# Synthesis and <sup>1</sup>H NMR studies of paramagnetic nickel(II) complexes containing bis(pyrazolyl)methane ligands with dendritic substituents<sup>†</sup>

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The substituted bis(pyrazolyl)methane ligands RCH(3,5-Me<sub>2</sub>pz)<sub>2</sub> (R = SiMe<sub>3</sub> (1), CH<sub>2</sub>Ph (2), G1 (3), G2 (4), and G3 (5); Gn = Fréchet-type dendritic wedges of generation n) have been prepared starting from H<sub>2</sub>C(3,5-Me<sub>2</sub>pz)<sub>2</sub>. Reaction of these didentate ligands with [NiBr<sub>2</sub>(DME)] is a straightforward procedure that allows the synthesis of the nickel(II) complexes [NiBr<sub>2</sub>{RCH(3,5-Me<sub>2</sub>pz)<sub>2</sub>] (**6–10**). The molecular structure of compound 7 (R = CH<sub>2</sub>Ph) has been determined by X-ray diffraction studies. The nickel centre coordinates two bromine and two nitrogen atoms in a tetrahedral environment, and the metallacycle Ni(NN)<sub>2</sub>C adopts a boat conformation with the benzyl group in an axial position. <sup>1</sup>H NMR studies have been carried out to characterize these paramagnetic nickel compounds in solution. Valuable information about the disposition of the ligands and dendritic wedges in solution has been obtained thanks to the influence of the paramagnetic centre on the proton resonances.

### Introduction

Since Trofimenko's pioneering work introducing poly(pyrazol-1yl)borate ligands,1 also known as scorpionates, the coordination chemistry of this type of polydentate N-donor ligands has been extensively developed. The versatility of their substitution allows the controlled modification of their steric and electronic properties and, therefore, of their coordination capability. In fact, scorpionates have been used to synthesize complexes of most metals of the periodic table, some of them with useful applications in a wide range of areas.<sup>2</sup> The neutral and isoelectronic poly(pyrazolyl)alkane ligands, however, received much less attention until a significant improvement of their synthesis was published.<sup>3</sup> This area of chemistry has subsequently generated new modified ligands and complexes, including those functionalized at the methine or methylene bridging carbon atom in tris-4-6 or bis-(pyrazolyl)methanes,7-9 respectively. The substitution of the reactive methine proton by other functional groups has led, for instance, to multitopic ligands and polynuclear compounds linked to a molecular core,<sup>4</sup> or to the preparation of ligands and complexes that are soluble and stable in water;<sup>5</sup> on the other hand, functionalization at the bridging CH<sub>2</sub> has offered the opportunity to design tailored heteroscorpionate systems such as hybrid scorpionate/cyclopentadienyl complexes.8b

Research on metallodendrimers<sup>10</sup> is now a prominent area of nanoscience with multiple applications, including catalysis as a main objective.<sup>11</sup> We have used N-donor ligands bonded at the focal point or at the periphery of carbosilane dendrimers to coordinate early<sup>12</sup> or late<sup>13,14</sup> transition metals. In a previous paper,

where we reported the synthesis of a tetranuclear compound with a carbosilane core along with four tris(pyrazolyl)methane molybdenum complexes, we concluded that a broader utilization of this type of N-heterocyclic donors in dendrimer chemistry requires the modification of the ligand in order to reduce steric crowding and to increase solubility.<sup>14</sup>

In light of this, we have undertaken new studies with the alkylated bis(pyrazolyl)methane  $[H_2C(3,5-Me_2pz)_2]$  as anchoring ligand, and have synthesized discrete models and Fréchet-type dendritic wedges by functionalizing the bridging  $CH_2$  group. We describe here the preparation and characterization of these didentate ligands, and the synthesis of monometallic nickel(II) complexes by metalation at the focal point of these wedges.

## **Results and discussion**

#### Synthesis of ligands

The deprotonation of bis(3,5-dimethylpyrazol-1-yl)methane with *n*BuLi was carried out as described by Otero *et al.* (Scheme 1).<sup>8</sup> Intermediate I was subsequently treated *in situ* with chlorotrimethylsilane or with the appropriate dendritic benzyl bromides Gn-Br, at low temperature, to form ligands 1–5. Alternatively, intermediate I can be isolated and stored in a dry-box, since it precipitates as an off-white solid when its preparation is carried out in diethyl ether and the mixture is allowed to warm to room temperature. This method for the isolation of I improves the purity of the crude compounds 1–5 and therefore raises the yields after the appropriate work up. These ligands were isolated as pale-yellow (1) or white (2–5), air-stable solids. Silane 1 and benzylic derivative 2 are soluble in all common organic solvents, whereas dendritic benzyl ethers 3–5 are scarcely soluble in alkanes.

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of compounds 1–5 show only one set of resonances for both pyrazolyl rings. Thus, these rings give rise to three singlets at about  $\delta = 2.0, 2.2, \text{ and } 5.7 \text{ ppm}$ , in a 3 : 3 : 1 ratio, corresponding to the Me<sup>3</sup>, Me<sup>5</sup>, and H<sup>4</sup> pyrazolyl

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<sup>†</sup> Electronic supplementary information (ESI) available: Fig. S1 and S2: MS spectral information of dendrimers **5** and **10**, respectively; Fig. S3 and S4: Curie and polynomial plots, respectively, for protons in compound **7**. See DOI: 10.1039/b607090f



Scheme 1

protons, respectively (see Scheme 1 for the numbering scheme). The resonance for the proton of the bridging CH group (RCHpz<sub>2</sub>) occurs at around  $\delta = 6.0$  ppm, and is observed as a singlet for 1 together with another singlet for the SiMe<sub>3</sub> group ( $\delta = 0.2$  ppm), and as a triplet for 2-5 due to coupling with the benzylic CH<sub>2</sub> protons of the R group, which appear as a doublet at around  $\delta =$ 3.8 ppm. The <sup>13</sup>C{<sup>1</sup>H} spectra show singlets at about  $\delta = 11$  (Me<sup>3</sup>), 14 (Me<sup>5</sup>), 106 (C<sup>4</sup>), 139 (C<sup>5</sup>), 147 (C<sup>3</sup>), and 72 ppm (bridging CH group,  $\delta = 68$  ppm for 1) for the bis(pyrazolyl)methane moieties in 1–5, at  $\delta = -1.2$  ppm for the SiMe<sub>3</sub> group in 1, and at  $\delta =$ 40 ppm for the benzylic carbon attached directly to the chelate ligand in 2–5. Two multiplets due to the phenyl group ( $\delta = 7.0$ – 7.2 ppm) are the remaining resonances observed in the <sup>1</sup>H NMR spectrum of 2. As described previously for this type of structure,<sup>15</sup> the polyether protons of dendrimers 3-5 give sets of resonances in three main regions, namely multiplets at  $\delta = 7.3-7.4$  ppm for the terminal phenyl groups (Ph), a doublet and a triplet at  $\delta =$ 6.2-6.7 ppm for each layer of internal aryl groups (Ar), and a singlet at  $\delta = 4.8-5.0$  ppm for each generation of  $-CH_2O$ -groups. Individual sets of resonances for each layer, which indicates slightly different chemical environments amongst them, are also observed in  ${}^{13}C{}^{1}H$  NMR spectroscopy. Thus, their corresponding spectra show one (3), two (4) or three (5) sets of singlets for the  $CH_2O$ , *p*-Ar, *o*-Ar, *ipso*-Ar, and *m*-Ar carbon atoms, at around  $\delta = 70$ , 101, 107, 139, and 160 ppm, respectively. The relative intensity of these sets of singlets increases on going from the focal point to the periphery of the dendrimer.

The IR spectra of ligands 1–5 show an absorption assigned to the asymmetric stretching of the C=N bond at around  $1555 \text{ cm}^{-1}$ ,

in the normal range for free pyrazolyl rings, which appears together with two absorptions at about 1600 and 1450 cm<sup>-1</sup> for compounds **2–5** due to the C=C bonds of the pyrazolyl and the aromatic rings, and with intense bands assigned to the C–O–C vibrations in the case of ligands **3–5**.

All ligands gave satisfactory elemental analyses, and their positive-ion electrospray mass spectra (ESI+/MS), carried out in 0.1% formic acid solution in MeOH, exhibit a peak assignable to the protonated molecular ion  $[M + H]^+$ , with peak isotope distributions that match the calculated patterns (see, for example, Fig. S1 in the ESI†). In addition, fragments corresponding to the loss of one or two pyrazolyl rings ( $[M - Me_2pz]^+$  or  $[M - 2Me_2pz]^+$ ) are also observed for compounds 1–4.

#### Synthesis of nickel complexes

The addition of a dichloromethane solution of chelates 1–5 to one equivalent of  $[NiBr_2(DME)]$  (DME = dimethoxyethane) in the same solvent readily leads to the formation of compounds 6–10 by displacement of the labile DME ligand (Scheme 1 and Fig. 1). In all the cases the initial orange suspension of the nickel compound quickly turned deep blue. Complexes 6–10 were isolated as purple paramagnetic solids that are stable to air in the solid and in solution and are insoluble in alkanes but soluble in polar, chlorinated, and aromatic solvents. Metalation at the periphery of the dendrimers usually results in systems with general properties that are determined by their polymetallic nature as the generation increases, whereas they approximate to those of the



Fig. 1 Metallodendrimer  $[NiBr_2{G3-CH(3,5-Me_2pz)_2}_2]$  (10).

free ligand in monometallic dendrimers functionalized at their focal point, like the nickel compounds described here.

The nickel complexes were characterized by <sup>1</sup>H NMR and IR spectroscopy, mass spectrometry, and elemental analysis. The molecular structure of compound 7 was also determined by X-ray diffraction studies. The crystal structure and NMR spectroscopic data are discussed below.

The IR spectra of compounds **6–10** are fairly similar to those of the free ligands, with the  $v_{asym}(C=N)$  absorption at around 1560 cm<sup>-1</sup> being the most significant. Intense bands assigned to the C=C and C–O–C vibrations are also clearly visible.

The nickel compounds gave satisfactory elemental analyses, and several fragmentation patterns could be detected when analyzing their ESI+/MS data obtained in acetonitrile. The molecular ion [M]<sup>+</sup> was only observed, as a low intensity peak, in the spectrum of complex 6. Peaks corresponding to the loss of one, or even two, bromine atoms ( $[M - Br]^+$  or  $[M - 2Br]^+$ ; low intensity), to dissociation and protonation of the free ligands ( $[LH]^+$ , L = 1-5), and even to the fragmentation of the latter by the loss of a pyrazolyl ring  $([L - Me_2pz]^+)$  were all commonly detected for complexes 6-10. Interestingly, a peak corresponding to loss of the bromo ligands and coordination of a third pyrazolyl ring and H<sub>2</sub>O is clearly observed in all the spectra (m/z = 447, 465, 677, 1101, and 1952,for 6-10, respectively). These observations are compatible with the formation of hydrated tris(pyrazolyl)methane nickel cations of general formula [Ni(H<sub>3</sub>O<sup>+</sup>){RC(Me<sub>2</sub>pz)<sub>3</sub>}] under these experimental conditions. Additionally, a fragment corresponding to a dicationic-bischelate  $[Ni{RCH(Me_2pz)_2}_2]^{2+}$  species was detected for compounds 9 and 10 (m/z = 960 and 1809, respectively). The MALDI-TOF mass spectrum for 10, recorded in dithranol (1,8,9-anthracenethiol,  $C_{14}H_{10}O_3$ ) as the matrix, shows peaks for the cation after the loss of one or two bromine atoms (m/z)1918 and 1829, respectively; Fig. S2 in the ESI<sup>†</sup>), and peaks due to dimetallic species containing halide bridges (i.e.,  $[M_2 Br^{+}$  and  $[(M - Br)_2]^+$ , with isotope distributions that match the calculated patterns. A fragmentation pattern with halide loss has been shown to occur for similar nickel compounds,<sup>16</sup> and a similar recombination leading to dimetallic structures is also known.<sup>13,17</sup>

Activation of 6-10 by MAO for ethylene polymerization was briefly evaluated. None of them show activity (room temp., 2 bar, toluene, 24 h, Al/Ni = 1000). This result contrasts

 Table 1
 Bond lengths [Å], angles [°], and torsion angles [°] for compound 7

with earlier findings using the bis(pyrazolyl)nickel(II) compounds						
with independent pyrazolyl rings described by Mapolie et al.,18						
or related complexes containing planar-conjugated chelates,13						
and is similar to the behavior reported by Jordan et al. for						
bis(pyrazolyl)methane-palladium(II) compounds.19						

#### Structure of $[NiBr_2{G0-CH(3,5-Me_2pz)_2}]$ (7)

Fig. 2 shows an ORTEP representation of the molecular structure of compound 7 in the solid state as determined by single-crystal X-ray diffraction studies; the relevant structural data are given in Table 1.



**Fig. 2** ORTEP diagram of the structure of compound **7** with thermal ellipsoids at 50% probability.

The molecular structure of 7 consists of a discrete molecule where the central nickel atom binds to two bromine atoms and two nitrogen atoms of a bis(pyrazolyl) chelate ligand, and exhibits a distorted tetrahedral geometry. Thus, the bond angles around the metal centre vary from  $118.17(5)^{\circ}$  for the bromine ligands to  $93.9(2)^{\circ}$  for the donor atoms of the pyrazolyl ligands, while the average Ni–Br (2.3648(14) Å) and Ni–N (1.996(6) Å) bond

Ni(1)–Br(1)	2.3549(14)	Ni(1)-Br(3)	2.3747(14)	
Ni(1) - N(1)	1.996(6)	Ni(1) - N(3)	1.996(6)	
N(1) - N(2)	1.385(7)	N(3)–N(4)	1.374(7)	
N(2)-C(11)	1.453(10)	N(4)-C(11)	1.446(9)	
C(11) - C(12)	1.541(10)	C(12) - C(13)	1.512(10)	
Br(1)-Ni(1)-Br(3)	118.17(5)	N(1)-Ni(1)-N(3)	93.9(2)	
Br(1)-Ni(1)-N(1)	112.81(17)	Br(1)-Ni(1)-N(3)	110.12(19)	
Br(3)-Ni(1)-N(1)	108.85(19)	Br(3)-Ni(1)-N(3)	110.37(17)	
Ni(1)-N(1)-N(2)	122.5(5)	Ni(1) - N(3) - N(4)	120.7(5)	
N(1)-N(2)-C(11)	119.9(6)	N(3)-N(4)-C(11)	120.4(6)	
N(2)-C(11)-N(4)	111.0(6)	C(11)-C(12)-C(13)	112.3(6)	
N(2)-C(11)-C(12)	110.6(6)	N(4)-C(11)-C(12)	112.4(6)	
Ni(1) - N(1) - C(1)	130.0(5)	Ni(1) - N(3) - C(6)	129.2(5)	
N(2)-N(1)-C(1)	106.2(6)	N(4)-N(3)-C(6)	106.0(6)	
Br(1)-Ni(1)-N(1)-N(2)	102.5(5)	Br(1)-Ni(1)-N(3)-N(4)	-109.1(5)	
Br(3)-Ni(1)-N(1)-N(2)	-124.3(5)	Br(3)-Ni(1)-N(3)-N(4)	118.6(5)	
N(3)-Ni(1)-N(1)-N(2)	-11.2(5)	N(1)-Ni(1)-N(3)-N(4)	6.8(5)	
N(1)-N(2)-C(11)-N(4)	59.6(8)	N(3)-N(4)-C(11)-N(2)	-65.8(8)	

distances fall in the usual range.<sup>18</sup> The value of these angles are about 120° and 99°, respectively, in the analogous compound with two independent monodentate pyrazolyl rings. The distortions in compound 7 are the result of both the steric repulsion between the large halide atoms and the presence of a chelate ligand with an acute N–Ni–N bite angle. The dihedral angle defined by the N(1)–Ni(1)–N(3) and Br(1)–Ni(1)–Br(3) planes is 88.4(1)°, almost a right angle. It is worth mentioning at this point that a related nickel(II) compound containing the  $CH_2(3,5-Me_2pz)_2$ ligand has been described and structurally characterized. In the solid state the structure of this complex consists of a dimeric molecule formed by bridging halides, each unit of which contains a five-coordinate metal centre in a geometry intermediate between trigonal bipyramidal and square pyramidal.<sup>20</sup>

The Ni(1)(NN)<sub>2</sub>C(11) nickellacycle formed by coordination of the didentate ligand presents a boat conformation in which the benzyl group attached to the methine carbon C(11) occupies an axial position, thus avoiding the steric hindrance that would arise between the benzyl group in the equatorial location and the adjacent methyl groups (Me<sup>5</sup>). A similar result has been reported for some palladium(II) complexes containing RCH(3,5- $Me_2pz_2$  ligands (R = phenyl or pyridyl), where the steric repulsion between the R and pz-methyl groups confers rigidity on the metallacycle as no boat-to-boat conformation exchange is observed in solution.<sup>21</sup> It is noteworthy that no matter what the Group 10 metal environment is-tetrahedral (Ni) or squareplanar (Pd)-the bridging substituent is always positioned axially in the solid state. The boat conformation is less pronounced on the side of the metal centre than on that of the methine bridge, as evidenced by the angles between the N(1)-N(2)-N(3)-N(4) plane and the planes N(1)-N(1)-N(3) and N(2)-C(11)-N(4) (7.8(3)° and  $51.5(4)^{\circ}$ , respectively).

The benzyl group is orientated asymmetrically towards the hemi-space that contains the N(3)–N(4) pyrazolyl ring, with a dihedral angle defined by the C(12)–C(13) bond and the Ni(1)…C(11) molecular axis of 114.6°. The two coordinated rings have different inclinations with respect to the coordination planes of the metal, probably as a result of the steric interaction of the phenyl group with one of the coordinated pyrazolyl rings. Thus, the dihedral angle between the N(1)–Ni(1)–N(3) plane and the pyrazolyl rings N(3)–N(4) and N(1)–N(2) are 25.0(2)° and 19.9(2)°, respectively. The asymmetric orientation of the benzyl group is accompanied by the presence of a short contact between one of the benzylic protons and the closest bromine atom [Br(1)…H12B = 2.94 Å].

#### <sup>1</sup>H NMR studies of paramagnetic complexes 6–10

High-resolution NMR spectra can be helpful for the characterization of paramagnetic complexes if the relaxation of the unpaired electron is fast enough with respect to the NMR timescale. In this case, the electronic magnetic field shortens the nuclear longitudinal relaxation times ( $T_i$ ) of the observed nuclei less effectively, thereby sharpening the broad resonances usually associated with paramagnetic species. First-row transition metal complexes with triply degenerate (T) ground states often have short electron-spin lifetimes that allow well-resolved NMR signals from which structural information can be retrieved.<sup>22</sup> Thus, nickel(II) complexes with tetrahedral or pseudo-tetrahedral, and high-spin pentacoordinate geometries typically produce sharper resonances than monomeric octahedral complexes, although the resonances of the latter are also sharpened because of zero-field splitting.<sup>23</sup>

The <sup>1</sup>H NMR spectra of compounds 6–10 show fairly well resolved and sharp signals ( $\Delta v_{1/2} < 120$  Hz) with hyperfine shifted resonances spread over a relatively narrow spectral window (about 80 ppm; Table 2). The presence of an effective plane of symmetry in the molecule, as defined by the metal centre and both bromine atoms, is confirmed by the chemical equivalence of both pyrazolyl groups. All the protons of  $[{Me_3SiCH(pz)_2}NiBr_2](6)$  have shorter  $T_1$  values (from 4 to 125 ms) and are strongly down- or upfield shifted from  $\delta = -18$  to 59 ppm with respect to their position in the diamagnetic free ligand 1. For complexes 7-10, comparably short  $T_1$  values and large hyperfine shifts are found for the protons located at the [CH<sub>2</sub>CH(pz)<sub>2</sub>NiBr<sub>2</sub>] moiety and at the ortho position of the aromatic ring adjacent to the methine bridge. The remaining protons of the dendritic substituents appear in ranges close to those found in the diamagnetic free ligands ( $\delta = 7.8-7.2$  vs. 7.4-7.2 (Ph), 6.7-6.2 vs. 7.0-6.5 (Ar), and 5.6-5.1 vs. 5.0-4.8 ppm (CH<sub>2</sub>)), with line widths (<8 Hz) and longitudinal relaxation rates progressively approaching those of diamagnetic compounds as the distance from the metal increases. For instance, the three CH<sub>2</sub>O methylene protons of the G3 complex 10 show  $\Delta v_{1/2}$  values of 7.7, 4.9, and 3.9 Hz, and  $T_1$  times of 84, 211, and 380 ms, going from the dendritic focal point to the periphery.

The full assignment of signals has been based on their position in the different spectra, on their relative areas, and on measurements of  $T_1$  values. Thus, for complex 7 (Table 3), the single resonance at  $\delta = -8.2$  ppm can be unequivocally assigned to the bridging CH group due to its integrated intensity, whereas the two resonances integrating for six protons are assigned to each of the methyl pyrazolyl groups (Me<sup>3</sup> and Me<sup>5</sup>) due to their measured  $T_1$  values.

**Table 2**  $\delta$  and  $T_1$  values for the nearest protons to the metal atom in 6–10 in CDCl<sub>3</sub> at 293 K<sup>a</sup>

Assignment	6		7		8		9		10	
	$\delta$ (ppm)	$T_1/\mathrm{ms}$	$\delta$ (ppm)	$T_1/ms$						
pz-H <sup>4</sup>	64.7	36	69.3	33	69.6	26	69.7	37	69.9	37
pz-Me <sup>3</sup>	38.5	4	21.4	5.2	21.4	5	21.4	5	21.2	5
pz-Me <sup>5</sup>	15.6	125	4.1	110	4.0	96	4.0	93	4.0	92
ĊH	-12.0	26	-8.2	23	-8.2	26	-8.5	17	-8.4	23
CH <sub>2</sub>			-9.1	4.6	-9.3	b	-9.5	5	-9.4	b
SiMe <sub>3</sub>	-4.4	22			_					_

<sup>a</sup> T<sub>1</sub> values were obtained at 300 MHz. <sup>b</sup> Fitting was unreliable.

Table 3<sup>1</sup>H NMR parameters in CDCl3 at 293 K for 7

Assign.	Relative area	$\delta$ (ppm)	$\Delta v_{1/2}^{a}/\mathrm{Hz}$	$T_1^{b}/\mathrm{ms}$	Ni · · · H (exp) <sup>c</sup> ∕Å	$\mathrm{Ni}\cdots\mathrm{H}~(\mathrm{calc})^{a}/\mathrm{\AA}$
pz-H <sup>4</sup>	2 H	69.3	18	33e	5.02	5.02 <sup>e</sup>
pz-Me <sup>3</sup>	6 H	21.4	84	5.2	3.66	3.7
pz-Me⁵	6 H	4.1	4	110	5.98	6.1
ĈH	1 H	-8.2	18	23	4.20	4.7
$CH_2$	2 H	-9.1	67	4.6	3.51	3.6
Ph, ortho	2 H	5.0	19	21	5.08	4.7
Ph, meta	2.11	7.2	ſ	f	7.00	_
Ph, para	3 H	1.2	ſ	ſ	7.80	_

<sup>*a*</sup> Line width at half-maximum. <sup>*b*</sup>  $T_1$  values were obtained at 300 MHz. <sup>*c*</sup> Crystallographic distances determined by X-ray diffraction. In the case of equivalent protons, the arithmetic average distance is given. <sup>*d*</sup> Average distances in solution obtained on the basis of a model taking into account a predominant dipolar relaxation mechanism. The Ni ··· H distances  $(d_{Ni...H})$  were calculated from the measured proton relaxation times  $(T_1)$  with respect to that of a reference resonance  $(T_{1ref})$ , according to the equation:  $d_{Ni...H} = d_{Ni...Href} (T_1/T_{1ref})^{1/6}$  (see ref. 24). The pyrazolyl proton pz-H<sup>4</sup> was used as reference. <sup>*c*</sup> Taken as reference. <sup>*f*</sup> *m*-Ph and *p*-Ph resonances overlap.

A COSY experiment was performed in order to assign the three resonances corresponding to the pz-H<sup>4</sup>, benzylic methylene, and *o*-Ph protons. A clear cross-peak is observed between the resonances at  $\delta = 7.2$  (*m*-Ph) and 5.0 ppm and thus the latter can be assigned to the *o*-Ph protons. The pz-H<sup>4</sup> and the CH<sub>2</sub> protons can clearly be assigned to the resonances at  $\delta = 69.3$  and -9.1 ppm, respectively, by comparison with the <sup>1</sup>H NMR spectrum of **6**, where a SiMe<sub>3</sub> group has replaced the benzyl group. Moreover, the large hyperfine shift to lower field of the former resonance is attributable to a contact contribution transmitted through the bonds from the unpaired electron density to the given nucleus, and therefore is more likely assignable to the pz-H<sup>4</sup> than to the methylene protons.

<sup>1</sup>H NMR parameters in paramagnetic complexes are particularly sensitive to the conformation adopted by the molecule in solution. At this point, it should be noted that data collected for the pyrazolyl, methine, and methylene protons of the G0 complex 7 virtually match those found for analogous nuclei in G1 to G3 dendrimers 8-10, with maximal differences of 0.5 ppm in the case of the chemical shifts (see Table 2). Larger differences are found between the chemical shifts of 6 and 7-10 and it is remarkable that the resonance for the distal methyl groups (pz-Me<sup>5</sup> protons) is significantly shifted in the case of compound 6 ( $\delta = 15.6$  ppm), and only slightly for 7–10 ( $\delta = 4.0-4.1$  ppm, see below). As mentioned for pz-H<sup>4</sup>, the hyperfine shifts for the protons closest to the Ni(II) centre must be due to a predominant contact contribution, whereas those of the methine and methylene (or  $SiMe_3$  for 6) protons must be a consequence of a larger dipolar input to the hyperfine shift. The differences in chemical shift for the protons of compound 6 when compared with their counterparts in the series 7-10 can be attributed to small conformational differences imposed by the steric bulk of the SiMe<sub>3</sub> group, which modifies the pseudocontact interaction of these protons with the metal centre, which, in turn, induces different dipolar shift contributions.

Assuming that the relaxation takes place predominantly through space by a dipolar mechanism, the longitudinal relaxation rates  $(T_1^{-1})$  of a given <sup>1</sup>H nucleus in a paramagnetic metal complex should be inversely proportional to the metal–proton distance to the sixth  $(d_{M...H}^{6})$ , according to the Solomon equation.<sup>24</sup> Therefore, relaxation rates and distance values can be calculated from each other using the equation  $T_{1 \text{ cale}}^{-1} = T_{1 \text{ ref}}^{-1}$   $(d_{M...H}/d_{M...H \text{ ref}})^{-6}$  and a given resonance as reference. Table 3

shows the Ni · · · H distances obtained for complex 7 in the solid state by X-ray diffraction and those estimated in solution on the basis of the measured  $T_1$  values. The pz-H<sup>4</sup> proton was chosen as reference because the distance to the nickel atom is essentially conformationally insensitive. The good qualitative agreement between the experimental and calculated distance values, with differences not exceeding 12%, supports the resonance assignements and the assumptions made for these calculations. As discussed previously, the boat conformation found in the solid state for 7 (Fig. 2) arranges the benzyl group in an apical position with the phenyl ring facing one of the pz-Me<sup>5</sup> groups. Since the experimental distances are derived from crystal data, it can be concluded that a similar conformation to that found in the solid state predominates in solution. Conformational calculations at the MM2 level gave a minimum energy for a disposition that closely resembles that found in the solid state. Thus, the dihedral angle,  $\theta$ , defined by Ni · · · CH–CH<sub>2</sub>–Ph is equal to 121.0° in the optimized MM2 structure versus 118.9° in the crystal structure. The maximal energy barriers for rotation of the phenyl group around the CHCH<sub>2</sub> axe are estimated to be 5-6 kcal mol<sup>-1</sup>. As pointed out above, the conformational characteristics of the corresponding metallacycle in 8-10 should be very similar to those described here for 7. The latter is also supported by the similarities of the  $T_1$  values found in solution for the protons nearest to the nickel atom in the full series of complexes 7–10 (see Table 2).

Examination of the <sup>1</sup>H NMR spectra of 7 over the temperature range 224-323 K reveals that the resonances move toward the diamagnetic region upon increasing the temperature, showing a typical Curie law behavior with linear fits of reasonably good quality and correlation coefficients greater than 0.99 (Fig. 3 and Table 4, full plot and Curie fits provided as ESI, † Fig. S3). The only exception is for the pz-Me<sup>5</sup> methyl protons and will be discussed later. However, deviations to the Curie law are suggested by the fact that intercepts at 0  $K^{-1}$  for the resonances corresponding to the CH<sub>2</sub>CH(3,5-Me<sub>2</sub>pz)<sub>2</sub> moiety differ significantly from the expected diamagnetic shifts ( $\delta_{dia}$  in the free ligand, Table 4). The fit quality improved when using a second-order polynomial procedure with fixed intercepts at the corresponding  $\delta_{dia}$  in the free ligand (Table 4; full plot in Fig. S4 in the ESI<sup>†</sup>). The chemical shift assigned to the pz-Me<sup>5</sup> protons of complex 7 shows a temperature dependence that does not fit into the range of temperatures studied in any of the



**Fig. 3** a) Observed chemical shift dependence *versus* reciprocal temperature for the most affected protons in complex **7**. The lines represent linear square-fit data (Curie law). b) Temperature dependence of the chemical shift of the pz-Me<sup>5</sup> protons, where the Curie least-square fit is shown by the dotted line.

preceding functions. A look at an expanded plot (Fig. 3b) reveals that this resonance shifts upfield to the diamagnetic region at low temperatures (Curie behavior), but the slope inverts at 266 K and the resonance shifts downfield at higher temperatures (anti-Curie behavior).<sup>25</sup> On the other hand, we have pointed out above that the hyperfine shift of pz-Me<sup>5</sup> protons in complexes **7–10** is small in comparison with that observed for the trimethylsilyl derivative **6**. Finally, we have postulated that the lowest-energy conformation in

7–10 situates the benzyl ring above the pz-Me<sup>5</sup> protons. A feasible explanation for these observations is that the phenyl ring shields the electron magnetic field at the pz-Me<sup>5</sup> protons in 7–10, thus explaining their upfield shifts. At high temperatures the ratio of molecules in the lowest-energy conformations would decrease and the phenyl shielding becomes less efficient.

The accessibility of the metal centres is an important question in metallodendrimers, particularly in catalytic reactions, and depends on the conformation adopted by the dendritic arms in solution. Following the calculation of distances discussed above, we wanted to know if the paramagnetic nickel centre might be used as a probe to get insights into the disposition of the dendritic arms. Unfortunately, the longer distances to the metal atom and the conformational flexibility of the dendritic part of the molecule complicate the data interpretation. Several conformations of similar energy with very different Ni ··· H distances are possible, and the diamagnetic contributions to the relaxation rates are no longer negligible. For the third-generation dendrimer 10, we first evaluated the paramagnetic relaxation rate  $(T_{1 \text{ para}}^{-1})$  subtracting the diamagnetic part  $(T_{1 \text{ dia}^{-1}})$  from the measured overall rate  $(T_1^{-1})$ . The diamagnetic rates were taken as those measured in the free ligand 5, and Ni ··· H distances were calculated from  $T_{1 \text{ para}}^{-1}$  according to the Solomon equation (Table 5). Secondly, a search of optimized structures corresponding to local minima was carried out by MM2 calculations, and the average distances derived from them [calculated as  $(1/d^6)_{average} = \sum (1/d^6)$  because of the dependence of rates on  $1/d^6$ ] were compared with the values estimated by NMR spectroscopy. Fig. 4 shows one of the optimized structures whose average Ni ··· H distances (Table 5) correlate acceptably ( $R^2 = 0.89$ ) with those calculated from  $T_1$ values, and therefore Fig. 4 gives a good picture of the accessibility of the metal centre in dendrimer 10.



Fig. 4 Space-filling model for G3 dendrimer 10.

#### Conclusions

Bis(3,5-dimethylpyrazol-1-yl)methane can be functionalized at the methylene bridge with dendritic Fréchet-type wedges of up to the third generation. These didentate ligands readily form nickel(II) paramagnetic complexes  $[NiBr_2\{RCH(3,5-Me_2pz)_2\}]$  upon reaction with  $[NiBr_2(DME)]$ . The nickel centre is tetrahedral and the

 Table 4
 Temperature dependence of chemical shifts for complex 7 in CDCl3

		Curie plot <sup>b</sup>		Polynomial plot <sup>e</sup>			
Assignment	$\delta^a$ (ppm)	$\overline{\delta_{\text{int}} \text{ (ppm)}}$	$a \times 10^{-3}/\mathrm{K}^{-1}$	$\delta_{\rm dia}~(\rm ppm)$	$a' \times 10^{-3}/\mathrm{K}^{-1}$	$b' \times 10^{-3}/{ m K}^{-2}$	-
pz-H <sup>4</sup>	69.3	-18.5	26.0	5.71	12.9	1.75	
pz-Me <sup>3</sup>	21.4	-10.0	9.3	2.03	2.8	0.88	
pz-Me <sup>5</sup>	4.1	đ	đ	2.20	e	e	
СН	-8.2	11.3	-5.8	6.20	-3.0	-0.37	
$CH_2$	-9.1	15.2	-7.2	3.87	-1.1	-0.82	
Ph, ortho	5.0	7.6	-0.77	7.17	-0.55	-0.03	
Ph, meta	7.20	6.9	0.08	6.95	0.07	0.00	
Ph, para	7.16	7.1	0.02	7.17	-0.02	0.00	

<sup>*a*</sup> Observed chemical shifts at 293 K. <sup>*b*</sup> Fit of change in chemical shift with temperature, according to the Curie Law ( $\delta_{obs} = \delta_{int} + a/T$ ), where  $\delta_{int}$  is the intercept at infinite temperature and *a* is the Curie slope. The correlation coefficient is greater than 0.99 in each case. <sup>*c*</sup> Fit of change in chemical shift with temperature, according to a polynomial function ( $\delta_{obs} = \delta_{dia} + a'/T + b'/T^2$ ), where  $\delta_{dia}$  is the observed diamagnetic shift in the free ligand. <sup>*d*</sup> Fitting was unreliable. <sup>*e*</sup> Erroneous fitting with intercept at  $\delta_{dia} = 2.20$ .

Table 5Ni  $\cdots$  H distances calculated from  $T_1$  data for 10

Assignment	$T_1^a/\mathrm{ms}$	$T_{1 \text{ para}}^{b}/\text{ms}$	$\operatorname{Ni}\cdots\operatorname{H}(\operatorname{calc})^c/\operatorname{\AA}$	$Ni \cdots H \ (model)^d / Å$
pz-H <sup>4</sup>	37	37	5.1 <sup>e</sup>	5.1
ĊH	23	24	4.8	4.3
$CH_2$	5	5	3.7	3.4
G0-o-Ar	23	24	4.8	4.6
G0-p-Ar	345	542	8.0	8.2
G1-CH <sub>2</sub>	84	122	6.2	7.7
G1-o-Ar	408	689	8.3	7.8
G1-p-Ar	570	1344	9.3	11.4
$G2-CH_2$	211	556	8.0	8.2
G2-o-Ar	575	1281	9.2	8.7
G2-p-Ar	945	2112	10.1	11.1
G3–CH <sub>2</sub>	380	982	8.8	8.5
o-Ph	854	1194	9.1	9.0

<sup>*a*</sup>  $T_1$  values obtained in CDCl<sub>3</sub> at 293 K and 300 MHz. <sup>*b*</sup> Estimated as  $T_{1para}^{-1} = T_1^{-1} - T_{1da}^{-1}$ , where the  $T_{1da}$  values were taken to be those of the free ligand **5**. <sup>*c*</sup> Average Ni ··· H distances ( $d_{Ni\cdots H}$ ) calculated from the measured proton paramagnetic relaxation rates ( $T_{1para}$ ) with respect to that of a reference resonance ( $T_{1ref}$ ), according to the equation:  $d_{Ni\cdots H} = d_{Ni\cdots Href} (T_{1para}/T_{1ref})^{1/6}$  (see ref. 24). The pyrazolyl proton pz-H<sup>4</sup> was used as reference, <sup>*d*</sup> Distances in the model for **10** represented in Fig. 4. In the case of equivalent protons, the average distance calculated as  $(1/d^6)_{average} = \sum (1/d^6)$  is given. <sup>*e*</sup> Taken as reference.

 $Ni-(NN)_2-C$  metallacycle adopts a boat structure in the solid state, which remains in solution, with the R groups in an axial position. The paramagnetic nature of these nickel complexes does not preclude their characterization by <sup>1</sup>H NMR spectroscopy as they yield spectra with fairly well-resolved and sharp signals with chemical shifts spread over a relatively narrow spectral window. In fact, the presence of the paramagnetic centre turns out to be a useful probe for gathering extra structural information that is not available in diamagnetic compounds. Thus, the conformational aspects of the nickel surroundings, as well as the average distances of the distal protons to the nickel atom, can be deduced in solution from longitudinal relaxation time determinations. Further work with this type of dendronized bis(pyrazolyl)methane ligand is currently underway.

# Experimental

# General remarks

All operations were performed under argon using Schlenk or drybox techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. The compounds H<sub>2</sub>C(3,5-Me<sub>2</sub>pz)<sub>2</sub>,<sup>3b,c</sup> [NiBr<sub>2</sub>(DME)],<sup>26</sup> and dendritic benzyl bromides Gn-Br,15 were prepared according to literature procedures. Solvents were previously dried and distilled under argon as described elsewhere.27 NMR spectra were recorded on Varian Unity 500+, VR-300, or 200 NMR spectrometers. Chemical shifts  $(\delta)$  are reported in ppm relative to SiMe<sub>4</sub>, and were referenced with respect to <sup>13</sup>C and residual <sup>1</sup>H resonances of the deuterated solvents. Coupling constants (J) are given in Hz. The following abbreviations/notations are used: Ph refers to aromatic ring of terminal benzyl groups, Ar to internal rings of benzyl ethers, and ipso refers to the first ring-position on going from the didentate pyrazolyl ligand. Longitudinal relaxation times  $(T_1)$ were measured using the inversion-recovery pulse sequence (180°- $\tau$ -90°) method. IR spectra were recorded with a Perkin-Elmer FT-IR Spectrum-2000 spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratories of the University of Alcalá on a Heraeus CHN-O-Rapid microanalyzer. ESI and MALDI-TOF mass spectra were recorded by the Research Services at the Universidad Autónoma de Madrid (SIDI) in Applied Biosystems spectrometers, API Qstar Pulsar I or 4700 Proteomics Analyzer, respectively, using MeOH + 0.1% HCOOH for ligands and MeCN for nickel complexes as the ionizing phase (ESI), or with dithranol as matrix (MALDI-TOF). Molecular modeling was carried out using Chem 3D Pro version 5.0 for Mac (CambridgeSoft, Cambridge, USA, 1999) and MM2 force field computations.

#### Syntheses

(trimethylsilyl)bis(3,5-dimethylpyrazolyl)-Preparation of methane [Me<sub>3</sub>SiCH(3,5-Me<sub>2</sub>pz)<sub>2</sub>] (1). nBuLi (3.1 mL, 1.6 M in hexanes, 4.96 mmol) was slowly added, from a funnel equipped with a bubbler, to a solution of  $H_2C(3,5-Me_2pz)_2$  (1.00 g, 4.9 mmol) in THF (40 mL) at -78 °C and the mixture was stirred for 2 h at that temperature. An excess of SiMe<sub>3</sub>Cl was then added (0.76 mL, 6.0 mmol) and the reaction mixture was allowed to warm to room temp. and stirred overnight. After removal of the solvent under vacuum the residue was extracted into pentane  $(2 \times 15 \text{ mL})$ , and compound 1 was isolated as a pale-yellow solid by evaporation of the filtrates to dryness under vacuum. Yield: 1.098 g (81%). Anal. Calc. for C<sub>14</sub>H<sub>24</sub>N<sub>4</sub>Si (276.46): C, 60.82; H, 8.75; N, 20.27%. Found: C, 60.72; H, 8.39; N, 20.05%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.20 (s, 9 H, SiMe<sub>3</sub>), 1.94 (s, 6 H, pz-Me<sup>3</sup>), 2.16 (s, 6 H, pz-Me<sup>5</sup>), 5.74 (s, 2 H, pz-H<sup>4</sup>), 5.87 ppm (s, 1 H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -1.2 (SiMe<sub>3</sub>), 10.8 (pz-Me<sup>5</sup>), 13.5 (pz-Me<sup>3</sup>), 68.5 (CH), 106.1 (pz-C<sup>4</sup>), 139.7 (pz-C<sup>5</sup>), 146.6 ppm (pz-C<sup>3</sup>). IR (KBr): v 1617 (m, C=C), 1550 cm<sup>-1</sup> (s, C=N). MS (ESI+ in MeOH/0.1% HCOOH): m/z 277 [M + H]<sup>+</sup>, 181 [M - Me<sub>2</sub>pz]<sup>+</sup>,  $85 [M - 2Me_2pz-H]^+$ .

Preparation of (benzyl)bis(3,5-dimethylpyrazolyl)methane [G0-CH(3,5-Me<sub>2</sub>pz)<sub>2</sub>] (2). *n*BuLi (3.1 mL, 1.6 M in hexanes, 4.96 mmol) was added dropwise to a solution of H<sub>2</sub>C(3,5-Me<sub>2</sub>pz)<sub>2</sub> (1.00 g, 4.9 mmol) in THF (15 mL) at  $-78 \degree$ C. The reaction mixture was stirred for 2 h at that temperature, then PhCH<sub>2</sub>Br was added (0.6 mL, 5.0 mmol) and the solution allowed to warm to room temp. The solvent was removed under vacuum, the crude solid dissolved in diethyl ether (30 mL) and washed with water (2  $\times$ 20 mL), and the organic layer dried with MgSO<sub>4</sub>. Removal of the volatiles followed by recrystallization from pentane led to ligand **2** as a white solid. Yield: 1.138 g (79%). Anal. Calc. for  $C_{18}H_{22}N_4$ (294.40): C, 73.44; H, 7.53; N, 19.03%. Found: C, 73.21; H, 7.47; N, 18.95%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.03 (s, 6 H, pz-Me<sup>3</sup>), 2.20 (s, 6 H,  $pz-Me^{5}$ ), 3.87 (d,  $J_{H,H} = 7.3 Hz$ , 2 H, CH<sub>2</sub>), 5.71 (s, 2 H,  $pz-H^{4}$ ), 6.20 (t, J<sub>H,H</sub> = 7.3 Hz, 1 H, CH), 6.95 (m, 2 H, *m*-Ph), 7.17 ppm (m, 3 H, o- and p-Ph).  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta$  11.2 (pz-Me<sup>5</sup>), 14.0 (pz-Me<sup>3</sup>), 40.1 (CH<sub>2</sub>), 72.2 (CH), 106.2 (pz-C<sup>4</sup>), 126.6 (p-Ph), 128.1 and 129.1 (o- and m-Ph), 136.3 (ipso-Ph), 139.2 (pz-C5), 147.6 (pz-C<sup>3</sup>). IR (KBr): v 1557 (s, C=N), 1604 (m, C=C), 1453 cm<sup>-1</sup> (s, C=C). MS (ESI+ in MeOH/0.1% HCOOH): *m*/*z* 295 [M + H]<sup>+</sup>,  $199 [M - Me_2 pz]^+$ .

**Preparation of G1-CH(3,5-Me<sub>2</sub>pz)**<sub>2</sub> **(3).** This compound was prepared according to the procedure described above for **2**, from LiCH(3,5-Me<sub>2</sub>pz)<sub>2</sub> (1.3 mmol), prepared *in situ*, and dendritic wedge G1–Br (0.50 g, 1.3 mmol) in THF (20 mL). The resulting yellow oil was stirred with pentane (15 mL) for several hours to give compound **3** as a white solid. Yield: 0.50 g (76%). Anal. Calc. for C<sub>32</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub> (506.65): C, 75.86; H, 6.76; N, 11.06%. Found: C, 75.69; H, 6.80; N, 10.88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.02 (s, 6 H, pz-Me<sup>3</sup>), 2.21 (s, 6 H, pz-Me<sup>5</sup>), 3.79 (d, J<sub>H,H</sub> = 7.3 Hz, 2 H, CH<sub>2</sub>), 4.87 (s, 4 H, PhCH<sub>2</sub>O), 5.73 (s, 2 H, pz-H<sup>4</sup>), 6.12 (t, J<sub>H,H</sub> = 7.3 Hz, 1 H,

CH), 6.18 (d,  ${}^{4}J_{\text{H,H}} = 2.2$  Hz, 2 H, o-Ar), 6.44 (t,  ${}^{4}J_{\text{H,H}} = 2.2$  Hz, 1 H, p-Ar), 7.3–7.4 ppm (m, 10H, Ph).  ${}^{13}\text{C}{}^{1}\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  11.0 (pz-Me<sup>5</sup>), 13.7 (pz-Me<sup>3</sup>), 40.2 (CH<sub>2</sub>), 69.8 (PhCH<sub>2</sub>O), 71.6 (CH), 101.2 (p-Ar), 106.3 (pz-C<sup>4</sup>), 108.1 (o-Ar), 127.4 and 128.5 (o- and m-Ph), 127.9 (p-Ph), 136.8 (*ipso*-Ph), 138.7 (*ipso*-Ar), 139.6 (pz-C<sup>5</sup>), 147.9 (pz-C<sup>3</sup>), 159.7 (m-Ar). IR (KBr):  $\nu$  1558 (s, C=N), 1595 and 1453 (s, C=C), 1261 and 1026 cm<sup>-1</sup> (vs, C–O–C). MS (ESI+ in MeOH/0.1% HCOOH): m/z 507 [M + H]<sup>+</sup>, 411 [M – Me<sub>2</sub>pz]<sup>+</sup>, 315 [M – 2Me<sub>2</sub>pz-H]<sup>+</sup>.

Preparation of G2-CH(3,5-Me<sub>2</sub>pz)<sub>2</sub> (4). This compound was prepared according to the procedure described above for 2, from LiCH(3,5-Me<sub>2</sub>pz)<sub>2</sub> (0.87 mmol), prepared in situ, and dendritic wedge G2-Br (0.7 g, 0.87 mmol) in THF. Ligand 4 was purified by addition of pentane to a stirred diethyl ether solution, which caused it to precipitate as an off-white solid. Yield: 0.632 g (78%). Anal. Calc. for C<sub>60</sub>H<sub>58</sub>N<sub>4</sub>O<sub>6</sub> (931.14): C, 77.40; H, 6.28; N, 6.02%. Found: C, 76,98; H, 6.37; N, 5.91%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.01 (s, 6 H, pz-Me<sup>3</sup>), 2.20 (s, 6 H, pz-Me<sup>5</sup>), 3.78 (d,  $J_{H,H} = 7.3$  Hz, 2 H, CH<sub>2</sub>), 4.80 (s, 4 H, ArCH<sub>2</sub>O), 5.01 (s, 8 H, PhCH<sub>2</sub>O), 5.71 (s, 2 H, pz-H<sup>4</sup>), 6.13 (t,  $J_{H,H} = 7.3$  Hz, 1 H, CH), 6.17 (d,  ${}^{4}J_{H,H} = 2.0$  Hz, 2 H, G0-o-Ar), 6.44 (t,  ${}^{4}J_{H,H} = 2.0$  Hz, 1 H, G0-p-Ar), 6.54 (t,  ${}^{4}J_{H,H} =$ 2.1 Hz, 2 H, G1-*p*-Ar), 6.61 (d,  ${}^{4}J_{H,H} = 2.1$  Hz, 4 H, G1-*o*-Ar), 7.3–7.4 ppm (m, 20H, Ph).  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta$  11.0 (pz-Me<sup>5</sup>), 13.8 (pz-Me<sup>3</sup>), 40.2 (CH<sub>2</sub>), 69.7 (ArCH<sub>2</sub>O), 70.1 (PhCH<sub>2</sub>O), 71.7 (CH), 101.3 (G0-p-Ar), 101.4 (G1-p-Ar), 106.2 (G1-o-Ar), 106.3 (pz-C<sup>4</sup>), 108.1 (G0-o-Ar), 127.5 and 128.6 (o- and m-Ph), 128.0 (p-Ph), 136.7 (ipso-Ph), 138.8 (G1-ipso-Ar), 139.3 (pz-C<sup>5</sup>), 139.6 (G0-ipso-Ar), 147.9 (pz-C3), 159.6 (G0-m-Ar), 160.1 ppm (G1-*m*-Ar). IR (KBr): v 1559 (s, C=N), 1595 and 1451 (vs, C=C), 1293 and 1262 (s, C-O-C<sub>as</sub>), 1156 and 1040 cm<sup>-1</sup> (vs, C-O-C<sub>s</sub>). MS (ESI+ in MeOH/0.1% HCOOH): m/z 931 [M + H]<sup>+</sup>, 835  $[M - Me_2pz]^+$ , 739  $[M - 2Me_2pz-H]^+$ .

Preparation of G3-CH(3,5-Me<sub>2</sub>pz)<sub>2</sub> (5). Dendritic wedge 5 was prepared according to the procedure described above for 2, starting from LiCH(3,5-Me<sub>2</sub>pz)<sub>2</sub> (0.6 mmol), prepared in situ, and G3-Br (1.0 g, 0.6 mmol) in THF. Purification was carried out by addition of pentane to a stirred toluene solution, which caused precipitation as an off-white solid. Yield: 0.775 g (72%). Anal. Calc. for C<sub>116</sub>H<sub>106</sub>N<sub>4</sub>O<sub>14</sub> (1780.14): C, 78.27; H, 6.00; N, 3.15%. Found: C, 78.14; H, 6.09; N, 2.90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.00 (s, 6 H, pz-Me<sup>3</sup>), 2.20 (s, 6 H, pz-Me<sup>5</sup>), 3.79 (d,  $J_{H,H} = 7.3$  Hz, 2 H, CH<sub>2</sub>), 4.81 (s, 4 H, G1-ArCH<sub>2</sub>O), 4.94 (s, 8 H, G2-ArCH<sub>2</sub>O), 5.00 (s, 16 H, PhCH<sub>2</sub>O), 5.71 (s, 2 H, pz-H<sup>4</sup>), 6.13 (t,  $J_{H,H} = 7.3$  Hz, 1 H, CH),  $6.17 (d, {}^{4}J_{H,H} = 2.2 Hz, 2 H, G0-o-Ar), 6.44 (t, {}^{4}J_{H,H} = 2.2 Hz, 1 H,$ G0-*p*-Ar), 6.51 (t,  ${}^{4}J_{H,H} = 2.2$  Hz, 2 H, G1-*p*-Ar), 6.54 (t,  ${}^{4}J_{H,H} =$ 2.2 Hz, 4 H, G2-*p*-Ar), 6.59 (d,  ${}^{4}J_{H,H} = 2.2$  Hz, 4 H, G1-*o*-Ar), 6.66 (d,  ${}^{4}J_{H,H} = 2.2$  Hz, 8 H, G2-o-Ar), 7.3–7.4 ppm (m, 40H, Ph).  ${}^{13}C{}^{1}H{} NMR (CDCl_3): \delta 11.0 (pz-Me^5), 13.7 (pz-Me^3), 40.2$ (CH<sub>2</sub>), 69.8 (G1-ArCH<sub>2</sub>O), 70.0 (G2-ArCH<sub>2</sub>O), 70.1 (PhCH<sub>2</sub>O), 71.7 (CH), 101.2 (G0-*p*-Ar), 101.4 (G1-*p*-Ar), 101.6, (G2-*p*-Ar), 106.2 (overlapping G1-o-Ar, G2-o-Ar and pz-C4), 108.2 (G0-o-Ar), 127.6 and 128.6 (o- and m-Ph), 128.0 (p-Ph), 136.8 (ipso-Ph), 138.9 (G1-ipso-Ar), 139.1 (G2-ipso-Ar), 139.3 (pz-C<sup>5</sup>), 139.6 (G0-ipso-Ar), 147.9 (pz-C<sup>3</sup>), 159.7 (G0-m-Ar), 160.1 (G1-m-Ar), 160.2 ppm (G2-*m*-Ar). IR (KBr): v 1560 (s, C=N), 1595 and 1452 (vs, C=C), 1295 (s, C-O-C<sub>asym</sub>), 1155 and 1051 cm<sup>-1</sup> (vs, C–O–C<sub>s</sub>). MS (ESI+ in MeOH/0.1% HCOOH): *m*/*z* 1781 [M + H]<sup>+</sup>.

Preparation of [NiBr<sub>2</sub>{Me<sub>3</sub>SiCH(3,5-Me<sub>2</sub>pz)<sub>2</sub>}](6). A solution of ligand 1 (80 mg, 0.29 mmol) in dichloromethane (15 mL) was added at room temp. to a suspension of [NiBr<sub>2</sub>(DME)] (78 mg, 0.25 mmol) in the same solvent (15 mL), and the mixture stirred for 2 h. During the course of the reaction the initial orange suspension changed rapidly to red, evolving to a deep-blue final color in 10 min. The solvent was removed in vacuo and the residue washed with pentane  $(2 \times 15 \text{ mL})$  to give 6 as a gravish purple paramagnetic solid, which was recrystallized from toluene. Yield: 110 mg (89%). Anal. Calc. for C<sub>14</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>4</sub>NiSi (494.96): C, 33.97; H, 4.89; N, 11.32%. Found: C, 34.15; H, 4.86; N, 11.23%. <sup>1</sup>H NMR  $(\text{CDCl}_3, 293 \text{ K}): \delta - 12.0 \text{ (br. s, } \Delta v_{1/2} = 16 \text{ Hz}, 1 \text{ H}, \text{CH}), -4.4 \text{ (br. s, } \delta + 12.0 \text{ (br. s)}, \delta = 100 \text{ Hz}, 1 \text{ H}, \delta = 100 \text{ Hz}, 1$  $\Delta v_{1/2} = 20$  Hz, 9 H, SiMe<sub>3</sub>), 15.6 (s,  $\Delta v_{1/2} = 8$  Hz, 6 H, pz-Me<sup>5</sup>), 38.5 (vbr. s,  $\Delta v_{1/2} = 117$  Hz, 6 H, pz-Me<sup>3</sup>), 64.7 ppm (br. s,  $\Delta v_{1/2} =$ 20 Hz, 2 H, pz-H<sup>4</sup>). IR (KBr): v 1625 (m, C=C), 1552 (s, C=N). MS (ESI+ in MeCN): m/z 447 [M - 2Br + Me<sub>2</sub>pz + H<sub>2</sub>O]<sup>+</sup>, 415  $[M - Br]^+$ , 333  $[M - 2Br - H]^+$ , 277  $[1 + H]^+$ , 181  $[1 - Me_2pz]^+$ .

Preparation of [NiBr<sub>2</sub>{G0-CH(3,5-Me<sub>2</sub>pz)<sub>2</sub>}] (7). Compound 7 was synthesized as described above for 6, starting from didentate ligand 2 (106 mg, 0.360 mmol) and [NiBr<sub>2</sub>(DME)] (110 mg, 0.356 mmol). Purple monocrystals of complex 7 were obtained after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane by the twolayers diffusion technique. Yield: 166 mg (91%). Anal. Calc. for C<sub>18</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>4</sub>Ni (512.90): C, 42.15; H, 4.32; N, 10.92%. Found: C, 42.67; H, 4.46; N, 10.64%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ –9.1 (vbr. s,  $\Delta v_{1/2} = 67$  Hz, 2 H, CH<sub>2</sub>), -8.2 (br. s,  $\Delta v_{1/2} = 18$  Hz, 1 H, CH), 4.13 (s,  $\Delta v_{1/2} = 4$  Hz, 6 H, pz-Me<sup>5</sup>), 5.0 (br. s,  $\Delta v_{1/2} =$ 19 Hz, 2 H, o-Ph), 7.16-7.19 (m, 3 H, m- and p-Ph), 21.4 (vbr. s,  $\Delta v_{1/2} = 84$  Hz, 6 H, pz-Me<sup>3</sup>), 69.3 ppm (br. s,  $\Delta v_{1/2} = 18$  Hz, 2 H, pz-H<sup>4</sup>). IR (KBr): v 1557 (s, C=N), 1605 (m, C=C) and 1463 cm<sup>-1</sup> (s, C=C). MS (ESI+ in MeCN): m/z 465 [M - 2Br + Me<sub>2</sub>pz +  $H_2O^{+}$ , 433  $[M - Br]^+$ , 371  $[M - 2Br + H + H_2O]^+$ , 351  $2Br - H]^+$ , 199 [2-Me<sub>2</sub>pz]<sup>+</sup>.

Preparation of [NiBr<sub>2</sub>{G1-CH(3,5-Me<sub>2</sub>pz)<sub>2</sub>}] (8). Compound 8 was also synthesized as described above for 6, starting from wedge 3 (210 mg, 0.414 mmol) and [NiBr<sub>2</sub>(DME)] (128 mg, 0.415 mmol). The purple solid was recrystallized from toluene. Yield: 269 mg (90%). Anal. Calc. for C<sub>32</sub>H<sub>34</sub>Br<sub>2</sub>N<sub>4</sub>NiO<sub>2</sub> (725.15): C, 53.00; H, 4.73; N, 7.73%. Found: C, 53.27; H, 4.84; N, 7.52%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  -9.3 (vbr. s,  $\Delta v_{1/2}$  = 89 Hz, 2 H, CH<sub>2</sub>), -8.2 (br. s,  $\Delta v_{1/2} = 23$  Hz, 1 H, CH), 3.9 (br. s, 2 H, partially overlapping, o-Ar), 4.02 (s,  $\Delta v_{1/2} = 6$  Hz, 6 H, pz-Me<sup>5</sup>), 5.59 (s,  $\Delta v_{1/2} = 5$  Hz, 4 H, PhCH<sub>2</sub>O), 6.47 (s,  $\Delta v_{1/2} = 4$  Hz, 1 H, *p*-Ar), 7.52 (d, 2 H,  $J_{H,H} = 7.3$  Hz, *p*-Ph), 7.64 (t, 4 H,  $J_{H,H} = 7.4$  Hz, *m*-Ph), 7.82 (t, 4 H,  $J_{H,H} = 7.5$  Hz, o-Ph), 21.4 (vbr. s,  $\Delta v_{1/2} = 102$  Hz, 6 H, pz-Me<sup>3</sup>), 69.6 ppm (br. s,  $\Delta v_{1/2} = 23$  Hz, 2 H, pz-H<sup>4</sup>). IR (KBr): v1559 (s, C=N), 1607, 1596 and 1464 (s, C=C), 1293 and 1058 cm<sup>-1</sup> (s, C–O–C). MS (ESI+ in MeCN): m/z 1151 [M + 3 – Br]<sup>+</sup>, 677  $[M - 2Br + Me_2pz + H_2O]^+, 645 [M - Br]^+, 583 [M - 2Br + H + H_2O]^+, 645 [M - Br]^+, 583 [M - 2Br + H_2O]^+, 645 [M - Br]^+, 645 [M - Br$  $H_2O^{+}_{2}$ , 507  $[3 + H]^+$ , 411  $[3 - Me_2pz]^+$ , 315  $[3 - 2Me_2pz]^+$ .

**Preparation of [NiBr<sub>2</sub>{G2-CH(3,5-Me<sub>2</sub>pz)<sub>2</sub>] (9).** Dendritic nickel complex 9 was synthesized as described above for 6, starting from ligand 4 (162 mg, 0.174 mmol) and [NiBr<sub>2</sub>(DME)] (54 mg, 0.175 mmol), and was isolated as a purple solid from toluene used as recrystallization solvent. Yield: 160 mg (80%). Anal. Calc. for  $C_{60}H_{58}Br_2N_4NiO_6$  (1149.64): C, 62.69; H, 5.09; N, 4.87%. Found: C, 62.35; H, 5.02; N, 4.79%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  –9.5 (vbr. s,  $\Delta v_{1/2} = 99$  Hz, 2 H, CH<sub>2</sub>), -8.5 (br. s,  $\Delta v_{1/2} = 24$  Hz, 1 H, CH), 3.9 (br. s,  $\Delta v_{1/2} = 24$  Hz, 2 H, G0-*o*-Ar), 3.98 (s, 6 H,  $\Delta v_{1/2} = 6$  Hz, pz-Me<sup>5</sup>), 5.18 (s, 8 H,  $\Delta v_{1/2} = 4$  Hz, PhCH<sub>2</sub>O), 5.47 (s, 4 H,  $\Delta v_{1/2} = 6$  Hz, ArCH<sub>2</sub>O), 6.42 (s, 1 H,  $\Delta v_{1/2} = 4$  Hz, G0-*p*-Ar), 6.80 (s, 2 H,  $\Delta v_{1/2} = 5$  Hz, G1-*p*-Ar), 7.04 (s, 4 H,  $\Delta v_{1/2} = 5$  Hz, G1-*p*-Ar), 7.04 (s, 4 H,  $\Delta v_{1/2} = 5$  Hz, G1-*o*-Ar), 7.38 (d,  $J_{\rm H,\rm H} = 7.0$  Hz, 4 H, *p*-Ph), 7.46 (t,  $J_{\rm H,\rm H} = 7.2$  Hz, 8 H, *m*-Ph), 7.56 (t,  $J_{\rm H,\rm H} = 7.4$  Hz, 8 H, *o*-Ph), 21.4 (vbr. s, 6 H,  $\Delta v_{1/2} = 99$  Hz, pz-Me<sup>3</sup>), 69.7 ppm (br. s, 2 H,  $\Delta v_{1/2} = 24$  Hz, pz-H<sup>4</sup>). IR (KBr): v 1559 (s, C=N), 1595 (vs) and 1451 (s, C=C), 1293 (m, C-O-O<sub>asym</sub>), 1156 and 1046 cm<sup>-1</sup> (vs, C-O-C\_s). MS (ESI+ in MeCN): m/z 1101 [M - 2Br + Me<sub>2</sub>pz + H<sub>2</sub>O]<sup>+</sup>, 1069 [M - Br]<sup>+</sup>, 960 [M + 4 - 2Br]<sup>2+</sup>, 931 [4 + H]<sup>+</sup>, 835 [4 - Me<sub>2</sub>pz]<sup>+</sup>, 739 [4 - 2Me<sub>2</sub>pz]<sup>+</sup>.

Preparation of [NiBr<sub>2</sub>{G3-CH(3,5-Me<sub>2</sub>pz)<sub>2</sub>}] (10). This complex was synthesized as described above for 6, from ligand 5 (200 mg, 0.112 mmol) and [NiBr<sub>2</sub>(DME)] (35 mg, 0.113 mmol), and was isolated as a purple solid from a mixture of toluene and pentane. Yield: 160 mg (80%). Anal. Calc. for C<sub>116</sub>H<sub>106</sub>Br<sub>2</sub>N<sub>4</sub>NiO<sub>14</sub> (1998.64): C, 69.71; H, 5.35; N, 2.80%. Found: C, 69.81; H, 5.10; N, 2.54%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  -9.4 (vbr. s, 2 H,  $\Delta v_{1/2}$  = 108 Hz, CH<sub>2</sub>), -8.4 (br. s, 1 H,  $\Delta v_{1/2} = 25$  Hz, CH), 3.9 (br. s, 2 H,  $\Delta v_{1/2} = 23$  Hz, G0-*o*-Ar), 3.99 (s, 6 H,  $\Delta v_{1/2} = 7$  Hz, pz-Me<sup>5</sup>), 5.01 (s, 16 H,  $\Delta v_{1/2} = 4$  Hz, PhCH<sub>2</sub>O), 5.08 (s, 8 H,  $\Delta v_{1/2} = 5$  Hz, G2-ArCH<sub>2</sub>O), 5.46 (s, 4 H,  $\Delta v_{1/2} = 8$  Hz, G1-ArCH<sub>2</sub>O), 6.41 (s, 1 H,  $\Delta v_{1/2} = 5$  Hz, G0-*p*-Ar), 6.59 (s, 4 H,  $\Delta v_{1/2} = 6$  Hz, G2-*p*-Ar), 6.73 (s, 2 H,  $\Delta v_{1/2} = 5$  Hz, G1-*p*-Ar), 6.77 (s, 8 H,  $\Delta v_{1/2} = 5$  Hz, G2-*o*-Ar), 6.99 (s, 4 H,  $\Delta v_{1/2} = 6$  Hz, G1-*o*-Ar), 7.30 (m, 24 H, *p*-Ph and *m*-Ph), 7.38 (m, 16 H, *o*-Ph), 21.2 (vbr. s, 6 H,  $\Delta v_{1/2} =$ 101 Hz, pz-Me<sup>3</sup>), 69.9 ppm (br. s, 2 H,  $\Delta v_{1/2} = 21$  Hz, pz-H<sup>4</sup>). IR (KBr): v 1559 (s, C=N), 1595 (vs) and 1448 (s, C=C), 1293 (m, C-O-O<sub>asym</sub>), 1155 and 1051 cm<sup>-1</sup> (vs, C-O-C<sub>s</sub>). MS (ESI+ in MeCN): m/z 1952 [M - 2Br + Me<sub>2</sub>pz + H<sub>2</sub>O]<sup>+</sup>, 1917 [M - $Br]^+$ , 1809  $[M + 5 - 2Br]^{2+}$ , 1781  $[5 + H]^+$ , 919  $[M - 2Br]^{2+}$ . MS (MALDI-TOF in dithranol): m/z 3917  $[M_2 - Br]^+$ , 3837  $[(M - M_2)^2 - M_2]^+$  $Br_{2}^{+}, 2096 [M + Br + H_{2}O]^{+}, 2078 [M + Br]^{+}, 1918 [M - Br]^{+},$  $1837 [M - 2Br]^+$ .

#### X-Ray crystallographic studies

Single crystals of **7** suitable for an X-ray diffraction study were obtained by slow diffusion of pentane into a toluene solution of the nickel complex at room temperature. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Table 6. A purple-blue crystal was glued to a glass fiber and mounted on a Kappa-CCD Bruker-Nonius diffractometer with an area detector, and equipped with an Oxford Cryostream 700 unit; data were collected using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 150 K, with an exposure time of 10 s per frame (five sets; 239 frames; phi scans 2° scan-width). Raw data were corrected for Lorenz and polarization effects.

The structure was solved by direct methods, completed by subsequent difference Fourier techniques and refined by fullmatrix least-squares on  $F^2$  with SHELXL-97.<sup>28</sup> Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. The hydrogen atoms were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system.<sup>29</sup> 
 Table 6
 Crystal data and structure refinement for compound 7

$C_{18}H_{22}N_4Br_2Ni$
512.90
Purple-blue
150.0(2)
0.71073
Monoclinic, $P2_1/n$
8.816(1)
16.318(1)
14.369(1)
90.00
97.29(1)
90.00
2050.2(3)
4, 1.662
4.852
1024
$0.50 \times 0.15 \times 0.15$
3.12 to 25.51
$-10 \le h \le 10, -19 \le k \le 19, -17 \le l \le 17$
$13369/3814 [R_{int} = 0.2191]$
$2098 [I > 2\sigma(I)]$
99.6
Full-matrix least-squares on $F^2$
3813/0/246
0.968
$R_1 = 0.0641, wR_2 = 0.1049$
$R_1 = 0.1451, wR_2 = 0.1252$
0.753 and -0.931

<sup>*a*</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \{ [\sum w(F_o^2 - F_c^2)] / [\sum w(F_o^2)^2] \}^{1/2}.$ 

CCDC reference number 606876.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607090f

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