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Synthesis, characterisation and polymerisation of vinylbenzene-substituted triazacyclododecanes and their transition metal complexes

Nicholas J. Long,[*a] **David G. Parker,**[b] **Paul R. Speyer,**[a] **Andrew J. P. White**[a] **and David J. Williams**[a]

[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY. E-mail: n.long@ic.ac.uk*
[b] *ICI Technology, Research and Technology Centre, P.O. Box 90, Wilton, Middlesborough, Cleveland, UK TS90 8JE*

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The synthesis of a range of methylated and non-methylated triazacyclododecane derivatives featuring the unsymmetrical incorporation of a 4-vinylbenzene side-arm is reported, along with the X-ray crystal structure of an amidinium salt precursor, and NMR characterisation of these ligands. The free amine, 1-(4-vinylbenzyl)-1,5,9-triazacyclododecane (**5**), has been reacted with a series of transition metal centres and the coordination chemistry is discussed, with structural analysis of an unusual triply-bridged (*via* one aqua and two chloride ligands) Ni(II) dimer and a mononuclear W(CO)$_5$ complex. Co-polymerisation studies on **5** and its metal complexes with varying percentages of styrene show the formation of low and high (*via* cross-linking) molecular weight polymers.

Introduction

Although the chemistry of aza-macrocycles is well established,[1] the development of new synthetic methodologies and applications continues to be of topical interest.[2] The selective functionalisation of these molecules for example, is still not straightforward, and although some elegant syntheses have been developed[3] there is scope for further development. Our aim has been to establish versatile and efficient synthetic routes to pendant arm macrocycles, focusing on polymerisable arms, leading to novel metal-free or metal-ion containing polymers following polymerisation of the macrocyclic monomers or copolymerisation with monomers such as styrene. It has been shown that the materials may act as anchors for metal complex-assisted catalysis and as polymer-supported metal ion filters.[4] This is an active area of interest with many potential applications, particularly environmental. For example, work involving polymerisation of metal-ion containing monomers featuring 1,4,7-triazacyclononane (the demetallated product being highly selective for Cu^{2+} ions),[5] oligonucleotide-tethered 1,5,9-triazacyclododecanes[6] and novel thiacrown polymers for extraction of Hg has been reported.[7]

Following our communication on some ligand syntheses,[8] this manuscript describes the synthesis and detailed characterisation of metal-free methylated and non-methylated triazacyclododecane derivatives featuring the unsymmetrical incorporation of a 4-vinylbenzene pendant arm. Some transition metal coordination chemistry with the free amine 1-(4-vinylbenzyl)-1,5,9-triazacyclododecane (**5**) is discussed, including X-ray structural characterisation of an unusual triply-bridged Ni(II) dimer and a mononuclear W(CO)$_5$ complex, along with polymerisation studies featuring the free ligand and its Ni and Zn complexes.

Results and discussion

Triazacyclododecane ligands

The Richman–Atkins cyclisation[9] has for many years, been the standard route for the formation of azamacrocycles and utilises tosyl-protecting groups. However, complete removal of these groups following cyclisation is difficult; yields are often variable and there can be unwanted monotosylated products. The use of a central carbon fragment to protect the nitrogen atoms from secondary electrophilic attack allows formation of monosubstituted triazamacrocycles and the intermediate triazatricyclo[7.3.1.0^{5,13}]tridecane **1** can be synthesised *via* the routes of Alder[10] or Haseltine.[11] We have taken this intermediate and demonstrated its versatility, particularly with reaction of cheap and readily available chloro-reagents. Thus, addition of 4-vinylbenzyl chloride to a stirred hexane solution of **1** at 60 °C gives the amidinium species 5-(4-vinylbenzyl)-1,5,9-triazabicyclo[7.3.1]tridecinium chloride (**2**) in 76% yield (Scheme 1).

X-Ray quality crystals were grown by dissolution in CH$_2$Cl$_2$ followed by the addition of an equal volume of acetone, and allowing the solution to slowly evaporate. The X-ray analysis of **2**, the precursor to the free ligand **5**, shows (Fig. 1) the molecule to have non-crystallographic C_s symmetry about a plane passing through C(7), C(13), N(1), C(14), C(15) and C(18) (the vinylic group being disordered about this "mirror plane"). The

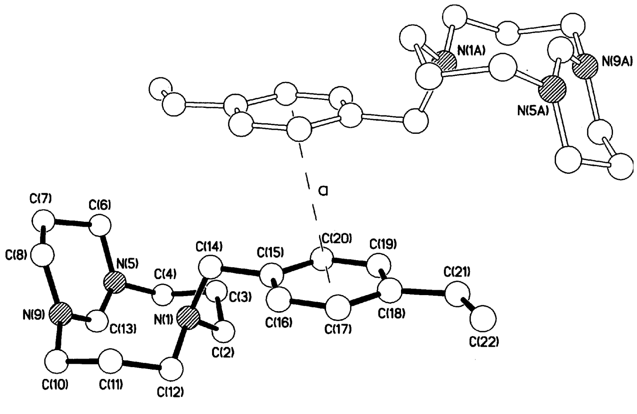

Fig. 1 One of the π-stacked "dimer pairs" of cations present in the structure of **2**. The centroid ··· centroid separation between the rings (**a**) is 3.96 Å.

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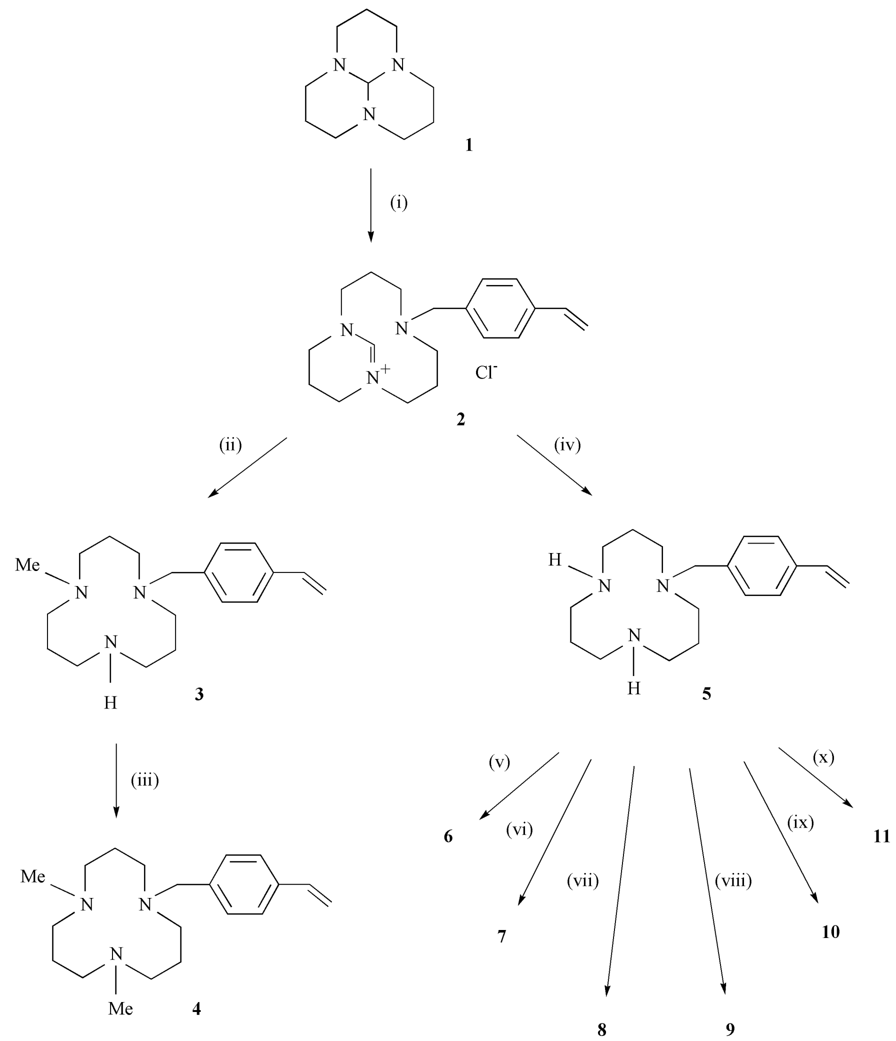


Scheme 1 Reagents and conditions: (i) 4-Vinylbenzyl chloride, hexane, 60 °C, 48 h (76%). (ii) Ethanol, $NaBH_4$, 0 °C, then reflux, 8 h, (84%). (iii) Methanol, formaldehyde (37–40%), $NaBH_4$, stir, r.t., 12 h (70%). (iv) 0.75 M NaOH, water : ethanol (2 : 1), 72 h (94%). (v) Methanol, $NiCl_2·6H_2O$, 48 h (29%). (vi) CH_2Cl_2, $Cu(CH_3CN)_4PF_6$, N_2 (30%). (vii) Methanol, $CuCl_2·2H_2O$ (30%). (viii) Methanol, $ZnCl_2·2H_2O$ (22%). (ix) Methanol, anhydrous $CoCl_2$ (11%). (x) THF, $W(CO)_5(THF)$, 8 h (45%).

Table 1 Selected bond lengths (Å) for **2**

N(1)–C(2)	1.467(3)	N(1)–C(12)	1.469(3)
N(1)–C(14)	1.479(2)	N(5)–C(4)	1.468(3)
N(5)–C(6)	1.452(3)	N(5)–C(13)	1.309(3)
N(9)–C(8)	1.463(3)	N(9)–C(10)	1.466(3)
N(9)–C(13)	1.310(3)		

conformation of the 10-membered ring has all three nitrogens on one face, defining a plane that is oriented parallel to the phenyl ring (4° between their planes). There is distinct partial double bond character in the N(5)–C(13) and N(9)–C(13) bonds [1.309(3) and 1.310(3) Å respectively] in the diazoprene ring (Table 1), consistent with the usual pattern of delocalisation observed in such systems; the ring has a sofa conformation. There is pyramidalisation at all three nitrogen centres, though this is most pronounced at N(1) where the nitrogen atom lies 0.37 Å out of the plane of its substituents *cf.* deviations of 0.15 and 0.17 Å at N(5) and N(9) respectively. Centrosymmetrically related pairs of molecules are oriented such that the phenyl rings enter into a parallel π–π stacking interaction, the mean interplanar and centroid ··· centroid separations being 3.40 and 3.96 Å respectively. A similar stacking is not observed for the related structure **5**, where the intermolecular interactions are dominated by N–H ··· O hydrogen bonds to the nitrate anion.[8] There are no other cation ··· cation interactions of note. Symmetry related chloride anions are bridged by hydrogen bonds from two water molecules to form a planar (maximum deviation 0.04 Å) eight-membered $[(OH_2)Cl]_2$ ring; the O ··· Cl, H ··· Cl distances (Å), O–H ··· Cl angle (°) are 3.21, 2.31, 179 and 3.17, 2.28, 171. The only cation ··· anion interaction of note is a weak C–H ··· Cl hydrogen bond between the methine hydrogen atom on C(13) of the diazoprene ring and the chloride anion; the C ··· Cl, H ··· Cl distances (Å), C–H ··· Cl angle (°) are 3.46, 2.64, 144.

Methylation of the N atoms by the Eschweiler–Clarke reductive alkylation using formaldehyde is a common procedure but can lead to cleavage of the macrocycle[12] and formation of a mixture of methylated species. We have found however, that the use of sodium borohydride can alleviate these problems. From **2**, the monomethyl derivative 1-methyl-5-(4-vinylbenzyl)-1,5,9-triazacyclododecane (**3**) can be formed in 84% yield using a large excess of $NaBH_4$ in refluxing ethanol.

Alder has communicated[10] a dimethylated derivative but with only limited experimental details and spectroscopic characterisation. We have adopted a variation of his procedure and thus, addition of 37–40% aqueous formaldehyde to **3** in methanol, followed by $NaBH_4$, gives the dimethylated 5,9-dimethyl-1-(4-vinylbenzyl)-1,5,9-triazacyclododecane (**4**) in 70% crude yield. It is an oil that solidifies on standing but it should be noted that, as with other non-acylated triazacyclododecane (tacd) derivatives produced, **4** is not amenable to column chromatography and could only be obtained in a fairly crude form. The CI (+ve) mass spectrum shows two notable peaks; that corresponding to 316 u is due to the capture of a proton by the macrocycle, whilst expulsion of the vinylbenzene side chain gives the 200 u fragmentation peak. ^{1}H and ^{13}C-{^{1}H} NMR spectra confirm the expected structure.

Compound **2** can be converted to the free amine-substituted macrocycle, 1-(4-vinylbenzyl)-1,5,9-triazacyclododecane (**5**) by addition of 0.75 M NaOH in a water : ethanol mixture (2 : 1) with prolonged refluxing (yield 94%) (Scheme 1). The product is a glassy amorphous solid, and appears to be unstable to polymerisation when stored at room temperature in daylight, but storage at low temperatures and in the absence of light keeps the molecule stable for several months. It is not amenable to either column chromatography or distillation/sublimation, but the CI (+ve) mass spectrum of the compound is consistent with the assigned structure, the major peak corresponding to the protonated molecule. The ^{13}C-{^{1}H} NMR is straightforward to interpret with the peaks due to the vinyl benzene side-chain little different to those of the starting material and assigned in the same manner. Similarly, in the ^{1}H NMR spectrum, the vinyl benzene side chain is again readily identifiable. The characteristic isolated singlet, ABX system and *pseudo* AB quartet are all analogous to those assigned for **2**. In this case however, the coupling between the two terminal olefin protons was too weak for resolution.

Metal complexes of 1-(4-vinylbenzyl)-1,5,9-triazacyclododecane (5)

Reaction with hydrated nickel(II) chloride. [μ-Aqua-di-μ-chloro-bis{1-(4-vinylbenzyl)-1,5,9-triazacyclododecanenickel(II)}] chloride (**6**) was synthesised *via* the addition of a methanolic solution of **5** to a freshly prepared solution (methanol) of hydrated nickel(II) chloride. A microcrystalline product formed upon slow evaporation of the solvent over a period of days and FAB(+ve) mass spectral evidence points to a dimeric chloride-bridged unit, with a strong peak at 798 u due to $L_2Ni_2Cl_3^+$.

Recrystallisation *via* slow evaporation of a CH_2Cl_2 solution of **6** produced small green prisms which were shown by X-ray crystallography to be the triply-bridged dimeric species illustrated in Fig. 2. There is an unexpected bridging water molecule, which is suspected to be present in other members of this family; the only previous report of halide-bridged Ni(II) triazacycloalkane complexes, which was non-structural, did not consider this possibility.[13] There are two crystallographically independent "dimers" in the asymmetric unit which, with the exception of the two phenyl rings **A** and **B** (which adopt slightly differing tilt angles), have essentially identical conformations. The complex has non-crystallographic C_s symmetry about a plane containing O(1), Cl(1) and Cl(2), and the two twelve-membered triazamacrocyclic rings have conformations that match to within 0.05 Å. This conformation, with its facial orientation of the three nitrogen centres, is distinctly different to that of the free ligand **5** which has a two-up, one-down relationship for the three nitrogen atoms.[8] The geometry at each nickel centre is distorted octahedral with *cis* angles ranging between 75.49(14) and 100.8(2)°, the acute angles being associated with the O–Ni–Cl linkages (Table 2). The Ni–N distances fall into two distinct groups, with those to the tertiary amino nitrogens N(1) and N(22) being, as expected, longer than those to the secondary amino nitrogens; the former are in the range 2.111(6)–2.125(7) Å whilst the latter range between 2.082(7) and 2.098(6) Å. Although there are statistically significant differences in the bridging Ni–Cl distances [that range between 2.433(2) and 2.502(2) Å], there is no systematic pattern of asymmetry in any of the bridges. The Ni–O bond lengths are typical of aqua-bridged species and range between 2.179(5) and 2.218(5) Å. The two chloride anions, Cl(3) and Cl(4), both of which lie on the molecular mirror plane, are linked to the cation *via* strong O–H ··· Cl hydrogen bonds from the bridging aqua ligand [the O ··· Cl distances range between 2.93(5) and 2.99(5) Å].

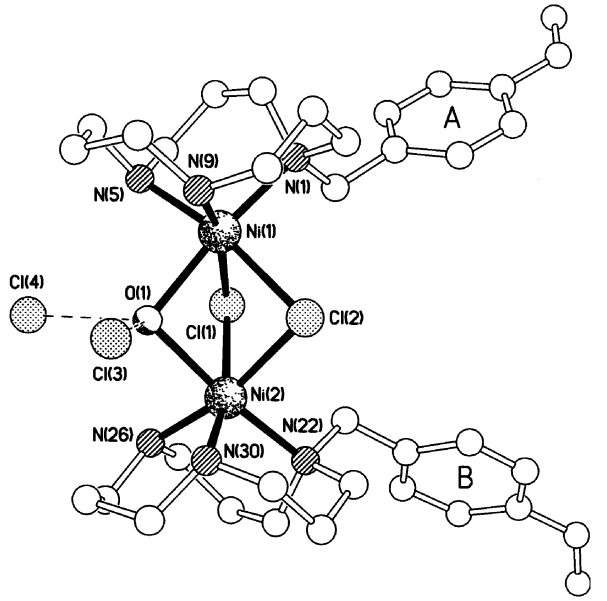


Fig. 2 One of the pair of crystallographically independent bridged dimers present in the structure of **6**. The geometries of the O–H ··· Cl hydrogen bonds are O ··· Cl, H ··· Cl distances (Å), O–H ··· Cl angle (°); 2.94, 2.08, 159 [Cl(3)]; 2.93, 2.04, 169 [Cl(4)]; and in the other independent dimer: 2.95, 2.07, 164 [Cl(3′)], 2.99, 2.17, 151 [Cl(4′)].

The two independent molecules have their pendant styryl arms interlocked asymmetrically such that the phenyl ring **A** of one molecule enters into a π-stacking interaction with its counterpart in the other (Fig. 3); the two rings are inclined by *ca.* 5° and have centroid ··· centroid and interplanar separations of 3.80 and 3.49 Å respectively. The other phenyl ring, **B**, is not involved in any intermolecular π-stacking interactions, nor are there any other intermolecular interactions of note.

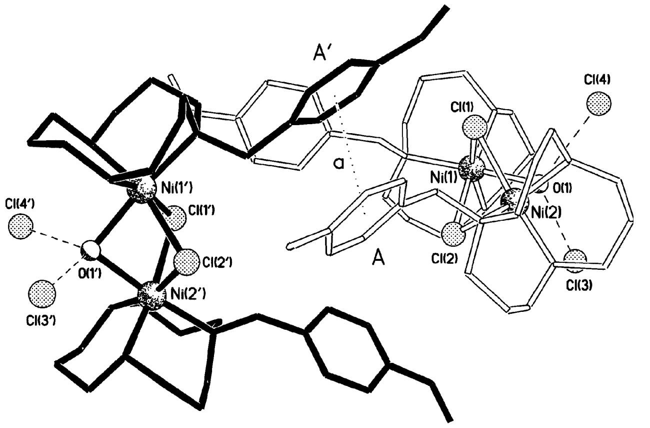


Fig. 3 The mutual interlocking of the pendant arms of pairs of independent molecules in the structure of **6**, showing also the π-stacking of rings **A**. The centroid ··· centroid separation (**a**) is 3.80 Å.

Reaction with copper(I) tetrakis(acetonitrile) hexafluorophosphate. Upon reaction of **5** with $Cu(CH_3CN)_4PF_6$ in dry CH_2Cl_2, a cream precipitate was initially formed along with a greenish solution. With exposure to air, the precipitate redissolved and the solution became deep blue, and eventually a blue microcrystalline powder was obtained. Elemental analysis of the compound (**7**) was consistent with a [di-μ-hydroxy-bis{1-(4-vinylbenzyl)-1,5,9-triazacyclododecanecopper(II)}] hexafluorophosphate formulation. Although crystals suitable for X-ray analysis were not obtained, it is thought that these would have a structure related to an allyl-substituted triazacyclododecane that features two bridging hydroxy moieties between the copper atoms.[14] FAB(+ve) mass spectral data indicate the presence of a strong LCu signal at 351 u and there is also a small peak assigned to LCuOH at 368 u. IR data show sharp N–H

Table 2 Selected bond lengths (Å) and angles (°) for the two independent molecules of **6**

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Ni(1)–N(1)	2.116(6)	2.111(6)	Ni(1)–N(5)	2.084(7)	2.082(7)
Ni(1)–N(9)	2.085(6)	2.098(6)	Ni(1)–O(1)	2.179(5)	2.218(5)
Ni(1)–Cl(1)	2.502(2)	2.437(2)	Ni(1)–Cl(2)	2.433(2)	2.476(2)
Ni(2)–N(22)	2.119(7)	2.125(7)	Ni(2)–N(26)	2.095(6)	2.097(6)
Ni(2)–N(30)	2.094(6)	2.089(7)	Ni(2)–O(1)	2.194(6)	2.209(5)
Ni(2)–Cl(1)	2.485(2)	2.444(2)	Ni(2)–Cl(2)	2.438(2)	2.457(2)
N(1)–Ni(1)–N(5)	94.3(3)	96.2(3)	N(1)–Ni(1)–N(9)	95.5(3)	95.0(2)
N(5)–Ni(1)–N(9)	96.9(3)	96.7(3)	N(1)–Ni(1)–O(1)	172.8(2)	173.4(2)
N(5)–Ni(1)–O(1)	90.7(2)	87.1(2)	N(9)–Ni(1)–O(1)	88.9(2)	90.4(2)
N(1)–Ni(1)–Cl(1)	99.7(2)	94.8(2)	N(5)–Ni(1)–Cl(1)	87.3(2)	92.4(2)
N(9)–Ni(1)–Cl(1)	163.9(2)	165.9(2)	N(1)–Ni(1)–Cl(2)	94.0(2)	100.1(2)
N(5)–Ni(1)–Cl(2)	168.0(2)	163.4(2)	N(9)–Ni(1)–Cl(2)	90.8(2)	85.2(2)
O(1)–Ni(1)–Cl(1)	75.49(14)	79.24(14)	O(1)–Ni(1)–Cl(2)	80.3(2)	76.44(14)
Cl(1)–Ni(1)–Cl(2)	82.84(7)	83.05(7)	N(22)–Ni(2)–N(26)	94.5(2)	97.0(3)
N(22)–Ni(2)–N(30)	95.7(3)	94.1(3)	N(26)–Ni(2)–N(30)	97.0(3)	96.8(3)
N(22)–Ni(2)–O(1)	173.3(2)	173.6(2)	N(26)–Ni(2)–O(1)	90.9(2)	87.9(2)
N(30)–Ni(2)–O(1)	87.6(2)	89.4(2)	N(22)–Ni(2)–Cl(1)	100.8(2)	96.7(2)
N(26)–Ni(2)–Cl(1)	86.4(2)	89.4(2)	N(30)–Ni(2)–Cl(1)	162.9(2)	166.9(2)
N(22)–Ni(2)–Cl(2)	94.2(2)	97.7(2)	N(26)–Ni(2)–Cl(2)	167.4(2)	164.2(2)
N(30)–Ni(2)–Cl(2)	91.2(2)	87.8(2)	O(1)–Ni(2)–Cl(1)	75.6(2)	79.25(14)
O(1)–Ni(2)–Cl(2)	79.87(14)	77.00(14)	Cl(1)–Ni(2)–Cl(2)	83.08(7)	83.29(7)
Ni(1)–O(1)–Ni(2)	93.4(2)	92.0(2)	Ni(1)–Cl(1)–Ni(2)	79.31(6)	81.40(7)
Ni(1)–Cl(2)–Ni(2)	81.59(7)	80.36(7)			

stretches at 3650 cm^{-1} and 3270 cm^{-1}, along with an O–H stretching vibration at 3280 cm^{-1}.

Reaction with copper(II) chloride. Addition of a methanolic solution of **5** to a solution of hydrated copper(II) chloride, also in methanol, resulted in the formation of a small amount of a brown precipitate. This was removed *via* filtration and the solution was dried *in vacuo* to yield a blue oil believed to be [aqua-dichloro-{1-(4-vinylbenzyl)-1,5,9-triazacyclododecane}copper(II)] (**8**). Dissolution in CH_2Cl_2 yielded another portion of the brown contaminant however; the blue solution was therefore filtered and removal of solvent *in vacuo* gave a light green powder. Elemental analysis of this powder is consistent with an [aqua-dichloro-{1-(4-vinylbenzyl)-1,5,9-triazacyclododecane}copper(II)] formulation. The FAB(+ve) mass spectrum has a fragmentation pattern with strong peaks due to LCu and LCuCl. IR data show the characteristic N–H and C=C stretches along with a broad signal at *ca.* 3325 cm^{-1} due to O–H stretching. An ESR spectrum contains a single peak consistent with a Jahn–Teller distorted octahedral copper(II) system and the proposed structure is shown in Fig. 4.

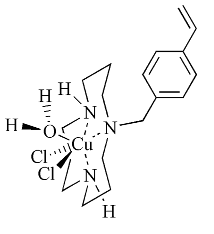


Fig. 4 Proposed structure of **8**.

Reaction with zinc(II)chloride. Reaction in methanol of equimolar amounts of **5** and hydrated zinc(II) chloride, lead to the isolation of a crude product which from FAB(+ve) MS and NMR data appears to involve one zinc(II) centre coordinated to the macrocyclic ligand *i.e.* [{1-(4-vinylbenzyl)-1,5,9-triazacyclododecane}zinc(II) chloride] (**9**). The product however, is very deliquescent and attempts to obtain accurate elemental analysis were unsuccessful. This failure is probably due to the labile nature of the d^{10} metal centre and the range of products that are possible. FAB (+ve) MS data indicate the presence of a LZnCl unit (388 u). In the IR spectrum, obtained as a KBr disc, typical ligand peaks are visible at 3460, 3200 and 1630 cm^{-1}. To explain the hydroscopic nature of the material it is postulated that a range of products may exist of the form $LZnCl_nH_2O_m$, where $n \leq 2$ and $1 \leq n + m \leq 3$. The possibility of incomplete macrocycle coordination cannot be dismissed however, due to lability at the zinc(II) centre; products with a tricoordinated macrocyclic arrangement are expected to dominate.

Reaction with cobalt(II) chloride. Addition of anhydrous or hydrated cobalt(II) chloride to **5** in methanol, produced an intense blue amorphous solid, thought to be [chloro-{1-(4-vinylbenzyl)-1,5,9-triazacyclododecane}cobalt(II)] chloride (**10**), but recurring problems with slow oxidation of the material made isolation of the pure product very difficult. FAB(+ve) mass spectra of freshly prepared crude samples indicate the presence of a LCoCl fragment. Although the majority of isolated product was an unstable amorphous solid, a small amount of stable blue crystalline product was obtained by recrystallisation under inert atmospheres, and microanalysis gave good agreement with the expected formulation.

Reaction with tungsten pentacarbonyl–tetrahydrofuran. Attempts to synthesise complexes of the form $LW(CO)_3$, where L is a triazamacrocyclic ligand, by heating **5** in decalin with tungsten hexacarbonyl failed. The use of $W(CO)_3(CH_3CN)_3$ also did not produce the desired product, so the $W(CO)_5$·THF adduct was used as an alternative starting material for W–N bond formation and to give, at least initially, monodentate coordination. The $W(CO)_5$·THF adduct was prepared by irradiating (using a 125 W medium pressure mercury lamp) a solution of tungsten hexacarbonyl in dry THF, whilst bubbling nitrogen through the solution. A water-cooled vessel was used to dissipate the heat produced in the process and irradiation was carried out for a period of around 10 minutes with the reaction being monitored in the IR carbonyl region. The adduct solution was added to a dry, degassed THF solution of **5** and the mixture stirred. The product was extracted from the reaction mixture after several hours by dissolution in CH_2Cl_2 and precipitation of unwanted side products in hexane. Removal of the solvent *in vacuo* led to the deposition of a yellow crystalline material (any excess starting material was removed by sublimation). Elemental analysis is correct for addition of one $W(CO)_5$ unit to the macrocycle and mass spectral data also indicate that the material is [**5**·$W(CO)_5$] (**11**), although the major tungsten fragmentation pattern (555) is due to

Table 3 Selected bond lengths (Å) and angles (°) for **11**

W–N(5)	2.318(5)	W–C(24)	2.043(7)
W–C(22)	1.975(8)	W–C(25)	2.042(7)
W–C(23)	2.034(8)	W–C(26)	2.014(7)
C(22)–W–N(5)	175.1(3)	C(23)–W–N(5)	92.0(3)
C(24)–W–N(5)	95.9(2)	C(25)–W–N(5)	88.3(2)
C(26)–W–N(5)	90.0(3)	C(22)–W–C(23)	90.6(3)
C(22)–W–C(24)	88.3(3)	C(22)–W–C(25)	88.9(3)
C(22)–W–C(26)	85.8(3)	C(23)–W–C(24)	87.7(3)
C(23)–W–C(25)	178.0(3)	C(23)–W–C(26)	89.1(3)
C(24)–W–C(25)	94.3(3)	C(24)–W–C(26)	173.3(3)
C(25)–W–C(26)	88.9(3)		

$[LW(CO)_3]^+$. The IR spectrum (CH_2Cl_2) shows two bands at 3600 and 3685 cm^{-1} due to N–H stretching, the latter being markedly stronger. As expected for the C_{4v} symmetry of $LW(CO)_5$, three C=O stretches are evident (1890, 1920 and 2065 cm^{-1}), with the one at 2065 cm^{-1} being substantially weaker; there is also the clearly identifiable C=C stretch at 1605 cm^{-1}.

The unsymmetrical coordination of **5** is borne out by the ^1H NMR spectrum. The side chain peaks are essentially unchanged from those of the free ligand but the peaks due to the macrocyclic protons have developed a complex fine structure. There appear to be three distinct multiplets for the trimethylene peaks centred around 1.54, 1.67 and 1.87 ppm although two of these overlap indicating that the tungsten is not bridging the two secondary amines. The protons on the methylene groups α to the nitrogens are visible as three complex multiplets in a 1 : 3 : 2 ratio. Interestingly, only one amino hydrogen is visible as a broad peak centred at 5.70 ppm overlaid with a vinyl proton.

Single crystal X-ray analysis indicated that the macrocycle had replaced the THF in the $W(CO)_5{\cdot}THF$ adduct, coordinating through a single secondary amine site [Fig. 5, Table 3], presumably due to steric constraints at the more basic tertiary amine N(1). The twelve-membered macrocyclic ring has a two-down, one-up arrangement of the three nitrogen atoms, a geometry observed in the free ligand (**5**),[8] though the overall conformation differs markedly. In the free ligand, however, the conformation was influenced by an intramolecular N–H ··· N hydrogen bond. Although the differences are not statistically significant, the two C–N bonds to the coordinated nitrogen N(5) [1.500(9) and 1.508(8) Å] are not surprisingly longer than those to the other two nitrogen atoms [where the C–N distances range between 1.449(9) and 1.481(10) Å]. The geometry at tungsten is slightly distorted octahedral with *cis* angles ranging between 85.8(3) and 95.9(2)°. The W–N bond is long [2.318(5) Å], though it is comparable with those seen in, for example, $W–NR_3$ species. The W–C bond *trans* to nitrogen is significantly shorter [1.975(8) Å] than those to the other carbonyl carbon atoms, which range between 2.014(7) and 2.043(7) Å. There are no noteworthy intermolecular π–π, C–H ··· π or C–H ··· O interactions.

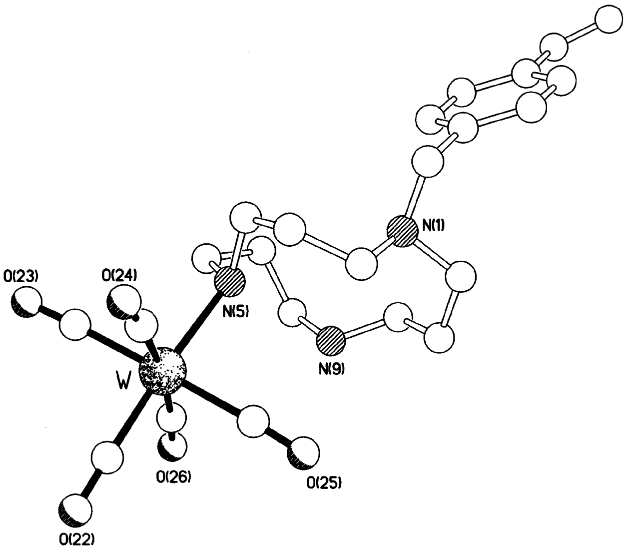


Fig. 5 The molecular structure of **11**.

Table 4 Polymerisation data for **P-1** to **P-4**

Polymers	M_w	M_n	Polydispersity
Ligand **5** (**P-1**)	4,630	1,480	3.1
	4,210	1,870	2.3
Ligand **5** + styrene (**P-2**)	7,450	4,540	1.6
	7,530	4,660	1.6
Ni complex + styrene (**P-3**)	3,540,000	3,570	990
	4,290,000	4,200	1,000
Zn complex + styrene (**P-4**)	166,000	24,200	3.1
	179,000	24,800	3.1

Polymerisations

Incorporation of triazamacrocycles into polymers is rare, so to investigate the possibilities for this, **5** was polymerised *via* radical polymerisation with AIBN (azoisobutyronitrile) alone and, along with its nickel and zinc complexes, co-polymerised with styrene.

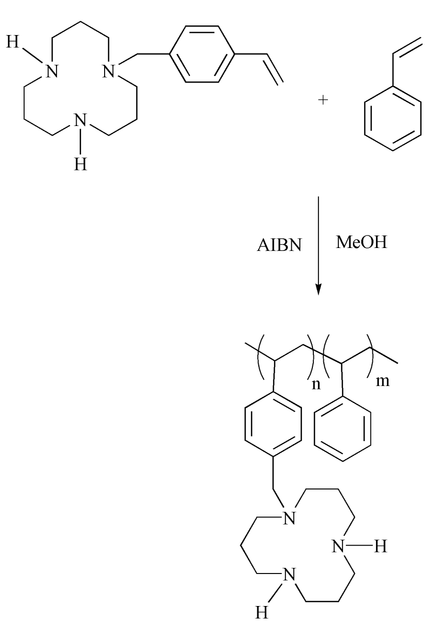
Homo-polymerisation of 5. Using ethanol and 4 mol% AIBN, an alcohol soluble polymeric material (**P-1**) was obtained in 25% yield after reprecipitation from methanol and diethyl ether. Analysis by ^1H NMR in d_4-methanol showed no evidence for the presence of unreacted starting material as shown by the lack of vinyl signals. Instead seven broad single peaks are seen at the expected positions in the spectrum with confirmatory integrals.

The polymeric material produced was partially soluble in chloroform and this allowed GPC measurements to be taken by RAPRA Technology Ltd. A sample solution was prepared by adding 10 mL of solvent to 20 mg of sample and leaving overnight to dissolve. On the following day, the solution was warmed at 50 °C for 30 minutes, a small amount of 1,2-dichlorobenzene was added as an internal marker and the solution thoroughly mixed. The solution was filtered through a 0.2 micron polyamide membrane prior to the chromatography. Polymer **P-1** did not completely dissolve, and this weak sample is probably responsible for the poor reproducibility of the results.

From the calculated molecular weights, it is clear that polymeric material is present (Table 4), although it is likely that higher molecular weight material was insoluble in the solvent and the actual numbers calculated must be treated as only applicable to the low RMM material. In addition, the data have been calculated with respect to a polystyrene standard, and this homo-polymer with large polarisable macrocycles in high concentration, is likely to have very different properties and hence the calculated masses are only estimates.

It appears from the slow degradation of stored samples of **5** that some spontaneous bulk polymerisation occurs. Supporting evidence that this is possible was obtained from an attempt at purification of the monomer by distillation under high vacuum. It was also clear that polymers with a high percentage of macrocycle have poor solubilities in aprotic solvents which lead to characterisation problems. Therefore, a series of copolymers with styrene and 1 mol% of the macrocycle or its nickel and zinc complexes were obtained (Scheme 2).

Co-polymerisation of 5 (1%) and its nickel and zinc complexes (1%) with styrene (P-2, P-3 and P-4 respectively). The 99% styrene polymers were all soluble in CH_2Cl_2, and could be reprecipitated by addition of hexane, or in the case of the nickel containing polymer (**P-3**), diethyl ether. In addition, the green colouration of **P-3** indicated that this polymer still contained



Scheme 2 Copolymerisation of **5** and styrene.

the metal ion. Whether this was due to the continued presence of the macrocycle complex as part of the polymer chain or simply the trapping of the salt within the polymer was not clear.

However, the solubility of these polymers in chlorinated solvents allowed for analysis by NMR and the acquisition of GPC data (Table 4, Fig. 6). GPC analysis (two runs, A and B, were performed for each sample) of the three samples (**P-2**, **P-3** and **P-4**) was provided by RAPRA Technology Ltd, using chloroform as solvent, calibrated with polystyrene. The results are therefore expressed as "polystyrene equivalent" molecular masses and it should be noted that there could be some differences between these and the actual molecular masses of the samples. The results are summarised in Table 4 and show the computed molecular weight distributions normalised to equal areas upon which these are based.

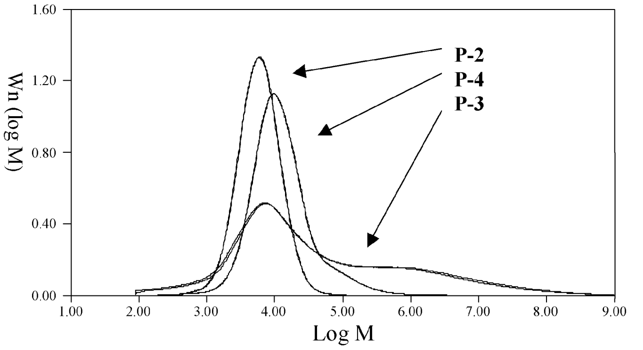


Fig. 6 GPC analysis of **P-2**, **P-3** and **P-4**.

On a simple level these results prove that these are polymeric samples. Polymer **P-2**, synthesised from the free macrocycle, behaves like a slightly polydisperse low weight polystyrene, and these data alone show no evidence of incorporation of the macrocycle within the polymer. However, both the metal containing polymeric samples have significant high molecular weight tails in the molecular weight distributions. This indicates a certain degree of cross-linking in these two samples, the origin of which is most obvious when one considers polymer **P-3**. If it is assumed that the metal complex maintains the same dimeric form within the polymer as is known to be exhibited by the monomer, then the dimeric unit can be thought of essentially as a cross-linking agent with two positions available for polymer growth. In the average case, assuming similar activity of the complex and styrene, only one unit in a hundred would be cross-linking. Hence, one would expect a mixture of low molecular weight polystyrene, with much higher molecular weight cross-linked metal containing polymer. This is manifest in the computed distribution by two apparently distinct distributions, one centred at $M \approx 6300$, superimposed with a highly polydisperse curve centred at $M \approx 10^6$. The first peak is equivalent to about 60 styrene units which fits this hypothesis, while the polydispersity of the rest of the sample is consistent with the presence of a low level of cross-linking agent. This is of course, an over simplification, ignoring the possibility of only one alkene on the nickel dimer being involved in polymerisation and assuming similar reactivities between the two monomers, but the results clearly show this to be an interesting area requiring further research.

The zinc-containing polymer **P-4**, has a less pronounced shoulder at the high molecular weight end of the distribution. This also suggests an element of cross-linking which is evidence of formation in solution of bis-macrocyclic complexes at the labile Zn(II) centres. Since the isolation of the monomeric complex has not been achieved, evidence for the coordination geometry at the Zn(II) atom or for the nature of the other ligands are not available, but an octahedral system with three coordinated aqua ligands is one species likely to be present in solution. The loss of a hydrated Zn(II) moiety to give the metal centre octahedrally coordinated to two macrocycles would account for this cross-linking. Whether this process is reversible or the steric bulk of the polymer essentially locks the system by preventing the approach of alternative donors is a topic of on-going debate. A similar situation has been postulated in a di-substituted triazacyclododecane Zn(II) co-polymer with styrene synthesised by Fish and co-workers.[5]

^{1}H NMR and ^{13}C-{^{1}H} NMR data have been obtained for all three of the copolymers in $CDCl_3$. Comparison of these data with the monomer and polystyrene shows evidence of the incorporation of the macrocycle and complexes within the copolymers. The informative region in both cases is that of the amine substituted macrocycle peaks. The ^{1}H NMR of the three polymers is dominated by broad signals from the main polystyrene chain, occurring in the alkyl region as two strong signals at around 1.4 and 1.8 ppm, with a weaker triplet signal at ≈0.9 ppm presumably due to the initiator residue. The only region in which unobscured signals from the macrocycle appear is the aminoalkyl region *i.e.* ≈ 2.1–3.4 ppm, although the upfield edge of this is also obscured. Broadened peaks are clearly visible in **P-2**, whilst **P-3** and **P-4** show evidence of very weak broadened signals in this area.

In conclusion, the coordination chemistry and novel polymerisation studies of the substituted macrocycle show great potential, and further work is in progress to elucidate interesting properties of the polymers.

Experimental

Air sensitive preparations were carried out using standard Schlenk tube techniques under a pre-dried nitrogen atmosphere.[15] Dry solvents were distilled from standard drying agents (THF, diethyl ether, toluene and hexane from Na/benzophenone, CH_2Cl_2 from CaH_2) under nitrogen directly prior to use. Starting materials were obtained from Aldrich, Lancaster or Acros chemical companies, and used as received. NMR spectra were recorded on a Delta upgrade of a JEOL JNM-EX 270 MHz spectrometer operating at 270.1 MHz (^{1}H) and 67.9 MHz (^{13}C-{^{1}H}) and chemical shifts (δ) are reported in ppm using $CDCl_3$ (^{1}H δ 7.25 ppm, ^{13}C-{^{1}H} δ 77.0 ppm) as reference for the spectra. IR spectra were recorded using Nujol mulls, KBr discs or NaCl solution cells (CH_2Cl_2) on a Mattson Polaris Fourier Transform IR Spectrometer and results expressed in cm^{-1}. FAB(+ve) mass spectra were recorded using an AutoSpec-Q mass spectrometer. The primary ion beam was 35 keV Cs+, and the matrix used was 3-nitrobenzyl alcohol.

Microanalyses were carried out at SACS, University of North London.

Ligands

1,5,9-Triazatricyclo[7.3.1.0$^{5.13}$]tridecane (1). **1** was formed *via* the following adaption of literature methods.[10,11] 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (1.03 g, 7.4 mmol), propan-1,3-diol ditosylate (3.42 g, 8.9 mmol) and sodium borohydride (0.30 g, 7.9 mmol) were mixed in dry toluene (45 mL), along with finely ground potassium hydroxide (1.25 g) and potassium bromide (1.25 g). After 3 days vigorous stirring at ambient temperature, ethyl acetate (50 mL) was added, and the mixture extracted with 1 M sodium hydroxide (4 × 25 mL). The combined aqueous extracts were washed with ethyl acetate (25 mL) that was back extracted with 1 M sodium hydroxide (25 mL). The combined aqueous extracts were saturated with sodium chloride, then extracted with dichloromethane (5 × 50 mL), dried over sodium sulfate, filtered and the solvent removed *in vacuo* to leave an amber coloured oil. The amber oil was taken up in diethyl ether, leaving a solid residue. The diethyl ether was decanted and dried over sodium sulfate. The product (a colourless oil which crystallised on cooling) was recovered by drying *in vacuo* (0.70 g, 52%).

5-(4-Vinylbenzyl)-1,5,9-triazabicyclo[7.3.1]tridecinium chloride (2). To **1** (0.50 g, 2.8 mmol) in hexane (40 mL) was added 4-vinylbenzyl chloride (0.55 mL, 3.0 mmol) and with stirring at 60 °C, the 4-vinylbenzyl chloride slowly dissolved. After 24 h, the reaction mixture went cloudy and a white solid formed upon the sides of the reaction vessel. After 48 h, a clear liquid was decanted off the tacky white solid. Upon evaporation of the solvent from the liquid, a white crystalline mass was formed which was recrystallised from CH_2Cl_2 (0.70 g, 2.1 mmol, 76%). IR (Nujol) 1680 ν(N=C); 1615 ν(C=C) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.35–1.40 [m, 2H, H_{3a}], 1.79 [m, 2H, H_{3e}], 2.12–2.28 [m, 2H, $H_{7a,7e}$], 2.95 [dd, 2H, H_{4a}, $^3J_{HH}$ = 14.6, 4.0], 3.10–3.14 [m, 2H, H_{6a}], 3.18–3.29 [m, 4H, $H_{6e,2e}$], 3.37 [br t, 2H, H_{4e}, $^3J_{HH}$ = 13], 3.59 [s, 2H, H_{14}], 4.44 [br t, 2H, H_{2a}, $^3J_{HH}$ = 13], 5.25 [ABX, H_{22a}, $^3J_{AX}$ = 10.9, $^2J_{AB}$ = 0.7], 5.74 [ABX, 1H, H_{22b}, $^3J_{BX}$ = 17.6, $^2J_{AB}$ = 0.7], 6.68 [ABX, 1H, H_{21}, $^3J_{AX}$ = 10.9, $^3J_{BX}$ = 17.6], 7.23 [AB, 4H, $H_{16,17}$], 10.06 [s, 1H, H_{13}]. ^{13}C-{^{1}H} NMR (67.5 MHz, $CDCl_3$) δ 19.8 [C_7], 23.9 [C_3], 42.3 [C_6], 54.9 [C_2], 55.5 [C_4], 56.8 [C_{14}], 114.4 [C_{22}], 126.2 [C_{16}], 130.6 [C_{17}], 135.5 [C_{18}], 136.2 [C_{21}], 137.1 [C_{15}], 159.1 [C_{13}]. MS (FAB +ve) 298 [100, M$^+$].

Crystal data for **2**. $C_{19}H_{28}N_3Cl\cdot H_2O$, M = 351.9, monoclinic, $P2_1/n$ (no. 14), a = 10.547(1), b = 12.712(1), c = 14.981(1) Å, β = 102.87(1)°, V = 1958.1(2) Å^3, Z = 4, D_c = 1.194 g cm^{-3}, μ(Cu-Kα) = 1.80 mm^{-1}, T = 293 K, clear prismatic needles; 3116 independent measured reflections, F^2 refinement, R_1 = 0.046, wR_2 = 0.111, 2548 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 126°$], 234 parameters.[16]

CCDC reference number 170670.

1-Methyl-5-(4-vinylbenzyl)-1,5,9-triazacyclododecane (3). **2** (1.36 g, 4.1 mmol) was dissolved in ethanol (50 mL) and cooled in an ice-bath. Sodium borohydride (1.60 g, 41.0 mmol) was added with stirring and the reaction flask was removed from the ice-bath. After 1 h, the mixture was heated to reflux for a further 8 h. The slush was allowed to cool then diethyl ether (500 mL) was added and the vessel placed in a freezer for 2 h. The mixture was then filtered to remove any solid material. Concentrated hydrochloric acid was added to the ethereal solution and a white precipitate formed, which was separated and dissolved in water (150 mL). Sodium hydroxide pellets were added to a give a pH of *ca.* 14 and the aqueous solution was extracted with CH_2Cl_2 (4 × 50 mL portions). The combined organic layers were dried over magnesium sulfate and the solvent was then removed *in vacuo* to leave a pale yellow oil (1.01 g, 3.4 mmol, 84%). IR (neat) 3400 ν(N–H); 1630 ν(C=C) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.45–1.81 (m, 6H, $CH_2C\mathit{H}_2CH_2$), 2.19 (s, 3H, $NC\mathit{H}_3$), 2.37 (t, 2H, $NC\mathit{H}_2CH_2$, ^3J 5.8), 2.41–2.51 (m, 4H, $NC\mathit{H}_2CH_2$), 2.56 (t, 2H, $NC\mathit{H}_2CH_2$, ^3J 5.6), 2.62 (t, 2H, $NC\mathit{H}_2CH_2$, ^3J 5.0), 2.83 (t, 2H, $NC\mathit{H}_2CH_2$, ^3J 5.0), 3.41 (s, 2H, $NC\mathit{H}_2C_6H_4$), 5.19 (ABX, 1H, –HC=CHH_A, $^3J_{AX}$ 10.9, $^2J_{AB}$ 1.0), 5.70 (ABX, 1H, –HC=CH_BH, $^3J_{BX}$ 17.6, $^2J_{AB}$ 1.0), 6.67 (ABX, 1H, –HC=CH_2, $^3J_{AX}$ 10.9, $^3J_{BX}$ 17.6), 7.23–7.37 (m, 4H, $C_6\mathit{H}_4$). ^{13}C-{^{1}H} NMR (67.5 MHz, $CDCl_3$) δ 23.8 ($CH_2\mathit{C}H_2CH_2$), 24.0 ($CH_2\mathit{C}H_2CH_2$), 24.2 ($CH_2\mathit{C}H_2CH_2$), 40.7 ($N\mathit{C}H_3$), 48.5 ($RHN\mathit{C}H_2CH_2$), 49.5 ($RHN\mathit{C}H_2CH_2$), 50.2 ($RR'N\mathit{C}H_2C_6H_6$), 54.3 ($RR'N\mathit{C}H_2CH_2$), 54.5 ($RR'N\mathit{C}H_2CH_2$), 57.4 (–(H_3C)$N\mathit{C}H_2CH_2$), 58.7 (–(H_3C)-$N\mathit{C}H_2CH_2$), 113.6 ($H_2\mathit{C}$=CH–C_6H_4), 126.3 (C_6H_4), 129.0 (C_6H_4), 136.5 (C_6H_4), 136.6 (H_2C=CH–C_6H_4), 139.1 (C_6H_4). MS (CI +ve [NH_4]) 302 [100, (M + H)$^+$], 184 [50, $C_{10}H_{22}N_3{}^+$].

5,9-Dimethyl-1-(4-vinylbenzyl)-1,5,9-triazacyclododecane (4). **3** (1.00 g, 3.4 mmol) was dissolved in methanol (25 mL) and 37–40% aqueous formaldehyde (2.5 mL, 30.0 mmol) was added and stirred for 2 min. Sodium borohydride (1.40 g, 37.0 mmol) was added rapidly and the mixture stirred for 12 h. The reaction mixture was added to diethyl ether (250 mL), and cooled to −20 °C for 3 h. The white precipitate formed was filtered and the filtrate was extracted with 10% hydrochloric acid solution. The aqueous solution was brought to pH 14 by addition of sodium hydroxide pellets and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed *in vacuo*, to give a clear oil which solidified on standing (0.76 g, 2.4 mmol, 70%). IR (KBr disc) 1650 ν(C=C) cm^{-1}. ^{1}H NMR (270 MHz, 343 K, $C_6D_5CD_3$) δ 1.45–1.90 (m, 6H, $H_{3,7}$), 2.06 (s, 6H, H_{22}), 2.29 (t, 4H, H_{16}, ^3J 3.1), 2.35 (t, 4H, H_6, ^3J 2.8), 2.56 (t, 4H, H_4, ^3J 5.4), 3.43 (s, 2H, H_2), 5.05 (ABX, H_{13}, $^3J_{AX}$ 10.9, $^2J_{AB}$ 1.1), 5.59 (ABX, 1H, $H_{21\text{-}cis}$, $^3J_{BX}$ 17.7, $^2J_{AB}$ 1.1), 6.60 (ABX, 1H, $H_{21\text{-}trans}$, $^3J_{AX}$ 10.8, $^3J_{BX}$ 17.8), 7.22–7.31 (m, 4H, $H_{15,16}$). ^{13}C-{^{1}H} NMR (67.5 MHz, 343 K, $CDCl_3$) δ 22.0 (C_3), 22.3 (C_7), 43.2 (C_{22}), 49.3 (C_4), 52.2 (C_6), 58.9 (C_{13}), 113.2 (C_{21}), 126.0 (C_{15}), 129.0 (C_{16}), 136.2 (C_{17}), 136.7 (C_{20}), 140.3 (C_{14}). MS (CI +ve[NH_4]) 316 [100, (M + H)$^+$].

1-(4-Vinylbenzyl)-1,5,9-triazacyclododecane (5). Sodium hydroxide (40.0 g, 1.0 mol) was dissolved in a 2 : 1 water : ethanol solution (450 mL), and **2** (3.00 g, 9.3 mmol) was added and the solution was refluxed for 72 h. The aqueous solution was extracted with CH_2Cl_2 (5 × 100 mL) and the combined extracts were dried over magnesium sulfate. The solvent was filtered and removed *in vacuo* to leave a pale yellow oil which solidified upon standing for several weeks (2.51 g, 8.7 mmol, 94%). IR (neat) 3400, 3270 ν(N–H); 1630 ν(C=C) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.70 [p, 4H, $CH_2C\mathit{H}_2CH_2$, $^3J_{HH}$ = 5.6], 1.80 [m, 4H, $CH_2C\mathit{H}_2CH_2$, $^3J_{HH}$ = 5.20], 2.48 [t, 4H, $NC\mathit{H}_2CH_2$, $^3J_{HH}$ = 5.8], 2.67 [t, 4H, $NC\mathit{H}_2CH_2$, $^3J_{HH}$ = 5.3], 2.86 [t, 4H, $NC\mathit{H}_2CH_2$, $^3J_{HH}$ = 5.2], 3.42 [s, 2H, $NC\mathit{H}_2C_6H_4$], 5.19 [ABX, 1H, –HC=CHH_A, $^3J_{AX}$ = 10.9], 5.70 [ABX, 1H, –HC=CH_BH, $^3J_{BX}$ = 17.6], 6.66 [ABX, 1H, –HC=CH_2, $^3J_{AX}$ = 10.9, $^3J_{BX}$ = 17.8], 7.22–7.35 [AB, 4H, $C_6\mathit{H}_4$]. ^{13}C –{^{1}H} NMR (67.5 MHz, $CDCl_3$) δ 25.3 [$CH_2\mathit{C}H_2CH_2$], 25.7 [$CH_2\mathit{C}H_2CH_2$], 46.8 [$RNH\mathit{C}H_2CH_2$], 49.7 [$RNH\mathit{C}H_2CH_2$], 52.5 [$RR'N\mathit{C}H_2CH_2$], 57.0 [$RR'N\mathit{C}H_2C_6H_6$], 113.5 [$H_2\mathit{C}$=CH–C_6H_4], 126.2 [C_6H_4], 129.2 [C_6H_4], 136.4 [C_6H_4], 136.6 [H_2C=CH–C_6H_4], 139.0 [C_6H_4]. MS (FAB +ve) 288 [100, (M + H)$^+$], 170 [40, $C_9H_{20}N_3{}^+$].

Complexes

[μ-Aqua-di-μ-chloro-bis{1-(4-vinylbenzyl)-1,5,9-triazacyclododecanenickel(II)}] chloride (6). To a 2.8 M methanolic solution of **5** (0.25 mL, 0.7 mmol) was added a 4.2 M methanolic solution of $NiCl_2\cdot 6H_2O$ (0.17 mL, 0.7 mmol). Upon standing for 2 days, intense green crystals were formed (0.08 g, 0.2 mmol, 29%) [X-ray quality crystals were obtained *via* slow evaporation of a CH_2Cl_2 solution of **6**]. mp 190–194 °C. Found: C, 49.7; H, 7.5; N, 9.3%. Calc. for $C_{36}H_{56}N_6ONi_2Cl_4$: C, 50.9; H, 6.6; N, 9.9%. IR (CH_2Cl_2) 3680, 3620 *v*(N–H); 3360 (br) *v*(O–H); 1610 *v*(C=C) cm^{-1}. MS (FAB +ve) 798 [30, $(C_{36}H_{58}N_6Ni_2Cl_3)^+$], 381 [100, $(C_{18}H_{29}N_3NiCl)^+$], 287 [55, $(C_{18}H_{29}N_3)^+$].

Crystal data for 6. $[C_{36}H_{56}N_6OCl_2Ni_2][Cl]_2\cdot 2.75CH_2Cl_2$, M = 1081.6, monoclinic, *C*2/*c* (no. 15), a = 18.828(1), b = 28.280(1), c = 38.356(3) Å, β = 92.75(1)°, V = 20400(2) $Å^3$, Z = 16 (two independent molecules), D_c = 1.409 g cm^{-3}, μ(Cu-Kα) = 5.78 mm^{-1}, T = 173 K, green prisms; 15145 independent measured reflections, F^2 refinement, R_1 = 0.088, wR_2 = 0.224, 10581 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 1102 parameters.[16]

CCDC reference number 170671.

[Di-µ-hydroxy-bis{1-(4-vinylbenzyl)-1,5,9-triazacyclododecanecopper(II)}] hexafluorophosphate (7). **5** (0.40 g, 1.4 mmol) was dissolved in dry CH_2Cl_2 (10 mL) under nitrogen and added dropwise with stirring to a solution of copper(I) tetrakis(acetonitrile) hexafluorophosphate (0.50 g, 1.3 mmol) in dry CH_2Cl_2 (10 mL) to form a cream precipitate. The solution was then exposed to air and the precipitate dissolved to form an intense blue solution. Within 10 min, a blue crystalline precipitate had formed which was filtered off, and washed with diethyl ether to give a blue microcrystalline powder (0.20 g, 0.2 mmol, 30%). Found: C, 41.9; H, 5.7; N, 7.9%. Calc. for $C_{36}H_{58}N_6Cu_2O_2P_2F_{12}$: C, 42.2; H, 5.7; N, 8.2%. IR (Nujol) 3650, 3270 *v*(N–H); 3280 *v*(O–H); 1607 *v*(C=C) cm^{-1}. MS (FAB +ve) 368 [2, $C_{18}H_{30}N_3CuO^+$], 351 [100, $C_{18}H_{29}N_3Cu^+$], 288 [8, $C_{18}H_{30}N_3{}^+$].

[Aqua-dichloro-{1-(4-vinylbenzyl-1,5,9-triazacyclododecane}-copper(II)] (8). **5** (0.41 g, 1.4 mmol) was dissolved in methanol (0.5 mL) and added to a solution of $CuCl_2\cdot 2H_2O$ (0.24 g, 1.4 mmol) in methanol (1 mL). A light brown oil formed, and addition of CH_2Cl_2 (10 mL) gave a green-blue solution and a brown precipitate, which was removed by filtration and solvent was removed *in vacuo* to leave a dark blue oil. This was redissolved in CH_2Cl_2 (10 mL) and a brown precipitate was separated. Following filtration and removal of solvent *in vacuo*, a light green powder was collected (0.42 g, 0.9 mmol, 30%). Found: C, 50.1; H, 7.1; N, 9.4%. Calc. for $C_{18}H_{31}N_3OCuCl_2$: C, 49.2; H, 7.1; N, 9.6%. IR (KBr disc) 3400, 3210 *v*(N–H); 3325 (br) *v*(O–H); 1630 *v*(C=C) cm^{-1}. MS (FAB +ve) 386 [10, $C_{18}H_{29}N_3CuCl^+$], 351 [75, $C_{18}H_{29}N_3Cu^+$], 288 [100, $C_{18}H_{30}N_3{}^+$].

Complex of [1-(4-vinylbenzyl)-1,5,9-triazacyclododecane] with zinc(II) chloride (9). **5** (0.77 g, 2.7 mmol) was dissolved in methanol (2 mL), and added with stirring to a solution of hydrated zinc chloride (0.37 g, 2.7 mmol) in methanol (10 mL). The solution was filtered to remove a small amount of white precipitate. Solvent was removed *in vacuo*, to give an oily solid. This crude product was dissolved in CH_2Cl_2 (5 mL), and diethyl ether added (10 mL) yielding a deliquescent, cream precipitate (0.25 g, 0.6 mmol, 22%). IR (KBr disc) 3460, 3200 *v*(N–H); 1630 *v*(C=C) cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 1.8–1.9 [br m, 4H, $CH_2CH_{2\alpha}CH_2$], 1.9–2.1 [br, 2H, $CH_2CH_{2\beta}CH_2$], 2.5–2.6 [br, 4H, $NCH_{2\alpha}CH_2$], 2.8–2.9 [br, 4H, $NCH_{2\alpha}CH_2$], 3.0–3.2 [br, 4H, $NCH_{2\chi}CH_2$], 3.5 [s, 2H, $NCH_2C_6H_4$], 5.22 [ABX, 1H, –HC=CHH_A, $^3J_{AX}$ = 10.9], 5.73 [ABX, 1H, –HC=CH_BH, $^3J_{BX}$ = 17.6], 6.65 [ABX, 1H, –*H*C=CH_2, $^3J_{AX}$ = 10.9, $^3J_{BX}$ = 17.6], 7.18–7.37 [AB, 4H, C_6H_4]. IR (KBr disc) 3460, 3200, 1628, 1597 cm^{-1}. MS (FAB +ve) 388 [25, $C_{18}H_{29}N_3ZnCl^+$], 288 [100, $C_{18}H_{30}N_3{}^+$].

[Chloro-{1-(4-vinylbenzyl)-1,5,9-triazacyclododecane}-cobalt(II)] chloride (10). A solution of **5** (0.10 g, 0.4 mmol) in dry methanol (1 mL) was added to a solution of anhydrous $CoCl_2$ (0.05 g, 0.4 mmol) also in dry methanol (1 mL). Removal of solvent *in vacuo* gave a blue oil in which pink spherelites formed but as the sample returned to room temperature a blue amorphous solid appeared. The blue solid was dissolved in dry CH_2Cl_2 (5 mL) and diethyl ether (5 mL) added. An opaque liquid formed above a blue amorphous solid. The blue solid decomposed slowly and resisted further attempts at purification, however from the opaque liquid, air-stable feathery blue crystals were formed (0.02 g, 0.03 mmol, 11%). Found: C, 52.1; H, 6.5; N, 10.2%. Calc. for $C_{18}H_{29}N_3CoCl_2$: C, 51.8; H, 7.0; N, 10.0%. MS (FAB +ve) 382 [27, M^+], 288 [100, $C_{18}H_{30}N_3{}^+$].

{1-(4-Vinylbenzyl)-1,5,9-triazacyclododecane}tungsten pentacarbonyl (11). **5** (0.25 g, 0.9 mmol) was dissolved in dry degassed THF (5 mL) in a pre-dried Schlenk tube under a nitrogen atmosphere. A solution of tungsten pentacarbonyl—tetrahydrofuran (18 mL, 0.7 mmol) was added with stirring (the tungsten pentacarbonyl—tetrahydrofuran was prepared by dissolving tungsten pentacarbonyl (2.0 g) in dry, degassed THF (150 mL), under a slow but constant flow of nitrogen, and irradiating with a 125 W medium pressure mercury lamp, for *ca.* 10 min). The solution was stirred for 8 h, and the solvent removed *in vacuo* from the brown solution. The solid residue was dissolved in dry CH_2Cl_2 (10 mL) and dry hexane (10 mL) added with the resultant brown precipitate being filtered from the yellow solution. Concentration of the solution *in vacuo* to ≈5 mL, lead to the growth from solution of a yellow crystalline product (**11**) suitable for X-ray analysis (0.24 g, 45%). Found: C, 44.9; H, 4.7; N, 6.8%. Calc. for $C_{23}H_{29}N_3O_5W$: C, 45.2; H, 4.8; N, 6.9%. IR (CH_2Cl_2) 3685, 3600 *v*(N–H); 2065, 1890, 1920 *v*(C=O); 1605 *v*(C=C) cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 1.42–1.71 [m, 4H, $CH_2CH_2CH_2$], 1.81–2.02 [m, 2H, $CH_2CH_2CH_2$], 2.28–2.41 [m, 2H, NCH_2CH_2], 2.49–2.82 [m, 6H, NCH_2CH_2], 2.99–3.40 [m, 4H, NCH_2CH_2], 3.45 [s, 2H, $C_6H_4CH_2N$], 5.21–5.25 [ABX, 1H, –HC=CHH_A], 5.70–5.77 [ABX + br s, 2H, –HC=CH_BH + N*H*], 6.65–6.76 [ABX, 1H, –*H*C=CH_2], 7.24–7.25 [AB + s, 2.5H, C_6H_4, $CHCl_3$], 7.36–7.39 [AB, 2H, C_6H_4]. ^{13}C-{^1H} NMR (67.5 MHz, $CDCl_3$) δ 25.5 [$CH_2CH_2CH_2$], 26.3 [$CH_2CH_2CH_2$], 26.7 [$CH_2CH_2CH_2$], 46.1[NCH_2CH_2], 50.7 [NCH_2CH_2], 55.6 [NCH_2CH_2], 57.8 [$NCH_2C_6H_4$], 65.3 [NCH_2CH_2], 113.7 [H_2C=CH–C_6H_4], 126.3 [C_6H_4], 129.2 [C_6H_4], 136.6 [C_6H_4, H_2C=CH–C_6H_4], 138.6 [C_6H_4], 191.2 [C=O_{ax}], 199.3 [C=O_{eq}, $^1J_{wc}$ = 65 Hz], 201.6 [$W(CO)_6$]. MS (FAB +ve) 611 [8, M^+], 555 [40, $(C_{21}H_{29}N_3O_3W)^+$], 288 [100, $(C_{18}H_{29}N_3)^+$].

Crystal data for 11. $C_{23}H_{27}N_3O_5W$, M = 609.3, triclinic, $P\bar{1}$ (no. 2), a = 8.690(1), b = 10.842(2), c = 13.733(2) Å, α = 90.26(1), β = 97.58(1), γ = 109.31(1)°, V = 1208.8(3) $Å^3$, Z = 2, D_c = 1.674 g cm^{-3}, μ(Mo-Kα) = 4.82 mm^{-1}, T = 293 K, yellow platy blocks; 5551 independent measured reflections, F^2 refinement, R_1 = 0.041, wR_2 = 0.091, 4706 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 55°$], 289 parameters.[16]

CCDC reference number 170672.

See http://www.rsc.org/suppdata/dt/b1/b108235n/ for crystallographic data in CIF or other electronic format.

Polymers

Poly[1-(4-vinylbenzyl)-1,5,9-triazacyclododecane] using 4 mol% AIBN in ethanol (P-1). **5** (0.20 g, 0.7 mmol) and AIBN (0.015 g, 0.03 mmol) were dissolved in degassed ethanol (5 mL) and heated to reflux under nitrogen for 12 h. After cooling, the solvent was removed *in vacuo*, and diethyl ether (10 mL) added. The supernatant liquid was removed from a sticky solid (0.12 g) which was dissolved in methanol (2 mL) and added to diethyl ether (10 mL). Again, the supernatant liquid was decanted from the precipitate which was washed with diethyl ether (10 mL) and dried *in vacuo* to leave an off-white powder (0.05 g, 25%). ^1H NMR (270 MHz, CD_3OD) δ 1.7–1.8 [br, 6H, $CH_2CH_2CH_2$], 2.4–2.6 [br, 4H, $NCH_{2\alpha}CH_2$], 2.7–2.8 [br, 4H, $NCH_{2\beta}CH_2$], 2.9–3.0 [br, 4H, $NCH_{2\chi}CH_2$], 3.4–3.7 [br, 4H, $NCH_2C_6H_4$], 6.3–6.5

[br, 2H, C_6H_4], 6.8–7.1 [br, 2H, C_6H_4]. MS (FAB +ve) 602 [6, $C_{38}H_{62}N_6^+$], 577 [4, $C_{36}H_{61}N_6^+$], 550 [3, $C_{35}H_{60}N_5^+$], 531 [10, $C_{34}H_{53}N_5^+$], 514 [7, $C_{34}H_{50}N_4^+$], 369 [8, $C_{23}H_{37}N_4^+$], 288 [10, $C_{18}H_{30}N_3^+$]. GPC: M_w 4400, M_n 1700, polydispersity 2.7.

Poly[1-(4-vinylbenzyl)-1,5,9-triazacyclododecane]-styrene copolymers. *Ligand **5** + 99 mol styrene (**P-2**).* **5** (0.05 g, 0.2 mmol) was dissolved in methanol (10 mL) and styrene (1.6 mL, 17.0 mmol) and AIBN (0.07 g, 0.4 mmol) were added. The mixture was degassed by 3 freeze–pump–thaw cycles, and then heated to reflux under nitrogen for 6 h. After cooling, the white precipitate formed was filtered off and washed with diethyl ether (2 × 20 mL) then air-dried (0.38 g, 21%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.9–1.1 [m, C–H], 1.2–1.6 [br m, CH_2], 1.7–1.9 [br, CH], 2.6 [br, NCH_2CH_2], 2.8 [br, NCH_2CH_2], 3.0 [br, NCH_2CH_2], 3.5 [br, $NCH_2C_6H_4$], 5.29–5.33 [$CH{=}CH_2$], 5.79–5.86 [$CH{=}CH_2$], 6.3–7.2 [br m, C_6H_4] ^{13}C-{^{1}H} NMR (67.5 MHz, $CDCl_3$) δ 25.3–28.1 [m, $CH_2CH_2CH_2$], 31.7, 32.0 [CH_2CH_3], 40.5 [CH], 41–47 [m, NCH_2CH_2], 113.9 [$CH{=}CH_2$], 125–128 [C_6H_4], 137.0 [$CH{=}CH_2$], 145–146 [C_6H_4]. GPC: M_w 7500, M_n 4600, polydispersity 1.6.

*Ni(II) complex + 99 mol styrene (**P-3**).* To a 0.1 M methanolic solution of **6** (2 mL, 0.1 mmol), styrene (0.95 mL, 10.0 mmol) and AIBN (0.03 g, 0.2 mmol) were added. The mixture was degassed by 5 freeze–pump–thaw cycles, then stirred at 60 °C for 14 h. A green solution was decanted from a small amount of solid, and the methanol removed *in vacuo*. The resultant solid was dissolved in CH_2Cl_2 and precipitated by addition of hexane, and dried *in vacuo*, to leave a light green powder (0.67 g, 58%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.8–0.9 [m, C–H], 1.12–1.6 [br m, CH_2], 1.7–1.9 [br, CH], 2.9 [vw, NCH_2CH_2], 3.5 [vw, $NCH_2C_6H_4$], 6.2–7.2 [m, C_6H_4]. ^{13}C-{^{1}H} NMR (67.5 MHz, $CDCl_3$) δ 14.3 [CH_3], 22.8 [$CH_2CH_2CH_2$], 31.7 [CH_2CH_3], 40.5 [CH], 41–46.6 [m, NCH_2CH_2], 53.6 [NCH_2CH_2], 125–128 [C_6H_4], 145–146 [C_6H_4]. GPC: M_w 3.9×10^6, M_n 3900, polydispersity 1000.

*Zn(II) complex + 99 mol styrene (**P-4**).* Hydrated zinc chloride (0.36 g, 2.7 mmol) in methanol (5 mL) was added to **5** (0.77 g, 2.7 mmol) also in methanol. To a portion of this solution (2 mL, 0.8 mmol), methanol (18 mL), styrene (7.9 mL, 75.0 mmol) and AIBN (130 mg, 0.8 mmol) were added. The mixture was degassed by 5 freeze–pump–thaw cycles, then heated to reflux for 18 h. The reaction mixture was cooled and the solvent removed *in vacuo*. The resultant oil was dissolved in CH_2Cl_2 (5 mL) and precipitated with hexane (15 mL). The solvent was decanted and the procedure repeated to give a white powder (4.44 g, 48%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.8–0.9 [m, C–H], 1.12–1.42 [br m, CH_2], 1.54–2.05 [br, CH], 2.2 [w, NCH_2CH_2], 2.4 [vw, NCH_2CH_2], 2.7 [vw, NCH_2CH_2], 3.1 [vw, $NCH_2C_6H_4$], 6.2–7.2 [m, C_6H_4]. ^{13}C-{^{1}H} NMR (67.5 MHz, $CDCl_3$) δ 14.3 [CH_3], 22–23, 26.7, 27.3, 28.0 [$CH_2CH_2CH_2$], 31.7 [CH_2CH_3], 40.5 [CH], 41–49.6 [m, NCH_2CH_2], 59.4 [$NCH_2C_6H_4$], 125–128 [C_6H_4], 145–146 [C_6H_4]. GPC: M_w 1.7×10^5, M_n 24500, polydispersity 3.1.

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