Keywords: adenine · bioinorganic chemistry · N ligands · nucleobases · ruthenium

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[7] **1a**·4.5H_2O: $C_{13}H_{28}Cl_3N_7O_2RuS_2 \cdot 4.5H_2O$, $M_r = 667.04$, crystal dimensions $0.30 \times 0.29 \times 0.06$ mm^3, triclinic, $P\bar{1}$, $a = 12.7288(11)$, $b = 14.7164(12)$, $c = 16.2058(14)$ Å, $\alpha = 93.525(2)$, $\beta = 111.256(2)$, $\gamma = 110.651(2)°$, $V = 2584.2(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.714$ g cm^{-3}, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $T = 160$ K, $\mu = 1.124$ mm^{-1}. 20192 (11193 unique, $2\theta < 55°$, $R_{int} = 0.0302$) data were collected on a Siemens SMART CCD area detector diffractometer using narrow frames (0.3° steps in ω) and the absorption effects were corrected semiempirically (transmission: 0.644–0.801). The structure was solved by Patterson synthesis and refined by full-matrix least-squares on F^2 values for all data (G. M. Sheldrick, SHELXTL manual, Siemens Analytical X-Ray Instruments, Madison, WI, **1994**, version 5) to give $wR = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1250$, conventional $R = 0.0525$ for F values of 8541 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.055$ for 661 parameters. The asymmetric unit contains two complex cations, two chloride ions, and approximately nine molecules of water some of these disordered. All non-H atoms were refined anisotropically. Hydrogen atom coordinates were refined for N-H atoms, riding for C-H atoms, and not included for O-H; a riding model was used for all U_{iso}(H). The residual electron density extremes were 1.09 and -0.93 e Å^{-3}. **1b**·H_2O: $C_{11}H_{21}Cl_2N_7ORuS.H_2O$, $M_r = 489.39$, crystal dimensions $0.22 \times 0.17 \times 0.04$, monoclinic, $P2_1/c$, $a = 9.2067(6)$, $b = 17.1639(11)$, $c = 12.0162(8)$ Å, $\beta = 105.421(2)°$, $V = 1830.5(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.776$ g cm^{-3}, $\mu = 1.283$ mm^{-1}; 11279 (4148 unique, $2\theta < 55°$, $R_{int} = 0.0356$) data, transmission: 0.815–0.962. The structure was solved by direct methods. $wR = 0.0991$, $R = 0.0382$ (3295 F values), $S = 1.117$ for 232 parameters. Coordinates of H atoms on N7, N10, and O2 were freely refined, all others were riding. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100265. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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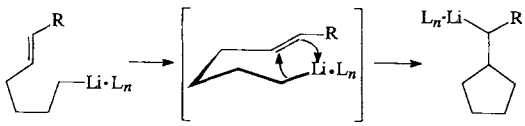
Synthesis of Enantiomerically and Diastereomerically Pure Cyclopentanols by Asymmetric Cyclocarbolithiation of 5-Alkenyl Carbamates**

Michael J. Woltering, Roland Fröhlich, and Dieter Hoppe*

Dedicated to Professor Hans J. Schäfer on the occasion of his 60th birthday

The intramolecular carbolithiation of 5-alkenyllithium compounds has become an important alternative to cyclizations of 5-alkenyl radicals (Scheme 1) due to the high 5-*exo-trig* selectivity and the facility of further functionalization of the resulting cyclopentylmethyl anion. Recently Marek, Normant et al. described an asymmetric variant of an intermolecular carbolithiation with cinnamyl alkoxides. Enantiofacial differentiation at the attacked double bond is achieved by the (−)-sparteine-mediated addition of non-stereogenic alkyllithium compounds.[3] However, the known methods do not allow control of the absolute configuration of the attacking nucleophilic carbon center. On the other hand, a wide variety of (*S*)-configurated (α-carbamoyloxy)alkyllithium derivatives are accessible by (−)-sparteine-mediated deprotonation.[4] Despite the presence of the reactive styrene moiety, we supposed that 6-phenyl-5-hexenyl carbamates would be lithiated regioselectively at the 1-position and then undergo stereoselective nucleophilic cycloalkylation to form the appropriate cyclopentanol derivatives.



Scheme 1. Intramolecular 5-*exo-trig*-carbolithiation [1, 2]. R = H or electron-withdrawing group; L = OEt_2.

Precursors **1a** and **1b** were prepared by Wittig olefination.[5, 6] They were deprotonated with *sec*-butyllithium/(−)-sparteine (**6**) in diethyl ether at −78 °C, the reaction mixture was stirred for 20 to 30 h at this temperature, and water or an electrophilic reagent was subsequently added (Scheme 2). With exception of the carboxylic acid ester **5g**, the diastereomerically and enantiomerically pure cyclization products **5** were obtained (Table 1). Decarbamoylation of **5a** provided (1*R*,2*S*)-2-benzylcyclopentanol;[11] the collected data correspond well to that in reference [12].

Substitution at the carbamate proceeds, as expected, with retention of configuration at the carbanionic center. The cyclization shows complete 5-*exo-trig* selectivity and leads with high diastereoselectivity to the *trans*-substituted cyclopentane **5** via intermediate **4**. Electrophilic attack at the benzylic carbanionic center also proceeds with high diastereoselectivity. The absolute configuration [1*R*,2*S*,2(1*S*)] was determined from the X-ray crystal structure of diol **8**, which was generated from **5e**

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[+] X-ray crystal structure determination

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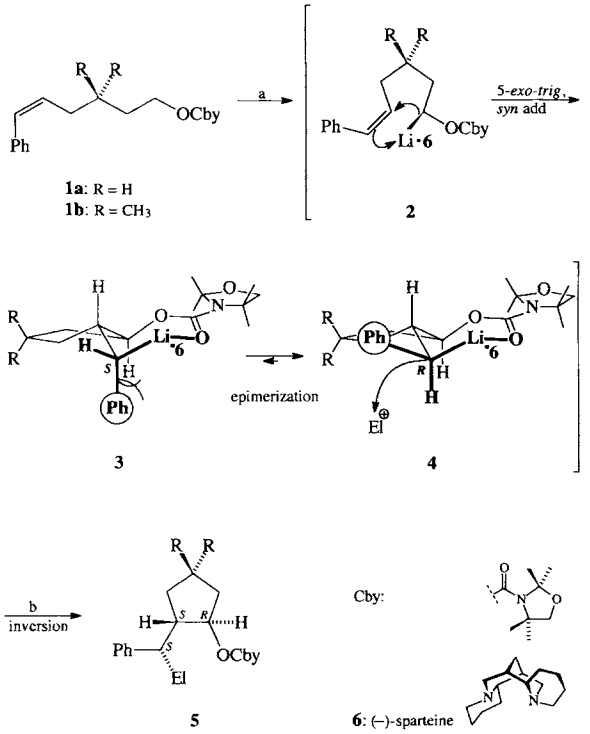


Scheme 2. Cyclocarbolithiation of **1** and scavenging reaction. a) *s*BuLi (1.5 equiv)/(–)-sparteine (**6**), Et_2O, –78 °C, 20–30 h; b) EIX, –78 °C → RT.

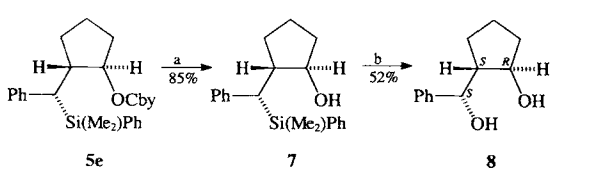
Table 1. Synthesis of cyclopentanol derivatives **5**.

Reagent	*t*[h]	EIX	Product[a]	Yield[%]	$[\alpha]_D^{20}$[b]	d.r.[f]
1a	20	HOH	**5a**	30	–20.9	>98:2
1a	26	Me_3SiCl	**5b**	32	–66.2	>98:2
1a	4	Bu_3SnCl	**5c**	14	–80.7	>98:2
1a	23	Me_3SnCl	**5d**[c]	17	–[g]	>98:2
1a	24	$PhMe_2SiCl$	**5e**	38	–79.7	>98:2
1b	23	HOH	**5f**	51	–29.0	>98:2
1b	23	CO_2	**5g**[d]	43	+19.2	92:8
1b	24	Bu_3SnCl	**5h**	30	–79.4	>98:2
1b	26	Me_3SiCl	**5i**[e]	38	–[g]	>98:2
1b	24	$PhMe_2SiCl$	**5j**	48	–59.4	>98:2

[a] Correct elemental analyses were obtained for all isolated products (C ±0.32, H ±0.26, N ±0.35 %). [b] $c = 0.96–1.01$ in CH_2Cl_2. [c] Mixture with **5a**. [d] Isolated as the methyl ester. [e] Mixture with **1b** and **5f**. [f] Determined by gas chromatography and ^1H NMR spectroscopy. [g] Not determined.

by deprotection of the hydroxy group and subsequent hydroxydesilylation (Scheme 3).[13, 14]

As stannylation, silylation, and carbonylation of several benzyllithium compounds occur with inversion of the configuration,[15–18] this can also be expected in our case. Therefore, the lithiated precursor **4** should have 2(1*R*) configuration. Since *syn* addition to the *cis* double bond leads to the primary adduct **3** with 2(1*S*) configuration, subsequent epimerization at the benzylic center is highly probable. The resulting epimer **4** is presumably thermodynamically more stable due to the equatorial position of the phenyl substituent within the bicyclic chelate. This is supported by the fact that the sequences of reactions starting from (*E*)-**1a**,**b** lead to the same diastereomers.



Scheme 3. Conversion of **5e** into diol **8**. a) $MeSO_3H$ (4 equiv), MeOH, reflux, 3 h, then K_2CO_3 (8 equiv), reflux, 20 h. b) $HBF_4 \cdot OEt_2$ (2 equiv), CH_2Cl_2, 0 °C, 10 min, then KF (2 equiv), $KHCO_3$ (10 equiv), 30% H_2O_2 (11 equiv), THF/MeOH, RT, 4.5 h.

The method described here allows the stereoselective formation of two C–C bonds and, therefore, three vicinal stereocenters of defined absolute configuration. The method might be interesting for the synthesis of cyclopentanoid natural products.[19]

Experimental Section

General procedure for cyclocarbolithiation: To **1a** or **1b** (0.5 mmol) and (–)-sparteine (0.75 mmol) in diethyl ether (3 mL) was added *s*BuLi (0.75 mmol) in cyclohexane/hexane at –78 °C, and the solution stirred for 20 to 30 h at –78 °C. The electrophile (0.75 mmol) was then added, and the reaction mixture warmed to room temperature over night. Water (3 mL) was added, the layers were separated, and the aqueous phase was extracted three times with ether. The combined organic fractions were dried over $MgSO_4$, the salts were filtered off, and the solvent removed from the filtrate in vacuo. The crude product was purified by flash chromatography on silica gel with ether/pentane.

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Keywords: asymmetric synthesis · carbanions · carbolithiations · cyclopentanols · (–)-sparteine

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[8] The crude carboxylic acid was converted into the methyl ester **5g** by treatment with diazomethane. A small amount of the carboxylate presumably epimerizes under the work-up conditions.

[9] The diastereomeric excesses of products **5** were determined by ^1H NMR spectroscopy and gas chromatography to be greater than 98%. After decarbamoylation of **5a** and acetylation of the resulting alcohol, the enantiomeric excess was determined by ^1H NMR shift experiments with tris[3-heptafluoropropylhydroxymethylene)camphorato]europium ([Eu(hfc)$_3$], 21 mol%) in $CDCl_3$ to be greater than 95%.

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[10] The by-products of the reactions of **1a** were the corresponding open-chain substitution product and the cyclopropane derivative resulting from intramolecular 1,3-elimination of the carbamate group. Reactions of **1b** delivered the cyclopropane derivative as well as the substrate. Therefore, in case of **1a** the yields are limited either by the rate of cyclization or the unfavorable equilibrium constant, whereas for **1b** the slow deprotonation step plays a crucial role. Other by-products were not identified.
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[16] However, protonations occur under retention of configuration [15, 17]. Therefore, for El = H the other benzylic epimer must be generated. As this is not of any significance for the examples described in here, the structure of 1′-*epi*-**5** is not shown.
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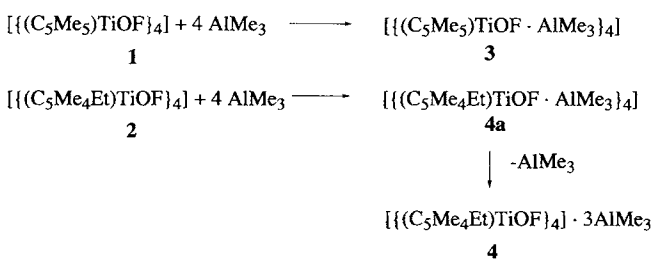
Activation of Ti–F Bonds in $[\{(C_5Me_5)TiOF\}_4]$ and $[\{(C_5Me_4Et)TiOF\}_4]$ with $AlMe_3$

Peihua Yu, Herbert W. Roesky,* Alojz Demsar, Thomas Albers, Hans-Georg Schmidt, and Mathias Noltemeyer

Dedicated to Professor Roald Hoffmann on the occasion of his 60th birthday

Substitution reactions proceed according to an S_N1 or S_N2 mechanism. For sterically shielded centers only an S_N1 mechanism is possible. It is assumed that in the latter the exit of the nucleophile can be electrophilically supported. This markedly facilitates the dissociation. Thus, C–F,[1] Si–F,[2] or P–F activations[3] have mainly been described with alkali metal and alkaline earth metal ions. Metallocenes of group 4 have been particularly intensively investigated in the last few years.[4, 5] Herein we report on the first step of a reaction of titanium fluoride oxide with $AlMe_3$.

As starting materials we chose the compounds $[\{(C_5Me_5)TiOF\}_4]$ (**1**) and $[\{(C_5Me_4Et)TiOF\}_4]$ (**2**),[6, 7] which each contain only one fluorine atom bound to each metal center. Compounds **1** and **2** were prepared by metathesis reactions from the corresponding chloride derivatives with Me_3SnF. When **1** and **2** are each allowed to react with four equivalents of $AlMe_3$ in toluene and hexane (1:1) at −10 °C, an immediate color change takes place from yellow to bright red. The solutions were stored at −20 °C, which led to red crystals of **3** and orange crystals of **4**, respectively. In the case of **4**, an intermediate is initially obtained (**4a**), which rearranges under dissociation to give **4** (Scheme 1). Both the color of the solution and that of the crystals is an indicator for the Ti–F activation in **3** and **4**.



Scheme 1.

The thermal decompositions of **3** and **4** do not afford $[\{(C_5Me_5)TiOMe\}_4]$ and $[\{(C_5Me_4Et)TiOMe\}_4]$, respectively. These compounds are only obtained when a slight excess of $AlMe_3$ is used.[8] Moreover, $(FAlMe_2)_3$ is formed. NMR and mass spectra reveal that the decomposition of **3** and **4** leads to mixtures of products containing fluorine atoms and methyl groups (MS: *m/z* 845 $[(C_5Me_5)_4Ti_4O_4FMe_2]$ and 901 $[(C_5Me_4Et)_4Ti_4O_4FMe_2]$). This confirms the lability of **3** and **4**.

The structure of **3** is shown in Figure 1. The four oxygen atoms and the four titanium atoms in this compound lie almost

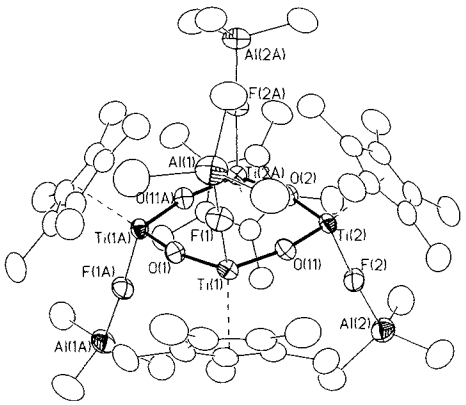


Figure 1. Crystal structure of **3**·3 toluene. Selected bond lengths [Å] and angles [°]: Ti(1)–F(1) 1.9593(13), Ti(2)–F(2) 1.9728(13), F(1)–Al(1) 1.8960(14), F(2)–Al(2) 1.8894(14), Ti(1)–O(1) 1.8282(7), Ti(1)–O(11) 1.8330(15), Ti(2)–O(11) 1.8245(15), Ti(2)–O(2) 1.8292(7); O(1)-Ti(1)-O(11) 105.24(8), O(1)-Ti(1)-F(1) 103.11(5), Ti(2)-O(11)-Ti(1) 164.67(9), Al(1)-F(1)-Ti(1) 175.90(8), Al(2)-F(2)-Ti(2) 175.62(8). The solvent molecules are not shown.

in a plane (deviation 0.02 Å). As expected the Ti–F bond lengths in **3** (av 1.965 Å) are considerably longer than those in the starting material[6] (av Ti–F 1.845 Å). Furthermore, the Ti-F-Al bond lengths (Ti–F 1.959, Al–F 1.896 Å) can be compared with the corresponding distances in $[\{(C_5H_4Me)_2TiF_2\}_3Al]$[9] (Ti–F 2.095, Al–F 1.812 Å).[10] These comparisons of the bond lengths clearly indicate that the coordinating effect of $AlMe_3$ leads to the extension of the Ti–F bonds. Moreover, the Al-F-Ti bonds are nearly linear (av 175.7°). The single-crystal structure analysis of **4** (Figure 2) shows that only three fluorine

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