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FLP behaviour of cationic titanium complexes with tridentate Cp, O, N-ligands: highly efficient syntheses and activation reactions of C-X bonds (X = Cl, F)⁺

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The synthesis of cationic titanium complexes **4a**,**b** with tridentate Cp,O,N-ligand frameworks, starting from the monopentafulvene complex $Cp^{*}Ti(Cl)(\pi-\eta^{5}:\sigma-\eta^{1}-C_{5}H_{4}CR_{2}$ (CR_{2} = adamantylidene) (**1**) and bidentate O,N-ligand precursors $CH_{3}C(O)CH_{2}CH_{2}NR_{2}$ (R = Et, $CH_{2}Ph$) (**L1a**,**b**), in a high-yielding and efficient twostep synthetic pathway is described. The β -aminoketones **L1a**,**b** were synthesized by a herein reported solvent- and catalyst-free reaction. The reaction pathway involves insertion reactions, subsequent methylations and final activations with $B(C_{6}F_{5})_{3}$. NMR investigations of the cationic titanium complex **4a** in deuterated dichloromethane revealed an ongoing selective reaction under formation of the cationic complex **5a**- d_{2} , which is the result of C–Cl bond cleavage. In addition to selective C–Cl bond activation reactions, $C(sp^{3})$ –F bonds were activated by **4a**,**b**, pointing out the special tm-FLP nature of **4a**,**b**.

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Introduction

The rapidly expanding chemistry of frustrated Lewis pairs (FLPs) has flourished into one of the main topics in the interdisciplinary field of inorganic and organic chemistry since the pioneering first description of this concept by Stephan and coworkers¹ several years ago.² Initial reports were based on Lewis acids and bases derived from main-group elements, in which the classic adduct formation is prevented either by steric or electronic properties. Thus, unique reactivity patterns and manifold stoichiometric and catalytic transformations were unveiled, relying heavily on Lewis acid and Lewis base cooperation in a spatially confined reaction compartment.³ As a consequence, manipulating the Lewis acidity or basicity of the components can be crucial for further reactivity.

Whereas main-group FLPs are usually focused on polyfluorinated arylboranes as the Lewis acid component, which limits the possibilities of tuning the Lewis acidity, a recent expansion was the development of transition metal based FLPs (tm-FLPs) where the electrophilic metal centres constitute the Lewis acidic component.⁴ This concept offers the advantage of versatile tuning potentials of the Lewis acidity because of the nearly endless scope represented by ligand design prospects, which has already allowed the combination of FLP-based small-molecule activation with the cornerstones of transition-metal based homogeneous catalysis.^{1–4} As recent outstanding examples with respect to tm-FLP chemistry, the activation of dinitrogen by late transition metal dinitrogen complexes with $B(C_6F_5)_3$ is especially worthy to note.⁵

Many examples of tm-FLPs with Zr,^{6–20} Hf,^{14,19,21} Ru,^{22,23} and rare-earth metals^{24–29} as central metal atoms have found their entry into the literature, whereas only a handful of titanium-based tm-FLPs **I–IV**, which show only limited reactivity (**I–III**), are reported (summarized in Scheme 1).^{30–33}

The scarceness of titanium-based FLPs is kind of ironic considering the early intramolecular example reported by Stephan *et al.* (Scheme 1, I).³⁰

In this context, it is highly desirable to focus on efficient syntheses of titanium-based FLPs, because titanium being the second most earth-abundant transition metal, of cost and environmental reasons, especially when compared to the chemistry of late transition metals like ruthenium or rareearth metals like scandium.^{34–36} Additionally, titanium is easy to recycle, considered to be nontoxic and environmentally benign.^{34–36}

We have put recent effort into the development of efficient and convenient syntheses of such systems by employing readily accessible monopentafulvene titanium complexes and appropriate bidentate ligand precursors (prepared in one step starting





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Scheme 1 Overview of titanium-based FLPs I–IV and motivation.^{30–33}

from commercially available starting materials) to give the corresponding cationic compounds in optimized two-step syntheses. It could be shown that complexes like IV show remarkable subsequent reactions in a tm-FLP fashion (Scheme 1).33,37,38 The fact, that the subsequent reactions take place at the Ti-N bond, emerged the question of introducing a nitrogen functionality at the hemilabile donor position (Scheme 1, bottom). This general concept includes the characteristics of hemilabile O,N-ligands, in which the unoccupied coordination site can become available for further reactions by dissociation of a donor atom to create an open coordination site for further reactions.⁶¹ The highly functionalized tridentate Cp, E, P-ligand frameworks (E = O, N) are built directly in the coordination sphere of the central metal atom, which underlines the efficient approach. This is in stark contrast to typical syntheses of tridentate ligand systems, which require multiple purification steps for the formation of comparable densely functionalized ligands.

With this in mind we investigated the reactivity of suitable bidentate O,N-ligand precursors, accessible by a herein reported solvent- and catalyst-free addition of various secondary amines to methyl vinyl ketone, their successful application in the two-step synthesis of cationic group 4 metal complexes with novel tridentate Cp,O,N-ligands, starting from a monopentafulvene titanium complex, and the subsequent tm-FLP chemistry of these compounds.

Results and discussion

Preparation of the β -amino ketones L1a,b

In order to start our investigations, an efficient synthesis of β -amino ketones as potential suitable ligand precursors was

targeted for the subsequent synthetic protocol in analogy to the β -keto phosphines, which were established as ligand precursors previously.³⁸

 β -Amino ketones can be prepared *via* the Mannich reaction through a carbon-carbon bond formation, starting from enolates and imines. However, this reaction requires equimolar amounts of base for the preparation of enolates, and often harsh reaction conditions accompanied by long reaction times.³⁹ The Aza-Michael reaction offers another way to prepare β-amino ketones through conjugated addition of amines to α , β -unsaturated carbonyl compounds, having the advantage of being much more atom economic than the Mannich reaction. Despite this benefit, Michael reactions in general require basic reaction conditions,^{40,41} the use of either stoichiometric or catalytic amounts of Lewis acids (e.g. Bi $(NO_3)_3$,⁴² CeCl₃·7H₂O,⁴³ SmI₂(THF)₂⁴⁴), and often (toxic) organic solvents, so that subsequent purification steps are indispensable. Another approach known from the literature suggests the use of micellar solutions.⁴⁵

Inspired by the preparation of the aforementioned β -keto phosphines by a solvent- and catalyst-free hydrophosphanation of methyl vinyl ketone⁴⁶ the β -amino ketones **L1a,b** were prepared by simple addition of the corresponding alkyl substituted secondary amines to methyl vinyl ketone (Scheme 2).

The diethyl substituted derivative **L1a** is obtained in nearly quantitative yield and on a multigram scale, and the exothermic reaction is complete after five minutes as shown by ¹H NMR measurements. The dibenzyl substituted ligand precursor **L1b** is obtained after 36 h of stirring at room temperature and removal of a small excess of the starting material as a colourless solid in 96% isolated yield (crystals suitable for single crystal X-ray diffraction of **L1b** where obtained from a saturated *n*-hexane solution of **L1b** at -26 °C; Fig. S11⁺⁴⁷). For the analytical data of **L1a,b** see the ESI.⁺⁴⁷

In effect, a highly desirable, solvent- and catalyst-free, and environmentally benign Aza-Michael reaction is possible by simple addition of secondary amines to methyl vinyl ketone.

Synthesis, characterization and reactivity of the complexes

The reactions of the monopentafulvene titanium complex $Cp^*Ti(Cl)(\pi-\eta^5:\sigma-\eta^1-C_5H_4=CR_2)$ **1**, featuring the sterically demanding adamantylidene substitution pattern at the exocyclic carbon atom (C_{exo}), with the bidentate *O*,*N*-ligand precursors **L1a,b** in *n*-hexane at room temperature were accompanied by colour changes of the reaction mixtures from yellow-brown to yellow-orange. Removal of all volatiles under reduced press-



Scheme 2 Solvent-and catalyst-free synthesis of the β -amino ketones L1a,b.

ures yield the products **2a,b** with Cp, $O \sigma$ - π -chelating ligands, as the result of the insertion of the carbonyl functional groups of **L1a,b** into the polarized Ti– C_{exo} bond as yellow or orange solids in isolated yields of up to 88% (Scheme 3).

Complexes **2a,b** are moderately soluble in aliphatic hydrocarbons like *n*-hexane and show good solubilities in aromatic and polar solvents (*e.g.* toluene, benzene or tetrahydrofuran). They can be stored in the solid state for months under inert conditions without indication of decomposition. Subsequent reactions to yield the corresponding singly methylated complexes **3a,b** proceed *via* reactions of **2a,b** with methyllithium in tetrahydrofuran at room temperature. After purification **3a,b** were isolated as pale yellow or pale orange solids in good yields, showing the same solubility properties as **2a,b**. Furthermore, **3a,b** can also be prepared in a one-pot procedure starting from **1** with the advantage of one less purification and isolation step in consistently good yields of up to 74%.

Complexes **2a,b** and **3a,b** were thoroughly characterized by NMR spectroscopy and single-crystal X-ray diffraction.

Due to strong similarities of the most important and characteristic structural parameters of the crystallized complexes, the X-ray data are exemplary discussed for complexes **2b** and **3b** and summarized for all in Table 1 (ORTEP presentations of **2a** and **3a** are presented in the ESI (S13,14)).⁺⁴⁷ The single crystals were obtained from saturated solutions in *n*-hexane or toluene at temperatures of $-4 \, ^{\circ}$ C or $-26 \, ^{\circ}$ C.

2b crystallizes in the triclinic space group $P\bar{1}$ and complex **3b** crystallizes in the monoclinic space group $P2_1/c$. The molecular structures of **2b** and **3b** (Fig. 1 and 2) display distorted tetrahedral coordination environments at the titanium atoms (*e.g.* Cl1-Ti1-O1 97.643(15)°, Ct1-Ti1-Ct2 134.0° for **2b**).

The Ti1–Cl1 bond length of 2.39082(19) Å in **2b** and the Ti1–C44 bond length of 2.185(3) Å in **3b** are typical of single bonds and lie in the same range as in related complexes with Cp, $O \sigma$ - π -chelating ligands.^{37,38,48–50} The newly formed bonds Ti1–O1 (1.8522(4) Å (**2b**), 1.8527(16) Å (**3b**)) and C16–C26 (1.6386(8) Å (**2b**), 1.635(3) Å (**3b**)) confirm the successful insertion reaction and are characteristic for complexes derived from insertion reactions of monopentafulvene complexes with multiple bond substrates.^{33,37,38} The Ti1–O1 bond lengths, which are slightly shortened compared to Ti–O single bonds, are

Table 1 Comparison of selected bond lengths (Å) of 2a,b and 3a,b

-					
	Ti-O	O–Cq	Cq,exo-Cq,ipso	C _{q,exo} –OC _q	
2a 2b 3a 3b	1.8713(8) 1.8522(4) 1.8654(7) 1.8527(16)	$\begin{array}{c} 1.4326(13)\\ 1.4298(7)\\ 1.4272(11)\\ 1.432(3) \end{array}$	1.5235(15) 1.5226(7) 1.5234(13) 1.530(3)	$\begin{array}{c} 1.6250(15)\\ 1.6386(8)\\ 1.6312(13)\\ 1.635(3)\end{array}$	



Fig. 1 Molecular structure of **2b** in the crystal. Thermal ellipsoids are drawn at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti1–Cl1 2.39082 (19), Ti1–O1 1.8522(4), O1–C26 1.4298(7), N1–C28 1.4775(7), Cl1–Cl6 1.5226(7), Cl6–C26 1.6386(8), C26–C27 1.5388(8), C26–C29 1.5311(8), C27–C28 1.5278(8), Cl1–Ti1–O1 97.643(15), Ct1–Ti1–Ct2 134.0, $\Sigma \angle$ C26 322.5 (O1–C26–C27 + O1–C26–C29 + C27–C26–C29), $\Sigma \angle$ N1 333.9 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

indicative for attractive $Ti(d_{\pi})$ -O(p_{π}) interactions.^{49,50} The strong ring strains, resulting from the formation of the *Cp*,*O* σ - π -chelating ligands cause exceptional elongations of the newly formed C16–C26 bonds between the former carbonyl carbon atom and the C_{exo} atom when compared to typical C(sp³)–C (sp³) single bonds,⁵¹ but are in the same range as reported for highly sterically crowded alkanes.⁵² Despite these significant elongations, the former carbonyl carbon atoms are sp³-hybridized as shown by the sum of angles around C26 in both cases



Scheme 3 Three-/two-step synthesis of cationic titanium complexes 4a,b.



Fig. 2 Molecular structure of **3b** in the crystal. Thermal ellipsoids are drawn at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti1-C44 2.185 (3), Ti1-O1 1.8527(16), O1-C26 1.432(3), N1-C28 1.472(3), C11-C16 1.530(3), C16-C26 1.635(3), C26-C27 1.547(4), C26-C29 1.536(3), C27-C28 1.530(3), C44-Ti1-O1 98.60(9), Ct1-Ti1-Ct2 136.0, \sum ∠C26 320.7 (O1-C26-C27 + O1-C26-C29 + C27-C26-C29), \sum ∠N1 330.1 (Ct1 = centroid of C1-C5; Ct2 = centroid of C11-C15).

(322.5° (**2b**), 320.7° (**3b**). The transition from the pentafulvene ligand in **1** to substituted cyclopentadienyl ligands in **2b** and **3b** is confirmed by the C11–C16 bond lengths, which are now typical of $C(sp^3)$ – $C(sp^2)$ single bonds with 1.5226(7) Å (**2b**) and 1.530(3) Å (**3b**) respectively.⁵¹

The solution NMR data of **2a,b** and **3a,b** are in accordance with their solid-state structures. Due to the prochirality of the bidentate *O*,*N*-ligand precursors **L1a,b**, a double set of signals is observed (**2b** is the exception) for these complexes, exhibiting two stereogenic centres at the titanium atoms and the former carbonyl carbon atoms. The ratios of the diasteroisomers were determined by integration of appropriate signals in the ¹H NMR spectra and lie between 4 : 1 and 10 : 1. Similar ratios of the diastereoisomers were reported for complexes with the *Cp*,*O*,*P*-ligand frameworks.^{37,38} The NMR data are discussed for the obtained diastereomerically pure derivative **2b**.

In the high field region of the 1H NMR spectrum the methyl group (δ^1 H = 1.29 ppm/ δ^{13} C{1H} = 31.2 ppm) located at the quaternary carbon atom of the former carbonyl group, together with the signals of the linking methylene groups between the oxygen and nitrogen atoms, and the signals of the adamantyl substituent are observed together with the signal of the methyl groups of the Cp* ligand (δ^1 H = 1.76 ppm/ δ^{13} C{¹H} = 12.6 ppm).

Of high diagnostic value are the signals of the methylene groups of the benzyl substituents, which show two doublet signals at $\delta^{1}H = 3.63$ and 3.98 ppm ($\delta^{13}C{^{1}H} = 60.1$ ppm) due to the diastereotopicity with characteristic coupling constants of ${}^{2}J_{H,H} = 14$ Hz each. The signals are shifted toward lower

field compared to the corresponding ligand precursor L1b $(\delta^{1}H = 3.36 \text{ (s, 4H) } ppm/\delta^{13}C\{^{1}H\} = 58.5 ppm)$. The ${}^{13}C\{^{1}H\}$ NMR chemical shifts of the quaternary C_{exo} ($\delta^{13}C$ {¹H} = 54.8 ppm) and C_{ipso} ($\delta^{13}C_{1}^{1}H_{1}^{1} = 156.9$ ppm) atoms of the former pentafulvene ligand are in the same range as for related complexes reported previously,^{37,38} and show significantly different chemical shifts compared to the starting material 1 ($\delta^{13}C_1^{(1)}H$) = 130.1 ($C_{q,exo}$) and 131.3 ($C_{q,ipso}$) ppm).⁵³ The four ¹H NMR signals for the C₅H₄ moiety range from 5.02 to 6.44 ppm. The signal of the terminal methyl group of the corresponding methylated complex 3b is observed at $\delta^{1}H =$ 0.10 ppm (δ^{13} C{¹H} = 34.8 ppm), which is in the same range as reported for other terminal methylated titanium complexes.^{33,38,54} The ¹⁵N NMR chemical shift at δ^{15} N = 48.4 ppm is only marginally different to L1b, clearly confirming identical chemical environments at the nitrogen atoms.

As mentioned above, complex $2\mathbf{b}$ was obtained diastereomerically pure and its X-ray structure reveals, that the titanium atom and the former carbonyl carbon atom are (*R*,*R*) and (*S*,*S*) configured.

The prepared methylated complexes **3a,b** were reacted with the highly Lewis acidic borane $B(C_6F_5)_3$ in toluene at room temperature and led to the isolation of the activated cationic complexes **4a,b** in isolated yields of up to 80% after purification as pale orange solids (Scheme 3).

The complexes are insoluble in aliphatic hydrocarbons such as *n*-hexane, which proves to be ideal for purification purposes. In aromatic solvents such as benzene or toluene only a marginal solubility is observed, which, during the reactions of **3a,b** with $B(C_6F_5)_3$, is reflected by the separation of two phases as soon as the stirring process is stopped. The previously reported complexes (*e.g.* derivatives of **IV**, Scheme 1) show good solubilites in dichloromethane and were stable without any indication of decomposition in dichloromethane solutions.^{33,37,38} Therefore CD_2Cl_2 was also chosen as solvent for multinuclear NMR spectroscopy of the current complexes.

Surprisingly, the ¹H NMR spectrum of the cationic complex **4a** shows initially a double set of signals, for which the relative ratios of the integrals change after one hour, indicating either an ongoing rearrangement or a subsequent reaction. After one day, only one set of signals remains. 2D- and 1D NMR spectroscopy reveals, that a subsequent clean reaction between CD_2Cl_2 and the cationic complex **4a** took place to yield the activation product **5a**-*d*₂ (summarized in Fig. 3).

In consequence of this unexpected reaction with CD_2Cl_2 , we attempted to obtain NMR data of **4a** in THF- d_8 and C_6D_5Br as the solvents, which also proved to be inadequate because of poor solubility of **4a**. However, **4a**,**b** are characterized by elemental analysis and the clean detection of the M⁺ signals with high-resolution ESI mass spectrometry. We started to prepare **4a**,**b** *in situ* for investigations of their further reactivity.

The reaction of *in situ* synthesized **4a** with non-deuterated dichloromethane was repeated and the corresponding activation product **5a** was obtained rapidly (reaction took less than five minutes, as indicated by a colour change to clear orange)



Fig. 3 Excerpt of the ¹H NMR spectrum of the reaction of 4a with CD_2Cl_2 (bottom: 300 MHz, CD_2Cl_2 , rt; middle, top: 500 MHz, CD_2Cl_2 , rt).

in 71% isolated yield as an analytically pure pale yellow solid, which shows similar solubility properties as **4a**.

Complex 5a is the result of addition of a chloride, abstracted from CH_2Cl_2 , to the titanium centre and addition of the remaining CH_2Cl moiety to the nitrogen, which then forms an ammonium functional group. The same reaction took place starting from **4b** to give the corresponding complex **5b** (Scheme 4).

5a,b are fully characterized by NMR measurements, ESI mass spectrometry (clean detection of the M⁺ signal), and for **5b**, single crystal X-ray diffraction, for which crystals were obtained by slow diffusion of *n*-hexane into a bromobenzene solution of **5b**. The molecular structure is shown in Fig. 4.

5b crystallizes in the triclinic space group $P\bar{1}$. The central titanium atom is in a distorted tetrahedral coordination environment (Cl1–Ti1–O1 96.10(3), Ct1–Ti1–Ct2 133.3). The newly formed Ti1–Cl1 bond length of 2.3856(4) Å and the Ti1–O1 bond length of 1.8749(8) Å are typical of single bonds and remain nearly unchanged compared to those of **2b** and **3b**.^{49,50} The second newly formed bond N1–C44 (1.5176(17) Å) is characteristic of a N–C(sp³) single bond and clearly confirms

4a: R = Et $4b: R = CH_Ph$ $5b: R = CH_Ph$

Scheme 4 Reactions of 4a,b with dichloromethane.



Fig. 4 Molecular structure of **5b** in the crystal. Thermal ellipsoids are drawn at the 50% probability level (hydrogen atoms except H44A, H44B and co-crystallized solvent have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti1–Cl1 2.3856(4), Ti1–O1 1.8749(8), O1–C26 1.4233(13), N1–C28 1.5332(16), N1–C44 1.5176(17), Cl2–C44 1.7644 (13), B1–C63 1.6333(19), C11–C16 1.5271(16), C16–C26 1.6277(16), C26–C27 1.5543(16), C26–C29 1.5350(16), C27–C28 1.5256(17), Cl1–Ti1–O1 96.10(3), Ct1–Ti1–Ct2 133.3, ∑∠C26 321.8 (O1–C26–C27 + O1–C26–C29 + C27–C26–C29), ∑∠N1 329.1 (C28–N1–C30 + C28–N1–C37 + C30–N1–C37) (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

the ammonium moiety.⁵¹ Due to the formation of the ammonium moiety, the N–C bond lengths are generally elongated compared to their non-cationic precursor complexes (*e.g.* N1–C28: 1.5332 (16) Å (**5b**), 1.4775(7) Å (2**b**), 1.472(3) Å (**3b**)). The molecular structure of **5b** proves, that the borate anion is noncoordinating. Additionally, the central metal atom and the C26 carbon atom both show *S*, or by applying crystal symmetry, *R* configuration, so that consequently **5b** is obtained diastereomerically pure as the (*S*,*S*) and (*R*,*R*) pair of enantiomers, which is confirmed by the single set of signals in the NMR spectra.

The signal of the methyl group (δ^{1} H = 0.49 ppm) located at the boron atom is characteristically broadened. This is caused by the high magnetic quadrupole moment of the boron atom, so that the corresponding chemical shift of the corresponding carbon atom had to be assigned by the ¹H/¹³C-HMQC spectrum. The ¹¹B{¹H} (δ^{11} B{¹H} = -14.9 ppm) and ¹⁹F{¹H} NMR chemical shifts (δ^{19} F{¹H} = -167.8 (*m*-F_{Ar}B), -165.2 (*p*-F_{Ar}B), -133.1 (*o*-F_{Ar}B) ppm; $\Delta\delta(m,p$ -F) = 2.6 ppm) are in accordance to other cationic complexes with this specific anion. Here, the $\Delta\delta(m,p$ -F) value is a good probe for the evaluation, whether the MeB(C₆F₅)₃⁻ anion is coordinating or not.^{13,19,33,37,38,55} As reported in the literature, the $\Delta\delta(m,p$ -F) value of 2.6 ppm (**5b**)

Table 2 Selected NMR parameters of complexes 2b, 3b, and 5b^a

	2 b	$3\mathbf{b}^b$	5 b
$\delta^{1}H/\delta^{13}C^{1}H$ ECH ₃	_	$0.10/34.8^{c}$	$0.49/10.0^d$
$\delta^{13}C{^1H}C_{\alpha ero}/C_{\alpha inso}$	54.8/156.9	55.0/151.5	55.3/156.8
$\delta^{1}H/\delta^{13}C{}^{1}H$ NCH ₂ Ph	3.63/3.69//60.1	3.57/3.69//60.2	4.49/4.55/5.00//63.2/64.0
2/нн	${}^{2}J_{\rm H \ H} = 13.9/14.0$	${}^{2}J_{\rm HH} = 13.9/14.0$	${}^{2}I_{\rm HH} = 13.4$
$\delta 1 H / \delta^{13} C \{ 1 H \} N C H_2 C l$			$\frac{4.81}{4.90}$
$\delta^{13}C{^1H} OC_a$	112.1	107.6	109.6
$\delta^1 H C_5 H_4$	5.03, 5.44 (2H), 6.44	4.85, 5.13, 5.28, 6.19	5.37, 5.45, 5.98, 6.39

^{*a*} Values are given in ppm and *J* values in Hz. Measurements were carried out in C_6D_6 (**2b**, **3b**) or CD_2Cl_2 (**5b**) at room temperature. ^{*b*} Product is obtained as a mixture of diastereoisomers; therefore signals of the main diastereoisomer are given. ^{*c*} E = Ti. ^{*d*} E = B.

is characteristic for the borate anion being noncoordinating in solution, which is also represented by its structure in the solid state.^{56,57,62} The other NMR data of **5b** are in the expected ranges and summarized together with those of **2b** and **3b** in Table 2 (for the data of the congener **5a** see the $\text{ESI}^{\ddagger 47}$).

Similar reactions with dichloromethane have been reported,^{6,9,30} for example for the intermolecular Ti⁺/P system reported by Stephan and coworkers (Scheme 1, I),³⁰ but in the light of to the entirety of FLP systems, those examples remain rare. Especially, until now, no main group based FLPs were capable of cleaving carbon–halogen bonds.⁶ On top of that, analogous titanium complexes with *Cp*,*O*,*P*- or *Cp*,*N*,*P*-ligands were completely inert toward dichloromethane, emphasizing the unique features of the *Cp*,*O*,*N*-ligand framework.^{33,37,38}

With this in mind, we further explored the reactivity toward other carbon–halogen substrates (Scheme 5).

The reaction of **4a** with benzyl chloride followed the same reactivity pattern, yielding complex **6** in 74% isolated yield as a pale yellow solid, which has been thoroughly characterized.⁴⁷ Even when alkyl fluorides are reacted with **4a** or **4b** under mild reaction conditions, an analogous reaction pathway is observed. Thus, treatment of **4a** and **4b** with stoichiometric amounts of 1-fluorodecane resulted in clean conversion to **7a** (70%) and **7b** (81%), respectively. They were also characterized by detection of the M⁺ signals by ESI mass spectrometry, and



Scheme 5 Enhanced reactivity studies of 4a,b.

multinuclear NMR spectroscopy.47 Complexes, which are capable of activating (inactivated) aliphatic C(sp³)-F bonds are scarce,^{6,9,58} so that the herein presented complexes might allow possible applications in defluorination or hydrodefluorination reactions.^{59,60} Above that, **4a,b** are the first titaniumbased cationic complexes, showing this reactivity. In addition, the chemistry concerning C-F bond activations by strong Lewis acids has been most successful in breaking (activated) C(sp²)-F bonds, employing late transition metals.⁶³ In the last years significant improvements have been reported in the field of activating (inactivated) C(sp³)-F bonds by e.g. strong main group Lewis acids.^{64a,b} Noteworthy, no C(sp²)-halogen cleavage reactions with any substituted substrates like chloro- or bromobenzene were observed, even when 4a and 4b were dissolved in excess of these substrates. These observations are in good agreement to previous reports.6,9

As demonstrated, the pendant amine functionalities, in contrast to the previously reported phosphorus containing counterparts,^{37,38} enable subsequent carbon-halogen bond activation reactions. This can be attributed to the higher basicity of the amine functionalities in 4a,b compared to the phosphine moieties, which, together with the Lewis acidic titanium centres, are capable of cooperatively activating these substrates at the Ti…N bond. In addition, a persistent covalent Ti-P bond is present in the previously reported complexes,^{37,38} which hampers subsequent reactions. This is further supported by the two other tm-FLP systems $(Zr^+/P, ^6 Zr^+/N^9)$ capable of activating carbon-halogen bonds, in which no or only a weak contact between the Lewis acidic metal centres and the Lewis basic functionalities are required for subsequent activation reactions. Thus, a higher grade of frustration between the amine functionalities and the titanium centres in 4a,b is an additional reason for the observed enhanced reactivity.

Conclusions

In summary, we report a novel solvent- and catalyst-free access to the β -aminoketones **L1a,b**, starting from methyl vinyl ketone and various secondary amines. The β -aminoketones **L1a,b** were successfully employed as ligand precursors in reactions with the titanium monopentafulvene complex **1** (Cp*Ti (Cl)(π - η^5 : σ - η^1 -C₅H₄CR₂: CR₂ = adamantylidene), and subsequent adoption in the previously established and optimized two-step synthetic pathway to yield the corresponding cationic complexes 4a,b. The two-step synthetic pathway involves insertion of the carbonyl functional group of L1a,b into the polarized Ti-Cexo bond, methylation, and final activation with the strong Lewis acid $B(C_6F_5)_3$ (insertion and methylation can be done in a one-pot procedure). The cationic complexes 4a,b feature the first tridentate Cp,O,N-ligand system, which is directly synthesized in the coordination sphere of the metal. This in an expansion of the series of tridentate ligands of the previously reported Cp,O,P- and Cp,N,P-congeners. The nitrogen, now localized at the hemilabile donor position, provides the ability of activating carbon-halogen bonds, whereas the Cp,O,P- and Cp,N,P-derivatives are completely inert toward dichloromethane, the cationic complexes 4a,b react cleanly and readily with dichloromethane to give the corresponding complexes 5a,b via C-Cl bond cleavage, addition of chloride to the titanium centres, and formation of ammonium functional groups by formal addition of CH_2Cl^+ to the nitrogen atoms. Furthermore, 4a,b selectively activate the $C(sp^3)$ -F bond of *n*-fluorodecane at room temperature under formation of 7a,b with Ti-F and ammonium functional groups, being the first titanium-based cationic complexes showing this reactivity. With the herein presented study, the special tm-FLP nature of 4a,b is demonstrated.

Conflicts of interest

There are no conflicts of interest to declare.

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