

Multiple ligand transfer to planar-chiral cyclopentadienylruthenium complexes inducing metal-centered chirality

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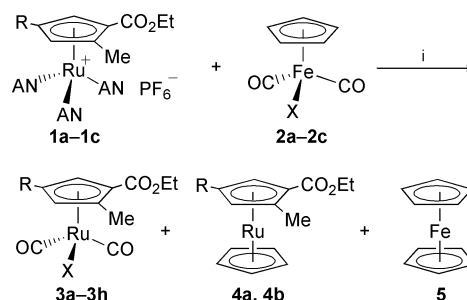
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Multiple ligand transfer reaction between planar-chiral cyclopentadienylruthenium complexes [Cp'Ru(AN)₃][PF₆] [(Cp' = 1-(CO₂Et)-2-Me-4-RC₅H₂, R = Me, Ph, Bu^t, AN = acetonitrile] and iron complexes CpFe(CO)(L)X (L = PMe₃, PPh₃; X = I, Br) results in formation of metal-centered chiral ruthenium complexes Cp'Ru(CO)(L)X with a diastereoselectivity (de) up to 68%.

Half-sandwich transition metal complexes CpML₃ with a three-legged piano stool structure are fascinating molecules owing to their potential as catalytic or stoichiometric mediators in precise organic syntheses and some of their chiral versions have recently been applied in asymmetric organic synthesis.¹ Although most chiral organometallic complexes have chiral organic groups on the ligands, chiral half-sandwich complexes can be formed in the absence of chiral ligands. While coordination of three different ligands to a metal generates a stereogenic center at the metal atom,² unsymmetrically substituted cyclopentadienyl ligands provide planar chirality.³ Studies on such chiral complexes give us fundamental and important information that serves for the development of novel asymmetric reactions.

We have been studying planar-chiral Ru complexes with trisubstituted cyclopentadienyl ligands.^{4,5} Recently we also reported a novel multiple ligand transfer reaction between [CpRu(L)(AN)₂][PF₆] [L = AN, CO, P(OMe)₃; AN = acetonitrile] and CpFe(CO)(L')X [L' = CO, PMe₃, PMe₂Ph, PMePh₂, PPh₃, P(OPh)₃; X = I, Br, Cl].⁶ Now, we have examined multiple ligand transfer reactions using planar-chiral cyclopentadienylruthenium complexes and found the induction of Ru-centered chirality by planar chirality on ligand transfer from Fe complexes.

Table 1 lists the results obtained from the reactions of the trisubstituted cyclopentadienyl ruthenium tris(acetonitrile) complex [Cp'Ru(AN)₃][PF₆] **1** with Fe complex **2** of the type CpFe(CO)₂X. Thus, treatment of Ru complex **1a** [Cp' = η⁵-1-(CO₂Et)-2,4-Me₂C₅H₂] with an equimolar amount of CpFe(CO)₂I **2a** in refluxing CH₂Cl₂ for 3 h produced a triple ligand transfer product, Cp'Ru(CO)₂I **3a**, in 76% yield (Scheme 1). Similar reactions of **1a** with CpFe(CO)₂Br **2b** and CpFe(CO)₂Cl **2c** gave Cp'Ru(CO)₂Br **3b** and Cp'Ru(CO)₂Cl **3c**, respectively. Ru complexes **1b** [Cp' = η⁵-1-(CO₂Et)-2-Me-



Scheme 1 Reagents and conditions: i, CH₂Cl₂, reflux, 3 h.

4-PhC₅H₂) and **1c** [Cp' = η⁵-1-(CO₂Et)-2-Me-4-Bu^tC₅H₂] also produced the corresponding dicarbonylruthenium complexes **3d-h**. The resulting Ru complex **3** was fully characterized by spectral analyses and X-ray crystallography.[†] The geometry around the metal atom is similar to those of analogous iron complexes (*R*)- and (*S*)-Cp'Fe(CO)₂I [Cp' = η⁵-1-(CO₂Men)-2-Me-4-PhC₅H₂; Men = (*l*)- or (*d*)-menthyl].⁷

When enantiomerically pure planar-chiral complexes (*R*)- and (*S*)-[Cp'Ru(AN)₃][PF₆] **1d** [Cp' = η⁵-1-(CO₂Adm)-2,4-Me₂C₅H₂; Adm = 2-adamantyl] were used as starting materials in the reaction with **2a**, the corresponding Ru complexes (*R*)- and (*S*)-Cp'Ru(CO)₂I **3i** were isolated, respectively, in an enantiomerically pure form [(*R*)-**3i**: [α]_D = +143° (c 0.100, CH₂Cl₂); (*R*)-**3i**: [α]_D = -142° (c 0.105, CH₂Cl₂)]. ¹H NMR experiments using a chiral shift reagent Eu(hfc)₃ unequivocally indicate that no racemization of the planar-chiral cyclopentadienyl ligand occurred in the multiple ligand transfer reactions.

Then, we investigated the influence of planar chirality of the cyclopentadienyl group on the stereochemistry at the Ru center of the triple ligand transfer product Cp'Ru(CO)(L)X **7** from the reaction with CpFe(CO)(L)X **6** (L = PMe₃, PPh₃; X = I, Br) (Scheme 2). As illustrated in Scheme 3, complex **7** contains two diastereomerically related pairs, each of which consists of enantiomers. Thus, the diastereoselectivity of metal-centered chirality affected by the planar chirality of cyclopentadienyl group was appraised by the diastereomer ratio of **7** (Table 2). Although other Ru complexes **3** and/or **4** were also produced as

Table 1 Triple ligand transfer reactions between [Cp'Ru(AN)₃][PF₆] **1** and CpFe(CO)₂X **2**

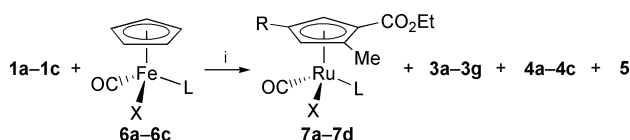
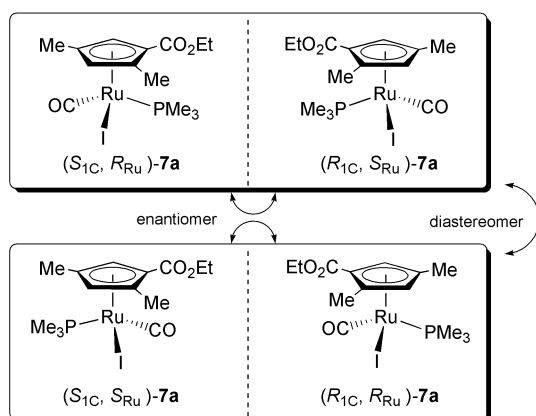
Run	Substrate		Isolated yields of products (%)			Recovery of 2
	Ru complex	Fe complex	Cp'Ru(CO) ₂ X 3 ^a	Cp'CpRu 4 ^a	Cp ₂ Fe 5 ^b	
1	1a (R = Me)	2a (X = I)	76 (3a)			21
2	1a	2b (X = Br)	91 (3b)			9
3	1a	2c (X = Cl)	47 (3c)	9 (4a)	43	
4	1b (R = Ph)	2a	71 (3d)		13	26
5	1b	2b	70 (3e)		26	
6	1b	2c	43 (3f)	7 (4b)	33	
7	1c (R = Bu ^t)	2a	72 (3g)		6	24
8	1c	2b	79 (3h)			

^a Yields are based on the starting Ru complex **1**. ^b Yields are based on the starting Fe complex **2**.

Table 2 Triple ligand transfer reactions between [Cp'Ru(AN)₃][PF₆] **1** and CpFe(CO)(L)X **6**

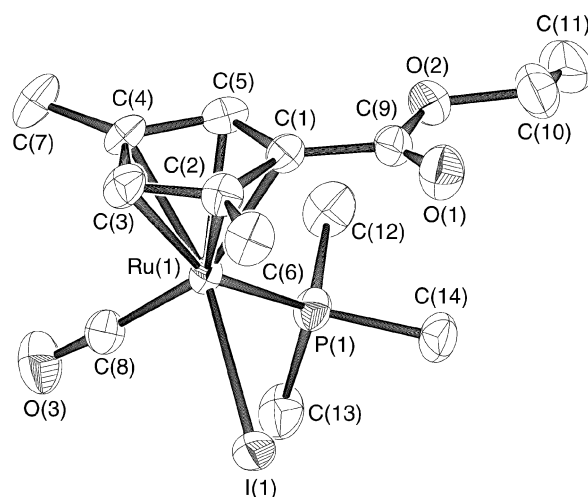
Run	Substrate		Isolated yields of products (%)				
	Ru complex	Fe complex	Cp'Ru(CO) ₂ X 7 ^a	Cp'Ru(CO) ₂ X 3 ^a	Cp'CpRu 4 ^a	Cp ₂ Fe 5 ^b	Recovery of 6
1	1a	6a (L = PMe ₃ , X = I)	49 (68) ^c (7a)	12 (3a)	6 (4a)	12	17
2	1a	6b (L = PPh ₃ , X = I)		35 (3b)	2 (4b)		24
3	1a	6c (L = PPh ₃ , X = Br)	12 (28) ^c (7b)	31 (3c)	12 (4c)	1	
4	1b	6a	36 (22) ^c (7c)	17 (3d)	2 (4a)	20	23
5	1c	6a	48 (40) ^c (7d)	18 (3g)		10	9

^a Yields are based on the starting Ru complex **1**. ^b Yields are based on the starting Fe complex **6**. ^c Parentheses indicate % de of **7** determined by ¹H and ³¹P NMR spectroscopy.

**Scheme 2** Reagents and conditions: i, CH₂Cl₂, reflux, 3 h.**Scheme 3** Stereoisomers of **7a**.

well as **7** in the reaction of **1** and **6**, they were easily separated by column chromatography on silica gel. Yields of products depended both on the substituents on the cyclopentadienyl group as well as the phosphine initially coordinated to Fe. Reactions with **6a** with PMe₃ gave desired complex **7** in moderate yields (runs 1, 4 and 5), while yields of **7** were low in the reactions with **6b** and **6c** having PPh₃ (runs 2 and 3). To our surprise, the best result (68% de) in the diastereoselectivity of **7** was observed in the reaction of **1a** having a small substituent (Me) on the cyclopentadienyl group with **6a** having a small phosphine ligand (PMe₃) (run 1). Reactions of **1b** and **1c** having a larger substituent (Ph or Bu^t) on the cyclopentadienyl group gave complexes **7c** and **7d** in 22 and 40% de, respectively (runs 4 and 5). Although asymmetric induction at a Ru center by a chiral organic group on the cyclopentadienyl ring has been attempted in the ligand exchange reaction of (η⁵-C₅H₄R*)Ru(CO)₂X (R* = neomenthyl) with phosphine and phosphite, the diastereoselectivities of products (η⁵-C₅H₄R*)Ru(CO)(PR₃)X were fairly low (up to 19% de).⁸

Fortunately single crystals of the major diastereomer selectively grew on recrystallization of a diastereomeric mixture of **7a** from Et₂O–hexane. As seen in Fig. 1 the molecular structure of the major diastereomer of **7a** was established by X-ray analysis to possess the configuration (R_{C1},S_{Ru})/(S_{C1},R_{Ru}).[†] Previously we also found the induction of metal-centered chirality by CO insertion into the Fe–C bond of planar-chiral Fe complexes giving Cp'Fe(CO)(PPh₃)(COMe) **8**.⁹ Facile isomerization of complex **8** around the metal center under the employed reaction conditions suggested that the selectivity of the resulting complex is controlled by thermodynamic factors. In contrast, no isomerization at a Ru center was observed for a CH₂Cl₂ solution of the major diastereomer of **7a**, isolated by recrystallization (*vide supra*), under reflux for 3 h. The reactions presented here provide the first induction of metal-centered

**Fig. 1** ORTEP diagram of (R_{C1},S_{Ru})/(S_{C1},R_{Ru})-**7a** (major diastereomer). Hydrogen atoms are omitted for clarity.

chirality in ligand transfer reactions. Further investigation focusing on the mechanism of asymmetric induction is now in progress.

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Notes and references

[†] Crystal data: for **3d**: C₁₇H₁₅IO₄Ru, *M* = 511.28, monoclinic, *P*1̄, *a* = 9.631(3), *b* = 11.246(3), *c* = 8.313(2) Å, α = 98.76(2), β = 100.410(8), γ = 93.71(3)°, *V* = 868.7(4) Å³, *Z* = 2, *D*_c = 1.954 g cm⁻³, μ(Mo–Kα) = 26.96 cm⁻¹, 6 < 2θ < 55°, *T* = –50 °C, *R* (*R*_w) = 0.029 (0.069) for 181 parameters vs. 3889 reflections with *I* > 3.0σ(*I*) out of 4122 unique reflections (*R*_{int} = 0.023), GOF = 1.35. For (R_{C1},S_{Ru})/(S_{C1},R_{Ru})-**7a**: C₁₄H₂₂IO₃PRu, *M* = 497.27, monoclinic, *P*2₁/n, *a* = 10.067(2), *b* = 9.951(2), *c* = 18.322(1) Å, β = 100.410(8)°, *V* = 1805.2(4) Å³, *Z* = 4, *D*_c = 1.830 g cm⁻³, μ(Mo–Kα) = 26.71 cm⁻¹, 6 < 2θ < 55°, *T* = –75 °C, *R* (*R*_w) = 0.037 (0.055) for 208 parameters vs. 3645 reflections with *I* > 3.0σ(*I*) out of 3990 unique reflections (*R*_{int} = 0.016), GOF = 1.35.

CCDC 182/1818. See <http://www.rsc.org/suppdata/cc/b0/b006458k/> for crystallographic files in .cif format.

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