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New Multidentate Pyrazolyl–Pyridine Ligands—Synthesis and Structures

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Five new multidentate ligands have been prepared containing *N,N*-bidentate pyrazolyl–pyridine units linked to a central aromatic spacer unit. The ligands 3,3′-bis(3-{pyridin-2-yl}-pyrazol-1-yl-methyl)-*p*-terphenyl (1), 4,4′-bis(3-{pyridin-2-yl}-pyrazol-1-yl)biphenyl (2), and 1,8-bis(3-{pyridin-2-yl}-pyrazol-1-yl-methyl)naphthalene (3) have two bidentate arms and are therefore potentially tetradentate; 2,6-bis(3-{pyridin-2-yl}-pyrazol-1-yl-methyl)pyridine (4) has two bidentate arms with an additional nitrogen-donor in the aromatic spacer unit (a pyridyl group) and is therefore potentially pentadentate; and 1,3,5-trimethyl-2,4,6-tris(3-{pyridin-2-yl}-pyrazol-1-yl-methyl)benzene (5) has three bidentate arms and is therefore potentially hexadentate. The X-ray crystal structures of all of these ligands have been determined.

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Introduction

The self-assembly of elaborate metallo-supramolecular architectures such as cages, helicates, grids, boxes, ladders, and rings from labile metal ions and simple multidentate heteronuclear ligands is becoming one of the most studied areas in supramolecular chemistry.[1–6] It has been shown that such architectures can be formed through the control of metal–ligand interactions, and that depending upon the preference of the metal ion for a specific coordination geometry, and the arrangement of donor sites and the flexibility of the ligand, it is possible to obtain—with a substantial degree of control in some cases—a variety of one-, two-, or three-dimensional architectures.[7] In the particular case of complexes which contain two- or three-dimensional cavities, there is also the possibility of templating effects associated with a central guest species, usually a counter-ion.[4,8]

The ligands most commonly used in the above examples of self-assembly are based on *N*-donor heterocycles. Our work has focussed in particular on ligands which contain two bidentate pyrazolyl–pyridine units separated by an aromatic spacer; these are exemplified by ligands L^A–L^C in Scheme 1 which have all been used for assembly of adamantoid M_4L_6 tetrahedral cage complexes which incorporate anions in their central cavities.[4,9,10] Related ligands, in which two or more pyrazolyl-based donors are pendant from a central spacer, have also been used in the self-assembly of some elaborate cage-like complexes by numerous groups,[11–17] in particular by Steel and coworkers.[13–17]

Given the popularity of ligands of this nature for studies in self-assembly, we have been interested in synthesizing further examples to study their coordination behaviour. We accordingly describe herein the synthesis, characterization, and X-ray crystal structures of five new ligands based on pyrazolyl–pyridine donor units.

Results and Discussion

The new ligands, (1)–(5) in Scheme 1, are prepared by a previously described method, involving the reaction of 3-(2-pyridyl)pyrazole with a halogenated aromatic core in the presence of hydroxide ion under phase-transfer conditions.[4,18] This is a simple and relatively general method that is only limited by the availability of suitable halogenated aromatic units to use as the central linker. Ligands (1)–(4) contain two bidentate pyrazolyl–pyridine units; within this group there are variations in the flexibility of the ligand, ligand (2); the length of the ligand due to the variation in the length of the spacer unit, ligand (1); and in the addition of a donor ligand within the central core, ligand (4). Ligand (5), in contrast, is a hexadentate tripodal ligand with three bidentate arms linked to the central aromatic spacer through methylene groups.

Ligands (1)–(5) have been fully characterized by standard techniques (see Experimental section) and the X-ray crystal structures have been determined. The molecular structures are shown in Figures 1–5, respectively; hydrogen atoms are omitted for clarity. In each case the pyrazolyl–pyridine units are arranged in an approximately *transoid* manner such that the adjacent lone pairs on the pyridyl and pyrazolyl rings avoid each other.

The packing diagram of (1) reveals that there are two distinct types of herringbone-like packing, a result of there being two independent half molecules in the asymmetric unit. Figure 6 shows a packing diagram for one of the independent molecules, with dotted lines indicating a 'T-stacking' arrangement of the molecules with a separation of 3.39 Å between

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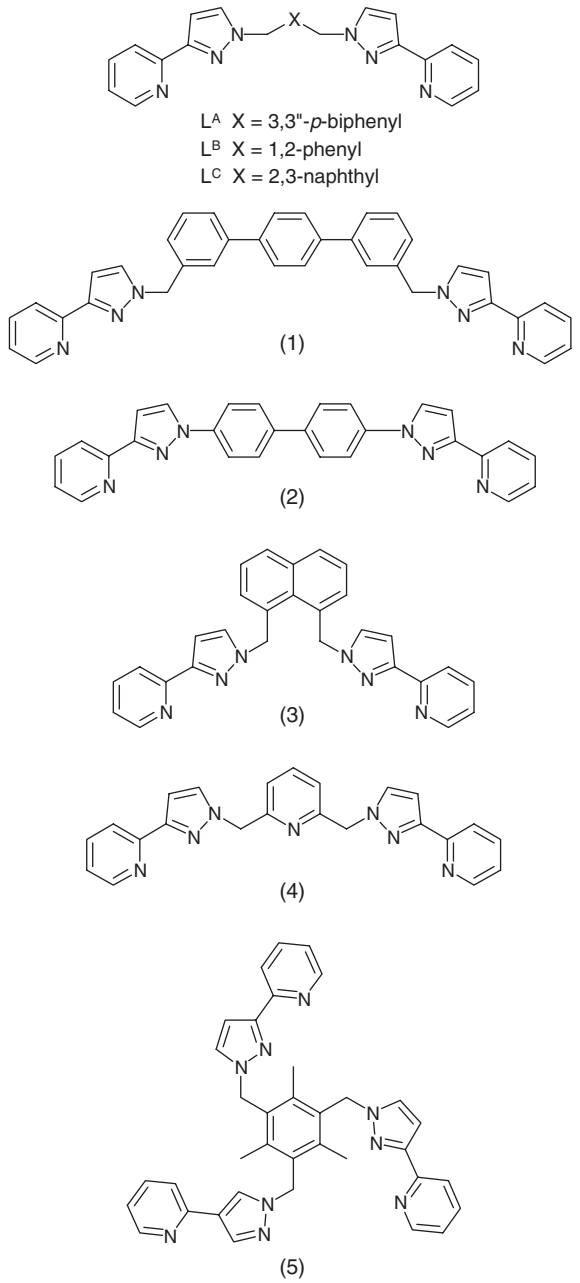


Scheme 1. Ligands (1)–(5).

H^5 of a pyrazole ring and the centre of the face of a phenyl ring from the terphenyl unit on the adjacent molecule. The terphenyl unit is not coplanar, with the central phenyl ring being twisted by 29.4 or 36.7° (depending on which disorder component is considered) from the plane of the two adjacent rings. The bidentate pyrazolyl–pyridine unit is also not coplanar, with a twist between the two rings of 4.1°. Figure 7 shows a packing diagram for the second independent molecule in the structure. Although it seems very similar to that illustrated in Figure 6, there are subtle differences that are in part due to the degree of disorder of the central phenyl ring in this molecule. The dotted lines indicate an interaction similar to those seen in the first molecule, but the H···π separation here is slightly longer at 3.52 Å. The twist of the central phenyl ring of the terphenyl spacer with respect

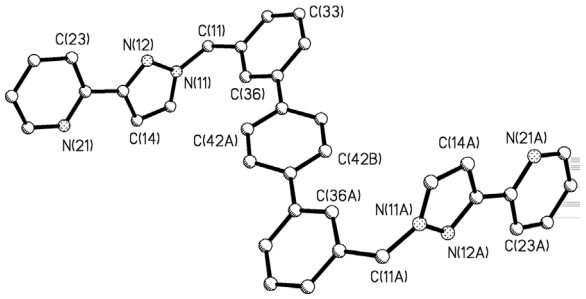


Fig. 1. Molecular structure of (1). Only one component of the disordered central phenyl ring is shown. There are two independent half-molecules in the asymmetric unit of which only one (grown to generate the whole molecule) is shown.

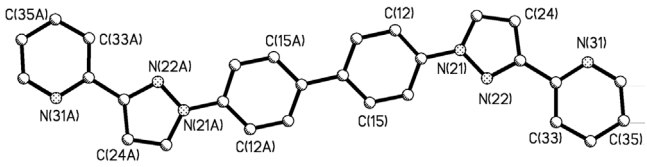


Fig. 2. Molecular structure of (2). The molecule lies on an inversion centre with only a half molecule in each asymmetric unit.

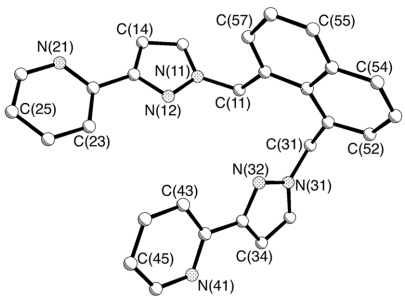


Fig. 3. Molecular structure of (3).

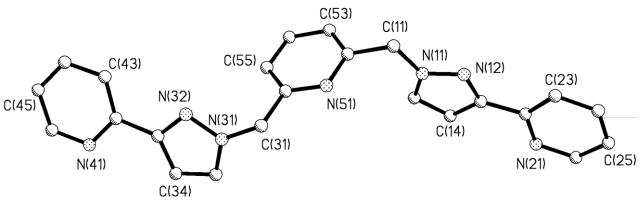


Fig. 4. Molecular structure of (4).

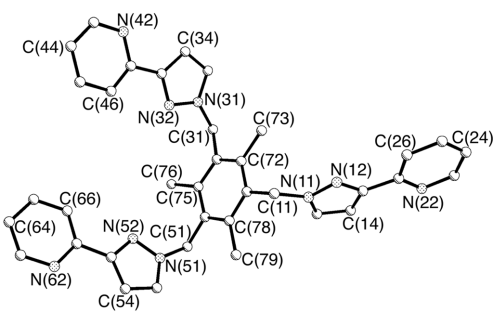


Fig. 5. Molecular structure of (5).

to the other two is either 27.8 or 59.2°, again depending on which disordered component is considered. The larger twist in the molecule generates the slightly different packing styles; adjacent molecules in the stack are slightly further apart, hence the longer C–H$\cdots\pi$ interaction. The bidentate pyrazolyl–pyridine units of this molecule have a twist angle of 7.5° between the rings. The chelating pyrazolyl–pyridine units of both molecules are nearly perpendicular to the external phenyl rings of the central spacer, the angles between them being 86.1 and 88.0° for the two independent molecules (1) and (2), respectively.

The packing of ligand (2) revealed extensive π–π stacking interactions (Fig. 8) between adjacent layers of ligands. The distance of this interaction is approximately 3.68 Å, and involves overlapping pyridine and pyrazole rings. There is also a weaker interaction (3.87 Å) between overlapping pyrazole rings of adjacent molecules (not shown in the Figure). The chelating units are again almost coplanar, with the angle between the pyrazolyl and pyridine rings being 3.4°. The central biphenyl unit is approximately planar; the angle between the mean planes of the pyrazolyl–pyridine and biphenyl units is 17.9°.

Ligand (3) (Fig. 9) crystallizes in the chiral space group $P2_1$. The molecule itself has a chiral, twisted conformation, with the angle between both chelating units and the plane of the naphthalene spacer unit being approximately 86°. The pyrazolyl–pyridine units themselves are not coplanar, with

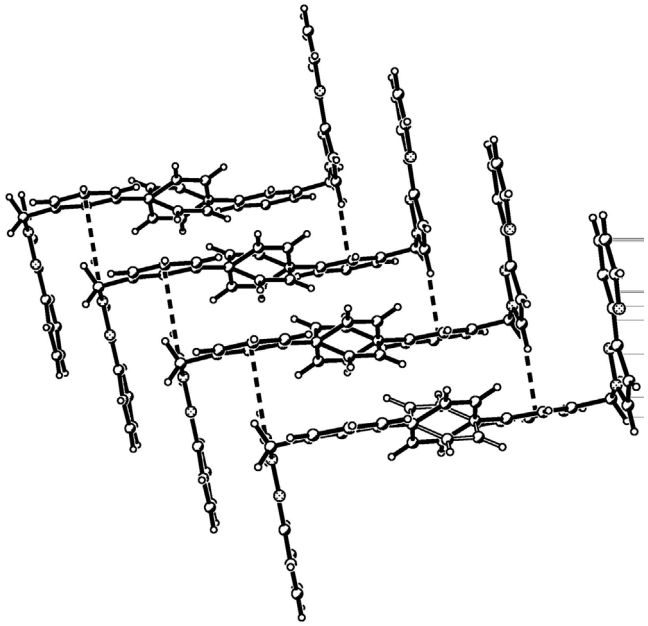


Fig. 6. Packing diagram showing the herringbone motif for one of the independent molecules of (1) (both disorder components of the central phenyl ring are shown).

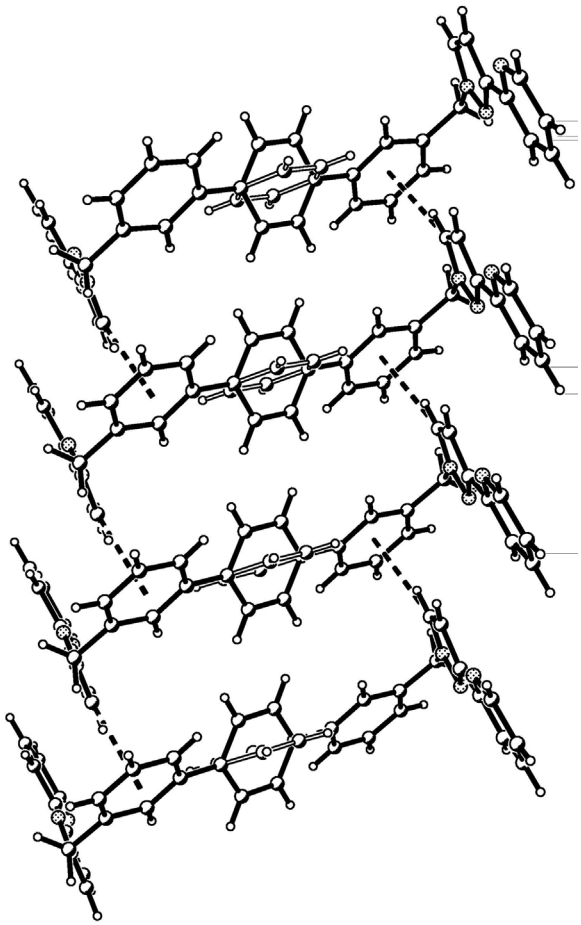


Fig. 7. Packing diagram showing the herringbone motif for the second independent molecule of (1) (both disorder components of the central phenyl ring are shown).

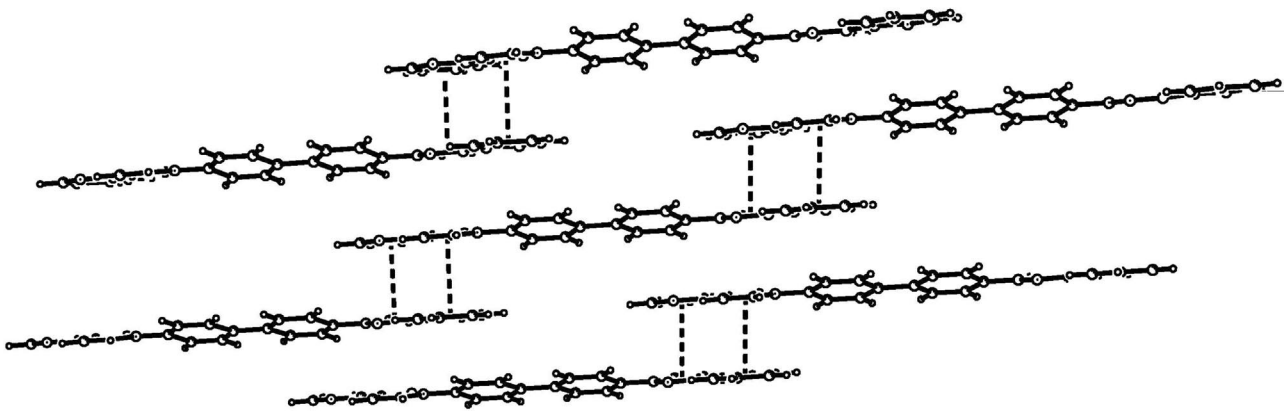


Fig. 8. Packing diagram of (2).

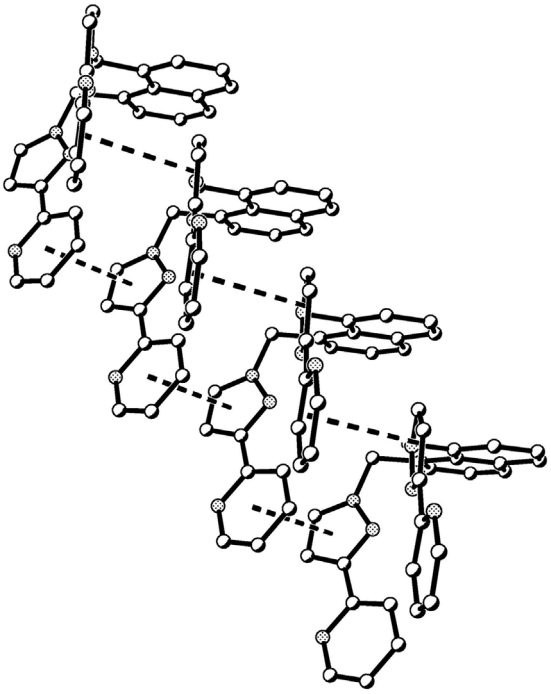


Fig. 9. Packing diagram of (3).

internal twist angles of 5.6 and 5.8°. There is an extensive array of π–π interactions between the pyrazole ring of one molecule and the pyridine ring of an adjacent molecule (Fig. 9). The average distance between the stacked units is 3.42 Å, the interactions being indicated with a dotted line in Figure 9.

The packing structure of (4) (Fig. 10) shows an array of weak C–H···N hydrogen-bonding interactions between adjacent molecules (shown in Figure 10 with dotted lines). There are three distinct types of interaction: (a) between the H^5 of a pyrazole ring and the nitrogen atom of the adjacent pyridine ring from the chelating unit (N···C distance 3.52 Å); (b) between the nitrogen of the pyridine ring and a hydrogen atom from a methylene unit on an adjacent molecule (N···C distance 3.68 Å); and (c) between a hydrogen atom from a methylene unit and the nitrogen atom of a pyrazole ring on an adjacent molecule (N···C distance 3.56 Å). As is clearly indicated in Figure 10, this results in a quadruple array of weak hydrogen-bonds connecting adjacent molecules.

The pyrazolyl–pyridine units of the ligand are not coplanar, with angles between pyrazolyl and pyridine rings in the two 'arms' being 9.0 and 11.5°. The angles between the mean planes of these 'arms' and the pyridyl ring are 85.1 and 59.8°, respectively.

The hexadentate ligand (5) shows no significant π–π, C–H···π, or C–H···N interactions in the packing arrangement, although, as for the other structures, the bidentate units are not exactly internally coplanar and are substantially twisted with respect to the plane of the central phenyl ring due to the effects of the methylene groups.

The coordination chemistry of ligand (3) has been discussed recently;[18] this ligand reacts with Co^{II} and Zn^{II} to generate dodecanuclear cage complexes $[M_{12}(\mu\text{-}(3))_{18}]X_{24}$

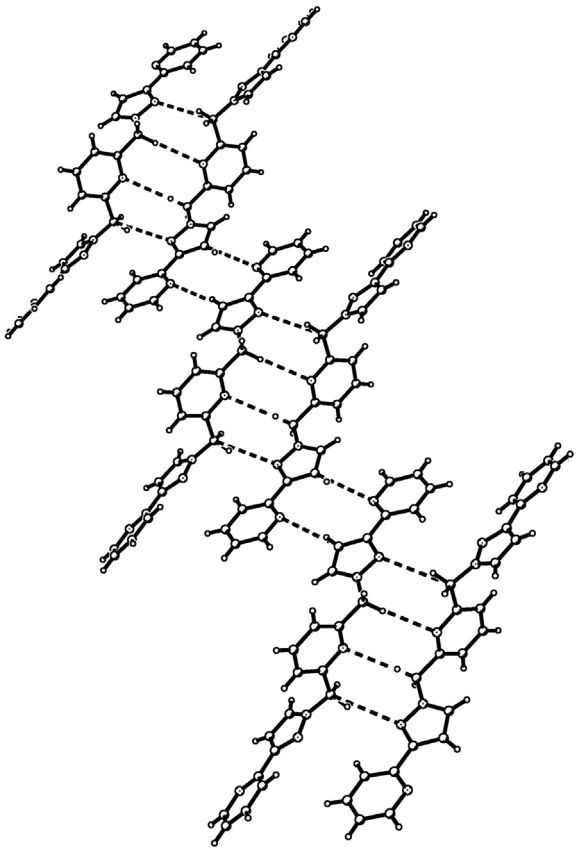


Fig. 10. Packing diagram of (4).

(where X = perchlorate or tetrafluoroborate), in which each of the 18 bridging ligands spans an edge of a truncated-tetrahedral M_{12} array. We expect the remaining new ligands to have comparably fruitful coordination behaviour, which will be discussed in due course.

Conclusions

This paper reports the syntheses and structures of five new multidentate ligands (1)–(5). The phase-transfer reaction is high yielding and has proved to be a simple and efficient way of synthesizing multidentate nitrogen-donor ligands, and appears to be limited only by the availability of the halogenated aromatic spacers.

Experimental

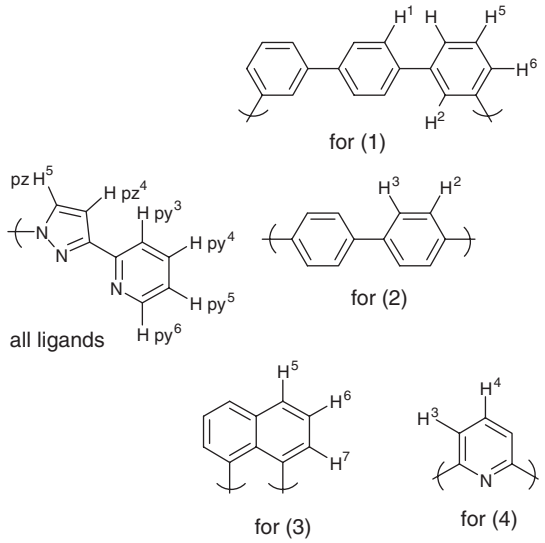
General Details

Proton NMR spectra were recorded on Jeol GX-270 or Lambda 300 spectrometers, assignments are shown in Scheme 2. Electron impact (EI) mass spectra were measured on a VG-Autospec instrument. Organic reagents were of the highest commercially available grade and were used as received.

Ligand (1)

1,4-Dibromo-2,5-diiodobenzene[19] was converted into 3,3″-dimethyl-*p*-terphenyl,[20] which was subsequently brominated to yield 3,3′-bis(bromomethyl)-[1,1′,4′,1″]terphenyl, as described below.

3,3′-Bis(bromomethyl)-[1,1′,4′,1″]terphenyl. 3,3″-Dimethyl-*p*-terphenyl (1.00 g, 3.9 mmol) and *N*-bromosuccinimide (1.73 g, 9.7 mmol) were added under an atmosphere of nitrogen to 20 mL of vigorously stirred carbon tetrachloride. To the resulting suspension



Scheme 2. Proton NMR spectroscopic assignments for ligands (1)–(5).

2,2′-azobis-(2-methylpropionitrile) (0.05 g) was added and the reaction mixture was heated to reflux with stirring for 4 h, after which time the reaction mixture was allowed to cool and was filtered. The filter cake was washed with carbon tetrachloride and the solvent was removed under vacuum to yield a yellow oil, which was recrystallized from diethyl ether to form a white crystalline solid (1.24 g, 76%).

Ligand (1) was then synthesized by further reaction with 3-(2-pyridyl)pyrazole.[13] A mixture of 3,3′-bis(bromomethyl)-[1,1′,4′,1″]-terphenyl (0.87 g, 2.1 mmol), 3-(2-pyridyl)pyrazole (0.64 g, 4.4 mmol), toluene (20 mL), $[Bu^n_4N][OH]$ (0.10 mL of a 40% aqueous solution), and aqueous NaOH (1.49 g dissolved in 3.50 mL of water) were heated to 85°C for 24 h with vigorous stirring. After cooling, the organic phase was separated, washed with water, and dried ($MgSO_4$). Removal of the solvent afforded a pale yellow oil, which, after recrystallization from dichloromethane/hexane (1 : 2), yielded the desired product as an off-white crystalline solid (0.74 g, 65%). X-ray quality crystals were grown by slow diffusion of acetone into a solution of (1) in chloroform. δ_H (300 MHz; $CDCl_3$) 5.41 (4 H, s, CH_2), 8.61 (2 H, d, J 5.8 Hz, py^6), 6.49 (2 H, dt, J 2.3, 9.2 Hz, py^4), 6.14 (2 H, td, J 2.3, 9.2 Hz, py^3), 7.29 (2 H, d, J 1.3 Hz, pz^5), 6.85 (2 H, d, J 1.3 Hz, pz^4), 6.15 (4 H, s, phenyl H^1), 7.02 (4 H, ddd, J 1.2, 5.8, 9.2, Hz, phenyl H^6), 7.39–7.55 (6 H, m, py^5, phenyl H^2, H^4, H^5). EI mass spectrums m/z 544 (M^+). (Found: C, 79.2; H, 5.3; N, 15.2%. $C_{36}H_{28}N_6$ requires: C, 79.4; H, 5.2; N, 15.4%.)

Ligand (2)

Preparation of (2) was based on a published method.[17] 4,4′-Dibromobiphenyl (0.50 g, 1.6 mmol), 3-(2-pyridyl)pyrazole (2.32 g, 16 mmol), CuI (0.790 g, 4.1 mmol), and K_2CO_3 (1.766 g, 12.8 mmol) in nitrobenzene (10 mL) were heated to reflux with stirring for 3 h. The solvent was removed under vacuum to yield a dark green residue which was purified by column chromatography (Alumina V, 99 : 0.5 : 0.5 CH_2Cl_2/hexane/pyridine). The desired product was obtained as a pale yellow crystalline solid after the removal of solvent (0.41 g, 58%). X-ray quality crystals were grown from slow evaporation of a saturated solution of (2) in dimethylformamide (DMF). δ_H (270 MHz; $CDCl_3$) 8.57 (2 H, d, J 6.4 Hz, py^6), 7.25 (2 H, t, J 4.6 Hz, py^5), 8.11 (2 H, dd, J 2.2, 7.6 Hz, py^4), 7.76 (2 H, d, J 8.6 Hz, py^3), 8.01 (2 H, d, J1.6 Hz, pz^5), 7.10 (2 H, d, J 1.7 Hz, pz^4), 7.69 (4 H, d, J 2.2 Hz, phenyl H^3), 7.83 (4 H, d, J 2.2, phenyl H^2). EI mass spectrums m/z 440 (M^+). (Found: C, 76.2; H, 4.6; N, 19.0%. $C_{28}H_{20}N_6$ requires C, 76.4; H, 4.6; N, 19.1%.)

Ligand (3)

1,8-Dimethylnaphthalene was brominated using the method described in the synthesis of 3,3′-bis(bromomethyl)-[1,1′,4′,1″]terphenyl (above). The crude solid was purified by column chromatography (silica, 1 : 1 CH_2Cl_2/hexane) to yield 1,8-bis(bromomethyl)naphthalene as a crystalline solid after the removal of solvent (1.55 g, 71%). δ_H (270 MHz; $CDCl_3$) 5.08 (4 H, s, CH_2), 7.74 (2 H, d, J 8.0 Hz, H^2), 7.43 (2 H, t, J 7.0 Hz, H^3), 7.18 (2 H,d, J 6.8 Hz, H^4). EI mass spectrums m/z 314 (M^+). (Found: C, 45.6; H, 3.2%. $Br_2C_{12}H_{10}$ requires C, 45.9; H, 3.2%.)

1,8-Bis(bromomethyl)naphthalene and 3-(2-pyridyl)pyrazole (2.1 equivalents) were reacted in the same manner used in the synthesis of (1). The crude solid was purified by recrystallization from dichloromethane/hexane to yield the desired product as an off-white crystalline solid (0.64 g, 44%). X-ray quality crystals were grown by the slow diffusion of hexane in to a solution of (3) in CH_2Cl_2. δ_H (300 MHz; $CDCl_3$) 5.87 (4 H, s, CH_2), 8.56 (2 H, d, J 5.6 Hz, py^6), 7.18 (2 H, t, J 5.6 Hz, py^5), 7.45 (2 H, t, J 8.6 Hz, py^4), 7.23 (2 H, d, J 7.5 Hz, py^3), 7.07 (2 H, d, J 3.8 Hz, pz^5), 6.80 (2 H, d, J 3.8 Hz, pz^4), 7.90 (2 H, d, J 7.5 Hz, H^7), 7.70 (2 H, td, J 1.9, 7.3 Hz, H^6), 7.99 (2 H, d, J 7.5 Hz, H^5). EI mass spectrum: m/z 442 (M^+). (Found: C, 76.3; H, 4.9; N, 19.3%. $C_{28}H_{22}N_6$ requires C, 76.0; H, 5.0; N, 19.0%.)

Ligand (4)

2,6-Bis(bromomethyl)pyridine and 3-(2-pyridyl)pyrazole (2.1 equivalents) were reacted in the same manner used for the synthesis of (1). The crude product was purified by column chromatography (alumina III, 33 : 1 CH_2Cl_2/methanol), giving the desired product as a pale yellow crystalline solid (0.51 g, 69%) following the removal of solvent. X-ray quality crystals were grown by the slow diffusion of hexane into a solution of (4) in CH_2Cl_2. δ_H (300 MHz; $CDCl_3$) 5.51 (4 H, s, CH_2), 8.64 (2 H, d, J 8.3 Hz, py^6), 7.38 (2 H, ddd, J 1.4, 5.2, 7.5 Hz, py^5), 7.92 (2 H, td, J 2.1, 8.3 Hz, py^4), 7.54 (2 H, d, J 7.5 Hz, py^3), 7.58 (2 H, d, J 2.8 Hz, pz^5), 7.88 (2 H, d, J 8.3 Hz, central pyridine H^3), 6.90–6.98 (3 H, m, pz^4, central pyridine H^4). EI mass spectrum m/z 393 (M^+). (Found: C, 70.2; H, 4.4; N, 24.8%. $C_{23}H_{19}N_7$ requires C, 70.2; H, 4.9; N, 24.9%.)

Ligand (5)

2,4,6-Tris(bromomethyl)mesitylene and 3-(2-pyridyl)pyrazole (3.2 equivalents) were reacted in the same manner used for the synthesis of (1). The crude product was purified by washing with diethyl ether to leave a white crystalline solid (0.56 g, 76%). X-ray quality crystals were grown by the slow diffusion of pentane into a solution of (5) in CH_2Cl_2. δ_H (300 MHz; $CDCl_3$) 2.45 (9 H, s, CH_3), 5.55 (6 H, s, CH_2), 8.63 (3 H, d, J 6.0 Hz, py^6), 7.20 (3 H, t, J 5.3 Hz, py^5), 7.72 (3 H, td, J 2.1, 8.6 Hz, py^4), 7.92 (3 H, d, J 8.6 Hz, py^3), 7.08 (3 H, d, J 2.1 Hz, pz^5), 6.83 (3 H, d, J 2.1 Hz, pz^4). EI mass spectrum m/z 591 (M^+). (Found: C, 73.3; H, 5.5; N, 21.1%. $C_{36}H_{33}N_9$ requires C, 73.1; H, 5.6; N, 21.3%.)

Crystal Structure Determinations

Suitable crystals were quickly transferred from the mother liquor to a stream of cold N_2 (173 K) on a Bruker SMART-CCD diffractometer. In all cases a hemisphere of data was collected at 173 K using graphite-monochromatized $Mo_{K\alpha}$ radiation. All of the structures studied were solved by direct methods. Ligand (1) crystallizes with two independent half molecules in the asymmetric unit. Ligands (1) and (2) have a crystallographic centre of inversion. The structural determination of (1) was complicated by disorder of the central phenyl ring. The disorder has been successfully modelled in two parts with 50% site occupancy for each part. The structural determinations for (2)–(5) were straightforward.

All hydrogen atoms were constrained to ideal geometries and assigned isotropic displacement parameters 1.2 times that of their adjacent carbon atom. Data collection: SMART; cell refinement: SAINT; data reduction, program(s) used to solve structure and program(s) used to refine structure: SHELXTL.[21] Crystal data and details of the data collection and processing for each crystal are given in Table 1. CIF files have been deposited in the Cambridge Crystallographic Data Centre (CCDC), nos. 186825–186829 for (1)–(5), respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-(0)1223-336033 or email:deposit@ccdc.cam.ac.uk.

Table 1. X-ray crystal data collection and refinement details for (1)–(5)

Parameter	(1)	(2)	(3)	(4)	(5)
Formula	$C_{36}H_{28}N_6$	$C_{28}H_{20}N_6$	$C_{28}H_{22}N_6$	$C_{23}H_{19}N_7$	$C_{36}H_{33}N_9$
M	544.64	440.50	442.52	393.45	591.71
Colour	colourless	colourless	colourless	colourless	colourless
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$	$C2/c$	$P2_1/c$
a (Å)	36.750 (18)	9.746 (2)	14.753 (4)	28.01 (2)	11.700 (3)
b (Å)	5.611 (3)	8.760 (2)	4.9545 (13)	6.702 (3)	23.730 (5)
c (Å)	13.618 (7)	12.528 (3)	14.853 (3)	21.686 (11)	10.977 (4)
β (deg)	100.65 (4)	93.777 (4)	98.00 (3)	107.28 (4)	95.61 (3)
U (Å^3)	2760 (2)	1067.2 (4)	1075.1 (5)	3888 (4)	3033.1 (14)
Z	4	2	2	8	4
D_{calc} (mg m^{-3})	1.311	1.371	1.367	1.344	1.296
Crystal size (mm^3)	0.5 × 0.3 × 0.2	0.3 × 0.2 × 0.1	0.5 × 0.2 × 0.2	0.5 × 0.2 × 0.1	0.35 × 0.2 × 0.05
Reflections collected: total, independent, R_{int}	17872, 6311, 0.0431	4972, 1847, 0.0652	6948, 4667, 0.03189	12093, 4444, 0.0802	16176, 5337, 0.0806
θ range for data (deg)	1.52–27.54	2.09–25.00	1.39–24.47	1.97–27.59	1.72–25.00
Data, restraints, parameters	6311, 0, 377	1847, 0, 154	4667, 1, 307	4444, 0, 271	5337, 0, 406
Final R_1, wR_2^A	0.0523, 0.1239	0.0411, 0.0778	0.0458, 0.0850	0.0494, 0.0912	0.0627, 0.1499

[A] Structure was refined on F_o^2 using all data; the value of R_1 is given for comparison with older refinements based on F_o with a typical threshold of $F \geq 4\sigma(F)$. The value of wR_2 is based on all data.

Acknowledgment

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