The Preparation and Metal Complexing Properties of Isonitrile-Functionalized Polystyrene Resins

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Preparation of cross-linked isonitrile-functionalized polystyrene resins of the type Ⓟ$-C_6H_5(CH_2)_nNC$ (n = 1,2) is described. The polymers extract a variety of normal oxidation state metals from aqueous tetrahydrofuran and anhydrous metal salts and organometallic complexes from tetrahydrofuran and toluene. Structures of the complexes species are assigned on the basis of analyses and infrared spectra.

1. Introduction

The immobilization of soluble metal complexes on suitably functionalized inorganic or organic supports offers potential advantages in catalysis and in metal separation and extraction [1a–c]. One of the most versatile ligands available to the transition metal chemist is the isonitrile; though most recent work has concentrated on mixed and homoleptic low valent mono and polymetallic complexes (some with interesting catalytic properties) [2a, b], older work demonstrates also the ability of isonitrile (unlike CO) to bind to metals in medium, but generally not high, oxidation states [3]. The alkyl or aryl substituent provides a site for attachment to both inorganic [4] and organic [5a–c] supports. We wish to present here complete details of our studies on the preparation and complexing properties of isonitrile functionalized polystyrenes. Since our initial communication [6] other reports have also appeared on the complexing properties of isonitrile functionalized organic polymers [7a–c].

2. Results and Discussion

(A) Polymer Preparation

To maximize the versatility in terms of functional group loading and polymer physical properties, two approaches have been adopted in the syntheses of the isonitrile functionalized polymers (**2**) and (**3**) (Schema 1):

(i) Chloromethylated polystyrene (**1**) (2% cross-linked) containing approximately 1 mmol g^{-1} chlorine was either purchased commercially or prepared by chloromethylation of polystyrene [8]. Though loadings approaching mono(chloromethylation) (5.2 mmol g^{-1}) have been attained [8], our work has been limited to materials with loadings of about 1 mmol g^{-1}. Treatment of **1** with $LiCH_2NC$, prepared *in situ* from BuLi and CH_3NC [9], yields **2** as a light yellow to brown powder. Though chlorine analyses indicate almost complete substitution, isonitrile-specific titrations with HSCN [10] indicate an isonitrile content in the range 0.6 to 0.9 mmol g^{-1} depending on sample. The loss in functionality may most likely be attributed to some polymerization; isonitriles are known to polymerize under free radical or acid conditions [12], and the yellow to brown colour of the polymers is consistent with this.

(ii) Use of the noxious CH_3NC may be avoided by suspension copolymerization of the phthalimide monomer (**5**) (prepared from commercially available meta/para-chloromethylstyrene) with styrene/divinylbenzene. In the absence of diluent, swellable gel-type resins (2 and 9% cross-linked) may be prepared, while in the presence of diluent, high cross-linked (52%) macroporous resins may be obtained which are potentially more suitable for chromatographic purposes. All polymers have a phthalimide content of about 1 mmol g^{-1}; this is consistently higher than the nominal combining monomer ratio, implying a greater rate of polymerization of **5** relative to styrene. Hydrazinolysis of 2 and 9% cross-linked **6** proceeds quantitatively to give the amine **7**, as established by picrate determination [13]. With macroporous **6**, conversion to amine is about 60% complete even after long reaction times, implying some chemical inaccessibilty of the phthalimide within the microporous structure.

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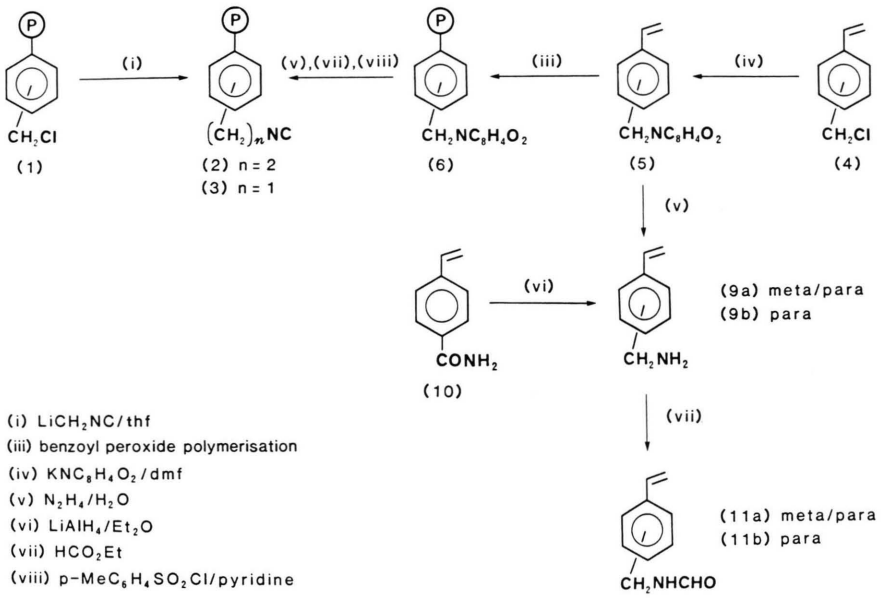
Conversion of **7** (2 and 9% cross-linked) to the formamide **8** followed by dehydration [7a] yields the isonitrile **3.** Best results in the dehydration are obtained using a large excess of pyridine, with aniline added to suppress polymerization of the isonitrile [14]. Even so, the yellow/brown colour and the titration figures (0.8 to 1.0 mmol g^{-1}) indicate a small amount of polymerization.

The formamide monomer **11** may also be prepared as a meta/para mixture *via* hydrazinolysis of **5** or as the pure para-isomer *via* reduction of **10** with $LiAlH_4$. Both syntheses are accompanied by some reduction of the vinyl group, but the saturated impurity may be removed by careful crystallization of **11b.** The formamide **11** may be homopolymerized and dehydrated to an isonitrile homopolymer [15], but both **9** and **11** possess too great a water solubility to be used in suspension polymerization.

Attempts to produce **3** by reaction of brominated polystyrene with $LiCH_2NC$ were unsuccessful.



(B) Metal complexation

Polymers **2** and **3** (2% and 9% cross-linked) may be swollen in organic solvents such as toluene, dichloromethane or tetrahydrofuran, thus enabling complexation of low valent, neutral organometallic complexes from toluene or tetrahydrofuran, and anhydrous metal chlorides from tetrahydrofuran. The polymers also retain sufficient swellability in 50% aqueous tetrahydrofuran such that metal salts which are soluble in this medium may also be complexed. Experiments with low-valent derivatives (vide infra) show little, if any, difference in complexing ability between **2** and **3,** and the results described below have been obtained with polymer **3** (9% cross-linked) unless otherwise stated.

(a) Complexation from aqueous tetrahydrofuran

Generally, polymer **3** was swollen in tetrahydrofuran and an appropriate three-fold molar excess (metal : isonitrile) of the metal salt dissolved in an equal volume of water was added. Quantitative complexation of the isonitrile is observed in all cases where metal complexation is found. The sharp NC vibration of **3** is replaced by a broadened band at higher wavenumber for all the positive oxidation state metal complexes; the spectrum of the $(RNC)_2PtCl_2$ complex is typical (Fig. 1). Metal and chlorine or phosphorus analyses are given in the experimental section; duplicate runs with samples of **3** containing different isonitrile loadings gave similar metal : chlorine and metal : isonitrile ratios. In combination with a comparison of the infrared spectra of "model compounds" (Table II), these results allow

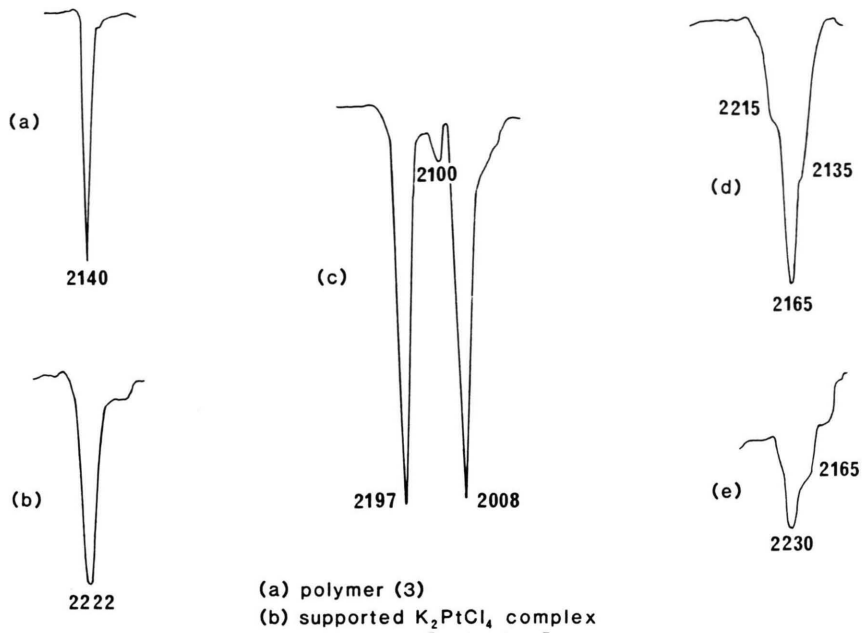


Fig. 1. Infrared spectra of supported complexes.

Table I. Analytical data.

Metal complex	Postulated complexation reaction	Analytical figures (mmol g^{-1}) Calculated M	Cl or P	Found M	Cl or P
$RhCl_3 \cdot xH_2O$	$RhCl_3 \cdot xH_2O + 2\,CNR \rightarrow RhCl_3(CNR)_2(H_2O) + (x-1)H_2O$	0.26	0.78	0.28	0.99
K_2PtCl_4	$K_2PtCl_4 + 2\,CNR \rightarrow PtCl_2(CNR)_2 + 2\,KCl$	0.40	0.80	0.41	0.79
$Na_2PdCl_4 \cdot 3\,H_2O$	$2\,Na_2PdCl_4 + 2\,CNR \rightarrow Pd_2Cl_4(CNR)_2 + 4\,NaCl$	0.85	1.70	0.95	1.44
$AgNO_3$	$AgNO_3 + 2\,CNR \rightarrow Ag(CNR)_2NO_3$	0.47	–	0.59	–
$AgPF_6$	$AgPF_6 + 2\,CNR \rightarrow Ag(CNR)_2PF_6$	0.40	0.40	0.40	0.35
$HgCl_2$	$HgCl_2 + 1.7\,CNR \rightarrow 0.7\,HgCl_2(CNR)_2 + 0.3\,HgCl_2(CNR)$	0.56	1.12	0.57	1.12
$CoCl_2$	$CoCl_2 + 2\,CNR \rightarrow CoCl_2(CNR)_2$	0.48	0.96	0.48	1.07
$FeCl_2$	$FeCl_2 + 2\,CNR \rightarrow FeCl_2(CNR)_2$	0.48	0.96	0.50	1.24
$CuCl_2 \cdot 2\,H_2O$	$2\,CuCl_2 + 5\,RNC + 2\,H_2O \rightarrow 2\,CuCl(CNR)_2 + HCl + CO_2 + RNH_3Cl$	0.40	0.60	0.30	0.54
$HAuCl_4 \cdot 3\,H_2O$	$HAuCl_4 + 2\,H_2O + 2\,RNC \rightarrow AuCl(CNR) + CO_2 + 2\,HCl + RNH_3Cl$	0.45	0.90	0.49	0.90
$Pt(cod)_2$	$Pt(cod)_2 + CNR \rightarrow Pt(CNR) + 2\,cod$	0.86	–	0.71	–
$Ni(cod)_2$	$Ni(cod)_2 + CNR \rightarrow Ni(CNR) + 2\,cod$	0.97 0.94*	–	1.07	–
$Pd(dba)_2$	$Pd(dba)_2 + 2\,CNR \rightarrow Pd(CNR)_2 + 2\,dba$	0.49	–	0.54	–
$(C_2H_4)Ni(PPh_3)_2$	$(C_2H_4)Ni(PPh_3)_2 + 2\,CNR \rightarrow (PPh_3)_2Ni(CNR)_2 + C_2H_4$	–	–	–	–
$[(cod)RhCl]_2$	$[(cod)RhCl]_2 + 4\,CNR \rightarrow (cod)RhCl(CNR) + RhCl(CNR)_3 + cod$	0.47	0.47	0.56	0.70
$[Rh(CO)_2Cl]_2$	$[Rh(CO)_2Cl]_2 + 3\,RNC \rightarrow Rh(CO)_2(CNR)Cl + Rh(CO)(CNR)_2Cl + CO$	0.61	0.61	0.69	0.86

* Calculated figure assuming oxidation to Ni(OCNR).

reasonable deductions to be made regarding the nature of the supported species (Table I). Several general points may be made:

- in no case are more than three isonitrile groups coordinated to a single metal atom
- the tendency towards metal reduction is reduced on the polymer compared to homogeneous solution
- there is a wide variation in the rates of complexation of different metal salts.

Table II. Infrared data.

Supported complex	Observed ν_{NC} (cm^{-1})	Model complex	Observed ν_{NC} (cm^{-1})	Reference
$RhCl_3 \cdot xH_2O$	2214	$[Rh(CNMe)_4]BPh_4$	2197	21
		$[Rh(CNMe)_4Cl_2]PF_6$	2280	45(b)
			2250	
		$[Rh(CNMe)_4I_2]BPh_4$	2265	21
		$Rh(CNMe)_3I_3$	2242	21
K_2PtCl_4	2222	*cis*-$PtCl_2(CNMe)_2$	2281	53
			2253	
		$[Bu_4N][PtCl_3(CNMe)]$	2240	53
		$[PtCl(CNMe)_3]PF_6$	2287	53
			2288	
			2308	
		$[Pt(CNMe)_4](PF_6)_2$	2322	53
			2314	
			2284	
$Na_2PdCl_4 \cdot 3H_2O$	2260	*cis*-$PdCl_2(CNMe)_2$	2280	53
		$[PdCl_2(CNp\text{-}tolyl)]_2$	2220	19
		$[PdCl(CNBu^t)_2]_2$	2166	18
$AgNO_3$	2220	$[Ag(CNCy)_2]ClO_4$	2215	23
$AgPF_6$	2238		2190	
		$[Ag(CNCy)_4]ClO_4$	2188	23
			2150	
		$[Ag(CNBu^t)_3]PF_6$	2241	26
			2184	
$HgCl_2$	2265	$HgCl_2(CNBu^t)$	2245	37
$CoCl_2$	2225	$CoCl_2(CNMe)_4$	2227	41
		$CoCl_2(CNMe)_2$	2260	41
		$[Co(CNMe)_5]ClO_4$	2198	54
			2139	
$FeCl_2$	2190	*cis*-$FeCl_2(CNp-MeOC_6H_4)_4$	2195	42(b)
			2160	
			2140	
$CuCl_2 \cdot 2H_2O$	2180	$[Cu(CNBu^t)_4(H_2O)_2](ClO_4)_2$	2233	27
		$[Cu(CNBu^t)_4]ClO_4$	2181	27
		$CuCl(CNp-MeOC_6H_4)_2$	2141	29
		$CuCl(CNCH_2SO_2C_6H_4Me)_2$	2193	55
			2152	
		$CuCl(CNBu^t)$	2189	30
$HAuCl_4 \cdot 3H_2O$	2250	$AuCl(CNCH_2Ph)$	2265	33
		$[Au(CNCy)_2]ClO_4$	2250	33
		$[Au(C_6F_5)_2(CNPh)_2]ClO_4$	2280	56
			2270	
$Pt(cod)_2$	2150	$Pt_3(CNBu^t)_6$	2155	47
			1714	
$Pd(dba)_2$	2197 (s)	$Pd_3(CNBu^t)_6$	2108	49
	2267 (sh)		1700	
		"$Pd(CNMe)_2$"	2185	51
$(C_2H_4)Ni(PPh_3)_2$	2015	$Ni(PPh_3)_2(CNBu^t)_2$	2048	57
			2000	
$[(cod)RhCl]_2$	2130 (sh)	$[(CNBu^t)_2RhCl]_2$	2230	58
	2165 (s)			
	2215 (sh)	RhCl(2,6-xylylNC)$_3$	2145	44(a)
			2105	
$[(CO)_2RhCl]_2$	2008* (s)	*cis*-$Rh(CO)_2(CNBu^t)Cl$	2223	45(a)
	2100* (w)		2101*	
	2197 (s)		2033*	
		trans-$Rh(CO)(CNBu^t)_2Cl$	2181	45(a)
			2011*	
		$[Rh(CNBu^t)_4]Cl$	2167	45(a)

* CO vibration.

(i) Nickel, platinum and palladium

Salts of both $PtCl_4^{2-}$ and $PdCl_4^{2-}$ are known to undergo substitution in aqueous solution with alkyl and aryl isonitriles to give highly coloured $[M(CNR)_4]MCl_4$ salts (also isolable as PF_6^- salts) which, at least in the case of Pt, undergo transformation on mild heating to give pale yellow, monomeric *cis*-$PtCl_2(CNR)_2$ (*trans* in the cases of the bromide and iodide) [16, 17]. Similar Pd complexes have been obtained from direct reaction of PdX_2 with isonitriles [18]. For the polymer supported Pt complex, the colour, analytical data and infrared are consistent with formulation as neutral, monomeric $PtCl_2(CNR)_2$. The stereochemistry is uncertain; the single infrared band may represent a *trans*-geometry or the broadness of the band may obscure the doublet structure expected for the *cis*-geometry. For the Pd complex, data show clearly a 1:1 Pd:CNR ratio, and as the intrared spectrum is not consistent with reduction to Pd(I), the supported complex seems best formulated as the dimer $Pd_2Cl_2(CNR)_2(\mu\text{-}Cl)_2$. Dimers of this type have been isolated from reaction of $PdCl_2(NCMe)_2$ with $PdCl_2(CNR)_2$ [19], and one other report of an analogues supported Pd-isonitrile complex also has a Pd:CNR ratio of 1:1 [7b].

Attempts to complex Ni(II) from aqueous tetrahydrofuran solutions of $NiCl_2 \cdot 6H_2O$ or from anhydrous tetrahydrofuran solutions of $NiCl_2$ yielded only unreacted polymer; Ni(II) is known to catalyse isonitrile polymerisation [20], but the recovered polymer shows no detectable decrease in the intensity of the NC stretching vibration.

(ii) Rhodium

Reaction of $RhCl_3 \cdot xH_2O$ with CH_3NC is known to yield initially a yellow solution from which $Rh(CNCH_3)_3I_3$ may be precipitated by addition of NaI, but which on standing undergoes reduction to yield salts of the $[Rh(CNCH_3)_4]^+$ cation [21]; these easily undergo oxidative addition with, for example, halogens to give $[Rh(CNCH_3)_4X_2]^+$ salts [22]. Data for the supported complex are consistent with formulation as unreduced $RhCl_3(CNR)_2(H_2O)$; though no exact model exists, infrared data are consistent with this stoichiometry, given the general decrease in NC stretching frequency with decreasing RNC:M ratio observed in model complexes of Pt and Pd. One molecule of water is included to maintain octahedral coordination; analytical data are not sufficiently precise to distinguish the presence of coordinated solvent or solvent of crystallization in any of the supported complexes described.

(iii) Copper, silver and gold

Reaction of silver salts with alkyl and aryl isonitriles generally is known to give complexes of stoichiometry $[Ag(CNR)_2]X$ and $[Ag(CNR)_4]X$ (X = ClO_4, NO_3, PF_6, BF_4) [23–25]. A crystal structure determination of an $[Ag(CNR)_2]PF_6$ derivative shows bidentate coordination of the PF_6^- anion [26]. Data indicate clearly that the supported silver complexes are $[Ag(CNR)_2]X$ (X = NO_3, PF_6).

Reactions of isonitriles with Cu(II) and Au(III) generally proceed with concomitant metal reduction and complexation. Though oxidation products of the isonitrile in homogeneous solution have not generally been well characterized, the half-cell may be regarded as a sequence of the reactions.

$$2RNC + 2H_2O \rightarrow 2RNCO + 4H^+ + 4e^- \quad (1)$$

$$RNCO + H_2O \rightarrow RNH_2 + CO_2 \quad (2)$$

$$RNH_2 + RNCO \rightarrow (RNH)_2CO \quad (3)$$

$$2RNC + 3H_2O \rightarrow CO_2 + (RNH)_2CO + 4H^+ + 4e^- \quad (4)$$

in which two electron oxidation to isocyanate is followed by hydrolysis and condensation to give the symmetrical urea.

Reaction (3) seems unlikely to occur on a polymer support and therefore the half-cell on the polymer seems best represented as

$$RNC + 2H_2O \rightarrow RNH_3^+ + H^+ + CO_2 + 2e^- \quad (5)$$

Though Cu(II)-isonitrile complexes are known [27], they decompose easily to yield $[Cu(CNR)_4]X$ where X is non-coordinating [27, 28]. Reaction of Cu(I) halides or pseudohalides with isonitriles yields a series of complexes $CuX(CNR)_y$ (y = 1–4) [24, 29–31] where y depends on both CNR and X. Infrared spectra of the supported complex clearly indicate Cu(I), and analytical data are most consistent with the reaction in Table I in which chlorine is retained on the polymer both as $CuCl(CNR)_2$ and RNH_3Cl. The presence of RNH_3Cl is not easily detected in the infrared due to a broad polymer absorption above 3100 cm^{-1}. There is certainly no trace of isocyanate (2250–2275 cm^{-1}) or urea (1660 cm^{-1}) absorptions.

Though unstable Au(III) complexes have been reported in early work [32], later work quotes only reduction to Au(I) in the presence of excess isonitrile [33] from which derivatives of stoichiometry AuCl(CNR) and $[Au(CNR)_2]X$ ($X = ClO_4$, BF_4) may be isolated [33, 34]. Infrared data for the polymer supported complex are clearly consistent with Au(I), and the reaction is best represented by reduction, followed by complexation as AuCl(CNR).

(iv) Zinc, cadmium and mercury

Though aryl isonitrile adducts of stoichiometry $MX_2(CNR)_2$ (M = Zn, Cd) are known [35, 32], we find no evidence for complexation of MCl_2 from aqueous tetrahydrofuran. Though the recovered polymer from the reaction with $ZnCl_2$ exhibits a pink colour, metal incorporation is negligible and the infrared spectrum shows only the NC stretching frequency of the starting polymer.

Mercury(II) complexes of stoichiometry $HgCl_2(CNR)_2$ and $HgCl_2(CNR)$ have been reported [24, 36, 37], but decompose to yield Hg_2Cl_2, polymerized isonitrile, and traces of products arising from transalkylation [38]; Hg(I)-isonitrile complexes are not isolated. Infrared and analytical data for the supported complex seem most consistent with a mixture of $HgCl_2(CNR)$ and $HgCl_2(CNR)_2$.

(v) Rates of complexation

Though kinetic data for homogeneous solution reactions are not available, complexation by the polymer supported isonitrile proceeds much more slowly, and at rates which differ greatly between metals, ranging from less than an hour for complete uptake of $HAuCl_4$ to several days for $RhCl_3 \cdot xH_2O$. From a qualitative analysis of the infrared spectra of samples taken before complete isonitrile uptake, the rates of precious metal complexation are in the order Rh<<Pd<Ag<Pt. With the possible exception of silver, this is not a result of differing rates of diffusion into the 9% cross-linked material, since a similar ordering (Rh<<Pd<Ag<Pt) and (with the exception of silver) similar rates are observed with 2% cross-linked material of similar loading. The results appear to reflect kinetic differences in the rates of substitution, and may be used as a basis for metal separation. Thus, the polymer recovered from extraction of metal from an equimolar solution of $RhCl_3 \cdot xH_2O$ and K_2PtCl_4 contains >96% platinum.

b) Complexation from organic media

Quantitative uptake of isonitrile is observed in the complexation of MCl_2 (M = Fe, Co) from anhydrous tetrahydrofuran solution to give complexes of stoichiometry $MCl_2(CNR)_2$. The reaction of Co(II) salts of non-coordinating anions with CH_3NC in aqueous is known to give salts of the $[Co_2(CNCH_3)_{10}]^{4+}$ dimer, though in solution in the presence of excess CH_3NC, $[Co(CNCH_3)_5H_2O]^{2+}$ may be detected [39]. Co(II) halides yield complexes of stoichiometry $CoX_2(CNR)_2$ and $CoX_2(CNR)_4$; the latter seem to possess monomeric *trans*-octahedral structures [40a–d] while the former are best formulated as $[Co(CNR)_4]CoX_4$ containing bridging halide [41]. Isolated Fe(II) complexes are of stoichiometry $Fe(CNR)_4X_2$ [40d, 42a–c], and no analogue of the polymer supported stoichiometry has been reported. Although a recent preparation of $MnX_2(CNBu^t)$ adducts has been described [43], we observe no complexation by **3** from tetrahydrofuran solutions of $MnCl_2$.

The Rh dimers $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) and $[Rh(CO)_2Cl]_2$ react rapidly with **3** in toluene to yield supported complexes whose infrared spectra are shown in Fig. 1. For the cod complex, gas chromatographic analysis of the supernatant liquid shows the release of about *one* mole of cod per mole of dimer; the results are consistent with initial bridge cleavage followed by partial displacement of cod to give a mixture of supported Rh(cod)(CNR)Cl and $Rh(CNR)_3Cl$. Reaction of $[Rh(cod)Cl]_2$ with isonitriles in solution generally yields salts of the $[Rh(CNR)_4]^+$ cation, though the reaction may be stopped at the $Rh(CNR)_3Cl$ stage in the case of bulky isonitrile ligands [44a, b]. Reaction of $[Rh(CO)_2Cl]_2$ with Bu^tNC is known to yield sequentially *cis*-$Rh(CO)_2(CNR)Cl$, *trans*-$Rh(CO)(CNR)_2Cl$ and $[Rh(CNR)_4]Cl$ [45a–c]; the band at 2100 cm^{-1} in the spectrum of the supported complex indicates the presence of $Rh(CO)_2(CNR)Cl$, though the most intense bands at 2008 and 2197 cm^{-1} may be assigned to $Rh(CO)(CNR)_2Cl$ [46]. This reaction also proceeds *via* bridge cleavage followed by partial ligand substitution (in this case, CO).

Zerovalent isonitrile derivatives of the nickel group have been intensively studied. Whereas $(cod)_2Pt$ reacts with alkyl isonitriles to give

$Pt_3(CNR)_6$ trimers [47], $Ni(cod)_2$ reacts with sterically demanding isonitriles to give $Ni(CNR)_4$, $Ni_4(CNR)_n$ (n = 6, 7; R = Bu^t, Pr^i) and $Ni_2(CNR)_3$ (R = Pr^i). Reaction with less bulky ligands yields $Ni(CNR)_4$ (R = Me, Et, Bu^n, CH_2Ph) together with insoluble, highly coloured polymers of approximate composition Ni(CNR) which exhibit bridging isonitrile stretching frequencies [48a, b]. The nickel complexes are particularly air sensitive, reacting with oxygen to give $(RNC)_2NiO_2$ adducts; oxygen transfer occurs easily with release of RNCO to give $Ni(RNCO)_n$ polymers. Displacement with further isonitrile to regenerate $Ni(CNR)_4$ provides a catalytic cycle for oxidation of isonitrile [49]. Reaction of $(cod)_2Ni$ and $(cod)_2Pt$ with polymer **3** occurs with quantitative displacement of cod (as shown by gas chromatography) to yield supported complexes of stoichiometry M(CNR), and a complex exhibiting an identical infrared spectrum can be obtained from the reaction of $Pt_3(CNBu^t)_6$ with **3,** a reaction which is accompanied by quantitative release of $CNBu^t$. While the supported Pt complex exhibits a well defined CN vibration, the Ni derivative shows only a very broad band centred at 2205 cm^{-1}, together with a small absorption at 2140 cm^{-1} due to free isonitrile. Due to unavoidable oxidation during preparation for spectroscopy, the infrared is most consistent with Ni(RNCO) as the supported species; long exposure to air results in a colour change from red to the green of Ni(II). There would appear to be no reported analogue of the supported Pt(CNR) stoichiometry; the absence of a bridging CN vibration may indicate the presence of coordinated toluene of intrapolymer coordination of the phenyl ring to the metal to maintain a higher coordinative saturation.

Complexes of stoichiometry $Pd(CNR)_2$, which appear to be trimeric and isostructural with $Pt_3(CNR)_6$, may be isolated from the reduction of Pd(II) with alkyl isonitriles [49, 50a, b] or from the reaction of $Pd(dba)_2$ with CH_3NC [51]. The latter reaction also yields, polymeric, insoluble complexes of unspecified stoichiometry which exhibit only terminal CN vibrations; the product obtained from the reaction of **3** with $Pd(dba)_2$, of stoichiometry $Pd(CNR)_2$, has an infrared spectrum consistent with this.

Reactions of all the organometallic complexes described in section (c) with polymer **2** yield products exhibiting identical infrared spectra; the difference in chain length appears to have no discernable effect on the complexing properties of the polymer.

(c) Catalysis [46]

The supported Rh(I) complexes have been investigated as potential catalysts for the hydrogenation of cyclohexene. Under the conditions used (1 atm H_2, 60 °C) only the complex derived from $[(cod)RhCl]_2$ was found to be active. Though the reaction proceeds cleanly with no loss of metal, observations indicate that some or all of the catalysis proceeds *via* reduction to metal accompanied by metal crystallite formation. Induction periods of about 100 min are observed, after which catalytic activity increases with time [52]. There is also a large decrease in the intensity of the CN vibration at 2165 cm^{-1} (Fig. 1), together with appearance of a band at 2230 cm^{-1}. These changes are similar to those seen on hydrogenation using a silica supported Rh-isonitrile complex [4] and are indicate of hydrogenation of isonitrile coupled perhaps with metal catalysed isomerisation to the nitrile.

III. Experimental

Polystyrene (2% cross-linked) and chloromethylated polystyrene (2% cross-linked, 1.04 mmol g^{-1}) were obtained from Eastman-Kodak and Peninsular Laboratories respectively. Methyl isonitrile [59], *p*-vinylbenzamide [60], $Ni(cod)_2$ [61], $Pt(cod)_2$ [62], $Pt_3(CNBu^t)_6$ [47], $(C_2H_4)Ni(PPh_3)_2$ [63], $Pt(dba)_2$ [64], $[Rh(CO)_2Cl]_2$ [65], and $[Rh(cod)Cl]_2$ [66] were prepared by literature methods. BuLi was titrated before use [67]. Other chemicals were obtained commercially; chloromethylstyrene was used as a 60/40 *meta/para* mixture.

NMR and infrared spectra were recorded on JEOL FX-100 and Pye Unicam SP2000 spectrometers, respectively. Metal, phosphorus and chlorine analyses were performed by the Microanalytical Laboratory, University of Manchester.

(a) Preparation of **2** *from chloromethylated polystyrene and* $LiCH_2NC$

A 500 ml flask was charged with 70 ml of sodium-dried THF under a nitrogen atmosphere and 11.2 ml of 1.64 M BuLi in hexane (18.4 mmoles) was added by syringe. After cooling to −70 °C, a solution of 1.0 ml of CH_3NC (0.76 g, 18.5 mmoles) in 20 ml dry THF was added dropwise by syringe and stirred for 30 min; some precipitation of the $LiCH_2NC$ so formed is observed. A swollen suspension of 10 g of chloromethylated polystyrene (**1**) (10.6 mmoles Cl) in 100 ml of dry THF was added slowly *via* a dropping funnel; after stirring for 30 min, the suspension

was allowed to warm to room temperature and refluxed for 1 h. After cooling, the polymer was filtered, washed with wet acetone (2×60 ml), water (2×60 ml) and dry acetone (2×40 ml) and dried under vacuum to give (**2**) as a light yellow powder.

Analysis

Calcd	C 89.8	H 7.7	N 1.6,
Found	C 90.9	H 7.5	N 1.6.

Titration of the isonitrile content was performed by suspension and swelling of 0.1 g of polymer in 5 ml of 1:1 ethyl acetate/dichloromethane, followed by addition of 3 ml of 0.1 M HSCN in ethyl acetate which had previously been standardized by titration against 0.1 M NEt_3. After standing for 30 min, indicator (0.2% solution of methylene blue and neutral red (1:1) in methanol) and dimethylformamide (2 ml) were added and the excess HSCN back-titrated against standard NEt_3. Isonitrile contents of various batches were in the range 0.6 to 0.9 mmol g^{-1}.

Infrared (KBr): ν_{NC} 2140 cm^{-1}.

(b) Monomer preparations

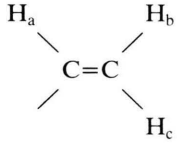
(i) N-(m/p-vinyl)benzylphthalimide (**5**): Potassium phthalimide (32 g, 0.17 mol) was dissolved at 40 °C in dimethylformamide (300 ml) previously dried and distilled from P_2O_5. Chloromethylstyrene (**4**) (25 g, 0.16 mol) was then added and the mixture stirred at 40 °C for 2 h and left overnight at room temperature. The resulting white precipitate was filtered and washed with dimethylformamide (100 ml). $CHCl_3$ (300 ml) was added to the filtrate which was mixed with water (600 ml). The aqueous layer was separated and washed with $CHCl_3$, and the combined organic layer was washed with 2 M NaOH. After drying over $MgSO_4$, solvent was removed under vacuum and the product crystallized from $CHCl_3$/petroleum ether (40–60) to give 36.8 g of (**5**) (85%).

Analysis

Calcd	C 77.5	H 4.94	N 5.32,
Found	C 77.7	H 4.97	N 5.34.

Infrared (KBr): ν_{CO} 1720 cm^{-1} (s), 1775 (w).

NMR ($CDCl_3$) 7.60–7.85 (m), phthalimide; 7.23–7.43 (m), Ph;



H_a 6.66 (dd), J_{ab} = 10.8 Hz;
H_b 5.20 (dd), J_{ac} = 17.6;
H_c 5.72 (dd), J_{bc} = 1.0.

(Resonances due to *m*-isomer only.)

(ii) (p-Vinyl)benzylformamide (**11b**): *p*-Vinylbenzamide (**10**) (11.9 g, 0.08 mol) was placed in the thimble of a sohxlet apparatus. $LiAlH_4$ (6.79 g, 0.18 mol) dissolved in dry Et_2O (750 ml) was placed in the flask and the contents of the thimble extracted by refluxing over a period of two days. Excess $LiAlH_4$ was destroyed by careful addition of water; after filtration, the aqueous layer was separated, washed with ether, and the combined organic layer dried over $MgSO_4$. Removal of solvent yielded 6.1 g of crude (**9b**) (57%) as a viscous liquid. A spectroscopically pure sample was microdistilled from KOH.

Infrared (thin film): ν_{NH} 3360 cm^{-1} (br).

NMR ($CDCl_3$): 7.23–7.41 (m), Ph; 3.80 (s), CH_2; 1.47 (s), NH_2; 6.63 (dd), H_a; 5.15 (dd), H_b; 5.65 (dd), H_c; J_{ab} = 10.8, J_{ac} = 17.7, J_{bc} = 1.1 Hz.

The crude amine (6.1 g, 0.046 mol) was cooled in ice in a 100 ml flask and ethyl formate (3.4 g, 0.0458 mol) was added dropwise with stirring. After refluxing for 2 h, the mixture was stirred at room temperature overnight. Ethanol and unreacted ethyl formate were removed under vacuum and the residue crystallized from $CHCl_3$/petroleum ether (40–60) to give 5.6 g of (**11b**) (76%).

Analysis

Calcd	C 74.5	H 6.83	N 8.70,
Found	C 74.7	H 6.63	N 8.75.

Infrared (KBr): ν_{CO}, 1670 cm^{-1}; ν_{NH}, 3300 cm^{-1}.

NMR ($CDCl_3$): 7.04–7.28 (m), Ph; 4.31 (d), CH_2 (J_{NH} = 5.8 Hz); 5.90 (s, br), NH; 8.10 (s), CHO; 6.55 (dd), H_a; 5.10 (dd), H_b; 5.60 (dd), H_c; J_{ab} = 10.7, J_{ac} = 17.7, J_{bc} = 0.9 Hz.

Minor resonances assignable to a small amount of *cis*-conformer may also be observed [68].

(iii) (m/p-Vinyl)benzylformamide (**11a**): The phthalimide (**5**) (10 g, 0.041 mol) was dissolved in ethanol (350 ml) at 40 °C; hydrazine hydrate (3 ml, 0.06 mol) was added and the mixture stirred overnight at 40 °C. The white solid which formed was filtered, suspended in water (200 ml) and stirred with dilute HCl (~50 ml) for 1 h. Remaining solid was filtered off, and the filtrate made basic by addition of 50% KOH. This was extracted with CH_2Cl_2 (3×50 ml) and dried over $MgSO_4$.

Ethanol was removed from the original filtrate under vacuum; the residual off-white solid was dissolved in MeOH/H_2O (300 ml) and filtered. After addition of CH_2Cl_2, the solution was treated with 50% KOH (50 ml), the organic layer separated, and the aqueous layer washed with CH_2Cl_2. After drying over $MgSO_4$, this was combined with the CH_2Cl_2 fraction above. Removal of solvent gave 2.1 g of **9a** (42%) as a viscous oil. This was converted into (*m/p*-vinyl)benzylformamide (**11a**) by the procedure described in (ii). NMR spectra are identical to those of

9b and **11b**, with additional resonances due to the meta isomer being observed.

(c) Polymerisation of **5**

This was performed under N_2 in 1 l baffled flask equipped with a high shear stirrer operating at 914 rpm.

The flask was charged with 500 ml of distilled water; after warming to 70 °C, surfactant [1.2 g of copoly(styrene-maleic anhydride)] was added. The monomer mix was prepared from appropriate amounts of styrene, divinylbenzene and the phthalimide (**5**) (see Table). After addition of benzoyl peroxide (0.5 g) and diluent (if used) the monomer mixture was added in one portion to the flask and stirred for 5 h at 70 °C. The product was collected by filtration and washed successively with water, 30 and 50% methylated spirit/water and finally acetone. After Soxhlet extraction with CH_2Cl_2, the white powder was dried under vacuum at 40 °C.

Infrared (KBr): ν_{CO} 1720 (s), 1775 (w) cm^{-1}.

Gel permeation chromatography of the macroporous 52% cross-linked material showed an exclusion limit of ~700 consistent with a pore size of approximately 50 Å.

(d) Preparation of **3**

Polymer supported phthalimide (**6**) (9% cross-linked; 27 g, 0.029 mol phthalimide) was suspended in ethanol (400 ml) and hydrazine hydrate (30 ml, 0.62 mol) was added. The mixture was stirred and refluxed for 24 h, filtered and washed with water to remove the white precipitate which had formed. The white polymer was then washed with ethanol, ether and dichloromethane, and dried under vacuum. Amine content was performed by picrate determination.

Polymer supported amine **7** (20 g, 0.029 mol amine) was converted to **8** by suspension in ethyl formate (170 ml), followed by refluxing for 24 h. The white polymer was filtered, washed with diethyl ether and pentane, and dried under vacuum.

Infrared (KBr): ν_{CO} 1670 cm^{-1}.

Polymer supported formamide **8** (7 g, 0.01 mol formamide) was converted to the isonitrile **3** by swelling in dichloromethane, (70 ml), followed by addition of *p*-toluenesulphonyl chloride (12.5 g, 0.066 mol, freshly recrystallized). Pyridine (280 ml, distilled from KOH) and aniline (2 ml) were added and the suspension stirred under N_2 for 16 h. The light yellow polymer was filtered, washed with water, ethanol and CH_2Cl_2, and dried under vacuum. Isonitrile content was determined by titration as previously described.

Infrared (KBr): ν_{NC} 2140 cm^{-1}.

Polymer data

	cross-linked 2%	9%	52%
Amount (**5**) (grams; mole %)	3.68 g 13.9%	7.89 g 14.1%	1.84 g 14.0%
Amount styrene (grams; mole %)	8.74 g 83.2%	15.9 g 71.9%	0.26 g 5.0%
Amount divinylbenzene (grams; mole %)	0.26 g 1.98%	2.46 g 8.83%	3.35 g 52.0%
Diluent	none	none	toluene (15 ml)
Analytical figures for **6**	C – 85.2 H – 6.25 N – 2.18	86.4 7.00 1.79	86.3 7.35 1.60
Phthalimide content of **6** ($mmol\,g^{-1}$)	1.56	1.27	1.14
Amine content of **7** ($mmol\,g^{-1}$)	1.86	1.21	0.77
Isonitrile content of **3** ($mmol\,g^{-1}$)	0.90	0.84	–

[a] Based on 63% divinylbenzene content of commercial sample.

(e) Metal complexation

Polymer **3** (0.2 g, 0.2 mmol NC) was swollen in tetrahydrofuran (5 ml) and $Na_2PdCl_4 \cdot 3H_2O$ (0.17 g, 0.49 mmol) dissolved in distilled water (5 ml) was added to the polymer and the mixture stirred overnight. The polymer was filtered, washed with water, ethanol, diethyl ether and CH_2Cl_2, and dried under vacuum for 24 h. The same procedure was followed for K_2PtCl_4, $RhCl_3 \cdot xH_2O$, $HAuCl_4 \cdot 3H_2O$, $AgPF_6$, $AgNO_3$, $CuCl_2 \cdot 2H_2O$ and $HgCl_2$. For rate measurement, samples were removed periodically and purified as above. Using a dry bag, the same procedure was followed for the complexation of anhydrous $CoCl_2$ and $FeCl_2$ from dry THF, except that the complexed polymer was washed with THF and CH_2Cl_2 before drying under vacuum.

Organometallic complexes were reacted with **3** in the same way under nitrogen in either dry THF [$Pd(dba)_2$, $(C_2H_4)Ni(PPh_3)_2$] or dry toluene [$Pt(cod)_2$, $Ni(cod)_2$, $Pt_3(CNBu^t)_6$, $[Rh(CO)_2Cl]_2$, $[Rh(cod)Cl]_2$] followed by washing with THF or toluene, then CH_2Cl_2 and drying under vacuum. Released cod and Bu^tNC were determined by gas chromatographic analysis by calibration with solutions of known concentration.

Analytical data

Metal complex	Product* colour	Isonitrile content of polymer used		
		Metal [%]	Cl or P [%]	
$RhCl_3 \cdot xH_2O$	pale orange	2.8	3.5	0.56
K_2PtCl_4	light brown	7.9	2.8	0.90
$Na_2PdCl_4 \cdot 3H_2O$	red brown	10.1	5.1	1.03
$AgNO_3$	off white	6.4	–	1.03
$AgPF_6$	off white	4.4	1.1	0.90
$HAuCl_4 \cdot 3H_2O$	off white	9.7	3.2	0.90
$CuCl_2 \cdot 2H_2O$	off white	1.9	1.9	1.03
$HgCl_2$	pale yellow	11.5	4.0	1.03
$CoCl_2$	turquoise	2.8	3.8	1.03
$FeCl_2$	pale yellow	2.8	4.4	1.03
$Pd(dba)_2$	dark brown	5.7	–	1.03
$Pt(cod)_2$	orange brown	13.9	–	1.03
$[(cod)RhCl]_2$	pale orange	5.8	2.5	1.03
$Ni(cod)_2$	red**	6.3	–	1.03
$(C_2H_4)Ni(PPh_3)_2$	red brown	–	–	0.5
$[(CO)_2RhCl]_2$	brown	7.0	3.1	1.03

* Colour of original polymer is yellow-orange;
** turns to yellow-green on prolonged air exposure.

(f) Hydrogenation of cyclohexene

The polymer supported $[(cod)RhCl]_2$ complex (2.4% Rh, 0.12 g) was swollen in toluene (2 ml) for 5 min and 1 ml of a 7.3 M solution of cyclohexene in toluene was added. The solution was rapidly stirred under 1 atm H_2 at 60 °C until H_2 uptake ceased. Complete conversion of cyclohexene to cyclohexane was confirmed by gas chromatography.

Rh analysis after catalysis: 2.4%.

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