

Self-discrimination of the racemic ligands in the self-assembly of $[(\text{dppp})\text{Pt}(\text{L})]_2^{4+}$

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Self-assembly of the racemic ligands, (*R*)- and (*S*)-1,1'-binaphthyl bis(isonicotinate) and Pt^{II} shows that the (*S*)-ligand stereospecifically recognises the (*R*)-ligand to give rise to an achiral heterodimeric complex.

Recently much progress has been achieved on the metal-assisted self-assembly of independent ligands.¹ A supramolecular assembly is manufactured from the information embedded in each preprogrammed molecular component.² The information stored in the rigid and chiral ligand systems can be used in the selective recognition of their partners in order to produce highly ordered supramolecular complexes from ligand mixtures in solution. In principle, the simplest situation arises from racemic ligands in which two extreme cases are possible. One is called ligand self-recognition, where each enantiomeric ligand selectively recognises itself to give a homochiral complex,³ and the other is known as ligand self-discrimination, in which one enantiopure ligand specifically perceives its enantiomer to generate an achiral complex. There have been several examples of self-recognition of achiral and chiral ligands.^{3,4} However, there exist few reports of ligand self-discrimination in which two different ligands form a heterodimeric complex.⁵ Herein we report a system that exhibits ligand self-discrimination in which the complex of racemic ligands with metal ions produces only an achiral 2:2 complex.

The design of the ligand **L** (Fig. 1) satisfies three requirements needed for ligand self-discrimination: restricted rotational degrees of freedom, a divergent array of two pyridyl groups for preclusion of intramolecular ligation of a single metal, and ligand chirality. These requirements are fulfilled by the incorporation of chiral 1,1'-binaphthol into the ligand backbone. Both the racemic ligand (*racL*) and the enantiomerically pure ligands (*S***L**, *R***L**) are readily prepared by ester condensation of the appropriate 1,1'-binaphthol and the acid chloride of isonicotinic acid. An equimolar mixture of $(\text{dppp})\text{M}(\text{OTf})_2$ ($\text{M} = \text{Pd}^{\text{II}}$, Pt^{II}) and **L** (*S***L**, *R***L**, *racL*) in acetone-*d*₆ was tested for the ligand chirality-induced self-discrimination process.[†]

¹H NMR titration spectra of *racL* with $(\text{dppp})\text{Pd}(\text{OTf})_2$ in acetone-*d*₆ show a highly symmetric single set of signals at a

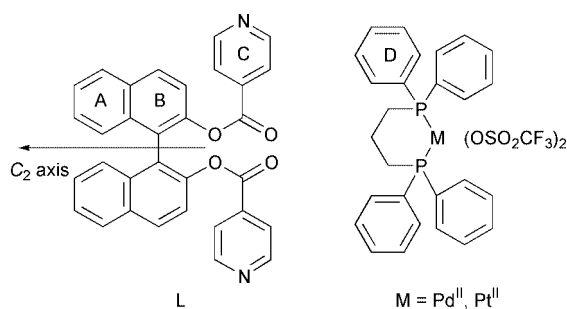
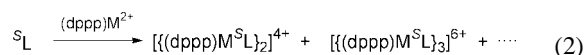
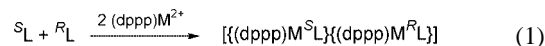


Fig. 1 Nomenclature of the ligands and metal complexes used in this work.

2:2 metal:ligand ratio. Addition of more $(\text{dppp})\text{Pd}(\text{OTf})_2$ to this 2:2 complex does not result in the generation of any new sets of signals, indicating the formation of a single metal complex. In contrast, ¹H NMR titrations of *S***L** with $(\text{dppp})\text{Pd}(\text{OTf})_2$ show complicated sets of resonances. The differences between ¹H NMR titrations of *racL* and *S***L**, respectively, with $(\text{dppp})\text{Pd}(\text{OTf})_2$ imply that *S***L** prefers to form an achiral, heterodimeric complex exclusively with *R***L**, [eqn. (1)] rather than a homochiral complex [eqn. (2)]. Interestingly, ¹H NMR titrations of **L** (*racL*



or *S***L**) with $(\text{dppp})\text{Pt}(\text{OTf})_2$ in acetone-*d*₆ do not produce any distinction between *racL* and *S***L**. It is reported that the Pt^{II} complex has the same coordination geometry as the Pd^{II} complex but the former cannot rapidly reach thermodynamic equilibrium at ambient temperature compared with the latter.⁶ In fact, heating an equimolar mixture of ligand and $(\text{dppp})\text{Pt}(\text{OTf})_2$ results in the generation of a similar ¹H NMR pattern to that of the Pd^{II} complex. The single set of ¹H NMR resonances of the racemic complex compared with those of the enantiopure complex indicates that this system is an example of self-discrimination of the racemic ligands: *S***L** stereospecifically recognises its counterpart, *R***L** (Fig. 2).

Careful interpretation of the HH-COSY of the achiral heterodimeric complex, $[(\text{dppp})\text{Pd}]_2(\text{S}L)(\text{R}L)]^{4+}$ reveals that

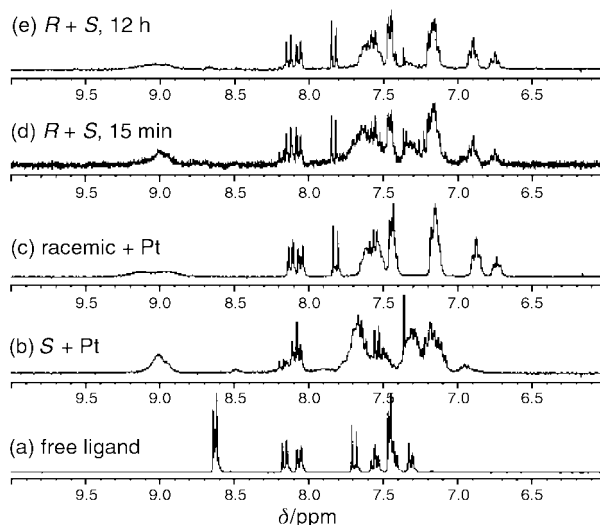


Fig. 2 Partial ¹H NMR spectra (300 MHz, acetone-*d*₆, aromatic protons) of (a) ligand **L**, (b) the complex of equimolar amounts of Pt^{II} and *S***L**, (c) the complex of equimolar amounts of Pt^{II} and *racL*. Monitoring of the reorganization of an equimolar mixture of 1:1 $\text{Pt}^{\text{II}}/\text{S}L$ and 1:1 $\text{Pt}^{\text{II}}/\text{R}L$ complexes (d) after 15 min and (e) after 12 h at 25 °C.

the signals for the four identical phenyl units of free dppp are split into two different sets. L has no symmetry plane due to its C_2 dissymmetry induced by 1,1'-binaphthol. Incorporation of the dissymmetric S L and R L into $[(\text{dppp})\text{Pd}]_2(^S\text{L})(^R\text{L})^{4+}$ should break one symmetry plane of dppp which includes two P atoms and bisects two adjacent phenyl rings. This intriguing phenomenon constitutes strong evidence for the formation of $[(\text{dppp})\text{Pd}]_2(^S\text{L})(^R\text{L})^{4+}$ in solution. In fact, the solubility of the enantiopure complex is different from that of the racemic complex: the enantiopure complex generally shows enhanced solubility in various solvent systems. In acetone solution, measurements of molecular weight by vapor pressure osmometry (VPO)⁷ give M^N (number averaged molecular weight) = 4000 g mol⁻¹ for an equimolar complex of S L and (dppp)Pd(OTf)₂, and M^N = 3400 g mol⁻¹ for an equimolar complex of S L and (dppp)Pt(OTf)₂.[‡] Calculated molecular weights of the 2:2 complex are 2627 and 2804 g mol⁻¹ for $[(\text{dppp})\text{Pd}]_2(^S\text{L})_2(\text{OTf})_4$ and $[(\text{dppp})\text{Pt}]_2(^S\text{L})_2(\text{OTf})_4$, respectively. Thus, VPO measurements show that the formation of homodimeric structures is excluded in the enantiopure case.

The crystal structure of an equimolar complex of (dppp)Pt(OTf)₂ with *rac*L supports the interpretation of the solution behavior of the complex.§ As expected from the ¹H NMR titrations, the racemic ligands generate a heterodimeric species, $[(\text{dppp})\text{Pt}]_2(^S\text{L})(^R\text{L})$ (Fig. 3). A crystal structure shows two crystallographically independent but chemically identical complexes in the unit cell. Both of them have crystallographic inversion centers with a C_{2h} point group. There are many existing reports on the formation of planar rectangular boxes by metal-assisted self-assembly.⁸ However, this complex has a particularly interesting structural variation from its predecessors. It forms a folded rectangular box: the two planes, N(2)–Pt(1)–N(1) and N(2A)–Pt(1A)–N(1A) are separated on the different spaces, making two steps of stairs. A rectangular cavity (6.8 × 7.2 Å) is in the center of the complex. Two triflate anions, captured in the center of the cavity, are in extensive van der Waals contact with the pyridyl groups of the ligand and are also in van der Waals contact with each other (F2A–F2A: 2.79, 2.91 Å). The remaining two triflate counter anions are in short contact with Pt(II) metal ions *via* an oxygen atom.

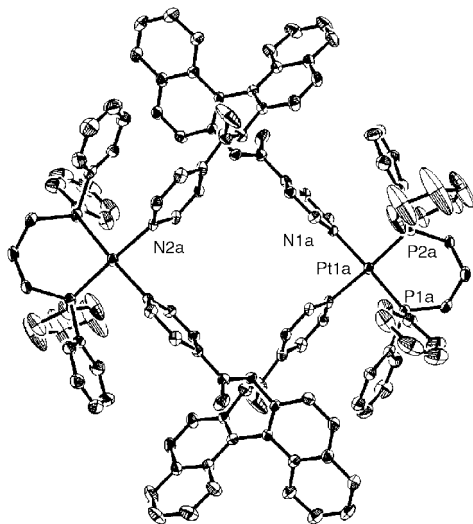


Fig. 3 An ORTEP representation of the structure of $[(\text{dppp})\text{Pt}]_2(^S\text{L})(^R\text{L})^{4+}$ perpendicular to the Pt–Pt vector (30% probability thermal ellipsoids). Selected average distances (Å) and angles (°): Pt–P 2.260, Pt–N 2.098; P–Pt–P 90.76, N–Pt–N 85.14, *cis* P–Pt–N 92.02, *trans* P–Pt–N 176.61. (Because of two independent but chemically identical complexes in the unit cell, average values are reported.)

It turns out that the racemic ligands combine to generate an achiral 2:2 complex with Pd^{II} or Pt^{II}, whereas the enantiopure ligands are not assembled into an entropically favorable homodimer, presumably due to the unfavorable strain energy involved in the formation of a homodimer. The destabilization of the homochiral dimer will be reduced by reorganization to less strained oligomeric complexes. In order to identify the reorganisation behavior of the homochiral complex, the ¹H NMR signal changes of a 1:1 mixture of equimolar $^R\text{L}/(\text{dppp})\text{Pt}(\text{OTf})_2$ and $^S\text{L}/(\text{dppp})\text{Pt}(\text{OTf})_2$ complexes are monitored (Fig. 2). The convergence into the racemic complex suggests that the reorganisation process is reversible in dynamic equilibrium and that the heterodimeric complex represents a thermodynamically stable product.

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Notes and references

[†] Selected data for $[(\text{dppp})\text{Pt}(^{\text{rac}}\text{L})_2](\text{OTf})_4$: ¹H NMR (500 MHz, acetone-*d*₆, 25 °C): δ 2.3 (br, 4H, CH₂–CH₂–CH₂), 3.3 (br, 8H, PCH₂), 6.73 (t, *J* 7.5 Hz, 4H, D¹-H), 6.89 (t, *J* 7.2 Hz, 8H, D²-H), 7.11–7.17 (m, 4 + 8 + 4H, A-H + D¹-H + D²-H), 7.40–7.44 (m, 8 + 4H, C-H + A-H), 7.50–7.57 (m, 8 + 4H, D²-H + A-H), 7.59 (br, 8H, D¹-H), 7.81 (d, *J* 9.0 Hz, 4H, B-H), 8.05 (d, *J* 8.2 Hz, 4H, A-H), 8.16 (d, *J* 9.1 Hz, 4H, B-H), 9.01 (br, 8H, C-H); ESIMS: *m/z* = 2655.3 (found), 2655 (calc. for major isotope peak for $[(\text{C}_{32}\text{H}_{20}\text{N}_2\text{O}_4)_2(\text{C}_{27}\text{H}_{26}\text{P}_2\text{Pt})_2(\text{CF}_3\text{O}_3\text{S})_3]^{4+}$); 1252.4 (found), 1253 (calc. for major isotope peak for $[(\text{C}_{32}\text{H}_{20}\text{N}_2\text{O}_4)_2(\text{C}_{27}\text{H}_{26}\text{P}_2\text{Pt})_2(\text{CF}_3\text{O}_3\text{S})_2]^{2+}$).

[‡] In acetone solution at 25 °C, the racemic complex crystallized out to inhibit the measurement of molecular weight by VPO, and polystyrene M_W = 2360 (M_N = 2250 in VPO, M_N = 2180 in GPC) was used as calibration standard.

[§] Crystal data for $[(\text{dppp})\text{Pt}(^{\text{rac}}\text{L})_2](\text{OTf})_4$ (0.27 × 0.42 × 0.73 mm, white transparent crystal): C₁₂₂F₁₂H₉₂N₄O₂₀P₄S₄Pt₂, M = 2804.39, triclinic, $P\bar{1}$, a = 15.714(3), b = 21.797(4), c = 22.380(5) Å; α = 68.33(3), β = 78.78(3), γ = 79.56(3)°; V = 6937(2) Å³, Z = 2, D_c = 1.530 g cm⁻³ (including solvent), $\mu(\text{Mo-K}\alpha)$, λ = 0.71073 Å = 2.211 mm⁻¹, $2\theta_{\text{max}}$ = 52.9°; 37 830 measured reflections, 27 063 unique of which 19 580 observables [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least squares calculations with SHELX-97. The final $R1$ = 0.0522 for 19 580 reflections of $I > 2\sigma(I)$, $R1$ = 0.0830, $wR2$ = 0.1388 for all 27 063 reflections; measurements: Siemens SMART CCD equipped with a graphite crystal incident-beam monochromator *Lp*.

CCDC 150517. See <http://www.rsc.org/suppdata/cc/b1/b100329l/> for crystallographic data in .cif or other electronic format.

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