cyclohexastannanes, $(R_2Sn)_6$, show $^1J_{^{119}Sn,^{117}Sn}$ coupling in the range 462 – 1339 Hz,[23] whereas the electron deficient borane-like Zintl ions display much smaller couplings (e.g *nido*-Sn_9^{4-}, $^1J_{^{119}Sn,^{117}Sn} = 254$ Hz , $[L_2PtSn_9]^{4-}$, $^1J_{^{119}Sn,^{117}Sn} = 79$ Hz).

In the solid state, the stannides show a rich chemistry that spans valence compounds containing discrete Zintl ions, to intermetallic phases characterized by delocalized bonding and metallic behavior.[24] Six-membered rings are found in several of these materials, including Li_5NaSn_4 (puckered 6-rings, chair conformation),[25] $BaSn_5$ (planar 6-rings),[26] and in α-tin itself. Each of these is derived from diamond or graphite related extended structures and does not contain isolated Zintl anions. Other compounds do contain isolated Zintl ions, such as the Sn_2^{6-} ion in $BaMg_2Sn_2$ with an ethane (or dihalogen) like structure and a short Sn–Sn bond of 2.87 Å.[27] The number of tin Zintl ions isolated from solution methods is low and the prospects of preparing new ones are limited by the apparent stability of the $E_9^{3/4-}$ clusters and their derivatives. However, through the use of appropriate transition metal precursors, other metal-stabilized Zintl ions may be accessible through cluster degradation reactions and internal electron transfer.

Experimental Section

Preparation of $[K(2,2,2\text{-crypt})]_2[(\eta\text{-}C_6H_5Me)NbSn_6Nb(\eta\text{-}C_6H_5Me)]\cdot en$. All reactions were performed in a nitrogen atmosphere dry box (Vacuum Atmospheres Company). In vial 1, K_4Sn_9 (50.0 mg, 0.041 mmol) and 2,2,2-crypt (46 mg, 0.12 mmol) were dissolved in en (ca. 3 mL). In vial 2, Nb(η-$C_6H_5Me)_2$ (11.3 mg, 0.041 mmol) was dissolved in toluene (ca. 1 mL) producing a red solution. The content of vial 2 was added to the vial 1 yielding a green-brown solution. The reaction mixture was stirred for 12 h and filtered through tightly packed glass wool in a pipette. Dark brown crystals formed in the reaction vessel after one week. Yield: 12 mg (15 %); NMR analysis of the reaction mixtures showed free toluene (^{1}H and ^{13}C NMR) as the only by-product of the reaction; ^{119}Sn NMR (186.5 MHz (en/toluene), 25 °C): $\delta = -149$; elemental analysis calcd (%) for $C_{52}H_{96}K_2N_6Nb_2Sn_6O_{12}$: C 31.64, H 4.87, N 4.26 %; found: C 30.53, H 5.00, N 4.33.

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Inversion of Enantioselectivity during the Platinum-Catalyzed Hydrogenation of an Activated Ketone**

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In the past few years there has been a remarkable progress in the enantioselective hydrogenation of α-functionalized (activated) ketones over chirally modified Pt catalysts. This development is reflected by the growing number of reactions in which enantiomeric excesses (*ee*) of 90 % or higher have been achieved. Even more promising is the shift from the early "trial-and-error" strategy to a more rational basis for designing new modifiers and discovering new applications through mechanistic investigations.[1–6] Several mechanistic

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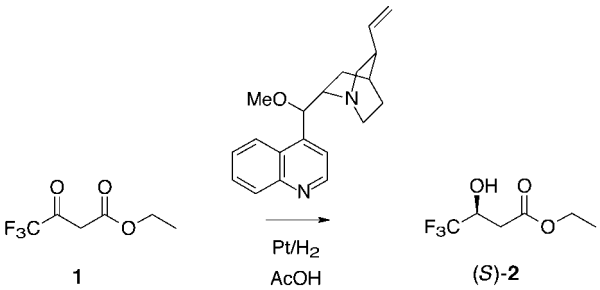
models have been suggested for rationalizing the observed enantiodifferentiation.[4–9] In one point all these models conform: the chiral modifier interacts on the Pt surface with the carbonyl group of the reactant. Other equilibrated species such as the enol form,[10] or the hemiketal in alcoholic solvents,[11] are considered as spectator species. Herein we show the first striking evidence against the general applicability of this assumption.

We have recently reported the facile hydrogenation of ethyl 4,4,4-trifluoroacetoacetate **1** in AcOH and in the presence of *O*-methylcinchonidine (MeOCD) as chiral modifier to afford β-hydroxyester **2** in 90% *ee* (Scheme 1).[12] Analysis of the



Scheme 1. Hydrogenation of ethyl 4,4,4-trifluoroacetoacetate (**1**).

influence of reaction conditions revealed a significant variation of *ee* value with conversion in the presence of even trace amounts of water. This variation was enlarged by catalytic amounts of a strong acid. The hydrogenation of **1** in THF containing small amounts of water (0.8 vol%) and trifluoroacetic acid (TFA; molar ratio: TFA/MeOCD = 8:1) is a typical example (Figure 1). The *ee* value decreased gradually

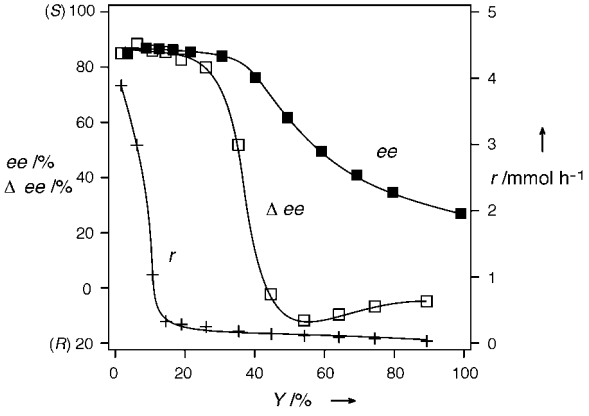
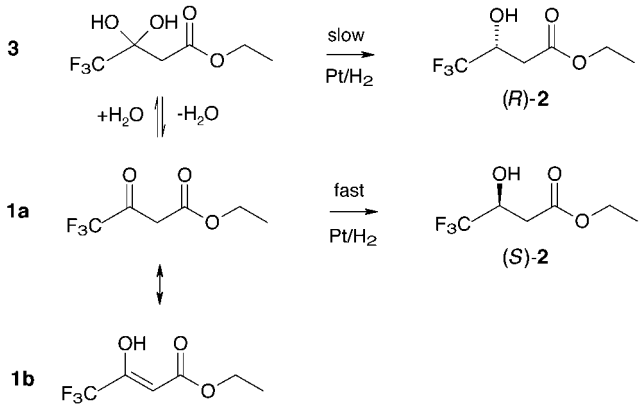


Figure 1. Changes in enantioselectivity and rate *r* during the course of the reaction (*Y*: yield). Standard reaction conditions (see Experimental Section) with preequilibration overnight; addition of TFA (10 μL) directly before initiating hydrogenation.

after an initial constant period (87% (*S*)) and dropped at full conversion to only 27% (*S*). The calculated actual or incremental *ee* (Δee) value shows that the sense of enantiodifferentiation inverted at around 50% yield (*Y*) and (*R*)-**2** became the dominant product. The highest Δee value in favor of (*R*)-**2** was 12%. To our knowledge, such an inversion has never been observed in the hydrogenation of any activated ketone over chirally modified Pt. No racemization of the product could be detected under the described reaction conditions. Note also the dramatic decrease in reaction rate (by a factor of >100) with conversion. With increasing water content in the system the product distribution shifted towards the dominance of (*R*)-**2**. With double amount of water (1.6 vol%) the final, cumulative *ee* value shifted from 27% (*S*) to 4% (*R*).

Evidently, at least two reacting species, dominating at different stages of the reaction and providing excess to the opposite enantiomers, are needed to explain the conversion-dependent changes in rate *r* and *ee*. NMR spectroscopic analysis revealed the equilibration of **1** as keto (**1a**), enol (**1b**), and hydrate (**3**, at $\delta = -87.3$ in the ^{19}F spectrum) species (Scheme 2). In the [D_8]THF used, only minor amounts of **3**



Scheme 2. Reaction scheme during hydrogenation of **1** in THF, in the presence of water.

(<5%) were detected, while the equilibrium was shifted towards **3** by addition of water. Rate of formation and equilibrium concentration of **3** under reaction conditions (0.8 vol% water) are shown in Figure 2. Though only

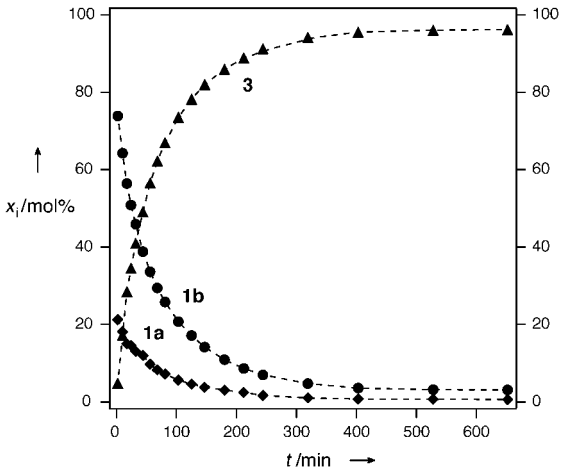


Figure 2. Hydrate (**3**) formation from **1** in THF; the equilibrium concentration x_i of component i in the mixture was determined by NMR spectroscopy. Concentrations according to general reaction conditions; the addition of 0.8 vol% water occurred at time $t = 0$ (water/**1** = 1.2).

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1.2 molar equivalents of water was present, in equilibrium the fraction of **3** was 95% and only 0.5% **1a** remained. Equilibration was three times slower in the absence of MeOCD and 20 times faster in AcOH (acid–base catalysis). The ratio of **1a**/**1b** remained constant, indicating that the keto–enol equilibration was much faster than hydrate formation.

On the basis of the catalytic and NMR data the inversion of enantioselectivity may be explained as follows. Hydrogenation of **1a** is fast and affords up to 87% *ee* (*S*). To judge the reactivity of **1a**, we have to point out that this is a minor species compared to **1b** and **3**, still, its hydrogenation determines the enantioselectivity at low conversions. This assumption is in accordance with all mechanistic models suggested for the enantioselective hydrogenation of activated ketones on a cinchona-alkaloid-modified Pt surface.[4–9] The high reactivity of the carbonyl group is partly due to the rate increase resulting from interaction with the chiral modifier MeOCD.[12]

Despite the relatively high concentration of **1b** in solution, it is likely a spectator species. In AcOH, in which hydration is much faster than in THF, a small drop in the **1a**/**1b** ratio at the beginning of equilibration (monitored by NMR spectroscopy) indicates that the rate of interconversion between **1a** and **1b** is in the same range as the initial rate of hydration ($>30\ \mathrm{mmol\,h^{-1}}$) under these conditions. Because this rate is considerably higher than even the initial rate of hydrogenation of **1** ($r = 4.3\ \mathrm{mmol\,h^{-1}}$, Figure 1), we can deduce that the **1a**/**1b** ratio remains constant during hydrogenation, and the observed changes in *ee* values with conversion cannot be attributed to a shift from the hydrogenation of **1a** to **1b**.

We suggest that hydrogenolysis of **3** leading to (*R*)-**2** is responsible for the inversion of *ee* at higher conversions. There has been no evidence yet available in the literature on the hydrogenation of a geminal diol, but it is well established that hydrogenolysis of a C–OH bond is much slower than hydrogenation of a ketone, and the rate of hydrogenolysis is dramatically enhanced by acids.[13] Our observations in Figure 1 may well be explained on this basis. In the early stage of the reaction the fraction of **1a** is high and hydrogenation of this reactive species governs the enantioselectivtiy. With increasing time and yield the ratio of **3**/**1a** strongly increases due to conversion of **1a** and to the proceeding equilibration to form **3** as the dominant species. At medium conversion, the hydrogenation of **3** affording (*R*)-**2** can compete with the hydrogenation of **1a** leading to (*S*)-**2**, and the product distribution is gradually shifted to the dominance of (*R*)-**2**.

The critical role of equilibration is demonstrated in Figure 3. When the hydrogenation is started without preequilibration (that is about 6 min after addition of water) the *ee* is high and almost constant in the initial period. In this region the hydrate concentration is low and hydrogenation of **1a** is almost exclusive. With increasing hydrate concentration the *ee* value gradually decreases. When the same reaction mixture is preequilibrated overnight, the initial *ee* value is lower (already significant hydrate concentration, hydrogenation of **1a** is dominant but not exclusive) and decreases from the beginning of the reaction.

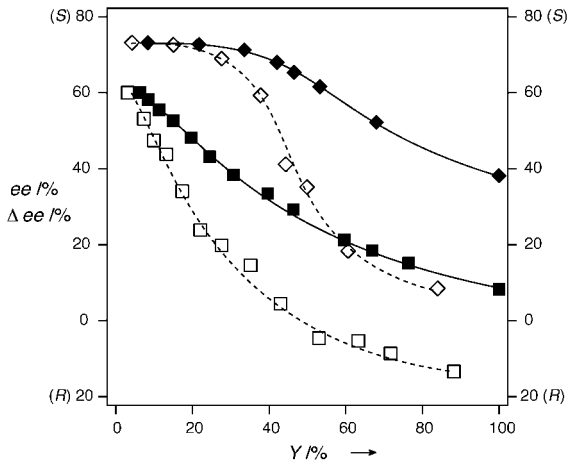

Figure 3. Influence of hydrate (**3**) formation on the conversion dependence of enantioselectivity, with (diamonds) and without preequilibration overnight (squares). Standard reaction conditions without TFA. Full symbols: cumulative (measured) *ee* values; open symbols: incremental (calcd) *ee* values.

To obtain unambiguous evidence for the hydrogenolysis of **3** over Pt, the experiment in Figure 3 (with preequilibration) has been repeated with a tenfold amount of water (8 vol%). In this mixture the molar ratio **3**/**1a** was 1975:1 as determined by NMR spectroscopy, and the initial (cumulative) *ee* value was 7% in favor of (*R*)-**2**. Evidently, hydrogenolysis of **3** over cinchona-alkaloid-modified Pt affords a small but significant *ee* value in favor of (*R*)-**2**, though the *ee* is diminished by the inevitable competition by the hydrogenation of **1a**. Interestingly, hydrogenation of all known activated ketones over Pt modified by cinchonidine or MeOCD afford the *R* enantiomer in excess.[5] The only exception is the hydrogenation of **1**, where the *S* enantiomer forms in excess, indicating a substantially different reactant–modifier interaction in this reaction. Understanding the formation of the *R* enantiomer from the hydrate **3** may help in developing a feasible model for the enantiodifferentiation in the hydrogenation of **1**.

The role of TFA is rather complex. It protonates the chiral modifier leading to higher initial *ee* values (compare Figure 1 and 3). Furthermore, TFA accelerates the equilibration of **1a** and **3**, and the hydrogenolysis of **3** to (*R*)-**2**. To sum up, TFA enhances the striking effect of water in the reaction mixture but its presence is not a necessary requirement for achieving an inversion of enantioselectivity during hydrogenation of **1**.

The crucial requirement is the high stability, and thus the high actual concentration, of the hydrate relative to the keto form in order to compensate the much higher reactivity of the latter. NMR spectroscopic analysis indicated that under identical conditions (in the presence of 1.2 molar equivalents of water), the molar fraction of hydrate was 0.95, 0.07, and 0.01 in case of **1**, trifluoroacetophenone, and ethyl pyruvate, respectively (Scheme 3). Considerable hydration of **1** is attributed to the extra stabilization by a hydrogen bond involving one of the F atoms.[14] We conclude that such a dramatic inversion of enantioselectivity as observed in the hydrogenation of **1** cannot be expected in general in the hydrogenation of activated ketones over cinchona-alkaloid-

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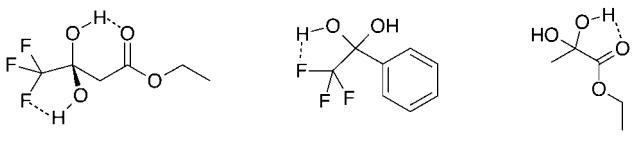

95 % 7 % 1 %

Scheme 3. Possible structures and the equilibrium fractions of the hydrates formed from different activated ketones. Values were measured by NMR spectroscopy in [D_8]THF containing 0.8 vol% water (water/reactant = 1.2:1).

modified Pt. Nevertheless, the frequently observed significant loss of *ee* with conversion of ethyl pyruvate in the best solvent AcOH (e.g. ref. [15]) may partly be attributed to the competing hydrogenolysis of the hydrate form, as this solvent generally has not been dried before use.

Experimental Section

Ethyl 4,4,4-trifluoroacetoacetate (**1;** Fluka, purum) was distilled before use, THF was dried over Na, and TFA was used as received. MeOCD was synthesized as described.[16] The 5 wt% Pt/Al_2O_3 catalyst (Engelhard 4759) was reduced in flowing hydrogen for 90 min at 400 °C before use.

The reactions were carried out at room temperature in an autoclave equipped with a 50 mL glass inlet and a PTFE cover. Prereduced catalyst (110 ± 3 mg) was added to a mixture of MeOCD (5.3 mg, 17.2 μmol) and reactant (0.34 g, 1.85 mmol) in 5 mL solvent. Water (40 μL; 0.8 vol%) was added either directly (6 min) or 15 h before the start of the reaction (preequilibration). Yields (Y) and *ee* values were dermined by direct gas chromatographic analysis of the reaction mixture using diglyme as an internal standard. The incremental *ee* was calculated as $\Delta ee = (ee_1 Y_1 - ee_2 Y_2)/(Y_2 - Y_1)$, where Y indicates yield to **2**, and index 2 refers to a sample taken subsequent to sample 1. Compounds **1a**, **1b**, and **3** were identified by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.[17] Relative amounts of the different compounds were calculated by integration of the peak areas in the ^{19}F NMR spectra.

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The Mechanism of the [Cp_2TiMe_2]-Catalyzed Intermolecular Hydroamination of Alkynes**

Frauke Pohlki and Sven Doye*

The addition of ammonia or primary and secondary amines to nonactivated alkenes and alkynes is a direct and efficient approach towards the synthesis of higher substituted nitrogen-containing products. Although this hydroamination reaction is extremely interesting for industrial applications, efforts to develop related processes have met with only limited success.[1]

Inspired by the work of Bergman et al.[2a,b] and Livinghouse et al.,[2c–f] we recently reported that [Cp_2TiMe_2][3] is a very efficient catalyst for the intermolecular hydroamination of alkynes.[4] By using [Cp_2TiMe_2] as the catalyst, primary arylamines as well as sterically hindered *tert*-alkyl- and *sec*-alkylamines can be coupled to alkynes in high yields. However, hydroamination reactions employing sterically less hindered amines such as benzylamine or *n*-hexylamine are very slow and the corresponding products could only be isolated in poor yields. To explain the mentioned differences in the behavior of different amines and to understand the mechanistic details of the reaction a kinetic investigation was carried out.

Initial studies showed that the reaction between 1-phenylpropyne (**1**) and 4-methylaniline (**2**) is suitable for kinetic experiments (Scheme 1). In the presence of ferrocene as internal standard, the changes in the concentrations of **1**, **2**, and **3** (two isomers) could be determined by ^{1}H NMR spectroscopy.[5] Representative plots of $c(\mathbf{1})\,c_0(\mathbf{1})^{-1}$ versus time t for different concentrations of [Cp_2TiMe_2] are shown in Figure 1.

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