

A chiral metallacyclophane for asymmetric catalysis†

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Chiral metallacyclophanes were self-assembled from *cis*-(PEt₃)₂PtCl₂ and enantiopure atropisomeric 1,1'-binaphthyl-6,6'-bis(acetylenes) and used in highly enantioselective catalytic diethylzinc additions to aldehydes to afford chiral secondary alcohols.

The design of functional supramolecular assemblies has received intense interest from synthetic and materials chemists.¹ Nanoscopic supramolecular assemblies can be expected to provide enhanced performance over their constituent building blocks.² The last decade has in particular witnessed tremendous progress in the synthesis of metallosupramolecular assemblies.³ These rigid supramolecular assemblies can provide better selectivity in sensory and catalytic applications. Fujita and coworkers have illustrated such advantages by performing cavity-directed synthesis of labile silanol oligomers and stereoselective [2 + 2] photodimerization of olefins.⁴

We have become interested in chiral supramolecular assemblies for potential applications in enantioselective processes. Our approaches combine rigid bridging ligands derived from 1,1'-bi-2-naphthol (BINOL) and appropriate metallo-corners to generate supramolecular assemblies that bear chiral functionalities. BINOL and its derivatives have been shown to be a 'privileged' ligand system for highly enantioselective catalytic processes and chiral separations.^{5,6} Herein we wish to report the self-assembly and characterization of novel chiral metallacyclophanes [*cis*-(PEt₃)₂Pt(L₁₋₃)]₂ (where L₁₋₃ is enantiopure 6,6'-bis(alkynyl)-1,1'-binaphthalene), and our preliminary results on the application of [*cis*-(PEt₃)₂Pt(L₃)]₂ in highly enantioselective diethylzinc additions to aldehydes to afford chiral secondary alcohols.

Enantiomerically pure atropisomeric bis(acetylenes) L₁ and L₃ were synthesized by modified literature procedures,⁷ while L₂ was synthesized by treating L₃ with acetic anhydride. Treatment of ligands L₁ and L₂ with one equiv. of *cis*-Pt(PEt₃)₂Cl₂ in the presence of catalytic amounts of CuCl in diethylamine at room temperature afforded chiral cycles [*cis*-(PEt₃)₂Pt(L₁)]₂ **1** and [*cis*-(PEt₃)₂Pt(L₂)]₂ **2** in 49 and 59% yield, respectively (Scheme 1). Treatment of L₃ with one equiv. of *cis*-Pt(PEt₃)₂Cl₂ under a variety of conditions gave the hydroxy cycle **3** in very low yields (<20%), presumably due to undesired competitive coordination of the dihydroxy groups of

L₃ to lead to intractable products. Instead, **3** can be obtained in quantitative yield by treating **2** with K₂CO₃ in a mixture of THF and methanol. Compounds **1–3** have been characterized by ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectroscopy, HR-MS, elemental analysis, and IR, UV-Vis, and circular dichroism (CD) spectroscopies.

NMR spectra of **1–3** indicated a single ligand environment, consistent with the formation of cyclic species. HR FAB-MS data showed the presence of molecular ions due to dinuclear species for **1–3**. The terminal acetylenic C–H stretches of L₁₋₃ at ~3280 cm⁻¹ disappeared upon the formation of **1–3**. The IR spectra of **1–3** exhibit expected C≡C stretches at ~2110 cm⁻¹. All these spectroscopic data are consistent with a cyclic dimeric structure of approximate D₂ symmetry. These results are in stark contrast with an earlier report where polymeric compounds were obtained when bis(alkynyl) ligand L₁ was treated with *trans*-Pt(PEt₃)₂Cl₂.^{7a,8}

A single-crystal X-ray diffraction study on compound **3** unambiguously demonstrated the formation of a chiral metallacyclophane.⁹ Compound **3** crystallizes in chiral monoclinic space group P2₁. Two *cis*-Pt(PEt₃)₂ units are linked by two enantiopure L₃ ligands to form a cyclic dinuclear structure (Fig. 1). Both Pt centers adopt slightly distorted square planar geometry with the *cis* angles around the Pt1 center ranging from 82.4(2) to 101.3(1)° and the *cis* angles around the Pt2 center ranging from 84.3(2) to 100.3(1)°. The rigid metallacyclophane structure of **3** is characterized by very small dihedral angles between the naphthyl rings within each L₃ ligand (62.18 and 73.45°).

The electronic spectra of L₁₋₃ show three major π→π* transitions: the naphthyl π→π* transitions at ~240 and ~255 nm and a weak absorption at ~290 nm due to acetylenic π→π* transition that has been delocalized into naphthyl ring systems. Upon the formation of metallacyclophanes **1–3**, a new peak appears at 230–240 nm, which can be assigned to the *cis*-Pt(PEt₃)₂ moiety. The naphthyl π→π* transitions and the acetylenic π→π* transition have significantly red-shifted (Fig. 2). Bathochromic shifts are well-established in platinum acetylides, assignable to the mixing of Pt p-orbitals into the acetylenic π→π* bands.¹⁰ The π→π* transitions at ~310 nm in **1–3** thus have significant ligand-to-metal charge transfer (LMCT) character. CD spectra of ligands L₁₋₃ exhibit one

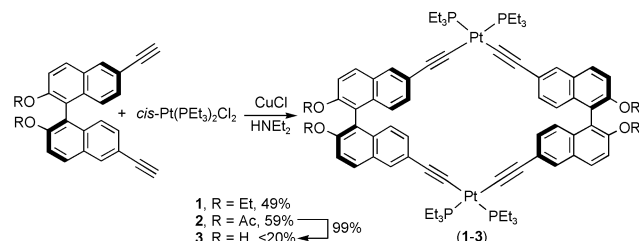
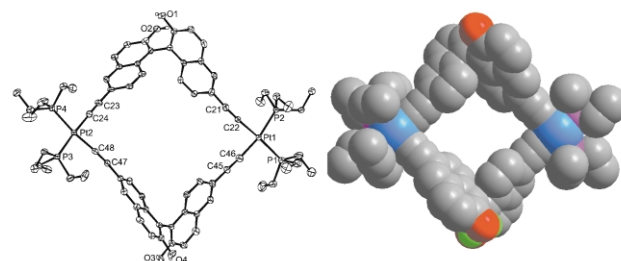
Scheme 1 Synthesis of **1–3**.

Fig. 1 (Left) ORTEP view of metallacyclophane **3**. Key bond distances (Å): Pt1–C22 1.983(8), Pt1–C46 2.016(9), Pt1–P1 2.306(2), Pt1–P2 2.310(2), Pt2–C24 1.989(9), Pt2–C48 1.999(8), Pt2–P4 2.314(2), Pt2–P3 2.316(2). (Right) A space-filling model of **3**.

† Electronic supplementary information (ESI) available: experimental details and analytical data for **2** and **3**, and general procedure for analysis. See <http://www.rsc.org/suppdata/cc/b2/b208324h/>

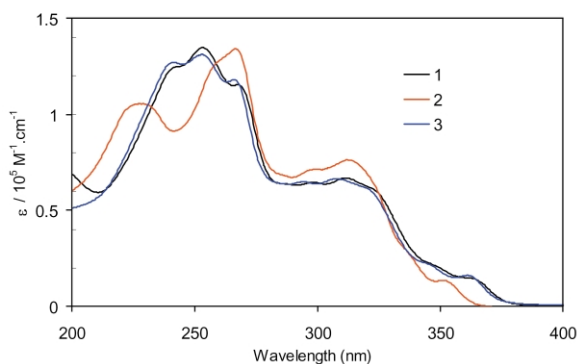


Fig. 2 UV-Vis spectra of 1–3 in acetonitrile.

major bisignate band corresponding to naphthyl $\pi \rightarrow \pi^*$ transitions at ~ 245 nm and one minor band at ~ 290 nm due to acetylenic $\pi \rightarrow \pi^*$ transition. CD spectra of metallacyclophanes 1–3 exhibit a bisignate band at ~ 260 nm due to the naphthyl $\pi \rightarrow \pi^*$ transitions and an intense band at 320 nm assignable to the acetylenic $\pi \rightarrow \pi^*$ transitions, along with a band at ~ 230 nm which can be attributed to the chiral arrangement of the PEt_3 groups on the Pt centers (Fig. 3). Interestingly, the intensities of the naphthyl $\pi \rightarrow \pi^*$ CD bands of coordinated L_{1-3} in 1–3 have decreased to $\sim 1/4$ of those of free L_{1-3} , probably a consequence of the reduction in their dihedral angles upon the formation of metallacyclophanes.

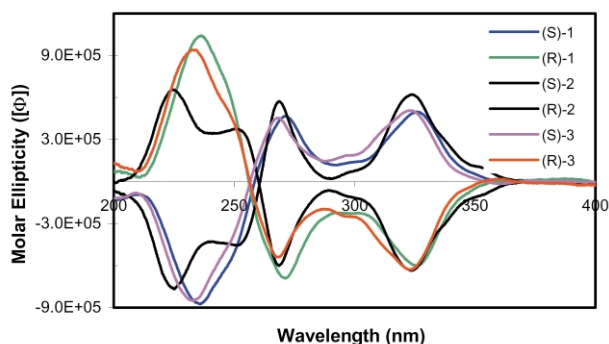
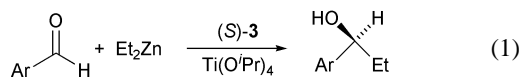


Fig. 3 Circular dichroism spectra of 1–3 in acetonitrile.

The presence of chiral dihydroxy groups in 3 has prompted us to examine its utility in asymmetric catalysis. We have carried out prototypical diethylzinc additions to aromatic aldehydes using a combination of 3 and $\text{Ti}(\text{O}^i\text{Pr})_4$ as the catalyst (eqn. 1).¹¹ As shown in Table 1, the $\text{Ti}(\text{iv})$ complexes of 3 are excellent catalysts for the additions of diethylzinc to 1-naphthaldehyde with 94% ee and $>95\%$ conversion at 0°C . The enantioselectivity has however dropped significantly when other smaller aromatic aldehydes were used as the substrates. This result differs from the performance of BINOL and a BINOL-derived organometallic triangle, both of which have a very broad substrate scope.¹¹ We believe that this difference is a direct consequence of much more rigid structure of 3; the dihedral angles of naphthyl rings in the $\text{Ti}(\text{iv})$ catalyst can no vary to accommodate aldehydes of various sizes to give high enantioselectivity. The chiral dihydroxy groups in 3 thus differ from those of BINOL, and may prove useful for mechanistic work owing to their rigid structure.



In summary, a family of novel chiral metallacyclophanes has been readily assembled based on robust Pt–acetylide linkages. Metallacyclophane 3 has been used as a chiral ligand for enantioselective catalytic diethyl zinc additions to aromatic

Table 1 Diethylzinc additions to aldehydes catalyzed by $\text{Ti}(\text{iv})$ complexes of 3

Aldehyde	Temp./K	Time/h	Conversion (%)	Ee (%)
	r.t.	16	>95	77
	0°C	16	>95	84
	r.t.	16	>95	91
	0°C	16	>95	94
	r.t.	16	>95	75
	0°C	16	>95	78
	r.t.	16	>95	77
	0°C	40	~ 40	78
	r.t.	16	>95	76
	0°C	40	~ 80	77
	r.t.	16	>95	75
	0°C	16	>95	78

aldehydes. Such a supramolecular approach will add a new dimension to the rapidly expanding field of asymmetric catalysis.

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Notes and references

† X-Ray single-crystal diffraction data for 3-EtAc-H₂O were collected on a Siemens SMART CCD diffractometer. *Crystal data*: monoclinic, space group $P2_1$, $a = 13.833(3)$, $b = 15.047(3)$, $c = 17.264(4)$ Å, $\beta = 92.105(5)^\circ$, $U = 3591.1(14)$ Å³, $Z = 2$, $D_c = 1.51$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 40.3$ cm⁻¹. Least-squares refinement based on 13710 reflections with $I > 2\sigma(I)$ and 802 parameters led to convergence, with a final $R1 = 0.050$, $wR2 = 0.105$, and GOF = 1.03. Flack parameter = $-0.02(6)$. See <http://www.rsc.org/suppdata/cc/b2/b208324h/> for crystallographic data in CIF or other electronic format.

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