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Synthesis and characterisation of heterometallic molecular triangles using ambidentate linker: self-selection of a single linkage isomer†

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The coordination driven self-assembly of discrete molecular triangles from a non-symmetric ambidentate linker 5-pyrimidinecarboxylate (5-pmc) and Pd(II)/Pt(II) based 90° acceptors is presented. Despite the possibility of formation of a mixture of isomeric macrocycles (linkage isomers) due to different connectivity of the ambidentate linker, formation of a single and symmetrical linkage isomer in both the cases is an interesting observation. Moreover, the reported macrocycles represent the first example of discrete metallamacrocycles of bridging 5-pmc. While solution composition in both the cases was characterised by multinuclear NMR study and electrospray ionization mass spectrometry (ESI-MS), the identity of the assemblies in the solid state was established by X-ray single crystals structure analysis. Variable temperature NMR study clearly ruled out the formation of any other macrocycles by [4 + 4] or [2 + 2] self-assembly of the reacting components.

Introduction

The self-assembly of molecular building blocks into discrete 2- and 3-dimensional molecular architectures through a directional bonding approach has developed into a mature field in the recent past.^{1,2} The bottom-up synthetic strategy whereupon small molecular motifs self-assemble has led to highly symmetric supramolecular entities of various geometries. For instances, a wide array of two-dimensional systems, such as rhomboids, squares, rectangles, triangles, *etc.*, and three-dimensional systems, such as trigonal pyramids, trigonal prism, cubes, cuboctahedra, double squares, adamantanoids, dodecahedra and a variety of other cages are reported.³ Many of these ensembles are finding application in various areas such as host–guest chemistry,⁴ chemosensing⁵ and cavity controlled catalysis.⁶

For the design and synthesis of such assemblies of finite shapes and sizes, Pd(II) and Pt(II) have long been used as the acceptors of choice in view of their rigid square planar coordination. Nitrogen donor symmetrical polypyridyl ligands have been widely used in coordination driven self-assembly. Recently, oxygen donor carboxylates have also been used to design neutral architectures.^{1,2} Ambidentate linkers, however, have not been exploited much in self-assembly *via* a directional bonding approach. This is due to the fact that, the use of ambidentate linkers containing two different donor sites, in principle, should lead to thermodynamically controlled self-sorting of the components resulting in a number of linkage isomers which are difficult to separate.⁷ Chi *et al.*^{3a} have

recently shown that ambidentate donor ligands can be successfully utilized to synthesise dimeric assemblies in combination with a Pt(II) acceptor.

In a recent communication, we have reported the formation of a heterometallic molecular triangle using an ambidentate ligand and Pd(II) acceptor, where self selection leads to the formation of a single linkage isomer.⁸ We have now extended this methodology to another non-rigid angular ambidentate ligand, 5-pyrimidinecarboxylate (5-pmc) in conjunction with rigid *cis*-(dppf)Pd(OTf)₂ as well as *cis*-(dppf)Pt(OTf)₂ acceptor units [where dppf = 1,1'-bis(diphenylphosphino)ferrocene; OTf = trifluoromethanesulfonate (CF₃SO₃[−])]. The present paper reports two new heterometallic molecular triangles [(dppf)₃Pd₃L₃](OTf)₃ (**1a**) [where L = 5-pyrimidinecarboxylate anion] and [(dppf)₃Pt₃L₃](OTf)₃ (**1b**) synthesised *via* coordination driven self-assembly of 90° Pt(II) and Pd(II) acceptor with an ~100° ambidentate ditopic donor linker pyrimidinecarboxylate (5-pmc). The assemblies **1a** and **1b** represent the first examples of metallamacrocycles containing bridging 5-pmc ligand. Moreover, the self-selection of a single isomeric triangle in both the cases despite the possibility of formation of other isomers is a rare observation.

Experimental

Materials and methods

All chemicals used in this work were purchased from commercial sources and used without further purification. All solvents used were distilled by standard methods. The complexes *cis*-[(dppf)M(OTf)₂] (M = Pd, Pt)⁹ and 5-pyrimidinecarboxylic acid (5-pmcH)¹⁰ were prepared by following the reported procedures. The KBr phase IR spectra of the complexes were recorded in the range of 4500–400 cm^{−1} using a Perkin Elmer Lambda 35 spectrometer. ¹H and ³¹P NMR spectra were recorded in a Bruker 400 MHz spectrometer. ³¹P{H} chemical shifts are reported relative to an external, unlocked sample of H₃PO₄

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† Electronic supplementary information (ESI) available: Synthesis, spectral characterisation of the starting acceptors and variable temperature NMR spectra of **1b**. CCDC reference numbers 715345 & 715346. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b900118b

($\delta = 0.0$ ppm) while ^1H NMR chemical shifts are referenced to TMS. Electrospray ionization mass (ESI-MS) measurements were made using a Bruker Daltonics (Esquire 300 Plus ESI model) spectrometer. Elemental analyses were performed using a Perkin-Elmer CHN analyzer.

Synthesis

[(dppf)₃Pd₃L₃](OTf)₃ (1a**).** To 1 mL methanolic solution of the sodium salt of 5-pyrimidinecarboxylic acid (12.2 mg, 0.084 mmol) was added a deep blue 1 mL methanolic solution of *cis*-(dppf)Pd(OTf)₂ (80.0 mg, 0.084 mmol). The mixture was stirred at room temperature for 2 hours and then at 45–50 °C for another 3 hours. A small amount of deep red precipitate was formed during this period. The reaction mixture was cooled down to room temperature and filtered. The supernatant was concentrated under vacuum following which cold diethyl ether was added to precipitate out **1a** as a deep red solid. The solid was dried under vacuum to yield a red powder. Yield: 54.0 mg (70%). The X-ray quality crystals were obtained by slow diffusion of diethyl ether into a nitromethane solution of the solid. The dried sample was analyzed as **1a**. Anal. Calcd. (Found), % for C₁₂₀H₉₃F₉Fe₃N₆O₁₅P₆Pd₃S₃: C, 51.50 (51.25); N, 3.00 (3.05); H 3.35 (3.20). ^{31}P NMR (CD₃OD, 121.4 MHz, ppm): 39.71, 32.49. ^1H NMR (CD₃OD; 400 MHz): δ (ppm) = 9.75 (s, 3H, 5-pmc); 9.53 (s, 3H, 5-pmc); 8.10 (s, 3H, 5-pmc); 8.42–6.77 (m, 60H, Ph); 5.12–3.2 (s, 24H, cp).

[(dppf)₃Pt₃L₃](OTf)₃ (1b**).** Synthesis of **1b** was accomplished by following analogous procedures to **1a**, but replacing *cis*-Pd(dppf)(OTf)₂ with *cis*-Pt(dppf)(OTf)₂ (88.0 mg, 0.084 mmol). The complex was isolated as a yellow solid by adding diethyl ether into the reaction mixture at room temperature. Yield: 63.0 mg (75%). The dried sample was analyzed as **1b**. Anal. Calcd. (Found), % for C₁₂₀H₉₃F₉Fe₃N₆O₁₅P₆Pt₃S₃: C, 47.03 (47.21); N, 2.74 (2.65); H 3.06 (3.01). ^{31}P NMR (CD₃OD, 121.4 MHz, ppm): 8.05, 2.64 (s). ^1H NMR (CD₃OD; 400 MHz): δ (ppm) = 9.87 (s, 3H, 5-pmc); 9.60 (s, 3H, 5-pmc); 8.12 (s, 3H, 5-pmc); 8.37–6.70 (m, 60H, Ph); 4.91–3.47 (s, 24H, cp).

X-ray crystallographic studies

Suitable single crystals of **1a** and **1b** were obtained by slow diffusion of diethyl ether into the nitromethane solution of the respective complexes. The diffraction data were collected with synchrotron radiation ($\lambda = 0.79999$ Å for **1a** and 0.69998 Å for **1b**) at the wiggler beamline 4A, Pohang Accelerator Laboratory. This multipole wiggler has 28 magnet poles with 2.02 Tesla and its periodic length and gap size are 14 cm and 14 mm, respectively. A fast speed CCD is installed for multi-wavelength

anomalous diffraction (MAD) experiments in the energy range of 6–18 keV. The *SADABS*¹¹ program was used for empirical absorption correction. The structures were solved by direct methods (*SHELXS-97*) and standard Fourier techniques, and refined on F^2 using full matrix least squares procedures (*SHELXL-97*) using the *SHELX-97* package¹² incorporated in *WinGX*.¹³ Structural illustrations were drawn using *POV-Ray*. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to either 1.5 (methyl hydrogen atoms) or 1.2 (all other hydrogen atoms) times the thermal parameter of the carbon atoms to which they were attached. A similar routine was adopted to refine the crystal structure of **1b**. To account for the unresolved solvent in the complexes **1a** and **1b**, the *SQUEEZE* program of *PLATON*¹⁴ was used. In **1a**, a void volume of 11670.1 Å³ was calculated to contain 2333 electrons per unit cell, or 18 molecules of nitromethane (solvent for crystallization) per molecular unit. For complex **1b**, it found a void volume of 1550.6 Å³ and 302 electrons per unit cell which translates to 5 nitromethane molecules per molecular unit.

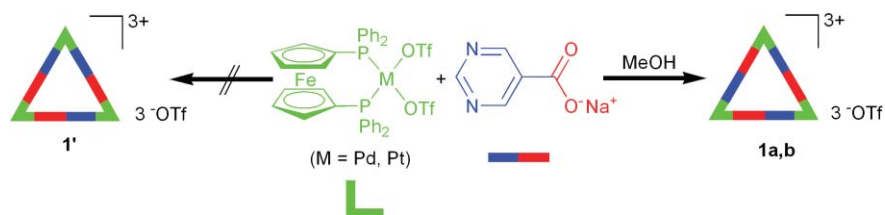
Results and discussions

Synthesis and characterisation

The cationic triangles, [(dppf)₃Pd₃L₃](OTf)₃ (**1a**) and [(dppf)₃Pt₃L₃](OTf)₃ (**1b**) were synthesized using 90° Pt(II)/Pd(II) acceptor in combination with an ~100° ambidentate ditopic donor linker 5-pyrimidinecarboxylate (Scheme 1).

When *cis*-(dppf)Pd(OTf)₂ was treated with one equivalent of sodium pyrimidinecarboxylate in methanol at 50 °C for 5 hours, molecular triangle **1a** was obtained as the exclusive product, while treatment of *cis*-(dppf)Pt(OTf)₂ with one equivalent of sodium pyrimidinecarboxylate under similar conditions led to the formation of molecular triangle **1b** as the only product. An immediate sharp change in color of *cis*-(dppf)Pd(OTf)₂ in methanol from deep blue to deep red upon addition of it into a colorless methanolic solution of sodium pyrimidinecarboxylate and finally the appearance of red precipitate are indications of the progress of the reaction for the formation of **1a**. Similar observations were also noticed in the case of **1b**.

Infra-red spectroscopic analysis of the complexes **1a,b** primarily indicate coordination of 5-pyrimidinecarboxylate (5-pmc) with nitrogen and carboxylate oxygen to the metal centres.¹⁵ The main IR group frequencies of the molecular triangles **1a,b** and 5-pmc are summarized in the Table 1. The strong broad $\nu(\text{C}=\text{O})$ band of 5-pmc assumed sharp strong peaks in the complexes with a wave number difference of around 25 cm⁻¹ (Fig. 1). Considerable shifts in the C=N stretching frequencies from $\nu(\text{C}=\text{N}) = 1380$ cm⁻¹ of

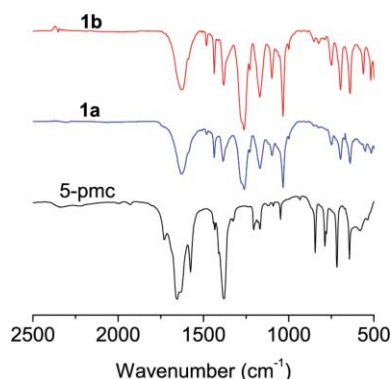


Scheme 1

Table 1 IR spectral data (cm⁻¹) of 5-pmc and **1a,b**

Compound	$\nu(\text{C}(7)=\text{O}(2))$	$\nu(\text{N}(1)=\text{C})$	$\nu(\text{N}(2)=\text{C})$
5-pmc	1653, 1631sb	1380s	1380s
Complex 1a	1627s	1261s	1385m
Complex 1b	1626s	1262s	1381m

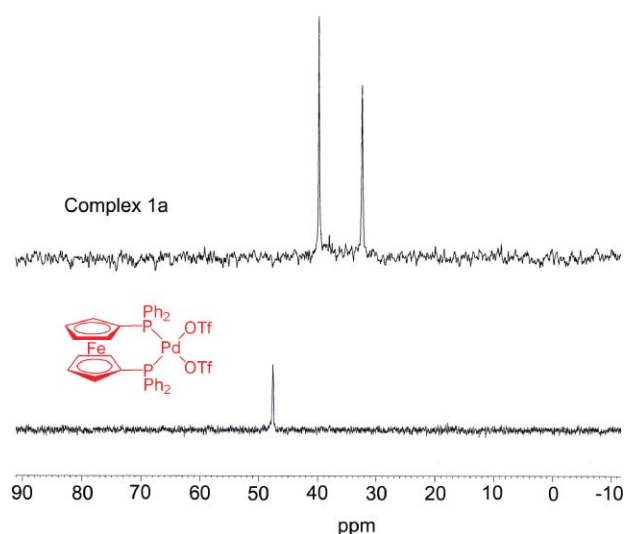
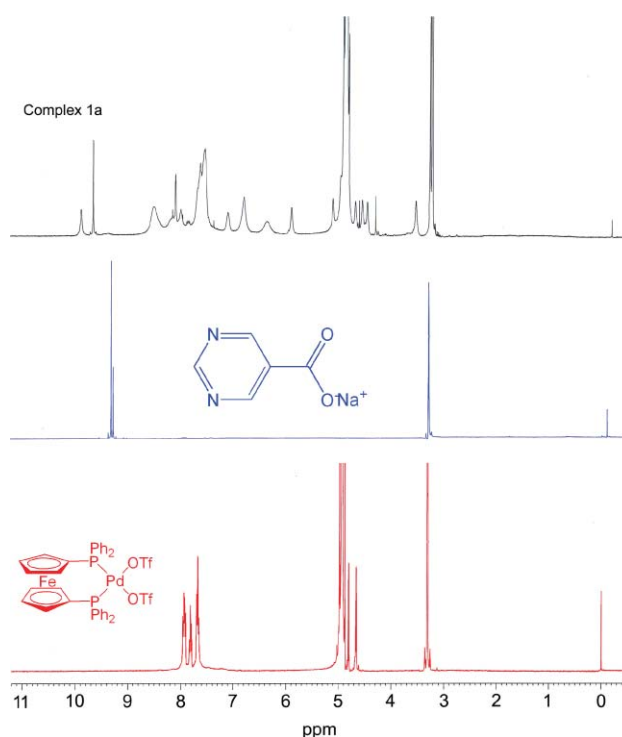
(S = strong, m = medium, b = broad)

**Fig. 1** KBr phase IR spectra of 5-pmc, **1a** and **1b**.

5-pmc to 1385, 1261 cm⁻¹ of complex **1a** and 1626, 1262 cm⁻¹ of **1b** is a clear indication of coordination of 5-pyrimidinecarboxylate-N to metal centres.

In principle, due to different bonding connectivity of the ambidentate ligand, self-assembly of the *cis*-blocked 90° acceptor with a linear ambidentate ligand should yield two linkage isomeric triangles (Scheme 1). Multinuclear NMR (³¹P and ¹H) spectroscopy is a handy tool to discriminate these molecular triangles. From Scheme 1, it is clear that in isomer **1**, all the metal centres (Pd/Pt) are identical but their coordinative chemical environment is different. Hence, due to two magnetically non-equivalent phosphorus nuclei, two peaks of equal intensity are expected in the ³¹P NMR spectra. But, in the case of isomer **1'** four such peaks of intensity ratios 1:1:2:2 are expected in the ³¹P NMR spectra.

³¹P NMR spectra (Fig. 2) of complex **1a** showed two peaks at 39.7 and 32.5 ppm. An upfield shift of 7 and 14 ppm with respect to *cis*-(dppf)Pd(OTf)₂ which appears at 46.3 ppm is indicative of ligand to metal coordination. The peak at 32.5 ppm corresponds to the phosphorus *trans* to the coordinated nitrogen, while the peak at 39.7 ppm is due to the phosphorus *trans* to the coordinated oxygen. As a Pd–O(OTf) bond is replaced by an another Pd–O(carboxylate) bond, less upfield shift (7 ppm) of the phosphorus peak is expected compared to the peak originating from the phosphorus *trans* to the coordinated nitrogen of 5-pmc. The fact that only two phosphorus peaks were observed showed the exclusive formation of a single linkage isomer **1a**. The ¹H NMR spectrum of **1a** was also indicative of the formation of a single linkage isomer and displayed significant spectroscopic differences from the precursor building block (Fig. 3). Large downfield shifts of the pyrimidyl protons ($\Delta\delta = 0.7$ ppm and 0.2 ppm for α and γ to carboxylate group, respectively) showed the coordination of the pyrimidyl moiety to the *cis*-Pd(dppf)²⁺ unit. Also, in complex **1b** complexation-induced shift of the ³¹P peaks to higher field is observed. The two phosphorus peaks were observed at 8.05

**Fig. 2** ³¹P NMR spectrum of **1a** and *cis*-(dppf)Pd(OTf)₂ in CD₃OD.**Fig. 3** ¹H NMR (400 MHz, CD₃OD, 293 K) spectrum of **1a**, Sodium 5-pyrimidine carboxylate and *cis*-(dppf)Pd(OTf)₂.

and 2.64 ppm with concomitant ¹⁹⁵Pt satellites. The significant difference in the ¹⁹⁵Pt–P coupling constants (¹J_{Pt-P} = 2762 Hz and 2610 Hz) of the complex **1b** from the precursor *cis*-(dppf)Pt(OTf)₂ (¹J_{Pt-P} = 3065 Hz) is a reliable indication of the coordination of the N- and O-donor sites to the metal centre (see ESI†). The ¹H NMR spectrum of **1b** also shows a small but significant chemical shift.

The [3 + 3] self-assembly of *cis*-blocked square planar metal complexes with non-rigid linear bidentate ligands leads to the formation of square and/or triangle with metal centres on the corners with ligands on the edges.^{16,17} The propensity to form one assembly over the other is guided by the entropy and enthalpy of

the reaction. For a linear rigid bidentate ligand, entropy favors the formation of a triangle while enthalpy favors the formation of a square because there is less ring strain. However, where the ligand is non-rigid, triangles become the major component in the square–triangle equilibrium by reducing the strain by allowing the ligand to bend. In the present study, the angle ($\sim 100^\circ$) between the two asymmetric donor sites in the 5-pyrimidine carboxylate ligand favours the exclusive formation of triangles over squares since it reduces the ring strain. Variable temperature ^{31}P NMR study for the complexes **1a** (Fig. 4) and **1b** (see ESI†) indeed showed that the triangle is the only product in both the cases as evident by the absence of peaks due to any other by-product. The steric bulkiness of the dppf ligand is also a driving force for the preferential formation of the triangle.

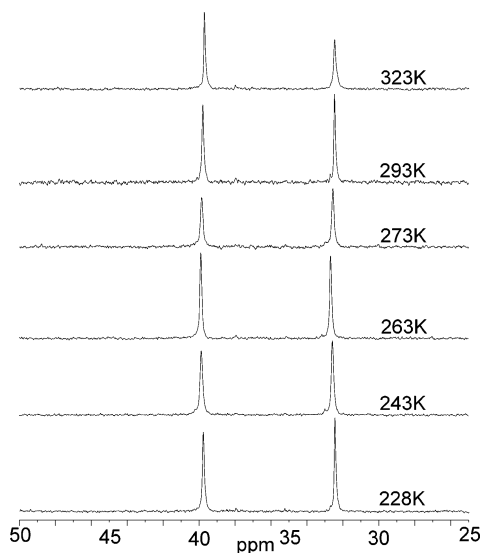


Fig. 4 Variable temperature ^{31}P NMR spectra of **1a** in CD_3OD .

ESI-MS analyses for the complexes **1a** and **1b** (Fig. 5) supports the formation of these complexes by the appearance of a series of prominent peaks for $[\mathbf{1a/b}-(\text{OTf})_n]^{n+}$. For the complex **1a**, peaks at m/z values of 1249.02, 742.0, 783.03 and 695.0 were assigned to $[\mathbf{1a}-2\text{OTf}]^{2+}/2$, $[\mathbf{1a}-3\text{OTf}]^{3+}/3$, $[\mathbf{1a}-2\text{OTf}-\text{C}_5\text{H}_3\text{O}_2\text{N}_2]^{3+}/3$ and $[\mathbf{1a}-2\text{OTf}-2(\text{dppf})]^{2+}/2$ respectively, and for the complex **1b** the prominent peaks at m/z values 872.09, 1806.07, 1105.6

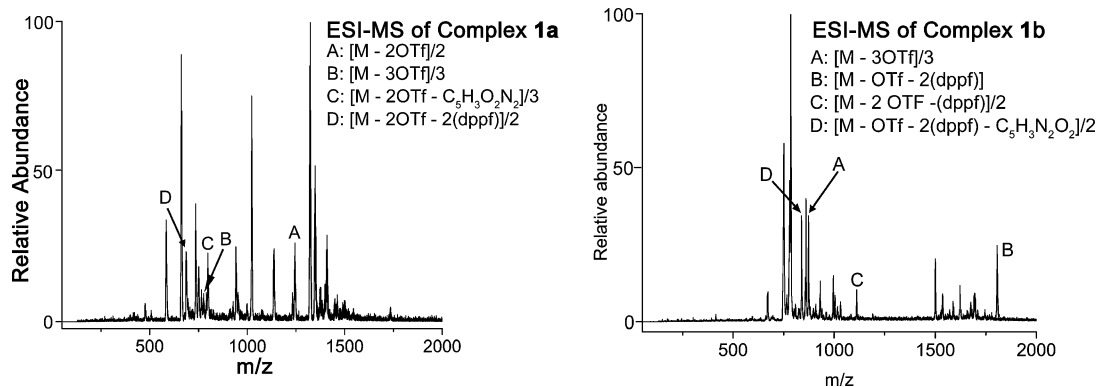


Fig. 5 ESI-MS spectra of **1a** (left) and **1b** (right).

Table 2 Crystallographic data and refinement parameters for **1a**· 18MeNO_2 and **1b**· 5MeNO_2

	1a	1b
Formula ^a	$\text{C}_{138}\text{H}_{150}\text{F}_9\text{Fe}_3\text{N}_{24}$ $\text{O}_{51}\text{P}_6\text{Pd}_3\text{S}_3$	$\text{C}_{125}\text{H}_{108}\text{F}_9\text{Fe}_3$ $\text{N}_{11}\text{O}_{25}\text{P}_6\text{Pt}_3\text{S}_3$
fw, g mol ^{-1a}	3900.62	3370.02
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
<i>T</i> , K	150	150
<i>a</i> , Å	20.528(4)	18.580(4)
<i>b</i> , Å	28.904(6)	18.840(4)
<i>c</i> , Å	53.724(11)	22.725(5)
α , deg	90	84.91(3)
β , deg	94.51(3)	75.09(3)
γ , deg	90	60.48(3)
<i>V</i> , Å ³	31778(11)	6682(2)
<i>Z</i>	4	2
ρ_{calcd} , g cm ⁻³	1.180	1.523
μ , mm ⁻¹	6.273	3.635
collected reflns	37435	38395
unique reflns	19454	25610
<i>R</i> _{int}	0.0202	0.0168
Final <i>R</i> 1 ^b , <i>wR</i> 2 ^c (<i>I</i> ≥ 2σ)	0.0977, 0.2742	0.0325, 0.0930
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1008, 0.2787	0.0331, 0.0936
GOF on <i>F</i> ²	1.093	1.038

^a Including solvate molecules. ^b $R1 = \sum \|F_o| - |F_c|\| / \sum |F_o|$. ^c $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ where $w = 1 / [\sum^2(F_o^2) + (aP)^2 + bP]$ with P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

and 841.58 correspond to $[\mathbf{1b}-3\text{OTf}]^{3+}/3$, $[\mathbf{1b}-\text{OTf}-2(\text{dppf})]^{1+}$, $[\mathbf{1b}-2\text{OTf}-\text{dppf}]^{2+}/2$ and $[\mathbf{1b}-\text{OTf}-2(\text{dppf})-\text{pmc}]^{2+}/2$, respectively.

Description of crystal structures

The molecular structures of **1a** and **1b** based on single crystal X-ray diffraction studies are shown in Fig. 6. Crystallographic data and refinement parameters are presented in Table 2. Selected bond distances and angles for complexes **1a** and **1b** are summarized in Table 3. While the complex **1a** crystallizes in the monoclinic $P2_1/c$ space group with two formula units included in the asymmetric unit, complex **1b** crystallizes in the triclinic $P\bar{1}$ space group having one formula unit in the asymmetric unit.

Each heterometallic molecular triangle consists of three Pd(II) or Pt(II) present at the vertices of an approximate triangle with three 5-pmc ligand bridging the metal centres in end-to-end fashion through pyrimidyl-N on one end and carboxylate-O on the

Table 3 Selected bond distances (Å) and angles for **1a**·18MeNO₂ and **1b**·5MeNO₂**Complex 1a**

Pd(1)–N(1)	2.085(13)	Pd(1)–O(1)	2.087(11)	Pd(1)–P(1)	2.251(5)
Pd(1)–P(2)	2.313(5)	Pd(2)–N(3)	2.086(12)	Pd(2)–O(3)	2.095(10)
Pd(2)–P(3)	2.253(4)	Pd(2)–P(4)	2.299(4)	Pd(3)–O(5)	2.042(11)
Pd(3)–N(5)	2.129(14)	Pd(3)–P(6)	2.260(5)	Pd(3)–P(5)	2.301(4)
Pd(4)–O(7)	2.069(11)	Pd(4)–N(7)	2.071(15)	Pd(4)–P(8)	2.237(5)
Pd(4)–P(7)	2.308(5)	Pd(5)–O(9)	2.072(11)	Pd(5)–N(9)	2.144(12)
Pd(5)–P(10)	2.257(4)	Pd(5)–P(9)	2.290(4)	Pd(6)–O(11)	2.062(11)
Pd(6)–N(11)	2.126(12)	Pd(6)–P(12)	2.262(5)	Pd(6)–P(11)	2.273(4)
N(1)–Pd(1)–O(1)	86.8(4)			N(1)–Pd(1)–P(1)	89.3(3)
O(1)–Pd(1)–P(1)	171.6(3)			N(1)–Pd(1)–P(2)	171.5(4)
O(1)–Pd(1)–P(2)	88.3(3)			P(1)–Pd(1)–P(2)	96.4(2)
N(3)–Pd(2)–O(3)	86.8(4)			N(3)–Pd(2)–P(3)	91.3(3)
O(3)–Pd(2)–P(3)	172.9(3)			N(3)–Pd(2)–P(4)	169.3(4)
O(3)–Pd(2)–P(4)	87.0(3)			P(3)–Pd(2)–P(4)	95.83(16)
O(5)–Pd(3)–N(5)	88.6(4)			O(5)–Pd(3)–P(6)	170.3(3)
N(5)–Pd(3)–P(6)	90.3(3)			O(5)–Pd(3)–P(5)	86.2(3)
N(5)–Pd(3)–P(5)	172.1(4)			P(6)–Pd(3)–P(5)	95.83(16)
O(7)–Pd(4)–N(7)	87.4(5)			O(7)–Pd(4)–P(8)	171.6(3)
N(7)–Pd(4)–P(8)	90.5(4)			O(7)–Pd(4)–P(7)	86.7(3)
N(7)–Pd(4)–P(7)	169.5(5)			P(8)–Pd(4)–P(7)	96.49(17)
O(9)–Pd(5)–N(9)	86.0(4)			O(9)–Pd(5)–P(10)	168.9(3)
N(9)–Pd(5)–P(10)	92.0(3)			O(9)–Pd(5)–P(9)	88.6(3)
N(9)–Pd(5)–P(9)	169.3(4)			P(10)–Pd(5)–P(9)	95.07(15)
O(11)–Pd(6)–N(11)	86.0(4)			O(11)–Pd(6)–P(12)	168.8(3)
N(11)–Pd(6)–P(12)	92.1(3)			O(11)–Pd(6)–P(11)	87.7(3)
N(11)–Pd(6)–P(11)	166.0(4)			P(12)–Pd(6)–P(11)	96.51(16)

Complex 1b

Pt(1)–O(1)	2.057(2)	Pt(1)–N(1)	2.098(3)	Pt(1)–P(1)	2.2350(11)
Pt(1)–P(2)	2.2588(11)	Pt(2)–O(3)	2.084(2)	Pt(2)–N(3)	2.089(3)
Pt(2)–P(3)	2.2433(10)	Pt(2)–P(4)	2.2938(11)	Pt(3)–O(5)	2.077(2)
Pt(3)–N(5)	2.092(3)	Pt(3)–P(6)	2.2392(10)	Pt(3)–P(5)	2.2716(10)
O(1)–Pt(1)–N(1)	85.36(11)			O(1)–Pt(1)–P(1)	169.86(7)
N(1)–Pt(1)–P(1)	92.57(9)			O(1)–Pt(1)–P(2)	85.34(9)
N(1)–Pt(1)–P(2)	167.01(9)			P(1)–Pt(1)–P(2)	98.14(4)
O(3)–Pt(2)–N(3)	84.23(10)			O(3)–Pt(2)–P(3)	174.13(7)
N(3)–Pt(2)–P(3)	91.16(8)			O(3)–Pt(2)–P(4)	87.77(7)
N(3)–Pt(2)–P(4)	169.94(8)			P(3)–Pt(2)–P(4)	97.18(4)
O(5)–Pt(3)–N(5)	86.26(10)			O(5)–Pt(3)–P(6)	169.41(7)
N(5)–Pt(3)–P(6)	92.80(8)			O(5)–Pt(3)–P(5)	83.60(7)
N(5)–Pt(3)–P(5)	163.81(7)			P(6)–Pt(3)–P(5)	99.45(4)

other. The ferrocenyl moieties occupy the most outlying sites on the partially distorted square planar Pd(II)/Pt(II) centres. Within the triangle, each metal (Pd or Pt) atom is coordinated to two phosphorus atoms from dppf, an oxygen atom and a nitrogen atom from two different pyrimidine ligands, completing the distorted square planar geometry around the metal centre.

The average interatomic bond distances around the Pd(II) ion in **1a** are typical, with Pd–O and Pd–N bond distances of 2.069 and 2.098 Å, respectively while the average Pd–P distances are 2.277 Å. The O–Pd–N bite angles lies within the range of 86.0(4)° to 88.6(4)° indicating a slight distortion from the ideal 90° angle expected for an ideal square planar system. The average Pd...Pd distance of 7.480 Å measures the cavity of the triangle and compares well with our earlier⁸ Pd₃Fe₃ triangle.

In **1b**, the plane made by the three non-coordinated N atoms of the pyrimidine rings makes a dihedral angle of 1.15° with the plane containing the three platinum metal centres. Moreover, the plane consisting of three iron metals in the ferrocene moieties makes a dihedral angle of 1.93° with the platinum containing

plane. One of the nitrogen atoms of the pyrimidine rings remains uncoordinated in both the molecules **1a** and **1b**. Interestingly, these free nitrogen atoms are disposed towards one side of the molecule. Thus, these molecular triangles themselves can now act as tritopic donor ligands towards the formation of more complex 3D supramolecular self-assemblies. The packing diagrams (Fig. 7) of the triangles **1a** and **1b** in solid state show that one of the counter anions occupies the cavity of the triangles.

Absorption spectroscopic analysis

UV-vis spectral analysis also supports the complex formations. The molar extinction coefficient (ϵ) of the deep-red coloured molecular triangle, **1a**, is $\sim 3.8 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$, at $\lambda_{\text{max}} = 502 \text{ nm}$ is almost six times larger than the starting linker [Pd(dppf)(OTf)₂]. In the characteristic spectra (Fig. 8) of Pd(dppf)(OTf)₂ recorded in CHCl₃, three bands appeared near λ_{max} 300 nm, 375 nm and 530 nm. The first one is owing to the LCMT band originating from charge transfer from the ferrocenyl ring to the Fe metal

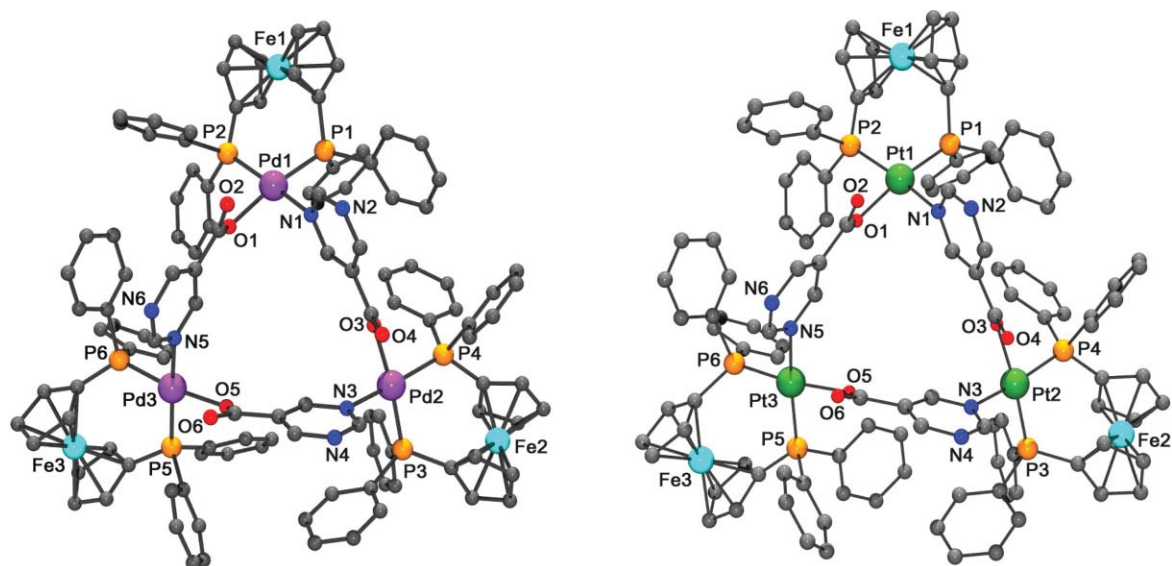


Fig. 6 Molecular structures of **1a** (left) and **1b** (right) in a ball and stick model with atom numbering scheme. Hydrogen atoms are omitted for clarity. Colour code: Pd, violet; Pt, green; Fe, cyan; P, golden; N, blue; O, red; C, gray.

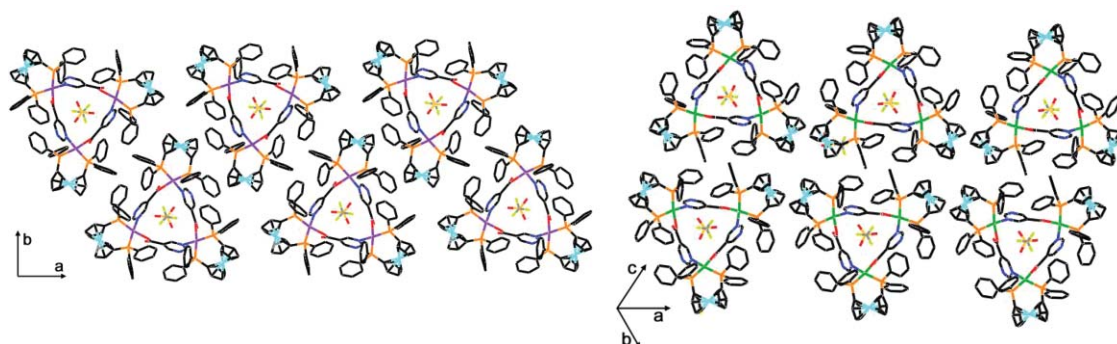


Fig. 7 Packing diagrams for **1a** (left) and **1b** (right). Colour code: Pd, violet; Pt, green; Fe, cyan; P, gold; N, blue; O, red; C, black.

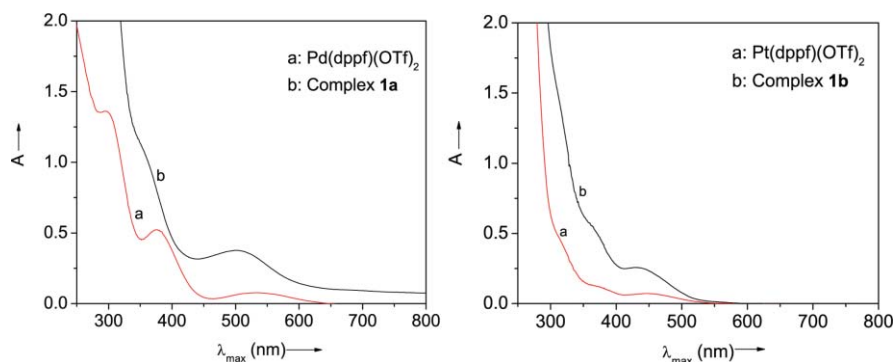


Fig. 8 UV-vis spectra of Pd(dppf)(OTf)_2 , molecular triangle **1a** (left) and Pt(dppf)(OTf)_2 , molecular triangle **1b** (right).

centre.⁸ The second and third bands are because of electronic d–d transitions in the Fe centre. The new band of extremely high absorbance appearing near λ_{max} (300 nm) is mainly because of π – π^* transitions originating from bridging pyrimidine carboxylate ligands. Considerable blue shifts of d–d bands in triangle **1a**, to near λ_{max} 500 nm and 350 nm from 530 nm and 375 nm in the starting linker indicate strong-field coordination of the nitrogen lone pair of the pyrimidine ring to the metal centre. Similar

spectral characteristics (Fig. 8) are also observed in the case of Pt(dppf)(OTf)_2 and triangle **1b**.

Conclusions

In conclusion, we have prepared two new discrete heterometallic triangles $[(\text{dppf})_3\text{Pd}_3\text{L}_3](\text{OTf})_3$ (**1a**) and $[(\text{dppf})_3\text{Pt}_3\text{L}_3](\text{OTf})_3$ (**1b**) by the directional self-assembly reaction of a $\sim 100^\circ$ ambidentate

linker 5-pyrimidinecarboxylate with *cis*-(dppf)Pd(OTf)₂ and *cis*-(dppf)Pt(OTf)₂, respectively. Despite the possibility of formation of a mixture of linkage isomers due to the different connectivity of the ambidentate donor, the selective formation of a single symmetrical isomeric triangle in both cases is an important observation. The triangles **1a** and **1b** represent the first examples of discrete metallamacrocycles containing 5-pyrimidinecarboxylate as the bridging ligand. While, due to the flexible nature of the ambidentate ligand other self-assembled [2 + 2] dimeric or [4 + 4] tetrameric macrocycles are expected to form, variable temperature NMR study along with ESI-MS analysis established the formation of the triangle as the sole product in the solution phase as well. Formation of three identical metal centres [Pd(II)/Pt(II)] in both cases implies that the equal electron density around the metal centres is a guiding factor for the formation of a symmetrical triangle.

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Synthesis and characterisation of heterometallic molecular triangles using ambidentate linker: self-selection of a single linkage isomer

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