The silyl complexes reported here, and others prepared similarly, should prove to be valuable in the characterization of Ln–Si bond reactivity. Initial reactivity studies indicate that these bonds are quite reactive. Both **1** and **2** react rapidly (≤5 min) with hydrogen (1 atm, benzene-d_6) to produce $[Cp^*_2LnH]_2$ and $SiH_2(SiMe_3)_2$, and with ethylene (1 atm, benzene-d_6) to produce polyethylene (by ^1H NMR spectroscopy). In the reactions with ethylene, all of **2** is consumed, but only 80% of **1**. Finally, **1** and **2** react much more rapidly with silanes than do the corresponding alkyls. For example, **1** reacts with $MesSiH_3$ (3 equiv, benzene-d_6) over 10 min at room temperature to afford $[Cp^*_2SmH]_2$, $SiH_2(SiMe_3)_2$, and $MesH_2SiSiH_2Mes$, while the analogous reaction of $Cp^*_2SmCH(SiMe_3)_2$ requires 10 min at 70 °C.

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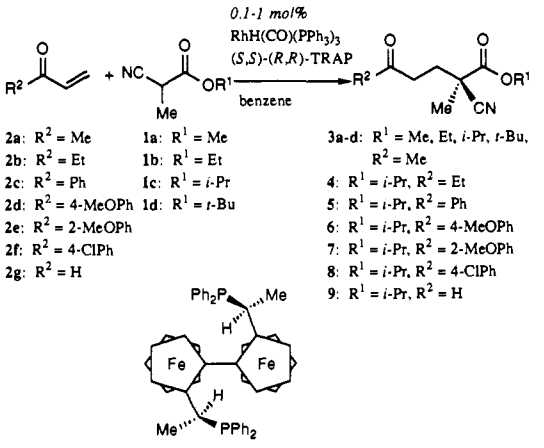
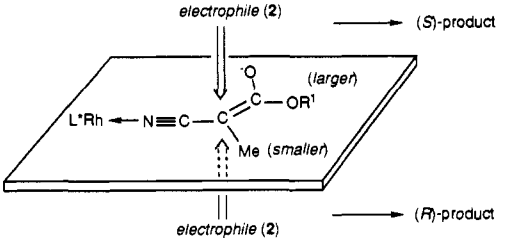
Supplementary Material Available: Experimental procedures and characterization data for **1** and **2** and tables of crystal, data collection, and refinement parameters, additional ORTEP drawings, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **1** (10 pages); listings of observed and calculated structure factors for **1** (9 pages). Ordering information is given on any current masthead page.

Scheme I



Scheme II



Catalytic Asymmetric Synthesis with Trans-Chelating Chiral Diphosphine Ligand TRAP: Rhodium-Catalyzed Asymmetric Michael Addition of α-Cyano Carboxylates

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The synthesis of well-designed chiral phosphine ligands has played a predominant role in the recent development of catalytic asymmetric synthesis promoted by transition metal complexes.[1] Recently, we designed and synthesized a trans-chelating chiral diphosphine ligand, 2,2″-bis[1-(diphenylphosphino)ethyl]-1,1″-biferrocene (abbreviated to TRAP), which possesses planar chiralities as well as stereogenic centers.[2–4] Herein, we wish to report a successful application of "TRAP" to transition metal catalyzed asymmetric synthesis, in which the rhodium complex prepared in situ from $RhH(CO)(PPh_3)_3$ and TRAP (0.1–1 mol %) was an effective catalyst for asymmetric Michael addition of α-cyano carboxylates (**1**) with vinyl ketones or acrolein (**2**) (Scheme I).[5] To the best of our knowledge, this is the first highly enantioselective Michael addition catalyzed by a chiral transition metal complex.[6,7]

Results are summarized in Table I. Enantioselectivities ranging from 83 to 89% were obtained for the reaction of **1c** with various vinyl ketones (**2a–f**) or acrolein (**2g**).[8,9] The enantioselectivity depends slightly on the structure of the ester group of **1** (entries 1–3, 5), with ispopropyl ester **1c** giving the highest selectivity.

(1) For review, see: (a) Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. (b) Noyori, R.; Kitamura, M. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1989; Vol. 5, p 115. (c) Brunner, H. *Synthesis* **1988**, 645.

(2) Sawamura, M.; Hamashima, H.; Ito, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 593.

(3) The trans geometry of $PdCl_2$(TRAP) and $PtCl_2$(TRAP) was confirmed by the NMR and molecular weight studies (ref 2). Recently, the X-ray crystal structure of $PdBr_2$(TRAP) has been determined, where TRAP chelates to the palladium in a P–Pd–P bite angle of 164.4°, and *trans*-RhCl(CO)(TRAP) has been synthesized from $[RhCl(CO)_2]_2$ and TRAP (unpublished results: Sawamura, M.; Hamashima, H.; Ito, Y.).

(4) It has been reported that a DIOXOP–rhodium complex can adopt trans geometry in the asymmetric hydrogenation of dehydroamino acids, but the ligand coordinates to Rh(III) as a tridentate ligand. See: (a) Brown, J. M.; Chaloner, P. A.; Descotes, G.; Glaser, R.; Lafont, D.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1979**, 611. (b) Descotes, G.; Lafont, D.; Sinou, D.; Brown, J. M.; Chaloner, P. A.; Parker, D. *Nouv. J. Chim.* **1981**, *5*, 167. Recently, Burk et al. have reported the synthesis of a series of multidentate chiral phosphorane ligands, some of which were shown to chelate to rhodium in a trans manner as tridentate ligands. See: (c) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Tetrahedron: Asymmetry* **1991**, *2*, 569.

(5) For the ruthenium-catalyzed aldol and Michael addition of activated nitriles, see: (a) Naota, T.; Taki, H.; Mizuno, M.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1989**, *111*, 5954. Recently, the Michael addition of cyanoacetate catalyzed by $RhH(CO)(PPh_3)_3$ has been reported. See: (b) Murahashi, S.-I.; Naota, T.; Maezaki, M. Presented at the 61th Annual Meeting of the Chemical Society of Japan, Yokohama, March 29–April 1, 1991, Paper 1C940. (c) Paganelli, S.; Schionato, A.; Botteghi, C. *Tetrahedron Lett.* **1991**, *32*, 2807.

(6) For catalytic asymmetric Michael addition, see: (a) Brunner, H.; Hammer, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 312. (b) Brunner, H.; Kraus, J. *J. Mol. Catal.* **1989**, *49*, 133. (c) Schionato, A.; Paganelli, S.; Botteghi, C.; Chelucci, G. *J. Mol. Catal.* **1989**, *50*, 1. (d) Botteghi, C.; Schionato, A.; Rosini, C.; Salvadori, P. *J. Mol. Catal.* **1990**, *63*, 155. (e) Botteghi, C.; Paganelli, S.; Schionato, A.; Boga, C.; Fava, A. *J. Mol. Catal.* **1991**, *66*, 7. (f) Desimoni, G.; Quadrelli, P.; Righetti, P. P. *Tetrahedron* **1990**, *46*, 2927. (g) Cram, D. J.; Sogah, G. D. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 625. (h) Yura, T.; Iwasawa, N.; Narasaka, K.; Mukaiyama, T. *Chem. Lett.* **1988**, 1025.

(7) For catalytic asymmetric conjugate addition of organometallic species to α,β-unsaturated ketones, see: (a) Villacorta, G. M.; Rao, C. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 3175. (b) Ahn, K.-H.; Klassen, R. B.; Lippard, S. J. *Organometallics* **1990**, *9*, 3178. (c) Soai, K.; Hayasaka, T.; Ugajin, S.; Yokoyama, S. *Chem. Lett.* **1988**, 1571. (d) Soai, K.; Yokoyama, S.; Hayasaka, T.; Ebihara, K. *J. Org. Chem.* **1988**, *53*, 4148. (e) Soai, K.; Hayasaka, T.; Ugajin, S. *J. Chem. Soc., Chem. Commun.* **1989**, 516. (f) Soai, K.; Okudo, M.; Okamoto, M. *Tetrahedron Lett.* **1991**, *32*, 95. (g) Jansen, J. F. G. A.; Feringa, B. L. *J. Org. Chem.* **1990**, *55*, 4168. (h) Bolm, C.; Ewald, M. *Tetrahedron Lett.* **1990**, *31*, 5011.

(8) Similar Michael addition of **1** with methyl acrylate or acrylonitrile took a longer reaction time, resulting in the formation of respective Michael adducts with low enantiomeric excesses (<15% ee).

(9) The reactions with aryl vinyl ketones (**2c–f**) or acrolein (**2g**) are very fast. In these cases, higher enantioselectivities are obtainable when a benzene solution of **2** is slowly added to a mixture of **1** and the catalyst in benzene.

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Table I. Asymmetric Michael Addition of 2-Cyanopropionates 1 with 2 Catalyzed by the Rhodium Complex with (*S*,*S*)-(*R*,*R*)-TRAP (Scheme I)[a]

entry	2, R^2	1, R^1	temp, °C	addition time, h[b]	time, h[c]	product (3–9) yield, %[d]	ee, %[e]	config[f]	$[\alpha]^{20}_D$, deg[g]
1	Me (**2a**)	Me (**1a**)	5	*i*	10	99 (**3a**)	72	*R*	+2.6
2	Me (**2a**)	Et (**1b**)	5	*i*	10	95 (**3b**)	81	*R*	+4.0
3	Me (**2a**)	*i*-Pr (**1c**)	5	*i*	10	99 (**3c**)	84	*R*[l]	+4.4
4	Me (**2a**)	*i*-Pr (**1c**)	3	*i*	10	97 (**3c**)	86	*R*[l]	+4.5
5	Me (**2a**)	*t*-Bu (**1d**)	5	*i*	10	95 (**3d**)	81	*R*	+2.7
6	Et (**2b**)	*i*-Pr (**1c**)	3	*i*	10	98 (**4**)	85	*R*	+4.5
7	Ph (**2c**)	*i*-Pr (**1c**)	5	1.5	2	95 (**5**)[j]	83[k]	*R*	+6.4
8	4-MeOPh (**2d**)	*i*-Pr (**1c**)	3	1.5	2	99 (**6**)[j]	89[k]	*R*	+5.4
9	2-MeOPh (**2e**)	*i*-Pr (**1c**)	3	1.5	2.5	98 (**7**)[j]	86[k]	*R*	+0.79[m]
10	4-ClPh (**2f**)	*i*-Pr (**1c**)	3	4	4.5	98 (**8**)[j]	85[k]	*R*	+6.7
11	H (**2g**)	*i*-Pr (**1c**)	3	2.5	3.5	88 (**9**)[j]	87	*R*	+3.1
12[h]	H (**2g**)	*i*-Pr (**1c**)	3	6	7	89 (**9**)	84	*R*	+3.1

[a] **1**/**2**/$RhH(CO)(PPh_3)_3$/TRAP = 100/150/1/1.1 unless otherwise noted. [b] Solution of **2** in benzene was added to a mixture of **1** and the catalyst over a given period. [c] Reaction time including the addition time. [d] Isolated yield by bulb-to-bulb distillation unless otherwise noted. [e] Determined by GLC analysis of the cyano ester with chiral capillary column Chiraldex G-TA (0.25 mm × 30 m, base line separation) unless otherwise noted. [f] Determined by the chemical correlation with (*R*)-**3c** unless otherwise noted (see the supplementary material). [g] *c* 5.0–5.1 in $CHCl_3$ unless otherwise noted. [h] **1**/**2**/$RhH(CO)(PPh_3)_3$/TRAP = 1000/1500/1/1.1. [i] Neat **2** was added within 1 min. [j] Isolated yield by MPLC. [k] Determined by HPLC analysis of *N*-(3,5-dinitrophenyl) amide derivatives with chiral stationary phase column Sumichiral OA-4400 (4 mm × 25 cm). [l] Determined by X-ray crystal structure of an amide derivative with (*S*)-[1-(1-naphthyl)ethyl]amine (see the supplementary material). [m] *c* 5.08 in EtOH.

Excellent catalyst turnover efficiency for the reaction with acrolein is shown in entry 12, where the [substrate]/[catalyst] ratio was raised to 1000/1 without significant loss of the enantiomeric purity of product.

A gram-scale experimental procedure is given for the reaction of **1c** with acrolein (**2g**) (entry 12); a mixture of $RhH(CO)(PPh_3)_3$ (9.2 mg, 0.010 mmol), (*S*,*S*)-(*R*,*R*)-TRAP (8.8 mg, 0.011 mmol), and **1c** (1.38 g, 9.80 mmol) in benzene (30 mL) was stirred at room temperature for a few minutes and then cooled to 3 °C. To the well-stirred slurry mixture was added a solution of **2g** (0.86 g, 15.3 mmol) in benzene (20 mL) over a period of 6 h at 3 °C, and the resulting mixture was stirred for 1 h. After the catalyst was removed by passing the solution through a short column of silica gel (3 × 3 cm, hexane/ethyl acetate = 1/1), bulb-to-bulb distillation gave 1.73 g (89%) of (*R*)-**9**, whose enantiomeric excess was determined to be 84% by GLC analysis with chiral capillary column Chiraldex G-TA (0.25 mm × 30 m, base line separation).

The Michael addition of **1b** with **2a** employing conventional cis-chelating chiral diphosphines such as BINAP, DIOP, or CHIRAPHOS was much less enantioselective (<17% ee),[10] suggesting that the trans-chelation of chiral ligand to rhodium is crucial for the highly stereoselective Michael addition, even if the possibility of other coordination modes of TRAP in catalytically active species cannot be excluded at this stage.[11] The X-ray crystal structure analysis[12] of *mer*-$RuH(NCCHCO_2Me)(NCCH_2CO_2Me)(PPh_3)_3$, formed by the oxidative addition of methyl cyanoacetate onto $Ru(C_2H_4)(PPh_3)_3$, reveals that the activated cyanoacetate ($NCCHCO_2Me$ group), which bonds to the ruthenium not through the methine carbon but through the cyano nitrogen, undergoes the Michael addition.[12] It may be conceived that the present rhodium-catalyzed Michael addition involves the similar enolate intermediate in which the enantioselective carbon–carbon bond formation would be accomplished at the carbon atom very distant from the metal center as shown in Scheme II. The remote enantiofacial differentiation may be achieved effectively by the concave chiral surroundings of TRAP rather than the convex chiral surroundings of cis-chelating diphosphine ligands.

Mechanistic studies and further synthetic applications of TRAP are now in progress in our laboratory.

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Supplementary Material Available: Listings of ^1H and ^{13}C NMR, IR, and analytical data for the Michael adducts **3–9**, details of the experimental procedure for the determination of the absolute configurations of **3–9**, and tables of data from the X-ray studies of the (*S*)-*N*-[1-(1-naphthyl)ethyl] amide derivative (10 pages). Ordering information is given on any current masthead page.

(10) The enantiomeric excesses in the reactions at 5 °C with the cis-chelating ligands were as follows: BINAP, 17% ee; DIOP, 12% ee; CHIRAPHOS, 3% ee.

(11) The ^{31}P NMR (toluene-d_8) spectrum of an equimolar mixture of $RhH(CO)(PPh_3)_3$ and TRAP (1.7×10^{-2} M) showed the existence of several undefined Rh–TRAP species at a temperature range from −60 to 0 °C.

(12) Mizuho, Y.; Kasuga, N.; Komiya, S. *Chem. Lett.* **1991**, 2127.

Hydride and Halide Ligand Effects on the Enthalpies of Protonation of Transition Metal Complexes

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In previous studies from this laboratory, the basicities of metals in transition metal complexes have been determined calorimetrically by measuring their enthalpies of protonation with CF_3SO_3H in 1,2-dichloroethane solvent. Using this method, the effects of different methyl-substituted cyclopentadienyl ligands in (η^5-$C_5Me_xH_{5-x}$)Ir(1,5-cyclooctadiene),[1] monodentate phosphines in (η^5-C_5H_5)Ir(CO)(PR_3) and $Fe(CO)_3(PR_3)_2$,[2] and the chelating phosphines in $Fe(CO)_3(P\frown P)$,[3a] $M(CO)_2(P\frown P)_2$ (M = Cr, Mo, W),[3b] and $W(CO)_3$(tridentate phosphine)[4] have been investigated. In the present communication we compare the different effects of halide and hydride ligands on the basicity of the metal in

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