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A chiral metallacyclophane for asymmetric catalysis†

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Chiral metallacyclophanes were self-assembled from *cis*-$(PEt_3)_2PtCl_2$ 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]

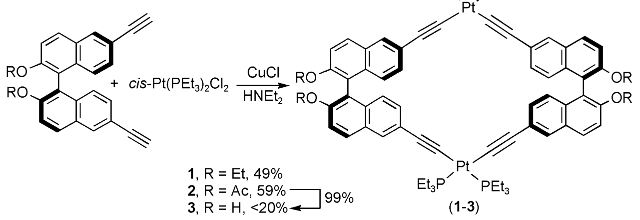
We have become interested in chiral supramolecular assemblies for potential applications in enantioselective processes. Our approaches combine rigid bridging ligands derived from 1,1′-bi-2-naphthol (BINOL) and appropriate metallo-corners to generate supramolecular assemblies that bear chiral functionalities. 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 $[cis\text{-}(PEt_3)_2Pt(\mathbf{L_{1-3}})]_2$(where $\mathbf{L_{1-3}}$ is enantiopure 6,6′-bis(alkynyl)-1,1′-binaphthalene), and our preliminary results on the application of $[cis\text{-}(PEt_3)_2Pt(\mathbf{L_3})]_2$ in highly enantioselective diethylzinc additions to aldehydes to afford chiral secondary alcohols.

Enantiomerically pure atropisomeric bis(acetylenes) $\mathbf{L_1}$ and $\mathbf{L_3}$ were synthesized by modified literature procedures,[7] while $\mathbf{L_2}$ was synthesized by treating $\mathbf{L_3}$ with acetic anhydride. Treatment of ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ with one equiv. of *cis*-$Pt(PEt_3)_2Cl_2$ in the presence of catalytic amounts of CuCl in diethylamine at room temperature afforded chiral cycles $[cis\text{-}(PEt_3)_2Pt(\mathbf{L_1})]_2$ **1** and $[cis\text{-}(PEt_3)_2Pt(\mathbf{L_2})]_2$ **2** in 49 and 59% yield, respectively (Scheme 1). Treatment of $\mathbf{L_3}$ with one equiv. of *cis*-$Pt(PEt_3)_2Cl_2$ 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 $\mathbf{L_3}$ to lead to intractable products. Instead, **3** can be obtained in quantitative yield by treating **2** with K_2CO_3 in a mixture of THF and methanol. Compounds **1–3** have been characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ 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 $\mathbf{L_{1-3}}$ 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 D_2 symmetry. These results are in stark contrast with an earlier report where polymeric compounds were obtained when bis(alkynyl) ligand $\mathbf{L_1}$ was treated with *trans*-$Pt(PEt_3)_2Cl_2$.[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 $P2_1$.‡ Two *cis*-$Pt(PEt_3)_2$ units are linked by two enantiopure $\mathbf{L_3}$ 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 $\mathbf{L_3}$ ligand (62.18 and 73.45°).

The electronic spectra of $\mathbf{L_{1-3}}$ show three major $\pi\rightarrow\pi^*$ transitions: the naphthyl $\pi\rightarrow\pi^*$ transitions at ~ 240 and ~ 255 nm and a weak absorption at ~ 290 nm due to acetylenic $\pi\rightarrow\pi^*$ 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*-$Pt(PEt_3)_2$ moiety. The naphthyl $\pi\rightarrow\pi^*$ transitions and the acetylenic $\pi\rightarrow\pi^*$ 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 $\pi\rightarrow\pi^*$ bands.[10] The $\pi\rightarrow\pi^*$ transitions at ~ 310 nm in **1–3** thus have significant ligand-to-metal charge transfer (LMCT) character. CD spectra of ligands $\mathbf{L_{1-3}}$ exhibit one



Scheme 1 Synthesis of **1–3**.

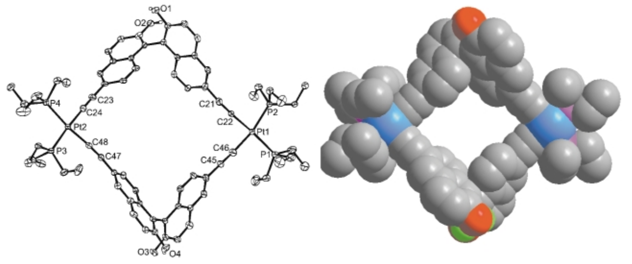


Fig. 1 (Left) ORTEP view of metallacyclophane **3**. Key bond distances (Å): Pt1–C22 1.983(8), Pt1–C46 2.016(9), Pt1–P1 2.306(2), Pt1–P2 2.310(2), Pt2–C24 1.989(9), Pt2–C48 1.999(8), Pt2–P4 2.314(2), Pt2–P3 2.316(2). (Right) A space-filling model of **3**.

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† Electonic 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/

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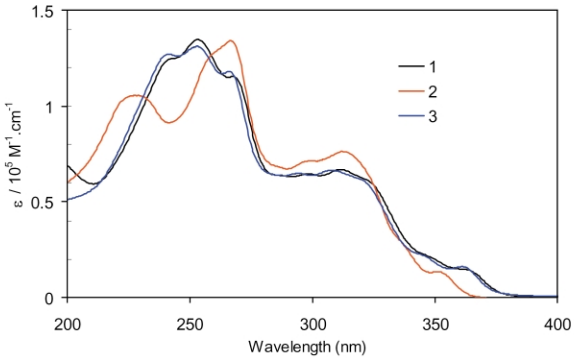


Fig. 2 UV-Vis spectra of **1**–**3** in acetonitrile.

major bisignate band corresponding to naphthyl π → π* transitions at ~245 nm and one minor band at ~290 nm due to acetylenic π→π* transition. CD spectra of metallacyclophanes **1**–**3** exhibit a bisignate band at ~260 nm due to the naphthyl π→π* transitions and an intense band at 320 nm assignable to the acetylenic π→π* transitions, along with a band at ~230 nm which can be attributed to the chiral arrangment of the PEt$_3$ groups on the Pt centers (Fig. 3). Interestingly, the intensities of the naphthyl π→π* CD bands of coordinated **L**$_{1-3}$ in **1**–**3** have decreased to ~1/4 of those of free **L**$_{1-3}$, probably a consequence of the reduction in their dihedral angles upon the formation of metallacyclophanes.

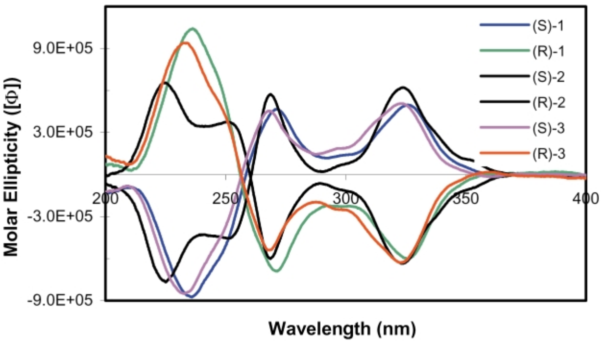
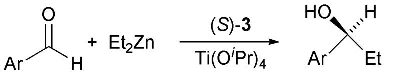


Fig. 3 Circular dichroism spectra of **1**–**3** in acetonitrile.

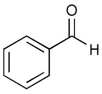
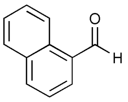
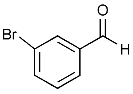
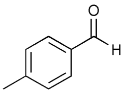
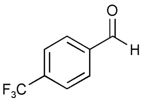
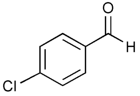
The presence of chiral dihydroxy groups in **3** has prompted us to examine its utility in asymmetric catalysis. We have carried out prototypical diethylzinc additions to aromatic aldehydes using a combination of **3** and Ti(O^{i}Pr)$_4$ as the catalyst (eqn. 1).[11] As shown in Table 1, the Ti(IV) 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 Ti(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.



(1)

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

Table 1 Diethylzinc additions to aldehydes catalyzed by Ti(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

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Notes and references

‡ X-Ray single-crystal diffraction data for **3**·EtAc·H_2O 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, β = 92.105(5)°, U = 3591.1(14) Å^3, Z = 2, D_c = 1.51 g cm^{-3}, μ(Mo-Kα) = 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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