1H), 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 anaylsis were grown by slow diffusion of hexanes into a solution of **3** in methylene chloride at 0 °C. Crystal Data (also see Supporting Information): $C_{19}H_{24}O_4Ru$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 24.3072(5)$, $b = 8.0591(3)$, $c = 8.8023(1)$ Å, $V = 1724.32(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.608$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\mu(Mo_{K\alpha}) = 9.29$ cm^{-1}, $T = -114$ °C. Siemens SMART CCD diffractometer, 7710 measured reflections, 2858 unique reflections, 2005 used ($4.64° < 2\theta < 49.38°$), $R_1 = 0.032$ (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 CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] [Cp*Ru(η^3-cinnamyl)]Cl_2 shows unsymmetrical bonding of the allyl group, with the Ph(H)C–Ru bond 0.2 Å longer: T. Kondo, H. Ono, N. Satake, T. Mitsudo, Y. Watanabe, *Organometallics* **1995**, *14*, 1945.

[9] a) D. J. Cole-Hamilton, G. Wilkinson, *Nouv. J. Chim.* **1977**, *1*, 141; b) B. N. Chaudret, D. J. Cole-Hamilton, G. Wilkinson, *Acta Chem. Scand. Ser. A* **1978**, *32*, 763.

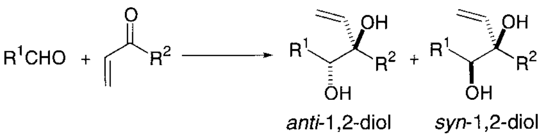
[10] A. Fürstner, H. Szillat, F. Stelzer, *J. Am. Chem. Soc.* **2000**, *122*, 6785.

[11] For a review see: a) L. Yet, *Chem. Rev.* **2000**, *100*, 2967. See also: b) L. Yet, *Tetrahedron* **1999**, *55*, 9439; c) A. Fürstner, *Top. Catal.* **1997**, *4*, 285; d) B. M. Trost, *Adv. Chem. Ser.* **1992**, *230*, 463.

Stereoselective Cross Pinacol-Type Coupling between α,β-Unsaturated Ketones and Aldehydes Mediated by Chromium(II) and R_3SiCl**

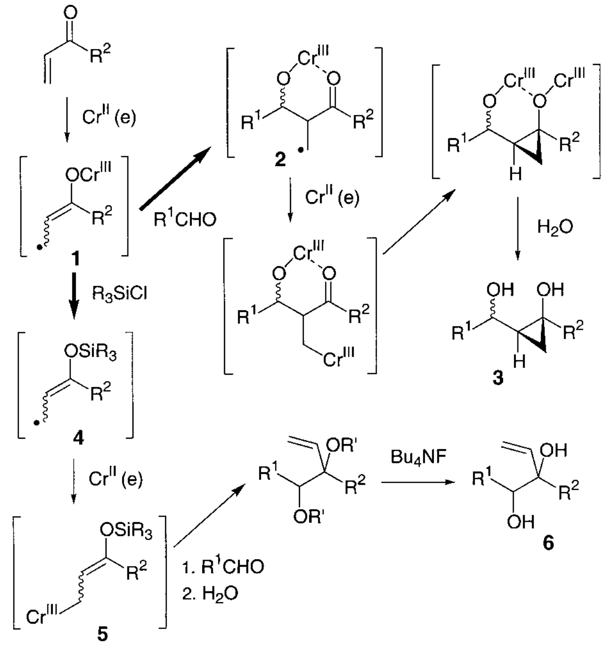
Kazuhiko Takai,* Ryotaro Morita, and Chika Toratsu

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)].



(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 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).



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

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

---

[*] Prof. Dr. K. Takai, R. Morita, C. Toratsu
Department of Applied Chemistry, Faculty of Engineering
Okayama University, Tsushima, Okayama 700-8530 (Japan)
Fax: (+81) 86-251-8094
E-mail: ktakai@cc.okayama-u.ac.jp

[**] Financial support by a Grant-in-Aid for Scientific Research on Priority Area No. 706 from the Ministry of Education, Culture, Sports, Science and Technology of Japan is gratefully acknowledged.

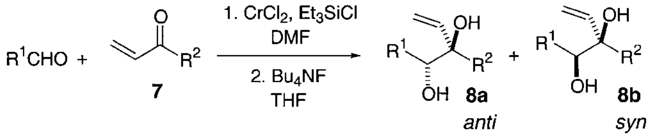
reduction of an α,β-unsaturated ketone with chromium(II) is conducted with Me_3SiCl, the radical enolate **1** will be trapped with Me_3SiCl to give the γ-siloxy-substituted allylic radical **4**. Such an allylic radical **4** can be reduced easily with chromium(II) to afford the corresponding allylic 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 tBuMe$_2$SiCl or iPr$_3$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 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

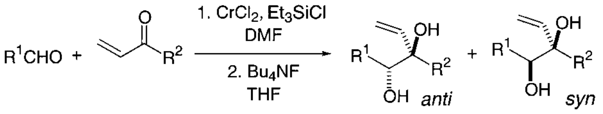
Table 1. Effects of reaction temperature on the diastereomeric ratios of cross pinacol-type reactions.[a]

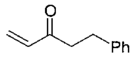
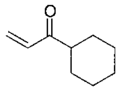
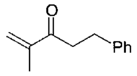
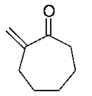


T [°C]	0	10	20	30	40	50	60	75
Time [h]	5	2	1	1	0.5	0.5	0.25	0.25
Yield [%]	99	97	96	93	90	86	84	85
anti:*syn*[b]	93:7	78:22	64:36	45:55	36:64	23:77	19:81	10:90

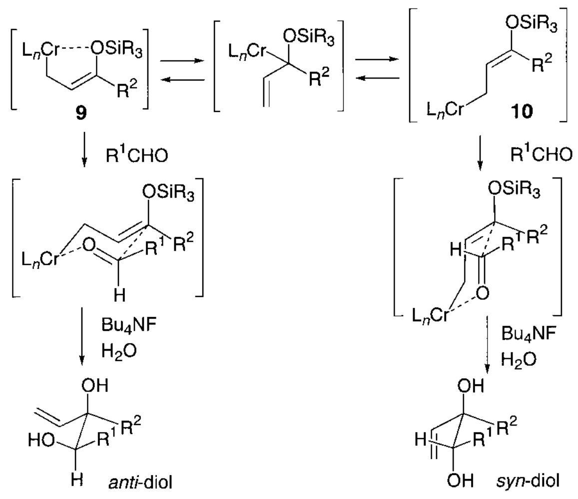
[a] The reactions were conducted on a 1.0-mmol scale. 5-Phenyl-1-penten-3-one (**7**, 2.0 mmol), $CrCl_2$ (8.0 mmol), and Et_3SiCl (6.0 mmol) were used per mmol of nonanal ($R^1 = n\text{-}C_8H_{17}$, $R^2 = Ph(CH_2)_2$. [b] Diastereomeric ratios were determined by isolation and/or by ^1H NMR spectroscopy.

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



Entry	R¹	Enone	0 °C Time [h]	 Yield [%]	 *anti*/*syn*[b]	75 °C Time [h]	 Yield [%]	 *anti*/*syn*[b]
1	$n\text{-}C_8H_{17}$	 **7**	5	99	93:7	0.25	85	10:90
2	$n\text{-}C_8H_{17}$	**7**	24	64[c]	70:30	6	42[c]	29:71
3	c-C_6H_{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	$n\text{-}C_8H_{17}$		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): Et_3SiCl (1.0 mL, 6.0 mmol) was added to a mixture of $CrCl_2$ (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 Bu_4NF 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).

Received: October 16, 2000
Revised: December 28, 2000 [Z15956]

---

[1] For pinacol coupling reactions of aliphatic aldehydes, see: a) Reviews: T. Wirth, *Angew. Chem.* **1996**, *108*, 65–67; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 61–63; A. Fürstner, B. Bogdanovic, *Angew. Chem.* **1996**, *108*, 2582–2609; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2442–2469; b) Ti: T. Mukaiyama, T. Sato, J. Hanna, *Chem. Lett.* **1973**, 1041–1044; T. Mukaiyama, H. Sugimura, T. Ohno, S. Kobayashi, *Chem. Lett.* **1989**, 1401–1404; T. A. Lipski, M. A. Hilfiker, S. G. Nelson, *J. Org. Chem.* **1997**, *62*, 4566–4567; c) Sm: J.-L. Namy, J. Souppe, H. Kagan, *Tetrahedron Lett.* **1983**, *24*, 765–766; G. A. Molander, C. Kenny, *J. Org. Chem.* **1988**, *53*, 2132–2134; E. Enholm, A. Trivellas, *Tetrahedron Lett.* **1989**, *30*, 1063–1066; T. Honda, M. Katoh, *Chem. Commun.* **1997**, 369–370; d) V: J. H. Freudenberger, A. W. Konradi, S. F. Pedersen, *J. Am. Chem. Soc.* **1989**, *111*, 8014–8016; T. Hirao, T. Hasegawa, Y. Muguruma, I. Ikeda, *J. Org. Chem.* **1996**, *61*, 366–367; e) Nb: J. Szymoniak, J. Besançon, C. Moïse, *Tetrahedron* **1994**, *50*, 2841–2848; f) Ta: K. Takai, Y. Kataoka, K. Utimoto, *J. Org. Chem.* **1990**, *55*, 1707–1708; g) Mg-graphite: R. Csuk, A. Fürstner, H. Weidmann, *J. Chem. Soc. Chem. Commun.* **1986**, 1802–1803; h) radical-intramolecular: D. S. Hays, G. C. Fu, *J. Am. Chem. Soc.* **1995**, *117*, 7283–7284.

[2] For some representative examples, see: a) Gibberellic acid: E. J. Corey, R. L. Danheiser, S. Chandrasekaran, P. Siret, G. E. Keck, J.-L. Gras, *J. Am. Chem. Soc.* **1978**, *100*, 8031–8034; E. J. Corey, R. L. Carney, *J. Am. Chem. Soc.* **1971**, *93*, 7318–7319; b) Taxol: K. C. Nicolaou, Z. Yang, J. J. Liu, H. Ueno, P. G. Nantermet, R. K. Guy, C. F. Claiborne, J. Renaud, E. A. Couladouros, K. Paulvannan, E. J. Sorensen, *Nature* **1994**, *367*, 630–634; I. Shiina, H. Iwadare, H. Sakoh, M. Hasegawa, Y.-i. Tani, T. Mukaiyama, *Chem. Lett.* **1998**, 1–2.

[3] a) D. Montgomery, K. Reynolds, P. Stevenson, *J. Chem. Soc. Chem. Commun.* **1993**, 363–364; b) J. B. Conant, H. B. Cutter, *J. Am. Chem. Soc.* **1926**, *48*, 1016–1030; c) A. B. Smith, III, P. A. Levenberg, J. Z. Suits, *Synthesis* **1986**, 184–189.

[4] C. Toratsu, T. Fujii, T. Suzuki, K. Takai, *Angew. Chem.* **2000**, *112*, 2837–2839; *Angew. Chem. Int. Ed.* **2000**, *39*, 2725–2727.

[5] a) A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 2533–2534; A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 12349–12357; b) A. Svatoš, W. Boland, *Synlett* **1998**, 549–551.

[6] K. Takai, N. Matsukawa, A. Takahashi, T. Fujii, *Angew. Chem.* **1998**, *110*, 160–163; *Angew. Chem. Int. Ed.* **1998**, *37*, 152–155.

[7] One approach to obtain cross pinacol-type 1,2-diols (or their derivatives) with carbon–carbon bond formation is the reaction of α-alkoxy or α-siloxy-substituted carbanions with carbonyl compounds. However, such carbanions and their vinylogous γ-alkoxy-allylic anions[8] usually require the preparation of their precursors in advance. Moreover, the preparation conditions of the reagents are not very moderate and the carbonyl compounds do not survive. T. Cohen, M. T. Lin, *J. Am. Chem. Soc.* **1984**, *106*, 1130–1131; W. C. Still, *J. Am. Chem. Soc.* **1978**, *100*, 1481–1486; D. Seebach, N. Meyer, *Angew. Chem.* **1976**, *88*, 484; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 438.

[8] a) D. A. Evans, G. C. Andrews, B. Buckwalter, *J. Am. Chem. Soc.* **1974**, *96*, 5560–5561; b) W. C. Still, T. L. Macdonald, *Tetrahedron Lett.* **1976**, *41*, 3620–3622; c) R. W. Hoffmann, B. Kemper, *Tetrahedron Lett.* **1980**, 4883–4886; d) M. Koreeda, Y. Tanaka, *J. Chem. Soc. Chem. Commun.* **1982**, 845–847; e) W. R. Roush, D. J. Harris, B. M. Lesur, *Tetrahedron Lett.* **1983**, *24*, 2227–2230; f) P. G. M. Wuts, S. S. Bigelow, *J. Org. Chem.* **1982**, *47*, 2498–2500; g) K. Takai, K. Nitta, K. Utimoto, *Tetrahedron Lett.* **1988**, *29*, 5263–5266.

[9] In the case of chromium(III), transfer of the silyl group from the enolate oxygen atom to the β-carbon atom did not occur. This observation is in sharp contrast to the case of lithium; see: H. Nakahira, I. Ryu, A. Ogawa, N. Kambe, N. Sonoda, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3361–3363.

[10] Strong reducing agents such as SmI_2 and low-valent titanium caused a competing homo coupling reaction of the aldehyde, and gave a complex mixture. a) SmI_2: A. Cabrera, R. Le Lagadec, P. Sharma, J. L. Arias, R. A. Toscano, L. Velasco, R. Gaviño, C. Alvarez, M. Salmón, *J. Chem. Soc. Perkin Trans. 1* **1998**, 3609–3617; b) Low-valent titanium and vanadium: J.-M. Pons, J.-P. Zahra, M. Santelli, *Tetrahedron Lett.* **1981**, *22*, 3965–3968.

[11] The effects of the substituents of the silyl reagents on the diastereomeric ratios of cross pinacol-type reactions between **7** and nonanal are as follows: Me_3SiCl, 0 °C, 5 h, 98 % (*anti*:*syn* = 82:18); 25 °C, 1 h, 99 % (40:60); $PhMe_2SiCl$, 0 °C, 5 h, 99 % (85:15); 25 °C, 1 h; 94 % (53:47).

[12] Authentic samples of *anti*-diols were prepared as follows: 1) α-Hydroxyketones ($R^1CHOHCOR^2$) were prepared following the Kagan SmI_2 coupling (J. Souppe, J.-L. Namy, H. B. Kagan, *Tetrahedron Lett.* **1984**, *25*, 2869–2872); 2) protection of the hydroxy group as tetrahydropyranyl or benzyl ether; 3) stereoselective addition of a vinyl Grignard reagent (W. C. Still, J. H. McDonald III, *Tetrahedron Lett.* **1980**, *21*, 1031–1034). The stereochemistry of the diols was also confirmed by NOE experiments on the corresponding acetonides.

[13] For catalytic pinacol coupling reactions using manganese or zinc as reductants, see: A. Gansäuer, D. Bauer, *J. Org. Chem.* **1998**, *63*, 2070–2071; A. Gansäuer, M. Moschioni, D. Bauer, *Eur. J. Org. Chem.* **1998**, 1923–1927; M. S. Dunlap, K. M. Nicholas, *Synth. Commun.* **1999**, *29*, 1097–1106; M. Bandini, P. G. Cozzi, P. Melchiorre, A. Umani-Ronchi, *Angew. Chem.* **1999**, *111*, 3558–3561; *Angew. Chem. Int. Ed.* **1999**, *38*, 3357–3359; M. Bandini, P. G. Cozzi, S. Morganti, A. Umani-Ronchi, *Tetrahedron Lett.* **1999**, *40*, 1997; U. Groth, M. Jeske, *Angew. Chem.* **2000**, *112*, 586–588; *Angew. Chem. Int. Ed.* **2000**, *39*, 574–576.

[14] a) It is known that there is a fast equilibrium between (*E*)- and (*Z*)-crotylchromium: C. T. Buse, C. H. Heathcock, *Tetrahedron Lett.* **1978**, 1685–1688; T. Hiyama, K. Kimura, H. Nozaki, *Tetrahedron Lett.* **1981**, *22*, 1037–1040; b) however, the equilibrium becomes very slow in the case of γ,γ-dialkyl-substituted allylic chromium compounds: C. Jubert, S. Nowotny, D. Kornemann, I. Antes, C. E. Tucker, P. Knochel, *J. Org. Chem.* **1992**, *57*, 6384–6386; S. Nowotny, C. E. Tucker, C. Jubert, P. Knochel, *J. Org. Chem.* **1995**, *60*, 2762–2772.

[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.

[16] F. Barbot, P. Miginiac, *Tetrahedron Lett.* **1975**, 3829–3832; J. Nokami, K. Yoshizane, H. Matsuura, S.-i. Sumida, *J. Am. Chem. Soc.* **1998**, *120*, 6609–6610; P. Jones, N. Millot, P. Knochel, *Chem. Commun.* **1998**, 2405–2406.

[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 alkylphosphanerhodium(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**)[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]

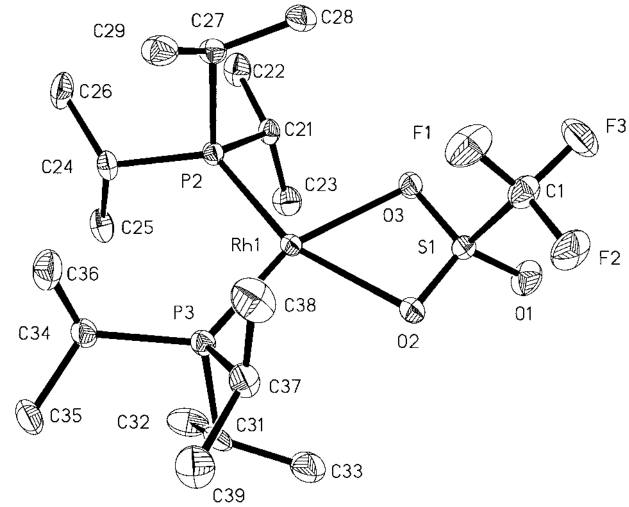


Figure 1. Structure of **1** (ORTEP plot; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1-O3 2.283(2), Rh1-O2 2.265(3), Rh1-P3 2.2099(11), Rh1-P2 2.2143(11); P3-Rh1-P2 105.41(4), P3-Rh1-O2 95.78(7), P2-Rh1-O2 158.82(7), P2-Rh1-O3 95.38(7), P3-Rh1-O3 158.96(7), O2-Rh1-O3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

---

[*] Prof. Dr. D. Milstein, R. Goikhman
Department of Organic Chemistry
The Weizmann Institute of Science
Rehovot, 76100 (Israel)
Fax: (+972) 8-9344142
E-mail: david.milstein@weizmann.ac.il

[**] This work was supported by the Israel Science Foundation, Jerusalem, Israel, by the MINERVA foundation, Munich, Germany, and by the Tashtiyot program of the Israeli Ministry of Science. D.M. is the holder of the Israel Matz Professorial Chair of Organic Chemistry. We thank Dr. L. Shimon and Dr. H. Rozenberg, Weizmann Institute of Science, for performing the X-ray structural analysis.