Reactions of Pentafulvene Complexes of Titanium with Carbonyl Compounds − Diastereoselective Synthesis of σ,π-Chelate Complexes with Cp~O Ligands

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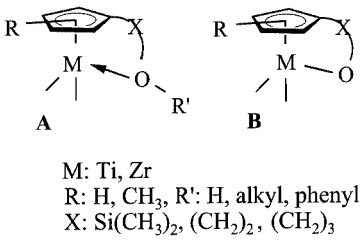
The compound Cp*Ti[η^6-$C_5H_4C(H)(t$Bu)]Cl (**1**) reacts with ketones, aldehydes, and esters to give σ,π-chelate complexes with Cp~O ligands through insertion of the carbonyl group into the Ti–C(H)(*t*Bu) bond. Starting from diastereomerically pure **1**, the reaction with symmetric ketones R_2CO led to the formation of two diastereomeric products. The diastereomeric ratio could be controlled by steric and electronic properties of the substituent R. Thus, this procedure provides an easy approach to complexes with Cp~O ligands where new chiral centres are formed directly in the coordination sphere of the metal atom through a side-differentiated attack of the carbonyl compound at the titanium atom. All products were thoroughly characterized. Crystal structure determinations were carried out on **2a**, **3a**, **5**, **6b**, and **9a**.

Introduction

Complexes with functionalized cyclopentadienyl chelate ligands have gained great importance in organo transition metal chemistry because they have been demonstrated to be useful catalysts (or precatalysts) in different kinds of reactions.[1] Generally, chelating Cp~O ligands can be classified as two principal types, ligands functionalized with a neutral O donor (mostly an ether group) (**A**) − forming a hemilabile ligand − and ligands with an anionic O donor (**B**) − leading to cyclopentadienylalkoxide σ,π-chelate complexes (Scheme 1). Diels−Alder reactions,[2] hydrogenations,[3] or the polymerization of olefins[4] and dienes,[5] as well as ring-opening metathesis polymerization reactions[6] are described for complexes of early transition metals exhibiting Cp~O ligands. However, in comparison to related *N*-functionalized cyclopentadienyl complexes, which proved to be remarkably successful in catalytic applications,[7] the use of *O*-functionalized species still seems to be underdeveloped.

Usually these complexes are available by two synthetic routes. Either a suitable transition metal ion is complexed by an already preformed *O*-functionalized cyclopentadienyl ligand,[8] or the ligand is prepared directly in the coordination sphere of the metal centre from a suitable precursor ligand. While the first route is well described,[4b,9] examples for the second one are rather rare.[10] Here we report on new titanium complexes with Cp~O ligands of the alkoxide type (**B**), which we were able to synthesize very efficiently by treating the diastereomerically pure pentafulvene complex Cp*Ti(η^6-$C_5H_4C(H)(t$Bu)]Cl (**1**) with various carbonyl compounds. This approach offers the opportunity to control the stereochemistry of the desired coordination compounds by steric and electronic effects of the carbonyl species, and that can be explained by a proposed mechanism.



Scheme 1

Results and Discussion

The reaction of diastereomerically pure Cp*Ti[η^6-$C_5H_4C(H)(t$Bu)]Cl (**1**)[11] with benzophenone in *n*-hexane at room temperature proceeded smoothly to give complex **2** as a mixture of diastereomers (Scheme 2), which could easily be separated by a simple filtration since diastereomer **2b** precipitated as a yellow nacreous solid, whereas **2a** proved to be well soluble and remained in solution. Thus, **2b** could be obtained as a yellow powder (81%) by washing the precipitate with a small amount of *n*-hexane. Complex **2a** was isolated as yellow-orange cube-shaped crystals (18%) by

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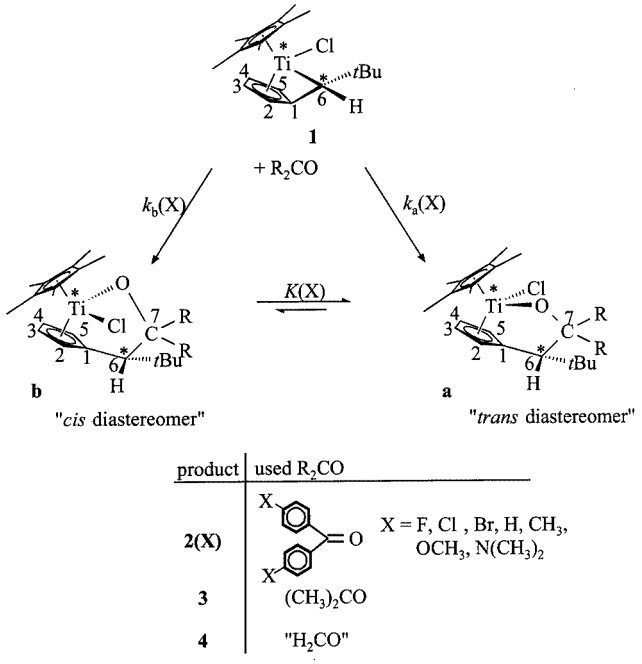
concentrating the filtrate and cooling to −20 °C. Complexes **2a** and **2b** differ in the relative arrangement of the exocyclic fulvene proton (6-H) to the titanium-bonded chlorine atom; **2a** was found to have a *trans*-arrangement and is therefore called the "*trans* diastereomer" and **2b** a *cis* arrangement and therefore named the "*cis* diastereomer".



Scheme 2

The two diastereomeric products were thermally stable and could be exposed to air for several hours. However, diastereomerically pure **2a** or **2b** underwent a very slow rearrangement upon storing as a solution in [D_6]benzene for several weeks to give noticeable amounts of the other diastereomer, respectively. After about 12 months these solutions of **2a** and **2b** had equilibrated. However, this equilibrium could be reached considerably faster in the presence of Lewis acids such as $AlMe_3$ or $B(C_6F_5)_3$.

X-ray Crystal Structure Analysis of Complex 2a

Crystals of **2a** suitable for X-ray structural analysis were obtained from a concentrated solution of **2a** in *n*-hexane at 0 °C, and the results are depicted in Figure 1. Two crystallographically independent, but remarkably similar, molecules of **2a** are present within the asymmetric unit. Due to this similarity only one molecule will be discussed in the following section.

The crystal structure reveals a characteristically bent metallocene arrangement of the ligands around the titanium atom. Distances from the metal atom to the ring centroids are 2.050 Å for the functionalized cyclopentadienyl group and 2.111 Å for the Cp* ring. The angle between the geometrical centres of both rings and the titanium atom is 132.9°. These data are in good agreement with those reported for other titanium complexes.[12] The distance Ti−O1 is 1.881(2) Å, similarly as short as those reported

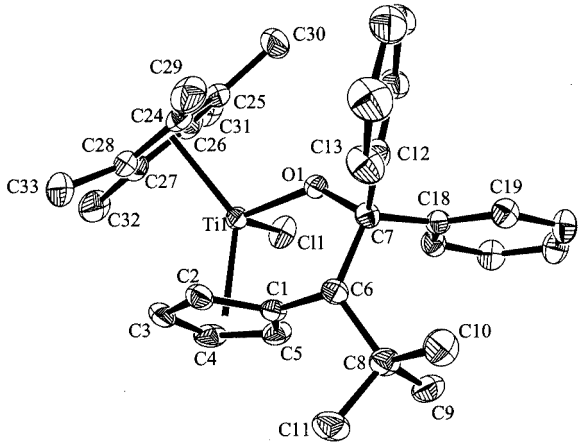


Figure 1. Molecular structure of **2a**; hydrogen atoms have been omitted for clarity; ORTEP ellipsoids represent 50% probability; selected bond lengths [Å] and angles [°]: Ti1−Cl1 2.398(1), Ti1−O1 1.881(2), O1−C7 1.439(3), C6−C7 1.601(3), C1−C6 1.515(3), Ti1−Ct1 2.050, Ti1−Ct2 2.111; Ti1−O1−C7 137.1(1), O1−C7−C6 106.8(2), C1−C6−C7 107.8(2), O1−Ti1−Cl1 100.1(1), Ct1−Ti1−Ct2 132.9; Ct1 = ring centroid of C1 to C5, Ct2 = ring centroid of C24 to C28)

for Ti−OH bonds in titanocene hydroxides,[13] and indicates metal−oxygen double-bond character caused by $O(p_\pi)\rightarrow Ti(d_\pi)$ interactions.[14] It is known from other *x*-membered metallacycles that a general correlation exists between the Ti−O bond length, the Ti−O−C angle, and the ring size. This is due to the attractive interaction between the oxygen lone pairs (located in the p_z orbital) and the lowest unoccupied molecular orbital (LUMO) of the metal atom, which increases with increasing Ti−O−C angle. In the case of the five-membered metallacycle **2a**, with its Ti−O bond length of 1.881(2) Å and its Ti−O−C angle of 137.1(1)°, there is a good agreement with these findings.[15] Furthermore, the significant elongation of the Ti−Cl distance in **2a** [2.398(1) Å] compared with the one found in **1** [2.354(1) Å][11] is noticeable, because it indicates a weakening of $Cl(d_\pi)\rightarrow Ti(d_\pi)$ interactions caused by a raised electron density at the titanium atom by $O(p_\pi)\rightarrow Ti(d_\pi)$ interactions. Whereas the O−C7 and C1−C6 distances are close to typical O−C and C−C single bonds, respectively,[16] the new C6−C7 bond shows a length [1.601(3) Å] that is significantly larger than a typical C−C single bond. This most probably indicates a higher ring strain. The hypothesis that this elongation of the C6−C7 bond is induced rather by ring strain than by steric effects of the substituents at the C6 and C7 atoms is further supported by the reaction products of **1** with several other ketones and aldehydes bearing substituents of varying steric bulkiness (Table 2). In all cases this C−C bond was significantly elongated.

Complex **2b** crystallised from all the usual solvents as fine needles, unsuitable for X-ray structure analysis. However, it could be identified unambiguously by NMR and MS data as well as elemental analysis.

Diastereoselectivity of the Insertion Reaction

In order to obtain an idea about the sense of the stereochemical induction and the underlying mechanism we

studied the reactions shown in Scheme 2 more closely by ^{1}H NMR spectroscopy. Benzophenone proved to be an especially suitable substrate for our purposes, because the proton signals of the pentamethylcyclopentadienyl ligand of **1** and the two diastereomeric products (**2a** and **2b**) were well separated from each other (Figure 2) and the reaction with **1** proceeded sufficiently slowly when we used starting concentrations of $c_{\mathbf{1}} = c_{\text{benzophenone}} = 0.071$ mol L^{-1}.[17] Thus, the concentration of all species involved in the reaction (**1**, **2a**, and **2b**) could be determined at any point during the reaction.

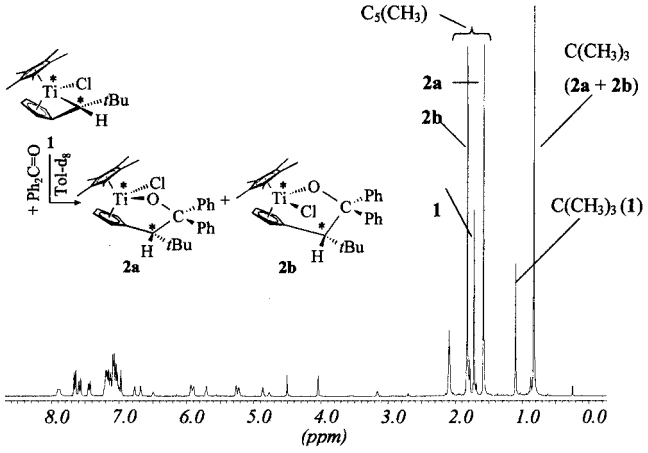


Figure 2. ^{1}H NMR spectra (300 MHz, [D$_8$]toluene) of the reaction of **1** with benzophenone after about 24 h

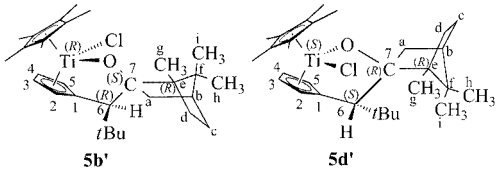
Furthermore, it was possible to insert activating (electron-donating) or deactivating (electron-accepting) substituents at the phenyl rings in the *para* position to the carbonyl group to study the influence of electronic effects on the reaction. As a preliminarily result,[18] the quotients of rate constants $k_b(X)/k_a(X)$ (cf. Scheme 2) for several disubstituted benzophenones [X = F, Cl, Br, (H), CH_3, OCH_3, $N(CH_3)_2$], which indicate the quantities of obtained "*cis* diastereomer" **2b(X)** and "*trans* diastereomer" **2a(X)**, are listed in Table 1.

Table 1. Ratio of single rate constants k_a and k_b at 300 K for the reactions shown in Figure 1 leading to "*trans* and *cis* diastereomers" **2a(X)** and **2b(X)**, respectively, and difference of the Gibbs energies between **2a(X)** and **2b(X)** [kJ mol^{-1}] at 298 K, showing the dependence on the benzophenone *para* substituent X

	F	Cl	Br	H	CH_3	OCH_3	$N(CH_3)_2$
$k_b(X)/k_a(X)$	3.67	1.74	–	1.39	0.95	0.69	0.23
$\Delta\Delta G_{(b-a)}$	−4.65	−4.85	−4.97	−4.90	−5.04	−5.11	−6.18

As mentioned above, **2a(X)** and **2b(X)** equilibrate after about 12 months with **2b(X)** being the thermodynamically more stable diastereomer in all cases. From equilibrium constant K ($K = c_{\mathbf{2b(X)},\infty}/c_{\mathbf{2a(X)},\infty}$) at 298 K the difference of free Gibbs energies between **2a(X)** and **2b(X)** could be calculated as given in Table 1. The *para* substituents in Table 1 are arranged in a manner that the activating effect increases to the right.

These data suggest two possible pathways for controlling the diastereomeric ratio, namely thermodynamic and kinetic control. While the thermodynamic effect is relatively small − the equilibrium between **2a(X)** and **2b(X)** shifts towards **2b(X)** with rising electron-donating effect of the *para* substituent − the kinetic effect is distinctively larger. The insertion, for example, of a benzophenone derivative with fluorine substituents, which remove electron density from the carbonyl group, led mainly to the "*cis* diastereomer" **2b(F)** ($k_{\mathbf{2b(F)}}/k_{\mathbf{2a(F)}} = 3.67$, according to Table 1), whereas the reaction with a benzophenone carrying the electron-donating Me_2N group yielded the "*trans* diastereomer" **2a(N(CH$_3$)$_2$)** as the major product ($k_{\mathbf{2b(NMe2)}}/k_{\mathbf{2a(NMe2)}} = 0.23$, according to Table 1). However, the diastereomeric ratio could be influenced, not only by electronic, but also by steric effects. In this context, reaction of **1** with small carbonyl compounds like acetone and formaldehyde led exclusively to "*trans* diastereomers" **3a** and **4a**, respectively. The "*cis* diastereomers" **3b** and **4b** could not be detected until the equilibration reaction was performed. However, the reaction with bulky *R*-(+)-camphor gave rise to the "*cis* diastereomers" **5b′** and **5d′** only (Scheme 3), and the "*trans* diastereomers" were not observed, even under the conditions mentioned above to reach equilibrium of the other insertion products.



Scheme 3

Structural analyses of three of these insertion products (**3a**, **5b′**, and **5d′**) revealed the bond lengths and angles of the metallacycle to be similar to those found for **2a** (Table 2). Corresponding ORTEP plots are depicted in the Supporting Information.

According to these results, the reaction of **1** with methyl isobutyrate, which has a significantly reduced electron density at the carbonyl oxygen atom, gave exclusively the "*cis* diastereomer" **6b** after β-elimination of MeOH (Scheme 4).

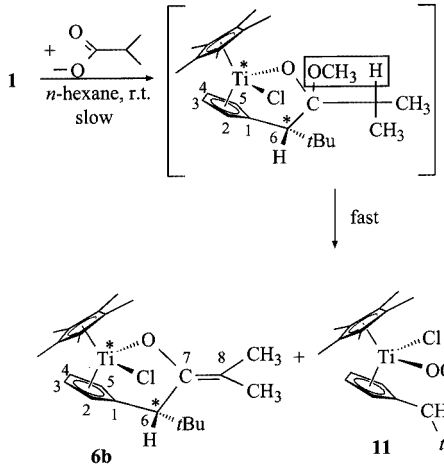
However, released MeOH also reacted with **1** to form compound **11**. Furthermore, since the primary insertion step of the carbonyl group into the Ti−C6 bond is comparatively slow, while the following β-elimination is very fast, the primary product was not observed, even in a ^{1}H NMR experiment. However, both products **6b** and **11** could be isolated by fractional crystallization.

Mechanistic Reflections

In pseudo-tetrahedral bent metallocene complexes of the Cp_2MR_2 type, eight out of the nine metal valence orbitals are used for coordinating the ligands. Two opposed spatial arrangements for the remaining ninth orbital, which determines the chemical reactivity of such complexes to a considerable content, have been discussed in a number of previous

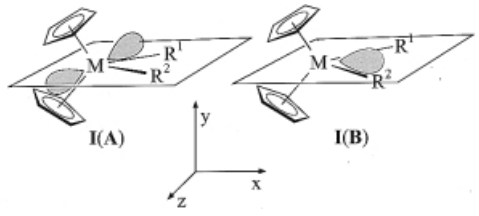
Table 2. Selected bond lengths [Å] and angles [°] in **2a**, **3a**, **5**, **6b**, and **9a**

	2a	**3a**	**5b′**	**5d′**	**6b**	**9a**
Ti−O	1.881(2)	1.854(1)	1.860(3)	1.862(3)	1.889(1)	1.870(2)
O−C7	1.439(3)	1.436(3)	1.438(5)	1.441(5)	1.371(2)	1.417(3)
C7−C6	1.601(3)	1.569(3)	1.612(6)	1.604(6)	1.534(2)	1.569(5)
C6−C1	1.515(3)	1.507(3)	1.524(6)	1.533(5)	1.515(2)	1.508(4)
Ti−Cl	2.398(1)	2.388(1)	2.407(2)	2.394(1)	2.369(1)	2.398(1)
Ti−Ct1	2.050	2.059	2.058	2.058	2.070	2.069
Ti−Ct2	2.111	2.094	2.138	2.114	2.085	2.110
Ti−O−C7	137.1(1)	132.0(1)	138.4(2)	134.4(2)	121.6(1)	134.9(2)
O−C7−C6	106.8(2)	105.1(2)	106.1(3)	106.8(3)	111.5(1)	107.5(2)
C1−C6−C7	107.8(2)	107.2(2)	107.2(3)	106.1(3)	103.4(1)	108.5(2)
Ct1−Ti−Ct2	132.9	133.2	131.9	133.4	134.4	134.2
O−Ti−Cl	100.1(1)	97.8(1)	98.1(1)	100.8(1)	95.8(1)	99.3(1)



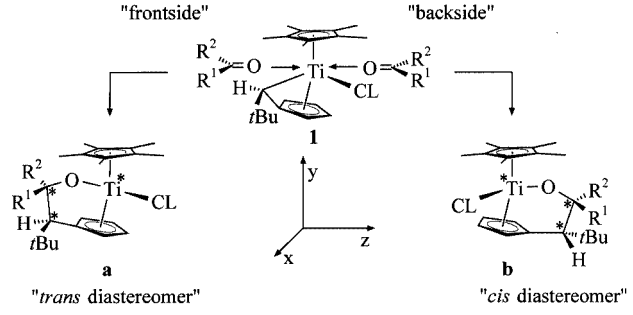
Scheme 4

publications (Scheme 5). Whereas Ballhausen and Dahl favoured a central position between the σ ligands R (**IB**),[19] Alcock et al. postulated a lateral position aligned along the *z* axis (**IA**).[20] Nowadays, recent results from several spectroscopic and theoretical studies unanimous support the lateral arrangement.[21]



Scheme 5

In case of metallocenes of group-IV metals (16 electron species) this "ninth" orbital is unoccupied (acceptor orbital). Assuming that the spatial arrangement of the acceptor orbital of **1** (16-electron species) is also in the lateral position, the nucleophilic attack of the lone pairs of the carbonyl oxygen atom at the titanium centre and the resulting interactions with the acceptor orbital can in principle proceed from two different sites (Scheme 6). Whereas the "frontal" attack leads to the "*trans* diastereomer", the "backside" attack results the "*cis* diastereomer".



Scheme 6

Calculations of the electrostatic potential[22] of **1** indicate a high electron density at the "backside" induced by the lone pairs of the chlorine atom (Figure 3). This suggests that from the electronic point of view the nucleophilic attack of the carbonyl oxygen atom from the "backside" is strongly disfavoured compared with the "frontal" attack, because the lone pairs of the oxygen and chlorine atoms should repel each other.

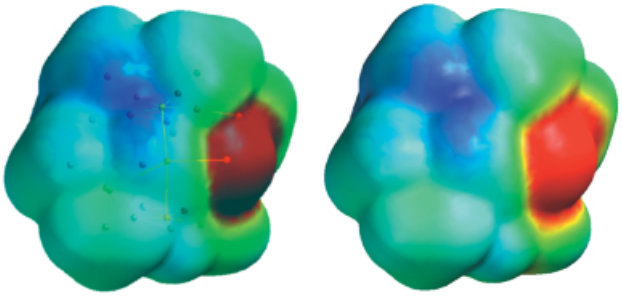


Figure 3. Electrostatic potential, molecular surface of **1** in colour-code form, red representing the negative, blue the positive maximum in charge density in relative terms (left hand semitransparent illustration)

On the other hand, the crystal structure of **1**[11] shows a slight deviation of both rings with respect to each other, and in consequence the titanium centre is sterically shielded from the "front" (Figure 4).

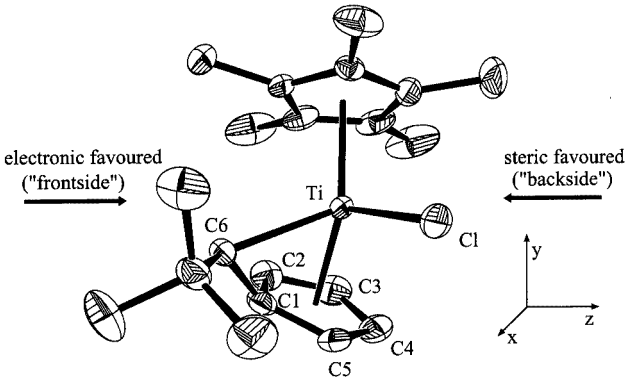


Figure 4. Molecular structure of **1**; hydrogen atoms have been omitted for clarity; ORTEP ellipsoids represent 50% probability

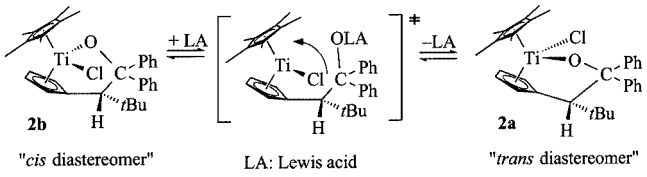
In solution (C_6D_6) strong NOE contacts between the pentamethylcyclopentadienyl protons and the protons at C2 and C3 atoms are observed,[11] indicating a similar deviation in solution. In consequence, an attack from the "front" should be disfavoured from a steric point of view. Thus, **1** is characterized by an electronically favoured "frontal" and a sterically favoured "backside". Therefore, benzophenone derivatives with activating (electron-donating) *para* substituents, e.g. X = NMe_2, attack mainly from the electronically favoured "front", whereas derivatives with deactivating (electron-accepting) substituents, e.g. F, attack from the sterically favoured "backside" [cf. $k_b(X)/k_a(X)$, Table 1]. Likewise, bulky carbonyl compounds like *R*-(+)-camphor approach the titanium centre from the sterically favoured, but electronically disadvantageous "backside", while small carbonyl compounds like acetone or formaldehyde from the electronic favoured "front". The "medium-sized" benzophenone attacks from both sides. According to these results, methyl isobutyrate, which has a considerably lower electron density at the carbonyl oxygen atom, reacts in terms of a "backside" attack exclusively to the "*cis* diastereomer" **6b**.

In order to further corroborate our proposed mechanism, we substituted the chlorine atom in **1** with a methyl group, which led to Cp*Ti[η^6-$C_5H_4C(H)(t\text{Bu})$]Me (**7**). If our mechanism is correct, this should eliminate the electronic disadvantages of the sterically favoured "backside", and in consequence the "*cis* diastereomer" **8b**, resulting from the "backside" attack, should be the main product of the reaction with "medium-sized" benzophenone. Indeed, only **8b** was found and **8a** could only be observed later as a consequence of the equilibration reaction. Insertion products in the Ti−Me bond of **7** were not observed.

Even the stereochemistry of the products, resulting from the reaction of **1** with asymmetric (prochiral) benzaldehyde, could be explained by our proposed mechanism if we take a pre-coordination[10b] of the carbonyl compound (Scheme 6 with R^1 = phenyl, R^2 = H) into account, which has already been suggested by Erker et al. Due to the deviation of the rings in **1**, the orientation of the benzaldehyde phenyl group out of the front of the *xz* plane is very likely, and thus leads to "*trans* and *cis* diastereomers" **9a** and **9b**, respectively.

Rearrangement of Diastereomers

As mentioned above all insertion products, except complexes **5b′** and **5d′**, slowly rearranged to give the corresponding diastereomer and finally reached an equilibrium after about 12 months. However, addition of stoichiometric as well as catalytic amounts of Lewis acids like $AlMe_3$ or $B(C_6F_5)_3$ made this equilibration reaction become considerably faster.[23] We found kinetics of pseudo-first order for the reaction **2b** → **2a** in the presence of $AlMe_3$, suggesting that the Lewis acid (LA) acts as a catalyst whose concentration does not change with time (Scheme 7). Furthermore, ^{1}H NMR spectra indicated that all involved species (**2a**, **2b**, and $AlMe_3$) existed unchanged in solution − since we did not see any permanent agglomeration products of $AlMe_3$. Also, the difference in the Gibbs free energy between the diastereomers [$\Delta\Delta G_{(b-a)}$] did not change.



Scheme 7

In principle, one could think of two different mechanisms for this rearrangement. An intramolecular rearrangement involving only a temporary cleavage of the Ti−O bond or an intermolecular exchange of carbonyl compounds between two titanium complexes which would need the permanent cleavage of the Ti−O bond and a C−C bond. Although the latter one seemed unlikely anyway, we further proved this assumption through cross-over experiments with **2a** or **2b** and **7**, as well as with **8a** or **8b** and **1**, which clearly showed, that there was no exchange of carbonyl compounds between two titanium complexes because all complexes remained unchanged even after several months.

However, we were able to confirm the kinetic lability of the Ti−O bond in **2a** and **2b**, respectively, which is the key factor for the probability of the intramolecular rearrangement mechanism proposed in Scheme 7. This was determined by ^{1}H NMR experiments made with **11**-type complexes and free alcohols. A fast exchange of the alkoxy group (methoxy versus ethoxy group) was observed upon addition of stoichiometric amounts of ethyl alcohol to a solution of **11** in [D_6]benzene.[24] Furthermore, no chloride/alkoxy exchange was observed, neither in experiments described above nor in a mixture of Cp*Ti($C_5H_4CH_2t\text{Bu}$)Cl_2 (**15**)[25] and EtOH, hence, also supporting the proposed mechanism.

Conclusion

A simple approach to complexes with Cp~O ligands has been presented, starting from diastereomerically pure Cp*Ti[η^6-$C_5H_4C(H)(t$Bu)]Cl (**1**) and several carbonyl compounds, and it has been demonstrated how the diastereomeric ratio of the product complexes could be controlled in a rather sensitive manner by the nature, nucleophilicity, and steric properties of the utilized carbonyl compounds. In all cases, the stereochemical outcome of this insertion could be explained by a side-differentiated attack of the carbonyl compound at the titanium atom. Thus, this procedure provides a convenient access to complexes with Cp~O ligands where the new chiral centres are formed directly in the coordination sphere of the metal atom in a well-defined manner.

Experimental Section

General Remarks: All operations were performed in nitrogen with rigorous exclusion of oxygen and moisture using glove-box or Schlenk techniques. Solvents were thoroughly dried and saturated with nitrogen. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AVANCE 500 spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz) or a Bruker AVANCE 300 spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.8 MHz), chemical shifts were referenced to residual protons or carbon atoms of the solvent. The notation of the nuclei follows the numbering in Scheme 2 and 3. Electron impact (EI) mass spectra were taken with a Finnigan-MAT 95 spectrometer. IR spectra were recorded with a BIO-RAD FTS-7 Spectrometer using KBr pellets. Elemental analyses were carried out by the Analytische Laboratorien in Lindlar (Germany). The complexes Cp*Ti[η^6-$C_5H_4C(H)t$Bu]Cl (**1**)[11] and Cp*Ti[η^6-$C_5H_4C(H)t$Bu]Me (**7**)[26] were prepared according to reported procedures. All carbonyl compounds were purchased from Aldrich and used as received. Diastereomers **3b**, **4b**, and **8a** resulted from the described equilibration reaction between the corresponding diastereomers and could not be isolated, but were characterized by NMR spectroscopy of the respective diastereomeric mixtures.

Complex 2: A solution of benzophenone (0.911 g, 5.0 mmol) in *n*-hexane (10 mL) was added dropwise to a stirred solution of Cp*Ti[η^6-$C_5H_4C(H)t$Bu]Cl (**1**) (1.764 g, 5.0 mmol) in *n*-hexane (20 mL) at room temperature. A yellow nacreous solid began to precipitate after about 8 h. After stirring for additional 52 h, the suspension was filtered. Washing the residue with *n*-hexane (4 × 10 mL) and drying in vacuo led to **2b** as a yellow powder (2.167 g, 81%). Concentration of the filtrate to 10 mL and cooling to −20 °C resulted in the isolation of **2a** as yellow-orange, cube-shaped crystals (0.321 g, 18%).

2a: M.p. 104 °C. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.84 [s, 9 H, $C(CH_3)_3$], 1.57 [s, 15 H, $C_5(CH_3)_5$], 4.03 (s, 1 H, 6-H), 5.21 (m, 1 H, C_5H_4), 5.24 (m, 1 H, C_5H_4), 6.01 (m, 1 H, C_5H_4), 6.78 (m, 1 H, C_5H_4), 7.00−7.24 (m, 6 H, *m*-H_{Ph}, *p*-H_{Ph}), 7.47 (m, 2 H, *o*-H_{Ph}), 7.68 (m, 2 H, *o*-H_{Ph}). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.5 [$C_5(CH_3)_5$], 30.1 [$C(CH_3)_3$], 34.5 [$C(CH_3)_3$], 58.0 (C6), 109.3 (C_5H_4), 110.8 (C_5H_4), 112.8 (C7), 117.1 (C_5H_4), 121.2 (C_5H_4), 124.8 [$C_5(CH_3)_5$], 127.0, 127.1, 127.3, 128.3, 130.2, 131.2 (CH_{Ph}), 149.0, 149.4 (*i*-C_{Ph}), 152.2 (C1). IR (KBr): ṽ = 3047 (m), 2957 (m), 2907 (m), 2894 (m), 1729 (s), 1660 (s), 1443 (s), 1261 (vs), 1095 (vs), 1024 (s), 995 (vs), 815 (s), cm^{-1} 801 (vs). EI MS: *m*/*z* (%) = 534 (5) [M$^+$], 399 (100) [M$^+$ − Cp*], 352 (6) [M$^+$ − $(Ph)_2CO$], 316 (36) [M$^+$ − $(Ph)_2CO$ + HCl], 218 (38) [M$^+$ − ($C_{10}H_{14}$ + Ph_2CO)], 182 (22) [Ph_2CO^+], 135 (30) [Cp*$^+$]. $C_{33}H_{39}ClOTi$ (534.99): calcd. C 74.09, H 7.35; found C 72.45, H 7.42 (lower carbon value due to e.g. TiC formation).

2b: Decomposition without melting at 244 °C. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.84 [s, 9 H, $C(CH_3)_3$], 1.81 [s, 15 H, $C_5(CH_3)_5$], 4.56 (s, 1 H, 6-H), 4.87 (m, 1 H, C_5H_4), 5.71 (m, 1 H, C_5H_4), 5.86 (m, 1 H, C_5H_4), 6.89 (m, 1 H, C_5H_4), 7.04−7.31 (m, 8 H, H_{Ph}), 7.68 (m, 2 H, H_{Ph}). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.8 [$C_5(CH_3)_5$], 30.4 [$C(CH_3)_3$], 30.2 [$C(CH_3)_3$], 59.3 (C6), 102.9 (C_5H_4), 109.5 (C_5H_4), 109.8 (C7), 117.9 (C_5H_4), 124.7 [$C_5(CH_3)_5$], 135.8 (C_5H_4), 126.6, 127.0, 127.5, 128.3, 129.2, 130.2 (CH_{Ph}), 139.1 (C1), 148.8 (both *i*-C_{Ph}). IR (KBr): ṽ = 3052 (m), 2955 (m), 2905 (m), 2892 (m), 1493 (s), 1488 (s), 1445 (s), 1393 (s), 1007 (vs), 1000 (vs), 899 (s), 880 (s), 824 (vs), 799 (vs), 783 (s), 764 (vs), 716 (vs), 698 (vs), cm^{-1} 687 (vs). EI MS: *m*/*z* (%) = 534 (2) [M$^+$], 399 (100) [M$^+$ − Cp*], 352 (4) [M$^+$ − $(Ph)_2CO$], 316 (38) [M$^+$ − $(Ph)_2CO$ + HCl], 218 (90) [M$^+$ − ($C_{10}H_{14}$ + Ph_2CO)], 182 (22) [Ph_2CO^+], 135 (30) [Cp*$^+$]. $C_{33}H_{39}ClOTi$ (534.99): calcd. C 74.09, H 7.35; found C 73.94, H 7.40.

Complex 3: A mixture of acetone (0.290 g, 5.0 mmol) in *n*-hexane (10 mL) was added dropwise to a stirred solution of Cp*Ti[η^6-$C_5H_4C(H)t$Bu]Cl (**1**) (1.764 g, 5.0 mmol) in *n*-hexane (20 mL) at room temperature. After 5 min, the colour of the solution turned from dark green to orange. After stirring for an additional 2 h, the solution was concentrated to 10 mL and cooled to −20 °C, **3a** was isolated as yellow-orange, cube-shaped crystals (1.397 g, 68%). M.p. 104 °C. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.97 [s, 9 H, $C(CH_3)_3$], 1.29 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 1.81 [s, 15 H, $(C_5(CH_3)_5$], 2.35 (s, 1 H, 6-H), 4.97 (m, 1 H, 2-H), 5.34 (m, 1 H, 3-H), 5.54 (m, 1 H, 4-H), 6.72 (m, 1 H, 5-H). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.6 [$C_5(CH_3)_5$], 27.1 (CH_3), 30.4 [$C(CH_3)_3$], 33.1 [$C(CH_3)_3$], 37.6 (CH_3), 63.6 ($^1J_{C,H}$ = 124.5 Hz, C6), 105.4 (C7), 109.5 (C2), 111.8 (C3), 114.3 (C4), 119.0 (C5), 123.9 [$C_5(CH_3)_5$], 148.3 (C1). IR (KBr): ṽ = 3088 (m), 2969 (m), 2911 (m), 2870 (m), 1478 (s), 1452 (s), 1437 (s), 1375 (s), 1358 (s), 1146 (s), 1123 (vs), 1020 (m), 974 (s), 826 cm^{-1} (vs). EI MS: *m*/*z* (%) = 410 (10) [M$^+$], 352 (22) [M$^+$ − $(CH_3)_2CO$], 316 (22) [M$^+$ − $(CH_3)_2CO$ + HCl], 275 (100) [M$^+$ − Cp*], 218 (90) [M$^+$ −$C_{10}H_{14}$ + $(CH_3)_2CO$], 135 (16) [Cp*$^+$]. $C_{23}H_{35}ClOTi$ (410.86): calcd. C 67.24, H 8.59; found C 67.06, H 8.47.

3b: ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.95 [s, 9 H, $C(CH_3)_3$], 1.25 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.81 [s, 15 H, $C_5(CH_3)_5$], 3.12 (s, 1 H, 6-H), 4.94 (m, 1 H, 4-H), 5.18 (m, 1 H, 2-H), 5.67 (m, 1 H, 3-H), 6.85 (m, 1 H, 5-H). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.6 [$C_5(CH_3)_5$], 29.6 (CH_3), 30.1 [$C(CH_3)_3$], 33.3 [$C(CH_3)_3$], 33.7 (CH_3), 62.7 (C6), 103.5 (C4), 103.7 (C7), 106.0 (C2), 116.3 (C3), 123.9 [$C_5(CH_3)_5$], 134.6 (C5), 139.6 (C1).

Complex 4: Powdered paraformaldehyde 0.300 g, 10.0 mmol) was added to a solution of Cp*Ti[η^6-$C_5H_4C(H)t$Bu]Cl (**1**) (1.764 g, 5.0 mmol) in THF (20 mL). The suspension was stirred under reflux. After 2 h, the colour of the solution turned from dark green to orange. The reaction mixture was stirred for an additional 2 h. After the THF had been removed, the residue was dissolved in 20 mL of *n*-hexane and separated from insoluble excessive paraformaldehyde by filtration. The filtrate was concentrated to 10 mL and cooled to −20 °C. Complex **4a** could be isolated as a yellow-orange, microcrystalline solid (1.340 g, 70%). **4a:** M.p. 108 °C. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.88 [s, 9 H, $C(CH_3)_3$], 1.83 [s, 15 H, $C_5(CH_3)_5$], 2.37 (dd, $^3J_{H6,H7}$ = 11.8, $^3J_{H6,H7'}$ = 6.1 Hz, 1 H, 6-H), 4.71 (dd, $^2J_{H7,H7'}$ = −9.1 Hz, 1 H, 7′-H), 5.10 (m, 1 H,

2-H), 5.34 (m, 1 H, 3-H), 5.50 (dd, 1 H, 7-H), 5.62 (m, 1 H, 4-H), 6.78 (m, 1 H, 5-H). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.5 [$C_5(CH_3)_5$], 29.0 [$C(CH_3)_3$], 32.3 [$C(CH_3)_3$], 55.7 (C6), 91.3 (C7), 109.6 (C2), 111.8 (C3), 115.8 (C4), 120.5 (C5), 124.5 [$C_5(CH_3)_5$], 148.2 (C1). IR (KBr): ṽ = 3094 (m), 2951 (m), 2889 (m), 2870 (m), 1489 (s), 1466 (s), 1447 (s), 1385 (s), 1364 (vs), 1045 (vs), 1022 (s), 1005 (s), 822 (vs), 791 cm^{-1} (s). EI MS: *m*/*z* (%) = 382 (34) [M$^+$], 352 (24) [M$^+$ − H_2CO], 316 (100) [M$^+$ − (H_2CO + HCl)], 247 (18) [M$^+$ − Cp*], 218 (72) [M$^+$ − ($C_{10}H_{14}$ + H_2CO)], 135 (66) [Cp*$^+$]. $C_{21}H_{31}ClOTi$ (382.86): calcd. C 65.89, H 8.16; found C 65.71, H 8.25.

4b: ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.84 [s, 9 H, $C(CH_3)_3$], 1.81 [s, 15 H, $C_5(CH_3)_5$], 3.23 (dd, 1 H, 6-H), 4.94 (dd, 1 H, 7′-H), 5.02 (dd, 1 H, 7-H), 5.03 (m, 1 H, 4-H), 5.06 (m, 1 H, 2-H), 5.65 (m, 1 H, 3-H), 6.95 (m, 1 H, 5-H). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.3 [$C_5(CH_3)_5$], 28.4 [$C(CH_3)_3$], 31.7 [$C(CH_3)_3$], 54.2 (C6), 91.2 (C7), 105.6 (C4), 106.7 (C2), 116.2 (C3), 124.2 [$C_5(CH_3)_5$], 133.4 (C5), 148.2 (C1).

Complex 5: A solution of *R*-(+)-camphor (0.761 g, 5.0 mmol) in *n*-hexane (10 mL) was added dropwise to a stirred solution of Cp* Ti(η^6-$C_5H_4C(H)tBu$)Cl (**1**) (1.764 g, 5.0 mmol) in *n*-hexane (20 mL) at room temperature. The reaction mixture was stirred under reflux for 7 d. The colour of the solution turned from dark green to orange. The solution was concentrated to 10 mL and cooled to −20 °C. A mixture of diastereomers **5b′** and **5d′** was isolated as yellow-orange, cube-shaped crystals (1.843 g, 73%; **5b′/5d′** = 50:50). M.p. 161 °C.

5b′: ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.86 (s, 3 H, $CH_{3,h}$), 1.13 (m, 1 H, H_d), 1.17 [s, 9 H, $C(CH_3)_3$], 1.27 (s, 3 H, $CH_{3,i}$), 1.31 (m, 1 H, H_d), 1.46 (s, 3 H, $CH_{3,g}$), 1.54 (m, 1 H, H_c), 1.59 (m, 1 H, H_c), 1.68 (m, 1 H, H_b), 1.83 [s, 15 H, $C_5(CH_3)_5$], 2.12 (m, 1 H, H_a), 2.23 (m, 1 H, H_a), 3.48 (s, 1 H, 6-H), 5.44 (m, 1 H, 3-H), 5.54 (m, 2 H, 2-H, 4-H), 6.49 (m, 1 H, 5-H). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 13.1 [$C_5(CH_3)_5$], 14.4 ($CH_{3,g}$), 22.8 ($CH_{3,h}$), 23.7 ($CH_{3,i}$), 27.6 (C_c), 31.9 [$C(CH_3)_3$], 32.6 (C_d), 34.4 [$C(CH_3)_3$], 46.4 (C_a), 46.7 (C_b), 48.1 (C_f), 55.9 (C6), 61.1 (C_e), 105.6 (C2), 113.2 (C3), 113.3 (C4), 122.0 (C5), 123.8 [$C_5(CH_3)_5$], 126.1 (C7), 152.4 (C1).

5d′: ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.90 (s, 3 H, $CH_{3,h/i}$), 0.96 (s, 3 H, $CH_{3,h/i}$), 1.22 [s, 9 H, $C(CH_3)_3$], 1.41 (m, 1 H, $H_{c/d}$), 1.43 (m, 1 H, $H_{c/d}$), 1.49 (s, 3 H, $CH_{3,g}$), 1.55 (m, 1 H, H_a), 1.64 (m, 1 H, H_b), 1.84 [s, 15 H, $C_5(CH_3)_5$], 2.57 (m, 1 H, H_a), 3.48 (s, 1 H, 6-H), 5.44 (m, 3 H, 3 C_5H_4), 6.66 (m, 1 H, C_5H_4). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.7 [$C_5(CH_3)_5$], 15.5 ($CH_{3,g}$), 21.0 ($CH_{3,h/i}$), 23.7 ($CH_{3,h/i}$), 28.4 ($C_{c/d}$), 28.8 ($C_{c/d}$), 31.9 [$C(CH_3)_3$], 35.8 [$C(CH_3)_3$], 46.3 (C_b), 48.9 (C_a), 50.4 (C_f), 56.7 (C6), 61.9 (C_e), 105.4 (C_5H_4), 111.7 (C_5H_4), 113.5 (C_5H_4), 123.1 (C7), 123.6 (C_5H_4), 123.6 [$C_5(CH_3)_5$], 151.1 (C1). Diastereomeric mixture **5b′/5d′**: IR (KBr): ṽ = 3097 (w), 2946 (m), 2909 (m), 1486 (s), 1474 (s), 1444 (s), 1372 (s), 1306 (w), 1038 (vs), 1022 (s), 1007 (s), 830 cm^{-1} (vs). EI MS: *m*/*z* (%) = 504 (20) [M$^+$], 468 (42) [M$^+$ − HCl], 369 (100) [M$^+$ − Cp*], 352 (5) [M$^+$ − $C_{10}H_{16}O$], 316 (100) [M$^+$ − ($C_{10}H_{16}O$ + HCl)], 218 (36) [M$^+$ − ($C_{10}H_{14}$ + $C_{10}H_{16}O$)], 135 (8) [Cp*$^+$]. $C_{30}H_{45}ClOTi$ (505.01): calcd. C 71.35, H 8.98; found C 71.36, H 8.97.

Complex 6: A solution of methyl isobutyrate (0.106 g, 2.5 mmol) in *n*-hexane (10 mL) was added dropwise to a stirred solution of Cp* Ti[η^6-$C_5H_4C(H)tBu$]Cl (**1**) (1.764 g, 5.0 mmol) in *n*-hexane (20 mL) at room temperature. After 12 h, the colour of the solution turned from dark green to claret red. After stirring for additional 48 h, the solution was concentrated to 10 mL and cooled to 0 °C; **6b** could be isolated diastereomerically pure as ruby coloured, acicular crystals (0.655 g, 62%). M.p. 139 °C. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 1.02 [s, 9 H, $C(CH_3)_3$], 1.71 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3), 1.83 [s, 15 H, $C_5(CH_3)_5$], 3.86 (s, 1 H, 6-H), 5.35 (m, 1 H, 2-H), 5.37 (m, 1 H, 4-H), 5.53 (m, 1 H, 3-H), 6.46 (m, 1 H, 5-H). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.6 [$C_5(CH_3)_5$], 17.7 (CH_3), 20.7 (CH_3), 29.8 [$C(CH_3)_3$], 35.2 [$C(CH_3)_3$], 51.5 (C6), 99.0 (C8), 107.1 (C2), 112.4 (C4), 114.7 (C3), 124.9 [$C_5(CH_3)_5$], 127.1 (C5), 145.6 (C1), 169.9 (C7). IR (KBr): ṽ = 2962 (m), 2948 (m), 2903 (m), 1653 (s), 1493 (s), 1480 (s), 1464 (s), 1438 (s), 1383 (s), 1169 (s), 1138 (vs), 1099 (s), 1022 (s), 937 (s), 827 (vs), 809 cm^{-1} (vs). EI MS: *m*/*z* (%) = 422 (80) [M$^+$], 386 (22) [M$^+$ − HCl], 352 (8) [M$^+$ − C_4H_6O], 329 (100) [M$^+$ − HCl + $C(CH_3)_3$], 316 (18) [M$^+$ − (C_4H_6O + HCl)], 218 (34) [M$^+$ − ($C_{10}H_{14}$ + C_4H_6O)], 135 (16) [Cp*$^+$]. $C_{24}H_{35}ClOTi$ (422.87): calcd. C 68.17, H 8.34; found C 68.08, H 8.26.

Complex 8: A solution of benzophenone (0.456 g, 2.5 mmol) in *n*-hexane (10 mL) was added dropwise to a stirred solution of Cp* Ti[η^6-$C_5H_4C(H)tBu$]Me (**7**) (0.831 g, 2.5 mmol) in *n*-hexane (10 mL) at room temperature. After 2 h, a yellow nacreous solid began to precipitate. After stirring for an additional 58 h, the suspension was filtered. Washing of the residue with *n*-hexane (4 × 10 mL) and drying in vacuo led to **8b** as a yellow powder (0.836 g, 65%).

8a: ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.66 (s, 3 H, CH_3), 0.93 [s, 9 H, $C(CH_3)_3$], 1.48 [s, 15 H, $C_5(CH_3)_5$], 4.05 (s, 1 H, 6-H), 4.64 (m, 1 H, C_5H_4), 5.36 (m, 1 H, C_5H_4), 5.58 (m, 1 H, C_5H_4), 6.54 (m, 1 H, C_5H_4), 7.01−7.24 (m, 8 H, H_{Ph}), 7.43 (m, 2 H, H_{Ph}). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 11.7 [$C_5(CH_3)_5$], 30.4 [$C(CH_3)_3$], 34.5 [$C(CH_3)_3$], 37.4 (CH_3), 58.6 (C6), 106.5 (C_5H_4), 113.6 (C_5H_4), 114.6 (C_5H_4), 116.2 (C_5H_4), 108.2 (C7), 119.4 [$C_5(CH_3)_5$], 125.6, 126.7, 126.9, 128.3, 128.5, 130.3 (CH_{Ph}), 136.8 (C1), 149.6, 152.6 (*i*-C_{Ph}).

8b: Decomposition without melting at 235 °C. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = −0.05 (s, 3 H, CH_3), 0.91 [s, 9 H, $C(CH_3)_3$], 1.72 [s, 15 H, $C_5(CH_3)_5$], 4.32 (s, 1 H, 6-H), 4.53 (m, 1 H, C_5H_4), 5.39 (m, 1 H, C_5H_4), 5.86 (m, 1 H, C_5H_4), 6.41 (m, 1 H, C_5H_4), 7.04−7.24 (m, 8 H, H_{Ph}), 7.59 (m, 2 H, H_{Ph}). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.1 [$C_5(CH_3)_5$], 30.5 [$C(CH_3)_3$], 34.4 [$C(CH_3)_3$], 34.7 (CH_3), 59.4 (C6), 102.4 (C_5H_4), 106.7 (C7), 107.3 (C_5H_4), 113.6 (C_5H_4), 119.2 [$C_5(CH_3)_5$], 128.9 (C_5H_4), 126.5, 126.8, 126.9, 128.7, 128.9, 130.2 (CH_{Ph}), 136.8 (C1), 149.1, 150.5 (*i*-C_{Ph}). IR (KBr): ṽ = 3053 (m), 2943 (m), 2908 (m), 2889 (m), 1492 (s), 1477 (s), 1443 (s), 1392 (s), 1035 (s), 1013 (vs), 808 (vs), 800 (vs), 763 (vs), 713 (vs), 700 (vs), 686 cm^{-1} (vs). EI MS: *m*/*z* (%) = 514 (24) [M$^+$], 261 (100), 135 (20) [Cp*$^+$]. $C_{34}H_{42}OTi$ (514.58): calcd. C 79.36, H 8.23; found C 79.09, H 8.09.

Complex 9: A mixture of benzaldehyde (0.531 g, 5.0 mmol) in *n*-hexane (10 mL) was added dropwise to a stirred solution of Cp* Ti[η^6-$C_5H_4C(H)tBu$]Cl (**1**) (1.764 g, 5.0 mmol) in *n*-hexane (20 mL) at room temperature. After 15 min, the colour of the solution turned from dark green to orange. After stirring for an additional 4 h, the solution was concentrated to 10 mL and cooled to −20 °C. A mixture of diastereomers **9a** and **9b** was isolated as a yellow-orange, microcrystalline solid (1.308 g, 57%; **9a/9b** = 25:75).

9a: ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.82 [s, 9 H, $C(CH_3)_3$], 1.76 [s, 15 H, $C_5(CH_3)_5$], 3.22 (d, $^3J_{H6,H7}$ = 8.5 Hz, 1 H, 6-H), 5.23 (m, 1 H, 2-H), 5.24 (m, 1 H, 3-H), 6.01 (m, 1 H, 4-H), 6.38 (d, 1 H, 7-H), 6.84 (m, 1 H, 5-H), 6.96−7.24, 7.89 (m, 5 H, H_{Ph}). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.4 [$C_5(CH_3)_5$], 29.3 [$C(CH_3)_3$], 33.5 [$C(CH_3)_3$], 61.0 (C6), 107.2 (C7), 109.7 (C3), 111.1

Table 3. Crystal data and structure refinement for **2a**, **3a**, **5**, **6b**, and **9a**

	2a	**3a**	**5**	**6b**	**9a**
Empirical formula	$C_{33}H_{39}ClOTi$	$C_{23}H_{35}ClOTi$	$C_{30}H_{45}ClOTi$	$C_{24}H_{35}ClOTi$	$C_{27}H_{35}ClOTi$
M_r	534.99	410.86	505.01	422.87	458.90
Cryst. size [mm]	0.55 × 0.36 × 0.31	0.50 × 0.40 × 0.20	0.47 × 0.41 × 0.36	0.65 × 0.32 × 0.25	0.69 × 0.14 × 0.04
Cryst. system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	P1	$P2_1/c$	$P2_1/c$
a [Å]	12.8007(9)	9.9744(4)	12.6661(14)	15.2868(7)	9.8168(5)
b [Å]	15.0494(11)	14.2277(8)	12.6773(15)	9.7894(4)	15.5485(11)
c [Å]	15.7150(13)	16.0204(6)	18.539(2)	16.0150(6)	15.2835(6)
α [°]	94.852(9)		70.535(14)		
β [°]	109.293(9)	100.635(4)	73.276(13)	113.114(5)	93.984(6)
γ [°]	99.189(9)		84.906(14)		
V [Å^3]	2789.9(4)	2234.45(18)	2687.9(5)	2204.23(16)	2327.2(2)
Z	4	4	4	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.274	1.221	1.248	1.274	1.310
μ [mm^{-1}]	0.426	0.511	0.438	0.521	0.499
F(000)	1136	880	1088	904	976
Θ_{range} [°]	2.10 to 26.17	2.08 to 26.04	2.33 to 25.86	2.50 to 25.88	2.46 to 25.92
Reflections coll.	34105	16309	32224	16754	17428
Independ. reflect.	10180 (R_{int} = 0.1012)	4076 (R_{int} = 0.0388)	19099 (R_{int} = 0.0793)	4037 (R_{int} = 0.0489)	4257 (R_{int} = 0.0959)
Observed reflect. [$I > 2\sigma(I)$]	7222	3135	14166	3274	2304
Refined parameters	601	235	1189	384	271
GOF	0.978	1.007	0.917	0.975	0.784
R_1	0.0410	0.0364	0.0474	0.0288	0.0396
wR_2	0.1064	0.0976	0.1061	0.0721	0.0788
Largest diff. peak/hole [eÅ^{-3}]	0.567/−0.359	0.760/−0.349	0.303/−0.580	0.381/−0.217	0.378/−0.277

(C2), 117.8 (C5), 120.3 (C4), 124.3 [$C_5(CH_3)_5$], 145.2 (C1), 127.7−128.3, 129.5 (CH_{Ph}), 147.7 (i-C_{Ph}).

9b: ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.78 [s, 9 H, $C(CH_3)_3$], 1.78 [s, 15 H, $C_5(CH_3)_5$], 2.50 (d, $^3J_{H6,H7}$ = 10.4 Hz, 1 H, 6-H), 5.07 (m, 1 H, 5-H), 5.44 (m, 1 H, 4-H), 5.62 (m, 1 H, 3-H), 6.24 (d, 1 H, 7-H), 6.89 (m, 1 H, 2-H), 6.96−7.24 (m, 5 H, H_{Ph}). ^{13}C NMR (125 MHz, C_6D_6, 300 K): δ = 12.7 [$C_5(CH_3)_5$], 29.9 [$C(CH_3)_3$], 33.4 [$C(CH_3)_3$], 60.1 (C6), 102.0 (C7), 108.8 (C5), 112.2 (C4), 115.3 (C3), 120.3 (C2), 124.8 [$C_5(CH_3)_5$], 147.0 (C1), 127.7−128.3, 129.5 (CH_{Ph}), 146.9 (i-C_{Ph}).

Crystal Structure Determinations. Single crystals of **2a**, **3a**, **5**(**b**′+**d**′), **6b**, and **9a** were obtained from saturated *n*-hexane solutions upon cooling to 0 °C. The crystal data were collected with a STOE-IPDS diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073). Intensity measurements were performed at 193(2) K on crystals in sealed glass capillaries. The structures of all complexes were solved by direct phase determination (SHELXS-97) and refined on F^2 (SHELXS-97)[27] with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms in **2a**, **3a**, **5**(**b**′+**d**′), and **6b** were calculated and refined as riding atoms; hydrogen atoms in **9a** refined freely. Details of data collection parameters and refinements results are listed in Table 3. CCDC-174560 (**2a**), -174562 (**3a**), -174561 (**5**), -174559 (**6b**) and -174563 (**9a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[23] For $c_{AlMe3} = c_{\mathbf{2b}} = 1 \cdot 10^{-3}$ mol L^{-1} and $c_{B(C6F5)3} = c_{\mathbf{2b}} = 1 \cdot 10^{-3}$ mol L^{-1} equilibrium state is reached in 1 h and 5 min.

[24] Further details are given in the Supporting Information.

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