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Highly selective induction of metal-centered chirality in the ligand exchange reaction of planar-chiral cyclopentadienyl–ruthenium complex bearing an anchor phosphine ligand†

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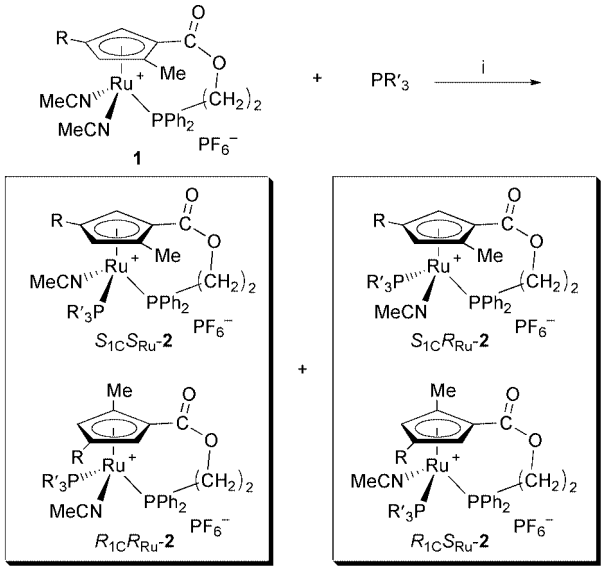
Treatment of planar-chiral cyclopentadienyl–phosphine ruthenium complexes with phosphine and phosphite induces metal-centered chirality with a high stereoselectivity (≥99 % de).

Planar-chiral cyclopentadienyl (Cp) complexes generated by coordination of unsymmetrically substituted Cp ligands to metal atoms have attracted much attention as novel asymmetric catalysts.[1] Although planar-chiral Cp complexes of early transition metals have been applied to asymmetric reactions with high selectivities, limited numbers of studies on such types of complex involving late transition metals are found in the literature. We have been investigating the synthesis, optical resolution and properties of planar-chiral organometallic complexes of Group 8 metals with trisubstituted Cp ligands.[2] Recently we prepared planar-chiral Cp–phosphine ruthenium complexes **1**,[3] which may serve as a good asymmetric environment around the ruthenium atom to prevent the rotation of the trisubstituted Cp ring by an anchor phosphine.[4] Now we examined the efficiency of the planar-chiral Cp–phosphine ligand on the induction of metal-centered chirality since the control of stereochemistry at a metal center is very important to develop highly enantioselective reaction using three-legged piano-stool complexes.[5]

Significant numbers of attempts to induce metal-centered chirality in three-legged piano-stool complexes have been found in the literature.[6] However, successive examples of the control of metal-centered chirality with a high selectivity are still limited. Very recently, with planar-chiral Cp and indenyl Rh and Ir complexes having anchor phosphine ligands it has been shown that the metal-centered chirality is induced by oxidative addition to the metal with high stereoselectivities.[7] Herein we report the thermodynamically or kinetically controlled induction of metal-centered chirality in the ligand exchange reactions of planar-chiral Cp–phosphine Ru complexes with various phosphines and phosphites.

Treatment of complex **1a** with 1.1 equiv. of PPh_3 in acetone at room temperature resulted in the replacement of one of the two MeCN ligands to give complex **2a** in quantitative yield. Resulting complex **2a** contained two diastereomers, each of which consists of a pair of enantiomers when racemic **1a** was used as the starting material (Scheme 1). Thus, the stereoselectivity at a chiral metal center was appraised by the ratio of the major diastereomer (**2a-1**) to the minor one (**2a-2**). ^1H and ^{31}P NMR spectra of **2a** clearly showed that the diastereoselectivity was 52% de. Fortunately, single crystals of **2a-1** were able to be grown in a CH_2Cl_2–ether solution of a mixture of the two diastereomers. The stereochemistry of **2a-1** was unequivocally identified by X-ray crystallography to be $S_{1C}S_{Ru}$/$R_{1C}R_{Ru}$ as shown in Fig. 1.‡

The stereoselectivity was then examined for the reactions of **1a**–**1c** with phosphines and phosphites (Table 1), and it was found that the selectivity depends upon the steric bulkiness of incoming phosphines and phosphites, and of the substituents on the Cp group. In the reactions with bulky phosphines, such as PPh_3 and PBu_3, the selectivities were higher than those with smaller ones such as PMe_3. The reaction of complex **1c** having a *t*-butyl group on the Cp ring gave products with a high selectivity relative to those for complexes **1a** and **1b**. Thus, the reactions of **1c** with bulky phosphines and phosphites (entries 11, 12 and 14) produced single diastereomers exclusively (> 99% de). The X-ray analyses of major products **2d-1**, **2f-1**, **2h-1**, **2m-1**, **2n-1** and **2o-1** revealed that all of them have the same stereochemistry as that of **2a-1**.†‡§ Similar reactions of planar-chiral Ru complexes **3** involving a $P(OMe)_3$ ligand instead of an anchor phosphine one were performed (Scheme 2, Table 2). Although the yields of products **4** were high, the



Scheme 1 *Reagents and conditions*: i, acetone, room temp., 3 h.

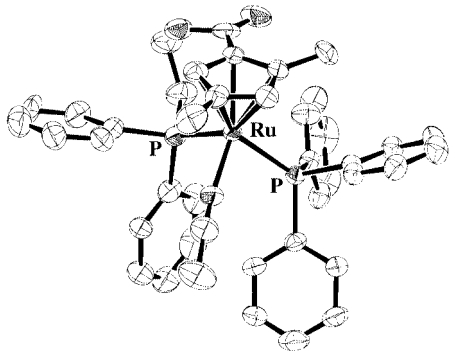


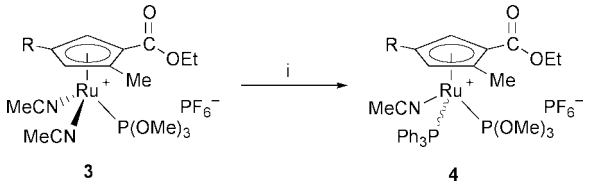
Fig. 1 Molecular structure of complex **2a-1**·$2CH_2Cl_2$. Hydrogen atoms, a counter anion and a solvent molecule are omitted for clarity.

† Electronic supplementary information (ESI) available: crystal data and ORTEP diagrams for complexes **1a**, **2d-1**, **2f-1**, **2h-1**, **2m-1**, **2n-1** and **2o-1**. See http://www.rsc.org/suppdata/cc/b0/b009412i/

Table 1 Reactions of complexes **1a**–**1c** with phosphines and phosphites

Entry	Complex	PR'_3	Product	Yield (%)[a]	% de[a]
1	**1a** (R = Me)	PPh_3	**2a**	100	52[b]
2	**1a**	PBu_3	**2b**	100	92
3	**1a**	PMe_3	**2c**	100	64
4	**1a**	$P(OPh)_3$	**2d**	100	38[b]
5	**1a**	$P(OMe)_3$	**2e**	100	40
6	**1b** (R = Ph)	PPh_3	**2f**	100	80[b]
7	**1b**	PBu_3	**2g**	96	86
8	**1b**	PMe_3	**2h**	100	46[b]
9	**1b**	$P(OPh)_3$	**2i**	100	42
10	**1b**	$P(OMe)_3$	**2j**	100	44
11	**1c** (R = Bu^t)	PPh_3	**2k**	91	> 99
12	**1c**	PBu_3	**2l**	100	> 99
13	**1c**	PMe_3	**2m**	100	70[b]
14	**1c**	$P(OPh)_3$	**2n**	100	> 99[b]
15	**1c**	$P(OMe)_3$	**2o**	96	82[b]

[a] Determined by ^{1}H and ^{31}P NMR spectroscopy. [b] The structures of major products were determined by X-ray crystallography.



Scheme 2 *Reagents and conditions*: i, 1.1 PPh_3, acetone, room temp., 3 h.

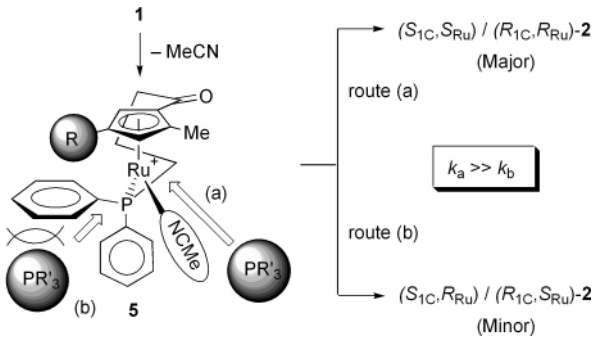
Table 2 Reactions of complexes **3a**–**3c** with phosphines

Entry	Complex	Product	Yield (%)[a]	% de[a]
1	**3a** (R = Me)	**4a**	92	28
2	**3b** (R = Ph)	**4b**	100	2
3	**3c** (R = Bu^t)	**4c**	100	34

[a] Determined by ^{1}H and ^{31}P NMR spectroscopy.

diastereoselectivities were very low (< 34% de) relative to those of **2**, suggesting that the anchor phosphine ligand has an important role in control of the stereochemistry at the metal center.

It should be noted that complexes **2a-1** and **2f-1** slowly isomerized into minor isomers **2a-2** and **2f-2**, respectively, in acetone at room temperature. For example, diastereomerically pure complex **2a-1** was converted into a mixture of complexes **2a-1** and **2a-2** in a 74:26 ratio (48% de), which is almost the same diastereoexcess as that observed for the reaction of **1a** with PPh_3. Since easy replacement of the MeCN ligands in **2a-1** and **2f-1** with CD_3CN was confirmed by means of ^{1}H NMR, the selectivities in these cases must be determined by the thermodynamic stability of the products. On the other hand, no epimerization at a metal center as well as no exchange of MeCN with CD_3CN were observed in other major products **2-1** in solution. These results strongly suggest that the selectivities of products **2**, except for **2a** and **2f**, were controlled kinetically. The kinetic preference of $S_{1C}S_{Ru}/R_{1C}R_{Ru}$ isomers to $S_{1C}R_{Ru}/R_{1C}S_{Ru}$ ones can be reasonably explained considering the stereochemistry of intermediate **5** as shown in Scheme 3. Ligand exchange reactions would proceed *via* unsaturated species **5**, which is generated by dissociation of MeCN from **1**. Coordination of incoming phosphines or phosphites from side (a) gives ($S_{1C}S_{Ru}/R_{1C}R_{Ru}$)-**2**, while coordination from side (b) produces ($S_{1C}R_{Ru}/R_{1C}S_{Ru}$)-**2**. The structures of planar-chiral ruthenium complexes with Cp–phosphine ligands including starting complex **1a**‡ clearly show that the attack of phosphines to the ruthenium center receives steric hindrance caused by the equatorial phenyl group and the substituent (R) on the Cp group. Thus, the attack from side (a) must be faster than that from side



Scheme 3

(b), resulting in the selective formation of ($S_{1C}S_{Ru}/R_{1C}R_{Ru}$)-**2**. This explanation is in good agreement with the steric influence of incoming phosphines and the substituents on the Cp group upon the selectivity of the reactions (*vide supra*).

In summary, we have disclosed here the first example of the kinetic control of metal-centered chirality by planar-chirality of the Cp group in the three-legged piano-stool complexes. Since the resulting complexes are conformationally stable, they may be applicable to novel asymmetric catalysts.

Notes and references

‡ *Crystal data* for complex **2a-1**·$2CH_2Cl_2$: $C_{44}H_{44}Cl_4F_6NO_2P_3Ru$, M = 1068.63, triclinic, $P\bar{1}$ (no. 2), a = 11.480(3), b = 19.232(5), c = 11.334(3) Å, α = 98.40(2), β = 107.45(2), γ = 80.66(2)°, V = 2342(1) Å^3, Z = 2, D_c = 1.515 cm^{-3}, μ(Mo-Kα) = 7.26 cm^{-1}, $2\theta_{max}$ = 55°, −50 °C, R (R_w) = 0.075 (0.137) for 550 parameters against 9502 reflections with I > 3.0σ(I) out of 11 004 unique reflections (R_{int} = 0.019), GOF = 1.53.

CCDC 147977–84. See http://www.rsc.org/suppdata/cc/b0/b009412i/ for crystallographic files in .cif or other electronic format.

§ In the reaction with PBu_3 and PMe_3, the assignments of configuration at a metal center (R_{Ru} or S_{Ru}) in resulting complexes **2b**, **2c**, **2g**, **2h**, **21** and **2m** are reversed relative to those of other complexes with the same conformation due to the change of the priorities of the anchor phosphine ligand and the incoming P ligands. Thus, the stereochemistries of **2b-1**, **2c-1**, **2g-1**, **2h-1**, **2l-1** and **2m-1** are $S_{1C}R_{Ru}/R_{1C}S_{Ru}$ whereas those of other major products are $S_{1C}S_{Ru}/R_{1C}R_{Ru}$.

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