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Preparation of Ti(IV) Fluoride *N*-Heterocyclic Carbene Complexes

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1,3,4,5-Tetramethylimidazol-2-ylidene (L^{Me}) and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (L^{iPr}) readily form complexes of *trans*-$TiF_4(L^{Me})_2$ (**1**) and of *trans*-$TiF_4(L^{iPr})_2$ (**4**) with TiF_4 in THF, respectively. Complex **1** has been used as a precursor for preparing the Ti(IV) fluoride carbene complexes $[\{TiF_2(L^{Me})(NEt_2)\}_2(\mu\text{-}F)_2]$ (**2**) and $(TiF_4(L^{Me})_2)(NacNacLi)$ (**3**) (NacNac = $HC(CMeN(2,6\text{-}iPr_2C_6H_3))_2$). Complex **2** was prepared from the reaction of 1−3 equiv of **1** and 1 equiv of $Ti(NEt_2)_4$ or by reacting TiF_4 with $Ti(NEt_2)_4$ and L^{Me} in toluene. Complex **3** has been prepared from **1** and NacNacLi in toluene. Reaction of **1** and $AlMe_3$ in toluene results in ligand transfer and formation of $AlMe_3(L^{Me})$. Complex **4** is unstable in solution at room temperature and degrades with formation of $[HL^{iPr}][TiF_5(L^{iPr})]$ (**5**). Complexes **1**, **2**·$2CH_2Cl_2$, **4**, and **5** were characterized by single crystal X-ray structural analysis, elemental analysis, IR and NMR spectroscopy, and mass spectrometry. The relative basicities of L^{Me}, L^{iPr}, and the donor ligands THF, pyridine, DMSO, and H_2O as well as $[Cl]^-$ and $[F]^-$ toward the Ti(IV) pentafluoride anion were established by NMR and confirmed by density functional theory (DFT) calculations. L^{Me} and L^{iPr} are more basic than the mentioned molecular donors and more basic than chloride, however less basic than fluoride.

Introduction

N-Heterocyclic carbene transition metal complexes have been prepared for nearly all transition metals[1] and found broad application in organic synthesis.[2] These complexes are supported by a wide range of ligands. However, the fluoride complexes containing *N*-heterocyclic carbene are less studied. The fluoride complexes supported by the *N*-heterocyclic carbene ligands were reported only for Au,[3] Ru,[4] boron, and group 15 elements (P, As, and Sb).[5] In the case of BF_3 and group 15 fluorides, only chlorinated imidazol-2-ylidenes are stable in combination with fluorides and a noncommon 1,3-bis(trifluoromethyl)benzene was used as a suitable reaction medium.[5]

Generally, the use of metal fluoride complexes as initiators in catalysis not only provides access to novel active species that result in higher selectivities but also provides an approach to novel catalytic cycles e.g. enantioselective

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Scheme 1. Preparation and Reactivity of **1**, Ar = 2,6-iPr$_2$C$_6$H$_3$

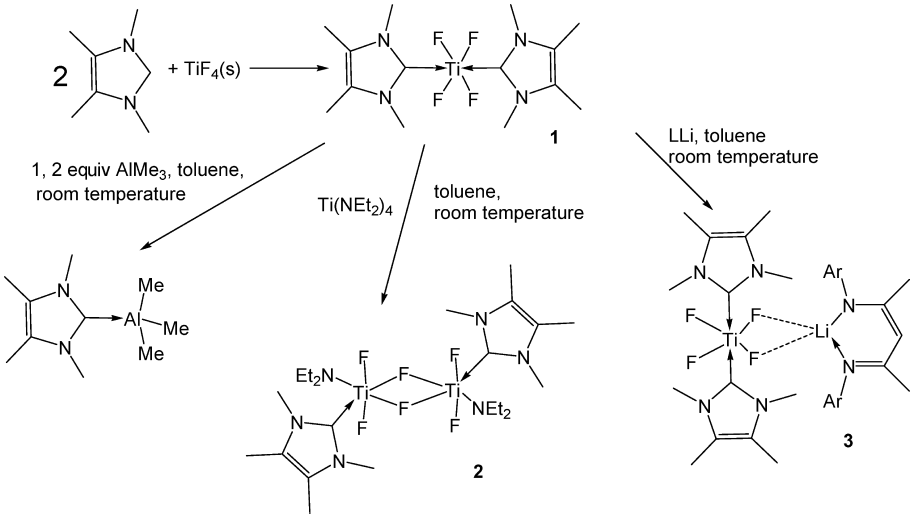

Table 1. Species Recorded in Solutions of **1** and **4** in Different Solvents by Means of ^{1}H and ^{19}F NMR and Species in Solution of **1** or **4** with 2 equiv Pyridine, Dimethylsulfoxide, and Water, Respectively, Recorded by ^{1}H and ^{19}F NMR

complex/reaction	solvent	detected species in solution (^{19}F and ^{1}H NMR)
trans-TiF$_4$(L^{Me})$_2$ (**1**)	C_6D_6	*trans*-TiF$_4$(L^{Me})$_2$
1	CD_3CN	*trans*-TiF$_4$(L^{Me})$_2$, [TiF$_5$(L^{Me})]$^-$, [TiF$_6$]$^{2-}$,[b] [H(L^{Me})]$^+$ [a]
1	$CDCl_3$	*trans*-TiF$_4$(L^{Me})$_2$, *cis*-TiF$_4$(L^{Me})$_2$, [TiF$_3$(L^{Me})$_3$]$^+$, [TiF$_5$(L^{Me})]$^-$ [c]
1 + 2 equiv pyridine	C_6D_6	*trans*-TiF$_4$(L^{Me})$_2$, pyridine[e]
1 + 2 equiv DMSO	C_6D_6	*trans*-TiF$_4$(L^{Me})$_2$, DMSO
1 + 2 equiv H_2O	C_6D_6	*trans*-TiF$_4$(L^{Me})$_2$, [TiF$_6$]$^{2-}$, H_2O
trans-TiF$_4$(L^{iPr})$_2$ (**4**)	C_6D_6	*trans*-TiF$_4$(L^{iPr})$_2$, [TiF$_5$(L^{iPr})]$^-$, [H(L^{iPr})]$^+$
4	CD_3CN	*trans*-TiF$_4$(L^{iPr})$_2$, [TiF$_5$(L^{iPr})]$^-$, [TiF$_6$]$^{2-}$, [H(L^{iPr})]$^+$
4 + 2 equiv pyridine	C_6D_6	*trans*-TiF$_4$(L^{iPr})$_2$, [TiF$_5$(L^{iPr})]$^-$, [H(L^{iPr})]$^+$, pyridine
4 + 2 equiv DMSO	C_6D_6	*trans*-TiF$_4$(L^{iPr})$_2$, [TiF$_5$(L^{iPr})]$^-$, [TiF$_6$]$^{2-}$, [H(L^{iPr})]$^+$, DMSO[a]
4 + 2 equiv H_2O	C_6D_6	*trans*-TiF$_4$(L^{iPr})$_2$, [TiF$_6$]$^{2-}$, [H(L^{iPr})]$^+$ [d]
[H(L^{iPr})][TiF$_5$(L^{iPr})] (**5**)	CD_3CN	[TiF$_6$]$^{2-}$, [H(L^{iPr})]$^+$
TiF$_4$ + 2 equiv pyridine + 2 equiv DMSO	CD_3CN	*cis*-TiF$_4$(Py)$_2$, *cis*-TiF$_4$(Py)(DMSO),[f] *cis*-TiF$_4$(DMSO)$_2$

[a] Unassigned resonances are present in the NMR spectrum. [b] Assignment to [TiF$_6$]$^{2-}$ is based on ref 21. [c] Assignment of *cis*-TiF$_4$(L^{Me})$_2$, [TiF$_3$(L^{Me})$_3$]$^+$, and [TiF$_5$(L^{Me})]$^-$ see the Supporting Information. [d] All H_2O reacted, unidentified μ-F complex present in solution. [e] Assignment of pyridine, DMSO, and H_2O is done according to ref 22. [f] Chemical shift of *cis*-TiF$_4$(Py)$_2$, *cis*-TiF$_4$(Py)(DMSO)—see Table 3 and the Supporting Information, chemical shift of *cis*-TiF$_4$(DMSO)$_2$ ref 23.

Mukaiyama aldol addition reactions[6] and carbon allylation of alcohols, silyl ethers, and acetals.[7] Although the Ti(IV) fluoride complexes are active in olefin polymerization,[8] conversion of fluoroalkyl–alkyl ethers to carbonyl compounds,[9] the most beneficial was the application of Ti(IV) fluoride complexes in the asymmetric organic synthesis.[10] TiF$_4$ in donor solvents is catalyzing the reaction of 2-trimethylsilylmethyl-1,5-dienes with aldehydes,[10a] enantionselective addition of allylsilanes to aldehydes,[7a,11] enantioselective addition of Me$_3$Al to aldehydes,[12] and the tri- and difluoromethylation of aldehydes.[10b] The Ti(IV) fluoride complexes obtained from TiF$_4$ and the donor ligands, namely (*R*)-2,2′-binaphthol,[10c] (*S*)-2,2′-binaphthol,[10f] bis-oxazolines,[13] and (*R*)-2-amino-1,1,2-triphenylethanol [7b]were successfully used as catalysts in the asymmetric organic synthesis. All these reactions were employed to obtain biologically active compounds and (or) in the total synthesis of natural products potentially important for drug design. The corresponding chloride complexes are less active.[10a,b,d] Therefore the preparation and characterization of Ti(IV) fluoride carbene complexes using available and suitable precursors are an important target from the theoretical and practical point of view. Moreover, carbene ligands were used for the preparation of a range of catalysts for asymmetric synthesis.[2]

The early transition metal fluorides are known as polymeric solids,[14] insoluble in many organic solvents, and the

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**, **2**, **4**, and **5**[a]

1		**2**		**4**		**5**	
C(1)−Ti(1)	2.255(4)	Ti−F(3)	1.8357(6)	Ti−F(2)	1.8337(8)	Ti(1)−F(5)	1.835(2)
Ti(1)−F(2)	1.831(3)	Ti−F(2)	1.8361(6)	Ti−F(1)	1.8378(8)	Ti(1)−F(2)	1.841(2)
Ti(1)−F(1)	1.835(2)	Ti−N(3)	1.8938(8)	Ti−F(3)	1.8394(8)	Ti(1)−F(1)	1.844(2)
F(2)−Ti(1)−F(2_2)	180.00(1)	Ti−F(1)	1.9940(6)	Ti−F(4)	1.8409(7)	Ti(1)−F(3)	1.846(2)
F(2)−Ti(1)−F(1)	89.41(11)	Ti−F(1_2)	2.1066(6)	Ti−C(12)	2.2781(12)	Ti(1)−F(4)	1.863(2)
F(1)−Ti(1)−C(1)	89.28(12)	Ti−C(1)	2.2367(9)	Ti−C(1)	2.2812(12)	Ti(1)−C(1)	2.310(3)
		F(1)−Ti−F(1_2)	74.26(3)	F(2)−Ti−F(1)	89.47(4)	F(2)−Ti(1)−F(1)	91.02(11)
		F(1)−Ti−C(1)	158.08(3)	F(1)−Ti−F(3)	177.57(4)	F(5)−Ti(1)−F(1)	94.05(10)
		F(2)−Ti−F(1)	94.11(3)	F(2)−Ti−C(1)	91.39(4)	F(5)−Ti(1)−C(1)	178.24(13)
		F(3)−Ti−F(1)	88.37(3)	F(2)−Ti−F(3)	90.71(4)	F(1)−Ti(1)−C(1)	86.02(11)
		N(3)−Ti−F(1)	101.34(3)	C(12)−Ti−C(1)	176.67(4)		
		N(3)−Ti−C(1)	100.06(3)				

[a] Symmetry transformations used to generate equivalent atoms _2 of **1**: $-x, -y + 1, -z + 1$. Those used to generate equivalent atoms _2 of **2**: $-x + 1, -y + 1, -z + 1$.

corresponding monomeric fluorides are regarded as strong electrophiles,[15,17] which might cause metathesis of the organic ligand attached to the metal center.[16] For instance, TiF_4 has a Lewis acid strength close to that of PF_5.[17] Due to these phenomena, the transition metal fluorides are obtained by multistep procedures using mainly chloride complexes as precursors and various fluorinating agents, such as $CH_2{=}CHF$,[18] $Et_3N{\cdot}3HF$,[3,4] Me_3SnF,[19] and others[18] for metathesis reaction. In recent years, our work was focused on the synthesis and investigation of Ti(IV) fluoride complexes[18,20] and we are reporting here the preparation and properties of the Ti(IV) fluoride *N*-heterocyclic carbene complexes.

Results and Discussion, Synthesis, and Reactivity

The 1,3,4,5-tetramethylimidazol-2-ylidene reacts with TiF_4 in THF under formation of *trans*-$TiF_4(L^{Me})_2$ (**1**) in high yield (Scheme 1). Compound **1** is weakly soluble in benzene, toluene, and THF and could be recrystallized from CH_2Cl_2 as colorless needles. Complex **1** is well soluble in $CDCl_3$ and CD_3CN; however, the solutions contained a mixture of complexes (Table 1), which degraded within several hours at room temperature.

In order to probe the properties of *trans*-$TiF_4(L^{Me})_2$ (**1**) and to obtain tetra- and trifluoro complexes, which are supported by *N*-heterocyclic carbenes and are soluble in benzene and toluene, we explored the reactivity of **1** toward $AlMe_3$, $Ti(NEt_2)_4$, and LLi ($L = HC(CMeN(2,6\text{-}iPr_2C_6H_3))_2$, NacNac)) (Scheme 1). Transmetalation was observed by reaction of **1** with $AlMe_3$ and complex $AlMe_3(L^{Me})$ was identified as a reaction product by means of ^1H NMR.[24] Complex **1** (1–3 equiv) reacted with $Ti(NEt_2)_4$ under formation of $[\{TiF_2(L^{Me})(NEt_2)\}_2(\mu\text{-}F)_2]$ (**2**), which was isolated by crystallization from CH_2Cl_2 (Scheme 1). Alternatively, compound **2** was obtained in better yield by interaction of 3 equiv TiF_4, 1 equiv $Ti(NEt_2)_4$, and 4 equiv L^{Me} in toluene followed by crystallization from CH_2Cl_2. Compound LLi and **1** in toluene formed a 1:1 adduct $(TiF_4(L^{Me})_2)$(NacNacLi) (**3**). The composition of **3** was deduced from the NMR and elemental analysis data as well as from mass spectrometry. Compound **3** is weakly soluble in C_6D_6 (ca. 0.1 g in 50 mL); although better than **1**, its solubility is approximately 5 times lower. The upfield shift of the ^{19}F NMR resonance from 145.3 ppm (for **1**) to 134.8 ppm (for **3**) is attributed to the coordination of *trans*-$TiF_4(L^{Me})_2$ to the lithium of LLi.

The reaction of diisopropyl-4,5-dimethylimidazol-2-ylidene and TiF_4 also affords *trans*-$TiF_4(L^{iPr})_2$ (**4**) in moderate yield, which was isolated from THF solution below 0 °C

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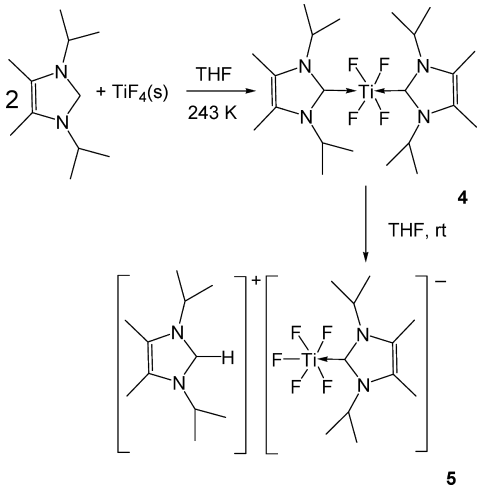
Scheme 2. Preparation of **4** and Transformation of **4** to **5** at Room Temperature



(Scheme 2). At room temperature, compound $[H(L^{iPr})][TiF_5(L^{iPr})]$ (**5**) crystallized from THF solution of **4** as a result of degradation of this compound. Complex **4** also degraded at room temperature in C_6D_6 and CD_3CN (Table 1) giving **5**. The slowest degradation of **4** was observed in C_6D_6 solution, while the concentration of **5** increased from 8 to 40% within 30 days. The ^{19}F resonances of **4** disappeared completely after 2 h at room temperature in CD_3CN solution. Therefore the *trans*-$TiF_4(L^{iPr})_2$ (**4**) is less stable, compared with the *trans*-$TiF_4(L^{Me})_2$ complex (**1**) containing the less bulky carbene ligand 1,3,4,5-tetramethylimidazol-2-ylidene. Obviously, the more bulky substituents (*i*Pr) decreased the stability of the tetrafluoro titanium complex.

Characterization of Complexes 1, 2, 4, and 5. The single crystal structures of *trans*-$TiF_4(L^{Me})_2$ (**1**), $[\{TiF_2(L^{Me})(NEt_2)\}_2(\mu\text{-}F)_2]$ (**2**), *trans*-$TiF_4(L^{iPr})_2$ (**4**), and $[H(L^{iPr})][TiF_5(L^{iPr})]$ (**5**) have been determined by X-ray crystallographic methods.

Complexes **1** and **4** are the first structurally characterized Ti(IV) tetrafluoro complexes having a ligand in the trans position to each other. The formation of *trans*-$TiF_4(L)_2$ with $L = L^{Me}$ and L^{iPr} is due to the bulkiness of these ligands. From the previously reported experimental data (NMR, IR)[20d–i,28d,e] it appears that *trans*-$TiF_4 \cdot 2$(donor) is formed only when there is sufficient steric interaction between the ligands to overcome the symmetry effects and the tendency to maximize the bonding between the fluorine and the Ti(IV) center.

Complexes **1** and **4** each contain a Ti(IV) center in a distorted octahedral environment, coordinated by four fluorine atoms and two carbon atoms (Figures 1 and 2). The C1N1C2C3N2 planes of coordinated L^{Me} in **1** are parallel to each other; while the C1N1C2C3N2 plane of L^{iPr} in **4** is rotated by 103.1° relative to the second plane (L^{iPr}). The Ti−C distance in **1** (2.255(4) Å) is shorter than that in **4** (2.2781(12) and 2.2812(12) Å) implying stronger Ti−C bonds in **1** than in **4**. Additionally, the Ti−C distances in **4** having two L^{iPr} are longer than those in $(L^{iPr})TiCl_3(\mu\text{-}O)TiCl_3(L^{iPr})$ (2.194(7) and 2.202(7) Å), where only one molecule of L^{iPr} is attached to each Ti(IV) center.[25] Moreover, the Ti−C (carbene) distance in the cationic complex $[Cp_2TiMe(L^1)]^+$ (L^1 = 1,3-diisopropylimidazol-2-ylidene) of 2.289(2) Å[26] is similar to that in **4**, hence the Ti−C distances depend on the type and size of ligands attached to the titanium center. The Ti−F bond lengths in **1** and **4** are in the normal range[20a,e] (Table 2).

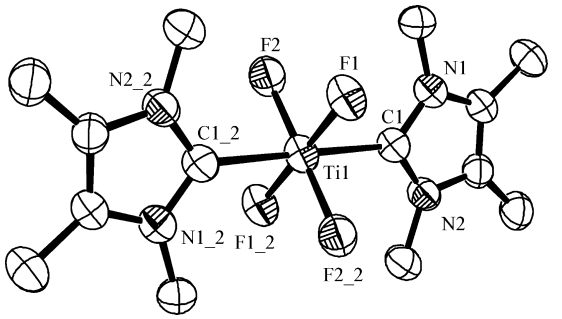


Figure 1. X-ray crystal structure of *trans*-$TiF_4(L^{Me})_2$ (**1**). Ellipsoids represent 50% probability levels.

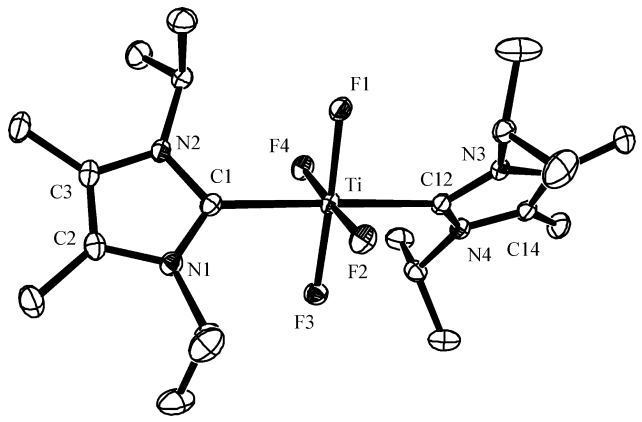


Figure 2. X-ray crystal structure of *trans*-$TiF_4(L^{iPr})_2$ (**4**). Ellipsoids represent 50% probability levels.

Complexes **1** and **4** are thermally stable (decomp. 227 and 169 °C, respectively) and do not change their appearance on storage in sealed ampoules at room temperature for several months. The ions detected in the EI-MS of **1** are mostly due to the cleavage of the ligand (Me, MeCCMe, *i*Pr) and elimination of fluorine. The ^{19}F NMR spectra of **1** and **4** (in C_6D_6) contain singlet resonances, and chemical shifts are presented (Table 1 in the Supporting Information). The ^{13}C NMR spectra of **1** and **4** are in agreement with the structures of the complexes. Resonances of carbon atoms attached to the titanium atoms appear (181.9 ppm for **1** and 184.3 ppm for **4**) in the same range as those for $[Cp_2TiMe(L^1)]^+$ (L^1 = 1,3-diisopropylimidazol-2-ylidene, 178.2 ppm),[26] $TiCl_4L$ (L = 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene,

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Table 3. ^{19}F NMR Chemical Shifts of the Fluoride Complexes at 240 K in MeCN used for the Estimation of Donor Numbers (DNs)

complex	δF_A	δF_X	$DN(SbCl_5)L$[37,38]	calcd DN (kcal·mol^{-1}) of L
$[TiF_5(TMP)]^-$ [39]	105.9	186.3	23.0	
$[TiF_5(TPPO)]^-$ [39]	104.0	173.0	27.0	
$[TiF_5(DMSO)]^-$ [23,40]	102.3[23]/101.3[40]	164.2[23]/163.7[40]	29.8	
$[TiF_5(HCNOEt_2)]^-$ [40]	105.1	171.2	30.9	
$[TiF_5Cl]^{2-}$ [21]	104.2	155.0	32.3	
$[TiF_5(L^{Me})]^-$	104.6[c]	118.9[c]		
	103.8	113.7		44.5; 30.1/37.3[b]
$[TiF_5(L^{iPr})]^-$	104.7[c]	123.0[c]		
	107.1	121.8		42.0; 25.7/33.8[b]

[a] TMP = $(MeO)_3PO$, TPPO = Ph_3PO, DMSO = Me_2SO. [b] Two numbers calculated using $\Delta\delta$ (^{19}F NMR) − $F_A([TiF_5L]^-)$ and $\Delta\delta$ (^{19}F NMR) − $F_X([TiF_5L]^-)$ relationships/average. [c] Measured at 298 K.

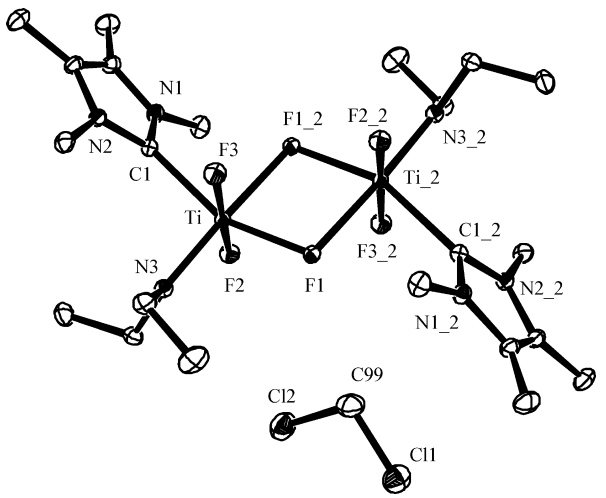

Figure 3. X-ray crystal structure of $[\{TiF_2(L^{Me})(NEt_2)\}_2(\mu\text{-}F)_2]$ (**2**)·$2CH_2Cl_2$. Ellipsoids represent 50% probability levels. Hydrogen atoms and one CH_2Cl_2 are omitted for clarity.

185.2−186.7 ppm),[25] and $TiCl_4L_2$ (180.7 ppm, L = 1,3-dimethylimidaxolin-2-ylidene).[27]

The dimeric complex $[\{TiF_2(L^{Me})(NEt_2)\}_2(\mu\text{-}F)_2]$ (**2**) crystallized with two molecules of CH_2Cl_2. Complex **2** has two Ti(IV) centers surrounded by L^{Me} and $[NEt_2]$ ligands in trans positions to the bridging fluorine atoms and by two terminal fluorine atoms in trans positions to each other, forming a distorted octahedral environment around each Ti(IV) center (Figure 3). Essentially, the mutual arrangement of the ligands in Ti(IV) (d^0) complexes is the result of the general trans effect in the octahedral complexes,[28] the weakest donor arranges in a trans position to the strongest donor (fluorine) to maximize the bonding between the fluorine and the Ti(IV) center.[29] However, complexes with bulky ligands do not follow this order. The location of both L^{Me} and NEt_2 ligands on the L^{Me}−Ti−(μ-F) and NEt_2−Ti−(μ-F) coordinates might be caused by the mutual repulsion of the ligands in **2**, since the basic property of L^{Me} is lower than that of terminal fluorine (see the next section). The trans arrangement of NMe_2 relative to the bridging fluorine atom is known and was observed in $[(Me_2N)_2TiF_2]_4$[30] and $[(Me_2N)_2TiF_2]_6$.[31]

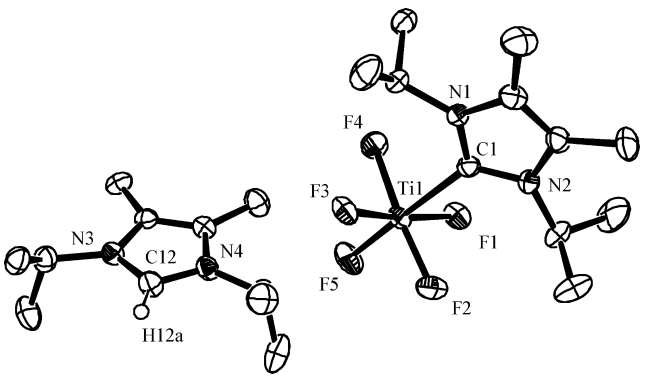

Figure 4. X-ray crystal structure of $[H(L^{iPr})][TiF_5(L^{iPr})]$ (**5**). Ellipsoids represent 50% probability levels.

The Ti−C distance in **2** (2.2367(9) Å) is close to that in **1** (2.255(4) Å). The Ti−F, Ti−(μ-F), and Ti−N bond lengths in **2** are in the normal range for the fluoride and amide complexes.[30,20a,d,e]

Compound **2** is thermally stable, and the appearance of the crystals was unchanged on storage in sealed ampoules at room temperature for several months. Elemental analysis of **2**·$2CH_2Cl_2$ is consistent with the formulation $[\{TiF_2(L^{Me})(NEt_2)\}_2(\mu\text{-}F)_2]$·$2CH_2Cl_2$. However, the ^{19}F NMR spectrum of **2** showed a mixture of complexes in solution. Five resonances were observed in the spectrum, when **2** was dissolved in C_6D_6, broad major resonances (144.2 ppm and −57.8 ppm) and minor resonances (121.2 and −2.3 ppm). The most downfield resonance (145.3 ppm) belonged to *trans*-$TiF_4L^{Me}_2$ (**1**). Formation of mixtures in solution is common for the Ti(IV) fluoride complexes. For instance, the organotitanium fluoride $[(C_5Me_5)TiF_3]_2$ revealed in toluene solution a mixture of five complexes, and the relative concentrations of the species depend on the temperature.[32]

Compound **5** contains discrete cations $[H(L^{iPr})]^+$ and anions $[TiF_5(L^{iPr})]^-$ (Figure 4). The shortest H(12)···F(4) contact in **5** (2.169 Å) is substantially less than 2.7 Å (the

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sum of van der Waals radii of hydrogen and fluorine)[33] suggesting the presence of weak hydrogen bonding in the crystal.[34] Consequently the Ti(1)−F(4) distance (1.863(2) Å) is longer than the other Ti−F bond lengths in **5** (1.835(2)–1.846(2) Å) and longer than the Ti−F distances in **1**, **2**, and **4** (1.831(3)–1.8409(7) Å). However, the H···F distance in **5** is longer than that of the normal hydrogen contacts found in other transition metal complexes, e.g. [*cis*-$TiF_4(H_2O)_2]_2$(18-crown-6) (1.633(3) Å),[20c] $CuF_2 \cdot 2H_2O$ (1.69 Å),[35] $FeSiF_6 \cdot 6H_2O$ (1.86 Å),[35c] and $[C_4H_{14}N_2][TiF_5(H_2O)]$ (O−H···F 1.74(4), 1.81(4) Å, and N−H···F 1.93 and 1.98 Å).[36] Compound **5** is the first reported complex containing discrete pentafluoro anions $[TiF_5(L^{iPr})]^-$. The Ti−C distance in **5** (2.310(3) Å) is longer than that in the molecular complexes **1**, **2**, and **4**, while the Ti−F(1–3) and Ti−F(5) distances are close to those in **1**, **2**, and **4** (Table 2).

Compound **5** is thermally stable, and the elemental analysis of **5** is consistent with the composition $[H(L^{iPr})][TiF_5(L^{iPr})]$. Pure **5** is very weakly soluble in C_6D_6 and toluene and strongly soluble in CD_3CN, although only $[TiF_6]^{2-}$ was detected in the ^{19}F NMR spectrum of a CD_3CN solution after 15 min of preparing the sample. The ^1H and ^{19}F NMR spectra of **5** in a solution of C_6D_6 can be interpreted as a mixture of **4** and **5**, with the major component $\{L^{iPr} \cdot (HF)\}$ **5a** together with undissolved **5**. The ions detected in the EI-MS of **5** are caused by the elimination of Me, NMe, and *i*Pr fragments from the cations $[H(L^{iPr})]^+$ and $[TiF_5(L^{iPr})]^+$.

Estimation of the Basic Properties of Carbene Ligands in the Titanium Fluoride Complexes. Previously, we have established a linear correlation between the $\Delta\delta$ (^{19}F NMR) of F_A and F_X in *cis*-TiF_4L_2 and $\Delta\delta$ (^{19}F NMR) of *fac*-$[TiF_3L_3]^+$ and the relative basicities of the molecular ligands L (L = donor ligands PhCN, MeCN, Et_2O, THF, $(MeO)_3PO$, H_2O, Ph_3PO, Me_2SO, etc.)[20e,f,37,38] and confirmed the order of relative basicities. This allowed us to estimate the donor properties of the carbenes toward Ti(IV) fluorides with the correlation between $\Delta\delta$ (^{19}F NMR) in $[TiF_5L]^-$ and the donor properties of ligand L.

However, the reported chemical shifts of $[TiF_5L]^-$ do not correlate linearly with the donor number of ligand L (TMP, TPPO, DMSO, $HCNOEt_2$, and pyridine toward $[SbCl_5]^-$). We propose that the relative basicity of $HCNOEt_2$ and pyridine toward $[TiF_5]^-$ is different from that reported for $SbCl_5$. In order to estimate the relative basicity of $HCNOEt_2$ and pyridine toward TiF_4, a linear relationship between chemical shifts of F_A and F_X of *cis*-TiF_4L_2 and the donor numbers (DNs) of L (Table 3)[20f] was used. The reported chemical shifts of $[TiF_5L]^-$ correlate linearly with the determined DN of L. The obtained correlation allowed us to estimate the donor numbers of the used carbenes toward $[TiF_5]^-$ ($DN(L^{Me}) = 37.3$, $DN(L^{iPr}) = 33.8$). The obtained numbers allow a comparison of the relative basicity of L^{iPr} and L^{Me} with the commonly used ligands of the Ti(IV) fluoride complexes to be made. The order of the relative basicities of the ligands was established to be THF < $(MeO)_3PO \approx Py < H_2O$[41] < $HCNOEt_2 \approx Ph_3PO < Me_2SO < [Cl]^- < L^{iPr} < L^{Me} < [F]^-$ (for further discussion, see the Supporting Information).

Gutmann represented the ability of a ligand to function as an electron pair donor toward $SbCl_5$ by the $-\Delta H$ value of the reaction in a dilute 1,2-dichloroethane solution with a donor number $DN(L) = -\Delta H$ reaction: $L + SbCl_5 = SbCl_5L$.[37] Unfortunately there is no experimental data to calculate the energy (ΔH and ΔG) for the formation of the $[TiF_5L]^-$. Therefore, we attempted to calculate the reaction energetics using the Turbomole[42] program (Table 4).

Table 4. Calculated Thermodynamic Values for the Reactions of $[TiF_5]^-$ with $[F]^-$, $[Cl]^-$, L^{iPr}, and L^{Me} [a]

reaction	ΔE (kcal·mol^{-1})
$[TiF_5]^- + [F]^- = [TiF_6]^{2-}$ (1)	−196.1
$[TiF_5]^- + [Cl]^- = [TiF_5Cl]^{2-}$ (2)	−18.0
$[TiF_5]^- + L^{iPr} = [TiF_5(L^{iPr})]^-$ (3)	−62.1
$[TiF_5]^- + L^{Me} = [TiF_5(L^{Me})]^-$ (4)	−62.8

[a] ΔE—difference of ab initio energies of the corresponding equilibrium structures, kilocalories per mole.

The calculated order of the relative basicities of L toward $[TiF_5]^-$ ($[Cl]^- < L^{iPr} < L^{Me} < [F]^-$) was in agreement with the experimental order extracted from the NMR data. Thus, density functional theory (DFT) calculations support our experimental data.

Conclusion

In summary, the Ti(IV) fluoride complexes *trans*-$TiF_4(L^{Me})_2$ (**1**) and *trans*-$TiF_4(L^{iPr})_2$ (**4**) are obtained in one step from the readily available 1,3,4,5-tetramethylimidazol-2-ylidene (L^{Me}), 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (L^{iPr}), and TiF_4 in THF. Complex **1** was used as a versatile precursor to prepare the Ti(IV) fluoride carbene complexes $[\{TiF_2(L^{Me})(NEt_2)\}_2(\mu\text{-}F)_2]$ (**2**) and $(TiF_4(L^{Me})_2)$-(NacNacLi) (**3**), while complex **4** degraded in solution at room temperature giving $[H(L^{iPr})][TiF_5(L^{iPr})]$ (**5**). It should be noted that the lability of the L^{Me} ligand (reaction of **1** with $AlMe_3$ in toluene) leads to the ligand transfer from the

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Table 5. Crystallographic Data and Structure Refinement Details for **1**, **2**, **4**, and **5**

	1	**2**	**4**	**5**
empirical formula	$C_{14}H_{24}F_4N_4Ti$	$C_{24}H_{48}Cl_4F_6N_6Ti_2$	$C_{22}H_{40}F_4N_4Ti$	$C_{22}H_{41}F_5N_4Ti$
M_r	372.27	772.28	484.48	504.49
temp [K]	203(2)	100(2)	100(2)	133(2)
radiation used (λ[Å])	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	7.9760(15)	8.7060(6)	14.3210(6)	9.1368(7)
b [Å]	8.3016(16)	9.4675(6)	12.2112(4)	9.5786(8)
c [Å]	8.3100(16)	11.9152(8)	15.0316(4)	16.9242(15)
α [deg]	116.763(14)	112.235(4)	90	88.349(4)
β [deg]	97.297(15)	105.096(4)	104.688(4)	99.143(7)
γ [deg]	113.598(14)	94.226(4)	90	90.213(7)
V [Å^3]	417.25(14)	861.24(10)	2542.77(15)	1308.62(19)
Z	1	1	4	2
ρ_{calcd} [g·cm^{-3}]	1.482	1.489	1.266	1.280
μ [mm^{-1}]	0.556	0.832	0.381	0.378
F (000)	194	400	1032	536
scan range Θ [°]	2.96−24.94	1.94−33.14	1.75−31.00	2.41−24.82
completeness to Θ_{max} [%]	69.1	99.3	99.8	98.7
index ranges	$-9 \le h \le 9$	$-13 \le h \le 13$	$-20 \le h \le 20$	$-10 \le h \le 10$
	$-9 \le k \le 9$	$-14 \le k \le 14$	$-17 \le k \le 16$	$-11 \le k \le 11$
	$-9 \le l \le 9$	$-18 \le l \le 18$	$-21 \le l \le 21$	$-19 \le l \le 19$
total reflections	4123	26753	70374	24855
unique reflections	1007	6530	8091	4469
R(int)	0.0973	0.0240	0.0437	0.1244
data/restrains/parameters	1007/0/110	6530/0/196	8091/0/292	4469/0/305
goodness-of-fit on F^2	1.060	1.047	1.023	0.978
$R1$, $wR2$[a] [$I > 2\sigma(I)$]	0.0535, 0.1485	0.0264, 0.0701	0.0357, 0.0894	0.0544, 0.1061
$R1$, $wR2$ (all data)	0.0668, 0.1605	0.0316, 0.0728	0.0540, 0.0983	0.0988, 0.1202
max, min electron density [e·Å^{-3}]	0.237, −0.399	0.531, −0.441	0.378, −0.424	0.341, −0.388

[a] $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[F_o^4])^{1/2}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, weight $= 1/[\sigma^2(F_o^2) + (AP)^2 + (BP)]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$; for **1** $A = 0.0535$, $B = 0.0000$; for **2** $A = 0.0347$, $B = 0.279$; for **4** $A = 0.0464$, $B = 0.8743$; for **5** $A = 0.1086$, $B = 0.0000$.

Ti(IV) to the Al(III) center. Thus, a controllable chemistry of Ti(IV) fluoride complexes can be accomplished with *N*-heterocyclic carbenes in common organic solvents at room temperature. The observed thermal stability of the tetrafluorocomplex *trans*-$TiF_4(L^{Me})_2$ with the less bulky *N*-heterocyclic carbene L^{Me} is higher compared to that of *trans*-$TiF_4(L^{iPr})_2$. This shows that the presence of bulky substituents at the *N*-heterocyclic carbene does not necessarily lead to an increase in stability of fluoride complexes. The applied carbenes are established to be strong molecular donors toward Ti(IV) fluorides; the order of relative basicities of the ligands in the Ti(IV) fluoride anionic complexes $[TiF_5L]^-$ was established to be THF < $(MeO)_3PO \approx Py \approx H_2O$[41] < $HCNOEt_2 \approx Ph_3PO < Me_2SO < [Cl]^- < L^{iPr} < L^{Me} < [F]^-$ and confirmed in part by DFT calculations.

Experimental Section

All operations were performed under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an MBrown MB-150B inert atmosphere glovebox. Solvents THF, toluene, hexane, and tetrahydrofuran were dried over Na/benzophenone and distilled under nitrogen prior to use. C_6D_6 was dried over K and degassed; CH_2Cl_2, pyridine, Me_2SO (DMSO), CD_3CN, and $CDCl_3$ were dried over CaH_2 and distilled prior to use. H_2O was degassed under nitrogen. The compounds LH with the ligand L = (2,6-iPr$_2$C$_6$H$_3$NC(Me))$_2$CH, NacNac, 1,3,4,5-tetramethylimidazol-2-ylidene (L^{Me}), and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (L^{iPr}) were prepared by the known literature methods.[43–45] The purity of all compounds was checked by ^{1}H and ^{13}C NMR spectra. TiF_4 (Acros Organics 99%), $Ti(NEt_2)_4$ (Aldrich), *n*BuLi (1.6 M) (Acros Organics), and $AlMe_3$ (2 M) (Acros Organics) were used as received. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded using Bruker Avance DPX 200, Bruker Avance DRX 500, and Varian INOVA-600 spectrometers. Chemical shifts are reported in δ units downfield from Me_4Si with the solvent as the reference signal. Mass spectra were recorded using a Finnigan MAT 8230 mass spectrometer, and elemental analysis were carried out at the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were measured in sealed capillary tubes under nitrogen and are not corrected.

***trans*-$TiF_4(L^{Me})_2$ (1).** A THF (20 mL) solution of TiF_4 (1.40 g, 11.3 mmol) was added to the THF (30 mL) solution of 1,3,4,5-tetramethylimidazol-2-ylidene (2.80 g, 22.6 mmol) at −79 °C under stirring. This mixture was stirred for additional 30 min at −79 °C and then allowed to warm to rt under continuing stirring for 6 h at rt and finally filtered. The recovered solid was washed with THF (30 mL) and dried under vacuum, yield 3.96 g (90%). Compound **1** can be further purified by recrystallization from CH_2Cl_2. Elemental analysis of $C_{14}H_{24}F_4N_4Ti$: calcd C, 45.16; H, 6.45; N, 15.05; found C, 45.32; H, 6.41; N, 14.95. Mp 227–228 °C. EI-MS: m/z (%) = 222 (2) [$M^+ - 2F - C_6H_{12}N_2$], 189 (4) [$M^+ - C_6H_{12}N_2 - C_4H_9N$], 173 (10) [$M^+ - 3F - C_6H_{12}N_2 - 2Me$], 124 (100) $[L^{Me}]^+$. ^{1}H NMR (200.13 MHz, C_6D_6, rt) δ_H (ppm) = 3.30 (s, 6H, N(1,3)-CH_3), 1.55 (s, 6H, C(4,5)-CH_3). ^{19}F NMR (188.34 MHz, C_6D_6, rt), δ_F (ppm) = 147.9 (s, *trans*-TiF_4(L^{Me})$_2$), ^{1}H NMR (200.13 MHz, $CDCl_3$, rt), δ_H (ppm) = 3.90 (s, N(1,3)-CH_3), 2.07 (s, C(4,5)-CH_3). ^{19}F NMR (188.34 MHz, $CDCl_3$, rt), δ_F (ppm) = 140.2 (s, *trans*-TiF_4(L^{Me})$_2$). ^{13}C NMR (125.712 MHz, $CDCl_3$, rt), δ_C (ppm) = 181.9 (C(2)), 123.5 (*C*(4,5)), 33.7 (N(1,3)-*C*H$_3$), 8.64 (C(4,5)-*C*H$_3$). The

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complex degrades in $CDCl_3$ in a period of several hours at room temperature; abbreviations are similar to those used in ref 45.

Reaction of 1 with $AlMe_3$ giving $AlMe_3(L^{Me})$. To compound **1** (0.57 g, 1.5 mmol) suspended in toluene (40 mL) was added drop by drop a toluene solution of $AlMe_3$ (1.53 mL, 2 M, 3.1 mmol). The suspension of **1** disappeared, and then a dark brown oily tar was deposited. The solution was filtered and concentrated, and the resulting solid was collected. ^{1}H NMR (200.13 MHz, C_6D_6, rt) δ_H (ppm) = 3.08 (s, 6H, N(1,3)-CH_3), 1.17 (s, 6H, C(4,5)-CH_3), −0.12 (s, 9H, Al-*Me*).

[{$TiF_2(L^{Me})(NEt_2)$}$_2$(μ-F)$_2$] (2). Method A. 1 (0.854 g, 2.3 mmol) and $Ti(NEt_2)_4$ (0.386 g, 1.2 mmol, 0.42 mL) have been stirred in toluene (40 mL) for 4 d at rt. Then the toluene was removed under vacuum and the residual dissolved in CH_2Cl_2 (40 mL). The resulting mixture was concentrated (20 mL) and left at 0 °C for 7 d. Crystals which deposited were washed with toluene (2 × 3 mL) and dried in vacuum. Yield (0.2 g). Crystals of **2** also deposited from a CH_2Cl_2 solution when 1 equiv of **1** and 1 equiv of $Ti(NEt_2)_4$ was used.

Method B. TiF_4 (0.7 g, 5.6 mmol) and $Ti(NEt_2)_4$ (0.636 g, 1.9 mmol, 0.68 mL) were stirred together for 2 h in toluene (40 mL) at rt, and then a toluene (20 mL) solution of 1,3,4,5-tetramethylimidazol-2-ylidene (0.94 g, 7.6 mmol) was added drop by drop. The resulting mixture was stirred for 5 d at rt, while an orange solid was formed. The resulting solid was filtered from the mother liquid (yield 1.50 g). This solid was dissolved in CH_2Cl_2 (60 mL), its solution was concentrated (30–40 mL), and **1** separated and was filtered off. The residual solution was concentrated (5–7 mL) and left at 0 °C for crystallization. The resulting crystalline solid was filtered off and washed with toluene (3 × 2 mL). Yield 1.15 g of **2**. Elemental analysis for $C_{24}H_{48}Cl_4F_6N_6Ti_2$: calcd C, 37.29; H, 6.21; N, 10.88; found C, 37.03; H, 6.04; N, 10.63. Mp 181–182 °C, decomp EI-MS: *m*/*z* (%) = 366 (10) [$M^+ - L^{Me} - 2Et - Me_2C_2$], 268 (10) [$M^+ - 2F - L^{Me} - NEt_2 - 2Et - Me_2C - Me$], 230 (30) $[TiF_3N_4C_5H_9]^+$, 215 (100) $[TiF_3N_4C_4H_6]^+$, 200 (15) $[TiF_3N_4C_3H_3]^+$, 162 (15) $[TiFN_4C_3H_3]^+$, 156 (30) $[TiF_2N_3C_2H_4]^+$. ^{1}H NMR (599.74 MHz, C_6D_6, rt), δ_H (ppm) = 4.55 (br, CH_2CH$_3$), 4.42 (q, J = 7.0 Hz, CH_2CH$_3$), 4.37 (br, CH_2CH$_3$), 4.28 (s, N(1,3)-CH_3), 4.22 (br, CH_2CH$_3$), 4.04 (br, CH_2CH$_3$), 3.86 (s, N(1,3)-CH_3), 3.83 (s, N(1,3)-CH_3), 3.70 (s, N(1,3)-CH_3), 3.66 (s, N(1,3)-CH_3), 3.63 (s, N(1,3)-CH_3), 3.55 (s, N(1,3)-CH_3), 1.39 (t, J = 7.0 Hz, CH$_2$CH_3), 1.35 (s, C(4,5)-CH_3), 1.30 (overlapped s + s, C(4,5)-CH_3), 1.26 (s, C(4,5)-CH_3), 1.20 (t, J = 7.0 Hz, CH$_2$CH_3), 1.17 (t, J = 7.0 Hz, CH$_2$CH_3), 1.04 (t, J = 7.0 Hz, CH$_2$CH_3). ^{13}C NMR (125.712 MHz, C_6D_6, rt), δ_C (ppm) = 123.2 (*C*(4,5)), 122.9 (*C*(4,5)), 122.8 (*C*(4,5)), 54.4 (*C*H$_2$CH$_3$), 53.3 (*C*H$_2$CH$_3$), 51.3 (*C*H$_2$CH$_3$), 34.7 (N(1,3)-*C*H$_3$), 34.4 (N(1,3)-*C*H$_3$), 34.3 (N(1,3)-*C*H$_3$), 33.9 (N(1,3)-*C*H$_3$), 16.5 (CH$_2$*C*H$_3$), 16.3 (CH$_2$*C*H$_3$), 15.2 (CH$_2$*C*H$_3$), 13.8 (CH$_2$*C*H$_3$), 13.4 (CH$_2$*C*H$_3$), 8.2 (C(4,5)-*C*H$_3$), 8.1 (C(4,5)-*C*H$_3$), 7.8 (C(4,5)-*C*H$_3$). ^{19}F NMR (188.34 MHz, C_6D_6, rt), δ_F (ppm) = 148.0 (s, *trans*-Ti*F*$_4$(L^{Me})$_2$, 3%), 144.2 (br, $\Delta\omega_{1/2}$ = 80 Hz, 59%), 121.2 (d, J = 30 Hz, 12%), −2.3 (br, weak, 4%), −57.8 (br, $\Delta\omega_{1/2}$ = 110 Hz, 22%). Note (a) selected crystals of **2** and bulk powder showed similar ^{19}F NMR spectra consisting of 5 resonances and (b) compound **2** is weakly soluble in C_6D_6 and always affords some amount of powder by dissolution, precluding quantitative study of solution equilibria.

($TiF_4(L^{Me})_2$)(NacNacLi) (3). An *n*-hexane solution of *n*BuLi (1.2 mL, 1.9 mmol, 1.6 M) was added drop by drop to a solution of LH (0.8 g, 1.9 mmol) in toluene (40 mL) at 0 °C. The resulting mixture was stirred overnight at rt and then added drop by drop to a toluene (20 mL) suspension of **1** (0.693 g, 1.9 mmol) at rt. Stirring continued for 3 d, the resulting suspension (0.92 g collected) was filtered off, and the solution concentrated. The colorless crystalline solid which deposited was filtered off and washed with *n*-hexane (6 × 3 mL). The insoluble (0.92 g) was suspended in toluene (60 mL) for 1 d, and then the solution was filtered and concentrated. The colorless crystalline solid which deposited was filtered off and washed with *n*-hexane (2 × 3 mL). Yield (0.10 g + 0.10 g). A further crop of **3** can be recovered by extraction of the crude reaction product with toluene. Elemental analysis for $C_{43}H_{65}F_4LiN_6Ti$: calcd C, 64.82; H, 8.17; Li, 0.88; N, 10.55; found C, 64.94; H, 8.22; Li, 0.89; N, 10.45. Mp 144 °C, decomp (turns dark above 120 °C). EI-MS can be interpreted that **3** is giving {($TiF_4(L^{Me})_2$)(NacNacLi)$_2$} (M^+ = 1221) by electron impact. EI-MS: *m*/*z* (%) = 1192–1197 (multipl.) 1195 (20) [M^+ − LiF], 1192 (15) [M^+ − LiF − 3H], 1177 (5) [M^+ − H*i*Pr], 1152 (5) [M^+ − LiF − *i*Pr], 1079 (5) [M^+ − 2LiF − *i*Pr − 2Me − CH_4], 1074 (30) [M^+ − F − LiF − 2*i*Pr − CH_4], 1070 (40) [M^+ − L^{Me} − LiF], 1044 (20) [M^+ − L^{Me} − 2LiF], 1029 (10) [M^+ − F − LiF − 3*i*Pr − CH_4], 951 (5) [M^+ − HF_2 − LiF − *i*Pr − $C_6H_3iPr_2$], 931 (10) [M^+ − L^{Me} − 2LiF − 2*i*Pr − MeC], 898 (5) [M^+ − 2$C_6H_3iPr_2$], 833 (20) [M^+ − 2$C_6H_3iPr_2$ − LiF − HF − F], 657 (30) [M^+ − 2$C_6H_3iPr_2$ − $NC_6H_3iPr_2$ − LiF − 2HF], 642 (5) [M^+ − 2$C_6H_3iPr_2$ − $NC_6H_3iPr_2$ − LiF − 2HF − Me], 418 (40) [NacNacH$^+$], 403 (100) [NacNacH$^+$ − Me]. ^{1}H NMR (599.74 MHz, C_6D_6, rt), δ_H (ppm) = 7.15–7.10 (m, aryl), 7.00–6.90 (m, aryl), 5.01 (s, 1H, C(CH$_3$)C*H*C(CH$_3$)), 3.50 (sept, 4H, J = 6.80 Hz, C*H*Me$_2$), 3.33 (s, 12H, N(1,3)-CH_3), 1.85 (s, 6H, C(CH_3)CHC(CH_3)), 1.33 (s, 12H, C(4,5)-CH_3), 1.26 (d, 12H, J = 6.80 Hz, CH*Me*$_2$), 1.08 (d, 12H, J = 6.80 Hz, CH*Me*$_2$).^{13}C NMR (125.712 MHz, C_6D_6, rt), δ_C (ppm) = 181.8 (C(2)), 163.4 (*C*(CH$_3$)CH*C*(CH$_3$)), 152.2 (*C*$_6$H$_3$), 141.7 (*C*$_6$H$_3$), 122.9 (C(4,5)), 122.6 (*C*$_6$H$_3$), 121.8 (*C*$_6$H$_3$), 92.7 (C(CH$_3$)*C*HC(CH$_3$), 33.5 (N(1,3)-*C*H$_3$), 28.0 (*C*HMe$_2$), 23.93 (C(*C*H$_3$)CHC(*C*H$_3$), 23.87 (*C*H$_3$), 23.4 (*C*H$_3$), 8.0 (C(4,5)-*C*H$_3$). ^{19}F NMR (188.34 MHz, C_6D_6, rt), δ_F (ppm) = 137.4 ($\Delta\omega_{1/2}$ 90 Hz, *trans*-TiF_4(L^{Me})$_2$·LLi).

***trans*-$TiF_4(L^{iPr})_2$ (4).** A THF (30 mL) solution of TiF_4 (0.6 g, 4.8 mmol) was added to the THF (30 mL) solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (1.74 g, 9.7 mmol) at −79 °C under stirring. This mixture was stirred for 30 min at −79 °C, then allowed to warm to rt, stirred for 3 h at rt, and finally filtered. The resulting solid was a mixture of **4** and [H(L^{iPr})][$TiF_5(L^{iPr})$] (50%:50%). The supernatant solution was concentrated (30 mL) and left at −30 °C for 3 d. The crystalline solid **4** was recovered by filtration. Yield of **4** (0.54 g). An additional crop of **4** (0.44 g) was obtained by further crystallization at −30 °C of the concentrated supernatant solution. Elemental analysis for $C_{22}H_{40}F_4N_4Ti$: calcd C, 54.49; H, 8.26; N, 11.55; found C, 54.28; H, 8.10; N, 11.46. Mp 169–170 °C. EI-MS: *m*/*z* (%) = 409 (5) [M^+ − 2CH_4 − *i*Pr], 385 (5) [M^+ − MeCN*i*Pr − Me], 340 (2) [M^+ − 3*i*Pr − Me], 315 (2) [M^+ − *i*Pr − N*i*Pr − CN*i*Pr], 297 (2) [M^+ − 4*i*Pr − Me], 273 (2) [M^+ − MeCC(Me)N*i*Pr − *i*Pr − 3F], 243 (2) [M^+ − MeCC(Me)N*i*Pr − *i*Pr − 3F − 2Me], 200 (5) [M^+ − MeCC(Me)N*i*Pr − 2*i*Pr − 3F − 2Me], 180 (100) [L^{iPr}]$^+$. ^{1}H NMR (599.74 MHz, C_6D_6, rt), δ_H (ppm) = 6.59 (sept, 4H, J = 7 Hz, N(1,3)-C*H*(CH$_3$)$_2$), 1.64 (s, 12H, C(4,5)-CH_3), 1.41 (d, 24H, J = 7 Hz, N(1,3)-CH(CH_3)$_2$). ^{13}C NMR (125.712 MHz, C_6D_6, rt), δ_C (ppm) = 184.3 (C(2)), 123.5 (C(4,5)), 50.8 (N(1,3)-*C*H(CH$_3$)$_2$), 21.8 (N(1,3)-CH(*C*H$_3$)$_2$), 9.90 (C(4,5)-*C*H$_3$). ^{19}F NMR (188.34 MHz, C_6D_6, rt), δ_F (ppm) = 149.4 (s, *trans*-TiF_4(L^{iPr})$_2$).

[H(L^{iPr})][$TiF_5(L^{iPr})$] (5). Crystals of **5** deposited from a solution of **4** (0.8 g) in THF (20 mL) at rt. over 14 days. Compound **5** crystallized as needles and rods, while compound **4** crystallized as small plates. The deposited **5**, which was contaminated with **4**, was filtered from the supernatant solution and washed with toluene (5 × 4 mL). Yield 0.35 g of **5**. Elemental analysis of $C_{22}H_{41}F_5N_4Ti$:

calcd C, 52.32; H, 8.13; N, 11.10; found C, 52.28; H, 8.10; N, 11.05. Mp 194–195 °C. EI-MS: spectrum can be interpreted that **5** is giving initially $[H(L^{iPr})]^+$, $[(TiF_4(L^{iPr}))_2]^+$, and $[F_2]^+$ by electron impact. *m*/*z* (%) = 479 (5) $[(TiF_4L^{iPr})_2^+ - 3iPr]$, 452 (5) $[(TiF_4L^{iPr})_2^+ - 2Ni\text{Pr} - i\text{Pr}]$, 437 (2) $[(TiF_4(L^{iPr}))_2^+ - 2Ni\text{Pr} - i\text{Pr} - \text{Me}]$, 409 (5) $[(TiF_4(L^{iPr}))_2^+ - 2Ni\text{Pr} - 2i\text{Pr}]$, 273 (5) $[(TiF_5(L^{iPr})) - F - 2CH_4]$, 180 (100) $[L^{iPr}]^+$. Pure **5** is very weakly soluble in C_6D_6 and toluene. NMR spectra can be interpreted that in solution L^{iPr}(HF) **5a** is the major component together with **4** and **5** and undissolved **5**.

5a. ^{1}H NMR (599.74 MHz, C_6D_6, rt), δ_H (ppm) = 12.20 (br, 1H, C(2)-*H*), 3.95 (sept, 2H, *J* = 6.5 Hz, N(1,3)-C*H*$(CH_3)_2$), 1.73 (s, 6H, C(4,5)-C*H*$_3$), 1.50 (d, 12H, *J* = 6.5 Hz, N(1,3)-CH(C*H*$_3)_2$). ^{19}F NMR (188.34 MHz, C_6D_6, rt), δ_F (ppm) = −131 (br); degradation of **4** was leading to a mixture of **4**, **5**, and **5a** (^{19}F NMR). The NMR spectrum of **5** was extracted from the spectrum containing resonances of **4**, **5**, and **5a**.

5. ^{1}H NMR (599.74 MHz, C_6D_6, rt), δ_H (ppm) = 10.20 (s, 1H, C(2)-*H*, $[H(L^{iPr})]^+$), 6.78 (sept, 2H, *J* = 7.1 Hz, N(1,3)-C*H*$(CH_3)_2$, $[TiF_5(L^{iPr})]^-$), 4.10 (br, 2H, N(1,3)-C*H*$(CH_3)_2$, $[H(L^{iPr})]^+$), 1.80 (s, 6H, C(4,5)-C*H*$_3$, $[TiF_5(L^{iPr})]^-$), 1.72 (br, 6H, C(4,5)-C*H*$_3$, $[H(L^{iPr})]^+$), 1.50 (d, 12H, *J* = 7.1 Hz, N(1,3)-CH(C*H*$_3)_2$, $[TiF_5(L^{iPr})]^-$), 1.47 (br, 12H, *J* = 7.1 Hz, N(1,3)-CH(C*H*$_3)_2$, $[H(L^{iPr})]^+$). ^{13}C NMR (125.712 MHz, C_6D_6, rt), δ_C (ppm) = 207.6 (C(2)), 125.3 (C(2) or C(2)-H),[46] 123.5 (C(4,5), or C(2)-H), 121.4 (C(4,5), or C(2)-H), 50.6 (N(1,3)-*C*H$(CH_3)_2$), 48.5 (N(1,3)-*C*H$(CH_3)_2$), 24.7 (N(1,3)-CH(*C*H$_3)_2$), 22.4 (N(1,3)-CH(*C*H$_3)_2$), 10.4 (C(4,5)-*C*H$_3$), 8.8 (C(4,5)-*C*H$_3$). ^{19}F NMR (188.34 MHz, C_6D_6, rt), δ_F (ppm) = 112.2 (q, 1F, *J* = 34 Hz), 118.9 (d, 4F, *J* = 34 Hz).

X-ray Crystallography. The crystallographic data and structure determinations of **1**, **2**, **4**, and **5** are summarized in Table 5. Intensities were collected on a Stoe image plate IPDS II-system for **1** and **4**. A Bruker APEX2 CCD diffractometer was employed for **2** and **4**. The structures were solved by direct methods, and refined against F^2 with nonhydrogen atoms anisotropic and hydrogen atoms with a riding model. The data was reduced (SAINT)[47] and corrected for absorption (SADABS).[48] All calculations were carried out using SHELXTL software.[49] All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated in idealized position.

Density Functional Calculations. The B-P86 functional,[50] def2-SVP basis set,[42,51] and COSMO model[52] and solvent acetonitrile have been applied for calculation using the Turbomole program.[42] In the first step, the compound was fully optimized to its equilibrium structure (coordinates are given in the ESI). The harmonic vibrational frequencies needed for the thermodynamic data were calculated. All molecules and anions represent a true minimum on the potential energy surface without negative IR frequencies.

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Supporting Information Available: X-ray crystallographic data files in CIF format; details of estimation of relative basicities of L, chemical shift of observed fluoride complexes at room temperature, NMR spectral data for **1** in $CDCl_3$ and CD_3CN and **4** in CD_3CN, IR spectra of **1**, **2**, **4**, and **5**, atomic coordinates of the optimized molecules L^{Me}, L^{iPr}, $[TiF_5]^-$, $[TiF_6]^{2-}$, $[TiF_5Cl]^{2-}$, $[TiF_5(L^{Me})]^-$, and $[TiF_5(L^{iPr})]^-$ in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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