generation of the same two peaks (1690 and 1550 cm^{-1}) that were observed by direct metalation of **10** with **1**. These were also replaced by the signal corresponding to adduct **8** after the addition of **7**.[15]

In summary we have shown that tol-binap–copper(I) complexes are active catalysts for the asymmetric addition of dienolate **1** to aldehydes. Utilization of CuO*t*Bu for the preparation of the catalyst permits a more direct entry into the catalytic cycle, avoids the introduction of spectator salts, and circumvents redox chemistry. Successful initiation of the reaction by CuO*t*Bu suggests that a copper(I) alkoxide is recursively generated throughout the reaction process. Additionally, we document spectroscopic and chemical evidence for the existence of a copper enolate as a reactive species. Such a process provides a conceptual and practical alternative to the well-established Lewis acid promoted stereoselective aldol reactions. The development of asymmetric, catalytic carbonyl additions that proceed through metalloenolates offers considerable opportunities for the design of new catalysts in asymmetric organic synthesis.

Received: June 16, 1998 [Z11993IE]
German version: *Angew. Chem.* **1998**, *110*, 3312–3314

Keywords: aldol reactions · asymmetric catalysis · C–C coupling · IR spectroscopy

---

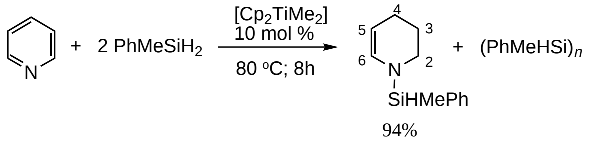
[1] For an extensive compilation of modern methods, see *Stereoselective Synthesis, Vol. 3* (Eds.: G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann), Thieme, Stuttgart, **1996**.
[2] a) E. J. Corey, D. Barnes-Seeman, T. W. Lee, S. N. Goodman, *Tetrahedron Lett.* **1997**, *38*, 6513; b) D. A. Evans, M. J. Dart, J. L. Duffy, M. G. Yang, *J. Am. Chem. Soc.* **1996**, *118*, 4322; c) B. W. Gung, Z. Zhu, R. A. Fouch, *J. Org. Chem.* **1995**, *60*, 2860; d) S. E. Denmark, W. Lee, *J. Org. Chem.* **1994**, *59*, 707; e) A. Bernardi, A. Cassinari, A. Comotti, M. Gardner, C. Gennari, J. M. Goodman, I. Paterson, *Tetrahedron* **1992**, *48*, 4183; f) M. T. Reetz, B. Raguse, C. F. Marth, H. M. Hugel, T. Bach, D. N. A. Fox, *Tetrahedron* **1992**, *48*, 5731.
[3] a) W. W. Ellis, B. Bosnich, *Chem. Commun.* **1998**, 193; b) T. K. Hollis, B. Bosnich, *J. Am. Chem. Soc.* **1995**, *117*, 4570; c) E. M. Carreira, R. A. Singer, *Tetrahedron Lett.* **1994**, *35*, 4323; d) P. J. Pospisil, S. R. Wilson, E. N. Jacobsen, *J. Am. Chem. Soc.* **1992**, *114*, 7585.
[4] (*S*)-Tol-BINAP = (*S*)-(−)-2,2′-bis(di-*p*-tolylphosphanyl)-1,1′-binaphthyl, a commercially available bisphosphane.
[5] J. Krüger, E. M. Carreira, *J. Am. Chem. Soc.* **1998**, *120*, 837.
[6] Shibasaki has reported an aldol addition reaction of benzophenone-derived enol silanes, mediated by Pd · BINAP/H$_2$O/molecular sieves, which is proposed to proceed via a Pd enolate intermediate: a) M. Sodeoka, K. Ohrai, M. Shibasaki, *J. Org. Chem.* **1995**, *60*, 2648; b) Y. M. A. Yamada, N. Yoshikawa, H. Sasai, M. Shibasaki, *Angew. Chem.* **1997**, *109*, 1942; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1871; c) Pd enolates have also been recently postulated in imine additions: E. Hagiwara, A. Fujii, M. Sodeoka, *J. Am. Chem. Soc.* **1998**, *120*, 2474; d) E. R. Burkhardt, R. G. Bergman, C. H. Heathcock, *Organometallics* **1990**, *9*, 30; e) G. A. Slough, R. G. Bergman, C. H. Heathcock, *J. Am. Chem. Soc.* **1989**, *111*, 938.
[7] For related processes wherein alkaline earth or lanthanide enolates are generated by deprotonation, see a) D. A. Evans, S. G. Nelson, *J. Am. Chem. Soc.* **1997**, *119*, 6452; b) M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem.* **1997**, *109*, 1290; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1237.
[8] A. Yanagisawa, Y. Matsumoto, H. Nakashima, K. Asakawa, H. Yamamoto, *J. Am. Chem. Soc.* **1997**, *119*, 9319.
[9] D. A. Evans, M. C. Kozlowski, C. S. Burgy, D. W. C. MacMillan, *J. Am. Chem. Soc.* **1997**, *119*, 7893.
[10] S. Kanemasa, Y. Oderaotoshi, S. Sakaguchi, H. Yamamoto, J. Tanaka, E. Wada, D. P. Curran, *J. Am. Chem. Soc.* **1998**, *120*, 3074.
[11] a) Y. Kobayashi, T. Taguchi, T. Morikawa, E. Tokuno, S. Sekiguchi, *Chem. Pharm. Bull.* **1980**, *28*, 262; b) F. H. Jardine, L. Rule, A. G. Vohra, *J. Chem. Soc. A* **1970**, 238.
[12] The depiction of **6** as an O-bound copper dienolate is not meant to suggest any detailed structural information regarding the nature of **6**.
[13] For the preparation of CuO*t*Bu, see T. Tsuda, T. Hashimoto, T. Saegusa, *J. Am. Chem. Soc.* **1972**, *94*, 658.
[14] The IR experiments were conducted with an ASI Applied Systems ReactIR 1000 spectrometer with a MCT detector (MCT = mercury cadmium telluride) and a DiComp probe.
[15] In these and all reactions the product was isolated in 91–94% *ee*, values which are similar to those we routinely obtain for this process under preparative conditions.
[16] In a control experiment, the quaternary ammonium dienolate was found to react rapidly with benzaldehyde at −78 °C to form racemic aldol adduct in 94% yield.
[17] [Cu(CH$_3$CN)$_4$]ClO$_4$ was prepared by the procedure described by Kubas: G. J. Kubas, *Inorg. Syn.* **1990**, *28*, 68.

Homogeneous Catalytic Hydrosilylation of Pyridines[**]

Leijun Hao, John F. Harrod,* Anne-Marie Lebuis, Ying Mu, Ronghua Shu, Edmond Samuel,* and Hee-Gweon Woo

Titanocene complexes are versatile catalysts for a large number of reactions.[1–11] The reaction of Me$_3$SiH with pyridine catalyzed by *heterogeneous* platinum-group catalysts was reported many years ago.[12] We now report the first examples of the hydrosilylation of pyridines with *homogeneous,* titanocene-based catalysts, and the first example of homogeneously catalyzed hydrosilylation of an aromatic substrate.

Typically, the reaction was carried out without solvent with a 2:1 molar ratio of silane to pyridine and 10 mol% of [Cp$_2$TiMe$_2$] (based on pyridine) at 80 °C [Eq. (1)], but an inert



(1)

---

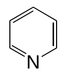
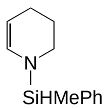
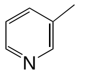
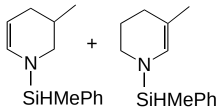
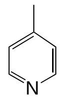
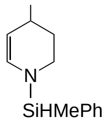
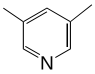
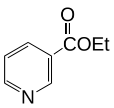
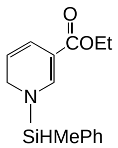
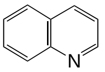
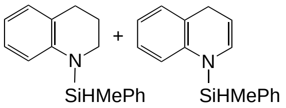
[*] Prof. Dr. J. F. Harrod, Dr. L. Hao, Dr. A.-M. Lebuis, Dr. Y. Mu, R. Shu, Dr. H.-G. Woo
Department of Chemistry, McGill University
Montreal, PQ H3A 2K6 (Canada)
Fax: (+1) 514-398-3797
E-mail: harrod@omc.lan.mcgill.ca
Dr. E. Samuel
Laboratoire de Chimie Organométallique de l'ENSCP
(URA 403 CNRS)
11 rue P. et M. Curie, 75005 Paris (France)
Fax: (+33) 1-4326-0061

[**] This work was supported by the Natural Sciences and Engineering Research Council (Canada) and the Fonds FCAR du Quebec. We thank Dr. J. Britten for collecting the X-ray data set of **1b**.

hydrocarbon solvent, such as toluene, may be added if desired. The ^1H NMR spectrum of the crude products showed that the yields of hydrosilylated pyridines were in the range of 80–100%.

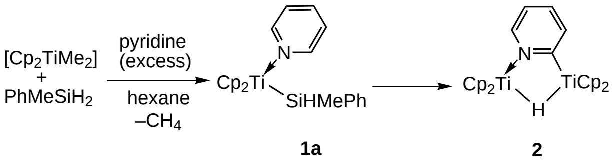
The results of the catalytic hydrosilylation of pyridine and several derivatives are summarized in Table 1. These show that 1) [Cp_2TiMe_2] is an effective precatalyst for the hydrosilylation of pyridines and quinoline, with the formation of a Si–N bond, 2) the reaction tolerates certain functional groups (entry 5), and 3) hydrogenation of the intermediate *N*-silyl-1,2-dihydropyridine sometimes occurs (entries 1–3) in a manner that is strongly dependent on the location of the substituents on the pyridine ring (entry 4). Substrates with methyl substituents in the 2- and/or 6-positions of the pyridine ring do not react under the conditions used.

Table 1. Titanocene-catalyzed hydrosilylation/hydrogenation of pyridines.[a]

Entry	Pyridine	Product	Yield [%][b]
1			94
2			85 (3:2)
3			83
4			70
5			100
6			74 (3:1)

[a] All reactions were carried out neat at 80 °C with 10 mol% [Cp_2TiMe_2] (relative to pyridine), the ratio of silane to pyridine was 2:1. [b] Based on the ^{29}Si NMR spectrum.

Model stoichiometric reactions provide insight into the general pathway of the catalytic hydrosilylation reactions. Reaction of [Cp_2TiMe_2] and $PhMeSiH_2$ (1:2 molar ratio) in the presence of excess pyridine in hexane/toluene (6/1) proceeded smoothly to give first the complex **1a**, as demonstrated by EPR spectroscopy and a color change of the solution from yellow to violet (Scheme 1). After one hour the violet solution had changed to dark brown, and brown-black, square-plate crystals of **2** precipitated when the solution was cooled to −20 °C for 24 h.



Scheme 1. Illustration of the sequential formation of **1a** and **2**.

When Ph_2SiH_2 or $PhSiH_3$ replaced $PhMeSiH_2$ in the reaction, **1b** or **1c** was obtained, respectively. However, unlike **1a**, **1b** and **1c** did not undergo further reaction to **2**, and they are stable for several days at ambient temperatures in the presence of excess pyridine. These differences in thermal stability are reminiscent of the analogous silylphosphane complexes: [$Cp_2Ti(SiH_2Me)(PMe_3)$] decomposes readily to give the hydride [$Cp_2TiH(PMe_3)$], whereas compounds of the type [$Cp_2Ti(SiHR_2)(PMe_3)$] ($R_2 = Ph_2$, PhH, H_2) are relatively stable under the same conditions.[13] Compounds **1b** and **1c** were isolated in good yield as dark violet crystals when the reaction was carried out in hexane.

[$Cp_2Ti(SiHMePh)(C_5H_5N)$] **1a**
[$Cp_2Ti(SiHPh_2)(C_5H_5N)$] **1b**
[$Cp_2Ti(SiH_2Ph)(C_5H_5N)$] **1c**
[$Cp_2Ti(\mu$-H)(1κN,2κC-pyridyl)$TiCp_2$] **2**

Complexes **1** exhibit characteristic EPR spectra. The spectrum of **1a** contains a pseudoquartet at $g = 1.9882$ due to the interaction of the unpaired electron with the ^{14}N nucleus ($a_N = 1.91$ G, $I = 1$) of the pyridine and the ^1H nucleus ($a_H = 2.16$ G, $I = 1/2$) of the silyl group, and well-resolved satellites due to the titanium nuclei ($a_{Ti} = 9.79$ G, ^{49}Ti, 7.75%, $I = 5/2$ and ^{47}Ti, 5.51%, $I = 7/2$). The spectrum of **1b** is, as expected, very similar to that of **1a** ($g = 1.9881$, $a_N = 1.92$ G, $a_H = 2.20$ G, $a_{Ti} = 9.75$ G), whereas the spectrum of **1c** contains a pseudoquintet at $g = 1.988$ with $a_N = 3.3$ G, $a_H = 2.30$ G, $a_{Ti} = 10.3$ G. Upon replacement of Si–H by Si–D, the spectra of **1** all simplify to a triplet (coupling to the ^{14}N nucleus) due to the much smaller (unresolved) superhyperfine coupling with D as opposed to H. The structure of **1b** was confirmed by X-ray crystallographic analysis (Figure 1).[14]

A single-crystal X-ray structure analysis of **2** revealed that it is a unique bimetallic titanocene(III) complex with one hydride and one pyridyl group as bridging ligands (Figure 2).[14] The Ti–Ti distance of 3.602(2) Å is too long for a metal–metal bond. The EPR spectrum of **2** in toluene displays a broad singlet ($g = 1.984$; $a_{Ti} = 12$ G; toluene, 250 K). The ^1H NMR spectrum of a saturated solution of **2** in toluene shows a very broad, paramagnetically shifted resonance at $\delta = 31.6$ ($\nu_{1/2} \approx 1080$ Hz), which is tentatively assigned to the Cp protons in **2**.

The formation of **2** can be rationalized according to Scheme 2. First, **1a** decomposes to generate the hydride **3**. Such a decomposition reaction has been seen in the analogous silylphosphane complexes.[13] The pyridine ligand of **3** then undergoes α-metalation and loss of H_2 to give **4**, which then

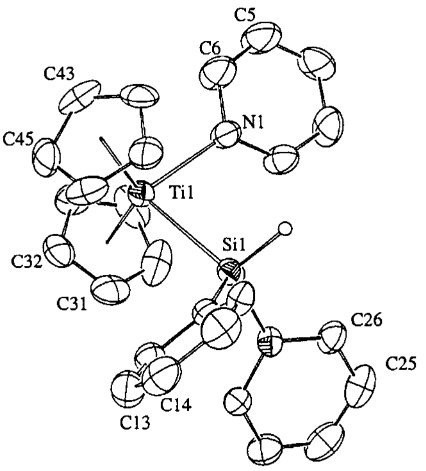


Figure 1. ORTEP drawing of the molecular structure of one of the two conformers of **1b** (thermal ellipsoids at the 30 % probability level). Selected bond lengths [Å] and angles [°]: Ti1–N1 2.292(8), Ti1–Si1 2.678(3); Si1-Ti1-N1 87.2(2), Cp-Ti1-Cp 135.49(9), angle between the Si-Ti-N plane and plane of the pyridine ring 28.8(4).

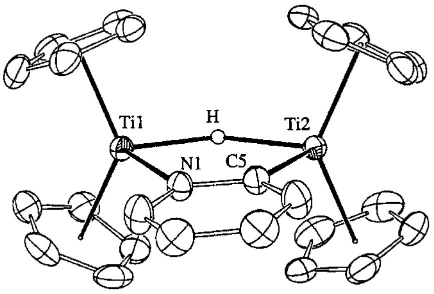
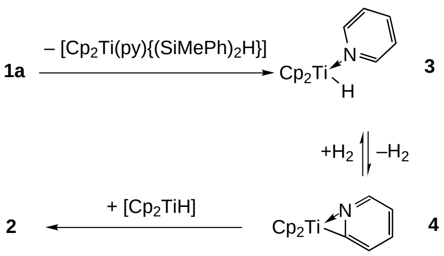


Figure 2. ORTEP drawing of the molecular structure of **2** (thermal ellipsoids at the 30 % probability level). Selected bond lengths [Å] and angles [°]: Ti1–H 1.92(2), Ti2–H 1.91(2), Ti1–N1 2.202(2), Ti2–C5 2.205(2); H-Ti1-N1 79.2(9), H-Ti2-C5 79.1(9), Cp-Ti1-Cp 131.38(2), Cp-Ti2-Cp 132.25(2).

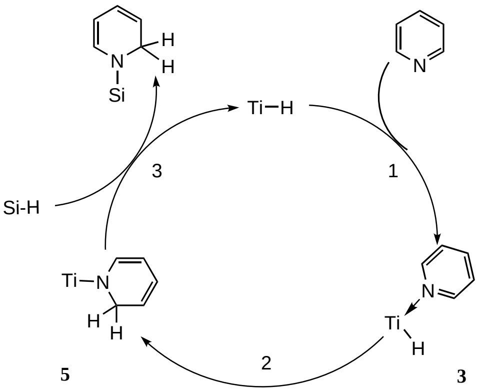


Scheme 2. Proposed mechanism for the formation of **2**.

reacts with another molecule of **3** to produce the pyridyl-bridged dimer **2**. A similar α-metalation process has also been reported for $[Cp_2Ti(alkyl)(py)]$ complexes.[15] *ortho*-Metalations of pyridine by other early transition metals have also been reported.[16–18] The hydride complex **3** was not observed directly in the hydrosilylation reactions, probably due to its high reactivity. A sample of **3**, generated from the reaction of $[\{Cp_2TiH\}_2]$[19] and pyridine at $-20\,^{\circ}C$, decomposes immediately upon warming to ambient temperatures to give **2** and a minor amount of **4** ($g = 1.9905$, which is close to the value of $g = 1.990$ for the analogous complex $[Cp_2Ti(\eta^2\text{-}N,C\text{-}2\text{-}MeC_5H_3N)]$).[15]

Experiments with $PhMeSiD_2$ and C_5H_5N, or $PhMeSiH_2$ and C_5D_5N gave products (entry 1, Table 1) in which H/D exchange was much more extensive at the 2- and 6-positions than at other positions of both the products and unchanged pyridine. Extensive H/D exchange also occurred at the 2- and 6-positions of pyridine when 1 atm of H_2 was applied to a solution containing 10 mol % of $[\{Cp_2TiH\}_2]$ in C_5D_5N.[19] Under 15 atm of H_2 complete exchange occurred at the 2- and 6-positions of the pyridine. These H/D exchange results support the mechanism depicted in Scheme 2, and can be easily rationalized by the reversibility between **3** and **4**.

These results show that the hydride **3** is, most likely, the key intermediate for the formation of **2**, H/D exchange, and hydrosilylation/hydrogenation reactions. The simplest mechanism for the hydrosilylation reaction, which conforms to all of the experimental data, is depicted in Scheme 3. In this mechanism, formation of **3** (step 1) is followed by insertion of the N=C bond into the Ti–H bond (step 2) to give **5,** which then undergoes σ-bond metathesis with silane to regenerate Cp_2TiH with release of *N*-silyl-1,2-dihydropyridine. The further facile hydrogenation of the latter to the observed products in the presence of excess silane is expected, since it is well known that olefinic substrates (and in particular dienes) are very efficient hydrogen traps in silane dehydrocoupling reactions.[9] In hydrosilations where further reduction of another double bond occurs, 1,2-dimethyl-1,2-diphenyldisilane and higher oligosilanes are always observed in amounts commensurate with dehydrocoupling/cohydrogenation. If only one mole of silane is used per mole of pyridine, the products remain the same, but the conversion is reduced to less than 50 %. In these cases, the hydrogenation step is more rapid than the hydrosilation step. Any absence of hydrogenation is explained by either steric hindrance (entry 4) or electronic deactivation (entry 5). When the reaction with 3,5-lutidine (entry 4) was carried out under 20 atm of H_2, and the reaction time extended to 8 days, diene and monoene were obtained in a ratio of 1:2.



Scheme 3. Proposed mechanism of the catalytic hydrosilylation.

In summary, we have demonstrated the unprecedented homogeneous catalytic hydrosilylation of an aromatic compound and followed several of the elementary steps of the reactions. Our homogeneous catalyst system has high selectivity towards the hydrosilylation of pyridines compared to the previous heterogeneous system, and tolerates some substituents. Study of the catalyst intermediates suggests that the hydride [Cp_2TiH] is a key reactant in the catalytic cycle, as previously proposed for a number of other titanocene-catalyzed reactions.

Experimental Section

1b: [Cp_2TiMe_2] (50 mg, 0.24 mmol) was dissolved in a mixture *n*-hexane/toluene (4/1, 5 mL), pyridine (0.10 mL, 1.2 mmol), and phenylsilane (0.11 mL, 0.72 mmol). Over about one hour, the solution slowly changed color from orange to dark violet. This was accompanied by a slow gas evolution and the formation of violet, needle-shaped crystals of **1b** $\cdot$ $0.25\,C_5H_5N$. The crystals were separated, washed several times with cold hexane, and dried under vacuum (yield: 95 mg, 87%). Elemental analysis for $C_{27}H_{26}NSiTi$ (440.47): found (calcd): C 72.83 (73.62); H 5.99 (5.95); N 3.22 (3.18); Si 5.98 (6.37); Ti 10.26 (10.87). The deuterated form of **1b** was prepared with Ph_2SiD_2 instead of Ph_2SiH_2.

2: [Cp_2TiMe_2] (120 mg, 0.58 mmol) was added to a solution of phenylmethylsilane (0.24 mL, 1.73 mmol) and pyridine (1.0 mL, 12.4 mmol) in *n*-hexane/toluene (6/1; 7.0 mL). The solution turned deep violet after 2 hr without stirring, and dark brown after about a further 1 h. The solution was held at ambient temperatures for another 4 h and at $-20\,^{\circ}C$ for 24 h to yield dark brown plates suitable for X-ray chrystallographic analysis (yield: 83 mg, 56%). Elemental analysis for $C_{26}H_{26}Ti_2N$ (448.25): found (calcd): C 66.27 (68.98); H 5.12 (5.79); N 3.04 (3.22); Ti 22.33 (22.01).

General procedure for the catalytic hydrosilylation/hydrogenation: $PhMeSiH_2$ (1.20 mL, 8.75 mmol) and pyridine (0.35 mL, 4.34 mmol) were added to [Cp_2TiMe_2] (0.45 g, 0.43 mmol) in a Schlenk tube. After a short time at room temperature the solution turned blue-violet, and gas was evolved. The mixture was stirred at 80 °C for 8 h and then distilled under vacuum to give pure *N*-(phenylmethylsilyl)-1,2,3,4-tetrahydropyridine (entry 1) (b.p. 57 °C/0.12 Torr; yield: 0.88 g, 50%). NMR analysis of the undistilled reaction mixture showed 94% conversion of pyridine. ^1H NMR (499.9 MHz, C_6D_6): $\delta = 0.28$ (d, 3H, $J = 3.3$ Hz, $SiCH_3$), 1.57 (m, 2H, C5-H), 2.00 (m, 2H, C4-H), 2.99 (m, 2H, C6-H), 4.62 (m, 1H, C3-H), 5.01 (q, 1H, $J = 3.3$ Hz, SiH), 6.28 (dt, 1H, $^3J = 7.8$ Hz, $^4J = 3.0$ Hz, C2-H), 7.20 (m, 3H, *m,p*-C_6H_5), 7.50 (m, 2H, *o*-C_6H_5); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = -0.50$ ($SiCH_3$), 22.16, 23.44, 43.79 (C2, C3, C4), 98.69, 123.49 (C5, C6), 128.18, 129.48, 130.13, 134.40 (Ph); ^{29}Si NMR (59.9 MHz, C_6D_6): $\delta = -9.10$; MS (70 eV): *m*/*z* (%): 203 (100) [M^+], 188 (18.5) [$M^+ - Me$], 121 (77) [$M^+ - C_5H_8N$].

Received: May, 25 1998 [Z11893IE]
German version: *Angew. Chem.* **1998**, *110*, 3314–3318

Keywords: homogeneous catalysis · hydrogenations · hydrosilylations · pyridines · titanium

---

[1] a) C. Aitken, J. F. Harrod, E. Samuel, *J. Organomet. Chem.* **1985**, *279*, C11; b) C. Aitken, J. F. Harrod, E. Samuel, *J. Am. Chem. Soc.* **1986**, *108*, 4059; c) L. S. Chang, E. R. Corey, *Organometallics* **1987**, *6*, 1595; d) L. S. Chang, J. Y. Corey, *Organometallics* **1989**, *8*, 1885; e) J. Y. Corey, X.-H. Zhu, T. C. Bedard, L. D. Lange, *Organometallics* **1991**, *10*, 924.

[2] C. Aitken, J. F. Harrod, A. Malek, E. Samuel, *J. Organomet. Chem.* **1988**, *349*, 285.

[3] H. Q. Liu, J. F. Harrod, *Organometallics* **1992**, *11*, 822.

[4] J. He, H. Liu, J. F. Harrod, R. Hynes, *Organometallics* **1994**, *13*, 336.

[5] H. Liu, J. F. Harrod, *Can. J. Chem.* **1990**, *68*, 1100.

[6] a) M. B. Carter, B. Schiott, A. Gutiérrez, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 11670; b) S. Xin, J. F. Harrod, *J. Organomet. Chem.* **1995**, *499*, 181; c) S. Xin, J. F. Harrod, *Can. J. Chem.* **1995**, *73*, 999.

[7] R. D. Broene, S. L. Buchwald, *J. Am. Chem. Soc.* **1993**, *115*, 12659.

[8] C. A. Willoughby, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 11631.

[9] J. F. Harrod, S. S. Yun, *Organometallics* **1987**, *6*, 1381.

[10] N. M. Kablaoui, S. L. Buchwald, *J. Am. Chem. Soc.* **1996**, *118*, 3182.

[11] T. Grasczyk, J. F. Harrod, *J. Polymer Sci. Part A* **1994**, *32*, 3183.

[12] N. C. Cook, J. E. Lyons, *J. Am. Chem. Soc.* **1965**, *87*, 3283; **1966**, *88*, 3396.

[13] L. Hao, A.-M. Lebuis, J. F. Harrod, *Chem. Commun.* **1998**, 1089.

[14] a) Crystal structure analysis of **1b** $\cdot$ $0.25\,C_5H_5N$: crystal dimensions $0.20 \times 0.11 \times 0.06$ mm^3, monoclinic, $P2_1/n$, $a = 18.991(1)$, $b = 8.356(1)$, $c = 31.381(2)$ Å, $\beta = 105.270(1)^{\circ}$, $V = 4804.3(4)$ Å^3, $T = 300(2)$ K, $Z = 8$ ($Z' = 2$), smart CCD P4 diffractometer (Siemens) $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 37192 measured reflections, 9317 independent and 3084 observed reflections [$I > 2\sigma(I)$], 573 refined parameters, $R_1 = 0.1327$, $wR_2 = 0.1446$.[14c] b) Crystal structure analysis of **2** $\cdot$ $0.5\,C_5H_5N$: crystal dimensions $0.75 \times 0.57 \times 0.21$ mm^3, monoclinic, $P2_1/n$, $a = 16.742(8)$, $b = 8.039(3)$, $c = 18.266(9)$ Å, $\beta = 114.03(1)^{\circ}$, $V = 2245(2)$ Å^3, $T = 220(2)$ K, $Z = 4$, CAD4 diffractometer (Enraf-Nonius), $Cu_{K\alpha}$ radiation ($\lambda = 1.54056$ Å), 18971 reflections measured, 4264 independent and 3876 observed reflections [$I > 2\sigma(I)$], 284 refined parameters, $R_1 = 0.0502$, $wR_2 = 0.1282$. The bridging hydrogen atom was located in the difference map.[14c] c) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-102515 (**2**) and CCDC-102516 (**1b**). 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).

[15] a) E. Klei, J. H. Teuben, *J. Organomet. Chem.* **1981**, *214*, 53; b) E. Klei, J. H. Teuben, *J. Chem. Soc. Chem. Commun.* **1978**, 659.

[16] K. H. Den Haan, Y. Wielstra, J. H. Teuben, *Organometallics* **1987**, *6*, 2053.

[17] L. C. Francesconi, D. R. Corbin, D. N. Hendrickson, G. D. Stucky, *Inorg. Chem.* **1978**, *17*, 2078; L. C. Francesconi, D. R. Corbin, D. N. Hendrickson, G. D. Stucky, **1979**, *18*, 3074; L. C. Francesconi, D. R. Corbin, D. N. Hendrickson, G. D. Stucky, *Inorg. Chem.* **1981**, *20*, 2059.

[18] R. Jungst, D. Sekutiwski, J. David, M. Luly, G. D. Stucky, *Inorg. Chem.* **1977**, *16*, 1645.

[19] a) J. E. Bercaw, H. H. Brintzinger, *J. Am. Chem. Soc.* **1969**, *91*, 7301; b) R. H. Marvich, H. H. Brintzinger, *J. Am. Chem. Soc.* **1971**, *93*, 2046.

Synthesis of β-Mannosides via Prearranged Glycosides**

Thomas Ziegler* and Gregor Lemanski

Although the chemical synthesis of oligosaccharides has reached a remarkable level several problematic cases of the diastereoselective formation of O-glycosidic bonds demand improvements. In particular, 1,2-*cis*-configurated O-glycosides are often realized solely with difficulties or with significant synthetic efforts. This is especially the case for saccharides that contain β-D-mannosidic and β-L-rhamnosidic linkages. Similarly, α-linked D-galactosyl and D-glucosyl residues are difficult to establish in some cases.

The Koenigs–Knorr reaction in combination with the silver silicate promotor developed by Paulsen et al. is still applied often to the synthesis of β-D-mannosidic and β-L-rhamnosidic linkages.[1] Since this glycosylation procedure and related

---

[*] Prof. Dr. T. Ziegler, Dipl.-Chem. G. Lemanski
Institut für Organische Chemie der Universität
Greinstrasse 4, D-50939 Köln (Germany)
Fax: (+49)221-470-5057
E-mail: Thomas.Ziegler@Uni-Koeln.de

[**] Prearranged Glycosides, Part 7. Part 6: T. Ziegler, G. Lemanski, *Eur. J. Org. Chem.* **1998**, 163–170.