Preparation and Characterisation of Some Nickel(II) Tetra-aza Macrocyclic Complexes bearing Pendant Polymerisable Groups as Part of the Ligand Superstructure

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The synthesis and characterisation of some new nickel(II) macrocyclic complexes of the 'lacunar' type have been performed where the ligand has, as part of the ligand superstructure, either 4-vinylphenyl or allyl groups capable of undergoing polymerisation reactions with selected comonomers. The n.m.r. spectra of a number of these new complexes show them to be fluxional on the n.m.r. time-scale and the nature of this fluxional behaviour is discussed. Some copolymerisation reactions of these complexes, with styrene or methyl methacrylate comonomers, have been performed.

The preparation and reactions of synthetic macrocyclic ligands have been topics of growing importance in co-ordination chemistry. Macrocyclic multidentate ligands are particularly useful species due to the high kinetic and thermodynamic stability of many of their complexes.[1] A variety of uses has been proposed for such complexes including the selective extraction of metal ions from solution[2] and the production of novel catalysts for diverse reactions, such as the hydrolysis or oxidation of organic substrates.[3] Recently Busch and co-workers have reported a series of papers concerning a family of 'lacunar cyclidene' complexes that illustrate the ease with which structural variation can be introduced into complexes *via* the peripheral substituents (or superstructure) of the parent ligand.[4] The cobalt(II) and iron(II) complexes of some of these ligands possess a defined molecular cavity about one co-ordination site of the metal ion and have proved to be very effective in the reversible binding of dioxygen in the solution phase.[5] This work has added to the growing list of complexes that reversibly interact with O_2 under controlled conditions.[6]

In general, however, solution-based carriers of dioxygen have restricted lifetimes which has limited the utility of these species. This is a result of two deleterious decomposition processes: (*a*) dimerisation of metal centres *via* a μ-peroxo bridge; (*b*) proton-promoted oxidation of the metal centre.[7] It has been proposed that incorporation of dioxygen-reactive complexes within synthetic polymer matrices will serve to inhibit the decomposition processes, utilising the bulk of the polymer (*i*) to keep the complexes apart and (*ii*) provide a hydrophobic environment for the co-ordinated O_2.[8] Four methods have been adopted for the inclusion of metal complexes into synthetic polymer structures: (1) simple dispersion of the complex; (2) binding *via* a co-ordinate bond from a polymer-bound ligand (for example, with copolymers of 4-vinylpyridine); (3) covalent attachment by reaction of a functionalised complex with a functionalised polymer, and (4) co-polymerisation of a complex bearing a polymerisable group with selected comonomers.

All of these methods have been used to incorporate oxygen-active complexes into polymer networks. While systems formed by methods (1) and (2) demonstrate that dioxygen will bind to a complex within a polymer matrix, the lifetimes of the active species are relatively short, presumably because the complexes have a high degree of mobility inside the polymer and thus dimerisation of metal centres is still possible.[9] Utilisation of methods (3) and (4) should serve to anchor the complexes to the polymer backbone and thereby substantially decrease their mobility. Very recently covalent attachment of complexes using methods (3) and (4) has been reported for some cobalt(II) Schiff-base complexes and an iron(II) porphyrin complex and reversible binding of O_2 has been demonstrated.[10–12]

Since we are interested in general in the covalent binding of macrocyclic complexes to synthetic polymers we have investigated the incorporation into polymer structures of non-porphyrin macrocyclic complexes of the lacunar type. In this paper we report the synthesis and characterisation of some new nickel(II) macrocyclic complexes which bear polymerisable groups as part of the ligand superstructure [structures (**I**)—(**III**)]. These species display some interesting fluxional behaviour on the n.m.r. time-scale. We also report the results of some copolymerisation reactions with these novel difunctional monomers.

Results and Discussion

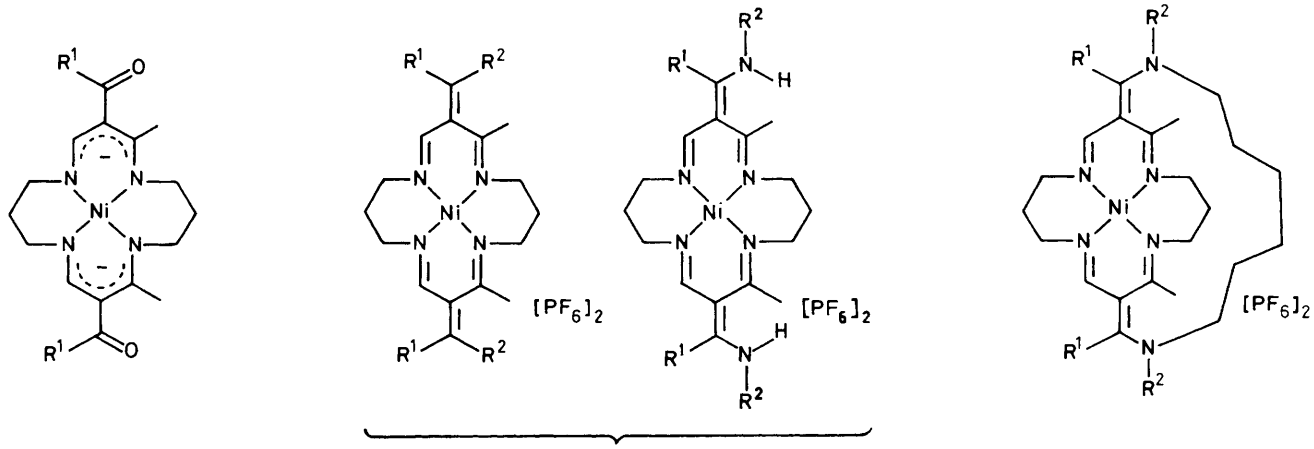
Synthesis of the Complexes.—Two new families of tetra-aza macrocyclic complexes are reported which bear polymerisable groups as part of the ligand superstructure. The new complexes (**2**)—(**6**) and (**8**)—(**10**) are illustrated in structures (**I**)—(**III**). The polymerisable groups selected for study in this work are (*a*) 4-vinylphenyl, in the R^1 position of the structure or (*b*) allyl in the R^2 position.

Both families of complexes are prepared using as the starting material the sixteen-membered macrocyclic complex (**1**), originally synthesised by Jäger,[13] and following procedures similar to those developed by Busch and co-workers.[5]

The preparation of the vinylphenyl-substituted family (**2**)—(**6**) and (**9**) is shown in Schemes 1 and 2. Complex (**11**), prepared from (**1**) by literature procedures,[14] reacts readily with 4-vinylbenzoyl chloride in the presence of triethylamine to produce complex (**2**) as a red solid. In common with other macrocyclic ligands with keto groups as part of their structure, complex (**2**) undergoes methylation at the keto oxygen atoms with powerful alkylating agents; in this case methyl trifluoromethanesulphonate proved to be a very efficient reagent. The product of methylation, the methyl vinyl ether complex (**3**), is a cationic species and is isolated as the hexafluorophosphate(V) salt.

Reaction of complex (**3**) in MeCN solution with either gaseous methylamine, n-propylamine, or isopropylamine produces the corresponding secondary amine substituted complexes (**4**)—(**6**) as orange solids.

Formation of the bridged complex (**9**) has been achieved by



(I) (II) (III)

R¹	R¹	R²	R¹	R²	R¹	R²
(1) Me	(3) 4-CH_2=CHC_6H_4	OMe	(4) 4-CH_2=CHC_6H_4	Me	(9) 4-CH_2=CHC_6H_4	Me
(2) 4-CH_2=CHC_6H_4			(5) 4-CH_2=CHC_6H_4	Pr^n	(10) Me	CH_2=$CHCH_2$
			(6) 4-CH_2=CHC_6H_4	Pr^i		
	(7) Me	OMe				
			(8) Me	CH_2=$CHCH_2$		

two routes: (*a*) direct reaction of the vinyl ether complex (**3**) with *N*,*N*′-dimethylhexane-1,6-diamine, in MeCN solution at high dilution, or (*b*) deprotonation of the secondary amine complex (**4**) with potassium t-butoxide followed by reaction with hexane-1,6-bis(toluene-*p*-sulphonate), again at high dilution. The products of the two reactions are spectroscopically identical but procedure (*b*) gave the material in higher purity. The lower purity of the product of route (*a*) is ascribed to partial hydrolysis of the methyl vinyl ether complex (**3**) during the relatively slow bridging reaction. This leads to a complex mixture of by-products including unbridged species which are difficult to separate from the desired product.

The allyl-substituted complexes (**8**) and (**10**) are also prepared by the procedure outlined in Scheme 2. Methylation of (**1**) with methyl trifluoromethanesulphonate produces the known complex (**7**) in very good yield. Reaction of (**7**) with allylamine proceeds smoothly to produce complex (**8**). An analogous complex has been reported starting from the corresponding fifteen-membered macrocyclic parent.[15] Complex (**8**) can be deprotonated and bridged by the procedure described above to produce (**10**) as yellow-orange crystals.

It is worthy of note that these synthetic procedures produce complexes capable of being incorporated into the polymer structure that are either neutral, (**2**), or charged, (**3**)—(**6**), and (**8**)—(**10**).

Characterisation.—Neutral complex (**2**).The electronic spectrum of complex (**2**) in chloroform solution has a band at $\lambda_{max.}$ 336 nm which is characteristic of this type of nickel(II) N_4 square-planar complex.[5] The i.r. spectrum has absorptions at 1 614 [ν(C=O)], 1 602 [ν(C=N)], and 1 565, 1 542, and 1 495 cm^{-1} [ν(C=C)].

The complex is most readily characterised by a combination of ^1H and ^{13}C n.m.r. spectroscopies. The relative simplicity of the spectra clearly indicates the mirror symmetry associated with complexes of this type. The ^{13}C n.m.r. spectrum is readily assigned with the aid of a DEPT (distortionless enhancement of polarisation transfer) pulse-sequence experiment. The chemical shifts and assignments of the spectra are given in Tables 1 (^{13}C) and 2 (^1H).

As expected the spectra are similar to those reported for other complexes of the same general structure. The successful incorporation of the vinylphenyl group into the macrocyclic ligand is indicated by the appearance of resonances characteristic of the vinyl moiety at 114.7 and 136.3 p.p.m. in the ^{13}C spectrum and at 5.28, 5.77, and 6.70, with the expected AMX splitting pattern, in the ^1H spectrum. The *para*-substituted aromatic ring of the vinylphenyl group appears as a sharp series of signals with the splitting pattern typical of a AA′BB′ spin system. The significance of this result is discussed below.

Unbridged complexes (**3**)—(**8**). The known vinyl ether complex (**7**) and the vinylphenyl substituted analogue (**3**) display characteristic bands in their i.r. spectra (Table 3) with a peak evident at *ca.* 1 030 cm^{-1}, assigned to the ν(C–O) vibration. Two bands, at 840 and 560 cm^{-1}, are due to vibrations of the PF_6^- counter ion. The complexes are further characterised by n.m.r. spectroscopy and the results are included in Tables 1 and 2. The most significant result is the appearance of resonances due to the OMe group, at *ca.* 60 p.p.m. in the ^{13}C spectrum and *ca.* 4 in the ^1H spectrum.

The i.r. spectra of the secondary amine complexes (**4**)—(**6**) (Table 3) show the appearance of a peak corresponding to the N–H vibration at *ca.* 3 400 cm^{-1}. The ^{13}C and ^1H n.m.r. spectroscopic data are included in Tables 1 and 2. The normal probe-temperature spectra of these three derivatives contain a number of broad signals which sharpen up considerably as the temperature is raised, indicating fluxional behaviour within the ligand superstructure. The nature of this fluxionality is discussed below. Despite the occurrence of these broad resonances, the complexes are adequately characterised by the n.m.r. spectroscopic data which indicate that the vinylphenyl group maintains its integrity during the formation of the secondary amine complexes and show the appearance of signals that can be assigned to the alkyl groups of the various amines. One feature that appears to be unique to these secondary amine

Table 1. Carbon-13 n.m.r. data for the complexes[a]

Complex	1	2	3	4	5	6	7	8	9	a	b	c	d	e	f	X
(2)[b]	192.2	115.1	160.6	167.6	19.7	54.5	50.1	30.4	29.1	138.9	128.6	125.7	142.3	136.3	114.7	
(3)	178.6	119.6	165.3	174.2	22.6	56.6	51.9	30.1	29.3	129.8	131.0	128.0	142.1	136.7	117.9	60.7 (OMe)
(4)	171.9[c]	111.0[c]	162.4	169.2	21.0	56.2	51.7	30.3[d]	30.3[d]	131.8[c,d]	131.8[c,d]	128.0	142.6[c]	136.8	117.8	35.6[c] (NHMe)
(5)	169.1[c,d]	114.0[c]	162.3	169.1[c,d]	20.8[c]	56.0	51.6	30.2[d]	30.2[d]	131.0[c,d]	131.0[c,d]	127.9	142.0[c]	136.7	117.7	49.1,[c] 23.8, 11.8[c] ($NHPr^n$)
(6)	169.0[c,d]	136.6[c]	162.2	169.0[c,d]	20.7[c]	55.9	51.7	30.2[d]	30.2[d]	130.8[c,d]	130.8[c,d]	127.9	141.7[c]	136.8	117.5	49.9,[c] 22.9[c] ($NHPr^i$)
(7)	180.6	117.8	164.2	173.7	22.5	57.1	51.6	30.2	29.3	16.0						58.3 (OMe)
(8)	168.8[d]	112.8[c]	160.1	168.8[c]	20.9	56.3	51.6	30.7	30.2	15.4[c]						138.5, 119.1, 47.9[c] (NH allyl)
(9)	173.5	112.7	162.9	168.7	21.0	56.0	51.4	30.5	29.9	133.8	131.3[c]	127.8[c]	141.7	136.7	117.4	57.4, 42.1, 24.9, 24.3 [2X = $MeN(CH_2)_6NMe$]
(10)	173.2	111.6	160.5	167.8	21.0	56.4	51.5	30.7	30.3	19.8						132.8, 120.9, 55.0, 55.5, 25.9, 24.6 [2X = $N(allyl)(CH_2)_6N(allyl)$]

[a] In CD_3CN solution, unless noted otherwise. [b] In $CDCl_3$ solution. [c] Broad. [d] Overlapping with another signal.

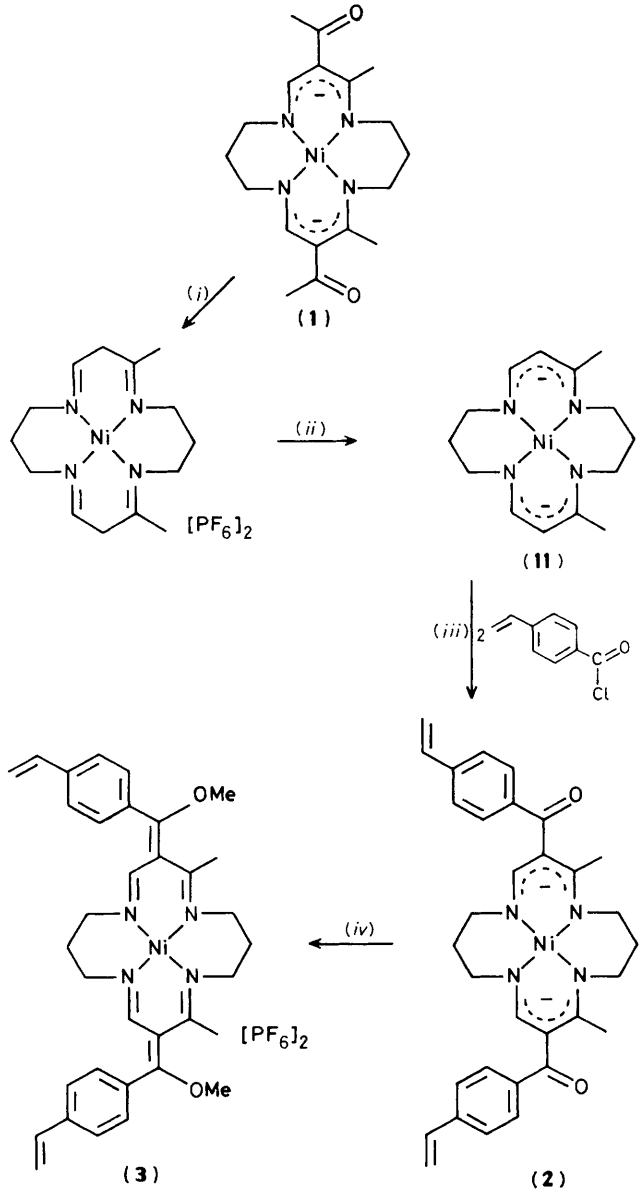
Table 2. Proton n.m.r. data for the complexes[a]

Complex	3	5	6	7	8	9	b,c	a	e	f	X
(2)[b]	7.21	2.08	2.98	2.90	1.80	2.90	7.45		6.70	5.28, 5.77	
(3)	7.15	2.44	3.33	3.22	2.19	2.19	7.62		6.91	5.48, 6.06	3.83 (OMe)
(4)	6.92[c]	2.10[c]	3.10[c]	3.10[c]	1.60	2.25[c]	7.60[c]		6.85	5.42, 5.97	3.15,[c] 7.33[c] (NHMe)
(5)	6.80[c]	2.20[c]	3.11[c]	3.11[c]	1.60	2.25[c]	7.55[c]		6.85	5.42, 5.96	3.45, 1.20, 0.90 ($NHPr^n$)
(6)	6.70[c]	2.20	3.11[c]	3.00[c]	1.60	2.30[c]	7.60[c]		6.85	5.41, 5.97	3.55, 1.25, 6.70[c] ($NHPr^i$)
(7)	7.75	2.40	3.52	3.08	2.15	2.15		2.20			4.05 (OMe)
(8)	7.52	2.31	3.36	3.05	1.87	3.05		2.15			7.55,[c] 5.95, 5.30, 4.10[c] [NH(allyl)]
(9)	6.57	2.18	3.0—3.3	2.65, 3.35	1.85	2.4	7.53[c]		6.85	5.41, 5.95	3.90, 3.50, 2.95, 1.85, 1.70 [2X = $MeN(CH_2)_6NMe$]
(10)	7.52	2.45	3.52	3.20	1.65	2.25		1.94			5.90, 5.37, 4.30, 3.60, 1.65, 1.48 [2X = $N(allyl)(CH_2)_6N(allyl)$]

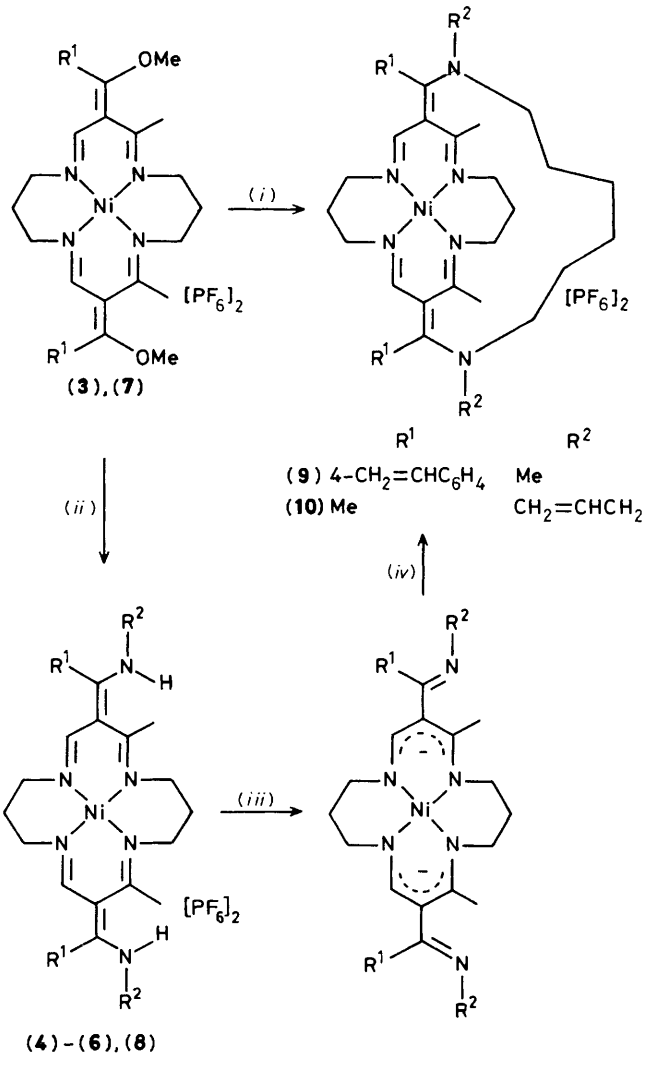
[a] In CD_3CN solution, unless otherwise noted. Number or letter refers to carbon atom to which a proton is bonded. [b] In $CDCl_3$ solution. [c] Broad.

Table 3. Infrared spectroscopic data (cm^{-1})

Complex	ν(N–H)	ν(C=N)	ν(C=C)	ν(C–O)	ν(PF_6^-)
(3)		1 625	1 564, 1 497	1 031	840, 560
(4)	3 401	1 611	1 575		840, 560
(7)		1 625	1 570	1 029	840, 560
(8)	3 390	1 580			840, 560
(9)		1 610	1 534		840, 560
(10)		1 608	1 530		840, 560



Scheme 1. (*i*) Toluene-*p*-sulphonic acid hydrate–methanol, then NH_4PF_6–water; (*ii*) 2KOBu^t–MeOH; (*iii*) NEt_3, Et_2O; (*iv*) $MeOSO_2CF_3$–CH_2Cl_2, then NH_4PF_6–EtOH



Scheme 2. (*i*) For R^1 = 4-CH_2=CHC_6H_4, MeHN$(CH_2)_6$NHMe–MeCN; (*ii*) R^3NH_2–MeCN; (*iii*) 2KOBu^t–MeOH; (*iv*) hexane-1,6-bis(toluene-*p*-sulphonate)–MeCN

complexes is that the ^{13}C n.m.r. spectra contain only one signal for carbon atoms 8 and 9. For all of the other complexes the two carbon atoms appear as separate signals, separated by *ca.* 0.5—1 p.p.m. (Table 1). While this equivalence may be the result of the fluxional nature of these species, the facts that (*a*) the carbon atoms in question are far removed from the groups involved in the molecular motion and (*b*) the signal is sharp tend to suggest that, by coincidence, these carbon atoms have the same chemical shift in these molecules.

The allylamine complex (**8**) has a band in the i.r. spectrum at 3 390 cm^{-1} indicating the presence of the N–H group. The complex is fully characterised by n.m.r. spectroscopy and the relevant data are included in Tables 1 and 2. Characteristic signals for the allyl grouping are observed at 47.9, 119.1, and 138.5 p.p.m. in the ^{13}C spectrum and at 4.10, 5.30, and 5.95 in the ^1H spectrum. In common with the vinylphenyl N–H complexes, the allyl derivative displays fluxional behaviour at the probe temperature with a number of resonances appearing as broadened signals. Another significant feature of the ^{13}C n.m.r. spectrum is that the signal due to carbon 1 shows an upfield shift of *ca.* 5 p.p.m. relative to other complexes of this type. As is evident from Table 1, while not always so pronounced, this shift seems to be a general feature of unbridged complexes containing the N–H grouping and may be associated with the ability of the amine to donate electron density to the macrocyclic ring *via* the lone pair on the nitrogen atom. This is further discussed below with regard to the fluxional behaviour of the complexes.

Bridged complexes (**9**) *and* (**10**). The i.r. spectra of the bridged materials are unremarkable but useful for the purpose of

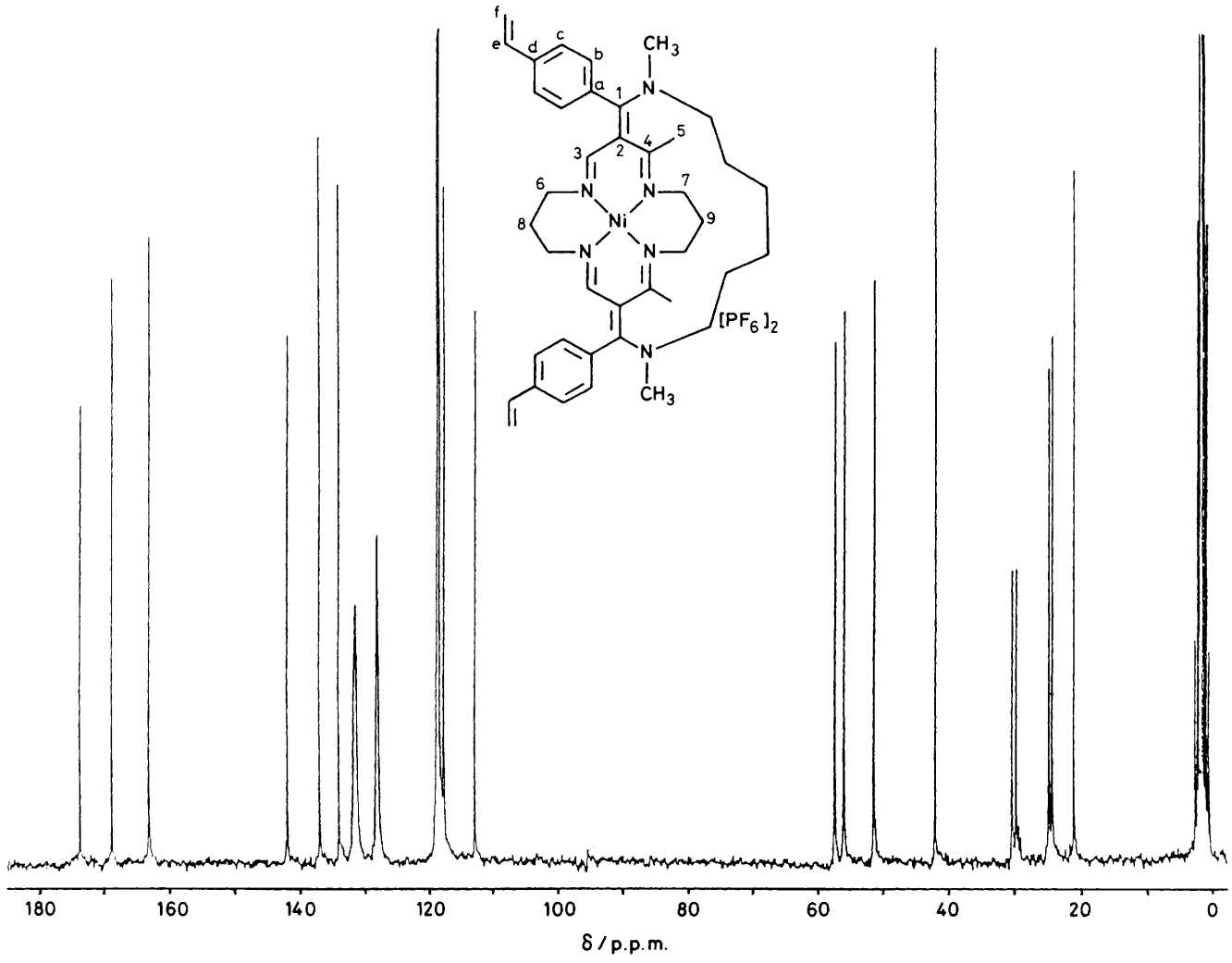


Figure 1. ^{13}C-$\{^1H\}$ N.m.r. spectrum of the bridged complex (**9**) in CD_3CN solution

identification. Representative data are included in Table 3. The electronic spectra display a band, $\lambda_{max.}$ *ca.* 395 nm, typical of nickel(II) N_4 square-planar complexes. A second band is observed at *ca.* 365 nm. Again, the most useful methods for characterisation are ^{13}C and ^1H n.m.r. spectroscopies and the data are included in Tables 1 and 2. The ^{13}C n.m.r. spectrum is shown in Figure 1. The assignment of the signals is accomplished with the aid of the results from a DEPT experiment and by measurement of the C–H correlation spectrum (Figure 2).

The ^{13}C n.m.r. spectra of the two bridged complexes are very similar to those of the known complex of structure (**III**) with $R^1 = R^2 = Me$ (**12**)[16] and clearly show the presence of the polymerisable groups in the macrocycle structure.

The spectrum of the vinylphenyl-containing complex (**9**) displays evidence for fluxionality in the ligand structure with the signals due to carbon atoms b and c of the vinylphenyl group being broadened. The fluxionality of the molecule is also evident from the ^1H n.m.r. spectrum which clearly shows broadening and an interesting splitting of the aromatic proton signals. This is further discussed below.

The other notable feature of the ^1H n.m.r. spectrum of (**9**) is the significant upfield shift of the signal due to the resonance of the ring methine proton, attached to carbon 3, in comparison with that observed for the known material (**12**); this signal appears at 6.57 for (**9**) compared to 7.50 for (**12**). This shift is presumably due to the shielding effect of the aromatic ring current on this proton which lies in close proximity to the vinylphenyl group. Further support for the close proximity of the methine proton to the aromatic group comes from measurement of the nuclear Overhauser effect (n.O.e.) difference spectrum while irradiating at the frequency of the methine proton resonance. The aromatic protons display a 9.1% enhancement in intensity. The only other signal to show enhancement is that ascribed to one of the protons attached to carbon atom 6 which has a 9.6% increase. While absolute distances cannot be obtained from the n.O.e. experiment, the results clearly indicate that the methine proton lies relatively close in space to both the aromatic and one of the ring NCH_2 protons and approximately equidistant from both. It is also interesting that the signal for the ring NCH_2 proton adjacent to the methine proton displays a small but significant upfield shift of some 0.5 relative to the same signal in complex (**12**). While the ring proton is rather far from the aromatic group, there does appear to be a shielding influence on its resonant frequency.

In contrast the spectra of the bridged complex bearing the allyl substituent are unremarkable and display no evidence for fluxional behaviour in this molecule. They do, however, confirm that the material has the desired structure.

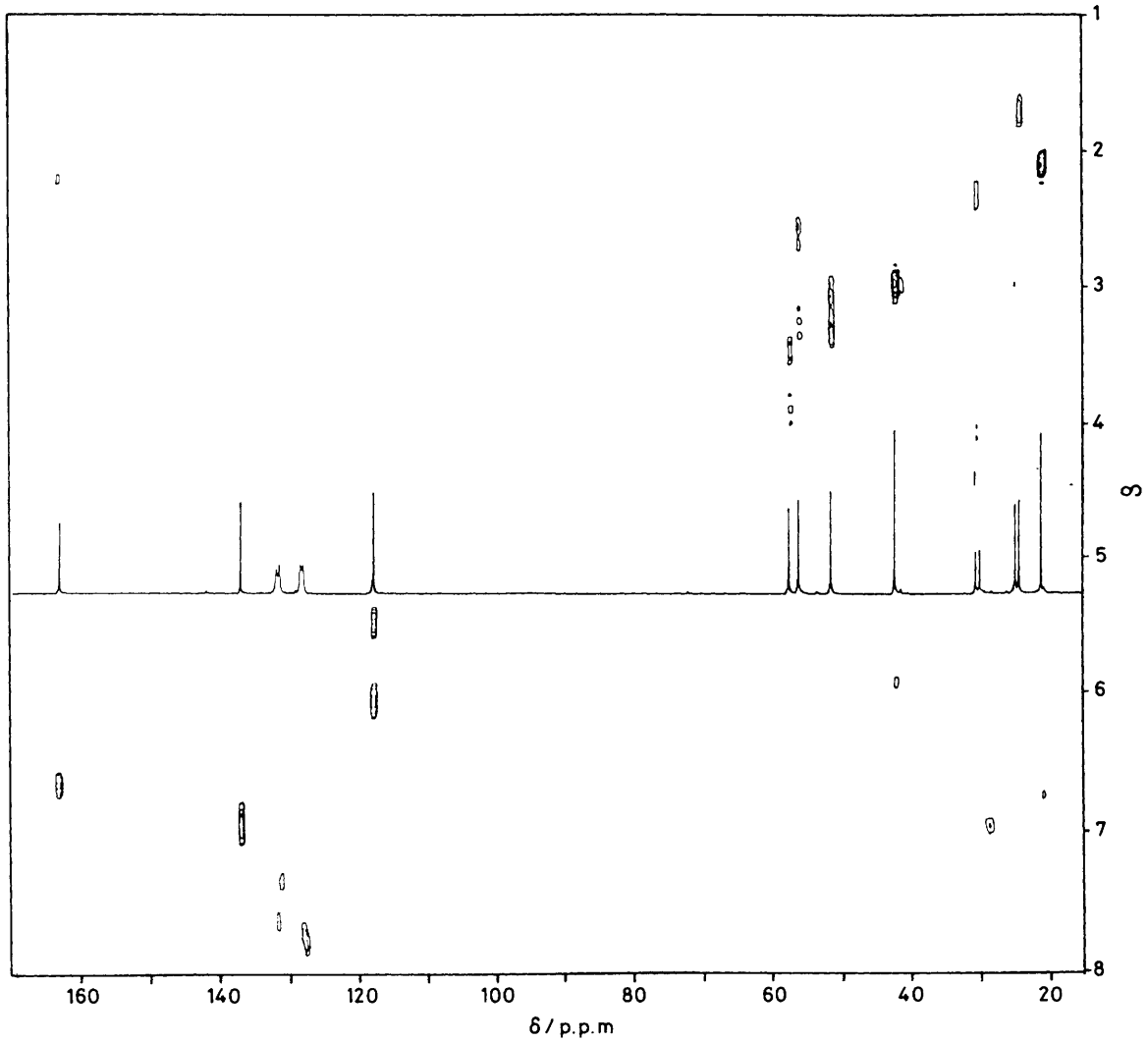
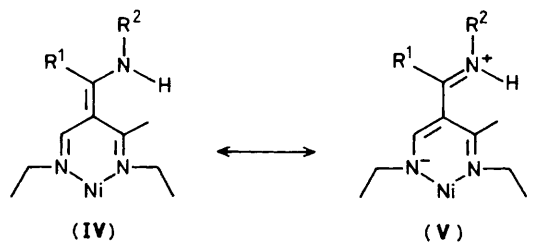


Figure 2. C–H Correlation n.m.r. spectrum for the bridged complex (**9**). Inset shows the ^{13}C DEPT spectrum

Fluxional Behaviour.—As described above a number of the new complexes display fluxional behaviour on the n.m.r. time-scale. This appears to be of two different types. For the unbridged secondary amine complexes (**4**)—(**6**) and (**8**) the ^{13}C n.m.r. spectra display broadening of the signals due to carbons 1 and 2 of the macrocycle, the carbon atom of R^2 next to the amine nitrogen atom, and either the Me carbon atom [R^1 = Me, (**8**)] or the carbon atoms a, b, and d (R^1 = vinylphenyl). In the case of complexes (**5**), (**6**), and (**8**), the signal due to carbon 1



is shifted to lower field and overlaps with the signal due to carbon 4. The ^1H n.m.r. spectra of the complexes mirror this behaviour with signals due to protons bonded to the above carbon atoms being broadened. In addition the macrocycle methine proton signal for complexes (**4**)—(**6**) is broadened. In earlier work Busch and co-workers [17] noted line broadening in the n.m.r. spectra of some lacunar complexes and this was attributed to restricted rotation about the C(1)–N(amine) bond of the ligand. In the present work such a rotation would not account for the observed broadening of the signal due to C(2) of the macrocycle. Rather it is proposed that the fluxional character derives from rotation about the C(1)–C(2) bond. Although this is formally a double bond, crystal structures of similar complexes [18] have shown that the amine nitrogen atom is in fact trigonal planar suggesting that the lone pair of the nitrogen atom is delocalised into the macrocyclic ring, presumably *via* resonance structures (**IV**) and (**V**). These suggest that the C(1)–C(2) bond has partial single-bond character thus allowing for the proposed restricted rotation. This motion, allied to a rapid rotation about the C(1)–C(a,aromatic) bond, readily accounts for the observed n.m.r. data. The temperature dependence of the n.m.r. spectra is clearly exemplified by complex (**4**). On warming from the probe temperature of *ca.* 303 K to first 323 then 348 K the ^1H n.m.r. spectrum is, as expected, seen to sharpen and at 348 K all of the signals are sharp and well resolved. The sharpening of the spectrum allows the observation of a signal due to the amine protons of the ligand, at 7.33.

Once the macrocycle has been bridged by the hexamethylene

unit the structure is altogether more rigid and rotation about C(1)–C(2) is no longer possible. In agreement with this the ^{13}C n.m.r. spectra of the bridged complexes have a sharp signal due to carbon atom 2. Complex (**9**), the vinylphenyl-substituted complex, does display some fluxional behaviour. In the ^{13}C n.m.r. spectrum this is seen as broadening of the aromatic C–H carbon atoms, b and c, but the effect is more clearly observed in the ^1H n.m.r. spectrum. The signal due to the protons (H_c,$H_{c'}$) bonded to carbon atoms c is broadened while that of the protons (H_b,$H_{b'}$) bonded to carbon atoms b is not only broadened but discernibly split [Figure 3(*a*)]. This effect appears to arise from rotation about the bond between C(1) and C(a,aromatic). At the probe temperature, this rotation is sufficiently slow that two separate environments are observed for H_b and $H_{b'}$. The environments of H_c and $H_{c'}$ are so similar that there is no evidence of splitting for this signal. As the sample is warmed to 323 K, the signals due to H_b and $H_{b'}$ coalesce [Figure 3(*b*)] and the signal due to H_c and $H_{c'}$ sharpens considerably. Further warming of the solution to 348 K causes the H_b,$H_{b'}$ signal to sharpen [Figure 3(*c*)] indicating that at this temperature the aromatic group is close to undergoing free rotation about C(1)–C(a,aromatic).

The fact that this type of fluxional behaviour is observed only in the bridged complexes suggests that, while free rotation of the aromatic ring occurs in unbridged species, when the bridge is introduced into the structure the barrier to rotation about C(1)–C(a,aromatic) increases, presumably as a result of steric constraints imposed on the structure by the bridging group. This type of phenomenon has been reported by Busch and co-workers[5] for a lacunar complex [structure (**III**), R^1 = 3,5-$(MeO)_2C_6H_3$, R^2 = Me but with a *m*-xylylene bridge]. This complex has extra resonances in its ^{13}C n.m.r. spectrum, indicating that the aromatic group cannot rotate about the C(1)–C(a,aromatic) bond. The results from all other known complexes with R^1 = aromatic grouping suggest that free rotation occurs about this bond. In this work it is not clear why there is a larger barrier to rotation for the vinylphenyl-substituted complex relative to the unsubstituted phenyl complex.

Copolymerisation Reactions.—Complexes (**2**), (**9**), and (**10**) have been copolymerised with either styrene or methyl methacrylate under free-radical polymerisation conditions. The results of these studies reveal a large difference in the reactivity of the styryl and allyl groups.

In polymerisation with the neat comonomers at 1% mol/mol loading of macrocycle complex, both vinylphenyl-substituted complexes (**2**) and (**9**) produce intractable copolymers. Although these polymers undergo swelling with solvent, they are completely insoluble. This establishes the high reactivity of

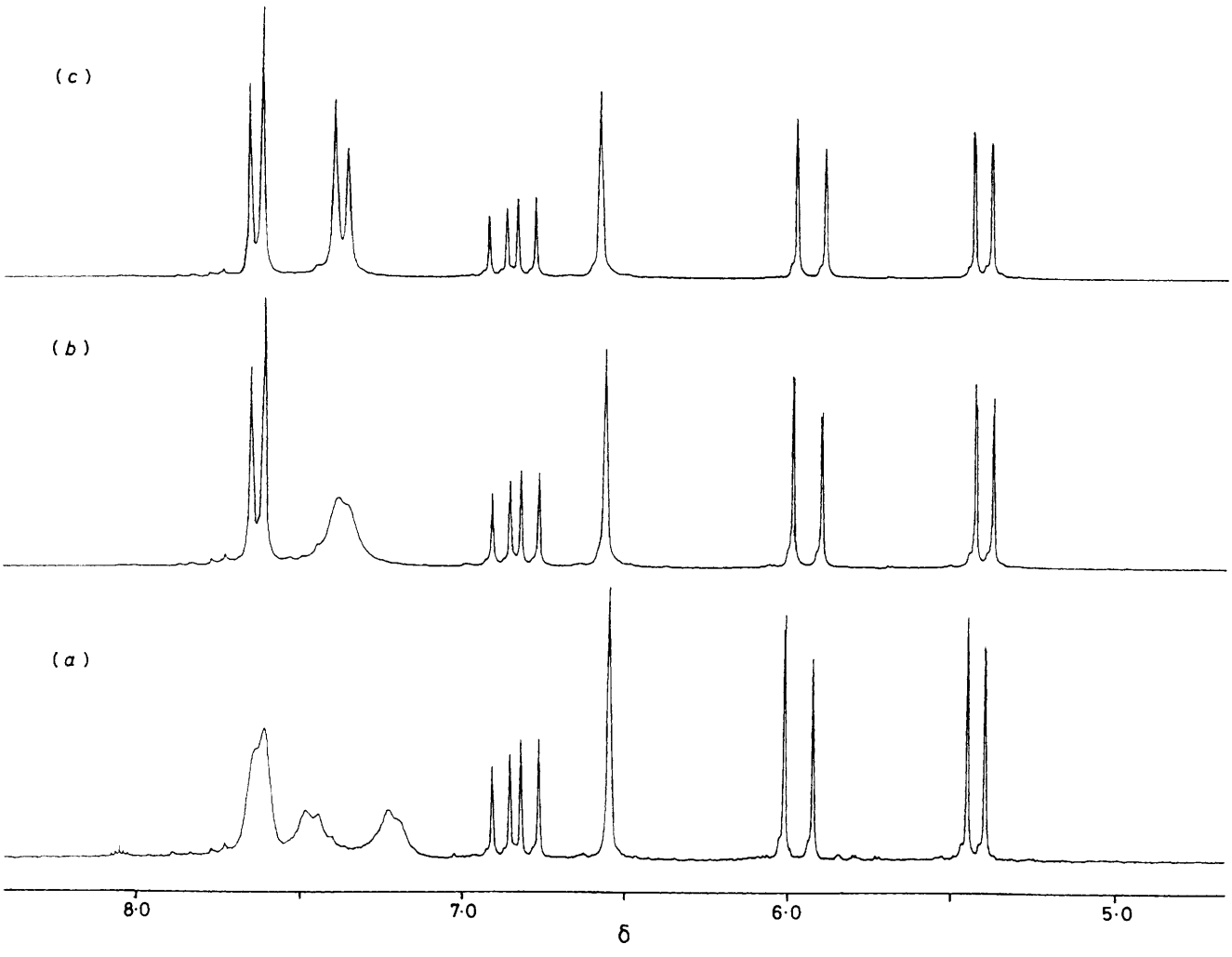


Figure 3. Part of the ^1H n.m.r. spectrum of the bridged complex, (**9**), at (*a*) 298, (*b*) 323, and (*c*) 348 K

the vinylphenyl group at both ends of these substituted complexes, resulting in copolymers that are extensively cross-linked by the macrocyclic group.

In contrast, the allyl-substituted complex (**10**), under the same conditions, produces soluble products which are essentially pure polystyrene or poly(methyl methacrylate) with very little of the macrocycle being incorporated into the polymers. This result is expected since the allyl group is known to be much less reactive in polymerisation reactions than either styryl or acrylate ester groupings.[19]

The degree of cross-linking by the vinylphenyl-substituted complexes can be controlled by limiting the extent of the polymerisation reaction. This has been done by carrying out the copolymerisations in a suitable solvent and results in the formation of soluble copolymers. The successful incorporation of the macrocycles into the polymer structures has been demonstrated by a combination of i.r., n.m.r., and electronic spectroscopies which each show signals unique to the macrocyclic complexes among those of the bulk polymers. Detailed studies of these and other polymerisation reactions will be the subject of a separate report.

Conclusions

A series of new macrocyclic complexes of nickel(II) have been successfully prepared and characterised. These complexes have polymerisable substituents as an integral part of their molecular architecture. The n.m.r. spectra of a number of these species reveal them to be fluxional on the n.m.r. time-scale and the fluxional behaviour appears to be of two distinct types, both involving rotation of peripheral groups of the macrocyclic ligand. The polymerisable groups undergo reaction with selected comonomers to produce copolymeric products, however, the allyl-substituted complex (**10**) is much less reactive than the vinylphenyl-substituted species (**2**) and (**9**). The vinylphenyl species are effective cross-linking reagents and the polymerisation reactions must be carefully controlled to produce soluble products.

Experimental

All materials were reagent grade and were used without further purification. Solvents were purified by standard methods.

Proton n.m.r. spectra were recorded on JEOL PX 60 (60 MHz) or Bruker WP 200 (200.133 MHz) spectrometers, ^{13}C n.m.r. spectra on a Bruker WP 200 (50.323 MHz) spectrometer. Chemical shifts are reported with respect to an external tetramethylsilane reference (positive shifts to low field). Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer, i.r. spectra as Nujol mulls using a Perkin-Elmer 580 spectrophotometer.

Preparation of Complexes.—[3,11-Diacetyl-2,12-dimethyl-1,5,9,13-tetra-azacyclohexadeca-1,3,9,11-tetraenato(2−)-κ^4N]nickel(II) (**1**), (2,12-dimethyl-1,5,9,13-tetra-azacyclohexadeca-1,4,9,12-tetraene-κ^2N)nickel(II) hexafluorophosphate, and [2,12-dimethyl-1,5,9,13-tetra-azacyclohexadeca-1,3,9,11-tetraenato(2−)-κ^4N]nickel(II) (**11**) were prepared by the literature procedures.[20]

2,12-*Dimethyl*-[3,11-*bis*(4-*vinylbenzoyl*)-1,5,9,13-*tetra-azacyclohexadeca*-1,3,9,11-*tetraenato*(2−)-κ^4N]*nickel*(II) (**2**). 4-Vinylbenzoyl chloride (8.2 g, 52.4 mmol) was added to a rapidly stirred solution of complex (**11**) (7.93 g, 26 mmol) and triethylamine (7.2 cm^3, 54 mmol) in anhydrous diethyl ether (300 cm^3). An orange solid and triethylamine hydrochloride precipitated immediately. After stirring for 1 h, the solids were collected by filtration and washed with water. The ether filtrate was evaporated to dryness. The orange solids were combined, dissolved in $CHCl_3$, and chromatographed on neutral alumina with $CHCl_3$ as eluant. The fast moving red-orange band was collected and evaporated to yield a red oil which was crystallised from CH_2Cl_2–ether to give orange crystals (11.4 g, 70%) (Found: C, 64.5; H, 6.9; N, 7.3. Calc. for $C_{32}H_{34}N_4NoO_2\cdot 2Et_2O\cdot 0.5CH_2Cl_2$: C, 64.4; H, 7.3; N, 7.4%).

[3,11-*Bis*(α-*methoxy*-4-*vinylbenzylidene*)-2,12-*dimethyl*-1,5,9,13-*tetra-azacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N]-*nickel*(II) *hexafluorophosphate* (**3**). To a solution of complex (**2**) (8.0 g, 14.2 mmol) in dry dichloromethane was added, with rapid stirring, methyl trifluoromethanesulphonate [**CAUTION**: very toxic reagent] (9 cm^3, 80 mmol). After 12 h the solution had changed colour from deep orange to olive green. The dichloromethane was removed by rotary evaporation and the oily residue redissolved in ethanol (100 cm^3). To this solution was added with rapid stirring a solution of ammonium hexafluorophosphate (4.9 g, 30 mmol) in ethanol (75 cm^3) resulting in formation of a yellow precipitate. This was crystallised from acetonitrile–ethanol (6.9 g, 60%).

[2,12-*Dimethyl*-3,11-*bis*(α-*methylamino*-4-*vinylbenzylidene*)-1,5,9,13-*tetra-azacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N]-*nickel*(II) *hexafluorophosphate* (**4**). Methylamine gas was bubbled through a solution of complex (**3**) (3.0 g, 0.34 mmol) in acetonitrile (100 cm^3) for 10 min, during which time the solution became deep red. The volume of acetonitrile was reduced by rotary evaporation and the residue was chromatographed on a column of neutral alumina with acetonitrile as eluant. The fast moving yellow-orange band was collected and the solvent removed to yield a yellow-orange crystalline product. This was recrystallised from acetonitrile–ethanol (2.86 g, 95%) (Found: C, 46.2; H, 4.6; N, 8.9; Ni, 7.0. Calc. for $C_{34}H_{42}F_{12}N_6NiP_2$: C, 46.2; H, 4.8; N, 9.5; Ni, 6.65%).

[2,12-*Dimethyl*-3,11-*bis*(α-*n-propylamino*-4-*vinylbenzylidene*)-1,5,9,13-*tetra-azacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N]*nickel*-(II) *hexafluorophosphate* (**5**). To a solution of complex (**3**) (3.7 g, 4.2 mmol) in dry acetonitrile (50 cm^3) was added, dropwise with stirring, a solution of n-propylamine (0.8 cm^3, 9.0 mmol) in MeCN (50 cm^3). After stirring at room temperature for 12 h the volume of the deep red solution was reduced to 10 cm^3 and this was chromatographed on a column of neutral alumina with MeCN as eluant. The fast moving deep orange band was collected and the product was precipitated by addition of ethanol. This precipitate was crystallised from acetone–ethanol (1:2) (3.4 g, 86%) (Found: C, 50.2; H, 6.1; N, 8.4; Ni, 5.9. Calc. for $C_{38}H_{50}F_{12}N_6NiP_2\cdot Et_2O$: C, 49.8; H, 6.0; N, 8.3; Ni, 5.8%).

[3,11-Bis(α-isopropylamino-4-vinylbenzylidene)-2,12-dimethyl-1,5,9,13-tetra-azacyclohexadeca-1,4,9,12-tetraene-κ^4N]nickel(II) hexafluorophosphate (**6**) was prepared in 89% yield by the procedure used for (**5**).

{3,10,13,19-*Tetramethyl*-2,11-*bis*(4-*vinylphenyl*)-3,10,14,18,21,25-*hexa-azabicyclo*[10.7.7]*hexacosa*-1,11,13,18,20,25-*hexaene*-κ^4N}*nickel*(II) *hexafluorophosphate* (**9**). *Method* (*a*). To a solution of complex (**4**) (1.5 g, 1.7 mmol) in dry MeCN (100 cm^3) was added a solution of KOBu^t (0.4 g, 3.6 mmol) in methanol–MeCN (1:1, 25 cm^3). The solution immediately became deep red. A solution of hexane-1,6-bis(toluene-*p*-sulphonate) (0.72 g, 1.7 mmol) in MeCN (125 cm^3) was prepared. These two solutions were added dropwise, simultaneously, under nitrogen to a rapidly stirred volume of dry MeCN (25 cm^3), heated at reflux. Addition was complete after 4 h and the solution was maintained at reflux for a further 72 h. The solvent volume was reduced and the residue was chromatographed on a column of neutral alumina with MeCN as eluant. The fast moving yellow-orange band was collected and the solvent evaporated to a small volume. Addition of ethanol gave the product as yellow-orange crystals (55%) (Found: C, 50.2; H, 5.6; N, 8.0; Ni, 5.0. Calc. for $C_{40}H_{52}F_{12}N_6NiP_2\cdot EtOH$: C, 49.9; H, 5.8; N, 8.3; Ni, 5.8%).

Method (*b*). Two solutions, one containing complex (**3**) (1.3 g, 1.47 mmol) in MeCN (100 cm^3) and the other *N*,*N*′-dimethylhexane-1,6-diamine (0.26 cm^3, 1.47 mmol) in MeCN (100 cm^3), were added dropwise, simultaneously, at the same rate, to a refluxing volume of MeCN (500 cm^3) under a blanket of nitrogen. Addition was complete after *ca.* 6 h. The volume of the reaction was reduced to *ca.* 10 cm^3 and this was chromatographed on a column of neutral alumina with MeCN as the eluant. The product was contained in the leading band from the column. Repeated chromatography was necessary to purify this product (0.106 g, 7%).

[2,12-*Dimethyl*-3,11-*bis*(α-*methoxyethylidene*)-1,5,9,13-*tetra-azacyclohexadeca*-1,4,9,12-*tetraene*-κ^4 N]*nickel*(II) *hexafluorophosphate* (**7**). This complex was prepared by a modification of the literature procedure, using methyl trifluoromethanesulphonate as the alkylating agent (yield 91%).[15]

[3,11-*Bis*(α-*allylaminoethylidene*)-2,12-*dimethyl*-1,5,9,13-*tetra-azacyclohexadeca*-1,4,9,12-*tetraene*-κ^4 N]*nickel*(II) *hexafluorophosphate* (**8**). To a solution of complex (**7**) (2.52 g, 3.56 mmol) in MeCN (50 cm^3) was added a solution of allylamine (0.54 cm^3, 7.2 mmol) in MeCN (25 cm^3) with rapid stirring. The colour of the solution changed from green-yellow to orange immediately upon addition of the amine. The solution was stirred for 1 h, then the acetonitrile was reduced to a small volume and the residue was chromatographed on a column of neutral alumina with MeCN as eluant. The fast moving yellow-orange band was collected and the solvent removed to yield a yellow-orange precipitate. This was crystallised from MeCN–ethanol (2.28 g, 84%) (Found: C, 37.9; H, 5.1; N, 11.1; Ni, 7.2. Calc. for $C_{24}H_{38}F_{12}N_6NiP_2$: C, 38.0; H, 5.0; N, 11.1: Ni, 7.7%).

{3,10-*Bis*(*allyl*)-2,11,13,19-*tetramethyl*-3,10,14,18,21,25-*hexa-azabicyclo*[10.7.7]*hexacosa*-1,11,13,18,20,25-*hexaene*-κ^4N}*nickel*(II) *hexafluorophosphate* (**10**). To a solution of complex (**8**) (4.0 g, 5.3 mmol) in dry MeCN (100 cm^3) was added a solution of KOBu^t (1.35 g, 12 mmol) in methanol–MeCN (1:1, 25 cm^3). The colour of the solution changed from deep orange to deep red. The solution was heated to reflux under nitrogen and a solution of hexane-1,6-bis(toluene-*p*-sulphonate) (2.26 g, 5.3 mmol) in MeCN (125 cm^3) was added dropwise with stirring. The solution was maintained at reflux for a further 48 h. The solvent was reduced to a small volume by rotary evaporation and the residue was chromatographed on a column of neutral alumina, with MeCN as eluant. The fast moving yellow-orange band was collected and the solvent evaporated to give yellow-orange crystals (2.52 g, 56%) (Found: C, 44.0; H, 6.2; N, 9.7; Ni, 6.6. Calc. for $C_{30}H_{48}F_{12}N_6NiP_2$·$Me_2CO$: C, 44.1; H, 6.05; N, 9.3; Ni, 6.5%).

4-*Vinylbenzoic Acid*.[21]—To a solution of 4-chlorostyrene (3.5 cm^3, 29 mmol) in anhydrous tetrahydrofuran (50 cm^3) was added magnesium turnings (1.4 g, 51 mmol) and two iodine crystals. The solution was heated to reflux under nitrogen. After 1 h the solution had become dark green. The reaction mixture was poured on to an excess of solid CO_2 and the resulting solution was acidified with aqueous H_2SO_4 (2 mol dm^{-3}, 10 cm^3). This mixture was extracted with ether (2 × 20 cm^3), then the organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness to leave a white product. This was crystallised from ether–light petroleum (b.p. 40—60 °C) (3.9 g, 88%). ^{1}H N.m.r. ($CDCl_3$): δ 5.35 (1 H, d, *J* 10, H_f), 5.82 (1 H, d, *J* 17, H_f), 6.75 (1 H, dd, *J* 17 and 10 Hz, H_e), 7.70 (4 H, m, aromatic H), and 11.7 (1 H, br s, acid H).

4-*Vinylbenzoyl Chloride*.—4-Vinylbenzoic acid was added to an excess of thionyl chloride and the reaction mixture was heated to reflux. When effervescence ceased, the remaining thionyl chloride was removed by distillation to leave the product as an oil. ^{1}H N.m.r. ($CDCl_3$): δ 5.40 (1 H, d, *J* 10, H_f), 5.85 (1 H, d, *J* 17, H_f), 6.72 (1 H, dd, *J* 17 and 10 Hz, H_e), and 7.69 (4 H, m, aromatic H).

Hexane-1,6-*bis*(*toluene*-p-*sulphonate*).—A solution of hexane-1,6-diol (3.0 g, 25 mmol) was dissolved in dry pyridine (25 cm^3) and cooled in an ice-bath. A solution of toluene-*p*-sulphonyl chloride (10.5 g, 54 mmol) in pyridine (75 cm^3) was added dropwise with rapid stirring over a period of 1 h. The reaction mixture was stored in a freezer overnight. After the addition of water (500 cm^3) at 0 °C, the crude white product was collected by filtration and crystallised from methanol (70%). ^{1}H N.m.r. ($CDCl_3$): δ 1.2—1.5 (8 H, m, CH_2), 2.32 (6 H, s, CH_3), 3.87 (4 H, t, *J* 6 Hz, CH_2O), and 7.40 (8 H, m, aromatic H).

Copolymerisation.—The copolymerisation reactions were carried out in evacuated, sealed tubes with α,α′-azobis(isobutyronitrile) (aibn) as the initiator. The temperature of the reaction was maintained at 60 °C. The reactions were carried out with styrene or methyl methacrylate as the comonomer. These were freshly distilled under vacuum immediately prior to use. Polymerisation was studied under two sets of conditions.

(*a*) *Bulk copolymerisation*. In a typical experiment, complex (**3**) (0.200 g, 0.36 mmol), methyl methacrylate (3.8 cm^3, 36 mmol), and aibn (0.02 g, 0.12 mmol) were placed in a polymerisation vessel. A small volume of benzene (*ca.* 3 cm^3) was required to solubilise the mixture. The vessel was heat sealed and warmed at 60 °C for *ca.* 4 h by which time the reaction mixture had become very viscous. The insoluble copolymer product was isolated after extraction of the reaction mixture with dichloromethane.

(*b*) *Solution copolymerisation*. These reactions were carried out as for the bulk reactions except that the reaction mixture was dissolved in benzene (25 cm^3). After heating at 60 °C for 15 h, the reaction mixture had become viscous. The contents of the vessel were extracted into dichloromethane and precipitated with an excess of cold methanol. Reprecipitation was repeated a further four times to yield a light orange product.

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