The First Chiral Organometallic Triangle for Asymmetric Catalysis

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Coordination-driven self-assembly of inorganic and organometallic cycles and cages has witnessed tremendous growth over the past decade.^{1–5} Numerous metallocorers such as *cis*-[M(phosphine)₂]²⁺,¹ *cis*-[M(en)]²⁺,³ *fac*-(CO)₃ReX,⁴ and M₂(carboxylate)₂ units⁵ have been utilized to construct metallosupramolecular assemblies that have not only exhibited interesting structures but also shown promises for applications in catalysis,⁶ chemical sensing,⁷ and selective inclusion of guest molecules.⁸ Despite the importance of asymmetric catalysis in the production of chiral compounds,⁹ there have been few reports on the design of chiral metallosupramolecular assemblies.¹⁰ Moreover, none of the known chiral metallosupramolecular assemblies have been explored for applications in asymmetric catalysis. We surmise that incorporation of a chiral ligand into a conformationally rigid metallosupramolecular system would lead to a well-defined enzyme-like chiral pocket or functionality, which could find applications in chiral sensing and asymmetric catalysis. Our proof of principle experiments use 1,1'-bi-2-naphthol (BINOL) as the key building block for the construction of functional chiral metallosupramolecular assemblies with the hope of taking advantage of the well-documented utility of its chirality for enantioselective processes.¹¹ We have recently reported a chiral molecular square that is capable of enantioselective sensing of chiral amino alcohols via fluorescence quenching.^{10a} We report here the self-assembly and characterization of the first chiral organometallic triangles [*cis*-(PEt₃)₂Pt(L_{1–4})]₃ (where L_{1–4} is enantiopure 4,4'-bis(alkynyl)-1,1'-binaphthalene) and their applications in highly enantioselective diethylzinc additions to aldehydes to afford chiral secondary alcohols.¹²

Enantiomerically pure atropisomeric 6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl-4,4'-bis(acetylene) **L**₁ was synthesized in two steps in 67% overall yield starting from 6,6'-dichloro-4,4'-dibromo-2,2'-diethoxy-1,1'-binaphthalene which was previously reported by us (Scheme 1).^{10a} Dimethoxy analogue **L**₂ and bis(*tert*-butyldimethylsilyl) analogue **L**₃ were similarly prepared, while dihydroxy analogue **L**₄ was prepared in quantitative yield by treating **L**₃ with tetra(*n*-butyl)ammonium fluoride (TBAF) in THF. All of these ligands have been characterized by ¹H and ¹³C{¹H} NMR, UV-vis, circular dichroism (CD) spectroscopies, and high-resolution mass spectrometry.

Treatment of ligand **L**_{1–3} with 1 equiv of *cis*-Pt(PEt₃)₂Cl₂ in the presence of CuI in a mixture of diethylamine and dichloromethane at room temperature afforded chiral cycles **1–3** in moderate yields (38–45%) after purification by silica gel column chromatography. Attempts to synthesize the hydroxy cycle **4** by treating **L**₄ with 1 equiv of *cis*-Pt(PEt₃)₂Cl₂ have failed, presumably due to competitive coordination of the 2,2'-dihydroxy groups to the Pt centers. Instead, cycle **4** was obtained in quantitative yield by treating **3** with TBAF in THF. Compounds **1–4** have been characterized by ¹H, ¹³C{¹H},

Scheme 1

and ³¹P{¹H} NMR spectroscopy, mass spectrometry, elemental analysis, and IR, UV-vis, and circular dichroism (CD) spectroscopies.

NMR data of **1–4** showed a single ligand environment, suggesting the formation of cyclic species. For example, the ³¹P{¹H} NMR spectrum of **1** exhibits a single peak at 3.51 ppm with a set of ¹⁹⁵Pt satellites (*J*_{Pt–P} = 2282.8 Hz). There is also only one single set of signals for the acetylenic and aromatic carbon atoms in its ¹³C{¹H} NMR spectrum. The aromatic region of ¹H NMR spectrum of **1** is deceptively simple with only three singlets, apparently a result of accidental overlap of H₇ and H₈ signals. Mass spectroscopic data showed the presence of molecular ions due to trinuclear species for **1–4** and thus unambiguously established their cyclic trimeric nature.¹³ The $\nu(\text{C}\equiv\text{C}-\text{H})$ stretches at $\sim 3280\text{ cm}^{-1}$ in **L**_{1–4} disappeared upon the formation of **1–4**, and the IR spectra of **1–4** exhibit expected $\nu(\text{C}\equiv\text{C})$ stretches at $\sim 2100\text{ cm}^{-1}$. The formulations of **1–4** are also supported by microanalysis results. All of these spectroscopic data are consistent with a cyclic trinuclear structure with approximate *D*₃ symmetry for **1–4**. Numerous attempts have however failed to produce X-ray diffraction quality single crystals of **1–4**.

The electronic spectra of **L**_{1–4} show three major $\pi \rightarrow \pi^*$ transitions at ~ 240 , ~ 300 , and $\sim 357\text{ nm}$. While the absorption at $\sim 240\text{ nm}$ is due to the naphthyl $\pi \rightarrow \pi^*$ transition, the absorptions at ~ 300 and $\sim 357\text{ nm}$ are probably due to acetylenic $\pi \rightarrow \pi^*$ transitions that have been delocalized into naphthyl ring systems. Upon the formation of metallocycles **1–4**, the absorption at $\sim 240\text{ nm}$ of **L**_{1–4} remains unshifted, while the lower energy transitions of **L**_{1–4} have red-shifted by more than 15 nm. Such bathochromic shifts have been well-established in platinum acetylides, owing to the mixing of Pt p-orbitals into the acetylenic $\pi \rightarrow \pi^*$ bands.¹⁴ A new band also appeared at $\sim 202\text{ nm}$, probably due to the *cis*-Pt-

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Figure 1. CD spectra of **L**₄ and **4** in acetonitrile.

Table 1. Diethylzinc Additions to Aldehydes Catalyzed by Ti(IV) Complexes of **4**^a

Entry	Aldehyde	Temp	Conversion ^b	e.e. (%) ^c
1		rt	>95%	91
2		rt	>95%	91
		0 °C	>95%	92
3		rt	>95%	90
4		rt	>95%	91
5		rt	>95%	89
6		rt	>95%	90

^a All reactions were carried out with 7 equiv of Ti(OⁱPr)₄ (on the basis of **L**₄). ^b Conversion was determined by ¹H NMR. ^c ee's were determined using a Chiralcel-OD HPLC column except for *p*-tolualdehyde (OJ column).

(PEt₃)₂ moieties. CD spectra of ligands **L**_{1–4} exhibit one major bisignate band corresponding to naphthyl $\pi \rightarrow \pi^*$ transitions and two minor bands due to the other two lower energy $\pi \rightarrow \pi^*$ transitions (Figure 1). CD spectra of **1–4** exhibited these three bands similar to **L**_{1–4}, but with red-shifts in energy and higher intensities. Interestingly, a new intense CD band appeared at ~ 202 nm, assignable to the transitions associated with *cis*-Pt(PEt₃)₂ moieties. This result suggests that triethylphosphines on the Pt centers adopt a propeller-type arrangement (relative to the naphthyl groups), apparently steered by chiral binaphthyl moieties.¹⁵ Enhanced lower energy CD signals for **1–4** are consistent with the presence of multiple ligands in each metallocycle, while their similarity with those of **L**_{1–4} indicates that the dihedral angles between naphthyl rings in **1–4** are quite similar to those of **L**_{1–4}.

With dihydroxyl groups present in **4**, we expect it to be applicable in asymmetric catalysis. We have thus carried out prototypical diethylzinc additions to aromatic aldehydes using a combination of **4** and Ti(OⁱPr)₄ (eq 1).¹⁶ As shown in Table 1, the Ti(IV) complexes of **4** are excellent catalysts for the additions of diethylzinc to aromatic aldehydes to generate chiral secondary

alcohols in very high selectivity, yield, and enantioselectivity. In comparison, when free ligand **L**₄ was used instead of **4**, a lower ee (80%) was obtained for the addition of diethylzinc to 1-naphthaldehyde. The broad substrate scope for catalytic diethylzinc additions using **4** and Ti(OⁱPr)₄ suggests that there is significant flexibility in the dihydroxy groups to accommodate aldehydes of various sizes. This result is entirely consistent with the CD data.

In summary, a family of chiral organometallic triangles has been readily assembled on the basis of robust Pt-acetylide linkage. Metallocycle **4** has been used for highly enantioselective catalytic diethylzinc additions to aromatic aldehydes.

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Supporting Information Available: Experimental procedures, analytical data, and seven figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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