Diels−Alder Synthesis of Rigid 60° Angular Bridging Ligands and X-ray Crystal Structures of their Silver Nitrate Complexes

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Using Diels–Alder chemistry, three bridging ligands (**2**–**4**) have been synthesised, each of which contains two pyridine nitrogen donors disposed at a 60° angle. X-ray crystal structures are reported for ligand **4** and two coordination polymers formed by the reaction of **2** and **3** with silver nitrate.

Introduction

The controlled self-assembly of two- and three-dimensional metallosupramolecular species has been the subject of enormous study in recent years.[1] The most common synthetic approach to such compounds has been to employ logical combinations of rigid linear and angular components in order to construct rationally designed architectures.[1] Within this context, molecular squares have proved to be particularly popular synthetic targets as they are readily assembled from combinations of linear, bridging ligands (such as pyrazine or 4,4′-bipyridine) and right-angular (90°) metal linkages (such as is provided by *cis*-coordination in a square-planar metal centre).[2] Similarly, molecular pentagons and hexagons are available using tetrahedral and trigonal linking components.[1] This concept has been extended into the third dimension with reports of molecular cubes,[3] dodecahedra,[4] and other polyhedra.[1]

Of the two-dimensional molecular polygons, triangles pose a particular problem.[1] Metal centres are not suitable for use as the angular components, since the requisite 60° angle is not readily provided by the subset of angular geometries offered by ligand coordination to transition metals. Consequently, the construction of metallosupramolecular triangles necessitates an inversion of approach, such that the metal provides the linear bridge (e.g. *trans* coordination to a square-planar metal centre) and the organic ligand provides the angular component (Figure 1a). A limited number of such species have been reported, the most common of which have employed pyrazolates as angular bridges linking linear metal centres, such as silver or gold (Figure 1b).[5] Intrinsically, the use of pyrazolates as the angular components allows no control over the dimension of the triangles assembled. Loeb and co-workers[6] have used 4,7-naphthyridine to construct larger molecular triangles in which the organic ligand provides the necessary 60° angular bridge linking doubly cyclometallated palladium-based linear bridges. However, such ligands are not amenable to control of the distance between the donor centres, and hence the size of the triangle produced. More recently, a number of isolated examples of metastable distorted triangles have been reported that used pyrazine[7] or larger, more flexible bridging ligands.[8]

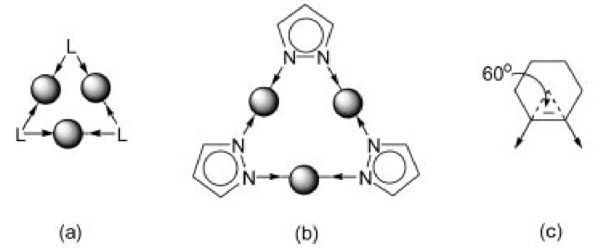

Figure 1. Molecular triangle components

Since the internal angle subtended by adjacent corners of a hexagon is 60°, we reasoned that a diverse range of triangular building blocks would be provided by organic ligands that incorporate donor groups with adjacent substitution in a cyclohexene or benzene ring (Figure 1c). We now report the synthesis of three such ligands that contain two 4-pyridyl substituents, each of which provides two nitrogen donors disposed at a 60° angle. Using a similar conceptual approach, Espinet and co-workers[9] recently reported the synthesis of an organometallic triangle derived from 1,2-phenylene diisocyanide, despite the fact that the corresponding diacetylide had led to an organometallic molecular square.[10] As we,[11] and others,[12] have found, reactions of bridging ligands with silver(I) species have led to a rich array of metallosupramolecular architectures. Thus, we have initially explored the coordination chemistry of these new

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ligands by examining their reactions with silver nitrate. Accordingly, we also report the synthesis and X-ray crystal structures of complexes formed from these ligands by reactions with silver nitrate.

Results and Discussion

The three ligands **2**−**4** were prepared by procedures based on the Diels−Alder reaction, as shown in Scheme 1. Di(4-pyridyl)acetylene (**1**) was prepared in 55% overall yield from commercially available 1,2-di(4-pyridyl)ethylene by bromination and dehydrobromination, according to a literature procedure.[13] In order to improve the dienophilicity of this compound, the pyridyl substituents were made more electron-withdrawing by conversion into the pyridinium species, through reaction with tetrafluoroboric acid. This methodology has previously been employed for the Diels−Alder reaction of **1** with cyclopentadiene.[14] Reaction of **1** with cyclohexa-1,3-diene gave the bicyclooctadiene **2**, albeit in a disappointing 12% yield.[15] Since mass spectrometry showed that this compound readily undergoes a retro-Diels−Alder reaction, with expulsion of ethylene, this strategy was used to prepare the disubstituted ligand **3**. Thus, heating **2** to 280 °C resulted in its smooth conversion into ligand **3**, which was isolated in 49% yield. This compound has previously been prepared by a Stille coupling procedure in the course of the synthesis of a large series of poly(4-pyridyl)-substituted aromatics.[16] The tetraphenyl derivative **4** was prepared by reaction of **1** with tetracyclone. In this case the free base was used, as Diels−Alder reactions of tetracyclone are well-known to proceed with inverse electron demand.[17] The intermediate adduct **5** underwent spontaneous expulsion of carbon monoxide to give the new ligand **4**.[18]

In order to confirm the structure of **4**, and to examine the relative orientations of the aryl rings, a single crystal X-ray crystal structure determination was carried out.[19] Figure 2 shows a perspective view of this new ligand, along with selected bond lengths and angles. Whereas the six peripheral aryl rings are all planar (to within 0.007 Å), the central ring displays an interesting distortion into a boat conformation, with C(3) and C(6) each displaced ca. 0.04 Å above the plane of the other four atoms of the ring. This in turn points the two attached phenyl rings above the plane of the central ring. As is the case in the crystal structure of hexaphenylbenzene,[20] the planes of the six external rings display a cooperatively correlated inclination with respect to the central benzene ring. The two pyridine rings are inclined at angles of 63.2 and 68.8° to the central ring, whereas the four phenyl rings are twisted by angles ranging from 65.9 to 76.1°. With respect to the centre of the central ring the two pyridine nitrogen donors subtend an angle of 62.6°.

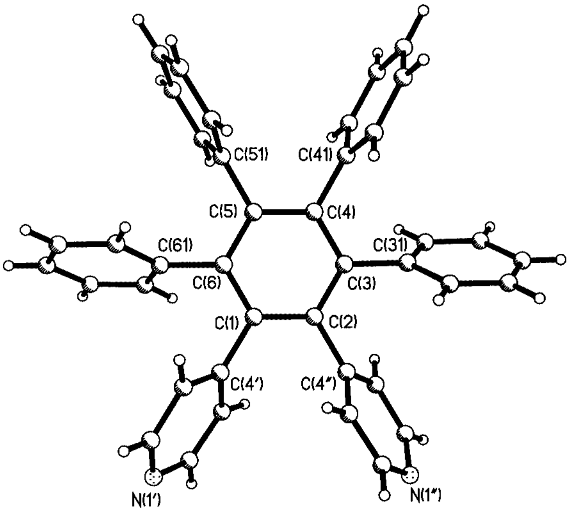
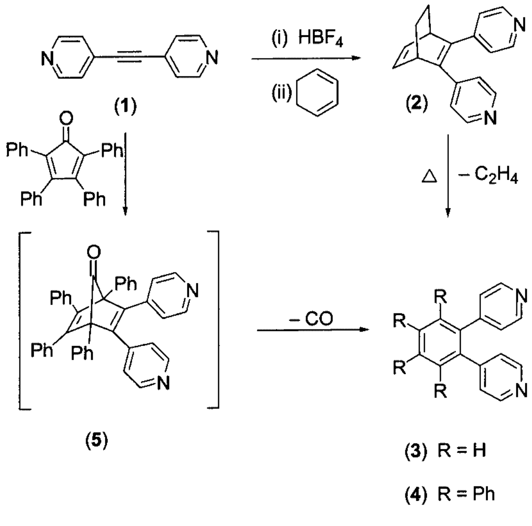


Figure 2. Perspective view of the X-ray crystal structure of ligand **4**; selected bond lengths (Å) and angles (°): C1−C2 1.411(3); C1−C6 1.409(3), C1−C4′ 1.501(3), C2−C3 1.408(3); C2−C4′′ 1.496(3), C3−C4 1.406(3), C3−C31 1.495(3), C4−C5 1.413(3), C4−C41 1.502(3); C5−C6 1.400(3), C6−C61 1.515(3); C2−C1−C6 119.9(2), C1−C2−C3 120.2(2), C2−C3−C4 119.4(2), C3−C4−C5 120.2(2), C4−C5−C6 120.1(2), C1−C6−C5 119.8(2)



Scheme 1

Ligands **2** and **3** were reacted with silver(I) nitrate in acetonitrile to give quantitative formation of complexes **6** and **7**, respectively, which on slow evaporation of the solutions furnished crystals suitable for an X-ray structure determination. In the case of the hexasubstituted ligand **4**, the low solubility of the ligand in acetonitrile required that the reaction be performed in methanol solution, which did not lead to X-ray quality crystals.

The structure[19] of the complex (**6**) formed from the bicyclo[2.2.2]octa-2,5-diene ligand **2** is surprisingly intricate. Figure 3 shows a perspective view of the contents of the asymmetric unit, which contains two silver atoms, two molecules of **2**, two nitrate anions and an acetonitrile solvate molecule. Each of the two independent ligands is bonded to three silver atoms through its two nitrogen donors and to the endo face of the more exposed double bond of the bicyclo[2.2.2]octa-2,5-diene moiety. Similarly, each silver atom is coordinated to three different ligands and also in-

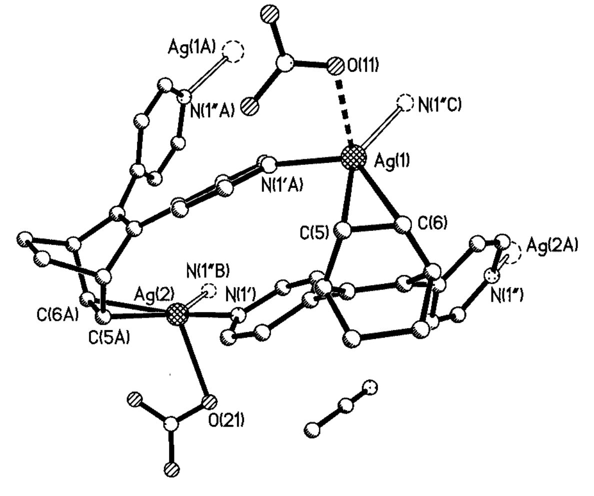


Figure 3. Perspective view of the contents of the asymmetric unit of the crystal structure of **6**; hydrogen atoms have been omitted for clarity; selected bond lengths (Å): Ag1−N1′A 2.328(5), Ag1−N1′′C 2.260(5), Ag1−C5 2.342(7), Ag1−C6 2.468(8), Ag1−O11 2.653(5), C5−C6 1.371(10), Ag2−N1′ 2.328(5), Ag2−N1′′B 2.292(5), Ag2−C6A 2.443(6), Ag2−C5A 2.457(7), Ag2−O21 2.565(5), C5A−C6A 1.403(8)

teracts weakly with one of the oxygen atoms of a nitrate counterion. The bridging nature of both the ligand and the metal results in an extension into a complex coordination polymer that propagates along the *a* axis.

Thus ligand **2** bridges three silver atoms with coordination to both the pyridine donors as well as a double bond of the bicyclooctadiene unit. To the best of our knowledge the only previously reported X-ray crystal structure which incorporates both of these features, is that of an ethylene adduct of a silver complex of a tris-pyrazolylborate.[21] As expected the nitrogen donors subtend angles [66.7(5) and 69.1(5)°] at the centroids of their attached bicyclooctane units which would be compatible with the formation of molecular triangles in the absence of these additional interactions.

The complex (**7**) formed from 1,2-di(2-pyridyl)benzene (**3**) is a zigzag coordination polymer. Figure 4 shows a perspective view of a section of this polymer, with selected atom labelling. In the crystal structure,[19] ligand **2** bridges two silver atoms, with an angle subtended at the centre of the benzene ring of 67.8°. The plane of the benzene ring is inclined to the planes of the attached pyridine rings at angles of 54.1 and 46.9°. By virtue of the coordination to the nitrate anion the silver atom deviates significantly from linear geometry.

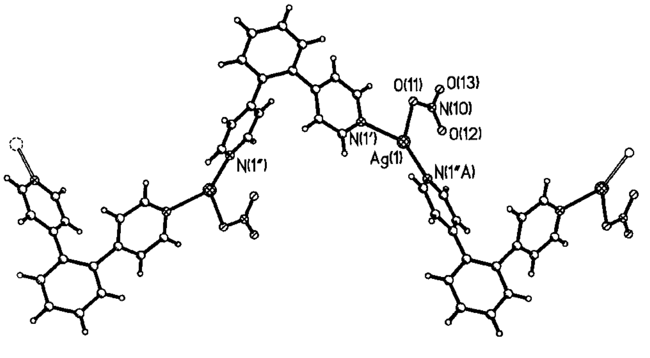


Figure 4. Crystal structure of a segment of the coordination polymer **7**; selected bond lengths (Å) and angles (°): Ag1−N1′ 2.279(2), Ag1−N1′′A 2.210(2), Ag1−O11 2.408(2); N1′−Ag1−N1′′A 132.13(6), N1′−Ag1−O11 87.90(5), N1′′A−Ag1−O11 138.23(5)

Table 1. X-ray crystal data and details of data collections and structure refinements

Compound	**4**	**6**	**7**
Formula	$C_{40}H_{28}N_2$	$C_{38}H_{35}Ag_2N_7O_6$	$C_{16}H_{12}AgN_3O_3$
Molecular weight	536.64	901.47	402.16
Crystal system	monoclinic	triclinic	monoclinic
Space group	*Cc*	$P\bar{1}$	$P2_1/n$
a (Å)	12.261(6)	10.738(7)	9.514(2)
b (Å)	21.343(11)	13.050(9)	10.940(3)
c (Å)	11.239(6)	13.825(10)	14.296(4)
α (°)	90	89.693(9)	90
β (°)	98.432(7)	67.692(9)	100.332(3)
γ (°)	90	87.084(10)	90
V (Å^3)	2909(3)	1790(2)	1463.8(6)
Z	4	2	4
D_c (Mg m^{-3})	1.225	1.673	1.825
F(000)	1128	908	800
Temperature (K)	168(2)	168(2)	168(2)
Crystal form	colourless prism	colourless needle	colourless block
Crystal size (mm)	0.36 × 0.16 × 0.12	0.64 × 0.03 × 0.02	0.86 × 0.21 × 0.17
μ (mm^{-1})	0.071	1.673	1.396
$2\theta_{max}$ (°)	50	50	53
Unique reflections	5111	6264	2989
Parameters	380	491	208
R[a] [$I > 2\sigma(I)$][a]	0.0386	0.0431	0.0201
wR[b] (all data)	0.0809	0.0814	0.0534

[a] $R = \Sigma (|F_0| - |F_c|)/\Sigma|F_0|$. [b] $wR = (\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2])^{1/2}$.

In conclusion, we have prepared three bridging ligands, each of which possesses two pyridine nitrogen donors disposed at a 60° angle, suitable for the self-assembly of molecular triangles. In their reactions with silver nitrate coordination polymers are formed as a result of the fact that the silver atoms do not behave as linear bridges due to additional interactions with the nitrate anions.

Acknowledgments

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[15] Preparation of **2**: Di(4-pyridyl)acetylene (500 mg) was converted into its di-HBF$_4$ salt by addition of 1 mL of 50% HBF$_4$ solution to a stirred solution of the acetylene in 350 mL diethyl ether. The white precipitate was filtered off, and dried under vacuum. This was added to 3.5 mL of cyclohexa-1,3-diene in 60 mL of dry acetonitrile and the mixture refluxed for 18 h. The solvent was removed in vacuo, leaving a brown/black residue, which was dissolved in 100 mL water, containing a small amount of HBF$_4$. This was washed with 4 × 45 mL dichloromethane, neutralised with NaHCO$_3$, then extracted with 4 × 60 mL dichloromethane. The dichloromethane solution was dried over MgSO$_4$ and the solvent removed in vacuo. After chromatography on alumina (10% methanol in ethyl acetate) the isolated product was recrystallised from petroleum ether/ethyl acetate to give 86.6 mg of a yellow solid. M.p. 124−126 °C. ^{1}H NMR (CDCl$_3$): $\delta = 8.44$ (d, 4 H), 6.95 (d, 4 H), 6.53 (dd, 2 H), 3.97 (br. s, 2 H), 1.62 (dd, 2 H), 1.53 (dd, 2 H) ppm. ^{13}C NMR (CDCl$_3$): $\delta = 149.8$, 146.7, 141.9, 134.4, 122.8, 43.7, 25.0. C$_{18}$H$_{16}$N$_2$ (260.3): calcd. C 83.04, H 6.20, N 10.76; found C 82.97, H 6.18, N 10.92.

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[18] Selected data for **4**: M.p. > 340 °C. ^{1}H NMR (CDCl$_3$): $\delta =$ 8.13 (d, 4 H), 6.88 (m, 12 H), 6.81 (m, 8 H), 6.78 (d, 4 H).

[19] The crystal data, data collection and refinement parameters for the X-ray structures are listed in Table 1. Data were collected with a Siemens SMART CCD area detector, using graphite monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods, and refined on F^2 using all data by full-matrix least-squares procedures.
CCDC-182307 to CCDC-182309 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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