

Synthesis and X-ray crystal structure of a bridging trispiran ligand

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Dedicated to Rod Rickards with admiration, affection and a Chupa Chup

Abstract

Spiro[3,3]heptane-2,6-dispiro-4,5-diazafluorene (**4**) has been synthesized in three steps from 1,10-phenanthroline. It crystallizes in the orthorhombic space group $P2_12_12_1$ and has the two 4,5-diazafluorene metal binding domains mutually orthogonal.

Keywords: Trispiran, diazafluorene, N-ligand, crystal structure.

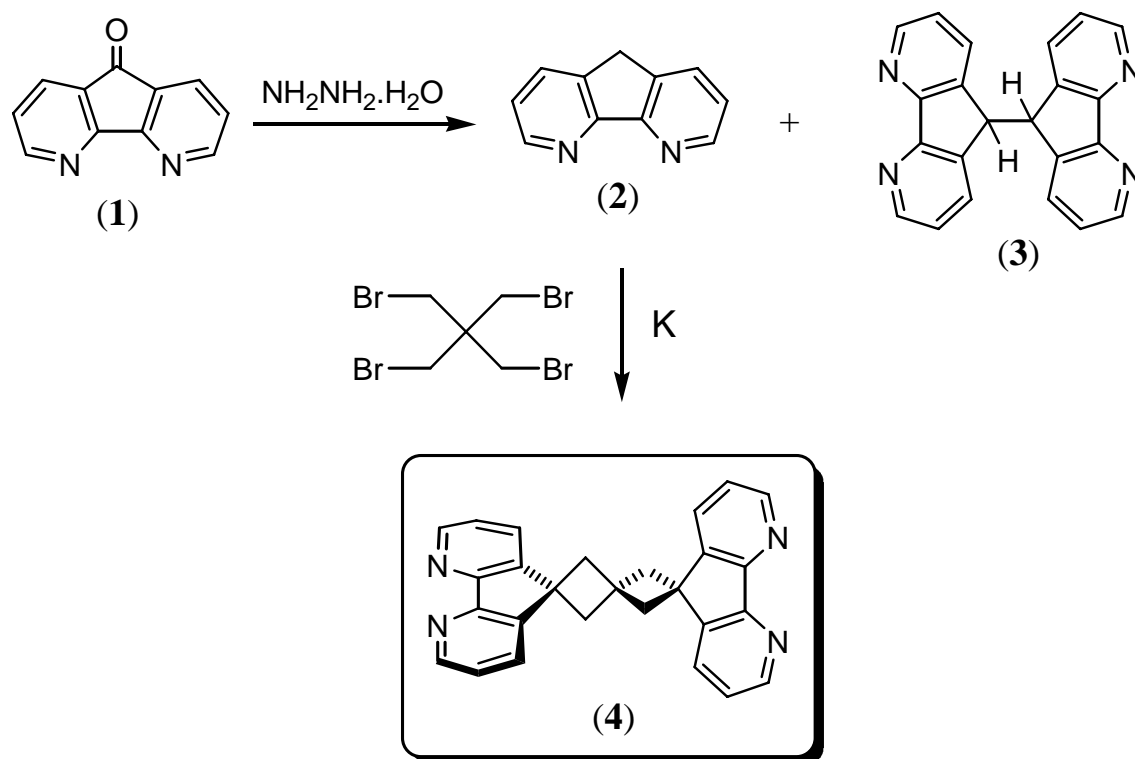
Introduction

Nitrogen-containing heterocyclic ligands are commonly used as bridges between metal centres and serve to facilitate communication between metals, such as energy or electron transfer or magnetic interactions.^{1,2} The magnitude of such interactions depends upon the distance between the metals, the extent of conjugation between the donor sites and the electronic properties of the heterocycles. In some cases surprisingly strong metal-metal interactions take place.³ Such ligands have found numerous applications in applied areas such as multi-electron catalysis, information storage, solar energy conversion, and artificial photosynthesis.

Ligands that contain two 2,2'-bipyridine (bpy) subunits coordinate to metal atoms with the formation of stable five-membered chelate rings and have been extensively used in coordination chemistry.⁴ Recently we described the synthesis and complexes of assorted ligands that contain di-2-pyridylmethane units linked by saturated and unsaturated bridges.⁵⁻⁸ We now describe the synthesis and X-ray crystal structure of the novel trispiro ligand **4**, which was designed to provide a ligand containing two mutually orthogonal bpy units separated by a rigid, saturated spacer group.

Results and Discussion

The synthetic procedure used to prepare **4** is shown in Scheme 1 and was based on the recently reported synthesis of the corresponding carbocyclic analogue.⁹ 4,5-Diazafluorenone (**1**), prepared by oxidation of 1,10-phenanthroline,¹⁰ was subjected to Wolff-Kishner reduction according to a literature procedure.¹¹ In our hands this resulted not only in the formation of the desired 4,5-diazafluorene (**2**) (36% yield) but also in the dimeric by-product 9,9'-bi-4,5-diazafluorene (**3**) (26% yield). This latter compound is itself a bridging ligand and useful precursor to the corresponding unsaturated 9,9'-bi-4,5-diazafluorenylidene.¹² Conversion of **2** to its potassium salt and treatment with pentaerythrityl tetrabromide furnished the trispiran **4**, albeit in somewhat disappointing yield (18%). This new compound was characterized by mass spectrometry and ¹H and ¹³C NMR. However, subsequent attempts to prepare complexes of **4** failed to provide any stable metal complexes. We became concerned about the identity of this compound and therefore carried out a single crystal X-ray structure determination, in order to establish unambiguously the structure.



Scheme 1. Synthesis of the title ligand **4**.

Crystals of **4**, suitable for X-ray crystallography, were obtained by recrystallisation from a mixture of dichloromethane and diethyl ether. The compound crystallizes in the chiral, orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The structure is confirmed as being the desired trispiran (Figure 1). Each spiro centre introduces an orthogonal orientation between the meanplanes of adjacent rings [90.8° at C(1), 90.6° at C(19) and 89.1° at C(39)] As a result the two 4,5-diazafluorene subunits are approximately orthogonal, but are still ideally placed to chelate to two metal atoms. Unlike the corresponding carbocyclic analogue,⁹ which has crystallographically imposed S_4 symmetry, the cyclobutane rings are slightly puckered, which introduces a small curvature to the ligand in the solid state. The strain within the structure is apparent in the large deviations of the bond angles about C(1) from the tetrahedral value (Figure 1). A consideration of the packing reveals that molecules of **4** pack in a herringbone arrangement, with edge-to-face π - π interactions between adjacent molecules.

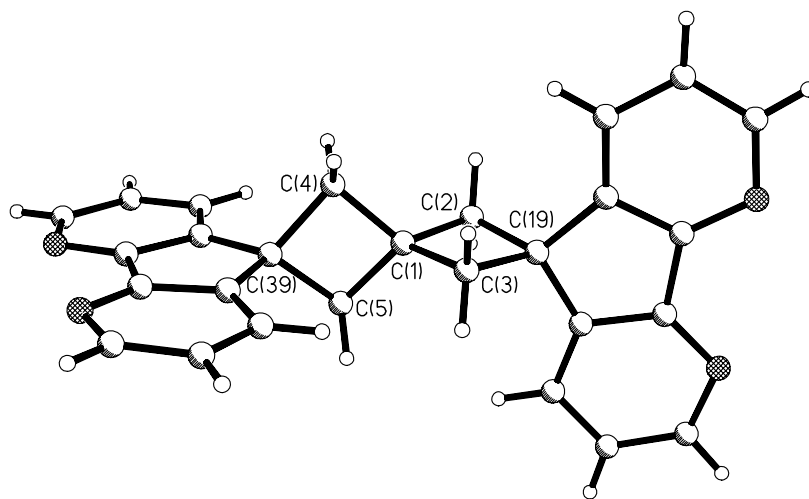


Figure 1. A perspective view of **4** shows the orthogonal arrangement of the two 4,5-diazafluorenyl ring systems. Selected bond lengths (Å) and angles (°): C(1)-C(2) 1.545(2), C(1)-C(5) 1.549(2), C(1)-C(4) 1.550(2), C(1)-C(3) 1.554(2), C(2)-C(19) 1.567(2), C(3)-C(19) 1.571(2), C(4)-C(39) 1.571(2), C(5)-C(39) 1.571(2), C(2)-C(1)-C(5) 121.26(14), C(2)-C(1)-C(4) 122.07(14), C(5)-C(1)-C(4) 88.66(11), C(2)-C(1)-C(3) 88.91(11), C(5)-C(1)-C(3) 119.39(14), C(4)-C(1)-C(3) 120.03(14), C(2)-C(19)-C(3) 87.53(11), C(5)-C(39)-C(4) 87.13(11).

Experimental Section

General Procedures. NMR spectra were recorded on a Varian 300 MHz NMR spectrometer. Melting points were performed on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell microanalytical laboratory at the University of Otago.

Spiro[3,3]heptane-2,6-dispiro-4,5-diazafluorene (4). To a suspension of potassium metal (160 mg, 4.09 mmol) in THF (10 mL), under argon, was added compound 4,5-diazafluorene (**2**) (350 mg, 2.08 mmol), dissolved in THF (15 mL). This gave a purple solution that was stirred for one hour. Pentaerythrityl tetrabromide (205 mg, 0.53 mmol) was then added in THF (15 mL) and the solution refluxed overnight. After cooling, the solvent was removed *in vacuo* and water (20 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 50 mL), the extracts dried over magnesium sulfate and the solvent removed *in vacuo*. The residue was dissolved in dichloromethane, run through a silica gel plug to give a purple solid, from which a significant amount of insoluble material was removed by subsequent elution through an alumina plug. Recrystallisation from dichloromethane-ether gave **4** as colourless crystals. Yield 38 mg (18%). M.p. 165-166°C. HRMS: calc. for C₂₇H₂₀N₄ 400.1688, found 400.1693. ¹H NMR (CDCl₃ + 3 drops CD₃CN) δ 8.69 (d, 4H, H3'), 8.00 (d, 4H, H1'), 7.37 (dd, 4H, H2'), 3.11 (s, 8H, CH₂). ¹³C NMR (CDCl₃ + 3 drops CD₃CN) δ 156.7, 149.2, 145.6, 130.4, 123.2, 44.57, 42.18, 31.00.

X-Ray Crystallography. Data were collected with a Siemens SMART CCD area detector, using graphite monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The intensities were corrected for Lorentz and polarization effects and for absorption.¹³ The structure was solved by direct methods using SHELXS¹⁴ and refined on F², using all data, by full-matrix least-squares procedures using SHELXTL.¹⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions, with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbons. Table 1 lists the final atomic coordinates. Complete crystallographic data, as a CIF file, have been deposited with the Cambridge Crystallographic Data Centre (CCDC No 228156). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for 4: C₂₇H₂₀N₄, MW 400.47, orthorhombic, P2₁2₁2₁, $a = 10.232(4)$, $b = 10.284(3)$, $c = 19.020(7) \text{ \AA}$, $V = 2001.5(12) \text{ \AA}^3$, $Z = 4$, $T = -105^\circ\text{C}$, $F(000) = 840$, μ (MoK α) = 0.080 mm⁻¹, $D_{\text{calcd}} = 1.329 \text{ g.cm}^{-3}$, $2\theta_{\text{max}} = 53^\circ$ (CCD area detector, 99.7% completeness), $wR(F^2) = 0.0722$ (all 4072 data), $R = 0.0347$ (2931 data with $I > 2\sigma$).

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5069(2)	6977(2)	-1246(1)	36(1)
C(2)	5351(2)	6056(2)	-1870(1)	41(1)
C(3)	4588(2)	8019(2)	-1779(1)	41(1)
C(4)	4183(2)	6569(2)	-623(1)	39(1)
C(5)	6148(2)	7336(2)	-709(1)	38(1)
C(11)	7383(2)	8085(2)	-2637(1)	42(1)
C(12)	8206(2)	8570(2)	-3153(1)	49(1)
C(13)	7793(2)	8602(2)	-3845(1)	50(1)
N(14)	6625(1)	8163(1)	-4070(1)	42(1)
N(15)	3872(1)	7014(1)	-4255(1)	43(1)
C(16)	2681(2)	6454(2)	-4183(1)	48(1)
C(17)	2131(2)	6125(2)	-3550(1)	51(1)
C(18)	2798(2)	6344(2)	-2928(1)	47(1)
C(19)	5035(2)	7154(2)	-2416(1)	35(1)
C(20)	6164(2)	7669(2)	-2842(1)	33(1)
C(21)	5845(2)	7709(2)	-3563(1)	33(1)
C(22)	4516(2)	7177(2)	-3650(1)	34(1)
C(23)	4041(2)	6863(2)	-2978(1)	34(1)
C(31)	4243(2)	9607(2)	-75(1)	40(1)
C(32)	3817(2)	10594(2)	361(1)	47(1)
C(33)	3826(2)	10409(2)	1079(1)	47(1)
N(34)	4270(2)	9344(1)	1405(1)	44(1)
N(35)	5512(1)	6739(2)	1832(1)	44(1)
C(36)	6058(2)	5560(2)	1864(1)	48(1)
C(37)	6336(2)	4790(2)	1291(1)	50(1)
C(38)	6045(2)	5232(2)	615(1)	43(1)
C(39)	5147(2)	7224(2)	-86(1)	32(1)
C(40)	4676(2)	8481(2)	233(1)	33(1)
C(41)	4704(2)	8413(2)	974(1)	36(1)
C(42)	5275(2)	7159(2)	1176(1)	36(1)
C(43)	5523(2)	6454(2)	556(1)	34(1)

Acknowledgements

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Graphical Abstract

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