Cationic Titanium Complexes Containing Alkoxide and Carboxylate Pincer Ligands; Noninnocent Role of the Anionic Moieties in Their Reactivity

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The reactions of [Cp*TiMe{(OCH$_2$)$_2$py}] (**1**) and [Cp*TiMe{(OOC)$_2$py}] (**2**) with triflic acid (HOTf) in the presence of a series of Lewis bases, such as water, pyridine, and *tert*-butylpyridine, give rise to the corresponding cationic species, namely [Cp*TiL{(OCH$_2$)$_2$py}]$^+$OTf$^-$ (**3**−**5**) and [Cp*TiL{(OOC)$_2$py}]$^+$OTf$^-$ (**6**, **7**). Similar processes with **1** and HOTf in the presence of 2,6-pyridinedimethanol and 2-pyridinemethanol lead to the binuclear complexes [{Cp*Ti((OCH$_2$)$_2$py)}$_2${μ-(HOCH$_2$)$_2$py}]OTf$_2$ (**8**) and [Cp*Ti{(OCH$_2$)$_2$py}{(HOCH$_2$)py}]OTf (**9**), respectively. In an unusual process, the reaction of **3** with NaBPh$_4$ or **1** with B(C$_6$F$_5$)$_3$ yields hydroxo-containing binuclear species, namely [{Cp*Ti((OCH$_2$)$_2$py)}$_2$(μ-OH)][BPh$_4$] (**10**) and [Cp*Ti(μ-OH){(OCH$_2$)$_2$py}][BMe(C$_6$F$_5$)$_3$] (**12**), respectively. The X-ray molecular structures of **10** and **12** have been established. Finally, the titanium−aluminum heterometallic complex [Cp*Ti{(OCH$_2$)$_2$py}(μ-O-AlMeOTf)] (**16**) has been prepared by reaction of **3** with AlMe$_3$.

Introduction

Several organometallic processes are concerned with enhancing the chemical reactivity of cationic metal complexes using weakly coordinating anions, whether for catalysis or for the stoichiometric synthesis of new complexes.[1] This activation is usually associated with a decrease in complex stability due to the electronic deficiency of the metal center. This can be prevented by using ligands with several donor atoms that can coordinate when necessary. In this way, oxygen donor ligands such as alkoxides, aryloxides, and carboxylates are extremely versatile, because appropriate substitution patterns allow substantial modification of the steric and electronic properties of the metal center.[2] Pyridinic alcohols and carboxylates have a nitrogen atom that facilitates coordination in a chelate fashion when necessary by providing the metal with additional electronic density.[3]

We are currently interested in this area, particularly developing synthetic protocols and studying the reactivity of new titanium cationic derivatives stabilized by pincer ligands with the appropriate counterions. With this aim in mind, we chose to investigate two of the most common anionic moieties, namely triflate and alkyl-/arylborate groups.[4] Although the latter species are usually considered as chemically inert, some exceptions have been reported—notably in relation to redox reactions,[5,6] complexation of phenyl rings to the metal center,[6] and transfer of phenyl[7] or biphenyl[8] groups to an organic ligand. Only a few examples of the activation of boron−carbon bonds in the anion have been reported.[9]

We report here the synthesis and reactivity of some cationic complexes of titanium that contain alkoxide or carboxylate pincer ligands and triflate or borate moieties as counterions. The nature of the anion proved to be decisive, as shown by an example where the borate anions play an important role and do not behave in the expected passive manner.

Results and Discussion

Synthesis and Structural Characterization. Our initial studies were directed toward the synthesis of cationic compounds of titanium(IV) containing the pincer ligands 2,6-pyridinedimethoxide and 2,6-pyridinedicarboxylate by starting

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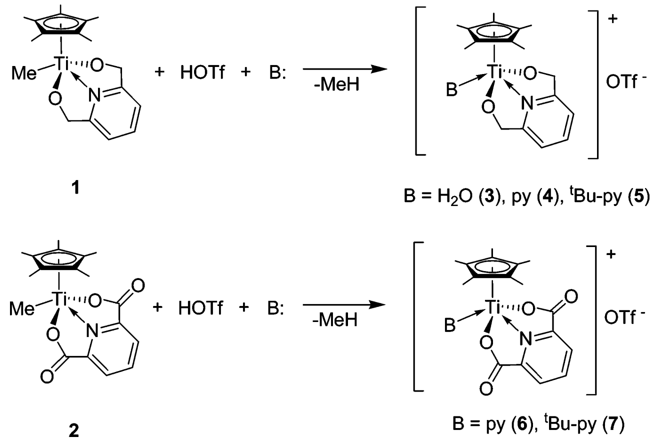
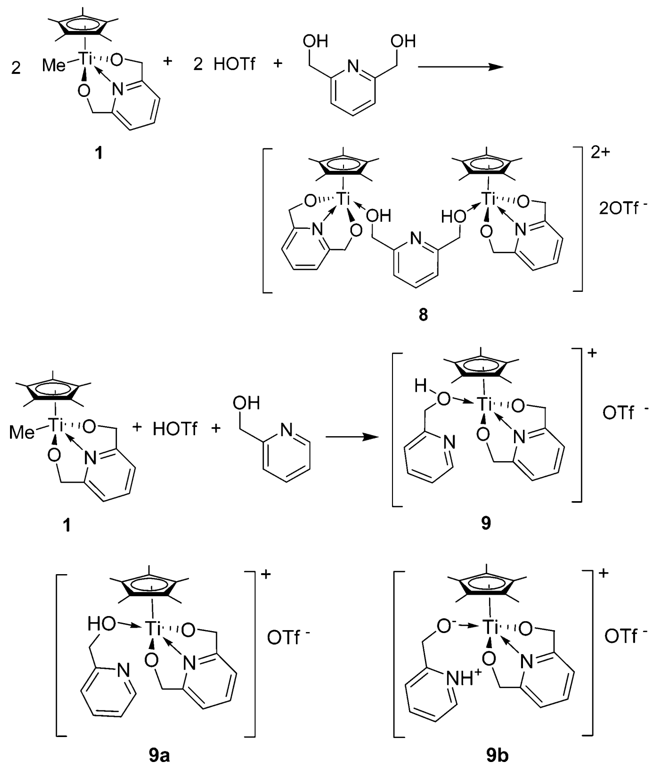
10.1021/om070119h CCC: $37.00

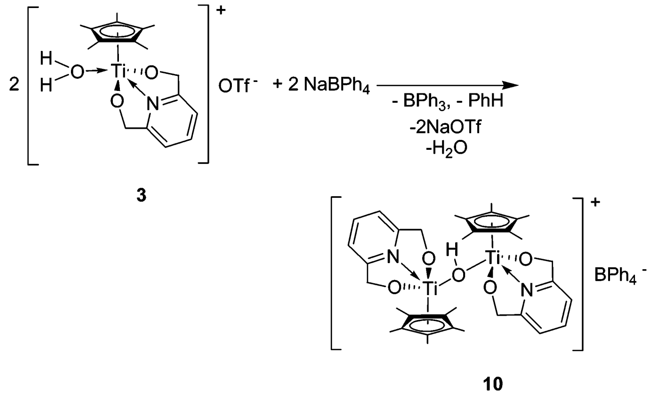
Scheme 1



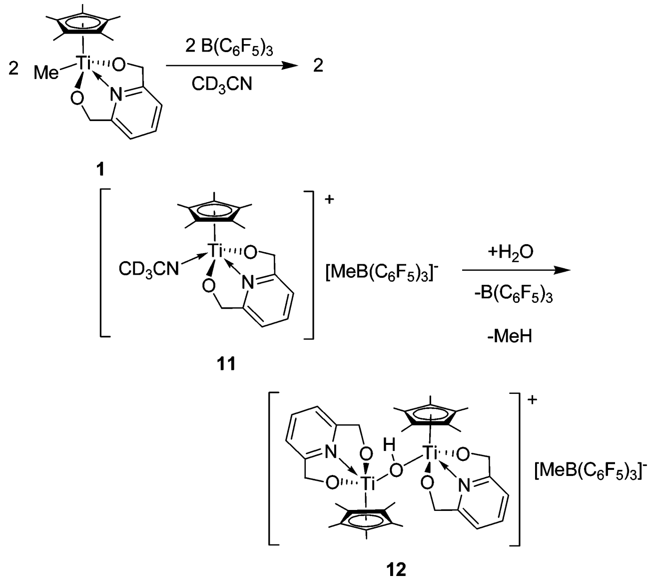
Scheme 2



Scheme 3



Scheme 4



from the previously described neutral methyl complexes [Cp*TiMe{(OCH$_2$)$_2$py}] (**1**)[10] and [Cp*TiMe{(OOC)$_2$py}] (**2**)[11] by their reactions with triflic acid (Scheme 1). This type of reactivity, namely protonolysis of the M−C bond, has been well documented,[12] and in several cases the appropriate cationic species with the triflate counterion has been isolated. It is well-known, however, that under certain conditions the classic ‘noncoordinating” anion $SO_3CF_3^-$ (OTf $^-$) coordinates to the metal center, making possible the isolation of neutral species.[13] However, in the reactions of **1** or **2** with triflic acid a mixture of unidentified complexes was detected, indicating that the additional donation of a pair of electrons from the nitrogen atom of the ligand to the metal center is not sufficient to stabilize the proposed cationic complexes either electronically or sterically, probably due to the constrained geometry of the pincer groups, which prevents them from filling the vacant metal orbital to form a stable piano chair titanium species.

Nevertheless, when the reaction of **1** or **2** with triflic acid was carried out in the presence of a Lewis base, such as water, pyridine, or *tert*-butylpyridine, the cationic complexes [Cp*TiL{(OCH$_2$)$_2$py}]$^+$OTf$^-$ (**3**−**5**) and [Cp*TiL{(OOC)$_2$py}]$^+$OTf$^-$ (**6**, **7**) were isolated as air- and moisture-sensitive orange solids (Scheme 1).

In contrast to the behavior of **1**, complex **2** reacts with water and triflic acid to yield the neutral oxo derivative [Cp*Ti{(OOC)$_2$py}]$_2$(O), which has recently been described by us.[11]

These complexes are soluble in chloroform, dichloromethane, and acetonitrile but insoluble in THF, toluene, pentane, and diethyl ether. The lack of solubility in nonpolar solvents is related to the cationic nature of this family of compounds.

Complexes **3**−**7** were characterized by spectroscopic techniques. In the ^{1}H NMR spectra the resonance for the Cp* ligand appears at ca. 1.8 ppm for the alkoxide complexes (**3**−**5**) and ca. 1.9 ppm for the carboxylate species (**6** and **7**). In both cases this signal is significantly upfield from those of the parent neutral methyl compounds (2.11 ppm (**1**),[10] 2.03 ppm (**2**)[11]). Additionally, the most remarkable feature of the resonances in the ^{1}H NMR spectra of the alkoxide ligand of complexes **3**−**5** is the

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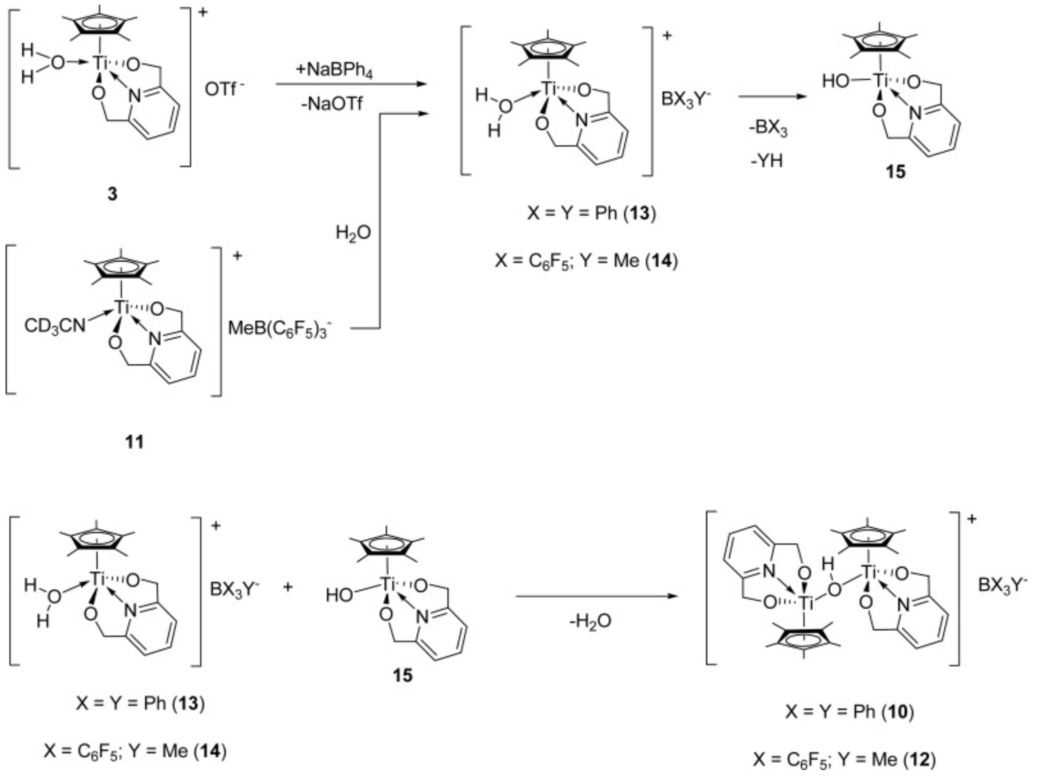
Scheme 5



presence of two doublets ($^2J_{H-H}$ = 18.32 Hz) at around 5.5 and 5.7 ppm, which correspond to the inequivalent protons of the methylene moiety, and two multiplet signals at around 7.4 and 7.9 ppm for the pyridinic aromatic protons. For complexes **6** and **7** the carboxylate pyridinic signals appear in the ^{1}H NMR spectra at around 8.1 and 8.3 ppm.

Given that both types of Lewis base (water and pyridines) stabilize the cationic compounds, it was decided to use 2,6-pyridinedimethanol and 2-pyridinemethanol as alternative bases, due to the presence of a pyridinic nitrogen and hydroxyl groups in these compounds. With this idea in mind, we synthesized compounds **8** and **9** (Scheme 2).

Complexes **8** and **9** were isolated as air- and moisture-sensitive orange solids. The complexes are soluble in chloroform, dichloromethane, and acetonitrile but insoluble in THF, toluene, pentane, and diethyl ether.

A binuclear formulation is proposed for **8**, with the 2,6-pyridinemethanol behaving as a bridging ligand. The ^{1}H NMR spectrum of **8** shows a broad signal at 4.87 ppm corresponding to the OH groups of the bridging ligand. Regarding the resonances of the methylene groups, while the equivalent methylenes of the bridging ligand give rise to a singlet at 5.01 ppm, the CH_2 groups from the pincer ligands exhibit an AB spin system (5.51 ppm, d, $^2J_{H-H}$ = 18.32 Hz and 5.75 ppm, d, $^2J_{H-H}$ = 18.32 Hz), which is consistent with the proposed coordination mode (see Scheme 2).

The spectroscopic data for compound **9** indicate the presence of 2-pyridinemethanol coordinated to the metal center. In the ^{1}H NMR spectrum the methylene group of the 2-pyridinemethanol ligand appears as a singlet at 5.84 ppm, while the signals of the pincer ligand appear as an AB system for the CH_2 groups and as an ABX system for the pyridinic protons. All these data point to a symmetrical disposition of the auxiliary alcohol in relation to the rest of the molecule, and a monodentate coordination of this ligand through the OH group with free rotation around the methylene fragment is proposed. Nevertheless, the spectroscopic data do not allow us to rule out an alternative coordination mode through the pyridinic nitrogen atom. Alternatively, taking account of the oxophilicity of titanium and the relative alcohol acidity and pyridine basicity,[14] a monodentate coordination through the O atom, with the proton transferred to the pyridinic nitrogen after coordination (see form **9b** in Scheme 2), cannot be ruled out.

Borate anions have been widely used as counterions to stabilize cationic titanium compounds. One of the most widely used synthetic strategies for the preparation of cationic complexes containing borate anions is the reaction of an alkyl complex with $B(C_6F_5)_3$[15] or borates.[16] However, it is also possible to generate these compounds through anion metathesis by reaction of a cationic complex with a borate.

The latter methodology was used when 1 equiv of sodium tetraphenylborate was added to a solution of complex **3** in dichloromethane and, in an unusual process, complex **10** was isolated as the only organometallic product (see Scheme 3).

In order to avoid the presence of water, we also tested the reaction of **1** with HOTf in the presence of $NaBPh_4$. In this case complex **10** was again isolated as the only organometallic compound.

In the same way, treatment of complex **1** with $B(C_6F_5)_3$ in pentane gave the cationic complex **12** (Scheme 4). Once again

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Table 1. Crystal Data and Structure Refinement Details for 10 and 12

	10	12
empirical formula	$[C_{34}H_{44}N_2O_5Ti_2]$-$[B(C_6H_5)_4]$	$[C_{34}H_{44}N_2O_5Ti_2]$-$[B(C_6F_5)_3CH_3]$
formula wt	975.72	1183.54
temp (K)	100(2)	100(2)
wavelength (Å)	1.541 78	0.710 73
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1$
a (Å)	12.3221(6)	9.3403(9)
b (Å)	13.4653(6)	13.891(1)
c (Å)	18.9223(9)	19.363(2)
α (deg)	87.364(2)	92.535(5)
β (deg)	79.293(2)	
γ (deg)	89.547(2)	
V (Å^3)	3081.7(3)	2509.8(4)
Z	2	2
calcd density (g/cm^3)	1.052	1.566
abs coeff (mm^{-1})	2.529	0.425
F(000)	1030	1206
cryst size (mm^3)	0.10 × 0.05 × 0.03	0.19 × 0.12 × 0.10
index ranges	$-14 \leq h \leq 13$ $-13 \leq k \leq 14$ $-19 \leq l \leq 21$	$-11 \leq h \leq 11$ $-15 \leq k \leq 17$ $-23 \leq l \leq 23$
no. of rflns collected	16 536	29 599
no. of indep rflns	8574 (R(int) = 0.0462)	9611 (R(int) = 0.0940)
no. of data/restraints/ params	8574/0/623	9611/1/714
goodness of fit on F^2	0.886	0.972
final R indices ($I > 2\sigma(I)$)	R1 = 0.0532, wR2 = 0.1253	R1 = 0.0546, wR2 = 0.1229
R indices (all data)	R1 = 0.0813, wR2 = 0.1351	R1 = 0.0879, wR2 = 0.1493
absolute structure param		−0.03(3)
largest diff peak, hole (e/Å^3)	0.463, −0.265	0.322, −0.537

Table 2. Bond Lengths (Å) and Angles (deg) for 10 and 12

10		12	
Bond Lengths			
Ti(1)−O(1)	2.099(2)	Ti(1)−O(1)	2.049(4)
Ti(1)−O(2)	1.898(2)	Ti(1)−O(2)	1.895(4)
Ti(1)−O(5)	1.829(3)	Ti(1)−O(5)	1.817(3)
Ti(1)−N(1)	2.173(3)	Ti(1)−N(1)	2.142(5)
Ti(1)−C(8)	2.386(4)	Ti(1)−C(8)	2.429(6)
Ti(1)−C(9)	2.349(4)	Ti(1)−C(9)	2.376(6)
Ti(1)−C(10)	2.332(4)	Ti(1)−C(10)	2.339(5)
Ti(1)−C(11)	2.372(4)	Ti(1)−C(11)	2.393(5)
Ti(1)−C(12)	2.390(5)	Ti(1)−C(12)	2.417(6)
Ti(2)−O(3)	1.906(2)	Ti(2)−O(3)	1.905(3)
Ti(2)−O(4)	2.070(2)	Ti(2)−O(4)	2.096(3)
Ti(2)−O(5)	1.816(3)	Ti(2)−O(5)	1.815(3)
Ti(2)−N(2)	2.162(3)	Ti(2)−N(2)	2.146(4)
Ti(2)−C(25)	2.410(4)	Ti(2)−C(25)	2.406(6)
Ti(2)−C(26)	2.438(4)	Ti(2)−C(26)	2.355(6)
Ti(2)−C(27)	2.414(4)	Ti(2)−C(27)	2.363(6)
Ti(2)−C(28)	2.349(3)	Ti(2)−C(28)	2.405(5)
Ti(2)−C(29)	2.336(3)	Ti(2)−C(29)	2.395(5)
Bond Angles			
O(1)−Ti(1)−N(1)	71.0(1)	O(1)−Ti(1)−N(1)	71.6(2)
O(2)−Ti(1)−N(1)	73.7(1)	O(2)−Ti(1)−N(1)	74.2(2)
O(5)−Ti(1)−N(1)	129.2(1)	O(5)−Ti(1)−N(1)	126.6(2)
O(2)−Ti(1)−O(1)	135.7(1)	O(2)−Ti(1)−O(1)	138.9(2)
O(5)−Ti(1)−O(1)	85.1(1)	O(5)−Ti(1)−O(1)	87.3(1)
O(5)−Ti(1)−O(2)	97.3(1)	O(5)−Ti(1)−O(2)	95.4(2)
O(3)−Ti(2)−N(2)	73.8(1)	O(3)−Ti(2)−N(2)	74.5(2)
O(4)−Ti(2)−N(2)	71.5(1)	O(4)−Ti(2)−N(2)	71.2(ss1)
O(5)−Ti(2)−N(2)	131.1(1)	O(5)−Ti(2)−N(2)	124.4(2)
O(5)−Ti(2)−O(3)	96.9(1)	O(5)−Ti(2)−O(3)	95.3(1)
O(5)−Ti(2)−O(4)	86.3(1)	O(5)−Ti(2)−O(4)	86.1(1)
O(3)−Ti(2)−O(4)	136.1(1)	O(3)−Ti(2)−O(4)	139.1(2)
Ti(2)−O(5)−Ti(1)	154.8(1)	Ti(2)−O(5)−Ti(1)	154.6(2)

the presence of adventitious water drives the process toward the formation of a hydroxo-containing binuclear species.

Complexes **10** and **12** were isolated as air- and moisture-sensitive orange solids that are soluble in THF, dichloromethane, and acetonitrile but insoluble in pentane and diethyl ether.

In order to avoid the presence of molecules of water, the reaction of **1** with $B(C_6F_5)_3$ was performed in an NMR tube by direct distillation of dry CD_3CN over the reactants. Under these conditions the formation of intermediate **11** can be observed spectroscopically (see Scheme 4), but all attempts to isolate this compound on a preparative scale were unsuccessful. Compound **12** was formed quantitatively when 1 equiv of water was added to the solution in the NMR tube.

It is worth noting that the cationic moieties in complexes **10** and **12** are identical.

An interesting point for discussion is the potential route for the formation of these complexes. It is well documented that borate anions $[BR_4]^-$ can decompose on reaction with the acidic protons of a ligand with elimination of the borane BR_3 and RH.[17] Taking into consideration this well-known behavior, it is reasonable to propose that the formation of intermediates **13** and **14** is followed by decomposition of the appropriate BX_3Y^- group to give BX_3, YH, and the intermediate **15**. The last species would subsequently react with a second molecule of **13** or **14** to generate the final product **10** or **12** (see Scheme 5).

A key step in this proposed route corresponds to protonolysis of the C−B bond in the appropriate borate in **13** and **14** by a proton from the coordinated water molecule. This process would give rise to the borane BX_3, YH, and **15**. On the basis of this explanation the important role played by water in the protonolysis process is very clear. The consumption of the proton in this process would displace the equilibrium to the right.

In order to gain an insight into the proposed mechanism, the reaction of complex **3** with $NaBPh_4$ was performed in $CDCl_3$ in an NMR tube. The formation of benzene and BPh_3 (^1H NMR ($CDCl_3$, 293 K) δ (ppm) 7.44−7.79; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ (ppm) 127.8, 131.7, 135.3) was confirmed.

The molecular structures of compounds **10** and **12** were established by X-ray diffraction methods, and these studies confirmed that their cationic moieties are almost identical. Some selected bond distances and angles for the two complexes are given in Table 2 and, as an example, an ORTEP view of the cationic moiety of **10** is shown in Figure 1.

The structural data for complexes **10** and **12** are very similar. The Ti−O(alkoxide) distances fall within the expected range for titanium complexes with alkoxide ligands.[18] The distances between the titanium atoms and the bridging oxygen are consistent with those reported for similar titanium μ-OH complexes.[19] With regard to the Ti−N distances, these are comparable to those found in related complexes.[11]

The most remarkable feature in both structures is the torsion existing in the coordination sphere of the titanium atoms, a phenomenon not observed in similar compounds.[11] This torsion causes differences between the O(alkoxide)−Ti−O(bridge) angles in each titanium moiety, which are around 8−12°. For example, in the structure shown in Figure 1 the angle O(5)−Ti(1)−O(1) is 85.1°, while the O(5)−Ti(1)−O(2) angle increases to 97.3°. For Ti(2) these angles are O(5)−Ti(2)−O(4) = 86.3° and O(5)−Ti(2)−O(3) = 96.9°.

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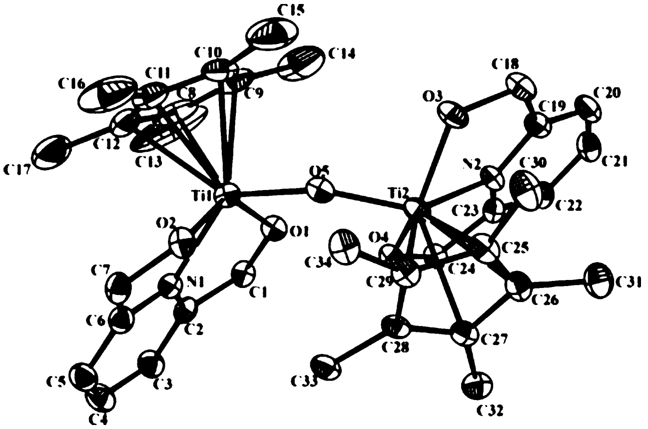


Figure 1. ORTEP drawing of the cationic moiety of compound **10** with thermal ellipsoids shown at 30% probability.

A similar situation is also observed in the difference between the two Ti−O(alkoxide) distances in each Ti−ligand moiety. For example, the Ti(1)−O(2) distance is 1.898 Å, whereas the Ti(1)−O(1) distance is slightly longer at 2.099 Å. For the Ti(2) atom these distances are Ti(2)−O(3) = 1.906 Å and Ti(2)−O(4) = 2.070 Å.

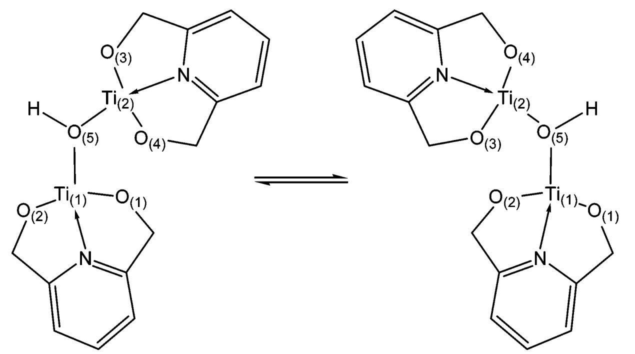
Comparable differences in angles and distances are also observed for the two titanium atoms of complex **12** (see Table 2).

These data could indicate the presence of a hydrogen atom linked to O(5) to form a bridging OH group that forces asymmetry on the molecule. This hydrogen atom has not been located.

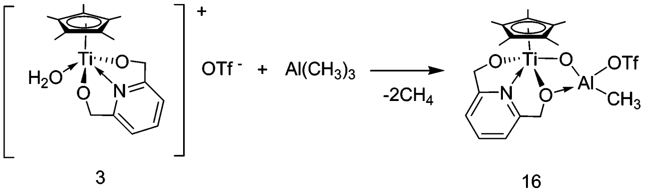
The ^{1}H NMR spectrum of **10** at 293 K shows a singlet at 1.75 ppm, and this corresponds to the methyl groups of the Cp* ring. The multiplets for the aromatic protons are observed at 6.90, 7.05, 7.49, and 7.69 ppm, while it was not possible to observe the resonance of the OH group. Moreover, the methylene groups of the pincer ligands appear as a very broad signal centered at 5.29 ppm, indicating that a dynamic behavior takes place in solution. In order to gain an insight into this fluxional process, a VTNMR experiment was carried out in $CDCl_3$. When the ^{1}H NMR spectrum was recorded at 218 K, four different doublet signals corresponding to the methylene groups of the pyridine ligand fragments were found, indicating that the twisting of the Ti−O−Ti fragment is hindered (Scheme 6). As the temperature increases, that twisting becomes easier, and at temperatures above the coalescence, 258 K, only two doublets are observed for the methylene groups. This coalescence temperature and the two site exchange equations[20] were used to estimate a value of $\Delta G^{\ddagger} = 11.8(3)$ kcal mol^{-1} for the exchange process ($\delta\nu = 209.486$ Hz).

Furthermore, the ^{1}H NMR spectrum of complex **12** in CD_2Cl_2 at room temperature shows two doublets ($^2J_{H-H} = 18.32$ Hz) at 5.52 and 5.79 ppm for the methylene groups of the pyridine ligand fragment, indicating that free rotation around the Ti−O−Ti fragment takes place at this temperature. In addition, singlets corresponding to the Cp* ligand protons at 1.82 ppm and methyl groups at 0.49 ppm are observed along with a broad signal attributable to the methyl group bonded to the boron atom. Finally, the multiplets due to the aromatic protons are observed at 7.47 and 8.05 ppm. As in the case of **10**, it was not possible to observe the resonance of the OH group of compound **12**.

Scheme 6



Scheme 7



Finally, the ability of the cationic complex **3** to form heterobimetallic complexes with aluminum was assessed, with the aim of improving our knowledge of the design and synthesis of new transition-metal precursors and main-group organometallic cocatalysts. In this field, Roesky and co-workers have recently prepared some stable heterobimetallic complexes of Al(III) with Zr,[21] Ti, and Hf,[22] respectively, binding through an oxygen bridge, and these complexes were active in olefin polymerization processes. It was found that complex **3** reacts with $AlMe_3$ to give the heterometallic complex **16** (see Scheme 7).

Complex **16** was isolated as an orange moisture-sensitive solid that is soluble in chloroform, dichloromethane, and acetonitrile but insoluble in THF, toluene, pentane, and diethyl ether.

The formation of **16** can be envisaged as being the result of a protonolysis process of two $Al-CH_3$ bonds by the coordinated water molecule to give a Ti−O−Al moiety. We propose a tetrahedral coordination for the Al center, as depicted in Scheme 7.

The NMR data are consistent with the proposed structural disposition. Indeed, the ^{1}H NMR spectrum shows a singlet at 0.98 ppm for the methyl group bonded to the aluminum atom and four different doublets for the protons of the two methylene groups, in accordance with an unsymmetrical disposition of the AlMeOTf fragment with respect to the pyridine-containing pincer ligand. This disposition was confirmed by the ^{13}C NMR spectrum, since two different signals are observed for the carbons of the methylene groups (see Experimental Section).

In summary, we report a series of cationic monocyclopentadienyl titanium complexes stabilized by a series of Lewis bases, such as pyridines, pyridinemethanol, and water, with the triflate counterion. In addition, the reaction of cationic (**3**) or neutral (**1**) complexes with $NaBPh_4$ and $B(C_6F_5)_3$ enabled the synthesis of cationic binuclear species containing an OH bridge; the noninnocent role of the borate anions in the reaction pathways of these latter processes constitutes one of the rare examples described for this kind of behavior. Furthermore, it

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(20) Abrahams, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*; Wiley: New York, 1988.

(21) Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449.

(22) Gurubasavaraj, P. M.; Mandal, S. K.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Noltemeyer, M. *Inorg. Chem.* **2007**, *46*, 1056.

was also discovered that **3** is an excellent building block for the preparation of an interesting heterometallic Ti−Al complex. Further studies aimed at expanding the chemistry of this type of complexes are in progress.

Experimental Section

The preparation and handling of the compounds described here was performed with exclusion of air and moisture under a nitrogen atmosphere using standard vacuum-line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere. The following reagents were prepared by literature procedures: $[Cp^*TiMe\{(OCH_2)_2py\}]$ (**1**),[10] $[Cp^*TiMe\{(O_2C)_2py\}]$ (**2**),[11] and $B(C_6F_5)_3$.[23] The commercially available compounds $(HOCH_2)_2py$, $(HOOCCH_2)_2py$, $Na[BPh_4]$, $AlMe_3$, pyridine, 4-*tert*-butylpyridine, and HOTf were used as received from Aldrich. ^1H and ^{13}C NMR spectra were recorded on a 200 Mercury Varian Fourier transform spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to $SiMe_4$. IR spectra were recorded in the region 4000−400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer.

Synthesis of $[Cp^*Ti(H_2O)\{(OCH_2)_2py\}]OTf$ (3). To a suspension of $[Cp^*TiMe\{(OCH_2)_2py\}]$ (**1**; 0.228 g, 0.679 mmol) in dichloromethane (5 mL) was slowly added triflic acid (0.060 mL, 0.679 mmol). The solution was stirred for 10 min at room temperature. H_2O (0.012 mL, 0.679 mmol) was added, and the resulting solution was stirred for 10 min at room temperature. The mixture was filtered, and the solvent was removed under vacuum. The resulting oil was washed with cool diethyl ether (5 mL) to afford an orange solid (0.188 g, 57%), which was characterized as complex **3**.

IR (KBr; cm^{-1}): 3432 (m), 2914 (m), 1608 (m), 1578 (w), 1441 (m), 1380 (w), 1256 (vs), 1285 (vs), 1236 (vs), 1162 (s), 1057 (s), 1030 (vs), 787 (m), 756 (m), 731 (m), 637 (s), 572 (w), 515 (w). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 1.79 (s, 15 H, Cp*), 2.20 (s, 2 H, H_2O), 5.55 (d, $^2J_{H-H} = 18.32$ Hz, 2 H), 5.77 (d, $^2J_{H-H} = 18.32$ Hz, 2 H), 7.45 (m, 2 H, Ar), 7.97 (m, 1 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): 12.0 (s, Cp*), 74.6 (s, CH_2), 119.1 (s, Cp*), 128.2 (s, Ar), 142.1 (s, Ar), 165.5 (s, Ar_{ipso}). $^{19}F\{^1H\}$ NMR ($CDCl_3$; δ (ppm)): −78.7. Anal. Calcd for $C_{18}H_{24}F_3NO_6STi$: C, 44.36; H, 4.96; N, 2.87. Found: C, 44.41; H, 4.91; N, 3.10.

Synthesis of $[Cp^*Ti(py)\{(OCH_2)_2py\}]OTf$ (4). To a suspension of $[Cp^*TiMe\{(OCH_2)_2py\}]$ (**1**; 0.310 g, 0.923 mmol) in dichloromethane (5 mL) was slowly added triflic acid (0.081 mL, 0.923 mmol). The resulting solution was stirred for 10 min at room temperature. Pyridine (0.074 mL, 0.923 mmol) was added, and the solution was stirred for 10 min at room temperature. The mixture was filtered and the solvent was removed under reduced pressure. The resulting oil was washed with cool pentane (5 mL) to afford an orange solid (0.455 g, 90%) which was characterized as complex **4**.

IR (Nujol/PET; cm^{-1}): 1601 (m), 1338 (w), 1277 (vs), 1223 (s), 1206 (w), 1152 (s), 1091 (m), 1062 (s), 1031 (s), 795 (w), 765 (w), 636 (s), 516 (w). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 1.78 (s, 15 H, Cp*), 5.53 (d, $^2J_{H-H} = 18.32$ Hz, 2 H), 5.76 (d, $^2J_{H-H} = 18.32$ Hz, 2 H), 7.43 (m, 2 H, Ar), 7.64 (m, 2 H, Ar-py), 7.95 (m, 1 H, Ar), 8.07 (m, 1 H, Ar-py), 8.57 (m, 2 H, Ar-py). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): 11.9 (s, Cp*), 74.7 (s, CH_2), 118.8 (s, Cp*), 126.5 (s, Ar), 127.4 (s, Ar-py), 141.9 (s, Ar), 146.8 (s, Ar-py); Ar_{ipso} was not found. $^{19}F\{^1H\}$ NMR ($CDCl_3$; δ (ppm)): −78.6. Anal. Calcd for $C_{23}H_{27}F_3N_2O_5STi$: C, 50.37; H, 4.96; N, 5.11. Found: C, 50.32; H, 4.81; N, 4.98.

Synthesis of $[Cp^*Ti(4\text{-}^tBu\text{-}py)\{(OCH_2)_2py\}]OTf$ (5). To a suspension of $[Cp^*TiMe\{(OCH_2)_2py\}]$ (**1**; 0.207 g, 0.616 mmol) in dichloromethane (5 mL) was slowly added triflic acid (0.054 mL, 0.616 mmol). The resulting solution was stirred for 10 min at room temperature. 4-^{t}Bu-py (0.091 mL, 0.616 mmol) was added, and the solution was stirred for 10 min at room temperature. The mixture was filtered, and the solvent was removed under reduced pressure. The resulting oil was washed with cool pentane (5 mL) to afford an orange solid (0.276 g, 74%), which was identified as **5**.

IR (Nujol/PET; cm^{-1}): 1650 (w), 1640 (m), 1608 (m), 1151 (s), 1093 (m), 1067 (vs), 631 (vs). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 1.39 (s, 9 H, ^{t}Bu), 1.79 (s, 15 H, Cp*), 5.55 (d, $^2J_{H-H} = 18.32$ Hz, 2 H), 5.78 (d, $^2J_{H-H} = 18.32$ Hz, 2 H), 7.44 (m, 2 H, Ar), 7.69 (m, 2 H, Ar-^{t}Bu-py), 7.94 (m, 1 H, Ar), 8.63 (m, 2 H, Ar-^{t}Bu-py). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): 11.9 (s, Cp*), 30.8 (s, ^{t}Bu), 36.7 (s, ^{t}Bu), 74.8 (s, CH_2), 118.8 (s, Cp*), 123.8 (s, Ar-^{t}Bu-py), 127.4 (s, Ar), 141.8 (s, Ar), 144.7 (s, Ar-^{t}Bu-py), 166.2 (s, Ar_{ipso}), 169.1 (s, Ar_{ipso}-^{t}Bu-py). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): −78.6. Anal. Calcd for $C_{27}H_{35}F_3N_2O_5STi$: C, 53.65; H, 5.84; N, 4.63;. Found: C, 53.89; H, 5.79; N, 4.55.

Synthesis of $[Cp^*Ti(py)\{(O_2C)_2py\}]OTf$ (6). To a suspension of $[Cp^*TiMe\{(O_2C)_2py\}]$ (**2**; 0.298 g, 0.820 mmol) in dichloromethane (5 mL) was slowly added triflic acid (0.072 mL, 0.820 mmol), and the solution was stirred for 10 min at room temperature. Pyridine (0.066 mL, 0.820 mmol) was added, and the resulting solution was stirred for 2 h at room temperature. The mixture was filtered and the solvent removed under reduced pressure. The resulting oil was washed with diethyl ether (5 mL) to afford an orange solid (0.409 g, 86%), which was characterized as complex **6**.

IR (Nujol/PET; cm^{-1}): 1330 (s), 1286 (s), 1226 (s), 1158 (s), 1030 (s), 757 (m), 684 (m), 644 (m), 636 (m), 576 (w), 519 (w). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 1.92 (s, 15 H, Cp*), 8.07 (m, 2 H, Ar), 8.12 (m, 2 H, Ar-py), 8.29 (m, 1 H, Ar-py), 8.51 (m, 1 H, Ar), 8.91 (m, 2 H, Ar-py). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): 12.7 (s, Cp*), 126.7 (s, Ar), 127.9 (s, Cp*), 132.0 (s, Ar-py), 142.7 (s, Ar-py), 145.6 (s, Ar), 146.6 (s, Ar_{ipso}-py), 150.3 (s, Ar_{ipso}), 166.5 (COO). ^{19}F $\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): −78.8. Anal. Calcd for $C_{23}H_{23}F_3N_2O_7STi$: C, 47.93; H, 4.02; N, 4.86. Found: C, 47.81; H, 3.98; N, 4.79.

Synthesis of $[Cp^*Ti(4\text{-}^tBupy)\{(O_2C)_2py\}]OTf$ (7). To a suspension of $[Cp^*TiMe\{(O_2C)_2py\}]$ (**2**; 0.173 g, 0.476 mmol) in dichloromethane (5 mL) was slowly added triflic acid (0.042 mL, 0.476 mmol), and the solution was stirred for 30 min at room temperature. 4-^{t}Bu-py (0.070 mL, 0.476 mmol) was added, and the resulting solution was stirred for 1 h at room temperature. The reaction mixture was filtered and the solvent removed under vacuum. The resulting oil was washed with cool diethyl ether (5 mL) to afford an orange solid (0.259 g, 86%), which was characterized as complex **7**.

IR (Nujol/PET; cm^{-1}): 1682 (vs), 1635 (s), 1608 (w), 1598 (w), 1340 (vs), 1282 (vs), 1230 (vs), 1162 (vs), 1077 (s), 1030 (s), 925 (m), 631 (s). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 1.43 (s, 9 H, ^{t}Bu), 1.91 (s, 15 H, Cp*), 7.97 (m, 2 H, Ar-^{t}Bu-py), 8.10 (m, 2 H, Ar-py), 8.25 (m, 1 H, Ar-py), 8.76 (m, 2 H, Ar-^{t}Bu-py). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): 12.7 (s, Cp*), 30.7 (s, ^{t}Bu), 37.5 (s, ^{t}Bu), 125.0 (s, Cp*), 126.7 (s, Ar), 132.0 (s, Ar-^{t}Bu), 141.7 (s, Ar), 145.6 (s, Ar-^{t}Bu), 150.3 (s, Ar_{ipso}-^{t}Bu), 166.6 (Ar_{ipso}), 173.6 (COO). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): −78.8. Anal. Calcd for $C_{27}H_{31}F_3N_2O_7STi$: C, 51.27; H, 4.94; N, 4.43. Found: C, 51.52; H, 4.96; N, 4.56.

Synthesis of $[\{Cp^*Ti((OCH_2)_2py)\}_2\{\mu\text{-}(HOCH_2)_2py\}]OTf_2$ (8). To a suspension of $[Cp^*TiMe\{(OCH_2)_2py\}]$ (**1**; 0.241 g, 0.717 mmol) in dichloromethane (5 mL) was slowly added triflic acid (0.063 mL, 0.717 mmol), and the solution was stirred for 15 min at room temperature. $(OHCH_2)_2py$ (0.049 g, 0.358 mmol) was added

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to this solution, and the resulting suspension was stirred for 2 h. The reaction mixture was filtered and the solvent removed under reduced pressure. The resulting oil was washed with diethyl ether (5 mL) to yield an orange solid (0.350 g, 90%), which was identified as **8**.

IR (Nujol/PET; cm^{-1}): 2365 (s), 2339 (s), 1635 (s), 1598 (s), 1577 (m), 1282 (vs), 1219 (s), 1062 (s), 1030 (vs), 783 (s), 641 (vs), 573 (s), 515 (s). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 1.77 (s, 30 H, Cp*), 4.87 (br, 2 H, μ-OH), 5.01 (s, br, 4 H, CH_2), 5.51 (d, $^2J_{H-H} = 18.32$ Hz, 4 H, CH_2), 5.75 (d, $^2J_{H-H} = 18.32$ Hz, 4 H, CH_2), 7.43 (m, 4 H, Ar), 7.78 (br, 2 H, Ar), 7.96 (m, 2 H, Ar), 8.36 (br, 1 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): 11.7 (s, Cp*), 61.3 (br, CH_2OH), 74.7 (br, CH_2O), 118.7 (s, Cp*), 124.4 (br, Ar), 125.3 (br, Ar), 127.4 (s, Ar), 141.9 (s, Ar), 143.2 (br, Ar), 144.5 (br, Ar), 158.3 (s, Ar_{ipso}), 166.0 (br, Ar_{ipso}). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): −78.6. Anal. Calcd for $C_{43}H_{53}F_6N_3O_{12}S_2Ti_2$: C, 47.92; H, 4.96; N, 3.90. Found: C, 47.74; H, 4.86; N, 3.87.

Synthesis of [Cp*Ti{(OCH$_2$)$_2$py}{(HOCH$_2$)py}]OTf (9). To a suspension of [Cp*TiMe{$(OCH_2)_2$py}] (**1**; 0.164 g, 0.488 mmol) in dichloromethane (5 mL) was slowly added triflic acid (0.043 mL, 0.488 mmol), and the solution was stirred for 15 min at room temperature. ($OHCH_2$)py (0.047 mL, 0.488 mmol) was added to this solution, and the suspension was stirred for 2 h. The reaction mixture was filtered and the solvent removed under reduced pressure. The resulting oil was washed with diethyl ether (5 mL) to yield an orange solid (0.157 g, 55%), which was identified as **9**.

IR (Nujol/PET; cm^{-1}): 2407 (m), 2307 (m), 1162 (s), 1077 (s), 1020 (s), 641 (m), 510 (m). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 1.79 (s, 15 H, Cp*), 5.04 (s, 1 H, OH), 5.56 (d, $^2J_{H-H} = 18.32$ Hz, 2 H, CH_2), 5.79 (d, $^2J_{H-H} = 18.32$ Hz, 2 H, CH_2), 5.84 (s, 2 H, CH_2), 7.43 (m, 2 H, Ar), 7.56 (br, 1 H, py), 7.72 (br, 1 H, py), 7.96 (m, 1 H, Ar), 8.29 (br, 1 H, py), 8.74 (br, 1 H, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): 11.8 (s, Cp*), 61.8 (br, CH_2OH), 74.7 (br, CH_2O), 118.7 (s, Cp*), 122.9 (br, Ar), 127.3 (s, Ar), 141.9 (s, Ar), 145.4 (br, Ar), 155.6 (s, Ar_{ipso}), 156.7 (br, Ar_{ipso}). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): −78.6. Anal. Calcd for $C_{24}H_{29}F_3N_2O_6STi$: C, 49.83; H, 5.05; N, 4.84 Found: C, 49.99; H, 5.12; N, 4.72.

Synthesis of [{Cp*Ti((OCH$_2$)$_2$py)}$_2$(μ-OH)][BPh$_4$] (10). To a suspension of [Cp*Ti(H_2O){$(OCH_2)_2$py}]OTf (**3**; 0.114 g, 0.233 mmol) in dichloromethane (5 mL) was added Na[BPh_4] (0.079 g, 0.233 mmol), and the mixture was stirred for 30 min at room temperature. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The resulting oil was washed with diethyl ether (5 mL) to yield complex **10** (0.096 g, 84%).

Slow diffusion of pentane into a THF solution of complex **10** at −30 °C afforded orange crystals of **10** suitable for an X-ray diffraction study.

IR (Nujol/PET; cm^{-1}): 1608 (m), 1566 (m), 1167 (m), 1088 (s), 1072 (vs), 1025 (vs), 505 (vs). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 1.75 (s, 30 H, Cp*), 5.29 (br, 8 H, CH_2), 6.90 (m, 4 H, Ar), 7.05 (m, 12 H, $ArBPh_4$), 7.49 (br, 8 H, $ArBPh_4$), 7.69 (m, 2 H, Ar). ^1H NMR ($CDCl_3$, 218 K; δ (ppm)): 1.75 (s, 30 H, Cp*), 4.79 (d, $^2J_{H-H} = 18.08$ Hz, 2 H, CH_2), 5.06 (d, $^2J_{H-H} = 18.08$ Hz, 2 H, CH_2), 5.52 (d, $^2J_{H-H} = 18.08$ Hz, 2 H, CH_2), 5.90 (d, $^2J_{H-H} = 18.08$ Hz, 2 H, CH_2), 6.95 (m, 4 H, Ar), 7.11 (m, 12 H, $ArBPh_4$), 7.52 (br, 8 H, $ArBPh_4$), 7.72 (m, 2 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): 11.9 (s, Cp*), (CH_2O not found), 118.7 (s, Ar), 122.5 (s, Ar), 126.3 (s, Ar), 127.3 (s, Ar), 128.0 (s, Cp*), 137.0 (s, Ar), 139.3 (s, Ar_{ipso}), 141.7 (s, Ar_{ipso}). Anal. Calcd for $C_{58}H_{65}BN_2O_5Ti_2$: C, 71.32; H, 6.71; N, 2.87. Found: C, 71.29; H, 6.56; N, 2.82.

Characterization by NMR of [Cp*Ti(CD_3CN){(OCH$_2$)$_2$py}][BMe(C_6F_5)$_3$] (11). To a solution of [Cp*TiMe{$(OCH_2)_2$py}] (**3**; 0.041 g, 0.122 mmol) in CD_3CN (freshly distilled) was added $B(C_6F_5)_3$ (0.062 g, 0.122 mmol), and immediate quantitative formation of **11** was detected by ^1H NMR spectroscopy.

^1H NMR (CD_3CN, 293 K; δ (ppm)): 0.50 (br, 3 H, Me−B), 2.04 (s, 15 H, Cp*), 5.66 (s, 4 H, CH_2), 7.30 (m, 2 H, Ar), 7.82 (m, 1 H, Ar). $^{13}C\{^1H\}$ NMR (CD_3CN, 293 K; δ (ppm)): 10.5 (s, Me−B), 11.6 (s, Cp*), 80.7 (s, CH_2), 116.7 (s, Cp*), 127.4 (s, Ar), 135.0 (br, $B(C_6F_5)_3$), 139.1 (s, Ar), 139.8 (br, $B(C_6F_5)_3$), 145.9 (br, $B(C_6F_5)_3$), 150.7 (br, $B(C_6F_5)_3$), 165.3 (s, Ar_{ipso}). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K; δ (ppm)): −134.2 (m, o-C_6F_5), −169.0 (m, p-C_6F_5), −167.6 (m, m-C_6F_5).

Synthesis of [{Cp*Ti((OCH$_2$)$_2$py)}$_2$(μ-OH)][BMe(C_6F_5)$_3$] (12). To a solution of [Cp*TiMe{$(OCH_2)_2$py}] (**1**; 0.128 g, 0.381 mmol) in pentane at −78 °C was added $B(C_6F_5)_3$ (0.195 g, 0.381 mmol), and the mixture was warmed to room temperature and then stirred for 3 h. The mixture was filtered, and the solvent was removed under vacuum to afford an orange solid (0.261 g, 80%), which was characterized as **12**. A diethyl ether solution at −30 °C afforded red crystals of complex **12**.

IR (Nujol/PET; cm^{-1}): 1650 (m), 1608 (m), 1577 (w), 1514 (s), 1083 (s), 1025 (m), 972 (s), 505 (m). ^1H NMR (CD_2Cl_2, 293 K; δ (ppm)): 0.49 (br, 3 H, Me−B), 1.82 (s, 30 H, Cp*), 5.52 (d, $^2J_{H-H} = 18.32$ Hz, 4 H, CH_2), 5.79 (d, $^2J_{H-H} = 18.32$ Hz, 4 H, CH_2), 7.47 (m, 4 H, Ar), 8.05 (m, 2 H, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K; δ (ppm)): 11.6 (s, Cp*), 56.6 (s, CH_2), 118.6 (s, Cp*), 127.6 (s, Ar), 134.9 (br, $B(C_6F_5)_3$), 140.1 (br, $B(C_6F_5)_3$), 141.9 (s, Ar), 146.3 (br, $B(C_6F_5)_3$), 150.9 (s, $B(C_6F_5)_3$); Me−B not found, Ar_{ipso} not found. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K; δ (ppm)): −136.5 (m, o-C_6F_5), −160.7 (m, p-C_6F_5), −166.0 (m, m-C_6F_5). Anal. Calcd for $C_{53}H_{48}BF_{15}N_2O_5Ti_2$: C, 53.74; H, 4.08; N, 2.37. Found: C, 53.67; H, 4.23; N, 2.41.

Synthesis of [Cp*Ti{(OCH$_2$)$_2$py}(μ-O-AlMeOTf)] (16). To a suspension of [Cp*Ti(H_2O){$(OCH_2)_2$py}]OTf (**3**; 0.148 g, 0.312 mmol) in dichloromethane (5 mL) at −40 °C was slowly added $AlMe_3$ (2 M in heptane) (188 μL, 0.376 mmol). The reaction mixture was warmed to room temperature and was stirred for 2 h. After filtration, the solvent was removed under vacuum and the residue was washed with diethyl ether (5 mL) to yield an orange solid (0.084 g, 51%), which was characterized as complex **16**.

IR (Nujol/PET; cm^{-1}): 1607 (m), 1578 (w), 1474 (w), 1446 (m), 1377 (w), 1340 (w), 1275 (s), 1239 (s), 1222 (s), 1158 (s), 1090 (m), 1067 (s), 1028 (vs), 785 (s), 745 (m). ^1H NMR ($CDCl_3$, 293 K; δ (ppm)): 0.98 (s, 3H, CH_3−Al), 1.88 (s, 15 H, Cp*), 5.00 (d, $^2J_{H-H} = 16.49$ Hz, 1 H, CH_2), 5.22 (d, $^2J_{H-H} = 16.49$ Hz, 1 H, CH_2), 5.78 (d, $^2J_{H-H} = 19.42$ Hz, 1 H, CH_2), 6.21 (d, $^2J_{H-H} = 19.42$ Hz, 1 H, CH_2), 7.39 (m, 1 H, Ar), 7.52 (m, 1 H, Ar), 8.03 (m, 1 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): −7.5 (s, Me−Al), 12.2 (s, Cp*), 69.4 (s, CH_2), 79.0 (s, CH_2), 118.9 (s, Ar), 119.4 (s, Ar), 129.5 (s, Cp*), 142.6 (s, Ar), 161.7 (s, Ar_{ipso}), 169.6 (s, Ar_{ipso}). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 293 K; δ (ppm)): −78.5. Anal. Calcd for $C_{19}H_{25}AlF_3NO_6STi$: C, 43.28; H, 4.78; N, 2.66 Found: C, 43.55; H, 4.85; N, 2.57.

X-ray Crystallography Data for 10 and 12. A summary of crystal data collection and refinement parameters for compounds **10** and **12** is given in Table 1.

A prismatic orange single crystal of **10** was mounted on a glass fiber and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer with a rotating anode (Cu Kα radiation, $\lambda = 1.541\,78$ Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA. X-ray data were collected at 100 K, with a combination of six runs at different φ and 2θ angles and 3600 frames. The data were collected using 0.3° wide ω scans (15 s/frame at $2\theta = 40°$ and 30 s/frame at $2\theta = 100°$), at a crystal-to-detector distance of 4.0 cm. A single crystal of a red block of **12** was placed in a Bruker-Nonius X8 APEXII CCD area-detector diffractometer, equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The data were collected using the full sphere data collection routine using 0.3° wide ω scans. For both compounds the substantial redundancy in data allows empirical absorption corrections (SADABS[24]) to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission: 0.573 341 for **10** and 0.7124 for **12**). The raw intensity data frames were integrated with the SAINT[25] program, which also applied corrections for Lorentz and polarization effects.

The software package SHELXTL[26] was used for space group determination, structure solution, and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by Patterson's method (SHELXS-97),[27] completed with difference Fourier syntheses, and refined with full-matrix least squares using SHELXL-97[28] minimizing $w(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit values S are based on F^2; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located in difference Fourier maps, but their positions were calculated geometrically and they were allowed to ride on their parent carbon atoms with fixed isotropic U values.

For **12**, the poor crystal quality led to a low value for completeness (only 87.4% for $\theta = 62.43°$). Above this value, we did not observe any reflections. Moreover, the crystal system is triclinic; for geometrical reasons, when the crystal system is triclinic, in our diffractometer it is very difficult to reach completeness above 92%.

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Supporting Information Available: Tables giving Cartesian coordinates (in Å) of the structures considered in this study and CIF files giving crystal data for **10** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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