Freezing Bond Rotation by a Pin in Cyclopentadienyl(cyclobutadiene)cobalt(I) Complexes. A New Type of Atropisomerism

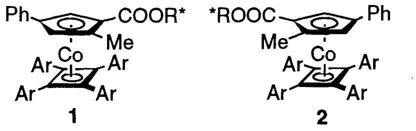
Mitsunari Uno, Kazuhiko Shirai, Katsuhiro Ando, Nobuko Komatsuzaki, Takanori Tanaka, Masami Sawada, and Shigetoshi Takahashi*
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567

(Received September 19, 1994)

The X-ray crystallographic and CD spectral analyses of $Cp^1Co(C_4Ar_4)$, **1** and **2**, reveal that the (–)-menthyl group on a C5 ring restricts the free rotation of single bonds between C4 ring and phenyl groups even in solution and induces a helical chirality on the C_4Ar_4 moiety; complexes **1~4** provide the new type of atropisomerism originating from freezing bond rotation by a pin stuck from the C5 ring into a four-blade windmill on the C4 ring.

Atropisomerism is referred to as an isomerism caused by freezing internal free rotation about a single bond in a molecule.[1] Since the discovery of the stable isomers due to restricted rotation,[2] numerous examples of the atropisomers have been reported.[3, 4] Most of them are related to biphenyl derivatives bearing at least one sterically hindered substituent, which works on the restriction of rotation, at a position neighbouring a pivot bond. In this paper we describe the new type of atropisomerism originating from freezing bond rotation by a pin in cyclopentadienyl(cyclobutadiene)cobalt complexes.[5]

Recently we have reported the first example of optically pure planar-chiral cyclopentadienyl-cobalt complexes $Cp^1Co(C_4Ar_4)$, **1** and **2** (Scheme 1).[6] The crystallographic analysis has revealed that **1a** has not only a planar (Cp^1-M moiety) and a carbon-centered [(–)-menthyl group] chirality but also a helical chirality which is induced by a four-blade windmill constructed with the four phenyl groups on a C4 ring. In order to seek the origin of the helical chirality, we have now carried out an X-ray crystallographic analysis for **2** and Circular-dichromism (CD) spectral analyses for **1**, **2**, and related complexes.



a: Ar=Ph **b**: Ar=3,5-$Me_2C_6H_3$ **c**: Ar=4-ClC_6H_4
R* = (–)-menthyl

Scheme 1.

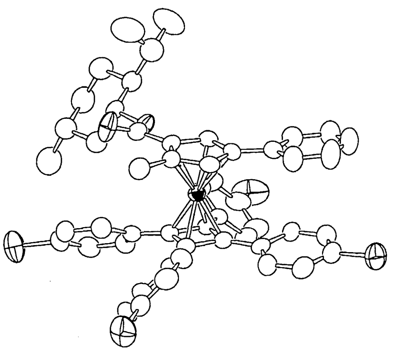
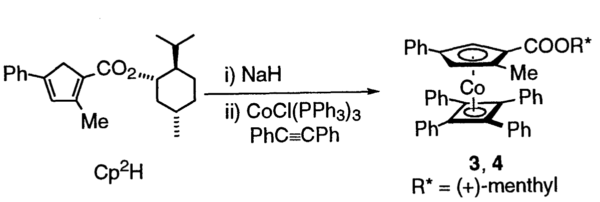


Figure 1. Molecular structure of **2c**.

Unfortunately single crystals of **2a** suitable for an X-ray crystallographic analysis were not grown, but good crystals of **2c** were obtained. Diastereomerically pure **2a** and **2c** clearly show similar CD spectra which indicate that both have the same absolute stereochemistry. The X-ray analysis informs that **2c** has also three different chiralities in a molecule and the (–)-menthyl group is located between two phenyl groups of the windmill as found for **1a** (Figure 1).[7] Bond distances and angles within **2c** are similar to those of **1a** except the orientation of the carbonyl group on a C5 ring. The absolute stereochemistries of planar (Cp^1-M moiety) and helical (C_4Ar_4 moiety) chirality have been determined to be 1*R* and *P*, respectively, based on the configuration of the (–)-menthyl group. As expected, the former configuration, 1*R*, is opposite to, whereas the latter, *P*, is the same as that of **1a**. These facts indicate that the menthyl group acts as a pin stuck into the C_4Ph_4 moiety from the C5 ring, which restricts the internal rotation of single bonds between C4 ring and phenyl groups, resulting in the induction of a helical chirality of the C_4Ph_4 in solid state.

CD spectral analyses have provided significant information regarding the structures of **1a** and **2a** in solution. The CD curve of **1a** is quite different from that of **2a** though a pair of the diastereomers of related $Cp^1Rh(cod)$ complexes,[8] which have planar and central chiralities but not a helical chirality, show a pair of symmetrical CD curves. (Figure 2) However, the enantiomer (+)-**5** derived from **1a** and the other, (–)-**5**, derived from **2a** show a pair of obviously symmetrical CD curves like those of $Cp^1Rh(cod)$ complexes, clearly indicating that the helical chirality found for **1a** and **2a** in solid state must be held even in solution and removal of the pin (menthyl group) from a cyclopentadienyl ligand resulted in loss of the restricted rotation around pivot bonds on a C_4Ph_4. In the ^1H NMR spectra of **1a** and **2a**, resonances due to one of the two methylene protons on the C6 position of a (–)-menthyl group appeared at δ 0.57 and 0.38, respectively, also supporting the postulated structure in solution. If the helical chirality is originated from freezing bond rotation by the menthyl group even in solution, the CD curves of complexes **3** and **4** having a (+)-menthyl group should be the same as the mirror image of those of **1** and **2**, respectively, as a result that they form a pair of enantiomers in respect of all the absolute stereochemistries found in the complexes. Thus, $Cp'Co(C_4Ph_4)$ complexes having a (+)-menthyl group have been synthesized from Cp^2H (Scheme 2).[9]



Scheme 2.

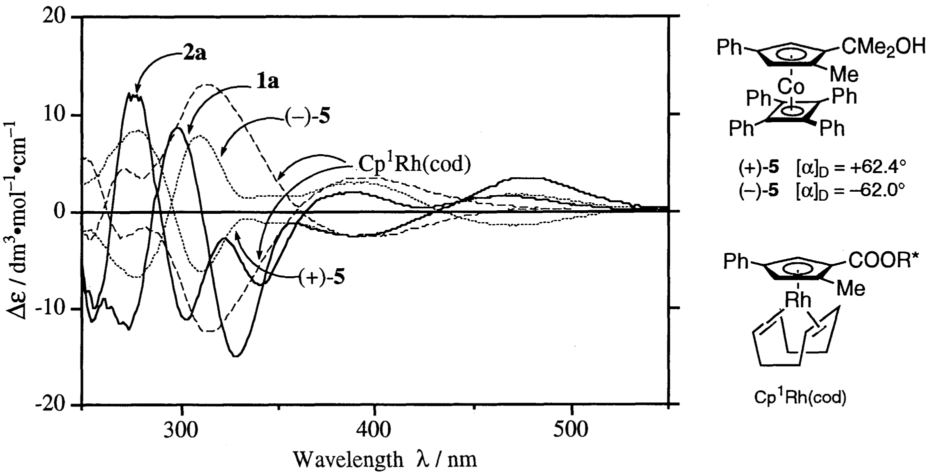


Figure 2. CD spectra of **1a**, **2a**, a pair of diastereomeric $Cp^1Rh(cod)$ complexes (in $CHCl_3$), and a pair of enantiomer (+)- and (–)-**5** (in Hexane).

Results are summarized in Table 1 along with their melting points and $[\alpha]_D$ values. As predicted, **3** showed the symmetrical CD curve to that of **1a**. In addition, **3** and **1a** show the same melting points and the absolute values of $[\alpha]_D$, indicating **3** and **1a** to be a pair of enantiomers. The same relation between **4** and **2a** was also observed.

From the standpoint of freezing the rotation about the single bonds between the C4 ring and the phenyl groups, the helical chirality induced by four phenyl groups offers the new type of atropisomerism. In this case, there are no sterically hindered groups neighbouring a pivot bond, but the menthyl group on the C5 ring acts as a pin which restricts the free rotation of a pivot bond and governs the absolute stereochemistry of the atropisomers.

This work was supported by Grant-in-Aid for Scientific Research No. 04640581 from Ministry of Education, Science and Culture.

Table 1. Synthesis of $Cp^2Co(C_4Ph_4)$ complexes.

Product	Yield / %^{a}	M. p. (°C)	$[\alpha]_D$ (deg.)^b (CHCl$_3$)
3	22	225.0 ~ 225.5	– 45.1 (*c* 0.537)
4	25	188.0 ~ 188.5	+ 8.9 (*c* 0.643)
1a^b	27	225.2 ~ 225.8	+ 44.4 (*c* 0.543)
2a^b	35	187.8 ~ 188.5	– 9.3 (*c* 0.710)

[a] Isolated yields based on $CoCl(PPh_3)_3$. [b] Temp 27 °C. [c] Previously reported.[6]

References and Notes

1 R. Kuhn in "Molekulare Asymmetrie. In Stereochemie" ed by H. Freudenberg, Franz Deutike, Leipzig-Wien (1933), p.803-824.

2 G. H. Christie and J. Kenner, *J. Chem. Soc.*, **121**, 614 (1922)

3 M. Oki, *Top. Stereochem.*, **14**, 1 (1983) and references therein.

4 Some recent reports. N. Nishino, T. Sakamoto, H. Kiyota, H. Mihara, T. Yanai, and T. Fujimoto, *Chem.. Lett.* 1993, 279; Y.-H. Lai, S.-Y. Wong, and D. H.-Y. Chang, *Tetrahedron*, **49**, 669 (1993); N. Harada, H. Ono, H. Uda, M. Parveen, N. U.-D. Khan, B. Achari, and P. K. Dutta, *J. Am. Chem. Soc.*, **114**, 7687 (1992); T. Kitamura, K. Harano, and T. Hisano, *Chem. Pharm. Bull.*, **40**, 2255 (1992).

5 Similar metallocenic chirality has been reported, but they show fluxional behavior in solution: L. Li, A. Decken, B. G. Sayer, M. J. McGlinchey, P. Brégaint, J.-Y. Thépot, L. Toupet, J.-R. Hamon, and C. Lapinte, *Organometallics*, **13**, 682 (1994) and references therein.

6 M. Uno, K. Ando, N. Komatsuzaki, T. Tanaka, M. Sawada, and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, **1993**, 1549; M. Uno, K. Ando, N. Komatsuzaki, T. Tsuda, T. Tanaka, M. Sawada, and S. Takahashi, *J. Organomet. Chem.*, **473**, 303 (1994).

7 Crystal data for **2c**: $C_{51}H_{45}Cl_4O_2Co$, M = 890.66, crystal dimensions 0.5 x 0.5 x 0.4 mm, orthorhombic, space groupe $P2_12_12_1$, a = 17.133(2), b = 29.948(5), c = 8.6422(7) Å, V = 4434 Å^3, Z = 4, D_C = 1.334 g cm^{-3}, Mo-Kα (graphite monochromated) radiation with λ = 0.7107 Å, μ(Mo-Kα) = 6.67 cm^{-1}. 7392 reflections were collected at 20 °C on a Rigaku AFC-5FOS four-circle diffractometer in the ω–2θ scan mode to $2\theta_{max}$ = 60°. The structure was solved by Patterson techniques and refined by full-matrix least squares to give R = 0.030, R_w = 0.038 for 3172 independent reflections [I > 3σ(I)]. Absolute stereochemistries were determined based on the the (–)-menthyl group on the cyclopentadienyl ring of **2c**.

8 M. Uno, K. Ando, N. Komatsuzaki, and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, **1992**, 964.

9 The new compounds were characterized by elemental analyses and IR, ^{1}H NMR, and Mass spectra.