

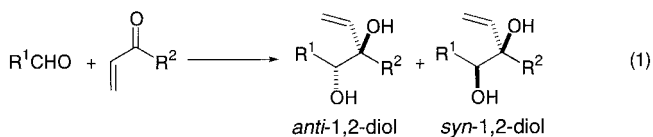
- 1 H), 1.88 (m, 1H), 1.81 (dd, $J = 13.4$, 6.2 Hz, 1H), 1.76 (dd, $J = 14.0$, 8.6 Hz, 1H), 1.42–1.22 (m, 2H), 1.13 (q, $J = 12.3$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 171.5$, 171.2, 86.2, 85.2, 84.7, 74.0, 57.3, 52.5, 52.5, 51.4, 49.3, 47.1, 34.3, 24.2, 22.0.
- [6] Several (1-3:5,6- η -cyclooctadienyl)ruthenium complexes have been reported, see: a) C. C. McComas, J. W. Ziller, D. L. Van Vranken, *Organometallics* **2000**, *19*, 2853; b) T. V. Ashworth, A. A. Chalmers, D. C. Liles, E. Meintjies, E. Singleton, *Organometallics* **1987**, *6*, 1543; c) N. Oshima, H. Suzuki, Y. Morooka, *Inorg. Chem.* **1986**, *25*, 3407; d) F. Bouachir, B. Chaudret, D. Neibecker, I. Tkatchenko, *Angew. Chem.* **1985**, *97*, 347; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 347; e) Y. V. Ashworth, M. Nolte, R. H. Reimann, E. Singleton, *J. Chem. Soc. Chem. Commun.* **1977**, 937.
- [7] Crystals of **3** suitable for X-ray analysis were grown by slow diffusion of hexanes into a solution of **3** in methylene chloride at 0 °C. Crystal Data (also see Supporting Information): $\text{C}_{19}\text{H}_{24}\text{O}_4\text{Ru}$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 24.3072(5)$, $b = 8.0591(3)$, $c = 8.8023(1)$ Å, $V = 1724.32(6)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.608$ g cm⁻³, $\text{MoK}\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{MoK}\alpha) = 9.29$ cm⁻¹, $T = -114$ °C. Siemens SMART CCD diffractometer, 7710 measured reflections, 2858 unique reflections, 2005 used ($4.64^\circ < 2\theta < 49.38^\circ$), $R_1 = 0.032$ (1850 reflexions, $I > 4\sigma(I)$), $wR_2 = 0.051$ (all data), GOF = 0.86. Minimum and maximum peaks in the final difference map -0.34 and -0.58 e Å⁻³. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158653. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [8] $[\text{Cp}^*\text{Ru}(\eta^3\text{-cinnamyl})]\text{Cl}_2$ shows unsymmetrical bonding of the allyl group, with the $\text{Ph}(\text{H})\text{C}-\text{Ru}$ bond 0.2 Å longer: T. Kondo, H. Ono, N. Satake, T. Mitsudo, Y. Watanabe, *Organometallics* **1995**, *14*, 1945.
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Stereoselective Cross Pinacol-Type Coupling between α,β -Unsaturated Ketones and Aldehydes Mediated by Chromium(II) and R_3SiCl **

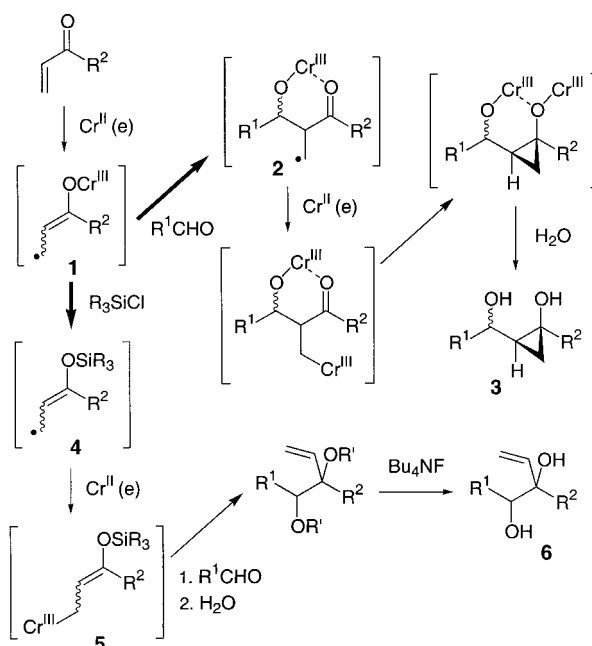
Kazuhiko Takai,* Ryotaro Morita, and Chika Toratsu

The Pinacol-type coupling of aliphatic carbonyl compounds to form 1,2-diols is an attractive and promising tool for organic synthesis.^[1, 2] In contrast to the case of aromatic carbonyl compounds, reagents for the coupling of aliphatic aldehydes are limited, and intermolecular cross coupling of two carbonyl compounds in a selective manner is especially difficult. We

report herein the cross pinacol-type coupling reaction between an α,β -unsaturated ketone and an aldehyde mediated by chromium(II) and R_3SiCl [Eq. (1)].



Aldehydes are usually unreactive to chromium(II) because of its moderate reducing ability. However, reactions promoted by a one-electron transfer from chromium(II) proceed with some carbonyl compounds, such as α,β -unsaturated aldehydes and ketones.^[3, 4] In the first step of these reactions, a radical enolate **1** is formed (Scheme 1). When the reaction is



Scheme 1. Mechanism of the coupling reactions; R = Me or Et, R' = SiR_3 or H.

conducted in the presence of an aldehyde under anhydrous conditions, an intermolecular aldol reaction, which leads to **2**, is followed by a cyclopropanation reaction to give the *cis*-hydroxyalkyl-substituted cyclopropanol **3**.^[4] In contrast, we have found that the reaction course changes dramatically with the addition of Me_3SiCl , producing cross-pinacol coupling products 1,2-diols **6**, after desilylation with Bu_4NF . For example, a mixture of 5-phenyl-1-penten-3-one (**7**, 2.0 equiv) and nonanal (1.0 equiv) in *N,N*-dimethylformamide (DMF) was added at 25 °C to a mixture of CrCl_2 (8.0 equiv) in DMF in the presence of Me_3SiCl (6.0 equiv), and the resulting mixture was stirred at 25 °C for 1 h. After workup with water followed by desilylation with Bu_4NF , 1-vinyl-substituted 1,2-diols **8** were obtained in almost quantitative yield (*anti/syn* = 40:60).

The key factor that leads to the cross pinacol-type coupling reaction is the fast trapping of an enolate with Me_3SiCl leading to a trimethylsiloxy compound.^[5] Therefore, when the

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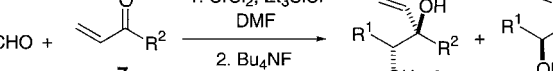
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reduction of an α,β -unsaturated ketone with chromium(II) is conducted with Me_3SiCl , the radical enolate **1** will be trapped with Me_3SiCl to give the γ -siloxy-substituted allylic radical **4**. Such an allylic radical **4** can be reduced easily with chromium(II) to afford the corresponding allylic chromium species **5**.^[6–9] Because the process is performed in the presence of an aldehyde,^[10] a coupling reaction takes place between the γ -siloxy-substituted allylic chromium complex **5** and the aldehyde. The coupling reaction leading to 1,2-diols **6** proceeds with Me_3SiCl , Et_3SiCl , Me_2SiCl_2 , and PhMe_2SiCl ; however, the addition of $t\text{BuMe}_2\text{SiCl}$ or $i\text{Pr}_3\text{SiCl}$ to the mixture does not afford the desired coupling products, probably owing to the slow trapping process of the chromium enolate with R_3SiCl .

The *anti/syn* ratio changed only slightly when using different substituents R of R_3SiCl .^[11] On the other hand, the reaction temperature influenced the ratio dramatically. At 0 °C, the *anti*-1,2-diol **8a** was produced selectively in a ratio of 93:7,^[12] but at higher temperatures the *anti/syn* ratio decreased gradually (Table 1), and the *syn* adduct **8b** was obtained as a major product at 75 °C in an *anti/syn* ratio of 10:90.

The results obtained with several kinds of α,β -unsaturated ketones and aldehydes are summarized in Table 2. Substituents on the carbon–carbon double bonds of the enones slowed down the reaction. Although α -substituted enones gave pinacol adducts in good yields (Table 2, entries 5 and 6), β -substituted enones did not afford the desired product. The diastereoselectivity also showed a similar temperature dependence to that described above, with the proportion of *syn* adduct increasing with increasing temperature. In contrast, reactions using 2-methylenecycloheptanone gave an *anti* adduct exclusively, irrespective of the reaction temperature

Table 1. Effects of reaction temperature on the diastereomeric ratios of cross pinacol-type reactions.^[a]



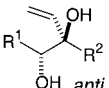
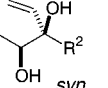
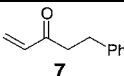
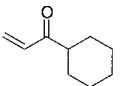
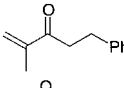
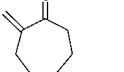
T [°C]	0	10	20	30	40	50	60	75
Time [h]	5	2	1	1	0.5	0.5	0.25	0.25
Yield [%]	99	97	96	93	90	86	84	85
<i>anti:syn</i> ^[b]	93:7	78:22	64:36	45:55	36:64	23:77	19:81	10:90

[a] The reactions were conducted on a 1.0-mmol scale. 5-Phenyl-1-penten-3-one (**7**, 2.0 mmol), CrCl_2 (8.0 mmol), and Et_3SiCl (6.0 mmol) were used per mmol of nonanal ($\text{R}^1 = n\text{-C}_8\text{H}_{17}$, $\text{R}^2 = \text{Ph}(\text{CH}_2)_2$). [b] Diastereomeric ratios were determined by isolation and/or by ^1H NMR spectroscopy.

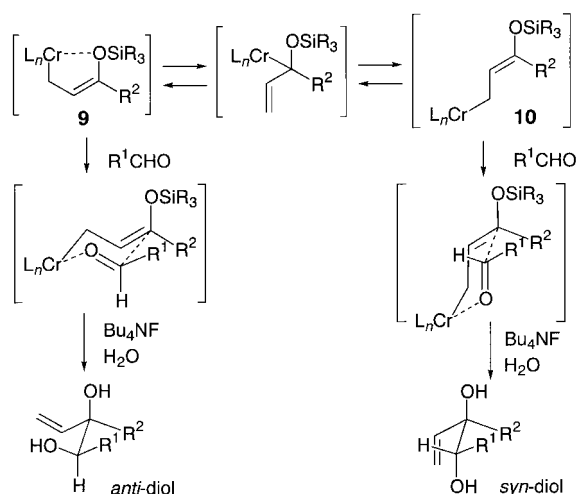
(Table 2, entry 6). To reduce the amount of chromium salt used in the reaction, we attempted a catalytic reaction using manganese as a reductant^[5, 13] of chromium(III). The reaction proceeded almost quantitatively at 25 °C; however, the yields decreased and the *anti/syn* ratios were not improved at either 0 or at 75 °C (Table 2, entry 2).

The addition of allylic chromium reagents to carbonyl compounds usually proceeds via a six-membered transition state with a chair form, and the diastereoselectivity reflects the configuration of the allylic chromium species (Scheme 2).^[14, 15] The formation of only the *anti* product from 2-methylenecycloheptanone, irrespective of the reaction temperature, suggests that the diastereoselectivity of the reaction also depends on the stereochemistry of the γ -siloxyallylic

Table 2. Formation of cross pinacol-type 1,2-diols from α,β -unsaturated ketones and aldehydes.^[a]

$\text{R}^1\text{CHO} + \text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{R}^2 \xrightarrow[\text{2. Bu}_4\text{NF, THF}]{\text{1. CrCl}_2, \text{Et}_3\text{SiCl, DMF}} \text{R}^1\text{CH}(\text{OH})\text{CH}(\text{OH})\text{R}^2$  <i>anti</i>  <i>syn</i>								
Entry	R ¹	Enone	Time [h]	0 °C Yield [%]	<i>anti/syn</i> ^[b]	Time [h]	75 °C Yield [%]	<i>anti/syn</i> ^[b]
1	<i>n</i> -C ₈ H ₁₇	 7	5	99	93:7	0.25	85	10:90
2	<i>n</i> -C ₈ H ₁₇	7	24	64 ^[c]	70:30	6	42 ^[c]	29:71
3	<i>c</i> -C ₆ H ₁₁	7	5	98	60:40	0.25	80	19:81
4	Ph(CH ₂) ₂		5	72	> 99: < 1	0.5	52	59:41
5	<i>n</i> -C ₈ H ₁₇		24	44	79:21	2	61	10:90
6	Ph(CH ₂) ₂		4	94 ^[d]	> 99: < 1	0.25	80 ^[d]	> 99: < 1

[a] The reactions were conducted on a 1.0-mmol scale. α,β -Unsaturated ketone (2.0 mmol), CrCl_2 (8.0 mmol), and Et_3SiCl (6.0 mmol) were used per mmol of aldehyde. [b] Diastereomeric ratios were determined by isolation and/or ^1H NMR spectroscopy.^[12] [c] CrCl_2 (0.8 mmol), Mn (4.0 mmol), and Et_3SiCl (6.0 mmol) were used per mmol of aldehyde. [d] Methylenecycloheptanone (4.0 mmol), CrCl_2 (16 mmol), and Et_3SiCl (12 mmol) were employed per mmol of aldehyde.



Scheme 2. Mechanism for diastereoselectivity.

chromium compounds formed, by virtue of which 2-methylenecycloheptanone can only form the *cis* isomer.

In the case of γ,γ -disubstituted allylic chromium species with a γ -siloxy group, the equilibrium between **9** and **10** is more quickly established^[17] than for γ,γ -dialkyl-substituted allylic species.^[14b] There are two possible reasons that account for the temperature dependence. One is a shift in the equilibrium from **9** to **10** by increasing the temperature.^[18] The other is that the addition rate of **10** to aldehydes could be increased more by temperature than that of **9**.^[19] In both cases, the mechanism also suggests that the equilibrium between **9** and **10** shifts to the *cis* isomer **9** when R^2 becomes bulkier. For example, the proportion of *anti*-diol derived from **9** was increased in the case of cyclohexyl vinyl ketone (Table 2, entry 4) as expected.

Experimental Section

8 (Table 2, entry 1, 0 °C): Et₃SiCl (1.0 mL, 6.0 mmol) was added to a mixture of CrCl₂ (0.98 g, 8.0 mmol; 99.9% purity, Aldrich) in dry, oxygen-free DMF (15 mL; Wako Pure Chemicals), and the mixture was stirred for 30 min. The mixture was cooled to 0 °C, and a solution of nonanal (0.14 g, 1.0 mmol) and 5-phenyl-1-penten-3-one (**7**, 0.32 g, 2.0 mmol) in DMF (5 mL) was added at 0 °C. After stirring for 5 h at 0 °C, the reaction mixture was poured into water (20 mL). The mixture was extracted with diethyl ether (3 × 20 mL), and the organic extracts were dried over anhydrous magnesium sulfate and concentrated. The crude mixture was diluted with THF (10 mL) and treated with a solution of Bu₄NF in THF (1.0 M, 4.0 mL) at 25 °C for 10 min, and then poured into water (5 mL). The mixture was extracted with diethyl ether (3 × 20 mL), and the organic extracts were dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel (hexane/ethyl acetate 50:1) gave 3-(2-phenylethyl)-1-dodecene-3,4-diols **8** in 99% yield (0.99 mmol, *anti/syn* = 93/7).^[20]

8 (Table 2, entry 1, 75 °C): The mixture was heated at 75 °C before the addition of a solution of nonanal (0.14 g, 1.0 mmol) and **7** (0.32 g, 2.0 mmol) in DMF (5 mL).

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- [15] There was no equilibrium between *anti*- and *syn*-diols through a retro addition of the allylic chromium species.^[16] This was confirmed by the following experiment: a mixture of adducts produced at 0 °C (*anti*/*syn* = 93/7) was heated at 75 °C for 30 min before quenching; the *anti*/*syn* ratio did not change.
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- [17] To examine the equilibrium between the *cis* and *trans* allylic chromium species **9** and **10**, the following experiment was conducted: two reaction mixtures containing the enone **7**, $CrCl_2$, and Et_3SiCl were heated at 75 °C for 5 min. Nonanal was added at 75 °C to one mixture and stirred at the same temperature. The other mixture was cooled to 0 °C before the addition of nonanal, followed by stirring at 0 °C. The *anti*/*syn* ratio of the reaction at 75 °C was 10:90. The reaction cooled to 0 °C gave a ratio of 93:7, which is the same ratio obtained when the reaction temperature is held constant at 0 °C (Table 1). The yield of **8** in the latter reaction decreased to 39% owing to the formation of 1,10-diphenyldecane-3,8-dione in 27% yield, and nonanal was recovered in 45% yield.
- [18] Coordination of a siloxy group in **9** possibly stabilizes the *cis* configuration, leading to an *anti* adduct. However, the siloxy group is bulky and this could push the equilibrium to the sterically less congested *trans* isomer **10**. At higher temperatures, this steric effect could be enhanced and the proportion of the *syn* isomer increased. One possibility is that the *anti*/*syn* ratios could reflect the *cis*/*trans* ratios, which depend on a balance between these factors.
- [19] For the temperature dependence of reaction rates, see: J. Otera, K. Sato, T. Tsukamoto, A. Orita, *Tetrahedron Lett.* **1998**, 39, 3201–3204; T. Sakai, I. Kawabata, T. Kishimoto, T. Ema, M. Utaka, *J. Org. Chem.* **1997**, 62, 4906–4907.
- [20] The following functional substrates were recovered under the standard reaction conditions (Table 2, entry 1, 0 °C) owing to the mild nucleophilicity of the organochromium reagent: 1-dodecene (94%), 1-dodecyne (98%), 1-chlorododecane (98%), ethyl octanoate (96%), nonanenitrile (96%), 4-phenyl-2-butanone (91%), 3-phenylpropyl acrylate (87%), and nonanal diethylene acetal (98%).

Ligand-Controlled Chemoselectivity in the Classical Oxidative Addition Reactions of MeI and Aldehydes to Rhodium(I) Complexes**

Roman Goikhman and David Milstein*

Rhodium(I) phosphane complexes are widely used in industrial and laboratory processes owing to their catalytic properties and high reactivities, particularly in oxidative addition reactions.^[1a] We report here a remarkable difference in the reactivity of similar alkylphosphane-rhodium(I) complexes bearing triflate and chloride ligands in classical oxidative addition reactions of aldehydes and MeI. High chemoselectivity in oxidative addition can be achieved by the choice of complex.

[[$(iPr_3P)_2RhOTf$]] (**1**) ($OTf = OSO_2CF_3$, triflate) was synthesized by a simple procedure involving chloride abstraction from [[$(iPr_3P)_2RhCl$]] (**2**)^[2] with Me_3SiOTf , according to our reported method;^[3] an alternative synthesis has also been described.^[4] Complex **1** was characterized by X-ray structure analysis, which confirmed that the geometry around the metal is square planar, and that an η^2 -bound triflate ligand is present (Figure 1).^[5] The structure is similar to that of another rhodium η^2 -triflate complex.^[4] Surprisingly, η^2 coordination of the triflate ligand in mononuclear late transition metal complexes was not reported until 1998, and the reactivity of these uncommon complexes has yet to be examined.^[4, 6]

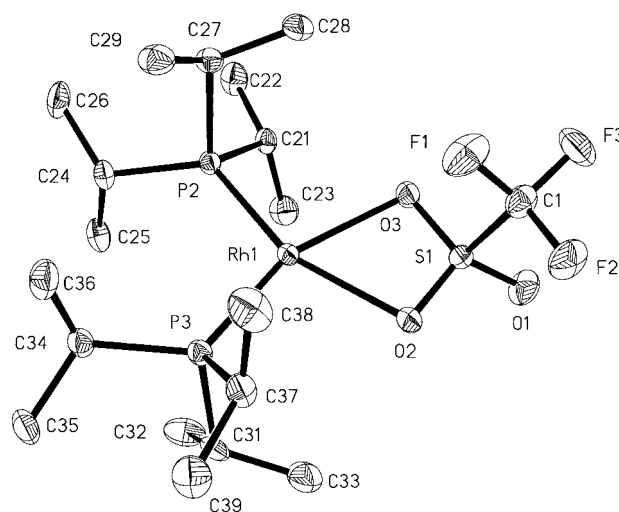


Figure 1. Structure of **1** (ORTEP plot; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–O3 2.283(2), Rh1–O2 2.265(3), Rh1–P3 2.2099(11), Rh1–P2 2.2143(11); P3–Rh1–P2 105.41(4), P3–Rh1–O2 95.78(7), P2–Rh1–O2 158.82(7), P2–Rh1–O3 95.38(7), P3–Rh1–O3 158.96(7), O2–Rh1–O3 63.48(9).

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