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Flexible dinucleating *N*,*N*,*N*-tridentate ligands based on a xanthene scaffold

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ABSTRACT

A versatile route to flexible ditopic ligands based on a 2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene scaffold, namely Williamson ether synthesis employing the 4,5-bis(chloromethyl) derivative of the xanthene and a phenol-substituted ligand donor, is demonstrated by the preparations of bis(terpyridine)xanthene L^1 and the bis(di(2-pyridylmethyl)amine)xanthene L^2 in good yields. The reaction of L^1 with $[Pd(PhCN)_2Cl_2]$ afforded the coordination complexes $[L^1(PdCl)_2][PF_6]_2$ (**4**$[PF_6]_2$) and $[L^1(PdCl)][PF_6]$ (**5**$[PF_6]$). The X-ray crystal structures of L^1 and **5**$[PF_6]$·solvate were determined and reveal intra- and intermolecular offset face-to-face stacking between terpyridine rings and intramolecular C–H…π-phenyl ring interactions. Variable temperature ^{1}H NMR studies show temperature-dependent chemical shift changes suggestive for face-to-face interactions between the terpyridines in **4**$[PF_6]_2$ and of **5**$[PF_6]$ being sustained in solution.

1. Introduction

In this paper we report a straightforward route to flexible ditopic ligands with terpyridine (L^1) or di(2-pyridylmethyl)amine (L^2) metal-binding domains spanned by a xanthene bridge, and the syntheses and characterisation of palladium chloride complexes of L^1.

As part of ongoing research into the emergent properties resulting from synergistic interactions between two metal centres in bimetallic complexes [1], we sought a simple route to flexible ditopic ligands constructed from a spacer proximally connecting two ligand donor domains. We required: (1) the synthetic methodology to be short with good yields and the versatility to allow introduction of different ligand donor domains. (2) The new ditopic ligands to be soluble, easily handled and to be sufficiently flexible to allow the interactions between the proximate metal centres in their metal complexes to optimize in response to changing conditions such as the charge or co-ligands on one or both metal centres. Therefore we developed, and report herein, a short route to flexible dinucleating ligands based on Rebek's 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene scaffold [2]. Rebek's xanthene bridge was chosen for its ease of synthesis and derivatisation, and for the solubility and ease of handling it confers on its more complicated derivatives [3].

The xanthene-bridged ligands described in this paper add to the large and growing number of ditopic bis(ligand domain)-spacer systems in the literature [3–9]. In bis(terpyridine)-spacer systems [3i,4,5], typically the two terpyridyl groups are separated by linear spacers such as phenyl, biphenyl or bis(imide) derivatives; *e.g.* L^{a-c}, Fig. 1. Ditopic ligands with proximal terpyridyl groups are more rare and include examples with angular and U-shaped geometries provided by more complex spacer scaffolds; *e.g.* L^{d-h}, Fig. 1. Terpyridines such as those in Fig. 1 and their metal complexes have application in a vast variety of fields including catalysis, sensors, supramolecular chemistry and material science. For instance, square-planar terpyridine–platinum(II) complexes have been extensively exploited for their characteristic photophysical properties in molecular sensors and switches and, as well, they are DNA intercalators [5a]. Although fewer studies of analogous palladium(II) complexes have been reported, the complexes which are analogous to those reported herein have shown remarkable molecular recognition abilities [5a]. Metal complexes of bis(dipicolinylamine)-spacer systems are increasingly studied, including as artificial phosphatases [7], as phosphoprotein recognition and inhibitor systems [8], and as fluorescent or electrochemical sensors for various biologically-relevant cations and anions [9].

2. Experimental

2.1. General procedures

Phenol-derivatized **1** [2b,3b,10] and **2** [11] (see Scheme 1), and $[Pd(PhCN)_2Cl_2]$ [12] were synthesized as described in the literature. Acetonitrile and methanol were taken from an Innovative Technology Pure Solvent Dispenser prior to use. All other reagents are commercially available and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300, Bruker Avance

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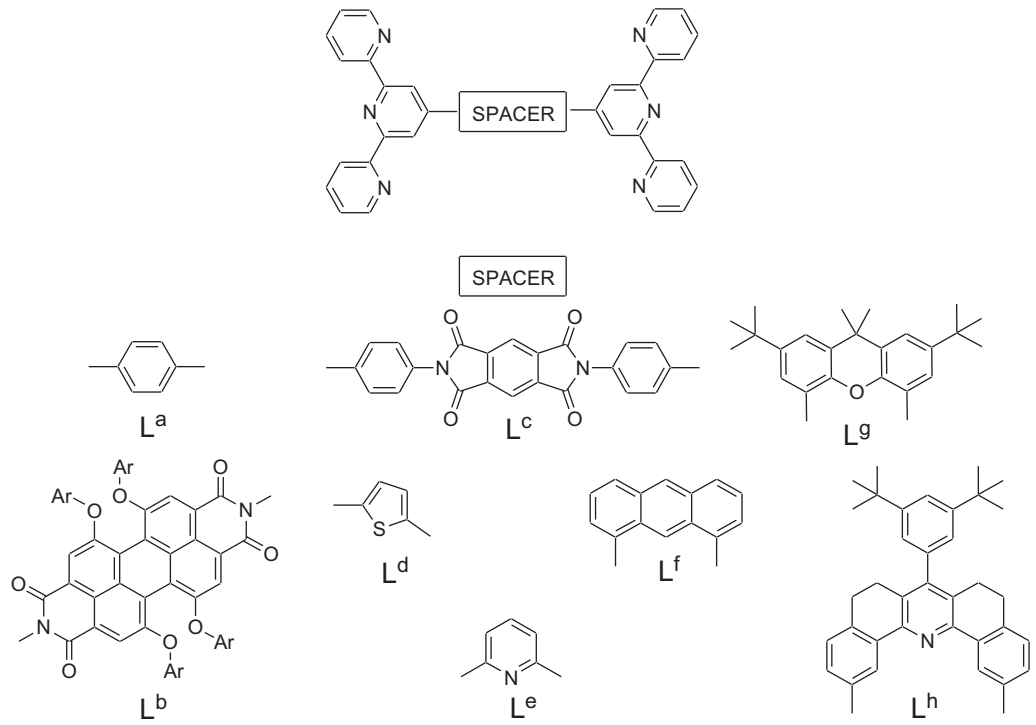
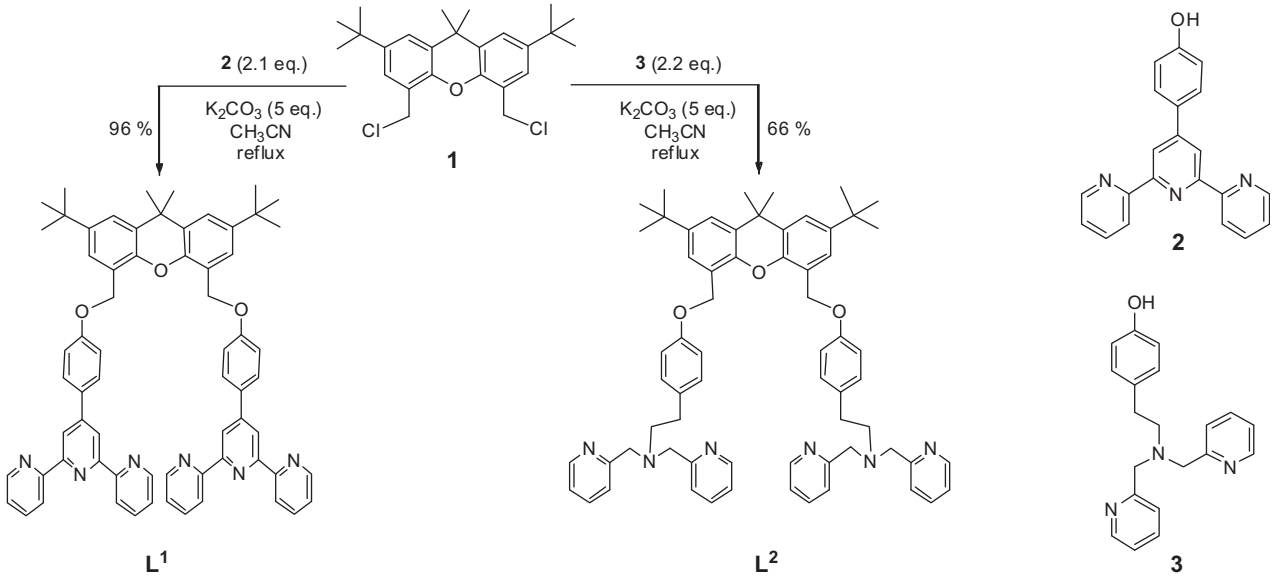


Fig. 1. Examples of bis(terpyridine) ligands described in the literature.



Scheme 1. Syntheses of dinucleating ligands L^1 and L^2.

III 500 or Bruker Avance III 600 spectrometers. High-resolution positive-mode ESI mass spectra were acquired in an Orbitrap Velos XL mass spectrometer in the Bioanalytical Mass Spectrometry Facility of the University of New South Wales.

2.2. Synthesis of L^1

A mixture of the bis(chloromethyl)xanthene **1** (220 mg, 0.52 mmol), the 4-terpyridylphenol **2** (359 mg, 1.10 mmol) and potassium carbonate (0.73 g, 5.32 mmol) in dry acetonitrile (18 mL) was heated to reflux for 3 days. The mixture was cooled to room temperature and the solvent removed under vacuum. The product was extracted into dichloromethane (20 mL) and washed with water (3 x 30 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent removed to give L^1 as a white solid (503 mg, 0.50 mmol, 96%).

L^1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (4H, ddd, J = 4.8, 1.8 and 0.8 Hz, py), 8.43 (4H, s, py), 8.35 (4H, dt, J = 7.8 and 1.1 Hz, py), 7.71–7.65 (8H, m, py), 7.47 (2H, d, J = 2.3 Hz, Ph–xanthene), 7.40 (2H, d, J = 2.3 Hz, Ph–xanthene), 7.14 (4H, ddd, J = 7.3, 4.8 and

1.1 Hz, py), 6.92 (4H, d, J = 8.9 Hz, Ph), 5.14 (4H, s, –O–CH_2), 1.72 (6H, s, CH_3), 1.37 (18H, s, ^{t}Bu). ^{13}C{H} NMR (150.9 MHz, $CDCl_3$): δ = 160.2, 156.4, 155.5, 149.5, 149.0 (CH, py), 146.6, 145.8, 136.6 (CH, py), 130.9, 129.8, 128.8 (CH, Ph), 125.3 (CH, Ph–xanthene), 123.6 (CH, py), 123.3 (CH, Ph–xanthene), 123.2, 121.3 (CH, py), 118.1 (CH, py), 115.0 (CH, Ph), 66.2 (O–CH_2), 35.0, 34.9, 32.8 (CH_3), 31.9 (^{t}Bu). (+)-HR-ESI-MS Calcd. for $[M+H]^+$ ($[C_{67}H_{60}N_6O_3]^+$): m/z 997.4710. Found: m/z 997.4777.

2.3. Synthesis of 4-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)phenol, 3

Under a nitrogen atmosphere, a solution of tyramine (0.549 g, 4.00 mmol) and 2-pyridinecarboxaldehyde (0.857 g, 8.00 mmol) in methanol (100 mL) was cooled using an ice bath. To this solution glacial acetic acid (0.83 mL, 14.8 mmol) followed by a solution of sodium cyanoborohydride (0.593 g, 9.43 mmol) in methanol (20 mL) were added. The resulting mixture was stirred at room temperature for four days, cooled in an ice bath and hydrochloric acid 5 M added until pH 5 was reached. After stirring for 30 min, a sodium bicarbonate aqueous solution was added until no further gas evolved. The mixture was extracted with dichloromethane, dried over sodium sulfate and the solvent was removed under vacuum to give an oily residue, which was purified by flash chromatography through silica using dichloromethane/methanol 9:1. Compound **3** was isolated as a brown oil (1.14 g, 3.57 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (2H, d, J = 5.0 Hz, py), 7.61 (2H, t, J = 7.7 Hz, py), 7.41 (2H, d, J = 7.7, py), 7.13 (2H, dd, J = 7.7 and 5.0 Hz, py), 6.92 (2H, d, J = 8.5 Hz, Ph), 6.70 (2H, d, J = 8.5 Hz, Ph), 3.88 (4H, s, NCH_2py), 2.76 (4H, s broad, NCH_2CH_2Ph). ^{13}C{H} NMR (75 MHz, $CDCl_3$): δ = 159.7, 155.3, 148.5 (CH, py), 136.9 (CH, py), 131.2, 129.8 (CH, Ph), 123.3 (CH, py), 122.2 (CH, py), 115.5 (CH, Ph), 60.1 (NCH_2py), 57.0 (NCH_2CH_2Ph), 33.2 (NCH_2-CH_2Ph). (+)-HR-ESI-MS Calcd. for $[M + H]^+$ ($[C_{20}H_{22}N_3O]^+$): m/z 320.1757. Found: m/z 320.1752.

2.4. Synthesis of L^2

Following the same procedure as for L^1, compound **1** (56.5 mg, 0.135 mmol), **3** (103 mg, 0.322 mmol) and potassium carbonate (224 mg, 1.62 mmol) were heated under reflux for four days. L^2 was isolated as a dark brown oil (87.6 mg, 0.089 mmol, 66%).

L^2: ^{1}H NMR (300 MHz, dmso-d_6): δ = 8.46 (4H, d, J = 4.8 Hz, py), 7.64 (4H, td, J = 7.9 and 1.8 Hz, py), 7.50 (2H, d, J = 2.3 Hz, Ph–xanthene), 7.39 (2H, d, J = 2.3 Hz, Ph–xanthene), 7.35 (4H, d, J = 7.9 Hz, py), 7.20 (4H, dd, J = 4.8 and 7.9 Hz, py), 6.91 (4H, d, J = 8.5 Hz, Ph), 6.71 (4H, d, J = 8.5 Hz, Ph), 5.03 (4H, s, –O–CH_2), 3.78 (4H, s, NCH_2py), 2.67 (8H, m, NCH_2CH_2Ph), 1.64 (6H, s, CH_3), 1.29 (18H, s, ^{t}Bu). ^{13}C{H} NMR (75 MHz, dmso-d_6): δ = 159.4, 156.7, 148.7 (CH, py), 145.4, 145.0, 136.4 (CH, py), 132.2 (CH, Ph), 129.9 (CH, Ph), 129.5 (CH, Ph), 124.5, 123.2, 122.7, 122.5 (CH, py), 121.3 (CH, py), 114.1 (CH, Ph), 64.8 (O–CH_2), 59.5 (NCH_2py), 55.6 (NCH_2 CH_2Ph), 34.9, 34.3 (NCH_2CH_2Ph), 34.2, 32.2 (CH_3), 31. 3 (^{t}Bu). (+)-HR-ESI-MS Calcd. for $[M+H]^+$ ($[C_{65}H_{73}N_6O_3]^+$): m/z 985.5739. Found: m/z 985.5716.

2.5. Synthesis of $[L^1(PdCl)_2][PF_6]_2$ ($4[PF_6]_2$)

$[Pd(PhCN)_2Cl_2]$ (104 mg, 0.27 mmol) was dissolved in dichloromethane (3 mL), added dropwise to a solution of L^1 (108 mg, 0.108 mmol) in dichloromethane (3 mL) and the resulting solution was stirred at room temperature overnight. The fine yellow precipitate was filtered off and dissolved in the minimum amount of dimethylsulfoxide. To this solution, a concentrated aqueous solution of $[NH_4][PF_6]$ was added to afford $\mathbf{4}[PF_6]_2$ as a bright yellow solid. The product was recrystallized by adding diethyl ether to a concentrated solution of $\mathbf{4}[PF_6]_2$ in acetonitrile (72.4 mg, 0.051 mmol, 47%). Yellow needles of the monometallic species $\mathbf{5}[PF_6]$·solvate were formed after slow evaporation of the filtrate of recrystallization (4.6 mg, <3%).

$\mathbf{4}[PF_6]_2$: ^{1}H NMR (600 MHz, dmso-d_6): δ = 8.65 (4H, d, J = 5.2 Hz, py), 8.62 (4H, s, py), 8.59 (4H, d, J = 7.9 Hz, py), 8.16 (4H, t, J = 7.3 Hz, py), 7.92 (4H, d, J = 8.1 Hz, Ph), 7.78 (4H, t, J = 6.6 Hz, py), 7.63 (2H, d, J = 2.2 Hz, Ph–xanthene), 7.46 (2H, d, J = 2.2 Hz, Ph–xanthene), 6.97 (4H, d, J = 8.1 Hz, Ph), 5.18 (4H, s, –O–CH_2), 1.72 (6H, s, CH_3), 1.35 (18H, s, ^{t}Bu). ^{13}C{H} NMR (100 MHz, dmso-d_6): δ = 162.3, 157.6, 154.2, 153.2, 153.0 (CH, py), 146.4, 145.7, 142.5 (CH, py), 130.1(CH, Ph), 129.7, 129.4 (CH, py), 126.8 (CH, Ph–xanthene), 125.9 (CH, py), 125.8 (CH, py), 124.4 (CH, Ph–xanthene), 122.5, 120.1 (CH, py), 115.1 (CH, Ph), 66.3 (–O–CH_2), 34.8, 34.8, 33.0 (CH_3), 31.8 (CH_3, ^{t}Bu). (+)-HR-ESI-MS Calcd. $[C_{67}H_{60}Cl_2N_6O_3Pd_2]^{2+}$: m/z 640.1083. Found: m/z 640.1072.

$\mathbf{5}[PF_6]$: ^{1}H NMR (400 MHz, dmso-d_6): δ = 8.55 (2H, d, J = 7.7 Hz, py), 8.50 (2H, s, py), 8.46 (2H, d, J = 8.0 Hz, py), 8.38 (2H, d, J = 5.7 Hz, py), 8.36 (2H, d, J = 4.9 Hz, py), 8.29 (2H, s, py), 8.06 (2H, td, J = 7.8 and 1.4 Hz, py), 7.89 (2H, d, J = 8.6 Hz, Ph), 7.85 (2H, td, J = 7.6 and 1.4 Hz, py),7.63 (1H, d, J = 1.9 Hz, Ph–xanthene), 7.59 (1H, d, J = 1.9 Hz, Ph–xanthene), 7.50–7.55 (4H, m, py and Ph), 7.48 (1H, d, J = 1.9 Hz, Ph–xanthene), 7.45 (1H, d, J = 1.9 Hz, Ph–xanthene), 7.27 (2H, dd, J = 6.6 and 4.9 Hz, py), 7.07 (2H, d, J = 8.6 Hz, Ph), 6.83 (2H, d, J = 8.5 Hz, Ph), 5.23 (2H, s, –O–CH_2), 5.07 (2H, s, –O–CH_2), 1.72 (6H, s, CH_3), 1.36 (9H, s, ^{t}Bu), 1.34 (9H, s, ^{t}Bu). ^{13}C{H} NMR (100 MHz, dmso-d_6): δ = 162.1, 160.1, 157.6, 155.1, 154.3, 154.2, 153.0, 152.0 (CH, py), 149.3 (CH, py), 148.8, 146.7, 146.0, 145.7, 141.9 (CH, py), 137.9 (CH, py), 130.0, 129.9 (CH, Ph), 129.8, 129.7, 128.7, 128.6 (CH, py), 128.2 (CH, Ph), 126.9 (CH, Ph–xanthene), 126.3, 125.9 (CH, Ph–xanthene), 125.4 (CH, py), 124.8 (CH, py), 124.4 (CH, Ph–xanthene), 123.9 (CH, Ph–xanthene), 122.9, 122.6, 121.4 (CH, py), 119.6 (CH, py), 116.5 (CH, py), 115.1 (CH, Ph), 115.0 (CH, Ph), 66.6 (–O–CH_2), 65.5 (–O–CH_2), 34.8, 34.8, 32.9 (CH_3), 31.8 (CH_3, ^{t}Bu). (+)-HR-ESI-MS Calcd. $[C_{67}H_{60}ClN_6O_3Pd]^+$: m/z 1137.3403. Found: m/z 1137.3445.

2.6. X-ray crystallography

Data for $\mathbf{5}[PF_6]$·solvate were recorded on a Bruker Kappa-Appex-II CCD diffractometer, and data for L^1 were collected on beamline MX2 at the Australian Synchrotron, Melbourne. The crystals were mounted in inert oil on cryoloops and transferred to the cold gas stream for the diffraction measurements. Data for $\mathbf{5}[PF_6]$·solvate were collected by using monochromated Mo Kα radiation (λ = 0.71073 Å) in ω-scans, and data for L^1 were measured at monochromated synchrotron radiation set to wavelength λ = 0.71085 Å. Absorption corrections based on multiple scans were applied only to data from $\mathbf{5}[PF_6]$·solvate by using SADABS [13]. The structures were solved by direct methods and refined on F^2 against ALL reflections using the SHELXL-97 program [14].

3. Results and discussion

3.1. Synthesis of ligands L^1 and L^2

The bis(terpyridine)xanthene derivative L^1 was obtained in excellent yield by treating bis(chloromethyl)xanthene **1** [2b,3b,10] with 4-terpyridinylphenol **2** [11] under standard Williamson ether synthesis conditions; Scheme 1. Ligand L^1 is a white solid that is highly soluble in chlorinated solvents, tetrahydrofuran, ethyl acetate and toluene, and is sparingly soluble in diethyl ether. Following the same methodology, ditopic ligand L^2 containing two bis(2-pyridylmethyl)amine groups, was obtained in moderate yield from **1** and dipicolinyltyramine **3** (Scheme 1). Dipicolinyltyramine **3**

is new and was readily available from the reductive amination of pyridine-2-carboxaldehyde with tyramine (89% yield).

The ^{1}H and ^{13}C NMR spectra of L^1 and L^2 are consistent with their C_s-symmetric structures: the requisite peaks corresponding to those anticipated for the ligand donor domains and the xanthene scaffold are observed in each case. For example, the ^{1}H NMR spectra of L^1 and L^2 in dmso-d_6 show one characteristic *O*-methylene singlet at δ 5.11 and 5.03, respectively, only slightly downfield relative to the methylene signal for the precursor xanthene **1** at δ 4.94.

A crystal of L^1 suitable for a single-crystal X-ray diffraction study was grown from a concentrated chloroform/diethyl ether solution at 278 K. Depicted in Fig. 2 are views of the molecular structure of L^1 and of the packing within the crystal. Table 1 presents the crystallographic structure and refinement data. The xanthene scaffold is slightly puckered as expected with the angle between the normal to the two phenyl rings being 11.8° (see Figs. S1A and S2 in the Supporting Information). The two phenolic rings are not parallel; the B phenolic ring lies approximately in the xanthene plane whereas the A phenolic ring is orthogonal to it, facilitating C–H edge-to-π-face inter-aryl interaction (see Fig. 2A). The distances between C4A, C5A and C6A from phenolic ring A and C7B, C6B from phenolic ring B are 3.65–4.02 Å (see Fig. S1A in the Supporting Information). The two terpyridyl groups are approximately parallel, and show significant offset face-to-face stacking interactions, with distances between the parallel terpyridyl rings varying 3.3–3.5 Å (see Fig. 2) [5b,5f,15]. In the crystal, pairs of L^1 molecules that are aligned head-to-head and related by crystallographic inversion pack into columns that lie parallel to the *x*-axis; see Figs. 2B and S2, Supporting Information. There are significant intermolecular offset face-to-face stacking interactions in the range 3.3–3.6 Å between the adjacent pairs in each column; see Figs. 2B and S2, Supporting Information. The overall crystal structure shows that the L^1 molecules form layers within the crystal lattice parallel to the *x*-axis (see Figs. S3 and S4 in the Supporting Information).

Table 1
Crystallographic structure and refinement data for L^1 and 5[PF_6]·solvate.

	L^1	5[PF_6]·solvate[a]
Empirical formula	$C_{67}H_{60}N_6O_3$	$(C_{67}H_{60}ClN_6O_3Pd)\cdot(F_6P)\cdot$solvate[a]
Crystal habit	thin light yellow plates	yellow plates
Crystal size (mm)	0.08 × 0.02 × 0.01	0.37 × 0.06 × 0.05
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.058(2)	21.035(6)
b (Å)	27.711(6)	13.514(4)
c (Å)	18.798(4)	25.839(7)
α (°)	90.00	90.00
β (°)	98.22(3)	105.904(15)
γ (°)	90.00	90.00
U (Å^3)	5185.4(18)	7064(3)
Z	4	4
D_{calc} (Mg m^{-3})	1.277	1.317
M	997.21	1400.83
F(000)	2112	2872
T (°C)	100	155
θ_{max} (°)	2.5–22.5	2.7–29.1
λ (Å)	0.71085	0.71073 (Mo Kα)
μ (mm^{-1})	0.079	0.0409
Absorpt. T_{min}–T_{max}	–	0.864–0.981
Reflections measured	67736	49865
Unique reflections	8769	12345
Observed reflections [$I > 2\sigma(I)$]	6965	6121
R_{int}	0.061	0.127
R [$F^2 > 2\sigma(F^2)$]	0.050	0.079
wR (F^2)	0.134	0.275
Reflections used	8769	12345
Parameters	693	923
Restraints	0	98[b]
S	1.06	1.05
Max./min. Δρ (e Å^{-3})	0.32, −0.27	1.01, −0.61

[a] The voids in the crystal lattice are filled by molecules of solvent from the crystallisation and refined to ¼ dichloromethane + ½ acetonitrile + ½ diethyl ether + $^{15}/_4$ C-atoms for ill-defined, disordered, solvent molecules.
[b] Restraints were only applied to the molecules of solvent in the crystal lattice.

3.2. Palladium complexes 4[PF_6]$_2$ and 5[PF_6]

Upon mixing ditopic ligand L^1 with 2.5 equiv. of [$Pd(PhCN)_2Cl_2$] at room temperature a bright yellow precipitate formed, which upon dissolution in dimethylsulfoxide and anion metathesis with [NH_4][PF_6] afforded the bimetallic complex [$L^1(PdCl)_2$][PF_6]$_2$ (**4**[PF_6]$_2$), Scheme 2. After **4**[PF_6]$_2$ was collected by filtration, the yellow acetonitrile–diethylether mother liquor was set aside. A few crystals of the monometallic complex [L^1(PdCl)][PF_6] (**5**[PF_6]) formed and were manually collected. Attempts to selectively

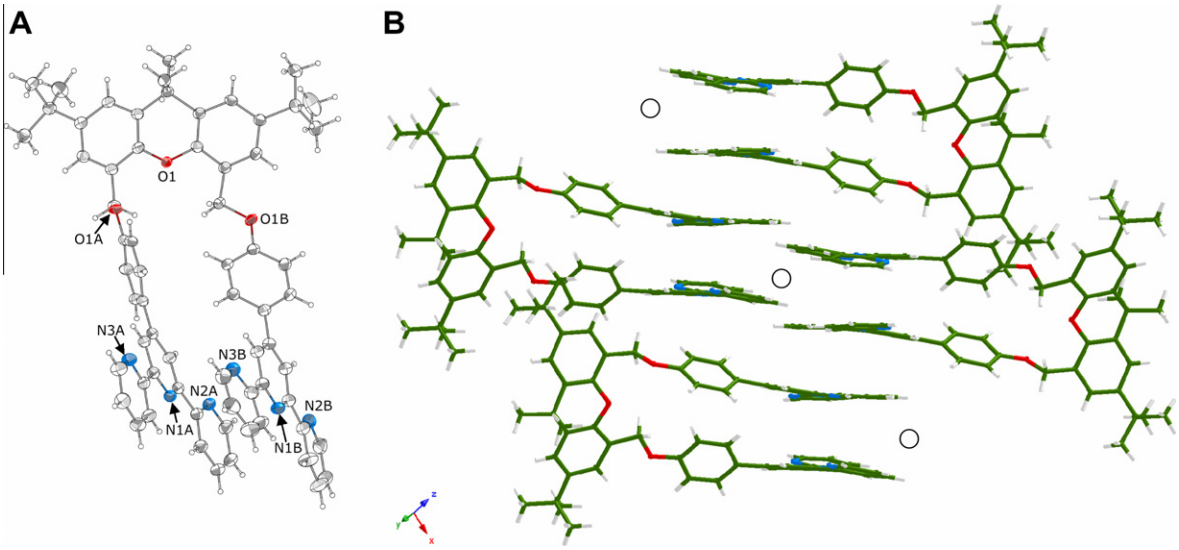
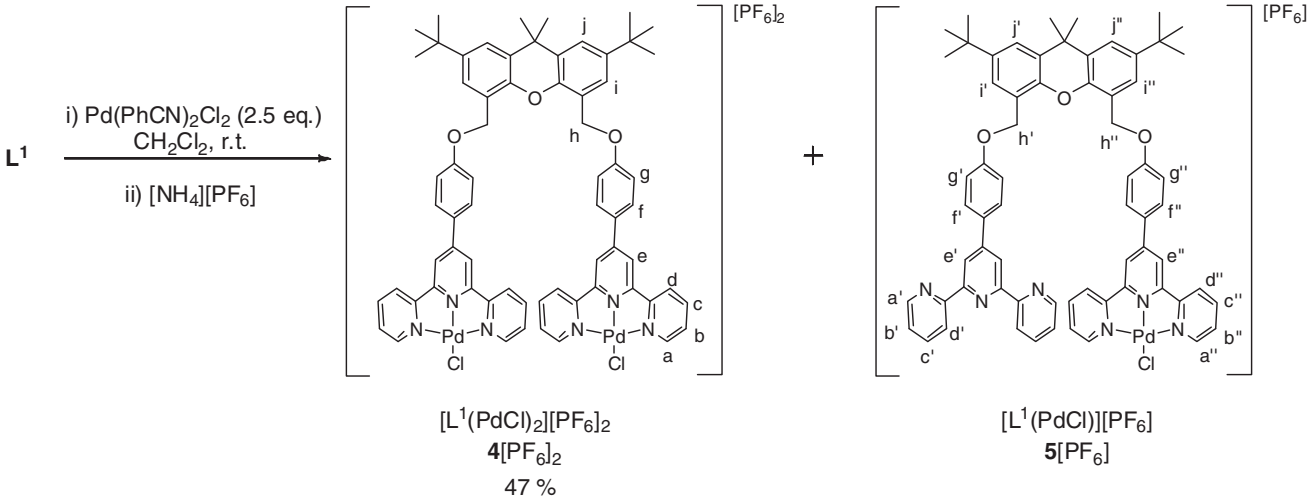


Fig. 2. (A) View of the molecular structure of L^1, showing the heteroatom labeling scheme and 50% thermal ellipsoids; (B) View of the crystal structure illustrating the face-to-face stacking parallel to the *x*-axis between a pair of L^1 molecules related by a crystallographic inversion and molecules of L^1 in the adjacent pairs (○ is a crystallographic inversion centre).



Scheme 2. Synthesis of palladium(II) complexes, 4$[PF_6]_2$ and **5**$[PF_6]$.

prepare $\mathbf{5}^{+}$ using slow dropwise addition of one equivalent of $[Pd(PhCN)_2Cl_2]$, shorter reaction times and various solvents were unsuccessful. Mixtures containing $\mathbf{4}^{2+}$, $\mathbf{5}^{+}$ and uncomplexed L^1 immediately formed that quickly began to precipitate bimetallic $\mathbf{4}^{2+}$ as its chloride salt. The low solubility of $\mathbf{4}(Cl)_2$ drives the formation of this product. Attempted crystallisations of $\mathbf{4}(Cl)_2$ and $\mathbf{4}[PF_6]_2$ always produced fibrous crystalline needles that were unsuitable for X-ray analysis.

Complexes $\mathbf{4}[PF_6]_2$ and $\mathbf{5}[PF_6]$ were characterized by ^1H and ^{13}C NMR spectroscopy, by high resolution mass spectrometry, and by X-ray crystallography for $\mathbf{5}[PF_6]$. The high resolution ESI mass spectrum of $\mathbf{4}[PF_6]_2$ showed an envelope of peaks for $\mathbf{4}^{2+}$ cation at *m/z* 640.1072 (calc. *m/z* 640.1083) and that of $\mathbf{5}[PF_6]$ exhibited an envelope of peaks for the $\mathbf{5}^{+}$ cation at *m/z* 1137.3445 (calc. *m/z* 1137.3403). The peaks for the $\mathbf{4}^{2+}$ and $\mathbf{5}^{+}$ parent ions displayed the anticipated isotope patterns.

The ^1H and ^{13}C NMR spectra for $\mathbf{4}[PF_6]_2$ and $\mathbf{5}[PF_6]$ are completely characteristic for each complex cation. Variable temperature (VT-) ^1H NMR spectra over the aromatic regions of complexes $\mathbf{4}[PF_6]_2$ and $\mathbf{5}[PF_6]$ in dmso-d_6 are presented in Fig. 3. Proton assignments were made with the aid of ^1H–^1H COSY and NOESY NMR experiments. The spectra for $\mathbf{4}[PF_6]_2$, Fig. 3A, reveal the C_2-symmetry of the $\mathbf{4}^{2+}$ complex ion: the two terpyridyl domains, and both halves of the complex ion, are equivalent. The spectra for $\mathbf{5}[PF_6]$ reveal the loss of symmetry and exhibit separate peaks for the protons of the uncomplexed (indicated by a " ′ ") and complexed (indicated by a " ″ ") terpyridyl domains. In the VT-^1H NMR spectra, the peaks for the terpyridyl protons also show notable temperature-dependent chemical shift changes. For example, as the temperature of the VT-^1H NMR spectrum is raised the peaks corresponding to the 6,6″-terpyridyl protons of the Pd(II)-coordinated terpyridine (labeled "e" for $\mathbf{4}^{2+}$ and "e″" for $\mathbf{5}^{+}$) move upfield while the 3′,5′-terpyridyl proton resonances (labeled "d" for $\mathbf{4}^{2+}$ and "d″" for $\mathbf{5}^{+}$) move downfield. The chemical shift changes are such that these resonances switch relative position in the high and low temperature spectra. It has been suggested that such chemical shift changes indicate face-to-face π-stacking interactions between terpyridyl groups in solution at the lower temperature(s) that weaken with increasing molecular freedom as the temperature is raised [1d,16]. No evidence for exchange of the PdCl centre between the occupied and unoccupied terpyridyl domains is seen in the VT NMR spectra for $\mathbf{5}[PF_6]$, Fig. 3B, over the temperatures surveyed (up to 380 K).

Crystals of $\mathbf{5}[PF_6]$·solvate grew upon slow evaporation of an acetonitrile–dichloromethane–diethyl ether solution. The molecular structure of $\mathbf{5}[PF_6]$·solvate was determined by single crystal

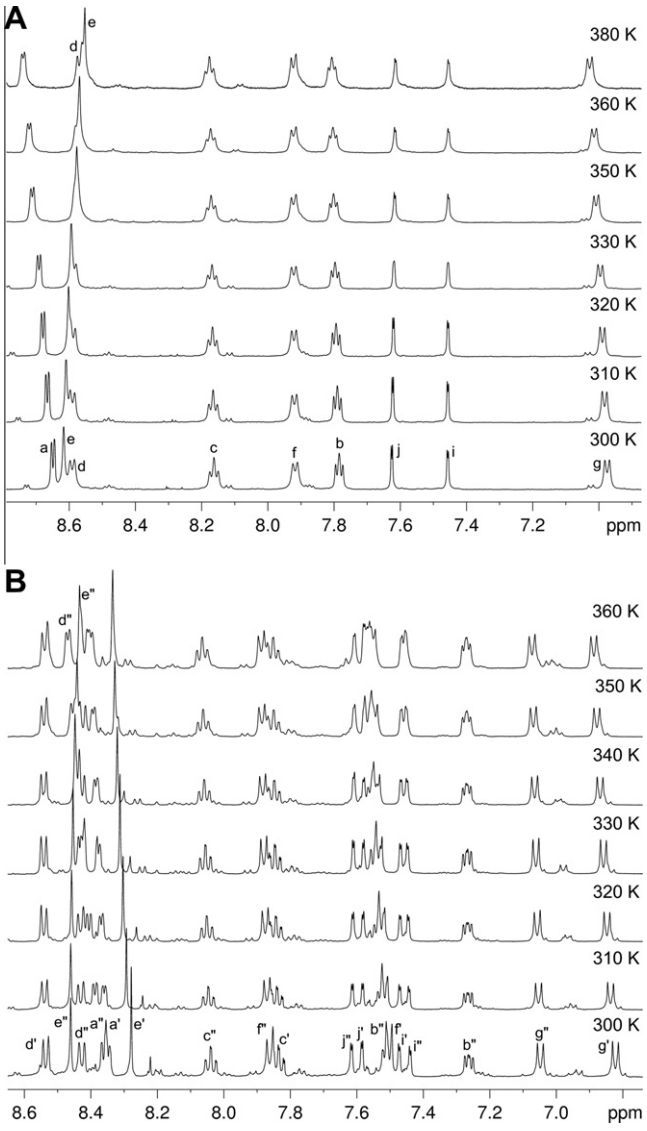


Fig. 3. Variable temperature ^1H NMR spectra in dmso-d_6: (A) $\mathbf{4}[PF_6]_2$ at 600 MHz; (B) $\mathbf{5}[PF_6]$ at 500 MHz. The labeling schemes adopted for the protons of ligand L^1 in the complexes are presented in Scheme 2.

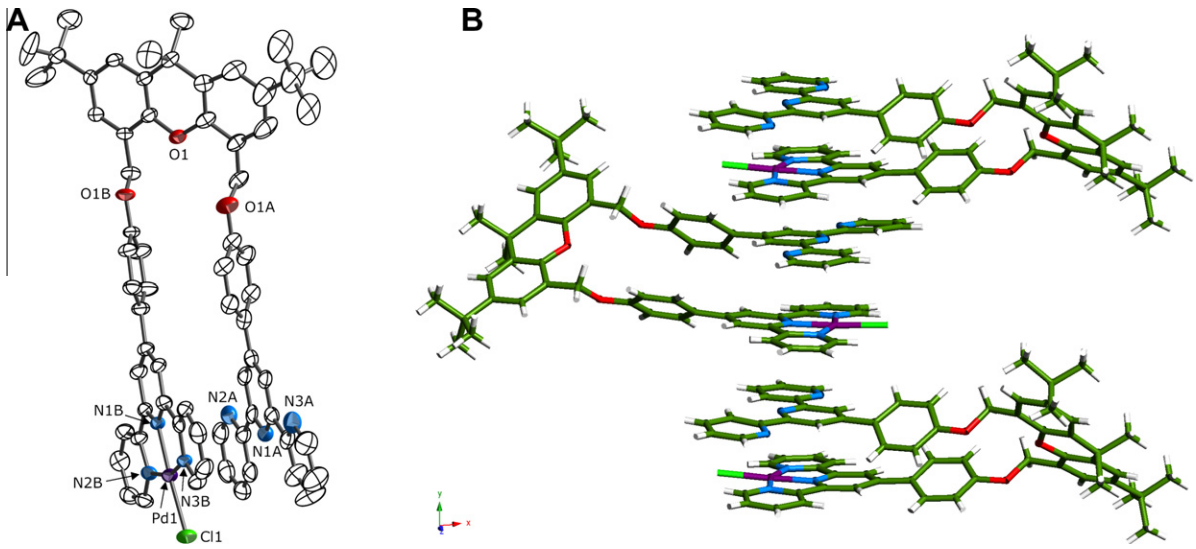


Fig. 4. (A) View of the structure of $\mathbf{5}^+$ in $\mathbf{5}[PF_6]$·solvate showing the heteroatom labeling scheme and 50% thermal ellipsoids at 155 K; for clarity, H-atoms are omitted and only the major (59%) orientation of the twofold rotationally disordered *tert*-butyl group on side A of the xanthene bridge is shown. (B) View orthogonal to the *x*-axis illustrating the columnar packing of $\mathbf{5}^+$ cations parallel to the *y*-axis. Key bond lengths (Å) and angles (°): N1B–Pd1 1.940(6), N2B–Pd1 2.048(8), N3B–Pd1 2.028(8), Pd1–Cl1 2.293(2); N1B–Pd1–N2B 80.8(3), N2B–Pd1–Cl1 100.7(2), N3B–Pd1–Cl1 97.7(2), N3B–Pd1–N1B 80.9(3).

X-ray crystallography. The crystal packing of the $\mathbf{5}^+$ ions creates voids that are filled with well-defined $[PF_6]^-$ counter-ions and with low-occupancy and disordered molecules of the crystallisation solvents (see Table 1, footnotes). The $\mathbf{5}^+$ ions dominate the structure solution and are excellently defined. The acute bond angles about the palladium ion sum to 360.1° indicative for square planar geometry (see Fig. 4). The bond distances and angles (Fig. 4) to palladium are unremarkable being exactly as expected for a terpyridine–palladium(II) complex [5a]. The xanthene-bridge flattens slightly in $\mathbf{5}^+$ with the angle between the normal to the two phenyl rings being 7.6° (*cf.* 11.8° in L^1, see above). A head-to-head intermolecular interaction between the metal-free terpyridine of one molecule and the terpyridine–Pd–Cl group of the other leads to columns of stacked antiparallel cations (Fig. 4B). Within each column, each of the two terpyridyl groups of $\mathbf{5}^+$ stack face-to-face with two parallel neighbouring terpyridines: the inter-plane distances between the terpyridines are 3.3 Å within $\mathbf{5}^+$ and 3.4 Å for the nearest inter-ion interactions (see Fig. 4 and Fig. S5 in the Supporting Information). Columnar stacking was also found for a platinum complex of the bis(terpyridine) ligand L^g (shown in Fig. 1) [3i]. The intermolecular interactions of $[L^g(PtCl)]^+$ differ from that of $[L^1(PdCl)]^+$ ($\mathbf{5}^+$) in that the contact is between two metal-free terpyridyl groups and two Pt atoms of adjacent cations. The strength of the d_{z^2}—d_{z^2} σ-interaction may determine whether M…M or inter-terpyridine face-to-face stacking interactions are observed. In $[L^g(PtCl)]^+$ [3i], the Pt…Pt interaction is strong and preferred over formation of the inter-terpyridine face-to-face stacking interactions, while in $[L^1(PdCl)]^+$ ($\mathbf{5}^+$) the Pd…Pd interaction would be weaker thus favouring the observed inter-terpyridine face-to-face interactions. Bimetallic palladium and platinum species derived from ligand L^h depicted in Fig. 1 also presented similar columnar crystal packing of terpyridyl groups [6c,6e,6f]. For example, $[L^h(PdCl)_2]^{2+}$ and $[L^h(PtCl)_2]^{2+}$ both crystallise in columns of interpenetrated pairs of cations where one terpyridine–Pd–Cl unit of one molecule lies in the middle of the two terpyridine–Pd–Cl groups of the other. This interlocked structure is possible for ligand L^h due to its wide span and rigidity.

In summary, condensation of the bis(chloromethyl) xanthene **1** with 4-phenol-substituted ligand donor domains under Williamson ether synthesis conditions provides a quick and general route to good yields of flexible ditopic ligands such as the bis(terpyridine) ligand L^1 and the bis(di(2-pyridylmethyl)amine) ligand L^2. Extensive intra- and intermolecular face-to-face interactions between the terpyridyl domains in L^1 and in its palladium complexes were observed by single crystal X-ray diffraction studies, and variable temperature NMR spectroscopy experiments suggest these interactions may remain for the complexes in solution. The straightforward syntheses of L^1 and L^2, and the wide versatility of terpyridine [3i,4,5] and di(2-pyridylmethyl)amine [7–9,17] domains as metal-ion binding groups, make these ditopic ligand promising precursors to bimetallic complexes for exploitation in the fields of catalysis, sensors and supramolecular chemistry.

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Appendix A. Supplementary material

CCDC 882845 (for L^1) and CCDC 882846 (for $\mathbf{5}[PF_6]$·solvate) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Atom labeling and additional crystallographic figures of L^1 and $\mathbf{5}[PF_6]$·solvate. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.12.040.

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