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A Back-to-Back Ligand with Dipyrazolylpyridine and Dipicolylamine Metal-Binding Domains

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Reaction of 4-bromomethyl-2,6-bis(pyrazol-1-yl)pyridine with dipicolylamine yields 4-bis(pyrid-2-ylmethyl)aminomethyl-2,6-bis(pyrazol-1-yl)pyridine (**L**). Treatment of **L** with [$MCl_2(NCPh)_2$] (M = Pd, Pt) in the presence of $AgPF_6$ affords [MCl(**L**)]PF_6, whose palladium or platinum centre is bound exclusively by the dipicolylamino moiety of **L**, as established by NMR spectroscopy. The pendant dipyrazolylpyridine residue in these compounds is complexed by iron(II) to form [Fe{MCl(μ-**L**)}$_2$][PF_6]$_4$ (M = Pd, **1**; M = Pt, **2**·$n$$H_2O$). The nitromethane solvate crystal of **1** contains low-spin iron centres at 150 K. However, dried **1** and **2**·$n$$H_2O$ are predominantly high-spin at room temperature, undergoing very gradual thermal spin transitions upon cooling to ≤ 50 % completeness. The platinum compound also undergoes a thermal spin transition in CD_3NO_2 solution, with $T_{1/2}$ = 253 K.

Introduction

Ditopic "back-to-back" ligands[1] are of continuing interest for the synthesis of metal-containing polymers,[2–4] dendrimers,[2,5] molecular wires[6] or other supramolecular structures.[7] The most versatile ligands for these applications are 2,2′:6′,2′′-terpyridine (terpy) derivatives, which can be readily prepared with a variety of substituents at the central or distal pyridine rings.[8] Derivatization at the 4′-position of the terpy scaffold, directly opposite a coordinated metal ion, is especially facile, which has allowed [$M(terpy)_2$]$^{2+}$ centres to be incorporated into all the types of structures mentioned above.[1–3,6,7]

A related tridentate heterocyclic ligand for metal ions is 2,6-bis(pyrazol-1-yl)pyridine (1-bpp), which can also be derivatized at its periphery with a variety of substituents.[9] Although they are less well studied than the terpy system, two classes of 1-bpp complex are receiving particular attention. First are lanthanide complexes of podands containing the 1-bpp moiety, which are efficient light emitters in solution.[10,11] Second are their iron(II) complexes, which often undergo thermal spin transitions[12] close to room temperature.[13] With both these applications in mind, several groups have prepared 1-bpp derivatives substituted at the pyridyl 4-position, yielding luminescent or spin-crossover compounds with a variety of different pendant functionalities.[11,14–21] In particular, two "back-to-back" ligands have been prepared so far, containing two 1-bpp residues linked by 1,2-ethenediyl[16] and 1,4-phenylenediyl[18,19] spacers. Complexation of these ligands by iron(II) yields 1-D coordination polymers of covalently linked [Fe(1-bpp)$_2$]$^{2+}$ centres; the 1,4-phenylene-linked iron polymer undergoes a cooperative spin transition just above room temperature.[18]

As a continuation of our own interest in [Fe(1-bpp)$_2$]$^{2+}$ chemistry,[13,15,16,22,23] we report here a new "back-to-back" ligand with covalently linked 1-bpp and dipicolylamine (dpa) moieties. While homoditopic derivatives of 1-bpp[16,18] and dpa[24,25] have been reported before, this is a rare example of a back-to-back bis-tridentate ligand with two different metal-binding sites.[26,27]

Results and Discussion

4-Bromomethyl-2,6-(dipyrazol-1-yl)pyridine is prepared from 2,6-dihydroxy-4-picolinic acid in six synthetic steps.[16] Reaction of this precursor with dpa in the presence of Na_2CO_3 and catalytic NBu_4Br affords 4-bis(pyrid-2-ylmethyl)aminomethyl-2,6-bis(pyrazol-1-yl)pyridine (**L**) as a pale brown oil (Scheme 1).

Complexation of **L** with 1 equiv. of [$MCl_2(NCPh)_2$] (M = Pd or Pt),[28] in the presence of 1 equiv. of $AgPF_6$, affords pale yellow solid products after the usual workup. These analyze as the expected compounds [MCl(**L**)]PF_6 (M = Pd, Pt), while electrospray mass spectrometry gave strong molecular ions at *m*/*z* 563.0 (M = Pd) and 652.0 (M = Pt) corresponding to the [$M^{35}Cl(\mathbf{L})$]$^+$ cations (M = ^{104}Pd or ^{195}Pt). ^{1}H NMR spectroscopy in CD_3NO_2 contained peaks

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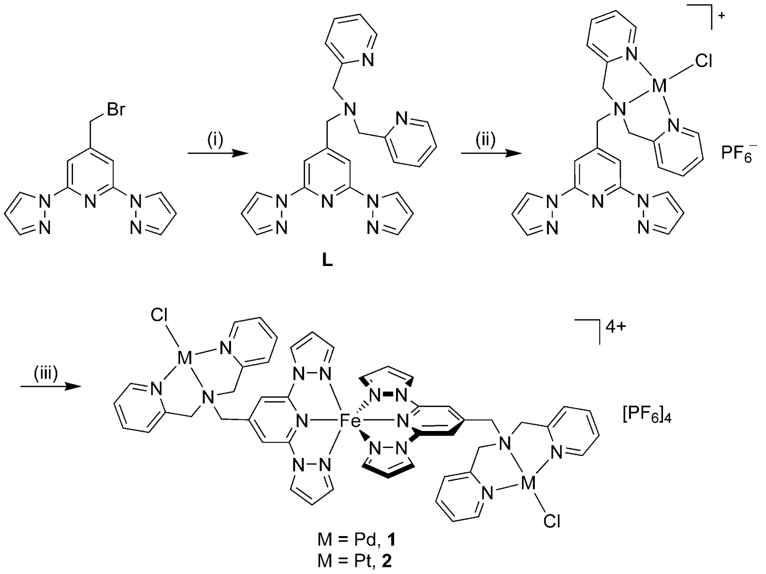

Scheme 1. Synthesis of **L** and its complexes. Reagents and conditions: (i) dpa, Na_2CO_3, NBu_4Br (cat), MeCN, reflux, 22 h. (ii) $[MCl_2(NCPh)_2]$ (M = Pd or Pt), $AgPF_6$, MeCN, 50 °C, 1 h. (iii) $FeCl_2$, 2 equiv. $AgPF_6$, MeCN, 50 °C, 1.5 h.

from just one **L** environment, with *m* or C_2 symmetry on the NMR timescale. Hence, the palladium and platinum centres are cleanly bound to one side of the **L** ligand. The structure shown in Scheme 1, with the metal ions bound to the dpa moiety in **L**, was assigned from the NMR resonances from the ligand methylene groups. In uncoordinated **L** these are observed as two singlets, with a 2:1 integral ratio. In [MCl(**L**)]PF_6, however, the NCH_2Py protons within the dpa fragment are observed as a pair of doublets, reflecting the diastereotopic nature of these groups when the conformation of the dpa fragment is locked by metal coordination.[29,30] The ^1H NMR spectrum of [PdCl(**L**)]PF_6 was unchanged upon heating to 353 K, suggesting that migration of the metal centre between the two tridentate domains in the ligand does not take place in solution.

Treatment of [MCl(**L**)]PF_6 with an acetonitrile solution of $Fe[PF_6]_2$ (generated in situ from $FeCl_2{\cdot}4H_2O$ and 2 equiv. $AgPF_6$) affords dark yellow solutions, which precipitate a yellow powder upon addition of diethyl ether. Microanalysis, ^1H NMR and IR spectroscopy support the formulation of the products as the desired [Fe{MCl(μ-**L**)}$_2$][PF_6]$_4$ (M = Pd, **1**; M = Pt, **2**; Scheme 1). Their ES mass spectra were identical to those of the corresponding [MCl(**L**)]PF_6 precursors, however, implying that the coordinated iron is lost under the conditions of the ES experiment. While **1** is a solvent-free powder after drying in vacuo, solid **2** analyzes consistently as a hydrate $\mathbf{2}{\cdot}nH_2O$ ($n \approx 6$). The presence of lattice water was confirmed by the observation of a broad $\delta_{\text{H-O-H}}$ peak at 1650 cm^{-1} in the IR spectrum of $\mathbf{2}{\cdot}nH_2O$, which was not shown by **1**.[31] The ^1H NMR spectra of the compounds in CD_3NO_2 are paramagnetically shifted, but again show one **L** environment with *m* or C_2 symmetry. The four peaks assignable to the 1-bpp fragment are contact shifted, occurring between 34 and 62 ppm. The seven remaining ^1H peaks, from the dpa moiety and the CH_2 group linking the two ligand domains, all lie within the diamagnetic region between 4.3 and 8.6 ppm. That is consistent with the structure in Scheme 1, where the diamagnetic palladium or platinum centres remain coordinated to the dpa residues of the two **L** ligands, while the paramagnetic iron ion is bound to the 1-bpp domain.

Vapour diffusion of diethyl ether into nitromethane solutions of **1** sometimes yielded brown crystals. An X-ray structure determination was achieved from one such crystal, which had the formula $\mathbf{1}{\cdot}6.8CH_3NO_2{\cdot}0.3(C_2H_5)_2O$. The analysis confirmed the proposed structure of the complex (Scheme 1), with a six-coordinate iron(II) centre coordinated by the 1-bpp domains of two **L** ligands (Figure 1). The bond lengths and angles about Fe(1) are in the range expected for a low-spin iron(II) centre with this ligand type (see the Supporting Information).[13] The palladium ions are bound to the dpa residues of the two **L** ligands, and show metric parameters that are typical of [PdCl(dpa)]$^+$ complexes.[25,30,32] The intramolecular Fe···Pd distances are 8.8587(8) and 8.8722(8) Å.

The two [PdCl(dpa)]$^+$ fragments in the molecule associate in the crystal through intermolecular stacking interactions (see the Supporting Information). The moiety centred on Pd(2) associates with two of its symmetry equivalents, related by the inversion centre –*x*, –*y*, 1 – *z* and the C_2 axis –*x*, *y*, 3/2 – *z*. These interactions combine to form non-helical stacks of [PdCl(dpa)]$^+$ centres zig-zagging parallel to the unit cell *c* axis. In contrast, the [PdCl(dpa)]$^+$ site centred on Pd(3) associates into centrosymmetric dimers with its symmetry equivalent, related by 1/2 – *x*, 1/2 – *y*, 2 – *z*. These dimersare oriented almost perpendicular to the Pd(2) stacks. Stacking interactions of this type are common in crystalline palladium(II) and platinum(II) complexes of heterocyclic ligands, being formed from a combination of π–π and M···M interactions. Of these interactions, only the distance Pd(3)···Pd(3^i) = 3.8455(6) Å [symmetry code (i) 1/2 – *x*, 1/2 – *y*, 2 – *z*] is significantly shorter than the sum

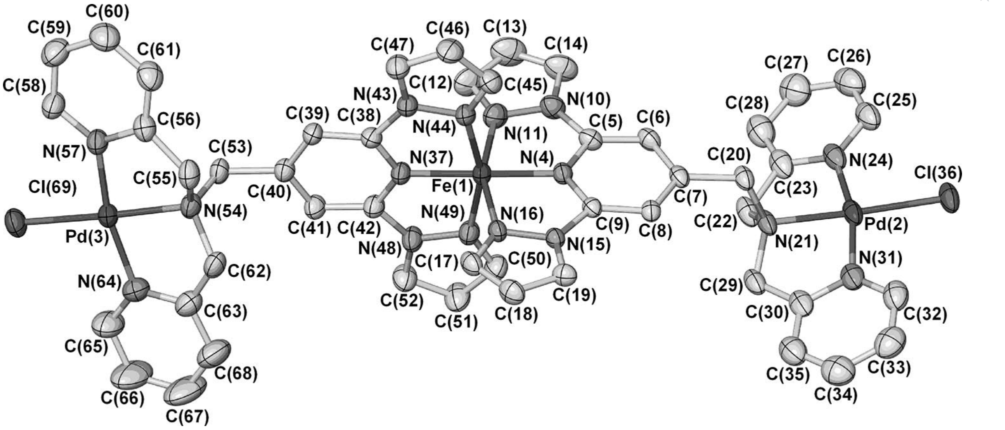

Figure 1. View of the $[Fe\{PdCl(\mu\text{-}\mathbf{L})\}_2]^{4+}$ cation in $\mathbf{1}\cdot 6.8CH_3NO_2\cdot 0.3(C_2H_5)_2O$, showing the atom numbering scheme employed. Thermal ellipsoids are at the 50% probability level, and H atoms have been omitted for clarity.

of the covalent radii for two palladium atoms (4.18 Å[33]). These stacking interactions give rise to a 2D network of channels parallel to the [011] and $[0\bar{1}1]$ crystallographic vectors, that are occupied by disordered anions and solvent. The channels are approximately 11.9 Å long, and 4.4 Å wide at each end but narrowing to 0.6 Å wide at the centre (see the Supporting Information). We tentatively suggest that the existence of similar channels in **2** might explain its moisture retention.

The brown solvate crystals of **1** decompose to a yellow powder on drying, that is similar in appearance to the freshly precipitated product. The magnetic moment of this powder, and of $\mathbf{2}\cdot n H_2O$, are very similar. At room temperature the powder exhibits $\chi_M T = 2.9$ (**1**) and 3.0 cm^{3}mol^{-1}K ($\mathbf{2}\cdot n H_2O$), slightly lower than the value expected for a fully high-spin compound (*ca.* 3.5 cm^{3}mol^{-1}K). These values decrease slowly upon cooling, before plateauing between 50–100 K (Figure 2). Hence the materials show extremely gradual thermal spin transitions that proceed to approximately 50% (**1**) and 43% ($\mathbf{2}\cdot n H_2O$) completeness. That being the case, the midpoints of the transitions can be estimated at 255 ± 5 K, close to the spin-transition temperatures shown by several other iron(II) complexes of 4-subsitituted bpp derivatives.[13,15,17,18,21] Below 50 K $\chi_M T$ decreases further, owing to zero-field splitting of the remaining high-spin fraction of the materials.[34] Fitting these data below 100 K allowed the magnitude of the zero-field splitting parameter to be estimated, giving $|D| = 12(1)$ cm^{-1} and $g = 2.16(1)$ for **1**, and $|D| = 9(1)$ cm^{-1} and $g = 2.17(1)$ for $\mathbf{2}\cdot n H_2O$. That may rule out one potential explanation for the incompleteness of the transition, which is that the fraction of the materials that remains high-spin adopts an angular Jahn–Teller distorted structure. Such structures are common in this class of compound, and trap the complex molecules in their high-spin state.[13,21,35] The values of $|D|$ shown by **1** and $\mathbf{2}\cdot n H_2O$ are in the range expected for undistorted high-spin compounds, but complexes showing the angular distortion often give $|D| < 8$ cm^{-1} from susceptibility data.[35] Hence, the incomplete nature of the transitions may instead be caused by kinetic trapping of the materials in their high-spin state at low temperatures. That is well-known in iron(II) compounds where the transition extends below 100 K.[23,36]

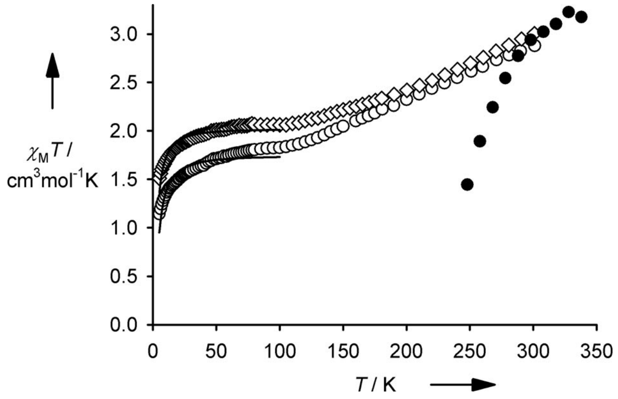

Figure 2. Variable-temperature magnetic-susceptibility data for solid **1** (○), solid $\mathbf{2}\cdot n H_2O$ (◇) and for $\mathbf{2}\cdot n H_2O$ in CD_3NO_2 solution (●). The lines show the fit of the low-temperature solid-state data to the equation deriving the zero-field splitting parameter. See the text for more details.

The magnetic properties of $\mathbf{2}\cdot n H_2O$ in CD_3NO_2 solution were also determined by Evans method.[37] The compound exhibits $\chi_M T$ = 3.2 cm^{3}mol^{-1}K at 338 K, which decreases increasingly rapidly on cooling, reaching 1.4 cm^{3}mol^{-1}K at 248 K, the lowest temperature accessible in that solvent (Figure 2). The midpoint of the spin transition is estimated at 253 ± 2 K, which is similar to $[Fe(1\text{-bpp})_2]^{2+}$ and other iron(II) complexes of 4-substituted 1-bpp derivatives.[13,21] A van ’t Hoff isochoric plot of these data yielded a good straight line, with ΔH = –21 kJ mol^{-1} and ΔS = +85 J mol^{-1} K^{-1} (see the Supporting Information). These are typical values for a thermal spin transition in an iron(II) compound, that imply the complex does not undergo significant ligand dissociation in solution (which would afford a higher value of ΔH).[38] This is additional evidence, that the iron and platinum ions do not exchange between the two domains of the **L** ligand in this solvent.

Conclusions

The heteroditopic bis-tridentate back-to-back ligand **L** has been synthesized and sequentially coordinated with palladium(II) or platinum(II), then with iron(II) (Scheme 1). The palladium and platinum reagents react preferentially with the dpa moiety of **L**, which is consistent with the higher basicity of the N-donor groups in dpa relative to those in the 1-bpp domain. The resultant complexes can then act as metalloligands to iron(II), yielding trimetallic complexes that undergo thermal spin transitions in solution and in the solid state.

Experimental Section

Instrumentation: Elemental microanalyses were performed by the University of Leeds School of Chemistry microanalytical service. Infra-red spectra were obtained as nujol mulls pressed between NaCl windows, between 600–4000 cm^{-1}, using a Nicolet Avatar 360 spectrophotometer. ^1H NMR spectra employed a Bruker DPX300 spectrometer operating at 300.2 MHz. UV/Vis/NIR measurements were performed with a Perkin–Elmer Lambda900 spectrophotometer in 1-cm quartz-solution cells, between 200–3000 nm. Electrospray mass spectra (ESI MS) were obtained with a Waters ZQ4000 spectrometer, from MeCN feed solutions. All mass peaks have the correct isotopic distributions for the proposed assignments. Susceptibility measurements were performed on a Quantum Design SQUID magnetometer, in an applied field of 1000 G. A diamagnetic correction for the sample was estimated from Pascal's constants;[39] a diamagnetic correction for the sample holder was also applied. Magnetic susceptibility measurements in solution were obtained by Evans method using a Bruker DRX500 spectrometer operating at 500.13 MHz.[37] A diamagnetic correction for the sample,[39] and a correction for the variation of the density of the CD_3NO_2 solvent with temperature,[40] were applied to these data.

Materials and Methods: Unless otherwise stated, all reactions were carried out in air using non-pre-dried AR-grade solvents. 4-Bromomethyl-2,6-bis(pyrazol-1-yl)pyridine,[16] $[PdCl_2(NCPh)_2]$ and $[PtCl_2(NCPh)_2]$[28] were prepared by the literature methods, and all other reagents were used as commercially supplied.

4-Bis(pyrid-2-ylmethyl)aminomethyl-2,6-bis(pyrazol-1-yl)pyridine (L): A mixture of 4-bromomethyl-2,6-bis(pyrazol-1-yl)pyridine (2.5 g, 8.2 mmol), dipicolylamine (1.6 g, 8.2 mmol), tetrabutylammonium bromide (20 mg) and sodium carbonate (5 g, 47 mmol) in dry acetonitrile (350 cm^3) was refluxed for 22 h. The solution was cooled, and 1 M sodium hydroxide (60 cm^3) was added. The solution was extracted with dichloromethane (3×100 cm^3), and the organic fractions dried with Na_2CO_3 and the solvents evaporated to dryness. The resultant pale brown oil retains solvent but is otherwise pure as established by ^1H NMR spectroscopy, and was used to make the complexes without further purification. Yield 1.4 g, 70%. $C_{24}H_{22}N_8$ (422.49): calcd. C 68.2, H 5.2, N 26.5; found C 67.2, H 5.5, N 24.0. ES mass spectrum: m/z = 423.2 [**L**H]$^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.89 (s, 2 H, NCH_2bpp), 3.92 (s, 4 H, NCH_2py), 6.52 (pseudo-t, J = 1.9 Hz, 2 H, bpp Pz H^4), 7.19 (dd, J = 5.2 Hz and 7.6 Hz, 2 H, dpa Py H^5), 7.65 (d, J = 7.8 Hz, 2 H, dpa Py H^3), 7.71 (dt, J = 1.8 and 7.8 Hz, 2 H, dpa Py H^4), 7.80 (d, J = 1.8 Hz, 2 H, bpp Pz H^3), 8.00 (s, 2 H, bpp Py $H^{3/5}$), 8.57 (dd, J = 0.8 and 5.2 Hz, 2 H, dpa Py H^6), 8.59 (d, J = 2.5 Hz, 2 H, bpp Pz H^5) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 58.0 (1 C, NCH_2bpp), 60.6 (2 C, NCH_2py), 108.3, 109.6 (both 2 C, bpp Pz C^4 and bpp Py $C^{3/5}$), 122.7 and 123.5 (both 2 C, dpa Py C^3 + C^5), 127.5 (2 C, bpp Pz C^3), 137.0 (2 C, dpa Py C^4), 142.7 (2 C, bpp Pz C^5), 149.5 (2 C, dpa Py C^6), 149.7 (1 C, bpp Py C^4), 155.7 (2 C, bpp Py $C^{2/6}$), 159.2 (2 C, dpa Py C^2) ppm.

[PdCl(L)]PF_6: A mixture of $[PdCl_2(NCPh)_2]$ (0.92 g, 2.4 mmol), **L** (1.00 g, 2.4 mmol) and $AgPF_6$ (0.61 g, 2.4 mmol) in acetonitrile (100 cm^3) was heated to 50 °C for 1 h. The solution was filtered to remove the AgCl precipitate, and the filtrate concentrated in vacuo. Addition of diethyl ether afforded a pale yellow precipitate, which was collected, washed with diethyl ether and dried with P_2O_5. Yield 0.51 g, 30%. $C_{24}H_{22}ClF_6N_8PPd$ (709.33): calcd. C 40.6, H 3.1, N 15.8; found C 40.6, H 3.1, N 15.5. ES mass spectrum: m/z = 563.0 [PdCl(**L**)]$^+$, 1273.1, [{PdCl(**L**)}$_2$PF$_6$]$^+$, 1983.2 [{PdCl(**L**)}$_3$(PF$_6$)$_2$]$^+$. ^1H NMR (300 MHz, CD_3NO_2): δ = 4.50 (s, 2 H, NCH_2bpp), 4.82 and 5.53 (both d, J = 16.0 Hz, 2 H, NCH_2bpp), 6.57 (dd, J = 1.6 and 2.6 Hz, 2 H, bpp Pz H^4), 7.35 (pseudo-t, J = 6.8 Hz, 2 H, dpa Py H^5), 7.58 (d, J = 7.8 Hz, 2 H, dpa Py H^3), 7.82 (d, J = 1.6 Hz, 2 H, bpp Pz H^3), 7.92 (pseudo-td, J = 0.6 and 7.8 Hz, 2 H, dpa Py H^4), 8.25 (s, 2 H, bpp Py $H^{3/5}$), 8.50 (dd, J = 0.6 and 4.8 Hz, 2 H, dpa Py H^6), 8.56 (d, J = 2.6 Hz, 2 H, bpp Pz H^5) ppm. UV/Vis (MeCN): λ_{max} (ε_{max}, 10^4 dm^3 mol^{-1} cm^{-1}) = 246 (4.4), 263 (2.7), 306 (1.9) nm.

[PtCl(L)]PF_6·H_2O: Method as for [PdCl(**L**)]PF$_6$, using $[PtCl_2(NCPh)_2]$ (1.13 g, 2.4 mmol). The product was a pale yellow solid. Yield 0.94 g, 48. $C_{24}H_{22}ClF_6N_8PPt·H_2O$ (816.01): calcd. C 35.3, H 3.0, N 13.7; found C 35.3, H 2.8, N 13.2. ES mass spectrum: m/z 652.0 [PtCl(**L**)]$^+$, 1450 [{PtCl(**L**)}$_2$PF$_6$]$^+$, 2249 [{PtCl(**L**)}$_3$(PF$_6$)$_2$]$^+$. ^1H NMR (300 MHz, CD_3NO_2): δ = 4.78 (s, 2 H, NCH_2bpp), 5.31 and 5.55 (both d, J = 16 Hz, 2 H, NCH_2py), 6.78 (dd, J = 1.6 and 2.6 Hz, 2 H, bpp Pz H^4), 7.58 (pseudo-t, J = 6.6 Hz, 2 H, dpa Py H^5), 7.79 (d, J = 7.9 Hz, 2 H, dpa Py H^3), 8.02 (d, J = 1.6 Hz, 2 H, bpp Pz H^3), 8.17 (pseudo-t, J = 7.8 Hz, 2 H, dpa Py H^4), 8.45 (s, 2 H, bpp Py $H^{3/5}$), 8.74 (d, J = 2.6 Hz, 2 H, bpp Pz H^5), 8.93 (br. d, 5.0 Hz {J_{Pt-H} = 27 Hz}, 2 H, dpa Py H^6) ppm. UV/Vis (MeCN): λ_{max} (ε_{max}, 10^4 dm^3 mol^{-1} cm^{-1}) = 243 (sh), 248 (3.7), 266 (sh), 293 (1.6), 313 (1.5) nm.

[Fe{PdCl(μ-L)}$_2$][PF$_6$]$_4$ (1): Solid $AgPF_6$ (0.14 g, 0.56 mmol) was added to $FeCl_2·4H_2O$ (0.056 g, 0.28 mmol) in acetonitrile (25 cm^3), and the mixture was heated at 50 °C for 30 min. The mixture was cooled and filtered. [PdCl(**L**)]PF$_6$ (0.32 g, 0.56 mmol) was then added to the filtrate, and the mixture was heated to 50 °C for a further 1 h. Addition of excess ethyl ether to the cooled solution afforded a yellow solid that was collected by filtration. The product was recrystallized from acetonitrile/diethyl ether. Yield 0.31 g, 62%. $C_{48}H_{44}Cl_2F_{24}FeN_{16}P_4Pd_2$ (1764.43): calcd. C 32.7, H 2.5, N 12.7; found C 32.5, H 2.7, N 11.9. ES mass spectrum: m/z 563.0 [PdCl(**L**)]$^+$, 1163.1 [{PdCl(**L**)}$_2$Cl]$^+$, 1273.1, [{PdCl(**L**)}$_2$PF$_6$]$^+$, 1983.2 [{PdCl(**L**)}$_3$(PF$_6$)$_2$]$^+$. ^1H NMR (300 MHz, CD_3NO_2): δ = 4.34 (s, 2 H, NCH_2bpp), 5.03 and 5.73 (both d, J = 17.0 Hz, 2 H, NCH_2bpp), 7.2 (br. s, 2 H, dpa Py H^5), 7.8 (br. s, 2 H, dpa Py H^3), 8.0 (br. s, 2 H, dpa Py H^4), 8.6 (br. s, 2 H, dpa Py H^6), 33.6 (br. s, 2 H, bpp Pz H^3), 36.2 (br. s, 2 H, bpp Py $H^{3/5}$), 55.5 and 62.0 (both br. s, 2 H, bpp Pz H^4 + H^5) ppm. UV/Vis (MeCN): λ_{max} = (ε_{max}, 10^4 dm^3 mol^{-1} cm^{-1}) = 243 (10.1), 247 (sh), 266 (5.2), 316 (3.9), 370 (sh) nm.

[Fe{PtCl(μ-L)}$_2$][PF$_6$]$_4$·nH$_2$O (2·nH$_2$O, $n\approx6$): Method as for **1**, using [PtCl(**L**)]PF$_6$·H$_2$O (0.46 g, 0.56 mmol). The yellow product was recrystallized from acetonitrile/diethyl ether, and dried in vacuo. Yield 0.38 g, 66%. $C_{48}H_{44}Cl_2F_{24}FeN_{16}P_4Pt_2·6H_2O$ (2049.85): calcd. C 28.1, H 2.7, N 10.9; found C 27.9, H 2.3, N 10.4. ES mass spectrum: m/z = 652.0 [PtCl(**L**)]$^+$, 1450 [{PtCl(**L**)}$_2$PF$_6$]$^+$, 2249 [{PtCl(**L**)}$_3$(PF$_6$)$_2$]$^+$. ^1H NMR (300 MHz, CD_3NO_2): δ = 4.7

(2 H, NCH_2bpp), 5.2 and 5.6 (both br. s, 2 H, NCH_2bpp), 7.3 (br. s, 2 H, dpa Py H^5), 7.9 (br. s, 2 H, dpa Py H^3), 8.1 (br. s, 2 H, dpa Py H^4), 8.9 (br. s, 2 H, dpa Py H^6), 33.2 (br. s, 2 H, bpp Pz H^3), 35.9 (br. s, 2 H, bpp Py $H^{3/5}$), 55.4 and 61.3 (both br. s, 2 H, bpp Pz H^4 + H^5) ppm. UV/Vis (MeCN): λ_{max} (ε_{max}, 10^4 dm^3 mol^{-1} cm^{-1}) = 244 (sh), 249 (10.1), 269 (5.2), 294 (4.1), 314 (3.9), 370 (sh) nm.

Crystal Data for 1·6.8CH$_3$NO$_2$·0.3(C$_2$H$_5$)$_2$O: $[C_{48}H_{44}Cl_2FeN_{16}Pd_2]^{2+}\cdot4[PF_6]^-\cdot6.8[CH_3NO_2]\cdot0.3[C_4H_{10}O]$, M_r = 2201.76 g mol^{-1}, brown plate, size 0.29 × 0.22 × 0.08 mm^3, monoclinic, space group $C2/c$, a = 76.201(5) Å, b = 15.5056(10) Å, c = 15.3306(10) Å, β = 99.471(3)°, V = 17867(2) Å^3, T = 150 K, Z = 8, $\rho_{calcd.}$ = 1.637 g cm^{-3}, μ (Mo-K_α) = 0.81 cm^{-1}, $F(000)$ = 8818, 138393 reflections in h(–105/99), k(–20/21), l(–21/21), measured in the range $1.63° \leq \theta \leq 29.49°$, completeness θ_{max} = 99.7 %, 24799 independent reflections, R_{int} = 0.0358, 18522 reflections with $F_o > 4\sigma(F_o)$, 1265 parameters, 139 restraints, R_{1obs} = 0.0568, wR_{2obs} = 0.1640, R_{1all} = 0.0787, wR_{2all} = 0.1855, GooF = 1.033, largest difference peak and hole: 1.747/–1.437 e Å^{-3}.

Diffraction data were collected with a Bruker X8 Apex diffractometer diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) generated by a rotating anode. The structure was solved by direct methods (SHELXS-97),[41] then developed by least-squares refinement on F^2 (SHELXL-97).[41] Crystallographic Figure were prepared using XSEED,[42] which incorporates POVRAY.[43]

The asymmetric unit contains one complex tetracation, four PF_6^- anions, eight fully or partially occupied nitromethane solvent sites whose occupancies sum to 6.8, and a partial diethyl ether molecule that was refined with occupancy 0.3. Two of the four PF_6^- anions are disordered, and were modelled with the refined restraints P–F 1.60(2) Å, and *cis*-F···F 2.26(2) Å. The solvent content of the lattice is as follows: two wholly occupied nitromethane molecules; three crystallographically ordered nitromethane molecules with a reduced occupancy of occupancy 0.7; two disordered nitromethane sites, with total occupancies of 0.6 and 0.7; and, a 0.4-occupied nitromethane and a 0.3-occupied diethyl ether molecule occupying the same region of the asymmetric unit. The following restraints were applied to the disordered nitromethane molecules: C–N 1.46(2), N–O 1.20(2), O···O 2.08(2) and C···O 2.30(2) Å. The partial diethyl ether molecule was modelled using C–C 1.54(2), C–O 1.43(2), 1,3-C···C 2.34(2) and 1,3-C···O 2.42(2) Å. All non-H atoms with occupancy >0.5 were refined anisotropically, while all H atoms were placed in calculated positions and refined using a riding model. The largest residual Fourier peak of +1.7 e Å^{-3} and deepest Fourier hole of –1.4 e Å^{-3} both lie within the same disordered anion.

CCDC-753873 contains 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.

Supporting Information (see footnote on the first page of this article): NMR spectra, and additional figures and tables of metric parameters for the crystal structure of **1**·6.8CH$_3$NO$_2$·0.3(C$_2$H$_5$)$_2$O.

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