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Communications

Enantiofacially Selective Olefin Coordination of α,β-Unsaturated Carbonyl Compounds to Chiral Bis(oxazolinyl)pyridineruthenium Fragments

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Summary: The reaction of [(p-cymene)$RuCl_2$]$_2$ and 2,6-bis(oxazolin-2-yl)pyridines (Pybox) in the presence of α,β-unsaturated carbonyl compounds as prochiral olefins gave η^2-olefin complexes as single conformations. From its NMR spectra and X-ray diffraction, these chiral (Pybox)$RuCl_2$ fragments not only discriminated the one enantioface (si-face) of the alkenes but also fixed the conformation of carbonyl moieties s-trans.

α,β-Unsaturated carbonyl compounds are widely used for organic synthesis because they have potentially reactive functions, a carbon−carbon double bond (C=C bond) and a carbon−oxygen double bond (C=O bond).[1] In terms of asymmetric synthesis, it is important that discrimination of the π-enantioface on the C=C bond or the C=O bond of substrates can be realized by certain chiral reagents or catalysts. Especially, prominent chiral Lewis acid complexes developed in recent years have been able to perfectly manipulate crucial selection of their π-enantioface by binding to the carbonyl oxygen.[2] Chiral transition metal complexes can mainly recognize the π-enantioface of C=C bonds by coordination accompanied with back-donation from the metal atoms.[3,4] However, strongly cationic transition metal complexes, such as some chiral rhenium complexes developed by Gladysz, can also capture the carbonyl groups just as Lewis acids.[5] Such a concept of transition metal Lewis acid complexes has been applied to asym-

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(2) Reviews: (a) Morrison, J. D. *Asymmetric Synthesis*; Academic Press: New York, 1984; Vol. 3B. (b) Noyori, R.; Kitamura, M. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1989; Vol. 5. (c) Bosnich, B. *Asymmetric Catalysis*; Martinus Nijhoff Publishers: Dordrecht, The Netherlands, 1986. For Lewis acid carbonyl complexation, see: (d) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256. (e) Shambayati, S.; Schreiber, S. L. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 1.

(3) Review: Gladysz, J. A.; Boone, B. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 550, and references therein.

(4) Recent representative papers: (a) Albano, V. G.; Demartin, F.; De Renzi, A.; Morelli, G. *Inorg. Chim. Acta* **1988**, *149*, 253. (b) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191. Pu, J.; Peng, T.-S.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2686. (c) Schmid, G.; Kilanowski, B.; Boese, R.; Blaser, D. *Chem. Ber.* **1993**, *126*, 899. (d) Cucciolito, M. E.; Jama, M. A.; Giordano, F.; Vitagliano, A.; de Felice, V. *Organometallics* **1995**, *14*, 1152. (e) Jedlicka, B.; Rulke, R. E.; Weissensteiner, W.; Fernandez-Galan, R.; Jalon, F. A.; Manzano, B. R.; Rodriguez-de la Fuente, J.; Veldman, N.; Kooijman, H.; Spek, A. L. *J. Organomet. Chem.* **1996**, *516*, 97. (f) Luecke, H. F.; Arndtsen, B. A.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 2517. (g) Quan, R. W.; Li, Z.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118*, 8156. (h) Erickson, L. E.; Hayes, P.; Hooper, J. J.; Morris, K. F.; Newbrough, K. F.; van Os, M.; Slangen, P. *Inorg. Chem.* **1997**, *36*, 284.

(5) (a) Quiros Mendez, N.; Mayne, C. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2323. (b) Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699.

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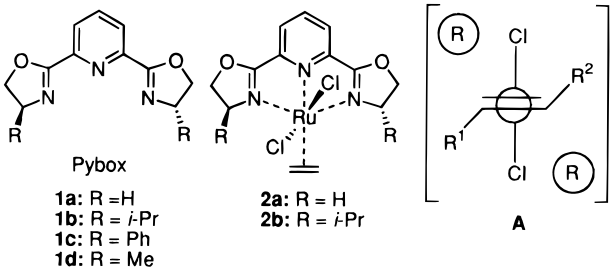
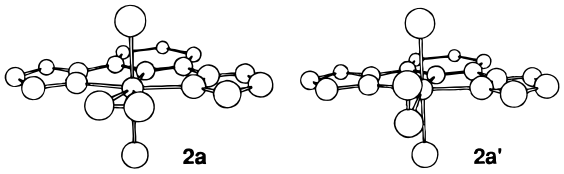
Chart 1



metric catalytic reactions.[1a,2c,6] In this situation, study of the coordination mode of α,β-unsaturated carbonyl compounds provides very important information to create new reaction systems and to elucidate reaction mechanisms. Very recently, as for enantiofacially selective coordination of simple olefins, Jacobsen disclosed chiral copper−olefin coordination.[4g]

We have recently reported that C_2-symmetric 2,6-bis-(2-oxazolin-2-yl)pyridines (Pybox) (**1**) are effective ligands for Ru(II)-catalyzed asymmetric cyclopropanation.[7] During the course of our studies on Ru-catalyzed cyclopropanation systems, in which chiral ethylene complex **2b** was used as a catalyst precursor, we successfully clarified the structure of nonchiral dihydroPybox (dH-Pybox) derived ethylene complex **2a** by X-ray analysis.[7b]



The ethylene moiety on **2a** is coordinated parallel to the Pybox plane and perpendicular to the Cl−Ru−Cl plane.[8] This result suggests that one enantioface (*si*-face) of substituted olefins could be discriminated by binding it to this Pybox−ruthenium (Pybox−Ru) fragment (**A**), Chart 1.[9] Now we wish to report the synthesis of several substituted olefins, such as α,β-unsaturated carbonyl compounds, -coordinated Pybox−Ru complexes, and the crystal structure of Me-Pybox-derived acrolein complex **8**.

At first, trans-substituted dimethyl fumarate complex **3** derived from Ph-Pybox was synthesized. To a stirred solution of $[(p\text{-cymene})RuCl_2]_2$[10] and dimethyl fumarate (2 equiv) in dichloromethane was added Ph-Pybox **1c**, and the mixture was stirred for 1 h at 25 °C under argon atmosphere. After the solvent was removed under reduced pressure, the residue was washed with ether−hexane (ca. 1:1) to remove an excess of the olefin and dissociated *p*-cymene, Scheme 1. The ^1H and ^{13}C NMR spectra of **3** showed a C_2-symmetric structure. The signals of olefinic protons and carbons of coordinated dimethyl fumarate appear at higher field than the uncomplexed (free) one (from δ 6.87 to 5.64 ppm in ^1H NMR and from δ 133.1 to 69.4 ppm in ^{13}C NMR). These results indicated that dimethyl fumarate is coordinated to the (Pybox)$RuCl_2$ fragment by the C=C bond; i.e., **3** is an η^2-olefin complex.[11] Even at a lower temperature (ca. −80 °C), complex **3** was the sole product observed. From the NOE spectra of complex **3**, 4−7% NOEs were observed between H_a and the aromatic protons of the phenyl substituents on the oxazoline rings of the Pybox ligand, while no NOEs were observed between H_a and H_b (Figure 1). Therefore, it can be concluded that one enantioface (*si*-face) of the alkene can be discriminated by using (*S*,*S*)-Pybox.

Scheme 1

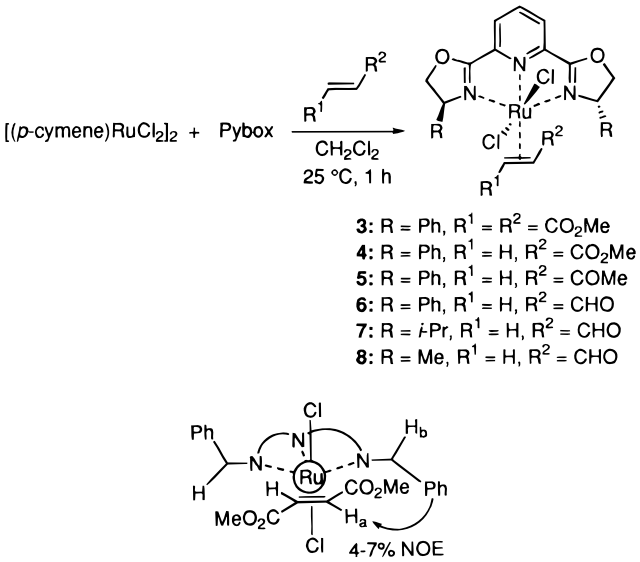


Figure 1.

The other (Pybox−Ru)(olefin) complexes **4**−**8** with monosubstituted α,β-unsaturated carbonyl compounds, such as methyl acrylate, methyl vinyl ketone, and acrolein, are synthesized and characterized in a similar manner (Table 1). In all of the experiments, the ^1H and ^{13}C NMR spectra of crude products **4**−**8**, with a single set of diastereotopic vinylic proton and carbon resonances present in the variable-temperature measurements (−80 to 25 °C), provide strong evidence for exclusive binding of one enantioface of the alkenes to the chiral (Pybox)$RuCl_2$ fragments. These results imply that these chiral (Pybox)$RuCl_2$ fragments not only discriminate the one enantioface of the alkenes but also fix the conformation of the carbonyl moieties either s-cis or s-trans.[12] Furthermore, these (Pybox)$RuCl_2$ frag-

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(7) (a) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223. (b) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247.

(8) Extended Hückel molecular orbital (EHMO) calculation of (dH-Pybox)$RuCl_2(C_2H_4$-0°) (**2a**) and (dH-Pybox)$RuCl_2(C_2H_4$-90°) (**2a′**) was carried out to show that isomer **2a** proved to be more stable than **2a′** by 1.48 eV (34.2 kcal/mol), see Supporting Information for input data for EHMO calculation.

(9) We recently reported propylene- and styrene-coordinated Pybox−Os complexes. The ^1H and ^{13}C NMR spectra of these complexes show a single set of diastereotopic vinylic proton and carbon resonances, see: Nishiyama, H.; Aoki, K.; Itoh, H.; Iwamura, T.; Kurihara, O.; Motoyama, Y. *Chem. Lett.* **1996**, 1071.

(10) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 223.

(11) Gladysz reported that chiral Cp*Re(NO)(PPh_3)(olefin) complexes exist in σ O=C, π O=C, and π C=C complex forms. These conformations are highly dependent on the reaction temperature and substitution patterns of the α,β-unsaturated carbonyl compounds, see: ref 5b.

(12) From the ab initio calculations of free (uncomplexed) acrolein, the s-trans conformation is preferred over the s-cis conformation. In the case of methyl acrylate, the s-cis/syn conformer is more stable than the s-trans/syn conformer, see: Loncharich, R. J.; Schwartz, R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14.

Table 1. Preparation of α,β-Unsaturated Carbonyl Compounds Coordinated to Pybox−Ru Complexes[a]

entry	complex	% yield[b]
1	(Ph-Pybox)$RuCl_2$(dimethyl fumarate) (**3**)	78[c]
2	(Ph-Pybox)$RuCl_2$(methyl acrylate) (**4**)	86
3	(Ph-Pybox)$RuCl_2$(methyl vinyl ketone) (**5**)	95
4	(Ph-Pybox)$RuCl_2$(acrolein) (**6**)	93
5	(*i*-Pr-Pybox)$RuCl_2$(acrolein) (**7**)	91
6	(Me-Pybox)$RuCl_2$(acrolein) (**8**)	96

[a] All reactions were carried out using 2 equiv of Pybox and 4 equiv of olefin based on $[(p\text{-cymene})RuCl_2]_2$ for 1 h under argon atmosphere at 25 °C. [b] Isolated yield by silica gel chromatography at −60 °C with CH_2Cl_2−acetone. [c] Based on the ^1H NMR.

ments can recognize the π-enantioface of alkenes despite the substituents on the Pybox ligands; even the Me group, which is the smallest substituent, can select the π-enantioface of alkenes perfectly. And these monosubstituted olefin complexes were stable enough to be purified by silica gel column chromatography at −60 °C with CH_2Cl_2−acetone as the eluent.[13]

Among the complexes **3**−**8**, the Me-Pybox-derived acrolein complex **8** could be crystallized and characterized by its X-ray analysis (Figure 2).[14] The C=C moiety of acrolein on **8** is coordinated by its *si*-face, parallel to the Pybox plane (ca. 4−8°), and the conformation of the carbonyl moiety is s-trans (torsion angle O3−C16−C15−C14 = 169(2)°). This s-trans conformation can be considered as a result of the dipolar repulsion between the carbonyl oxygen and the chloride atom at the apical position of the (Pybox)$RuCl_2$ fragments.[15] From the NOE spectra of **8**, the s-trans conformation of acrolein in the X-ray crystal structure is also present in solution. This preferential complexation is due to not the substituents on the Pybox ligand but the structure of the (Pybox)$RuCl_2$ fragment, since the conformation of acrolein, coordinated to nonsubstituted dH-Pybox complex **9**, is also s-trans. All of the NOE results are collected in Table 2.

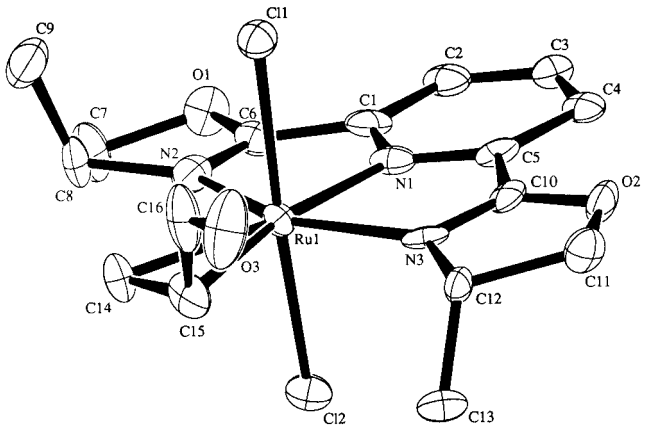
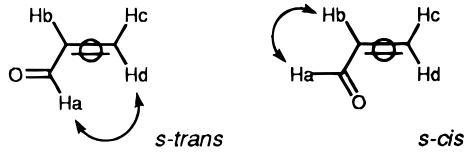


Figure 2. Molecular structure of (Me-Pybox)$RuCl_2$(η^2-acrolein) complex **8**.

Table 2. Summary of NOE Data for Acrolein Complexes[a]



	NOE (saturated/obsd, %)			
complex	H_a/H_b	H_a/H_d	H_d/H_a	H_b/H_a
8		3	13	
7	0	7	12	−5
9	4	−1	16	2

[a] In $CDCl_3$ (25 °C, TMS).

To our knowledge, using these (Pybox)$RuCl_2$ fragments is the first case demonstrating that one enantioface and conformation of α,β-unsaturated carbonyl compounds can be discriminated.

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Supporting Information Available: Text giving the experimental procedures for the synthesis of the olefin complexes and tables of crystal data and structure refinement, atomic coordinates, displacement parameters, and bond lengths and angles for **8** and input data of **2a** for EHMO calculation (18 pages). Ordering information is given on any current masthead page.

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(13) These α,β-unsaturated carbonyl compounds coordinated to the (Pybox)$RuCl_2$ fragments were slowly dissociated in solution at 25 °C.

(14) Crystal data of **6d**: $C_{16}H_{19}N_3O_3Cl_2Ru$, monoclinic, $P2_1$ (No. 4), a = 7.149(1) Å, b = 10.669(2) Å, c = 11.928(1) Å, V = 900.7(2) Å^3, β = 98.10(1)°, Z = 2. Of the 2350 reflections collected (Mo Kα, 2θ (max) = 54.9°, 300 K), 2184 were independent and 1245 were observed. R = 0.047 and R_w = 0.042. Selected bond distances (Å) and angles (deg): Ru(1)−N(1) 2.02(2), Ru(1)−N(2) 2.13(2), Ru(1)−N(3) 2.16(2), Ru(1)−C(14) 2.20(1), Ru(1)−C(15) 2.24(2), C(14)−C(15) 1.42(4), C(16)−O(3) 1.20(2), N(2)−Ru(1)−N(3) 152.5(6), Cl(1)−Ru(1)−Cl(2) 176.3(2).

(15) From the X-ray analysis of the (dmphen)PtCl($SnMe_2Cl$)(η^2-dimethyl fumarate) [dmphen = 2,9-Me_2-1,10-phenanthroline] complex, the conformation of the CO_2Me group facing the chloride was s-trans, while in the (dmphen)Pt(η^2-dimethyl fumarate) complex, which has no chloride at the apical position on Pt, the conformation of coordinated dimethyl fumarate was s-cis, see: Albano, V. G.; Castellari, C.; Monari, M.; De Felice, V.; Panunzi, A.; Ruffo, F. *Organometallics* **1996**, *15*, 4012.