Titanium *Lewis* Acids for Asymmetric Catalysis: Synthesis and Structural Characterization of Dichloro[diolato(2−)-κ*O*,κ*O*′]bis(solvent)titanium ([$TiCl_2$(diolato)(solvent)$_2$]) Complexes

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The complexes [$TiCl_2$]{(*R*,*R*)-TADDOLato}(DME)]·MeCN (**3**), and [$TiCl_2$]{(*R*,*R*)-1-Nph-TADDOLato}$(MeCN)_2$]·CH_2Cl_2 (**4b**) (DME = 1,2-dimethoxyethane; (*R*,*R*)-TADDOLato = (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato(2−)-κ*O*,κ*O*′; (*R*,*R*)-1-Nph-TADDOLato = (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetra(naphthalen-1-yl)-1,3-dioxolane-4,5-dimethanolato(2−)-κ*O*,κ*O*′) were prepared and isolated in high yield as stable crystalline materials (*Scheme 1*). They constitute ideally suited and easy-to-handle catalyst precursors for a large number of Ti-catalyzed asymmetric reactions, for which they have been previously generated *in situ*. The X-ray crystal structures of **3** and **4b** show a distorted octahedral geometry around Ti with the chloro ligands in mutual *trans* positions (*Figs. 5* and *6*). The new chiral diols α-(1*S*,3*R*)-3-hydroxy-2,2,3-trimethylcyclopentyl]-α-phenylbenzenemethanol (**13a**), derived from camphoric acid (**5**), and (*M*)-6,6′-dimethyl-α,α,α′,α′-tetraphenyl[1,1′-biphenyl]-2,2′-dimethanol (**15**) were prepared (*Schemes 3* and *4*). These new ligands are able to form mononuclear complexes with the $Ti^{IV}Cl_2$ fragment. The corresponding complex **14** derived from **13a** was characterized by X-ray as a mixed THF/MeCN adduct.

1. Introduction. – Complexes of the general formula [$TiCl_2(OR)_2$] serve as *Lewis* acid catalysts or mediators (*i.e.*, in stoichiometric amounts) in allylation reactions of aldehydes in the presence of allylstannanes, hetero-*Diels-Alder* reactions, ene reactions, *Michael* additions, *Mukaiyama* silyl-aldol condensations, and other reactions (see review [1]). Of particular interest are those complexes derived from an enantiomerically pure chelating diol. Thus, [$TiCl_2$(BINOLato)] complexes (BINOLato = [1,1′-binaphthalene]-2,2′-diolato(2−)-κ*O*,κ*O*′) have found specific use in enantioselective *Mukaiyama* aldol reactions [2], cyanosilylation of aldehydes [2], carbonyl-ene reactions [3], carbonyl allylsilane or allylstannane additions [4–6], ene cyclizations [7], (hetero)-*Diels-Alder* reactions [8], and others (for a review, see [9]). Complexes of the type [$TiCl_2$(TADDOLato)][1]) serve as catalysts in enantioselective cyanosilylations [10], (hetero)-*Diels-Alder* [11–15], [2 + 2] cycloadditions [16–18], [2 + 3] cycloadditions [19], 1,3-dipolar cycloadditions [20], nitro-aldol reactions [21], fluorinations [22], and others (for reviews, see [9][23]).

When inspecting the procedures for the generation of the titanium catalysts used in the reactions mentioned above, one notes that they are prepared *in situ* according to

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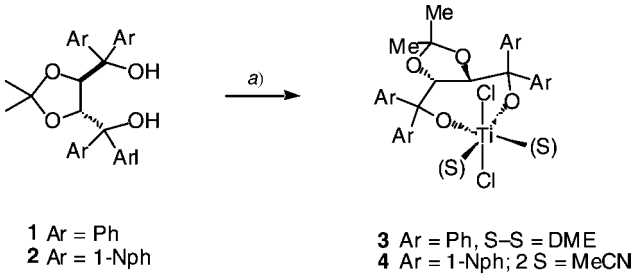
[1]) (*R*,*R*)-TADDOL **1** = (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol; (*R*,*R*)-1-Nph-TADDOL **2** = (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetra(naphthalen-1-yl)-1,3-dioxolane-4,5-dimethanol; (*R*,*R*)-TADDOLato = (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato(2−)-κ*O*,κ*O*′; (*R*,*R*)-1-Nph-TADDOLato = (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetra(naphthalen-1-yl)-1,3-dioxolane-4,5-dimethanolato(2−)-κ*O*,κ*O*′.

different protocols and sometimes in the presence of molecular sieves, the role and mode of action of which remains unclear [11][21][23]. In connection with our recent work on catalytic enantioselective fluorination [22], chlorination, and bromination [24], we explored in some detail the synthesis and complex chemistry of [$TiCl_2$(TADDOLato)(solvent)] species. This led to the isolation and characterization of the complexes [$TiCl_2$(TADDOLato)(DME)]·MeCN (**3**; DME = 1,2-dimethoxyethane) and [$TiCl_2$(1-Nph-TADDOLato)(MeCN)] (**4a**) (*Scheme 1*)[1]). These materials proved to be handy catalyst precursors for the enantioselective halogenation reactions. Our interest in chiral dichloro(diolato)titanium *Lewis* acids with potential use in asymmetric catalysis led us to study additional systems as well. Thus, two enantiomerically pure diols were prepared from (+)-camphoric acid (**5**) and converted to the corresponding $TiCl_2$ complex derivatives. Furthermore, we explored for the first time an enantiomerically pure $\alpha,\alpha,\alpha',\alpha'$-tetraphenyl[1,1′-biphenyl]-2,2′-dimethanol and its unstable Ti complex.

Scheme 1



1 Ar = Ph
2 Ar = 1-Nph

3 Ar = Ph, S–S = DME
4 Ar = 1-Nph; 2 S = MeCN

1-Nph = naphthalen-1-yl, DME = 1,2-dimethoxyethane

a) 1. [$TiCl_2(O^iPr)_2$], MeCN. 2. Evaporation. 3. ¼MeCN, DME (for **3**). Complex **3** crystallized with *ca.* 1 equiv. of MeCN as solvent of crystallization.

2. Results and Discussion. – 2.1. *Preparation and Characterization of Complexes Containing TADDOLato Ligands.* For the synthesis of dichloro(diolato)titanium complexes, the most popular *in situ* preparation method is the reversible ligand-exchange reaction starting from [$TiCl_2(O^iPr_2)$] and the diol ligand in, *e.g.*, toluene [25]. This reaction is sometimes performed in the presence of powdered molecular sieves, or with subsequent evaporation of the solution. The second method was thought to azeotropically remove ^{i}PrOH from the equilibrium, whereas the role of the molecular sieves is not clear [11][23][26]. However, when we prepared complex solutions starting from the simple (*R*,*R*)-TADDOL[1]) (**1**) and [$TiCl_2(O^iPr)_2$] in toluene, we found by ^{1}H-NMR spectroscopy that ^{i}PrOH was still present in materials obtained after evaporation, probably as ligand completing the coordination sphere of Ti ([$TiCl_2$(TADDOLato)(^{i}PrOH)$_n$]; $n \leq 2$). However, these materials were not crystalline and still contained impurities. On the other hand, if the ligand-exchange reaction was carried out in the coordinating solvent MeCN[2]), a single evaporation of the reaction solution removed most of the ^{i}PrOH and yielded a material of the composition

[2]) We note that TADDOL **1** is hardly soluble in MeCN, but slowly dissolves on addition of [$TiCl_2(O^iPr)_2$] to a suspension of the ligand in the same solvent, thus indicating that complex formation is relatively fast.

$[TiCl_2(TADDOLato)(MeCN)_n]$ ($n \approx 2$). This material was not easily purified due to its high solubility in MeCN and loss of coordinated solvent on drying, but it could be converted to the highly crystalline complex $[TiCl_2(TADDOLato)(DME)] \cdot MeCN$ (**3**) by simple addition of a stoichiometric amount of DME (1,2-dimethoxyethane) to the *in situ* prepared MeCN solution, whereupon **3** precipitated and could, thus, be isolated analytically pure in a yield of up to 90%.

Complex **3** was characterized by X-ray, NMR, and elemental analysis (C, H, N, Cl). It is a white crystalline material that can be handled for prolonged periods in air and stored in closed vessels for months. It is soluble in CH_2Cl_2, $CHCl_3$, and THF, but only sparingly so in MeCN. The MeCN molecule (actually only *ca.* 0.8 equiv. per complex unit are present, as shown by X-ray and ^{1}H-NMR) is not coordinated to the metal center, but is solvent of crystallization. Under high vacuum at room temperature, some MeCN, but no DME was lost. The stability of **3** is also reflected by its melting point of 200° (with decomposition; browning from 190°). The ^{1}H- and ^{13}C-NMR spectra of **3** give the sets of signals expected for a C_2-symmetric species (*Fig. 1*). The signal patterns remain unchanged at low temperature (233 K in $CDCl_3$), thus indicating that the species actually observed is the most stable isomer containing the Cl ligands in mutual *trans*-diaxial position, as observed for the solid-state structure (*vide infra*).

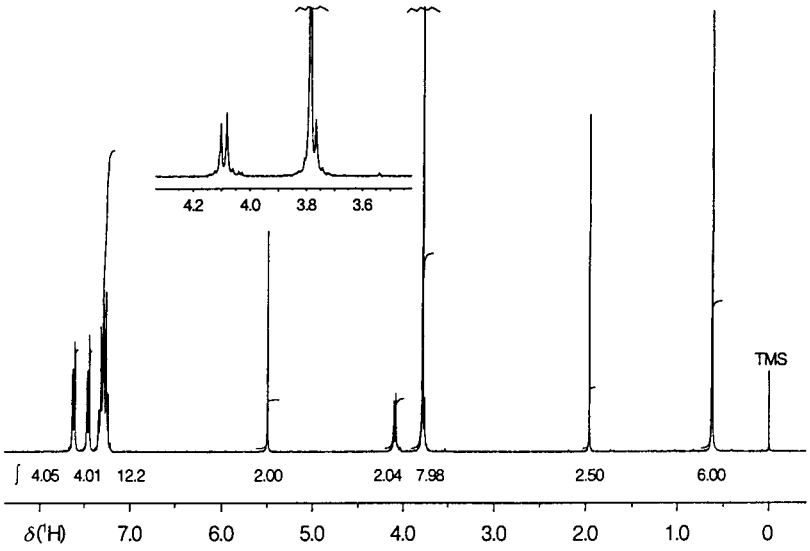


Fig. 1. *^{1}H-NMR* (300 MHz, $CDCl_3$) *of* $[TiCl_2(TADDOLato)(DME)] \cdot MeCN$ (**3**)

Upon addition of 1-Nph-TADDOL[1]) (**2**) to $[TiCl_2(O^iPr)_2]$ in MeCN, rapid ligand exchange occurred, as indicated by a color change from almost colorless to yellow. Slow evaporation under high vacuum of such solutions led to the precipitation of a beige powder of the composition $[TiCl_2(1\text{-Nph-TADDOL})(MeCN)_n]$ ($n \approx 2$) that is only sparingly soluble in many solvents ($CDCl_3$, CH_2Cl_2, MeCN, THF, C_6H_6)[3]). Although

[3]) Precipitation or crystallization may sometimes also occur spontaneously, without previously evaporating solvents.

this material was easily prepared and isolated in good yield, we were not able to obtain a consistent elemental analysis, possibly due to loss of MeCN on drying under high vacuum. Redissolution of this material in CH_2Cl_2/MeCN yielded, on evaporation of CH_2Cl_2, a bright yellow powder of the composition [$TiCl_2$(1-Nph-TADDOLato)-(MeCN)] (**4a**). Under an inert atmosphere, this compound is stable for at least several months, but it slowly deteriorates in air as shown by the darkening of samples stored in vessels occasionally opened to air. However, even these samples performed in our catalytic fluorination reaction [22] with reactivity and selectivity equal to fresh samples. The substance **4a** is only slightly soluble in $CDCl_3$, CH_2Cl_2, MeCN, and THF, and its exact structure is not known. Upon slow evaporation from MeCN/CH_2Cl_2 solutions, the complex [$TiCl_2$(1-Nph-TADDOLato)$(MeCN)_2$]·CH_2Cl_2 (**4b**) was obtained as transparent yellow crystals suited for an X-ray-crystal-structure study (*vide infra*). It is thus reasonable to assume that the species containing two coordinated MeCN molecules is dominant in solution with excess MeCN, whereas, at lower MeCN concentration, the monosolvated form precipitates.

Crystalline mixed solvates [$TiCl_2$(1-Nph-TADDOLato)$(THF)_n(MeCN)_{2-n}$]·CH_2Cl_2 were obtained by slow evaporation from MeCN/CH_2Cl_2/THF solutions, but the addition of DME or of the less volatile 1-(benzyloxy)-2-methoxyethane to **4a** in MeCN/CH_2Cl_2 did not afford the corresponding ether complexes. This is in contrast to the case of **3**, which is, apparently, a very stable complex with DME. We assume that the increased steric demand of the naphthalenyl-substituted TADDOL is responsible for the relative instability of the corresponding adducts with chelating diethers.

2.2. *Synthesis of a Camphor-Derived Ligand and Formation of Titanium Complexes.* Several enantiomerically pure diol ligands can be derived in a few steps from (+)-camphoric acid (**5**). Camphoric anhydride (**6**) reacted with PhMgBr to yield a 1.6:1 mixture of regioisomeric diphenylcampholides **7a** and **7b**, after cyclization of the intermediate hydroxy acids [27] (*Scheme 2*)[4]).

It has been described in the older literature that the main isomer **7a** is the only product isolated from the reaction of dimethyl camphorate (**8**) with PhMgBr [27], and, indeed, on repetition of this reaction under these conditions, we could not detect the minor isomer **7b** in the crude product, meaning that the regioselectivity in that case must be in the range of **7a**/**7b** $\geq$ 50:1. The difference in regioselectivity for the reaction of **6** or **8** can be rationalized by comparing the different directions of attack, according to the *Felkin-Ahn* model (*Fig. 2*). The energetically most-favored pathway of attack to **8** (case **A**) cannot be realized analogously for **6** (case **B**), as the carbonyl groups are fixed in a ring system.

$LiAlH_4$ Reduction of campholide **7a** afforded the 1,5-diol **9** as a new potential ligand. An *in situ* complex was generated upon reaction with [$TiCl_2(O^iPr)_2$] in MeCN, followed by evaporation. The ^{1}H-NMR analysis gave clear evidence of the formation of a single complex species **10**. In particular, a single set of new signals, shifted with respect to those of the free ligand **9**, is observed (*Fig. 3*). Furthermore, a *singlet* at 2.03 ppm is assigned to coordinated MeCN, and broadened signals due to one of the Ph groups

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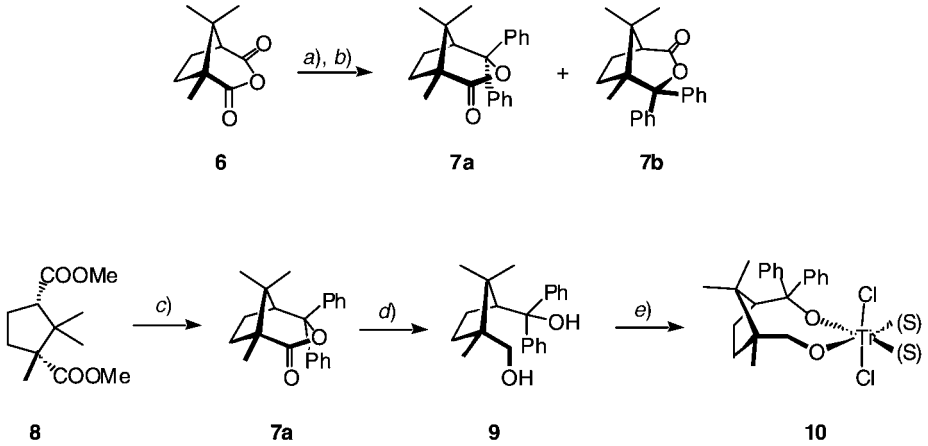
[4]) The regioisomer ratio was determined from a small-scale reaction with PhMgCl at 0°, cyclization of the hydroxy acids with Ac_2O, and ^{1}H-NMR analysis of the crude product. In the large-scale reaction, the isomers were isolated, after purification, in a ratio **7a**/**7b** of 3:1.

Scheme 2



a) PhMgCl or PhMgBr, THF. *b*) Ac_2O, CH_2Cl_2, 50°; 57% **7a** + 18% **7b**. *c*) PhMgCl, THF, 83%. *d*) $LiAlH_4$, ^{t}BuOMe; 82%. *e*) $[TiCl_2(O^iPr)_2]$, MeCN; evaporation.

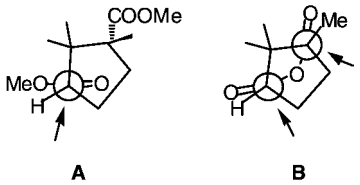


Fig. 2. *Regioselectivity of the PhMgCl attack rationalized by the* Felkin-Ahn *model:* **A** *from* **8** *and* **B** *from* **6**

indicate hindered rotation. This same phenomenon is observed in the diphenylcampholide **7a**, where the Ph_2C fragment is part of a ring system. The hindered rotation of one Ph group of **10** is, therefore, taken as an indication of chelate-ring formation.

We have used the *in situ* formed complex **10** for the catalytic fluorination reaction, however, with only limited success [28]. In a first attempt to prepare a chiral diol with increased steric requirements, the reaction of campholide **7a** with an excess of MeMgCl gave only the methyl ketone **11** (*Scheme 3*) in low yield, instead of the expected bis-tertiary alcohol. Finally, an isomeric mixture of the diphenylmethanols **13a**/**13b** could be obtained from the corresponding mixture of campholytolactones **12a**/**12b** (derived form $Pb(OAc)_4$ oxidation of (+)-camphoric acid (**5**) [29–31]) upon reaction with PhMgBr (*Scheme 3*). Compounds **13a**/**13b** could easily be separated by chromatography.

The diol **13a** was submitted to *in situ* complex formation with $[TiCl_2(O^iPr)_2]$ in MeCN, as usual. However, it is interesting to note that a crystalline compound **14** could be obtained only from solvent mixtures of THF and MeCN. This material was shown by X-ray analysis (*vide infra*) to be a MeCN/THF 1:1 solvate, [$TiCl_2$ (**13a**-ato)(THF)-(MeCN)]·MeCN (**14**).

2.3. *A Chiral Bis(trityl alcohol)* (=α,α,α′,α′-*Tetraphenyl[1,1′-biphenyl]-2,2′-dimethanol*) *Ligand*. When one considers the frequent occurrence of both the 1,1′-biaryl unit

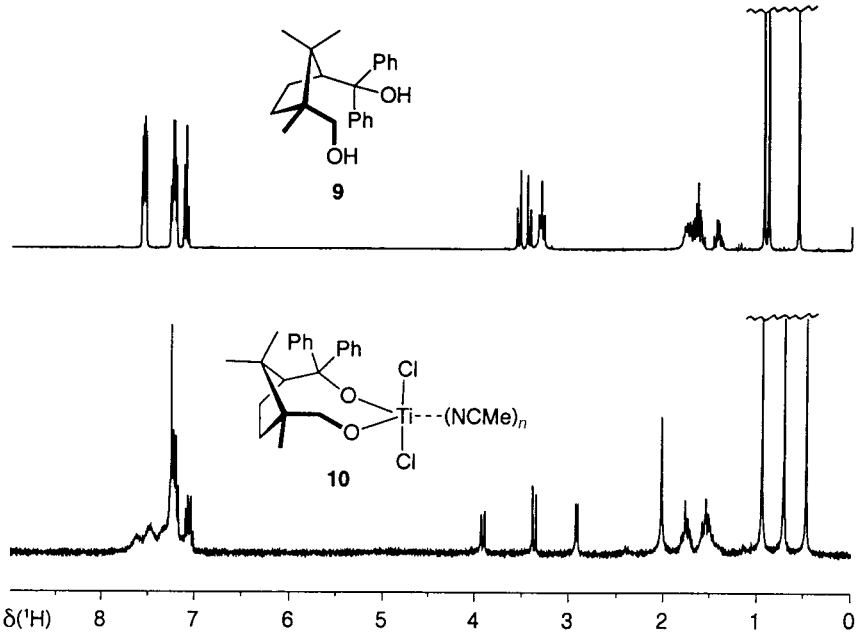


Fig. 3. *^{1}H-NMR* (300 MHz, $CDCl_3$) *Spectra of diol* **9** *and the* in situ *formed complex* **10**

and the diphenylmethanol moiety [23] in ligands for asymmetric catalysis, it is somewhat surprising that these two structural elements have not yet been combined into one ligand. We present here a new enantiomerically pure bis(trityl alcohol) derivative **15**, easily obtained in high yield from double addition of a [1,1′-biaryl]-2,2′-diyldilithium (generated from the diiodo compound **16** and ^{t}BuLi) to benzophenone (*Scheme 4*)[5]).

On treating diol **15** with an equimolar amount of $[TiCl_2(O^iPr)_2]$ in MeCN and THF (added to increase solubility), the resulting 'catalyst' solution was inactive in a fluorination reaction [22], and by TLC analysis, **15** could no longer be detected in the reaction mixture, although it was used in slight excess. Most probably, **15** had cyclized to the corresponding ether under the influence of traces of HCl, as previously described by *Wittig* and *Petri* for a similar diol [32]. We, thus, repeated the *in situ* preparation of the complex in the presence of the sterically hindered base 2,6-di(*tert*-butyl)pyridine which is known to remove traces of protic acid without blocking *Lewis* acid metal centers [34][35]. This time, the corresponding solution gave a single TLC spot for the ligand **15**, and it catalyzed a fluorination reaction, albeit with low activity and stereoselectivity [28]. We are, thus, confident that a complex **17** had formed in solution, and that such species may find future applications in *Lewis* acid catalyzed reactions.

2.4. *Solid-State Structure of TADDOL Complexes* **3** *and* **4b** *and of Complex* **14**. The structure of some (TADDOLato)titanium complexes has been determined by X-ray

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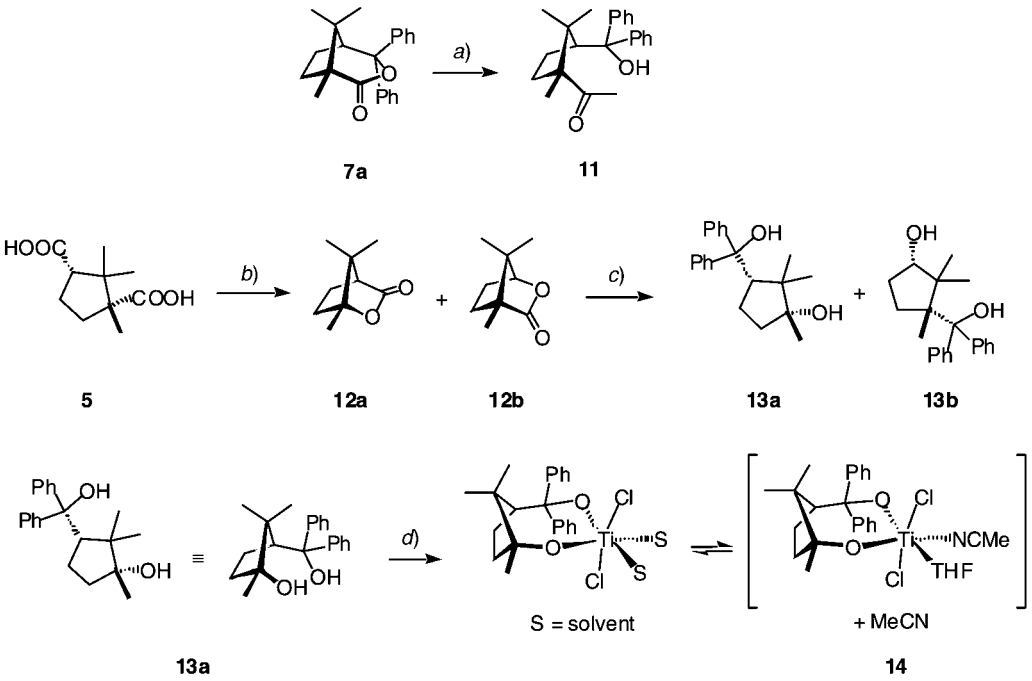
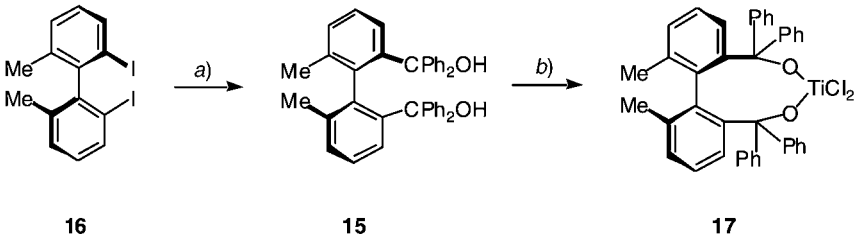
[5]) A similar substance has been prepared in a enantiomerically pure state by *Wittig* and *Petri* in 1933 [32]. A series of related racemic substances have been reported in 1996 [33]. In both cases, the use of these molecules as ligands for catalysis was not considered.

Scheme 3



a) MeMgCl, THF, 90°, 3 d; 34% (36% **7a** re-isolated). *b*) [31]. *c*) PhMgBr, THF; 51% **13a** + 18% **13b**. *d*) $[TiCl_2(O^iPr)_2]$, MeCN; then THF, MeCN.

Scheme 4



a) 1. ^{t}BuLi, THF, −78°. 2. Ph_2CO; 94%. *b*) $[TiCl_2(O^iPr)_2]$, 2,6-di(*tert*-butyl)pyridine, MeCN, THF.

crystallography previously. Thus, known derivatives include the spirocyclic alkoxide $\{3[Ti(TADDOLato)_2]\}\cdot 0.5\ Et_2O$ [36], the chloro-cyclopentadienyl complexes $[TiCl(\eta^5\text{-cp})(TADDOLato)]$ [37] and $[\{Ti(\eta^5\text{-cp})(TADDOLato)\}_2(\mu^2\text{-O})]$ [38], the latter being a partial hydrolysis product of the former. Most important for our study are the $[TiCl_2(TADDOLato)]$ derivatives $[TiCl_2(TADDOLato)\{(3\text{-cinnamoyl})\text{-}1,3\text{-oxazolidin-2-one}\}]\cdot CH_2Cl_2$ (**18**) [39], $[TiCl_2(TADDOLato)(diphos)]$ (**19**) [40a], and $[TiCl_2(TADDOLato)(THF)_2]$ (**20**) [40b] described more recently (*Fig. 4*). The structure of compounds **3** and **4** has been reported in preliminary form from our laboratories in conjunction with the first catalytic asymmetric fluorination [22]. We note

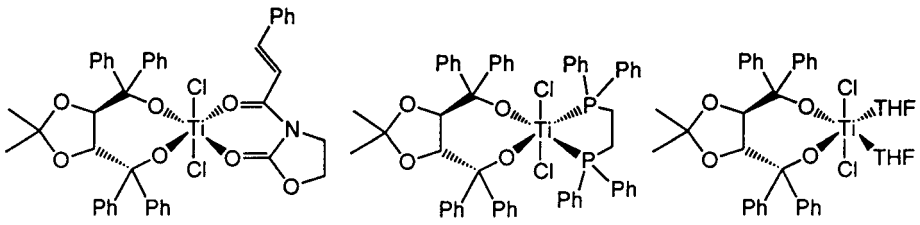


Fig. 4. *Three [$TiCl_2$(TADDOLato)] complexes whose crystal structures have been reported previously:* **18** [39], **19** [40a], *and* **20** [40b]

that **4** is the first reported structure of a [Ti(TADDOLato)] complex where the TADDOL ligand is different from **1**. The *Table* provides a summary of important bond distances and angles for the three complexes **3**, **4b**, and **14**. One notes that the bonding parameters of the three compounds define a distorted octahedral geometry around the Ti-center, with the two Cl ligands in mutual axial positions, with respect to the equatorial plane containing the diol O-atoms and solvent donor atoms. The extent of the distortion is very similar for **3**, **4b**, and **14**. Therefore, the most-relevant geometrical features will be pointed out explicitly for **3** only.

Complex **3** crystallizes in form of colorless transparent platelets of up to millimeter size. The X-ray structural analysis was complicated by the presence of MeCN solvent of crystallization forming layers, through which it can diffuse. As a result, there are solvent positions with partial occupancy. This observation is in line with the ^{1}H-NMR quantification of MeCN, where less than 1 equiv. was found. Crystals belong to the orthorhombic crystal system, space group $P2_12_12_1$, and the unit cell contains one and a half independent molecular units. In the fully asymmetric unique molecule, shown in *Fig. 5*, the coordinated solvent DME assumes a pseudo-*meso* configuration, *i.e.*, with the two Me groups in mutual *cis* orientation. The axial Cl ligands and the Ti-atom span an angle Cl(1)–Ti–Cl(2) of 164.97(10)°. This deviation from an idealized 180° for an octahedral geometry is typical for all $[TiCl_2(OR)_2(L)_2]$ complexes so far structurally characterized, as reflected also by the corresponding parameter of, *e.g.*, **18** (164.4° [39]) and **19** (157.2° [40a]). The Ti–O(olato) bond lengths, as well as the angles around the olato O-atom (each 147.0(4)°) are in line with partial multiple-bond character for the Ti–O bonds. The relatively long bond distances to the DME O-atoms from Ti (Ti–O(5) 222.5(5) pm; Ti–O(6) 216.4(6) pm) and the acute angle O(5)–Ti–O(6) of 73.7(2)° constitute a geometric indication that the solvent molecule is only weakly bound to Ti. It is also known that O-donors forming 5-membered chelate rings usually do not afford very stable mononuclear complexes with Ti^{IV} [25]. The position of the Ph groups can be defined as pseudo-axial and pseudo-equatorial, respectively, relative to the plane of the dioxolane ring. However, relative to the main coordination plane of Ti (TiO_4), they show pseudo-mirror symmetry, and the coordination plane is bisecting the angles C(12)–C(1)–C(18) and C(30)–C(4)–C(24). However, the relevant aspect concerning the aryl substituents in complexes of TADDOLs being very important when discussing chiral induction in catalytic reactions is their orientation with respect to an axial coordination site, here occupied by a Cl ligand. Thus, one observes that the

Table. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for the Complexes* **3**, **4b**, *and* **14**

	3	**4b**	**14**
Bond distances:			
Ti–Cl(1)	2.337(2)	2.3343(13)	2.3610(16)
Ti–Cl(2)	2.342(3)	2.3622(13)	2.3772(16)
Ti–O(1)	1.752(5)	1.780(3)	1.755(4)
Ti–O(2)	1.765(5)	1.773(3)	1.764(3)
Ti–O(5)/Ti–O(6)	2.225(5)/2.164(6)		
Ti–N(1)/Ti–N(2)		2.283(4)/2.264(4)	
Ti–N(1)/Ti–O(6)			2.313(6)/2.222(4)
Bond angles:			
Cl(1)–Ti–Cl(2)	164.97(10)	162.11(5)	156.32(7)
O(1)Ti–O(2)	98.6(2)	97.18(12)	95.17(16)
O(5)–Ti–O(6)	73.7(2)		
N(1)–Ti–N(2)		83.25(14)	
N(1)–Ti–O(6)			86.16(16)
Ti–O(1)–C	147.0(4)	145.8(2)	147.6(3)
Ti–O(2)–C	147.0(5)	148.0(2)	150.6(3)

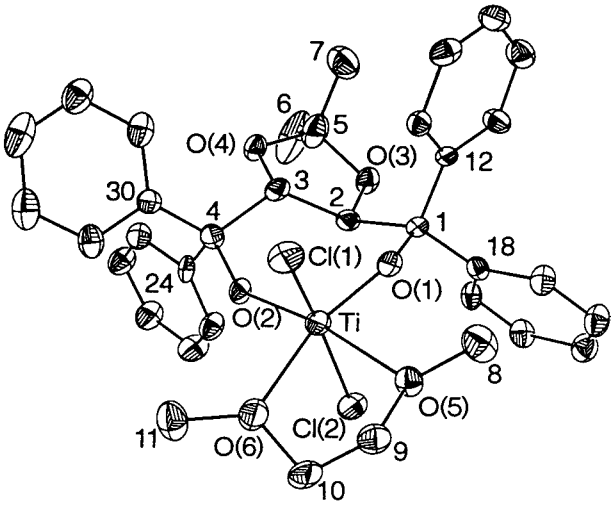


Fig. 5. *ORTEP View* (30% probability ellipsoids) *of the unique independent complex molecule in* $[TiCl_2(TADDOLato)(DME)]\cdot MeCN$ (**3**). H-Atoms and solvent of crystallization are omitted. C-Atoms are numbered without bearing atom symbols.

four aryl groups are pairwise characterized by an 'edge-on and 'face-on' orientation, respectively, as previously noted also in the structure of free TADDOLs [23], as well as for chiral chelating diphosphines.

As illustrated in *Fig. 6*, the same description applies to the bis(acetonitrile) solvate $[TiCl_2(1\text{-Nph-TADDOLato})(MeCN)_2]\cdot CH_2Cl_2$ (**4b**; obtained as orthorhombic crystals, space group $P2_12_12_1$) where the distinction between 'edge-on' and 'face-on' naphthalenyl group is particularly pronounced. The 'edge-on' naphthalenyl groups point away from Ti and toward the dioxolane ring where they come in close proximity to the Me groups. This is also reflected in the ^{1}H-NMR spectrum of **4** in $CDCl_3$ (with

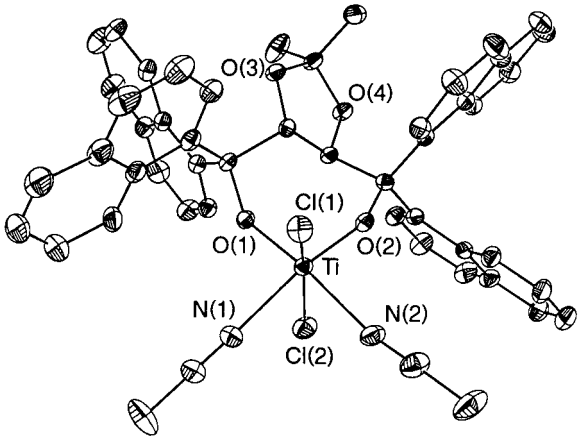


Fig. 6. *ORTEP View* (30% probability ellipsoids) *of* $[TiCl_2(1\text{-}Nph\text{-}TADDOLato)(MeCN)_2]\cdot CH_2Cl_2$ (**4b**). H-Atoms and solvent of crystallization are omitted for clarity.

excess CD_3CN for solubilization) by a shift to lower frequency of the signals for the Me groups ($\delta(H) = -0.27$). As we reported elsewhere [41], the 'face-on' naphthalenyl groups are a key factor in determining stereoselectivity in the catalytic fluorination reaction of β-keto esters by virtue of their shielding of one enantioface of the coordinated enolate.

The coordinating solvent molecules in **14** (monoclinic crystals, space group $P2_1$) occupy the two different coordination sites in the equatorial plane of Ti according to their steric requirements: the small linear MeCN lies *cis* to the sterically demanding Ph_2CO unit, whereas the THF molecule resides next to the primary alcoholato function (*Fig. 7*). The bond lengths Ti–O(olato) are shorter than typical Ti–O single bonds (*ca.* 185 pm

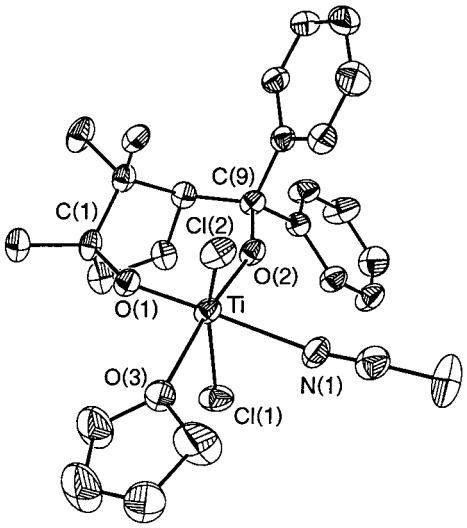


Fig. 7. *ORTEP View* (30% probability ellipsoids) *of* $[TiCl_2$(**13a**-*ato*)*(THF)(MeCN)*$]\cdot MeCN$ (**14**)

[42]), but consistent with data from the TADDOL complexes discussed above. This applies also to all other features of the distorted octahedral geometry around the Ti-atom.

3. Conclusions. – It has been pointed out by *Duthaler* and *Hafner* that, to obtain stable complexes of the dichlorotitanium/chelating diolato type, the chelating diol should be of the 1,3, 1,4, or 1,5 type [25]. Complexes with 1,2-diols tend to form multinuclear species with alcoholato ligands bridging two metal centers, whereas diols with rather distant coordinating groups tend to form polymeric complexes [25][43]. TADDOL-Type 1,4-diol ligands are well-pre-organized for complex formation with Ti-centers, but complexes can also easily be obtained from other diols fulfilling the requirements mentioned above. Although it is common practice to prepare such species *in situ*, our experience is that they can often be isolated as crystalline materials, when the choice of solvent and co-ligands (very often these are coordinating solvent) is appropriate. We worked with MeCN as solvent, and it seems that this was a good choice for preparing the titanium species in question. As a first beneficial consequence, the displacement of ^{i}PrOH (which is liberated during the ligand-exchange reaction of diol ligands with $[TiCl_2(O^{i}Pr)_2]$) was never a problem, whereas it is not possible to remove ^{i}PrOH by azeotropic distillation or under high vacuum when toluene is used as solvent for complex synthesis, because the alcohol remains strongly coordinated to the Ti-atom. Second, the presence of excess sterically undemanding MeCN ligands assures coordinative saturation and, thus, makes the dichlorotitanium entity less susceptible towards hydrolysis. Still, the strength of coordination of MeCN is not too high to prevent ligand exchanges, with substrates (and thus catalytic processes) to take place. Third, the coordination of solvents may convert otherwise amorphous or polymeric metal species into mononuclear, crystalline complexes of defined composition. These may be useful as catalyst precursors that are easy to handle. Given the wide range of solvents available, it should be possible to find one that favors the formation of a crystalline product. However, sometimes a suitable combination of solvents is necessary. This is exemplified by the highly crystalline complexes **3** (both MeCN and DME necessary) or **14** (THF and MeCN). Obviously, a fine balance of co-ligands at the central metal is necessary to obtain crystalline materials, and one approach to find the suitable ones is to use a 'multiple choice' approach in which the complex species is exposed to a mixture of several coordinating solvents.

The complexes **3** and **4** are easily prepared catalyst precursors. They are stable compounds that can be stored for prolonged times. Unlike many *in situ* prepared catalysts, they need not be prepared each time just before a catalytic experiment. Our own experience in catalytic enantioselective fluorination reactions has shown that the results of catalytic experiments were of better reproducibility, and that the enantiomer excess of the products was often a few % ee higher, when these crystalline complexes were used in catalysis, as opposed to *in situ* prepared catalysts [22]. While there is no definitive explanation for this, one may assume that the high purity (also the enantiomer purity!) and uniformity of the crystalline catalyst precursors is responsible. We propose that complexes **3** and **4** are applicable in all reactions published in the literature, where *in situ* prepared [$TiCl_2$(TADDOLato)] species have been used previously [23].

L. H. thanks *Solvias AG*, Basel, for financial support.

Experimental Part

General. TADDOL ligands **1** and ((4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetra(naphthalen-1-yl)-1,3-dioxolane-4,5-dimethanol; **2**) were obtained from *Fluka* and *Aldrich* resp.; other TADDOLs were prepared according to *Beck et al.* [44]. $[TiCl_2(O^iPr)_2]$ was prepared according to [45] and used either as pure substance or as 1M soln. in MeCN. Dimethyl camphorate (**8**) was obtained by dimethyl sulfate alkylation of (+)-camphoric acid (*Acros*), as described in [46]; camphoric anhydride (=(1*R*,5*S*)-1,8,8-trimethyl-3-oxabicyclo[3.2.1]octane-2,4-dione; **6**) was obtained commercially or from (+)-camphoric acid and Ac_2O. PhMgCl was prepared according to [47], (*M*)-2,2′-diiodo-6,6′-dimethyl-1,1′-biphenyl (**16**) was available from earlier work. Syntheses of metal complexes were performed under an inert atmosphere and air-sensitive substances handled in a glove box. DME = 1,2-dimethoxyethane; Nph = naphthyl; h.v. = high vacuum (≤0.01 mbar); NMR Spectra: at 300 (^{1}H) and 75.5 MHz (^{13}C) in $CDCl_3$, if not stated otherwise; δ in ppm, referenced to $SiMe_4$ (=0 ppm; ^{1}H) or solvent signal (^{13}C; δ ($CDCl_3$) 77.0), *J* in Hz.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publications no. CCDC 145414 (**3**), CCDC 145415 (**4b**), and CCDC 172511 (**14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223336-033; e-mail: deposit@ccdc.cam.ac.uk).

*Dichloro[1,2-di(methoxy-κO)ethane][(4*R,5R*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato(2−)-κO,κO′]titanium-Acetonitrile* ($[TiCl_2$(TADDOLato)(DME)]·MeCN; **3**). To a suspension of (*R*,*R*)-TADDOL (**1**; 2.59 g, 5.55 mmol) in MeCN (10 ml) 1M $[TiCl_2(O^iPr)_2]$ in MeCN (5.55 ml, 5.55 mmol) was added and the mixture stirred for 1 d at r.t. After evaporation and drying of the remaining crust for 1 d under h.v., the solid was redissolved in MeCN (40 ml) at 50° and the resulting soln. evaporated to almost dryness. Fresh MeCN was added to reach a total volume of 20 ml. To this soln., DME (0.65 ml, 6.25 mmol) was added at r.t. under vigorous stirring. As soon as a homogeneous soln. was obtained, the stirring was stopped and the soln. set aside for crystallization (which started within seconds!). The mother liquor was removed with a filter stick at −20°, and the crystals were washed twice with MeCN (20 ml) at −20°. The product was dried for 1 d under h.v. (0.002 mbar), whereupon it lost some solvent of crystallization (MeCN): 3.507 g (89%) of **3** as $[TiCl_2$(*R*,*R*-TADDOLato)(DME)]·0.86 MeCN. M.p. 200–202° (dec.; browning at 190°). IR (fluorolube, NaCl plates): 3053*w*, 2978*w*, 2939*w*, 2904*w*, 2250*w*, 1598*w*, 1495*m*, 1444*s*, 1383*m*, 1371*s*. ^{1}H-NMR (400 MHz): 0.62 (*s*, 6 H, 2 Me); 1.97 (*s*, 2.58 H, MeCN); 3.79 (*d*, *J* = 6.0, 2 H, CH_2CH_2); 3.78 (*s*, 6 H, 2 MeO); 4.09 (*d*, *J* = 6.0, 2 H, CH_2CH_2); 5.50 (*s*, 2 H, 2 CH); 7.23–7.36 (*m*, 12 arom. H); 7.44–7.48 (*m*, 4 arom. H); 7.60–7.64 (*m*, 4 arom. H). ^{13}C-NMR (100.6 MHz): 1.8 (Me, *Me*CN); 27.2 (Me); 63.5 (Me (DME)); 71.7 (CH_2 (DME)); 80.0 (CH); 102.4 (C); 111.5 (C); 116.4 (br. *s*, Me*C*N); 127.0 (CH); 127.3 (CH); 127.6 (CH); 127.7 (CH); 127.9 (CH); 129.9 (CH); 142.7 (C); 143.6 (C). Anal. calc. for $C_{35}H_{38}Cl_2O_6Ti \cdot 0.86\ C_2H_3N$ (708.801): C 62.22, H 5.77, N 1.70, Cl 10.00; found: C 62.50, H 5.91, N 1.70, Cl 9.77.

Crystals suitable for an X-ray determination were grown by diffusion of a complex soln. in a CH_2Cl_2/MeCN mixture against heptane.

*(Acetonitrile)dichloro[(4*R,5R*)-2,2-dimethyl-α,α,α′,α′-tetra(naphthalen-1-yl)-1,3-dioxolane-4,5-dimethanolato(2−)-κO,κO′]titanium* ($[TiCl_2$(TADDOLato)(MeCN)]; **4a**). In MeCN (15 ml), 1-Nph-TADDOL (**2**; 1.022 g, 1.533 mmol; *Aldrich*) and $[TiCl_2(O^iPr)_2]$ (1.6 mmol) were stirred for 1 d at r.t. The yellow soln. was slowly (40 min) evaporated to *ca*. 4 ml (r.t./h.v.) under stirring whereupon precipitation of a bright beige powder set in. The volume was further reduced until a thick suspension was obtained. To this, MeCN (5 ml) was added, stirring was continued for 1 h at −10°, and the yellow mother liquor was removed with a filter stick. The fine powder was again suspended in MeCN (5 ml) and the (almost colorless) mother liquor removed. This material corresponds most probably to the formula $[TiCl_2$(TADDOLato)$(MeCN)_2]$, but a correct elemental analysis was not obtained due to loss of coordinated solvent in the dry state. The powder was dried for 1 h under h.v. and then further purified by recrystallization. Suspension in MeCN (5 ml), and adding a total of 25 ml of CH_2Cl_2 gave a soln. that was filtered and then slowly evaporated to 5 ml under h.v. under stirring. Bright yellow crystals of **4b** separated. Filtration and drying of the crystals for 12 h under h.v. yielded 923 mg (73%) of **4a** as $C_{47}H_{36}Cl_2O_4Ti + C_2H_3N$ (M_r 824.61). Dark yellow powder. ^{1}H-NMR ($CDCl_3/CD_3CN$ 4:1): −0.27 (*s*, 6 H, 2 Me); 1.97 (*s*, 3 H, MeCN); 6.30 (*s*, 2 H, CH); 6.71 (*ddd*, *J* = 8.9, 6.7, 1.5, 2 arom. H); 6.94 (*ddd*, *J* = 8.7, 6.7, 1.3, 2 arom. H); 7.07 (*ddd*, *J* = 8.0, 6.7, 1.0, 2 arom. H); 7.20 (*ddd*, *J* = 8.1, 6.7, 1.0, 2 arom. H); 7.54 (*d*, *J* = 9.0, 2 arom. H); 7.63 (*dd*, *J* = 8.3, 1.1, 2 arom. H); 7.68 ('*t*', *J* = 7.7, 2 arom. H); 7.72–7.92 (*m*, 8 arom. H); 8.13 (*d*, *J* = 8.7, 2 arom. H); 8.33 (*d*, *J* = 7.3, 2 arom. H); 9.15 (*dd*, *J* = 7.2, 1.5, 2 arom. H). ^{13}C-NMR ($CDCl_3/CD_3CN$): 0.9 (Me, MeCN); 25.8 (Me); 80.9 (CH); 100.8 (C); 111.7 (C); 123.1 (CH); 123.4 (CH); 123.8 (CH); 124.0 (CH);

124.2 (CH), 124.3 (CH), 125.1 (CH); 126.6 (CH); 127.2 (CH); 127.3 (CH); 127.6 (CH); 127.8 (CH); 128.5 (CH); 128.5 (CH); 130.9 (C); 132.1 (C); 133.5 (C); 134.0 (C); 139.1 (C); 139.5 (C). Anal. calc. for $C_{49}H_{39}Cl_2NO_4Ti$ (824.61); C 71.37, H 4.77, N 1.70; found: C 71.20, H 4.91, N 1.66 (sample sealed in glovebox).

*(1*R*,5*S*)-1,8,8-Trimethyl-4,4-diphenyl-3-oxabicyclo[3.2.1]octan-2-one* (**7a**) *and (1*S*,5*R*)-5,8,8-Trimethyl-4,4-diphenyl-3-oxabicyclo[3.2.1]octan-2-one* (**7b**) *from Camphoric Anhydride* (**6**). To a suspension of **6** (2.00 g, 10.98 mmol) in THF (10 ml) PhMgBr (30 mmol) in THF (12 ml) was added within 15 min at 0°. On warming to r.t., an exothermic reaction set in (caution! cooling advisable). After 2 h of stirring at r.t., the mixture was heated for 30 min at 70°, cooled to r.t., and quenched with 2M HCl (8 ml). Workup with ^{t}BuOMe/H_2O gave, after drying and evaporation, 3.527 g of a white foam, consisting of isomeric hydroxy acids (TLC, NMR). To the crude material Ac_2O (3 ml) and CH_2Cl_2 (3 ml) were added, and the mixture was stirred overnight at 50°. After evaporation, the residue was separated by FC (^{t}BuOMe/hexane 1:15): **7a** (1.992 g, 57%), **7b** (0.649 g, 18%), and some mixed fractions (< 100 mg).

Campholide **7a** *from Dimethyl Camphorate* (**8**) [27]. To a soln. of **8** [46] (20.2 g, 88.5 mmol) in THF (50 ml), a soln. of PhMgCl (350 mmol) in THF (120 ml) was added at 0° within 1.5 h. The mixture was stirred and warmed to r.t. overnight and then carefully quenched by the addition of sat. NH_4Cl soln. (20 ml) and 2M H_2SO_4 (100 ml). After workup with ^{t}BuOMe and H_2O, washing with H_2O, drying ($MgSO_4$) and evaporation, a crude yield of 28.84 g of a slightly yellow solid was obtained. Crystallization from hot EtOH (40 ml) gave a solid mass that was triturated with pentane (50 ml), filtered, and washed with additional pentane: 23.406 g (83%) of **7a**. White powder.

Data of **7a**: TLC (^{t}BuOMe/hexane 1:10): R_f 0.28. M.p. 152–153° ([58]: 154–155°). $[\alpha]_D = +149.3$ ($c = 0.99$, MeOH). IR (KBr): 3067*w*, 3053*w*, 2981*m*, 2969*m*, 2937*m*, 2873*w*, 1723*s*, 1448*m*, 1316*m*, 1217*m*, 1152*s*, 1083*m*, 742*m*, 702*s*, 653*m*. ^{1}H-NMR: 0.61 (*s*, 1 Me); 1.04 (*s*, 1 Me); 1.17 (*s*, 1 Me); 1.43–1.55 (*m*, 1 H); 1.62–1.75 (*m*, 1 H); 1.84–2.03 (*m*, 2 H); 3.23 (*d*, $J = 6.7$, 1 H); 7.08 (br. *s*, 1 arom. H); 7.09–7.18 (*m*, 2 arom. H); 7.20–7.32 (*m*, 4 arom. H); 7.51 (br. *s*, 1 arom. H); 7.72 (br. *s*, 2 arom. H). ^{13}C-NMR: 14.3; 23.2; 24.3; 24.4; 33.9; 43.9; 49.9; 53.2; 89.6; 123.5 (br.); 125.1 (br.); 126.4; 126.7; 128.5 (br.); 146.0; 146.1; 176.3. EI-MS (pos.): 320 (100, M^+), 243 (24, $[M - C_6H_5]^+$), 193 (87), 183 (81), 138 (86), 105 (93), 95 (48). Anal. calc. for $C_{22}H_{24}O_2$ (320.43): C 82.46, H 7.55; found: C 82.37, H 7.53.

Data of **7b**: TLC (^{t}BuOMe/hexane 1:10): R_f 0.19. M.p. 136–139°. $[\alpha]_D = -121.9$ ($c = 0.99$, MeOH). IR (KBr): 3062*w*, 3050*w*, 3011*w*, 2980*m*, 2963*m*, 2921*m*, 2881*m*, 1741*s*, 1478*m*, 1444*m*, 1386*w*, 1313*m*, 1259*s*, 1083*s*, 755*m*, 702*s*, 460*s*. ^{1}H-NMR: 0.80 (*s*, 1 Me); 0.96 (*s*, 1 Me); 1.55 (*ddd*, $J = 14.6, 12.1, 5.4$, 1 H); 1.68 (*s*, 1 Me); 1.80 (*ddd*, $J = 13.9, 9.9, 5.4$, 1 H); 2.02 (*dddd*, $J = 13.9, 12.1, 6.9, 4.4$, 1 H); 2.25 (*ddd*, $J = 14.6, 9.8, 4.5$, 1 H); 2.60 (*d*, $J = 6.9$, 1 H); 7.12–7.31 (*m*, 6 arom. H); 7.52–7.58 (*m*, 2 arom. H); 7.74–7.79 (*m*, 2 arom. H). ^{13}C-NMR: 20.0; 22.7; 25.1; 26.0; 35.6; 46.3; 51.1; 54.1; 93.8; 126.7; 126.7; 126.8; 127.2; 127.7; 127.8; 144.3; 145.3; 174.6. FAB-MS: 1537 (50, $[2M - Cl]^+$), 786 (27, M^+), 750 (92, $[M - Cl]^+$), 714 ($[M - 2\,Cl]^+$, 100), 630 (74). Anal. calc. for $C_{22}H_{24}O_2$ (320.43): C 82.46, H 7.55; found: C 82.44, H 7.78.

*(1*S*,3*R*)-2,2,3-Trimethyl-α,α-diphenylcyclopentane-1,3-dimethanol* (**9**). A soln. of **7a** (1.00 g, 3.12 mmol) in ^{t}BuOMe (10 ml) was added dropwise to $LiAlH_4$ (80 mg, 2.11 mmol) in ^{t}BuOMe (5 ml). Additional $LiAlH_4$ (120 mg, 3.16 mmol) was added in portions to the mixture (TLC control). After 1 h stirring at r.t., the excess reagent was destroyed by dropwise addition of H_2O, followed by workup with 2M KOH and ^{t}BuOMe. Drying of the org. phase (Na_2SO_4) and evaporation gave 1.049 g of a colorless resin (quant.), containing some ^{t}BuOMe (^{1}H-NMR). The material was dissolved in EtOH (2 ml) and slowly evaporated by standing in air. Large colorless crystals separated that were collected and washed with ^{t}BuOMe. The remaining material was dissolved in ^{t}BuOMe (10 ml), the soln. filtered, evaporated to *ca.* 2 ml, and overlayered with pentane (4 ml). After crystallization at −20° (in the presence of a trace of the crystalline material) the mother liquor was decanted, and the colorless crystals were washed with pentane. Total yield: 829 mg (82%) of **9**. TLC (^{t}BuOMe/hexane 1:1): R_f 0.25. M.p. 120.0–120.6°. $[\alpha]_D = -99.5$ ($c = 0.92$, MeOH). IR (KBr): 3577*s*, 3462*s* (br.), 3055*w*, 2996*w*, 2965*s*, 2872*m*, 1599*w*, 1493*w*, 1474*w*, 1447*s*, 1379*m*, 1344*m*, 1317*m*, 1266*m*, 1185*m*, 1158*m*, 1069*m*, 1049*m*, 1027*m*, 1004*m*, 980*m*, 916*w*, 890*w*, 868*w*, 757*s*, 748*s*, 707*s*, 698*s*. ^{1}H-NMR: 0.57 (*s*, 1 Me); 0.89 (*s*, 1 Me); 0.94 (*s*, 1 Me); 1.36–1.48 (*m*, 1 H); 1.57–1.81 (*m*, 3 H); 1.80 (br. *s*, CH_2OH, exchange with D_2O); 3.27–3.35 (*m*, 1 H); 3.33 (br. *s*, $C(Ph)_2OH$, exchange with D_2O); 3.43 (*d*, $J = 10.7$, 1 H, CH_2OH); 3.54 (*d*, $J = 10.7$, 1 H, CH_2OH); 7.07–7.15 (*m*, 2 arom. H); 7.20–7.29 (*m*, 4 arom. H); 7.53–7.59 (*m*, 4 arom. H); in fresh $CDCl_3$, a coupling of OH (δ 1.80, $J \approx 5$) to $CH_2(\alpha')$ was observed. ^{13}C-NMR: 25.1; 20.5; 25.1; 28.1; 33.5; 45.1; 49.3; 54.8; 69.5; 79.8; 125.3; 125.7; 125.9; 126.1; 127.7; 128.1; 146.7; 149.6. EI-MS (pos.): 306 (11, $[M - H_2O]^+$), 288 (3), 273 (4), 247 (3), 219 (7), 183 (100), 167 (12), 105 (24). Anal. calc. for $C_{22}H_{28}O_2$ (324.46): C 81.44, H 8.70; found: C 81.36, H 8.88.

*1-[(1*R*,3*S*)-3-(Hydroxydiphenylmethyl)-1,2,2-trimethylcyclopentyl]ethanone* (**11**). At 0°, 3M MeMgCl in THF (1.3 ml, 3.9 mmol) was added to a soln. of **7a** (3.62 mmol) in THF (5 ml). After stirring overnight at r.t., no

product was detected by TLC. After a new addition of MeMgCl (3.5 ml, 10.5 mmol) the mixture was refluxed for 3 d at 90°. Workup with sat. NH_4Cl soln., H_2O, and ^{t}BuOMe gave, after drying of the org. phase ($MgSO_4$), 1.277 g of crude product that was separated by FC (^{t}BuOMe/hexane 1:10): 412 mg (36%) of **7a** and 415 mg (34%) of **11** as colorless crystals. For analysis, the sample **11** was crystallized from CH_2Cl_2/hexane by slow evaporation. TLC (^{t}BuOMe/hexane 1:5): R_f 0.25. M.p. 110.6–112.5°. $[\alpha]_D = -99.5 \pm 1.3$ ($c = 1.455$, MeOH). IR (KBr): 3496*s*, 3058*w*, 2968*m*, 1682*s*, 1598*w*, 1491*w*, 1446*m*, 1373*m*, 1354*m*, 1255*m*, 1167*m*, 1062*w*, 985*w*, 883*w*, 760*m*, 746*m*, 786*s*, 642*w*. ^{1}H-NMR: 0.69 (*s*, 1 Me); 0.87 (*s*, 1 Me); 1.20 (*s*, 1 Me); 1.45 (*ddd*, $J = 14.7$, 8.8, 5.9, 1 CH); 1.58–1.91 (*m*, 2 CH); 2.11 (*s*, MeCO); 2.22 (*ddd*, $J = 13.2$, 10.1, 6.4, 1 CH); 3.28 (*s*, OH); 3.31 (*t*, $J = 9.5$, 1 CH); 7.08–7.16 (*m*, 2 arom. H); 7.20–7.30 (*m*, 4 arom. H); 7.54–7.59 (*m*, 4 arom. H). C-NMR: 20.5; 21.9; 25.0, 27.5; 29.3; 32.9; 46.8; 54.2; 61.9; 79.5; 125.3; 125.8; 126.0; 126.2; 127.7; 128.2; 146.4; 149.5; 214.9. EI-MS: (pos.): 336 (0.4, M^+), 318 (17, $[M - H_2O]^+$), 234 (17), 219 (16), 193 (27), 183 (100), 167 (37), 154 (16), 105 (39). Anal. calc. for $C_{23}H_{28}O_2$ (336.47): C 82.10, H 8.39; found: C 82.04, H 8.18.

*α-[(1*S*,3*R*)-3-Hydroxy-2,2,3-trimethylcyclopentyl]-α-phenylbenzenemethanol* (**13a**) *and α-[(1*R*,3*S*)-3-Hydroxy-1,2,2-trimethylcyclopentyl]-α-phenylbenzenemethanol* (**13b**). To a soln. of campholytolactones **12a/b** (2.640 g, 17.1 mmol) – obtained in the ratio 81:19 by lead tetraacetate oxidation of (+)-camphoric acid (**5**) as reported [31] (*cf.* also [29][30]) – in THF (20 ml) at r.t., 2.5M PhMgBr in THF (50 ml, 125 mmol) was added, and the resulting soln. was refluxed for 40 h (required reaction time may be much shorter). After workup with ^{t}BuOMe, sat. NH_4Cl soln., and H_2O, the org. phase was washed with sat. NH_4Cl soln., sat. NaCl soln., dried (Na_2SO_4), and evaporated leaving a few ml of a yellow oil. By FC (^{t}BuOMe/hexane 1:10, 1:5, and 1:3), impurities (biphenyl and phenol) were separated and the following 4 fractions were obtained. *Fr. 1:* **13a** and some PhOH (550 mg); *Fr. 2:* pure **13a** (2.521 g); *Fr. 3:* mixture **13a/b** (71 mg); *Fr. 4:* pure **13b**. *Fr. 1* and *2* were crystallized separately from ^{t}BuOMe/pentane at −20° to yield 0.478 and 2.246 g, resp., of colorless crystals of **13a**, total 2.724 g (51.3%). *Fr. 4* was dissolved in ^{t}BuOMe, the soln. concentrated to *ca.* 3 ml, overlayered with pentane (7 ml), and left for 1 d for crystallization at −20°. Decantation and washing with pentane yielded 0.973 g (18.3%) of **13b** as white crystalline powder. The product alcohols retained traces of H_2O and were thus sublimed, **13a** at 120°/0.002 mbar and **13b** at 100°/0.003 mbar, for elemental analysis and Ti-complex syntheses.

Data of **13a**: TLC (^{t}BuOMe/hexane 1:5): R_f 0.24. M.p. 153.2–154.4° (before sublimation), 153.0–154.2° (after sublimation). $[\alpha]_D = +6.8 \pm 0.6$ ($c = 1.14$, MeOH). IR (KBr): 3562*m*, 3509*w*, 3333*s* (br.), 3062*w*, 3018*w*, 2969*s*, 1596*w*, 1489*m*, 1472*m*, 1449*s*, 1394*m*, 1370*w*, 1314*w*, 1170*m*, 1146*m*, 1086*m*, 1010*m*, 934*w*, 811*w*, 898*w*, 770*m*, 745*s*, 786*s*, 661*w*, 636*w*, 539*w*. ^{1}H-NMR: 0.58 (*s*, 1 Me); 1.01 (*s*, 1 Me); 1.16 (*s*, 1 Me); 1.49–1.85 (*m*, 4 H); 2.21 (br. *s*, 1 OH); 3.43 (*t*, $J = 7.8$, 1 H); 5.66 (br. *s*, 1 OH); 7.01–7.13 (*m*, 2 arom. H); 7.17–7.29 (*m*, 4 arom. H); 7.54–7.68 (*m*, 4 arom. H). ^{13}C-NMR: 19.6 (Me); 21.4 (Me); 24.4 (CH_2); 31.4 (Me); 37.5 (CH_2); 47.8 (C); 55.5 (CH); 78.9 (C); 84.0 (C); 125.4 (CH); 125.5 (CH); 125.5 (CH); 125.6 (CH); 127.8 (CH); 149.3 (C); 149.5 (C). EI-MS (pos.): 310 (0.4, M^+), 292 (3, $[M - H_2O]^+$), 274 (11), 259 (7), 219 (16), 183 (100), 167 (15), 105 (44). Anal. calc. for $C_{21}H_{26}O_2$ (310.44): C 81.25, H 8.44; found: C 81.14, H 8.58.

Data of **13b**: TLC (^{t}BuOMe/hexane 1:5): R_f 0.13. M.p. 163.6–163.9° (before sublimation), 163.0–164.3° (after sublimation). $[\alpha]_D = -70.9 \pm 1.0$ ($c = 1.05$, MeOH). IR (KBr): 3358*s* (br.), 3096*w*, 3057*w*, 2994*m*, 2970*s*, 1597*w*, 1493*m*, 1467*m*, 1444*m*, 1388*m*, 1366*m*, 1264*w*, 1194*m*, 1068*s*, 1035*s*, 892*w*, 840*w*, 759*m*, 730*m*, 698*s*, 578*w*. ^{1}H-NMR: 0.73 (*s*, 1 Me); 0.86 (*s*, 1 Me); 1.18–1.26 (*m*, 1 CH); 1.28 (*s*, 1 Me); 1.59 (*dddd*, $J = 14.7$, 9.2, 5.2, 4.1, 1 CH); 1.96–2.12 (*m*, 2 CH); 2.89–3.01 (*m*, CH); 3.77 (br. *s*, 2 OH); 7.12–7.34 (*m*, 6 arom. H); 7.51–7.57 (*m*, 2 arom. H); 7.71–7.77 (*m*, 2 arom. H). ^{13}C-NMR: 21.0 (Me); 24.5 (Me); 25.5 (Me); 29.5 (CH_2); 34.5 (CH_2); 54.6 (C); 82.3 (CH); 83.1 (C); 126.4 (CH); 126.4 (CH); 127.1 (CH); 127.3 (CH); 128.3 (CH); 128.8 (CH); 146.8 (C); 146.9 (C). EI-MS (pos.): 292 (3, $[M - H_2O]^+$), 274 (2), 259 (1), 220 (2), 205 (4), 191 (2), 183 (100), 105 (24). Anal. calc. for $C_{21}H_{26}O_2$ (310.44): C 81.25, H 8.44; found: C 81.04, H 8.22 (sublimed sample).

*(*M*)-6,6′-Dimethyl-α,α,α′,α′-tetraphenyl[1,1′-biphenyl]-2,2′-dimethanol* (**15**). To a soln. of (*M*)-2,2′-diiodo-6,6′-dimethyl-1,1′-biphenyl (**16**; 2.049 g, 4.72 mmol) in 10 ml THF, 1.6M ^{t}BuLi in pentane (12.2 ml, 19.5 mmol) was added dropwise at −78°, and the resulting yellow suspension was stirred for 30 min. Still at −78°, a soln. of benzophenone (2.00 g, 11.0 mmol) in THF (5 ml) was added dropwise to the mixture, resulting in a green coloration. After 1 h stirring, the cooling bath was removed and the mixture stirred for an additional 3 h at r.t. Quenching with 10 ml sat. NH_4Cl soln. was followed by workup with H_2O (100 ml), ^{t}BuOMe (100 ml), and CH_2Cl_2 (50 ml). The org. phase was washed with H_2O, sat. $NaHCO_3$ soln., and sat. NaCl soln., dried (Na_2SO_4), and evaporated to yield a semi-crystalline mass that was triturated with pentane (2 × 10 ml and 1 × 5 ml), yielding 2.417 g (94%) of **15**. White powder. TLC (^{t}BuOMe/hexane 1:10): R_f 0.23. M.p. 270–275°. $[\alpha]_D = +117.9$ ($c = 0.615$, CH_2Cl_2). IR (KBr): 3504*m*, 3428*m*, 3056*m*, 3023*w*, 2913*w*, 1942*w*, 1879*w*, 1810*w*, 1598*w*, 1492*m*, 1446*s*, 1322*w*, 1162*m*, 1042*m*, 1032*m*, 1007*m*, 786*m*, 764*s*, 757*s*, 750*m*, 733*m*, 698*s*, 649*m*, 638*s*. ^{1}H-NMR (250 MHz): 0.74 (*s*, 2 Me); 4.69 (*s*, 2 OH); 6.86–6.91 (*m*, 4 arom. H); 7.11 (*dd*, $J = 8.2$, 7.2, 2 arom. H); 7.16–

7.31 (*m*, 20 arom. H). ^{13}C-NMR (62.9 MHz): 18.4; 84.3; 126.2; 126.8; 127.3; 127.6; 127.7; 128.0; 128.7; 128.8; 129.4; 138.2; 138.3; 143.3; 143.7; 148.9. EI-MS: 528 (41, $[M - H_2O]^+$), 451 (100), 435 (57), 374 (47), 346 (29), 331 (48), 105 (36). Anal. calc. for $C_{40}H_{34}O_2$ (546.71): C 87.88, H 6.27; found: C 87.93, H 6.44.

In situ *Preparation of Bis(acetonitrile)dichloro[(1*S*,3*R*)-2,2,3-trimethyl-α,α-diphenylcyclopentane-1,3-dimethanolato(2−)-*κ*O,*κ*O′]titanium* (**10**) *from Diol* **9**. To a soln. of **9** (330 mg, 1.02 mmol) in MeCN (20 ml; dist. from P_2O_5), 3-Å molecular sieves (*pulvis*; 250 mg) and 1M $[TiCl_2(O^iPr)_2]$ in MeCN (0.98 ml, 0.98 mmol) were added. The suspension was stirred overnight, heated to 70°, and slowly evaporated under h.v. (1 h), followed by drying for 5 h under h.v. A sample of the solid was dissolved in dry $CDCl_3$ (in the glove box) and analyzed spectroscopically. ^{1}H-NMR: 0.47 (*s*, 1 Me); 0.71 (*s*, 1 Me); 0.95 (*s*, 1 Me); 1.44–1.62 (*m*, 2 H, CH_2); 1.68–1.85 (*m*, 2 H, CH_2); 2.03 (*s*, 3 H, >1 MeCN–Ti); 2.92 (*d*, *J* = 6.3, 1 H); 3.37 (*d*, *J* = 10.9, 1 H, CH_2OTi); 3.92 (*dd*, *J* = 11.0, 1.2, 1 H, CH_2OTi); 7.00–7.13 (*m*, 2 arom. H); 7.15–7.29 (*m*, 3 arom. H); 7.34 (br. *s*, 2 arom. H); 7.38 (br. *s*, 2 arom. H); 7.62 (br. *s*, 2 arom. H); due to slow relaxation, the integral for coordinated MeCN protons may be low.

In-situ *Preparation of Ti-Complex from Diol* **13a**, *and Crystallization of (Acetonitrile)dichloro{α-[(1*S*,3*R*)-3-(oxylato-*κ*O)-2,2,3-trimethylcyclopentyl]-α-phenylbenzenemethanolato(2−)-*κ*O}(tetrahydrofuran)titanium-Acetonitrile* ([$TiCl_2$ (**13a**-ato)(THF)(MeCN)]·MeCN; **14**). To a soln. of **13a** (101 mg, 0.325 mmol) in MeCN (5 ml), 1M $[TiCl_2(O^iPr)_2]$ in MeCN (0.31 ml, 0.31 mmol) was added dropwise. After stirring the faint beige soln. for 30 h at r.t., it was evaporated and the remaining foam dried 3 h under h.v. The material was dissolved in THF (5 ml) and the resulting soln. evaporated and dried under h.v. overnight. When the glassy solid was treated with MeCN (5 ml), it dissolved to immediately crystallize in large pieces that only slowly dissolved in the total volume of MeCN. On cooling to −20°, colorless crystals formed reproducibly from the soln. One of the crystals was used for an X-ray structure analysis.

In situ *Preparation of Dichloro{(*M*)-6,6′-dimethyl-α,α,α′,α′-tetraphenyl[1,1′-biphenyl]-2,2′-dimethanolato(2−)-*κ*O,*κ*O′]titanium* (**17**) *from Diol* **15**. To **15** (273 mg, 0.50 mmol) in THF (10 ml), 2,6-di(*tert*-butyl)pyridine (23 µl) and 1M $[TiCl_2(O^iPr)_2]$ in MeCN (0.48 ml, 0.48 mmol) was added and the soln. stirred 15 h at r.t.

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