

## Synthesis and Structure of Planar-chiral Cyclopentadienyl–Cobalt(II) Complexes: Three Different Chiralities in One Molecule

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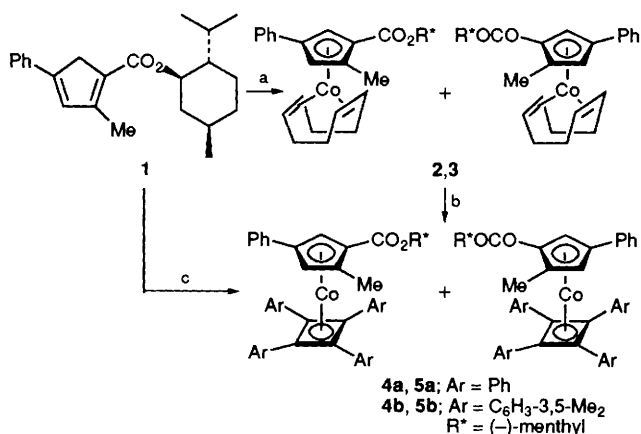
Diastereoisomerically pure planar-chiral cyclopentadienyl–cobalt complexes, **4** and **5**, were prepared by the reaction of a trisubstituted cyclopentadiene bearing a (–)-menthyl group with [CoCl(PPh<sub>3</sub>)<sub>3</sub>] and acetylenes, and removal of the menthyl group from **4a** and **5a** afforded the optically pure enantiomers, (+)- and (–)-**6**, respectively; an X-ray structural analysis of **4a** has revealed that there exist three different chiralities (planar, carbon-centred and helical) in one molecule.

Cyclopentadienyl–metal complexes play an important role in organic syntheses.<sup>1</sup> In the past few years, planar-chiral cyclopentadienyl–metal complexes have been regarded with much interest as mediators of enantioselective organic reactions and as a host–guest system.<sup>2</sup> Recently, we have synthesized enantiomerically pure planar-chiral ferrocenes and cyclopentadienyl–rhodium complexes by use of a trisubstituted cyclopentadiene bearing a removable chiral auxiliary, a (–)-menthyl group.<sup>3</sup> Here, we report the synthesis and structure of the first optically pure planar-chiral cyclopentadienyl–cobalt complexes,<sup>4</sup> which contain three different chiralities: planar, carbon-centred and helical.

We first synthesized planar-chiral cyclopentadienyl(cycloocta-1,5-diene)cobalt complexes using the chiral cyclopentadiene **1**(HL)<sup>3</sup> by a reported method<sup>5</sup> and obtained [Co(L)(cod)] as a mixture of two diastereoisomers **2** and **3** after purification by column chromatography (Scheme 1). Attempted optical resolution of the two diastereoisomers with preparative HPLC on silica failed, though complete resolution for the Rh analogues has already been achieved by the same method.

We then converted **2** and **3** to the [Co(L)(tetraphenylcyclobutadiene)] complexes **4a** and **5a** by treatment with diphenylacetylene (Scheme 1). The resultant diastereoisomers **4a** and **5a** were easily separated by column chromatography on silica. Isolated yields are summarized in Table 1 along with [α]<sub>D</sub> values. We also tried the direct synthesis of [Co(L)(tetraaryl-cyclobutadiene)] complexes starting from [CoCl(PPh<sub>3</sub>)<sub>3</sub>], the cyclopentadiene **1** and acetylenes, and isolated **4** and **5** in moderate yields (Scheme 1, Table 1).

The chiral auxiliary, the (–)-menthyl group, was removed from the diastereoisomeric complex **4a** by reaction with MeLi (Scheme 2), which afforded the enantiomeric complex, (+)-**6**, in good yield. Conversion of the diastereoisomer **5a** to (–)-**6** was accomplished similarly. The enantiomers thus obtained showed the same m.p.s and absolute values of [α]<sub>D</sub> (Table 2). The CD spectrum of (+)-**6** is the mirror image of that of (–)-**6**.



**Scheme 1** a, NaH, [CoCl(PPh<sub>3</sub>)<sub>3</sub>], cod, toluene–thf; b, PhC≡CPh, xylene reflux; c, NaH, [CoCl(PPh<sub>3</sub>)<sub>3</sub>], ArC≡CAr, toluene–thf (thf = tetrahydrofuran, cod = cycloocta-1,5-diene)

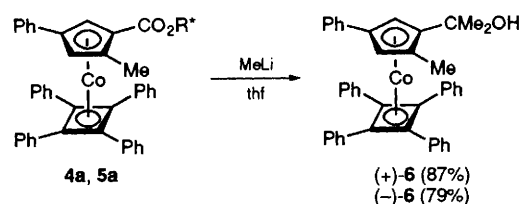
In the presence of a chiral shift reagent, (*R*)-(–)-2,2,2-trifluoro-1-(9-anthryl)ethanol<sup>6</sup> (fivefold excess), <sup>1</sup>H NMR analysis indicated (+)- and (–)-**6** to be a pair of pure enantiomers,<sup>†</sup> which provide the first examples of optically pure planar-chiral cyclopentadienyl–cobalt complexes.

In order to establish the absolute configuration of the complexes, we carried out an X-ray structural analysis for **4a**, knowing the absolute configuration of the (–)-menthyl group

**Table 1** Synthesis of planar chiral [Co(L)(Ar<sub>4</sub>C<sub>4</sub>)] complexes

Product	Ar	Path <sup>e</sup>	Yield (%)	[α] <sub>D</sub> (in CHCl <sub>3</sub> )
<b>4a</b>	Ph	A	28 <sup>a</sup>	+46 (c 0.502) <sup>c</sup>
<b>5a</b>			36 <sup>a</sup>	–5.6 (c 0.547) <sup>c</sup>
<b>4a</b>	Ph	B	27 <sup>b</sup>	
<b>5a</b>			35 <sup>b</sup>	
<b>4b</b>	3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	B	29 <sup>b</sup>	+93 (c 0.515) <sup>d</sup>
<b>5b</b>			32 <sup>b</sup>	–7.7 (c 0.521) <sup>d</sup>

<sup>a</sup> Isolated yield based on [Co(L)(cod)]. <sup>b</sup> Isolated yield based on [CoCl(PPh<sub>3</sub>)<sub>3</sub>]. <sup>c</sup> Temp. 16 °C. <sup>d</sup> Temp. 31 °C. <sup>e</sup> Path A, through step b; Path B, through step c in Scheme 1.



**Scheme 2**

<sup>†</sup> New compounds were characterized by elemental analyses and IR, <sup>1</sup>H NMR, and mass spectra.

**Selected data:** **4a:** <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 0.55–1.86 (m, 9H), 0.64 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 7.3 Hz, 3H), 1.80 (s, 3H), 4.57 (dt, *J* = 10.6, 4.3 Hz, 1H), 4.95 (d, *J* = 2.0 Hz, 1H), 5.58 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 6.9 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 2H) and 7.09–7.25 (m, 21H); MS (EI, 70 eV): *m/z* 752 (M<sup>+</sup>).

**5a:** <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 0.38 (q, *J* = 11.2 Hz, 1H), 0.70 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 3H), 0.87 (d, *J* = 7.3 Hz, 3H), 0.75–1.86 (m, 8H), 1.90 (s, 3H), 4.49 (dt, *J* = 10.6, 4.0 Hz, 1H), 4.99 (d, *J* = 2.0 Hz, 1H), 5.37 (d, *J* = 2.0 Hz, 1H), 6.92 (d, *J* = 6.9 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 2H) and 7.08–7.25 (m, 21H); MS (EI, 70 eV): *m/z* 752 (M<sup>+</sup>).

**(+)-6:** <sup>1</sup>H NMR (360 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.34 (s, 3H), 1.36 (s, 3H), 1.48 (s, 1H), 2.10 (s, 3H), 4.76 (d, *J* = 1.9 Hz, 1H), 5.17 (d, 1H, *J* = 1.9 Hz), 6.92–7.04 (m, 17H) and 7.51 (dd, *J* = 7.9, 1.6 Hz, 8H); MS (EI, 70 eV): *m/z* 628 (M<sup>+</sup>).

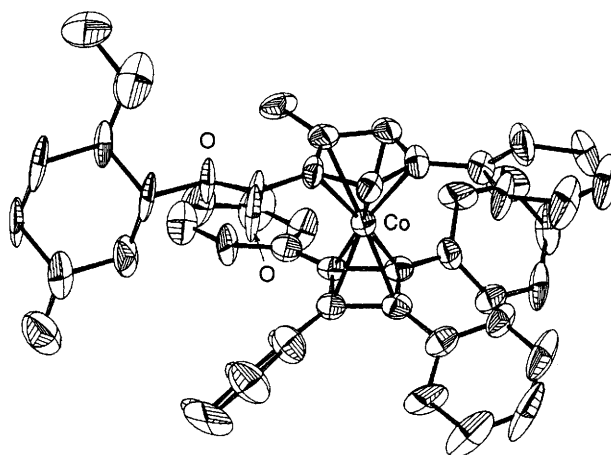
**(–)-6:** <sup>1</sup>H NMR (360 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.34 (s, 3H), 1.36 (s, 3H), 1.48 (s, 1H), 2.10 (s, 3H), 4.76 (d, *J* = 1.9 Hz, 1H), 5.17 (d, 1H, *J* = 1.9 Hz, 1H), 6.92–7.04 (m, 17H) and 7.51 (dd, *J* = 7.9, 1.6 Hz, 8H); MS (EI, 70 eV): *m/z* 628 (M<sup>+</sup>).

**Table 2** Selected physical data of (+)- and (-)-**6**

	M.p./°C	$[\alpha]_D^{15}$ (in C <sub>6</sub> H <sub>6</sub> )
(+)- <b>6</b>	172.0–172.5	+62.4 (c 0.535)
(-)- <b>6</b>	172.0–172.5	+62.0 (c 0.534)

on the cyclopentadienyl ligand. Fig. 1 depicts an ORTEP drawing of the molecular structure of **4a**.<sup>‡</sup> The configurations of the cyclopentadienyl and cyclobutadiene ligands around cobalt are essentially the same as those found for achiral [M( $\eta$ -C<sub>5</sub>H<sub>5</sub>) (cyclobutadiene)] (M = Co, Rh) complexes.<sup>7</sup> The absolute configuration of **4a** (around the L–M moiety) has been determined to be *S* based on the configuration of the (-)-menthyl group. The crystallographic analysis showed that **4a** has an interesting structure, in which the four phenyl groups on the cyclobutadiene ring are twisted in only one direction about their bonds to the cyclobutadiene ring, forming a unique four-blade windmill arrangement. This windmill unit has no asymmetric carbon atom but induces a helical chirality (point group: *D*<sub>4</sub>). The absolute configuration of the windmill moiety has been determined to be *P* based on the (-)-menthyl group. In the molecular structure of **4a**, the location of the menthyl group between the two phenyl groups on the C<sub>4</sub> ring implies that the helical chirality may be controlled remotely by the (-)-menthyl group on the cyclopentadienyl ligand. Further work is now in progress to ascertain the origin of the stereocontrol.

To our knowledge, diastereoisomers **4** and **5** are not only first optically pure planar-chiral cyclopentadienyl–cobalt complexes but also the first compounds containing three different

**Fig. 1** ORTEP drawing of the molecular structure of **4a**

chiralities: planar (L–M moiety), carbon-centred [(–)-menthyl group] and helical (Ph<sub>4</sub>C<sub>4</sub> moiety).

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## References

- 1 S. G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis*, Pergamon, Oxford, 1982.
- 2 R. L. Halterman, *Chem. Rev.*, 1992, **92**, 965, and references therein; T. Hayashi, A. Yamamoto, M. Hojo, K. Kishi, Y. Ito, E. Nishioka, H. Miura and K. Yanagi, *J. Organomet. Chem.*, 1989, **370**, 129; R. C. Pettey and C. I. Milberg, *Tetrahedron Lett.*, 1989, **30**, 5085.
- 3 M. Uno, K. Ando, N. Komatsuzaki and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1992, 964.
- 4 Related chiral cyclopentadienyl–cobalt complexes have been reported, but not yet optically resolved: N. E. Murr and E. Laviron, *Can. J. Chem.*, 1976, **54**, 3357; R. Boese, D. Bläser, R. L. Halterman and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 553.
- 5 Y. Wakatsuki and H. Yamazaki, *Inorg. Synth.*, 1989, **26**, 189.
- 6 W. H. Pirkle, D. L. Sikkenga and M. S. Pavlin, *J. Org. Chem.*, 1977, **42**, 384.
- 7 G. G. Cash, J. F. Helling, M. Mathew and G. J. Palenik, *J. Organomet. Chem.*, 1973, **50**, 277; M. D. Raush, E. F. Tokas, E. A. Mintz, A. Clearfield, M. Mangion and I. Bernal, *J. Organomet. Chem.*, 1979, **172**, 109.

<sup>‡</sup> Crystal data for **4a**: C<sub>51</sub>H<sub>49</sub>O<sub>2</sub>Co, *M* = 752.88, crystal dimensions 0.3 × 0.2 × 0.25 mm, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 18.602(10), *b* = 15.629(3), *c* = 13.893(3) Å, *V* = 4039 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.239 g cm<sup>-3</sup> (*D*<sub>m</sub> = 1.239 g cm<sup>-3</sup>), *F*(000) = 398, Mo–K $\alpha$  radiation with  $\lambda$  = 0.7107 Å,  $\mu$ (Mo–K $\alpha$ ) = 4.85 cm<sup>-1</sup>. 5461 reflections were collected at 20 °C on a Rigaku AFC-5FOS four-circle diffractometer (graphite-monochromated Mo–K $\alpha$  radiation) in the  $\omega$ –2 $\theta$  scan mode to  $2\theta_{\max}$  = 55°. The structure was solved by direct methods (MULTAN 80; Rigaku RASA system on FACOM S-3500) and refined to *R* = 0.051, *R*<sub>w</sub> = 0.057 for 3643 independent reflections [*F* > 3 $\sigma$ (*F*)]. The absolute configuration was determined based on that of the (-)-menthyl group on the cyclopentadienyl ring of **4a**.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.