitrogen atom, that is, upon the acidic character of the alcohol. We have already noted that the pK_a of EtOH is greater than that of MeOH. It has also been observed that the reaction between $[NiL^1(NCPh)]$ and MeOH takes place very slowly at room temperature. The reason can be understood by taking into consideration the resonating structure of PhCN shown above. Clearly, other competing sites of nucleophilic attack impede the reaction rate.

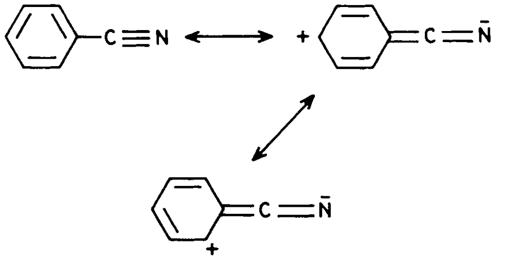


Table 4. Kinetic data for the formation of $[\mathrm{NiL\{NH{=}C(OR')R\}}]^+$ at different concentrations of the catalyst, NaOR′, at 25 ± 0.1 °C

Product	$[\mathrm{NaOR'}]$/mmol dm^{-3}	$10^4k_{\mathrm{obs.}}$/s^{-1}	10^5k^1/s^{-1}	k^2/dm^3 mol^{-1} s^{-1}
$[\mathrm{NiL^1\{NH{=}C(OMe)Me\}}]^{+\,a}$	0.16	4.27 ± 0.05	9.8 ± 2.1	2.03 ± 0.03
	0.32	7.36 ± 0.16		
	0.48	10.64 ± 0.22		
	0.64	14.44 ± 0.31		
	0.80	17.08 ± 0.52		
	0.96	20.46 ± 0.66		
$[\mathrm{NiL^1\{NH{=}C(OMe)Me\}}]^{+\,b}$	0.16	0.40 ± 0.01	0.6 ± 0.4	0.24 ± 0.01
	0.32	0.81 ± 0.01		
	0.48	1.38 ± 0.02		
	0.64	1.55 ± 0.02		
	0.80	1.93 ± 0.02		
	0.96	2.39 ± 0.04		
$[\mathrm{NiL^1\{NH{=}C(OMe)Et\}}]^{+\,a}$	0.30	4.98 ± 0.16	9.8 ± 3.2	1.33 ± 0.05
	0.40	6.62 ± 0.26		
	0.60	8.59 ± 0.31		
	0.80	11.59 ± 0.29		
	1.0	14.24 ± 0.14		
$[\mathrm{NiL^3\{NH{=}C(OMe)Me\}}]^{+\,a}$	0.20	1.04 ± 0.03	4.5 ± 0.60	0.34 ± 0.01
	0.40	1.88 ± 0.07		
	0.60	2.59 ± 0.07		
	0.80	3.19 ± 0.11		
	1.0	3.80 ± 0.12		

[a] [MeOH] = 12.34 mol dm^{-3}. [b] [EtOH] = 8.59 mol dm^{-3}.

Kinetics of the Alkoxide Catalysed Imino-ether Complex Formation.—The formation of $[\mathrm{NiL\{NH{=}C(OR')R\}}]^+$ ($\mathrm{L = L^1}$ or $\mathrm{L^3}$, R = Me, R′ = Me; $\mathrm{L = L^1}$, R = Me, R′ = Et; $\mathrm{L = L^1}$, R = Et, R′ = Me) catalyzed by sodium alkoxide were investigated at a fixed RCN to R′OH ratio and at varying concentrations of NaOR′ (4—25 mol% of the complex). The rate constants obtained from pseudo-first-order kinetic plots are given in Table 4. The plots of $k_{\mathrm{obs.}}$ *vs.* [OR′] gave straight lines with positive intercepts, which indicate that in addition to the alkoxide catalysed path, the reaction also proceeds through the solvent path, *i.e.* equation (vi), That is, where k^1 and k^2 are

$$k_{\mathrm{obs.}} = k^1 + k^2[\mathrm{OR^-}] \qquad \text{(vi)}$$

uncatalyzed and catalyzed rate constants, respectively. In this case, similar to the base hydrolysis of $[\mathrm{M(NH_3)_5(NCR)}]^{3+}$, the alkoxide ion attacks the nitrile carbon atom directly. The solvent path is the one shown in the Scheme. Although the two rate constants, k^1 and k^2, are not directly comparable, qualitatively they indicate that the alkoxide catalysed path is more than four orders of magnitude faster than the solvent mediated path.

The rate data related to the alkoxide catalysed and solvent mediated paths (Table 4) show the expected trend for the formation of imino-ether complexes. It may be noted that the rates of formation of $[\mathrm{NiL^3\{NH{=}C(OMe)Me\}}]^+$ and $[\mathrm{NiL^1\{NH{=}C(OEt)Me\}}]^+$ by the alkoxide catalysed path are not much different. From these results it is clear that for the preparation of imino-ether complexes, especially those of electron-rich nitriles and alcohols, sodium alkoxide should be used as a catalyst.

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