

## The First Chiral Organometallic Triangle for Asymmetric Catalysis

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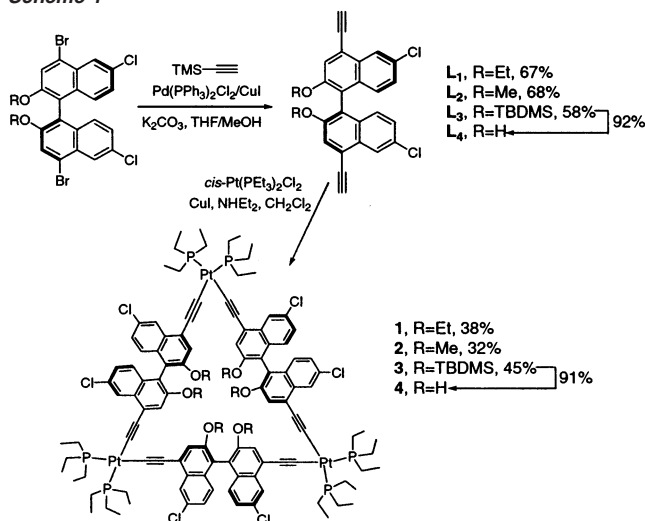
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Coordination-driven self-assembly of inorganic and organometallic cycles and cages has witnessed tremendous growth over the past decade.<sup>1–5</sup> Numerous metallocorners such as *cis*-[M(phosphine)<sub>2</sub>]<sup>2+</sup>,<sup>1</sup> *cis*-[M(en)]<sup>2+</sup>,<sup>3</sup> *fac*-(CO)<sub>3</sub>ReX,<sup>4</sup> and M<sub>2</sub>(carboxylate)<sub>2</sub> units<sup>5</sup> have been utilized to construct metallosupramolecular assemblies that have not only exhibited interesting structures but also shown promises for applications in catalysis,<sup>6</sup> chemical sensing,<sup>7</sup> and selective inclusion of guest molecules.<sup>8</sup> Despite the importance of asymmetric catalysis in the production of chiral compounds,<sup>9</sup> there have been few reports on the design of chiral metallosupramolecular assemblies.<sup>10</sup> 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.<sup>11</sup> We have recently reported a chiral molecular square that is capable of enantioselective sensing of chiral amino alcohols via fluorescence quenching.<sup>10a</sup> We report here the self-assembly and characterization of the first chiral organometallic triangles [*cis*-(PEt<sub>3</sub>)<sub>2</sub>Pt(L<sub>1–4</sub>)<sub>3</sub>] (where L<sub>1–4</sub> is enantiopure 4,4'-bis(alkynyl)-1,1'-binaphthalene) and their applications in highly enantioselective diethylzinc additions to aldehydes to afford chiral secondary alcohols.<sup>12</sup>

Enantiomerically pure atropisomeric 6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl-4,4'-bis(acetylene) L<sub>1</sub> 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).<sup>10a</sup> Dimethoxy analogue L<sub>2</sub> and bis(*tert*-butyldimethylsilyl) analogue L<sub>3</sub> were similarly prepared, while dihydroxy analogue L<sub>4</sub> was prepared in quantitative yield by treating L<sub>3</sub> with tetra(*n*-butyl)ammonium fluoride (TBAF) in THF. All of these ligands have been characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR, UV-vis, circular dichroism (CD) spectroscopies, and high-resolution mass spectrometry.

Treatment of ligand L<sub>1–3</sub> with 1 equiv of *cis*-Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> 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<sub>4</sub> with 1 equiv of *cis*-Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> 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 <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H},

Scheme 1



and <sup>31</sup>P{<sup>1</sup>H} 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 <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 1 exhibits a single peak at 3.51 ppm with a set of <sup>195</sup>Pt satellites (*J*<sub>Pt–P</sub> = 2282.8 Hz). There is also only one single set of signals for the acetylenic and aromatic carbon atoms in its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The aromatic region of <sup>1</sup>H NMR spectrum of 1 is deceptively simple with only three singlets, apparently a result of accidental overlap of H<sub>7</sub> and H<sub>8</sub> 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.<sup>13</sup> The  $\nu(\text{C}\equiv\text{C}-\text{H})$  stretches at  $\sim 3280\text{ cm}^{-1}$  in L<sub>1–4</sub> 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*<sub>3</sub> 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<sub>1–4</sub> show three major  $\pi \rightarrow \pi^*$  transitions at  $\sim 240$ ,  $\sim 300$ , 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  $\sim 300$  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<sub>1–4</sub> remains unshifted, while the lower energy transitions of L<sub>1–4</sub> 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.<sup>14</sup> A new band also appeared at  $\sim 202\text{ nm}$ , probably due to the *cis*-Pt-

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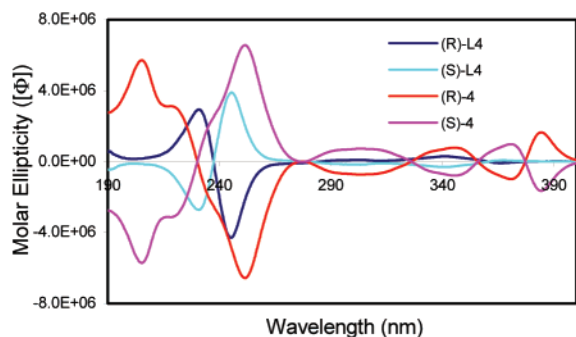


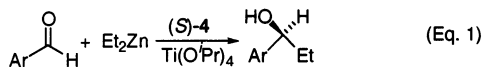
Figure 1. CD spectra of **L**<sub>4</sub> and **4** in acetonitrile.

Table 1. Diethylzinc Additions to Aldehydes Catalyzed by Ti(IV) Complexes of **4**<sup>a</sup>

Entry	Aldehyde	Temp	Conversion <sup>b</sup>	e.e. (%) <sup>c</sup>
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

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

(PEt<sub>3</sub>)<sub>2</sub> moieties. CD spectra of ligands **L**<sub>1–4</sub> exhibit one major bisignate band corresponding to naphthyl π → π\* transitions and two minor bands due to the other two lower energy π → π\* transitions (Figure 1). CD spectra of **1–4** exhibited these three bands similar to **L**<sub>1–4</sub>, 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(PEt<sub>3</sub>)<sub>2</sub> 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.<sup>15</sup> 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**<sub>1–4</sub> indicates that the dihedral angles between naphthyl rings in **1–4** are quite similar to those of **L**<sub>1–4</sub>.



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(O<sup>*i*</sup>Pr)<sub>4</sub> (eq 1).<sup>16</sup> 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**<sub>4</sub> 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(O<sup>*i*</sup>Pr)<sub>4</sub> 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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