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Convenient Synthesis of Cationic Titanium Complexes with Tridentate *Cp,N,P*-Ligand Framework: FLP-Like Reactivity at the Ti−N Bond and Unexpected Ligand Hydrogenation Reaction

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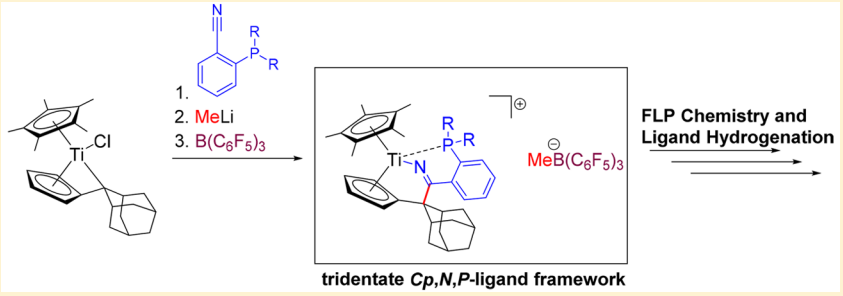
Supporting Information



ABSTRACT: The convenient synthesis of cationic titanium complexes **4a,b** is reported, starting from the titanium monopentafulvene complex **1** (Cp*Ti(Cl)(π-η^5:σ-η^1-C_5H_4=CR_2; CR_2 = adamantylidene) and the bidentate *P,N*-ligand precursor compounds **L1** and **L2** (2-$R_2PC_6H_4CN$; R = Ph, ^{i}Pr) with a nitrile functional group each and differently substituted phosphine moieties. In effect, **4a,b** feature novel tridentate *Cp,N,P*-ligand systems, which were introduced directly into the coordination sphere of the titanium in conclusive two-step syntheses. Complexes **4a,b** react under mild conditions with acetone and phenylacetylene selectively at the Ti−N bond in a FLP-like manner to give the corresponding complexes **5a,b** and **6a,b** via protonation of the nitrogen and addition of the anionic enolate and acetylide moieties to the titanium. Addition of dihydrogen to a solution of **4b** at room temperature results in an unexpected hydrogenation reaction of the C=N bond of the ancillary *Cp,N,P*-ligand framework to yield complex **7b**. In order to obtain further insight into the ligand design with respect to enabling subsequent reactions, another cationic titanium complex **10** was prepared with a bidentate *Cp,N*-ligand framework bearing no phosphine functional group, starting from **1** and 4-chlorobenzonitrile. **10** does not react with acetone, phenylacetylene, or dihydrogen, and consequently only **10** could be reisolated, even under harsher reaction conditions, showing that the phosphorus donor side is mandatory for subsequent reactions in a FLP-like manner.

INTRODUCTION

The chemistry of frustrated Lewis pairs (FLPs) is based on the prevention of the formation of classic Lewis adducts either by steric or, although less often, by electronic features within these systems.[1] This topic is one of the most expanding fields in main-group chemistry in which the Lewis acid is usually a polyfluorinated arylborane.[1] Several groups have started to replace the Lewis acid by high-valent electrophilic group 4 complexes[2−4] to combine FLP-based small-molecule activation with homogeneous catalysis. Such transition-metal FLPs (tm-FLPs) have shown the activation of e.g. H_2[5,6] and carbon−halogen bonds and have been used as catalysts for amine−borane dehydrocoupling[7] and for the hydrogenations of alkenes,[8,9] alkynes,[8,9] and imines.[10]

The idea of integrating group 4 metal complexes as the Lewis acid component in FLP chemistry was recognized by Stephan et al. in 2005, who demonstrated that a titanium-based cationic phosphinimide complex, namely [CpTi(N=P^{t}Bu$_3$)Me][B(C_6F_5)$_4$] (**I**), did not undergo a Lewis acid−Lewis base interaction with the sterically encumbered phosphine P(*o*-tolyl)$_3$ (Scheme 1A).[11] Instead, on the basis of today's knowledge about FLPs, this system shows the activation of dichloromethane and reacts like an intermolecular Ti^+/PR_3 FLP. Ironically, due to this early example, titanium has been neglected as the Lewis acid component in FLP chemistry, whereas numerous examples involving Zr,[5,7−9,12−21] Hf,[15,20,22] and Ru[22−24] Lewis acids have been described in the literature. Later, Wass et al. reported on the synthesis of the cationic titanium phosphinoaryl oxide complex [$Cp_2TiOC_6H_4P^tBu_2$]-[$B(C_6F_5)_4$] (**II**) and its reactivity toward dihydrogen, one of the classic substrates used in FLP chemistry.[25] Interestingly, the reaction yielded the cationic titanium(III) hydride complex **III**, showing that the special redox properties of titanium can have a strong influence on the reactivity (Scheme 1B). In 2015, Erker and co-workers reported a series of cationic titanium aryloxy complexes with a pendant phosphine, which were unreactive toward dihydrogen and carbon dioxide. However, among these

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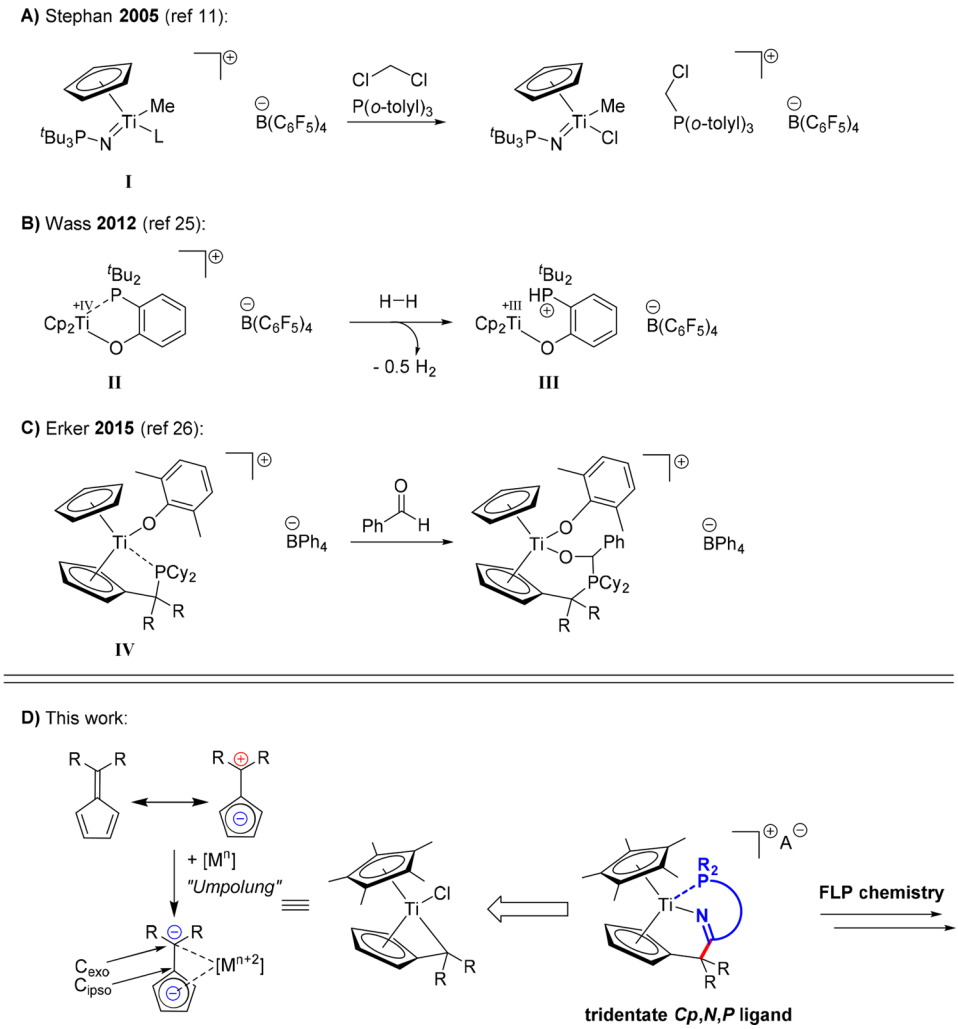
Scheme 1. Examples of Cationic Titanium-Based FLPs (A–C) and π-η^5:σ-η^1-bonding Mode and Attempted Synthesis of Cationic Titanium Complexes Bearing a Tridentate *Cp,N,P*-Ligand Framework (D)



complexes, [CpCp^{P}TiO(2,6-MeC$_6$H$_3$)][BPh$_4$] (**IV**) reacts with both benzaldehyde and an α,β-unsaturated carbonyl compound to form typical FLP activation products (Scheme 1C).[26]

We think that titanium-based FLPs are highly desirable, due to titanium being the secondmost abundant, and therefore rather inexpensive, transition metal in the earth's crust.[27,28]

We have recently presented a convenient, high-yielding, three-step synthesis of cationic group 4 complexes utilizing the special features of monopentafulvene complexes [Cp*M(Cl)-(π-η^5:σ-η^1-C$_5$H$_4$=CR$_2$)] and reacting those with bidentate *O,P*-ligand precursors to form a tridentate *Cp,O,P*-ligand framework directly in the coordination sphere of the particular group 4 metal.[29]

Herein, we report on an expansion of this synthetic strategy to form cationic complexes of titanium with a novel tridentate *Cp,N,P*-ligand framework with characteristics of tm-FLPs. In this regard the reactivity of these complexes toward dihydrogen, phenylacetylene, and acetone is presented and the first example of Ti–N metal–ligand cooperativity is found (Scheme 1D).

RESULTS AND DISCUSSION

Synthesis of Cationic Titanium Complexes with a *Cp,N,P*-Ligand Framework. We synthesized[30] and used the adamantylidene-substituted monopentafulvene complex **1** and the readily accessible bidentate *N,P* ligand precursors **L1** and **L2**, with different substitution patterns at the phosphorus, which were synthesized according to procedures known in the literature in a slightly modified way (Scheme 2).[31,32] Both ligand precursors were obtained in good yields of 60% and 87% as colorless (**L1**) and pale yellow (**L2**) solids, respectively. NMR data were recollected in C$_6$D$_6$ for reasons of comparison (δ(^{31}P{^{1}H}) −8.2 ppm (**L1**), 6.7 (**L2**)). It is worth noting that the air- and moisture-sensitive alkyl-substituted phosphanitrile **L2** was previously described as a yellow oil,[32] and therefore the melting point was measured additionally. Furthermore, crystals suitable for single-crystal X-ray diffraction were obtained and the X-ray structure was determined.[33]

The reactions of the monopentafulvene complex **1** with **L1** and **L2** in *n*-hexane at room temperature were accompanied by color changes to red and yielded the titanium complexes **2a,b** in very good to good isolated yields of 96% (**2a**) and 86% (**2b**). The reactions result from the insertion of the CN group into the Ti–C$_{exo}$ bond (Scheme 2). Whereas **2a** is nearly insoluble in aliphatic and aromatic solvents, **2b** shows very high solubilities in these solvents. Therefore, THF-d_8 was used as a solvent for the NMR experiments in the case of **2a**. The insertion reaction leads to the envisaged formation of a *Cp,N* σ,π-chelating ligand, directly in the coordination sphere of the

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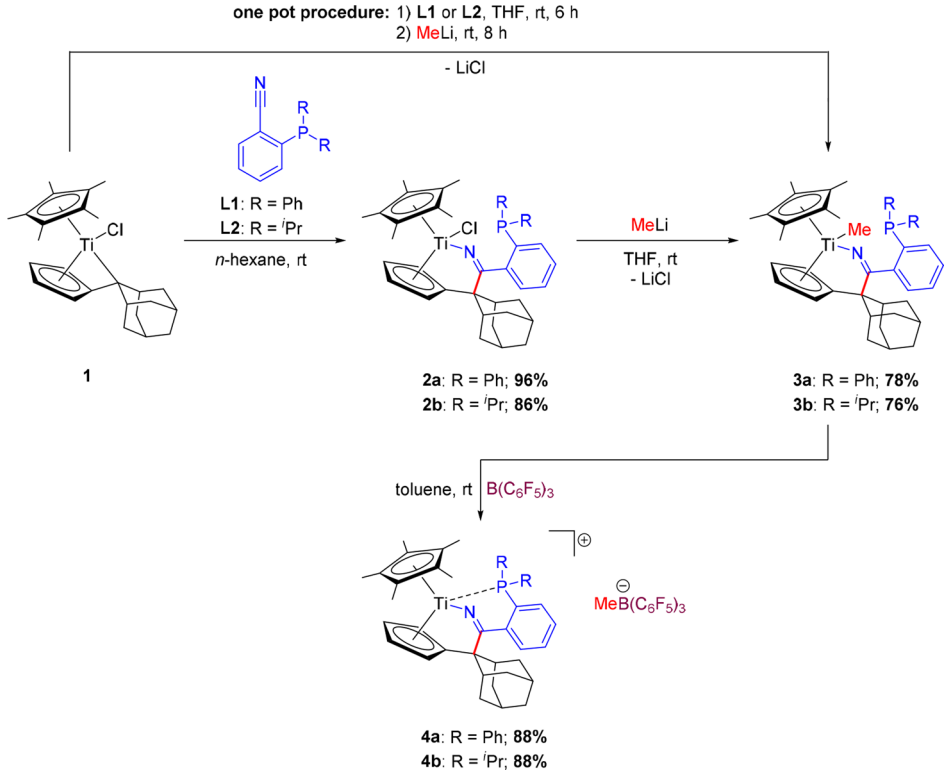
Scheme 2. Three-/Two-Step Synthesis of Cationic Titanium Complexes 4a,b



titanium center due to the formation of a new C−C bond between the C_{exo} and the carbon atom of the nitrile functional group.

Subsequent methylation of **2a,b** with methyllithium in THF under mild reaction conditions readily yielded the corresponding complexes **3a,b** in good yields of 78% and 76%, respectively, as red solids after purification. The solubility of **3a** in aliphatic and aromatic solvents is significantly increased in comparison to **2a**. The methylated complexes **3a,b** can also be prepared in a one-pot procedure.[33]

The air- and moisture-sensitive compounds **2a,b** and **3a,b** were thoroughly characterized by NMR analyses and, in the case of **2a** and **3a**, single-crystal X-ray diffraction.

Complexes **2a** and **3a** both crystallize in the monoclinic space group $P2_1/n$. The molecular structures (Figure 1) display pseudotetrahedral coordination environments at the titanium centers (Cl1−Ti1−N1 96.48(7)° (**2a**), N1−Ti1−C45 93.91(3)° (**3a**), Ct1−Ti1−Ct2 133.1° (**2a**), 134.6° (**3a**)).

The newly formed Ti1−N1 bonds in **2a** and **3a** with bond lengths of 1.948(2) and 1.9576(7) Å, respectively, are slightly shortened in comparison to typical Ti−N single bonds,[34,35] indicating attractive Ti(d_π)−N(p_π) interactions. Those values are comparable to those of titanaazavinylidenes[36] and similar complexes with *Cp,N σ,π*-chelating ligands[37] reported previously. The Ti1−Cl1 bond length of 2.3970(9) Å and the Ti1−C45 bond length of 2.1862(9) Å are typical of single bonds.[35] Furthermore, the N1−C26 distances of 1.267(3) Å (**2a**) and 1.2712(10) Å (**3a**) are in accordance with C=N double bonds (1.28 Å).[38] Due to strong ring strains as the result of the *σ,π*-chelating ligand, the newly formed C−C bonds C16−C26 (1.570(4) Å (**2a**), 1.5709(11) Å (**3a**)) are slightly elongated in comparison to a typical C(sp^3)−C(sp^3) single bond.[38] The carbon atom of the former nitrile functional group is now sp^2 hybridized in **2a** and **3a**, as indicated by the sum of angles around C26 (approximately 360°), and the C11−C16 bond lengths are elongated in comparison to the starting material **1**. They are now characteristic of C(sp^2)−C(sp^3) single bonds.[38]

The NMR data of **2a,b** and **3a,b** are consistent with the information obtained from the X-ray structures. It is worth noting that the NMR analyses of **2a** and **3a,b** show a double set of signals. The same was observed for the recently reported complex **V**,[29] but in contrast to **V**, the use of nonprochiral phosphanitriles does not lead to the generation of a second stereogenic center in addition to that of the titanium atom (Scheme 3). Therefore, a variable-temperature NMR experiment (−80 to +80 °C) of **3b** in toluene-d_8 was performed. At higher temperatures only one set of signals remains, indicating that the double set of signals is caused by the existence of two rotamers (Scheme 3). At higher temperatures only one of the rotamers is observed.[33]

The NMR data are summarized in Table 1 and are discussed as an example for **2b**. The ^{1}H NMR spectrum of **2b** shows at higher field four separate signals for the methyl groups and two signals for the C−H groups (masked by the signals of the adamantyl group) of the isopropyl moieties due to the diastereotopicitiy with characteristic coupling constants (e.g., $^3J_{P,H}(CH_3)$ = 12.7−13.8 Hz). Of high diagnostic value is the $^{13}C\{^1H\}$ chemical shift of the C_{exo} atom $\delta(^{13}C\{^1H\})$ 62.6 ppm, which is in the same range as for complex **V** and also significantly shifted toward higher field in comparison to **1**.[30] The $^{13}C\{^1H\}$ chemical shifts of the former nitrile carbon atom at $\delta(^{13}C\{^1H\})$ 198.8 ppm and of the C_{ipso} atom at $\delta(^{13}C\{^1H\})$ 154.1 ppm are in the same range as for related complexes reported previously.[37] The same relation applies for the Cp* and C_5H_4 moieties, and the carbon atoms close to the phosphorus show the expected characteristic coupling patterns. The $^{31}P\{^1H\}$ NMR spectrum of **3a** contains one resonance at

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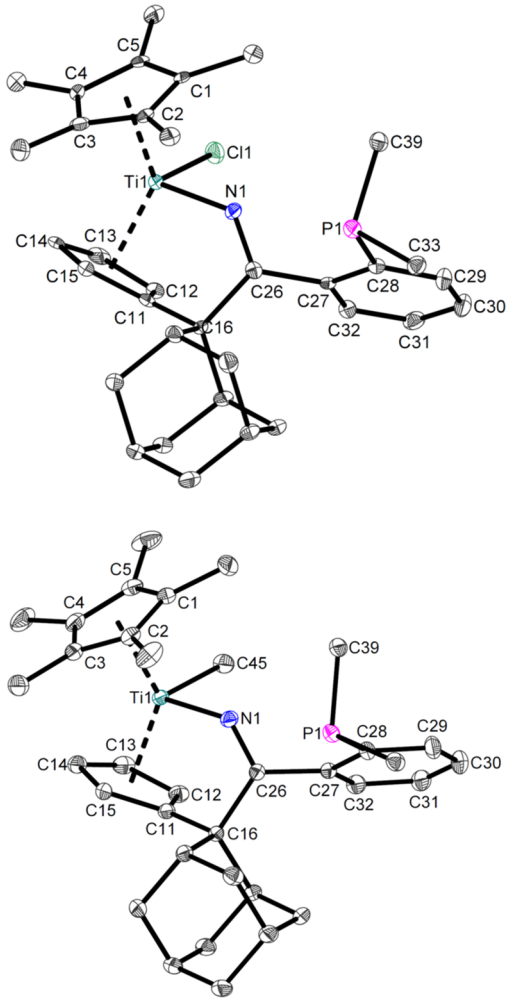


Figure 1. Molecular structures of **2a** (top) and **3a** (bottom). Hydrogen atoms and the phenyl groups of the phosphine moieties are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): **2a**, Ti1−N1 1.948(2), Ti1−Cl1 2.3970(9), Ti1···P1 5.38, N1−C26 1.267(3), P1−C39 1.831(3), C11−C16 1.524(4), C16−C26 1.570(4), Ti1−N1−C26 127.41(19), Cl1−Ti1−N1 96.48(7), Ct1−Ti1−Ct2 133.1 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15); **3a**, Ti1−N1 1.9576(7), Ti1−C45 2.1862(9), Ti1···P1 5.33, N1−C26 1.2712(10), P1−C39 1.8291(9), C11−C16 1.5243(11), C16−C26 1.5709(11), Ti1−N1−C26 123.58(6), N1−Ti1−C45 93.91(3), Ct1−Ti1−Ct2 134.6 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15).

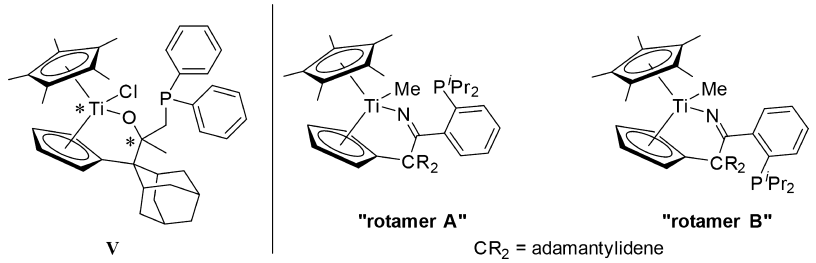
$\delta^{31}P\{^1H\}$ 1.1 ppm, which is in the same range as for the free **L2** ($\delta^{31}P\{^1H\}$ 6.7 ppm), indicating the same chemical environment at the phosphorus atom. The ^1H and $^{13}C\{^1H\}$ NMR signals of the terminal titanium methyl groups of **3a**,**b** are in the range for terminal monomethylated complexes of titanium.[29,39,40]

The abstraction of the methyl groups of **3a**,**b** with the highly Lewis acidic borane $B(C_6F_5)_3$ in toluene at room temperature resulted in the clean formation of the corresponding cationic complexes **4a**,**b** in isolated yields of 88% each as air- and moisture-sensitive pale yellow (**4a**) or pale orange (**4b**) solids (Scheme 2). The targeted tridentate *Cp*,*N*,*P*-ligand framework is directly introduced in the coordination sphere of the metal. **4a**,**b** are perfectly stable in the solid state and can be stored for months under inert conditions. Complexes **4a**,**b** are nearly insoluble in aromatic and aliphatic hydrocarbons, clearly indicating the formation of ionic species. Fortunately, **4a**,**b** both show adequate stability and solubility in dichloromethane, enabling multinuclear NMR spectroscopy for further characterization.

^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR data clearly confirm the abstraction of the methyl group by formation of the weakly coordinating anion $MeB(C_6F_5)_3^-$ (e.g., $\delta(^{11}B\{^1H\})$ −14.9 ppm; $\delta(^{19}F\{^1H\})$ −167.9 (*m*-F_{Ar}B), −165.4 (*p*-F_{Ar}B), −133.1 (*o*-F_{Ar}B) ppm; $\delta(^1H)$ 0.49 ppm). According to Horton et al. the $\Delta\delta(m,p\text{-F})$ values of 2.5 ppm confirm, that the borate anions are noncoordinating.[41,42] These parameters are in accordance with many other cationic complexes with this borate anion.[14,20] Of high diagnostic value are the $^{31}P\{^1H\}$ resonances of complexes **4a** ($\delta(^{31}P\{^1H\})$ 41.1 ppm) and **4b** ($\delta(^{31}P\{^1H\})$ 55.5 ppm), which are significantly shifted toward lower field (approximately 56 ppm in both cases) in comparison to their methylated precursor complexes **3a**,**b**. The low-field shift is an indicator for the persistent interaction between the Lewis acidic titanium center (as the result of cationization) and the Lewis basic phosphine moiety in both cases. This was also observed for the previously reported complexes derived from monopentafulvene complexes and bidentate *O*,*P*-ligand precursors[29] and other cationic complexes of group 4 metals with phosphorus side arms as cited in the Introduction. Other chemical shifts in the ^1H and $^{13}C\{^1H\}$ NMR spectra of the cationic titanium complexes **4a**,**b** are in the expected ranges, and the characteristic coupling patterns for the nuclei close to the phosphorus are observed, as well as signal splitting for the diastereotopic moieties (e.g., four signals in the ^1H NMR spectrum for the methyl groups of the isopropyl groups in **4b**). In addition, the formations of **4a**,**b** are positively supported by the results of high-resolution ESI mass spectrometry (clear detection of the M^+ signals).

Reactions of Cationic Complexes 4a,b with Acetone. Next, we envisaged to investigate the general reactivity of **4a**,**b** toward typical substrates that react with classic main-group- and tm-FLPs. In this context Wass et al. reported on the reaction of the zirconium tm-FLP **VI** with acetone.[5] It has been shown that

Scheme 3. Stereogenic Centers in V and Rotamers of 3b



V

CR$_2$ = adamantylidene

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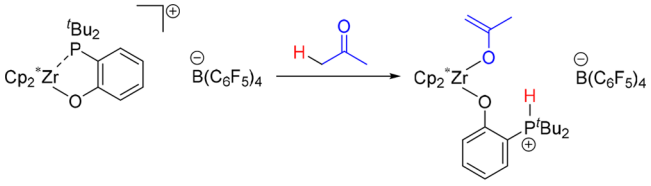
Table 1. Selected ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR Data of 2a,b and 3a,b[a]

	2a[b]	2b	3a[b]	3b
$\delta(^{1}H)/\delta(^{13}C\{^{1}H\})$ CH_3 ($^{3}J_{P,H}$)		1.04, 1.14, 1.21, 1.26 (12.7−13.8)		0.71, 1.00, 1.12, 1.22 (11.8−13.8)
$\delta(^{1}H)/\delta(^{13}C\{^{1}H\})$ $TiCH_3$			0.14	0.32
$\delta(^{13}C\{^{1}H\})$ $C_{q,exo}/C_{q,ipso}$	60.5/149.0	62.6/154.1	60.8/144.1	62.9/150.4
$\delta(^{13}C\{^{1}H\})$ CN	197.7	198.8	196.1	197.7
$\delta(^{31}P\{^{1}H\})$	−17.0	1.1	−15.0	0.2

[a]Values are given in ppm and J values in Hz. Measurements were carried out in C_6D_6 (**2b**, **3a**), toluene-d_8 (**3b**), and THF-d_8 (**2a**) at room temperature. [b]Only signals of the main rotamer are given.

the coordination of a remote functional group such as the carbonyl oxygen in acetone enables the deprotonation of the relatively acidic α-C−H group in acetone by the intramolecular phosphine group, leading to the zirconium enolate complex **VII** with a corresponding phosphonium functional group (Scheme 4).

Scheme 4. Reaction of Acetone wih the Zirconium tm-FLP VI by Wass et al.[5]



VI VII

In contrast, the reactions of **4a,b** with acetone lead surprisingly to the formation of the cationic titanium complexes **5a,b** as the result of deprotonation not by the phosphorus but by the nitrogen of the tridentate *Cp,N,P*-ligand and addition of the anionic enolate group to the titanium center (Scheme 5).

The reactions are accompanied by marginal color changes of the reaction mixtures after addition of acetone. Compounds **5a,b** show solubility properties similar to those of **4a,b** and are obtained as beige or yellow solids in isolated yields of up to 72%.

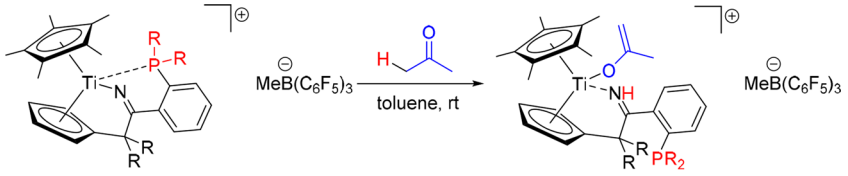
5a,b have been fully characterized by NMR measurements, and their M^+ signals were detected by high-resolution ESI mass spectrometry.

The addition of one α-hydrogen atom of the acetone to the nitrogen of the tridentate ligand framework is clearly demonstrated by the $^{1}H/^{15}N$ HMQC spectra, which reveal one signal each with chemical shifts of 273.9 (**5a**) and 276.8 (**5b**) ppm. These values are in the range of η^{1}-imine complexes of titanium.[36] The corresponding hydrogen atoms of the HN=C_q moieties are localized at $\delta(^{1}H)$ 8.63 (**5a**) and 8.74 (**5b**) ppm. These conspicuous low-field shifts can be explained by the previously described strong Ti(d_π)−N(p_π) interactions, which result in significant deshielding of the NH hydrogen atoms. The same interaction presumably leads to a shift toward lower field of the carbon atom of the HN=C_q moieties ($\delta(^{13}C\{^{1}H\})$ 214.5 (**5a**) and 216.2 (**5b**) ppm). The localization of the enolate groups at the titanium centers is verified by their ^{1}H and $^{13}C\{^{1}H\}$ chemicals shifts (e.g., for **5a** $\delta(^{1}H)$ 1.65 (s, 3H, OC_qCH_3), 3.86−3.88 (m, 2H, $OC_q=CH_2$) ppm and $\delta(^{13}C\{^{1}H\})$ 24.1 (OC_qCH_3), 87.5 ($OC_q=CH_2$), 170.8 (OC_q) ppm), which are in good agreement with complex **VII**.[5] The $^{31}P\{^{1}H\}$ NMR spectra of **5a,b** contain one resonance each, shifted to higher field at $\delta(^{31}P\{^{1}H\})$ −14.0 and −2.0 ppm, respectively. These values are only marginally different from the methylated complexes **3a,b**, which clearly indicates the absence of the coordination of the phosphorus to the metal center (Figure S73[33]).

Reactions of Cationic Complexes 4a,b with Phenylacetylene. After the successful activation of acetone at the Ti−N bond in **4a,b**, we were interested in the reactivity of **4a,b** toward a terminal acetylene, which is another substrate typically activated by Zr−P tm-FLPs and main-group FLPs in analogy to Scheme 5. By reaction of **4a,b** with phenylacetylene in toluene at room temperature an immediate but slight color change to red is observed, and after workup of the reaction mixtures the products **6a,b** were obtained as reddish solids in yields of 85% (**6a**) and 82% (**6b**) (Scheme 6).

Evaluation of the analytical data show that a typical frustrated Lewis pair reaction had taken place, but not at the M−P bond as previously described for numerous Zr−P tm-FLPs.[5,7−9,12−21] Instead, as for the reactions with acetone, the terminal alkyne is deprotonated by the nitrogen of the Ti−N moiety, and the resulting alkynyl units are bonded σ to the titanium atoms, which was verified by multinuclear NMR spectroscopy. As for **5a,b** the ^{1}H NMR HN=C_q resonances are located at $\delta(^{1}H)$ 8.09 (**6a**) and 8.28 (**6b**) ppm and the $^{1}H/^{15}N$ HMQC resonances are located at 282.6 (**6a**) and 284.2 (**6b**) ppm. The phosphorus leaves the coordination environment of the titanium centers, as indicated by the significant shift toward higher field ($\delta(^{31}P\{^{1}H\})$ −13.2 (**6a**) and 0.7 (**6b**) ppm). The

Scheme 5. Reactions of 4a,b with Acetone To Give the Cationic Titanium−Enolate Complexes 5a,b[a]



4a: R = Ph
4b: R = ^{i}Pr

5a: R = Ph; **61%**
5b: R = ^{i}Pr; **72%**

[a]CR_2 = adamantylidene.

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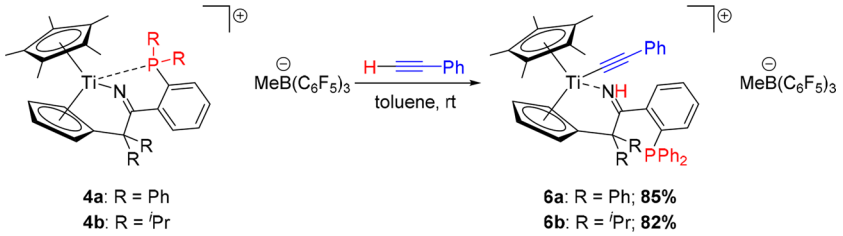
Scheme 6. Reactions of 4a,b with Phenylacetylene To Give the Cationic Titanium−Acetylide Complexes 6a,b[a]

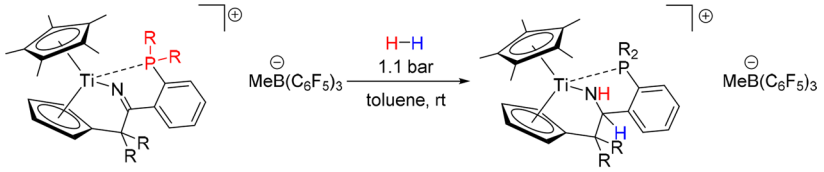


4a: R = Ph
4b: R = ^{i}Pr

6a: R = Ph; **85%**
6b: R = ^{i}Pr; **82%**

[a]CR_2 = adamantylidene.

Scheme 7. Reactions of 4a,b with Dihydrogen[a]

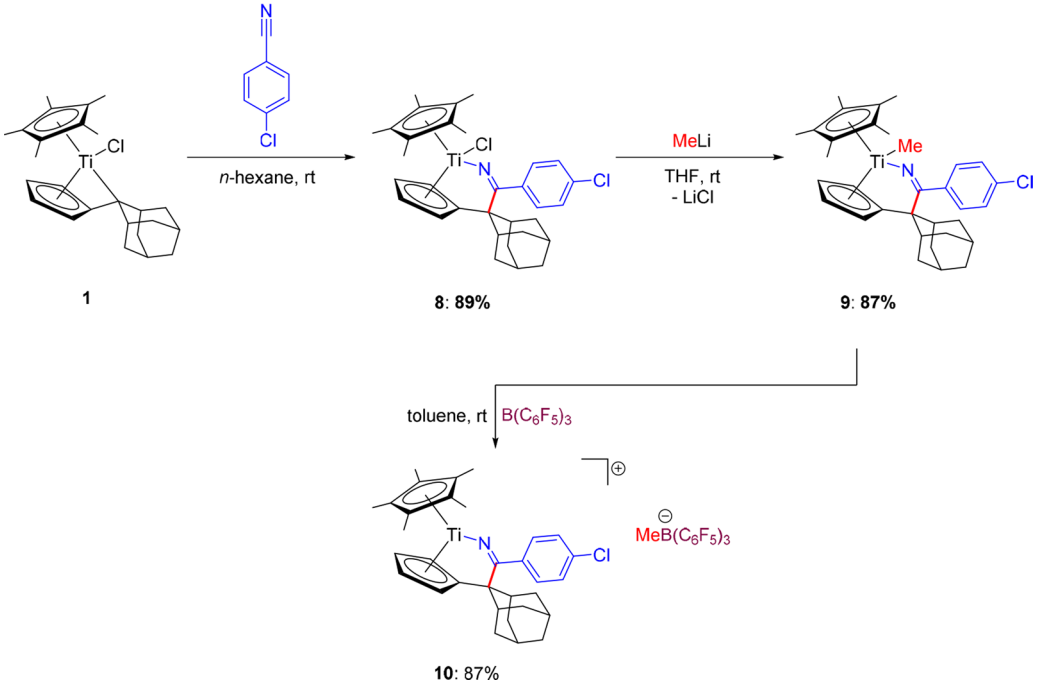


4a: R = Ph
4b: R = ^{i}Pr

7a: R = Ph; **no reaction**
7b: R = ^{i}Pr; **66%**

[a]CR_2 = adamantylidene.

Scheme 8. Synthesis of Cationic Titanium Complex 10 without the Phosphorus Side Arm



1

8: **89%**

9: **87%**

10: 87%

$^{13}C\{^{1}H\}$ resonances of the terminal alkynyl groups as well as the $\tilde{\nu}$(CC) stretching frequencies at 2061 (**6a**) and 2062 (**6b**) cm^{-1} are in good agreement with terminal titanium alkynyl complexes.[43,44]

Reactions of Cationic Complexes 4a,b with Dihydrogen. The heterolytic cleavage of dihydrogen to give the corresponding Zr−H phosphonium complexes in high yields and under mild conditions is one of the benchmark reactions of zirconium tm-FLPs.[5,6] The outcome of this reaction proves to be very sensitive to the nature of the ancillary ligand system. For example, the Cp_2 congener of **VI** is not able to cleave dihydrogen heterolytically, in contrast to the Cp_2* bearing **VI** itself. The only example of this reaction in the coordination sphere of titanium has been investigated for the titanium complex **II** mentioned in the Introduction and leads to the cationic Ti(III) hydride species **III**, indicating strong influence of redox properties.[11]

The addition of H_2 at 1.1 bar and room temperature to a solution of complex **4b** in toluene resulted in a slow color change. The $^{31}P\{^{1}H\}$ NMR spectrum reveals clean conversion to the new diamagnetic species **7b** with a chemical shift of $\delta(^{31}P\{^{1}H\})$ 58.4 ppm (Scheme 7).

The marginal shift toward lower field in comparison to starting complex **4b** ($\delta(^{31}P\{^{1}H\})$ 55.5) indicates that the phosphorus still shows a persistent interaction with the Lewis acidic titanium center. Interestingly, the addition of H_2

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occurred at neither the Ti−P nor the Ti−N bond. Instead, the C═N functional group of the tridentate *Cp,N,P*-ligand is selectively hydrogenated. To the best of our knowledge no other example of a hydrogenation of the pendant ligand system is known for cationic titanium complexes. The ^{1}H NMR spectrum of **7b** shows the two characteristic signals for the NHCH moiety, which are localized at $\delta(^{1}H)$ 5.67−5.70 ppm (m, 1H, NHCH; $\delta(^{13}C\{^{1}H\})$ 93.1 (d, $^{3}J_{C,P}$ = 2.1 Hz) ppm) and 9.62−9.63 ppm (m, 1H, NH; $\delta(^{15}N/^{1}H(HMQC))$ 324.8 ppm) and confirmed by ^{1}H/^{13}C HMQC and HMBC experiments. The latter shows the significant shift toward lower field. Furthermore, the M^{+} signal was detected by high-resolution ESI mass spectrometry.

Interestingly, the phenyl-substituted derivative **7a** was not obtained under the same reaction conditions, and even heating the reaction mixture to 70 °C for 5 days only led to isolation of the starting complex **4a**. Hence, the activation of dihydrogen seems to be highly sensitive to the nature of the ancillary ligand system so that the reaction of **4a** with dihydrogen does not result in the hydrogenation of the C═N moiety of the tridentate *Cp,N,P*-ligand framework. This ligand hydrogenation reaction of **4b** shows a new reaction pathway and is in contrast to the previously described titanium FLP-like system **VI** by Wass et al. and its reaction with dihydrogen which led to titanium(III) hydride species, showing that the special redox properties of titanium can occur quickly.

Insights into the Role of the Phosphorus: Synthesis of Cationic Titanium Complexes with a *Cp,N*-Ligand Framework. To obtain further insight into the role of the phosphorus, we prepared the cationic titanium complex **10** with a free coordination side, bearing a bidentate phosphorus-free *Cp,N* ligand, by reacting **1** with 4-chlorobenzonitrile and following the established route of methylation and final abstraction of the methyl group by $B(C_6F_5)_3$ (Scheme 8).

Compounds **8**−**10** were thoroughly characterized by multinuclear NMR spectroscopy among other analyses. The NMR data are in accordance with the other complexes reported herein.[33] In addition, we were able to determine the molecular structure of **9** by single-crystal X-ray diffraction, which is shown in Figure 2.

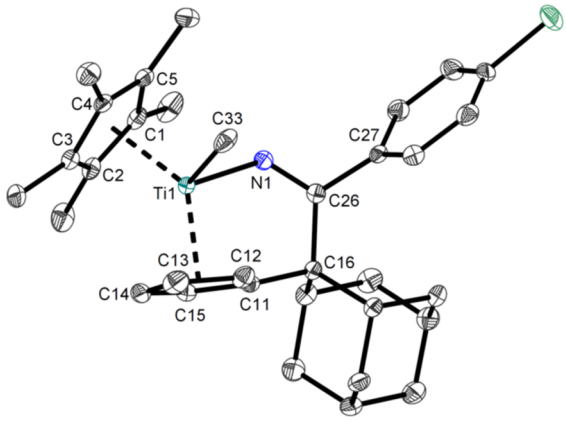

Figure 2. Molecular structure of **9**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1−N1 1.959(2), Ti1−C33 2.232(3), N1−C26 1.267(3), C11−C16 1.522(3), C16−C26 1.566(3), C26−C27 1.505(3), Ti1−N1−C26 123.78(17), C33−Ti1−N1 93.59(10), Ct1−Ti1−Ct2 134.9 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15).

We tested the reactions of **10** with acetone, phenylacetylene, and dihydrogen using the same reaction conditions as for the corresponding reactions of **4a,b**. Interestingly, no reaction yielded conversions to complexes related to the reactivities of **4a,b**. Only the starting complex **10** was reisolated in all cases, even when the reaction mixtures were heated for several days at 60 °C. These results lead to the conclusion that, although the reactions take place at the Ti−N bond, the phosphorus plays an important role in the reaction pathways, thus increasing the significance of the proper ancillary ligand framework.

SUMMARY AND CONCLUSION

In summary, we have discovered a convenient three-/two-step synthetic route, under very mild conditions, to yield the electrophilic cationic d^{0} complexes **4a,b**, starting from the corresponding monopentafulvene complex **1** and the bidentate *P,N*-ligand precursors **L1** and **L2**. Complexes **4a,b** feature a novel tridentate *Cp,N,P*-ligand system, which is built directly in the coordination sphere of the titanium by utilization of the general reactivity of **1**, subsequent methylation, and eventual generation of the cationic species by abstraction of the methyl group with $B(C_6F_5)_3$. It has been demonstrated that **4a,b** show efficient FLP-like reactivities in reactions with acetone and phenylacetylene by cooperativity between the earth-abundant first-row metals titanium and nitrogen. This is highly noteworthy due to the very limited number of tm-FLPs based on titanium so far. Additionally, reacting **4b** with dihydrogen results in the selective hydrogenation of the C═N bond of the ancillary tridentate *Cp,N,P*-ligand. This unexpected hydrogenation reaction might be relevant for reactions in which **4b** serves as catalytic hydrogenation precursor and shows a new reaction pathway of cationic d^{0} titanium complexes. Furthermore, the fact that **4a** does not react with dihydrogen, even under harsher reaction conditions, distinguishes the high sensitivity of the nature of the ancillary ligand system.

The fact that the reactions take place at the Ti−N bond, and not at the Ti−P bond, can be explained by the overall higher basicity of the nitrogen. The role of the phosphorus, however, and thereupon the decisive factors for the reactivities of the cationic titanium complexes **4a,b** are currently under investigation. Initial results reported herein, concerning the cationic titanium complex **10** with a *Cp,N*-ligand framework, missing the phosphine functional group, underline that, although the phosphorus does not directly take an observable part in the subsequent reactions, it seems to play an important role in the FLP-like reactivity.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an inert atmosphere of argon or nitrogen with rigorous exclusion of oxygen and moisture using standard glovebox and Schlenk techniques. The glass equipment was stored in an oven at 120 °C and evacuated prior to use. Solvents and liquid educts were dried according to standard procedures. Solvents were distilled over Na/K alloy and benzophenone or CaH_2 under nitrogen atmosphere. Solid materials were stored and weighed in a glovebox or dried under high vacuum before use. The methyllithium was used as a 1.6 M solution in diethyl ether, and the *n*-butyllithium was used as a 1.6 M solution in *n*-hexane.

The pentafulvene complex **1** was synthesized according to a literature procedure.[30] 2-Fluorobenzonitrile, 2-bromobenzonitrile, 4-chlorobenzonitrile, $ClPPh_2$, $ClP^{i}Pr_2$, and $HPPh_2$ were purchased from commercial sources. 2-Fluorobenzonitrile, 2-bromobenzonitrile, and 4-chlorobenzonitrile were used as received. $ClPPh_2$, $ClP^{i}Pr_2$, and $HPPh_2$ were distilled over $CaCl_2$ and stored under nitrogen.

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High-resolution mass spectra were measured on a Finnigan-MAT95 spectrometer using ESI.

Infrared spectra were performed on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

NMR spectra were recorded on Bruker Avance 300, Bruker Avance 500, and Bruker Avance III 500 spectrometers. ^{1}H NMR spectra were referenced to the residual solvent resonance as internal standard (benzene-d_6 (C_6D_6), $\delta(^{1}H)$ (C_6D_5H) 7.16 ppm; dichloromethane-d_2 (CD_2Cl_2), $\delta(^{1}H)$ ($CDHCl_2$) 5.32 ppm; toluene-d_8 (C_7D_8), $\delta(^{1}H)$ (C_7D_7H) 2.08 ppm (methyl group); tetrahydrofuran-d_8, $\delta(^{1}H)$ (C_4D_7HO) 1.72, 3.58 ppm) and $^{13}C\{^{1}H\}$ spectra were referenced by using the central line of the solvent signal (benzene-d_6 (C_6D_6), $\delta(^{13}C\{^{1}H\})$ (C_6D_6) 128.06 ppm; dichloromethane-d_2 (CD_2Cl_2), $\delta(^{13}C\{^{1}H\})$ (CD_2Cl_2) 53.84 ppm; toluene-d_8 (C_7D_8), $\delta(^{13}C\{^{1}H\})$ (C_7D_8) 20.43 (methyl group); tetrahydrofuran-d_8 $\delta(^{13}C\{^{1}H\})$-(C_4D_8O) 25.31, 67.21 ppm). $^{11}B\{^{1}H\}$ NMR, $^{19}F\{^{1}H\}$ NMR, and $^{31}P\{^{1}H\}$ NMR spectra were referenced against external standards ($BF_3{\cdot}OEt_2$, ($\delta(^{11}B\{^{1}H\})$ ($BF_3{\cdot}OEt_2$) 0.0 ppm; $CFCl_3$, $\delta(^{19}F\{^{1}H\})$ ($CFCl_3$) 0.0 ppm; H_3PO_4, $\delta(^{31}P\{^{1}H\})$ (H_3PO_4) 0.0 ppm). The given chemical shifts of ^{15}N NMR spectra resulted from $^{15}N/^{1}H$ HMQC/HMBC NMR experiments with nitromethane as external standard (δ 378.9 vs NH_3).

Elemental analyses were carried out on a EuroEA 3000 Elemental Analyzer. The carbon value in the elemental analysis is often lowered by carbide formation. The hydrogen value is found in some cases to be higher, due to residual traces of solvents.

Melting points were determined using a "Mel-Temp" apparatus by Laboratory Devices, Cambridge, U.K.

Synthesis and Characterization of Compounds. *Synthesis of L1.* (A) Compound **L1** was synthesized according to a slightly modified literature procedure.[31] To a suspension of KOH (1.940 g, 29.73 mmol; 86%) and 40 mL of DMSO was added diphenylphosphine (4.3 mL, 24.77 mmol). The suspension was stirred for 1 h, resulting in a color change to red followed by addition of 2-fluorobenzonitrile (2.7 mL, 24.77 mmol). The suspension was stirred for another 10 min, resulting in a color change to yellow. Addition of water results in the precipitation of a colorless solid. The solid was filtered, washed with water (3 × 10 mL), and recrystallized from methanol to obtain **L1** as a colorless solid.

(B) Compound **L1** was synthesized according to a slightly modified literature procedure.[32] To a solution of 2-bromobenzonitrile (1.963 g, 10.79 mmol) in 20 mL of THF was slowly added *n*-butyllithium (4.3 mL, 10.79 mmol; 2.5 M in hexane) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C followed by addition of chlorodiphenylphosphine (2 mL, 10.79 mmol) at −78 °C. The reaction mixture was stirred for 1 h, slowly warmed to room temperature, and stirred for another 16 h. All volatiles were removed under vacuum, and the residue was filtered and washed with toluene (3 × 12 mL). The solvent was removed under vacuum and the residue recrystallized from methanol to yield **L1** as a colorless solid.

Data for **L1** are as follows. Yield: 4.271 g (60%; procedure A); 1.282 g (41%; procedure B). ^{1}H NMR (500 MHz, C_6D_6, 299 K): δ 6.62−6.65 (m, 1H, C_6H_4), 6.74−6.77 (m, 1H, C_6H_4), 6.92−6.94 (m, 1H, C_6H_4), 7.01−7.03 (m, 6H, 4 × *o*-CH_{Ph}P, 2 × *p*-CH_{Ph}P), 7.08−7.10 (m, 1H, C_6H_4), 7.26−7.29 (m, 4H, 4 × *m*-CH_{Ph}P) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 299 K): δ 117.6 (d, $^{3}J_{C,P}$ = 4.0 Hz, CN), 118.7 (d, ^{2}JC,P = 33.1 Hz, $C_{q,C6H4}$CN), 128.7 (C_6H_4), 129.0 (d, $^{3}J_{C,P}$ = 7.2 Hz, 4 × *m*-CH_{Ph}P), 129.5 (2 × *p*-CH_{Ph}P), 131.9 (C_6H_4), 133.3 (C_6H_4), 133.7 (d, $J_{C,P}$ = 4.8 Hz, C_6H_4), 134.4 (d, $^{2}J_{C,P}$ = 20.6 Hz, 4 × *o*-CH_{Ph}P), 135.4 (d, $^{1}J_{C,P}$ = 2 × $C_{q,PhP}$), 143.3 (d, $^{1}J_{C,P}$ = 20.7 Hz, $C_{q,C6H4}$P) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 299 K): δ −8.2 ppm.

Synthesis of L2. Compound **L2** was synthesized according to a slightly modified literature procedure.[32] To a solution of 2-bromobenzonitrile (2.290 g, 12.58 mmol) in 20 mL of THF was slowly added *n*-butyllithium (5.0 mL, 12.58 mmol; 2.5 M in hexane) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C followed by addition of chlorodiisopropylphosphine (2 mL, 12.58 mmol) at −78 °C. The reaction mixture was stirred for 1 h, slowly warmed to room temperature, and stirred for another 16 h. All volatiles were removed under vacuum, and the residue was filtered and washed with toluene (3 × 12 mL). The solvent was removed under vacuum to yield **L2** as a yellow solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at −26 °C.

Data for **L2** are as follows. Yield: 2.400 g (87%). ^{1}H NMR (500 MHz, C_6D_6, 299 K): δ 0.75 (dd, $^{3}J_{P,H}$ = 11.5 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.93 (dhept, $^{2}J_{P,H}$ = 15.3 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 2H, $CH(CH_3)_2$), 6.68−6.73 (m, 1H, C_6H_4), 6.87−6.92 (m, 1H, C_6H_4), 7.08−7.12 (m, 1H, C_6H_4), 7.17−7.21 (m, 1H, C_6H_4) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 299 K): δ 19.0 (d, $^{2}J_{C,P}$ = 9.7 Hz, $CH(CH_3)_2$), 20.0 (d, $^{2}J_{C,P}$ = 19.4 Hz, $CH(CH_3)_2$), 23.7 (d, $^{1}J_{C,P}$ = 14.5 Hz, $CH(CH_3)_2$), 118.6 (d, $^{3}J_{C,P}$ = 3.4 Hz, CN), 121.6 (d, $^{2}J_{C,P}$ = 31.9 Hz, $C_{q,C6H4}$CN), 128.9 (C_6H_4), 131.0 (C_6H_4), 133.5 (d, $J_{C,P}$ = 1.2 Hz, C_6H_4), 133.8 (d, $J_{C,P}$ = 5.4 Hz, C_6H_4), 140.9 (d, $^{1}J_{C,P}$ = 29.2 Hz, $C_{q,C6H4}$P) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 299 K): δ 6.7 ppm.

Synthesis of 2a. Complex **1** (0.500 g, 1.199 mmol) and ligand precursor **L1** (0.345 g, 1.199 mmol) were suspended in 12 mL of *n*-hexane, resulting in a color change to red. The reaction mixture was stirred for 16 h at room temperature. The solvent was removed under vacuum to yield complex **2a** as a red solid. No further purification steps were required.

Due to poor solubility in C_6D_6 and toluene-d_8 and decomposition in CD_2Cl_2, THF-d_8 was used to for the NMR analyses.

Complex **2a** was obtained as a mixture of rotamers. Therefore, only the clearly assignable signals of the main rotamer (A) and the minor rotamer (B) are given in the analyses of the NMR data.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated toluene solution at −4 °C.

Data for **2a** are as follows. Yield: 0.815 g (72%). Mp: 102−104 °C dec. IR (ATR): $\tilde{\nu}$ 3052, 2956, 2905, 2852, 1587, 1478, 1470, 1452, 1434, 1373, 1310, 1237, 1205, 1163, 1116, 1100, 1063, 1044, 1026, 999, 984, 940, 924, 902, 902, 869, 847, 829, 804, 769, 741, 696, 676, 648, 632 cm^{-1}. ^{1}H NMR (500 MHz, THF-d_8, 305 K): δ(rotamer A) 1.74 (s, 15H, C_5Me_5), 5.30−5.32 (m, 1H, C_5H_4), 5.72−5.74 (m, 1H, C_5H_4), 5.82−5.84 (m, 1H, C_5H_4), 6.44−6.45 (m, 1H, C_5H_4) ppm; δ(rotamer B) 1.86 (s, 15H, C_5Me_5), 5.50−5.52 (m, 1H, C_5H_4), 5.61−5.63 (m, 1H, C_5H_4), 6.06−6.08 (m, 1H, C_5H_4), 7.00−7.02 (m, 1H, C_5H_4) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, THF-d_8, 305 K): δ(rotamer A) 12.66 (C_5Me_5), 60.5 ($C_{q,exo}$), 105.2 (C_5H_4), 111.3 (C_5H_4), 115.6 (C_5H_4), 117.2 (C_5H_4), 123.9 (C_5Me_5), 149.0 ($C_{q,ipso}$), 197.7 (C═N) ppm; δ(rotamer B) 12.72 (C_5Me_5), 62.7 ($C_{q,exo}$), 108.0 (C_5H_4), 108.4 (C_5H_4), 119.3 (C_5H_4), 119.8 (C_5H_4), 123.7 (C_5Me_5), 149.3 ($C_{q,ipso}$), 197.9 (C═N) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, THF-d_8, 305 K): δ(rotamer A) −17.0 ppm; δ(rotamer B) −15.8 ppm. HR/MS: calculated *m*/*z* 668.2926 [M − Cl$^-$]; measured (ESI) *m*/*z* 668.2930.

Synthesis of 2b. Complex **1** (0.515 g, 1.235 mmol) and ligand precursor **L2** (0.271 g, 1.235 mmol) were dissolved in 12 mL of *n*-hexane, resulting in a clear solution and a color change to red. The reaction mixture was stirred for 16 h at room temperature. The solvent was removed under vacuum to yield complex **2b** as a red solid. No further purification steps were required.

Data for **2b** are as follows. Yield: 0.672 g (86%). Mp: 56−58 °C dec. IR (ATR): $\tilde{\nu}$ 2948, 2903, 2860, 2361, 2342, 1588, 1453, 1374, 1261, 1234, 1202, 1155, 1122, 1100, 1063, 1040, 1022, 984, 925, 874, 850, 812, 793, 769, 749, 704, 689, 678, 634 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 305 K): δ 1.04 (dd, $^{3}J_{P,H}$ = 12.7 Hz, $^{3}J_{H,H}$ = 7.2 Hz, 3H, $CH(CH_3)_2$), 1.14 (dd, $^{3}J_{P,H}$ = 13.0 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.21 (dd, $^{3}J_{P,H}$ = 12.9 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.26 (dd, $^{3}J_{P,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.33−1.36 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 1.48−1.66 (m, 7H, $CH(CH_3)_2$, 6 × $CH_{Ad}/CH_{2,Ad}$), 1.82 (s, 15H, C_5Me_5), 1.92−1.99 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 2.06−2.18 (m, 2H, $CH(CH_3)_2$, $CH_{Ad}/CH_{2,Ad}$), 2.27−2.31 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.63−2.70 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.75−2.82 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.76−3.80 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 5.15−5.18 (m, 1H, C_5H_4), 5.47−5.50 (m, 1H, C_5H_4), 6.41−6.43 (m, 1H, C_5H_4), 6.99−7.03 (m, 1H, *p*-CH_{C6H4}P), 7.09−7.14 (m, 1H, *p*-CH_{C6H4}CN), 7.19−7.24 (m, 1H, *o*-CH_{C6H4}CN), 7.29−7.34 (m, 1H, *o*-CH_{C6H4}P), 7.35−7.39 (m, 1H, C_5H_4) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 305 K): δ 12.9 (C_5Me_5), 20.0 (d, $^{2}J_{C,P}$ = 13.4 Hz, $CH(CH_3)_2$),

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21.2 (d, $^{2}J_{C,P}$ = 16.9 Hz, $CH(CH_3)_2$), 21.3 (d, $^{2}J_{C,P}$ = 14.3 Hz, $CH(CH_3)_2$), 22.1 (d, $^{2}J_{C,P}$ = 14.4 Hz, $CH(CH_3)_2$), 24.7 (d, $^{1}J_{C,P}$ = 14.3 Hz, $CH(CH_3)_2$), 27.8 (CH_{Ad}), 28.1 (CH_{Ad}), 28.9 (d, $^{1}J_{C,P}$ = 14.7 Hz, $CH(CH_3)_2$), 33.8 ($CH_{2,Ad}$), 33.9 ($CH_{2,Ad}$), 34.0 (CH_{Ad}), 35.5 ($CH_{2,Ad}$), 35.8 ($CH_{2,Ad}$), 36.3 (CH_{Ad}), 39.2 ($CH_{2,Ad}$), 62.6 ($C_{q,exo}$), 106.4 (C_5H_4), 108.1 (C_5H_4), 116.4 (d, $^{TS}J_{C,P}$ = 12.4 Hz, C_5H_4), 121.4 (C_5H_4), 123.1 (C_5Me_5), 126.3 (*p*-CH_{C6H4}P), 127.8, (*p*-CH_{C6H4}CN)*, 128.5 (d, $^{3}J_{C,P}$ = 7.9 Hz, *o*-CH_{C6H4}CN), 132.0 (d, $^{2}J_{C,P}$ = 2.3 Hz, *o*-CH_{C6H4}P), 136.9 (d, $^{1}J_{C,P}$ = 20.5 Hz, $C_{q,C6H4}$P), 151.9 (d, $^{2}J_{C,P}$ = 33.6 Hz, $C_{q,C6H4}$CN), 154.1 ($C_{q,ipso}$), 198.8 (CN) ppm. * = overlap with C_6D_6 signal. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 305 K): δ 1.1 ppm. Anal. Calcd for $C_{38}H_{51}ClNPTi$: C, 71.75; H, 8.08; N, 2.20; Found: C, 71.38; H, 8.72; N, 2.12. HR/MS: calculated *m*/*z* 600.3239 [M − Cl^-]; measured (ESI) *m*/*z* 600.3234.

Synthesis of ***3a***. To a solution of complex **2a** (0.500 g, 0.710 mmol) in 15 mL of tetrahydrofuran was added a methyllithium solution (0.4 mL, 0.710 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 10 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 12 mL). All volatiles were removed under vacuum to give complex **3a** as a red solid.

Complex **3a** was obtained as a mixture of rotamers. Therefore, only the clearly assignable signals of the main rotamer (A) and the minor rotamer (B) are given in the analyses of the NMR data.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at −4 °C.

Data for **3a** are as follows. Yield: 0.381 g (78%). Mp: 116−118 °C dec. IR (ATR): $\tilde{\nu}$ 3051, 2901, 2853, 1586, 1479, 1451, 1433, 1374, 1308, 1239, 1204, 1185, 1161, 1117, 1099, 1063, 1026, 998, 983, 940, 923, 904, 865, 848, 808, 778, 767, 741, 694, 677, 651, 633 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 305 K): δ(rotamer A) 0.14 (s, 3H, $TiCH_3$), 1.67 (s, 15H, C_5Me_5), 5.00−5.01 (m, 1H, C_5H_4), 5.49−5.50 (m, 1H, C_5H_4), 5.64−5.65 (m, 1H, C_5H_4), 6.35−6.36 (m, 1H, C_5H_4) ppm; δ(rotamer B) −0.06 (s, 3H, $TiCH_3$), 1.71 (s, 15H, C_5Me_5), 4.78−4.79 (m, 1H, C_5H_4), 5.55−5.56 (m, 1H, C_5H_4), 5.90−5.91 (m, 1H, C_5H_4), 7.28−7.29 (m, 1H, C_5H_4) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 305 K): δ(rotamer A) 12.25 (C_5Me_5), 34.3 ($TiCH_3$)*, 60.8 ($C_{q,exo}$), 104.7 (C_5H_4), 107.7 (C_5H_4), 111.1 (C_5H_4), 114.7 (C_5H_4), 119.4 (C_5Me_5), 144.1 ($C_{q,ipso}$), 196.1 (C═N) ppm; δ(rotamer B) 12.28 (C_5Me_5), 42.1 ($TiCH_3$)*, 63.0 ($C_{q,exo}$), 105.8 (C_5H_4), 106.9 (C_5H_4), 114.0 (C_5H_4), 116.1 (C_5H_4), 119.1 (C_5Me_5), 150.0 ($C_{q,ipso}$), 196.5 (C═N) ppm. * = assignment by $^{1}H/^{13}C$ HMQC/HMBC spectra. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 305 K): δ(rotamer A) −15.0 ppm; δ(rotamer B) −12.1 ppm. HR/MS: calculated *m*/*z* 684.3239 [M + H^+]; measured (ESI) *m*/*z* 684.3234.

Synthesis of ***3b***. To a solution of complex **2b** (0.500 g, 0.786 mmol) in 15 mL of tetrahydrofuran was added a methyl lithium solution (0.5 mL, 0.786 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 12 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 12 mL). All volatiles were removed in vacuum to give complex **3b** as a pale red solid.

Complex **3b** was obtained as a mixture of rotamers (ratio approximately 1:1).

A variable-temperature NMR experiment in toluene-d_8 was performed. Therefore, NMR data of the main rotamer at 353 K is given.

Data for **3b** are as follows. Yield: 0.367 g (76%). Mp: 76−78 °C dec. IR (ATR): $\tilde{\nu}$ 2949, 2901, 2856, 1585, 1451, 1374, 1261, 1099, 1063, 1022, 983, 867, 849, 803, 767, 744, 711, 692, 677, 654, 633, 592 cm^{-1}. ^{1}H NMR (500 MHz, toluene-d_8, 300 K)**: δ 0.32 (s, 3H, $TiCH_3$), 0.71 (dd, $^{3}J_{P,H}$ = 11.8 Hz, $^{3}J_{H,H}$ = 7.2 Hz, 3H, $CH(CH_3)_2$), 1.00 (dd, $^{3}J_{P,H}$ = 13.1 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.12 (dd, $^{3}J_{P,H}$ = 13.1 Hz, $^{3}J_{H,H}$ = 7.1 Hz, 3H, $CH(CH_3)_2$), 1.22 (dd, $^{3}J_{P,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.52−1.64 (m, 9H, $CH(CH_3)_2$, 8x$CH_{Ad}/CH_{2,Ad}$), 1.72 (s, 15H, C_5Me_5), 1.90−2.04 (m, 4H, $CH(CH_3)_2$, 3x$CH_{Ad}/CH_{2,Ad}$), 2.73−2.80 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.82−2.88 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.53−3.55 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 4.71−4.73 (m, 1H, C_5H_4), 5.52−5.54 (m, 1H, C_5H_4), 5.96−5.99 (m, 1H, C_5H_4), 6.93−6.96 (m, 1H, C_6H_4)*, 7.02−7.07 (m, 1H, C_6H_4), 7.12−7.15 (m, 1H, C_6H_4), 7.17−7.19 (m, 1H, C_5H_4), 7.21−7.24 (m, 1H, C_6H_4) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, toluene-d_8, 300 K)**: δ 12.2 (C_5Me_5), 20.5 (d, $^{2}J_{C,P}$ = 15.2 Hz, $CH(CH_3)_2$), 21.2 (d, $^{2}J_{C,P}$ = 21.5 Hz, $CH(CH_3)_2$), 22.1 (d, $^{2}J_{C,P}$ = 14.8 Hz, $CH(CH_3)_2$), 25.0 (d, $^{2}J_{C,P}$ = 14.0 Hz, $CH(CH_3)_2$), 28.0 (CH_{Ad}), 28.4 (CH_{Ad}), 28.6 (d, $^{1}J_{C,P}$ = 14.7 Hz, $CH(CH_3)_2$), 32.6 (CH_{Ad}), 33.5 (d, $^{1}J_{C,P}$ = 14.1 Hz, $CH(CH_3)_2$), 33.99 ($CH_{2,Ad}$), 34.0 ($CH_{2,Ad}$), 35.7 ($CH_{2,Ad}$), 36.2 (CH_{Ad}), 36.5 ($CH_{2,Ad}$), 39.5 ($CH_{2,Ad}$), 41.9 ($TiCH_3$), 62.9 ($C_{q,exo}$), 105.1 (C_5H_4), 107.1 (C_5H_4), 115.3 (C_5H_4), 115.9 (d, $^{TS}J_{C,P}$ = 11.8 Hz, C_5H_4), 118.9 (C_5Me_5), 125.8 (C_6H_4), 128.0 (C_6H_4)*, 128.7 (d, $J_{C,P}$ = 7.9 Hz, C_6H_4)*, 131.7 (d, $J_{C,P}$ = 2.4 Hz, C_6H_4), 135.7 (d, $^{1}J_{C,P}$ = 19.2 Hz, $C_{q'C6H4}$P), 150.4 ($C_{q,ipso}$), 153.4 (d, $^{2}J_{C,P}$ = 33.6 Hz, $C_{q'C6H4}$CN), 197.7 (CN) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, toluene-d_8, 300 K)**: δ 0.2 ppm. * = overlap with toluene-d_8 signals. ** = after variable-temperature NMR experiment. Anal. Calcd for $C_{39}H_{54}NPTi$: C, 76.08; H, 8.84; N, 2.27; Found: C, 71.38; H, 8.73; N, 2.14.

Note. Complexes **3a**,**b** can also be prepared in a one-pot procedure: complex **1** (1.0 equiv) and the respective ligand precursor **L1** or **L2** (1.0 equiv) were dissolved in THF (2 mL per 0.100 g of **1**). The reaction mixture was stirred for 6 h at room temperature. A methyllithium solution (1.0 equiv; 1.6 M in diethyl ether) was added slowly, and the reaction mixture was stirred for 8 h at room temperature. The solvent was completely removed, and the residue was dissolved in toluene (4 mL per 0.100 g of **1**). The solution was filtered, and the residue was washed with toluene (2 × 4 mL per 0.100 g of **1**). All volatiles were removed under vacuum to give complexes **3a**,**b**.

Synthesis of ***4a***. A mixture of complex **3a** (0.200 g, 0.293 mmol) and $B(C_6F_5)_3$ (0.150 g, 0.293 mmol) was stirred in 10 mL of toluene. When the stirring process is stopped after a few minutes, the development of two phases can be observed due to the formation of the cationic complex **4a**. The solvent was removed under vacuum, and the residue was washed with *n*-hexane (3 × 10 mL) and dried under vacuum to give complex **4a** as a yellow solid.

Data for **4a** are as follows. Yield: 0.307 g (88%). Mp: 92−94 °C dec. IR (ATR): $\tilde{\nu}$ 2912, 2859, 1640, 1509, 1450, 1381, 1267, 1081, 965, 952, 875, 829, 803, 745, 696, 660, 641 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 305 K): δ 0.48 (s(br), 3H, BCH_3), 1.55−1.82 (m, 9H, 9 × $CH_{Ad}/CH_{2,Ad}$), 1.88 (s, 15H, C_5Me_5), 2.07−2.25 (m, 4H, 4 × $CH_{Ad}/CH_{2,Ad}$), 2.79−2.82 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 4.59−4.60 (m, 1H, C_5H_4), 4.88−4.89 (m, 1H, C_5H_4), 5.12−5.15 (m, 1H, C_5H_4), 6.38−6.43 (m, 2H, C_5H_4, CH_{Aryl}), 7.13−7.17 (m, 1H, CH_{Aryl})*, 7.27−7.33 (m, 2H, 2 × CH_{Aryl})*, 7.37−7.48 (m, 5H, 5 × CH_{Aryl}), 7.64−7.67 (m, 4H, 4 × CH_{Aryl}), 8.06−8.09 (m, 1H, CH_{Aryl}) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 305 K): δ 9.9 (BCH_3)**, 13.0 (C_5Me_5), 27.2 (CH_{Ad}), 28.0 (CH_{Ad}), 33.0 (CH_{Ad}), 33.3 ($CH_{2,Ad}$), 33.5 ($CH_{2,Ad}$), 35.2 (CH_{Ad}), 35.8 ($CH_{2,Ad}$), 37.5 ($CH_{2,Ad}$), 38.7 ($CH_{2,Ad}$), 59.7 (d, $^{4}J_{C,P}$ = 3.5 Hz, $C_{q,exo}$), 102.6 (C_5H_4), 108.9 (d, $^{TS}J_{C,P}$ = 3.2 Hz, C_5H_4), 109.0 (C_5H_4), 119.7 (C_5H_4), 124.0 (C_5Me_5), 129.0 (d, $J_{C,P}$ = 6.4 Hz, CH_{Aryl}), 129.1 ($C_{q,ArB}$)**, 129.4 (d, $^{1}J_{C,P}$ = 29.6 Hz, $C_{q,C6H4}$P), 129.8 (CH_{Aryl}), 130.3 (d, $J_{C,P}$ = 9.2 Hz, CH_{Aryl}), 130.4 (d, J = 5.0 Hz, CH_{Aryl}), 130.9 ($C_{q,ipso}$), 131.2 (CH_{Aryl}), 132.0 (CH_{Aryl}), 132.7 (d, $J_{C,P}$ = 11.1 Hz, CH_{Aryl}), 133.7 (d, $^{1}J_{C,P}$ = 28.8 Hz, $C_{q,Ph}$P), 134.6 (d, $^{1}J_{C,P}$ = 36.9 Hz, $C_{q,Ph}$P), 136.9 (dm, $^{1}J_{C,F}$ = 242.5 Hz, $C_{q,ArF}$F), 138.0 (dm, $^{1}J_{C,F}$ = 242.6 Hz, $C_{q,ArF}$F), 139.7 (CH_{Aryl}), 143.1 (d, $^{2}J_{C,P}$ = 14.8 Hz, $C_{q,C6H4}$CN), 188.8 (CN) ppm. * = overlap with toluene signals (residue). ** = assignment by $^{1}H/^{13}C$ HMQC/HMBC spectra.[11] $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 305 K): δ −14.9 ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, CD_2Cl_2, 305 K): δ −167.9 (m, 6F, *m*-$F_{Ar}B$), −165.4 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.1 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 305 K): δ 41.1 ppm. HR/MS: calculated *m*/*z* 668.2926 [M^+]; measured (ESI) *m*/*z* 668.2932.

Synthesis of ***4b***. A mixture of complex **3b** (0.300 g, 0.487 mmol) and $B(C_6F_5)_3$ (0.249 g, 0.487 mmol) was stirred in 12 mL of toluene. When the stirring process is stopped after a few minutes, the development of two phases can be observed due to the formation of the cationic complex **4b**. The solvent was removed under vacuum, and

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the residue was washed with *n*-hexane (3 × 10 mL) and dried under vacuum to give complex **4b** as an orange solid.

Data for **4b** are as follows. Yield: 0.484 g (88%). Mp: 88−90 °C dec. IR (ATR): $\tilde{\nu}$ 3021, 2994, 2930, 2857, 1640, 1509, 1449, 1382, 1265, 1082, 1022, 978, 965, 951, 934, 872, 830, 803, 756, 733, 707, 695, 659, 641, 608 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ 0.02 (dd, $^3J_{P,H}$ = 14.1 Hz, $^3J_{H,H}$ = 6.8 Hz, 3H, $CH(CH_3)_2$), 0.49 (s(br), 3H, BCH_3), 1.11 (dd, $^3J_{P,H}$ = 11.6 Hz, $^3J_{H,H}$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.17 (dd, $^3J_{P,H}$ = 19.2 Hz, $^3J_{H,H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.45 (dd, $^3J_{P,H}$ = 12.5 Hz, $^3J_{H,H}$ = 7.4 Hz, 3H, $CH(CH_3)_2$), 1.54−1.82 (m, 11H, $CH_{Ad}/CH_{2,Ad}$), 2.07 (s, 15H, C_5Me_5), 2.33−2.41 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 2.59−2.68 (m, 1H, $CH(CH_3)_2$), 2.71−2.79 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.08 (dhept, $^2J_{P,H}$ = 21.7 Hz, $^3J_{H,H}$ = 7.1 Hz, 1H, $CH(CH_3)_2$), 5.07−5.11 (m, 1H, C_5H_4), 5.60−5.63 (m, 1H, C_5H_4), 5.79−5.83 (m, 1H, C_5H_4), 6.38−6.41 (m, 1H, C_5H_4), 7.58−7.66 (m, 3H, 3 × C_6H_4), 7.93−7.98 (m, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ 10.0 (BCH_3)*, 13.3 (C_5Me_5), 16.9 (d, $^2J_{C,P}$ = 8.1 Hz, $CH(CH_3)_2$), 20.1 (d, $^2J_{C,P}$ = 14.0 Hz, $CH(CH_3)_2$), 20.3 (d, $^2J_{C,P}$ = 13.6 Hz, 2x$CH(CH_3)_2$), 23.9 (d, $^1J_{C,P}$ = 9.0 Hz, $CH(CH_3)_2$), 27.1 (CH_{Ad}), 27.9 (d, $^1J_{C,P}$ = 11.8 Hz, $CH(CH_3)_2$), 28.0 (CH_{Ad}), 33.0 (CH_{Ad}), 33.5 ($CH_{2,Ad}$), 33.7 ($CH_{2,Ad}$), 34.8 (CH_{Ad}), 35.9 ($CH_{2,Ad}$), 37.2 ($CH_{2,Ad}$), 38.6 ($CH_{2,Ad}$), 59.8 ($C_{q,exo}$), 104.0 (C_5H_4), 104.4 (C_5H_4), 106.0 (C_5H_4), 117.4 (C_5H_4), 124.0 (C_5Me_5), 128.4 (d, $J_{C,P}$ = 5.6 Hz, C_6H_4), 129.0 ($C_{q,ArB}$)*, 129.5 (C_6H_4), 130.2 (d, $J_{C,P}$ = 4.3 Hz, C_6H_4), 130.5 ($C_{q,ipso}$), 132.3 (C_6H_4), 133.0 (d, $^1J_{C,P}$ = 28.1 Hz, $C_{q,C6H4}P$), 136.8 (dm, $^1J_{C,F}$ = 237.3 Hz, $C_{q,Ar}F$), 137.9 (dm, $^1J_{C,F}$ = 242.8 Hz, $C_{q,Ar}F$), 139.8 (d, $^2J_{C,P}$ = 8.8 Hz, $C_{q,C6H4}CN$), 148.7 (dm, $^1J_{C,F}$ = 242.3 Hz, $C_{q,Ar}F$), 190.0 (d, $^3J_{C,P}$ = 3.5 Hz, CN) ppm. * = assignment by $^1H/^{13}C$ HMQC/HMBC spectra. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 299 K): δ −14.9 ppm. $^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 299 K): δ −167.9 (m, 6F, *m*-$F_{Ar}B$), −165.4 (t, $^3J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.1 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ 55.5 ppm. Anal. Calcd for $C_{57}H_{54}BF_{15}NPTi$: C, 60.71; H, 4.83; N, 1.24. Found: C, 59.21; H, 4.22; N, 1.38. HR/MS: calculated *m*/*z* 600.3239 [M^+]; measured (ESI) *m*/*z* 600.3239.

Synthesis of ***5a***. Complex **4a** (0.080 g, 0.067 mmol) was suspended in 8 mL of toluene. Acetone (0.01 mL, 0.136 mmol) was added, and the reaction mixture was stirred for 16 h at room temperature. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane (3 × 5 mL). The residue was dried under vacuum to give complex **5a** as a slightly yellow solid.

Data for **5a** are as follows. Yield: 0.052 g (61%). Mp: 86−88 °C dec. IR (ATR): $\tilde{\nu}$ 2913, 2864, 1640, 1610, 1566, 1509, 1454, 1383, 1366, 1263, 1082, 1030, 978, 965, 952, 935, 891, 877, 832, 804, 767, 745, 697, 659, 642 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 300 K): δ 0.49 (s(br), 3H, BCH_3), 1.65 (s, 3H, OC_qCH_3), 1.67−1.72 (m, 4H, 4 × $CH_{Ad}/CH_{2,Ad}$), 1.75 (s, 15H, C_5Me_5), 1.78−1.86 (m, 3H, 3 × $CH_{Ad}/CH_{2,Ad}$), 1.95−1.98 (m, 2H, 2 × $CH_{Ad}/CH_{2,Ad}$), 2.11−2.19 (m, 3H, 3 × $CH_{Ad}/CH_{2,Ad}$), 2.50−25.1 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.28−3.29 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.86−3.88 (m, 2H, OC_q=CH_2), 5.78−5.79 (m, 1H, C_5H_4), 5.95−5.97 (m, 1H, C_5H_4), 6.37−6.39 (m, 1H, C_5H_4), 6.78−6.80 (m, 1H, C_5H_4), 6.98−7.01 (m, 2H, 2 × CH_{Aryl}), 7.26−7.30 (m, 2H, 2 × CH_{Aryl})*, 7.35−7.43 (m, 7H, 7 × CH_{Aryl}), 7.53−7.59 (m, 3H, 3 × CH_{Aryl}), 8.63 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 300 K): δ 10.0 (BCH_3)**, 12.4 (C_5Me_5), 24.1 (OC_qCH_3), 27.0 (CH_{Ad}), 27.1 (CH_{Ad}), 32.8 ($CH_{2,Ad}$), 33.9 ($CH_{2,Ad}$), 35.0 (CH_{Ad}), 35.06 (CH_{Ad}), 35.1 ($CH_{2,Ad}$), 35.4 ($CH_{2,Ad}$), 38.3 ($CH_{2,Ad}$), 59.0 ($C_{q,exo}$), 87.5 (d, $^{TS}J_{C,P}$ = 4.9 Hz, OC_q=CH_2), 111.7 (C_5H_4), 114.5 (C_5H_4), 115.2 (C_5H_4), 117.2 (C_5H_4), 126.9 (d, $J_{C,P}$ = 8.0 Hz, CH_{Aryl}), 127.0 (C_5Me_5), 129.0 ($C_{q,ArB}$)**, 129.4 (d, $J_{C,P}$ = 7.0 Hz, 2 × CH_{Aryl}), 129.7 (d, $J_{C,P}$ = 6.5 Hz, 2 × CH_{Aryl}), 130.0 (CH_{Aryl}), 130.1 (CH_{Aryl}), 130.3 (CH_{Aryl}), 131.4 (CH_{Aryl}), 133.6 (d, $J_{C,P}$ = 18.0 Hz, 2 × CH_{Aryl}), 134.1 (d, $J_{C,P}$ = 18.0 Hz, 2 × CH_{Aryl}), 134.3 (d, $^1J_{C,P}$ = 14.8 Hz, $C_{q,C6H4}P$), 135.2 (d, $^1J_{C,P}$ = 10.1 Hz, $C_{q,Ph}P$), 135.6 (d, $^1J_{C,P}$ = 8.6 Hz, $C_{q,Ph}P$), 136.78 (CH_{Aryl}), 136.8 (dm, $^1J_{C,F}$ = 236.2 Hz, $C_{q,Ar}F$), 137.9 (dm, $^1J_{C,F}$ = 245.0 Hz, $C_{q,Ar}F$), 147.5 (d, $^2J_{C,P}$ = 35.8 Hz, $C_{q,C6H4}C$=NH), 148.7 (dm, $^1J_{C,F}$ = 238.9 Hz, $C_{q,Ar}F$), 150.7 ($C_{q,ipso}$), 170.8 (OC_q), 214.5 (C=NH) ppm. * = overlap with residue of toluene. ** = assignment by $^1H/^{13}C$ HMQC/HMBC spectra. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 300 K): δ −14.9 ppm. $^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 300 K): δ −167.8 (m, 6F, *m*-$F_{Ar}B$), −165.3 (t, $^3J_{F,F}$ = 20.4 Hz, 3F, *p*-$F_{Ar}B$), −133.1 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 300 K): δ −14.0 ppm. ^{15}N NMR (51 MHz, CD_2Cl_2, 300 K) δ 273.9 ppm. HR/MS: calculated *m*/*z* 726.3344 [M^+]; measured (ESI) *m*/*z* 726.3342.

Synthesis of ***5b***. Complex **4b** (0.100 g, 0.089 mmol) was suspended in 8 mL of toluene. Acetone (0.01 mL, 0.136 mmol) was added, and the reaction mixture was stirred for 16 h at room temperature. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane (3 × 5 mL). The residue was dried under vacuum to give complex **5b** as a fawn yellow solid.

Data for **5b** are as follows. Yield: 0.076 g (72%). Mp: 62−64 °C dec. IR (ATR): $\tilde{\nu}$ 2914, 2868, 1710, 1640, 1573, 1509, 1453, 1382, 1366, 1263, 1082, 978, 965, 952, 934, 890, 875, 831, 803, 766, 705, 658, 605 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 305 K): δ 0.49 (s, 3H, BCH_3), 0.83 (dd, $^3J_{P,H}$ = 10.2 Hz, $^3J_{H,H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 0.91 (dd, $^3J_{P,H}$ = 14.5 Hz, $^3J_{H,H}$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.14 (dd, $^3J_{P,H}$ = 15.1 Hz, $^3J_{H,H}$ = 7.2 Hz, 3H, $CH(CH_3)_2$), 1.29 (dd, $^3J_{P,H}$ = 13.9 Hz, $^3J_{H,H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.58−1.72 (m, 11H, $CH(CH_3)_2$, 10x$CH_{Ad}/CH_{2,Ad}$), 1.84 (s, 3H, OC_qCH_3), 1.93 (s, 15H, C_5Me_5), 2.23−2.39 (m, 5H, $CH(CH_3)_2$, 4x$CH_{Ad}/CH_{2,Ad}$), 3.96−3.97 (m, 1H, OC_q=CH2), 4.14 (d, $^2J_{H,H}$ = 2.6 Hz, 1H, OC_q=CH_2), 5.90−5.92 (m, 1H, C_5H_4), 6.08−6.11 (m, 1H, C_5H_4), 6.26−6.28 (m, 1H, C_5H_4), 6.85−6.88 (m, 1H, C_5H_4), 7.48−7.59 (m, 3H, 3 × C_6H_4), 7.69−7.74 (m, 1H, C_6H_4), 8.74 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 305 K): δ 9.9 (BCH_3)*, 12.6 (C_5Me_5), 18.7 (d, $^2J_{C,P}$ = 5.1 Hz, $CH(CH_3)_2$), 19.7 (d, $^2J_{C,P}$ = 15.9 Hz, $CH(CH_3)_2$), 20.6 (d, $^2J_{C,P}$ = 13.7 Hz, $CH(CH_3)_2$), 22.1 (d, $^2J_{C,P}$ = 16.4 Hz, $CH(CH_3)_2$), 24.5 (d, $^1J_{C,P}$ = 12.1 Hz, $CH(CH_3)_2$), 24.9 (d, $J_{C,P}$ = 3,1 Hz, OC_qCH_3)*, 26.9 (CH_{Ad}), 27.18 (d, $^1J_{C,P}$ = 13.7 Hz, $CH(CH_3)_2$), 27.2 (CH_{Ad}), 32.9 ($CH_{2,Ad}$), 33.7 (CH_{Ad}), 33.8 (CH_{Ad}), 34.0 ($CH_{2,Ad}$), 34.7 ($CH_{2,Ad}$), 35.8 ($CH_{2,Ad}$), 38.2 ($CH_{2,Ad}$), 59.5 ($C_{q,exo}$), 89.1 (d, $^{TS}J_{C,P}$ = 9.6 Hz, OC_q=CH_2), 112.8 (C_5H_4), 113.6 (C_5H_4), 115.3 (C_5H_4), 117.8 (C_5H_4), 126.8 (C_5Me_5), 126.9 (C_6H_4), 129.0 ($C_{q,ArB}$)*, 129.9 (C_6H_4), 130.7 (C_6H_4), 134.5 (C_6H_4), 135.1 (d, $^1J_{C,P}$ = 23.8 Hz, $C_{q,C6H4}P$), 136.9 (dm, $^1J_{C,F}$ = 244.3 Hz, $C_{q,Ar}F$), 137.9 (dm, $^1J_{C,F}$ = 241.8 Hz, $C_{q,Ar}F$), 148.8 (dm, $^1J_{C,F}$ = 237.2 Hz, $C_{q,Ar}F$), 149.4 (d, $^2J_{C,P}$ = 33.8 Hz, $C_{q,C6H4}C$=NH), 151.6 ($C_{q,ipso}$), 170.8 (OC_q), 216.2 (C=NH) ppm. * = assignment by $^1H/^{13}C$ HMQC/HMBC spectra. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 305 K): δ −14.9 ppm. $^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 305 K): δ −167.9 (m, 6F, *m*-$F_{Ar}B$), −165.4 (t, $^3J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.1 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 305 K): δ −2.0 ppm. ^{15}N NMR (51 MHz, CD_2Cl_2, 305 K) δ 276.8 ppm. HR/MS: calculated *m*/*z* 658.3657 [M^+]; measured (ESI) *m*/*z* 658.3662.

Synthesis of ***6a***. Complex **4a** (0.080 g, 0.067 mmol) was suspended in 8 mL of toluene. Phenylacetylene (0.01 mL, 0.067 mmol) was added, and the reaction mixture was stirred for 16 h at room temperature. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane (3 × 5 mL). The residue was dried under vacuum to give complex **6a** as a reddish solid.

Data for **6a** are as follows. Yield: 0.074 g (85%). Mp: 78−80 °C dec. IR (ATR): $\tilde{\nu}$ 2911, 2856, 2061, 1640, 1596, 1556, 1509, 1453, 1382, 1267, 1207, 1081, 1026, 977, 965, 952, 935, 890, 873, 831, 803, 746, 730, 692, 659 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 300 K): δ 0.40 (s(br), 3H, BCH_3), 1.54−1.66 (m, 8H, 8 × $CH_{Ad}/CH_{2,Ad}$), 1.76 (s, 15H, C_5Me_5), 2.07−2.20 (m, 4H, 4 × $CH_{Ad}/CH_{2,Ad}$), 2.31−2.32 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.42−3.43 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 5.85−5.87 (m, 1H, C_5H_4), 5.92−5.94 (m, 1H, C_5H_4), 6.09−6.10 (m, 1H, C_5H_4), 6.74−6.77 (m, 2H, 2 × CH_{Aryl}), 6.88−6.92 (m, 2H, 2 × CH_{Aryl}), 6.96−6.99 (m, 1H, CH_{Aryl}), 7.07−7.09 (m, 2H, 2 × CH_{Aryl})*, 7.13−7.16 (m, 2H, 2 × CH_{Aryl})*, 7.25−7.42 (m, 8H, 8 × CH_{Aryl}), 7.48−7.49 (m, 1H, C_5H_4), 7.53−7.56 (m, 1H, CH_{Aryl}), 8.09 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 300 K): δ 10.1 (BCH_3)**, 13.2 (C_5Me_5), 27.0 (CH_{Ad}), 27.3 (CH_{Ad}), 32.9 ($CH_{2,Ad}$), 33.3 ($CH_{2,Ad}$), 35.1 (CH_{Ad}), 35.3 ($CH_{2,Ad}$), 35.4 (CH_{Ad}), 35.7 ($CH_{2,Ad}$), 38.4 ($CH_{2,Ad}$), 59.8 ($C_{q,exo}$), 113.4 (C_5H_4), 114.1 (C_5H_4), 117.7 (C_5H_4), 120.4 (C_5H_4), 125.7 (TiCC), 126.4 (d, $J_{C,P}$ = 8.2 Hz, CH_{Aryl}), 128.0 (C_5Me_5), 128.9 ($C_{q,ArB}$)**, 129.0 (CH_{Aryl}), 129.3 (d, $J_{C,P}$ = 6.7 Hz, CH_{Aryl}), 129.4 (d, $J_{C,P}$ = 7.2 Hz, CH_{Aryl}), 129.5 (CH_{Aryl}), 129.8

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(CH_{Aryl}), 129.9 (CH_{Aryl}), 130.2 (CH_{Aryl}), 131.2 (CH_{Aryl}), 132.6 (CH_{Aryl}), 133.2 (d, $J_{C,P}$ = 10.2 Hz, $C_{q,Aryl}$), 133.5 (d, $J_{C,P}$ = 18.5 Hz, CH_{Aryl}), 134.0 (d, $J_{C,P}$ = 19.8 Hz, CH_{Aryl}), 134.5 (d, $J_{C,P}$ = 8.9 Hz, $C_{q,Aryl}$), 135.4 (d, $J_{C,P}$ = 4.7 Hz, $C_{q,Aryl}$), 136.2 (d, $J_{C,P}$ = 1.6 Hz, CH_{Aryl}), 136.8 (dm, $^{1}J_{C,F}$ = 244.2 Hz, $C_{q,Ar}F$), 137.9 (dm, $^{1}J_{C,F}$ = 245.9 Hz, $C_{q,Ar}F$), 142.3 ($C_{q,Ph}$), 147.1 (d, $^{2}J_{C,P}$ = 35.9 Hz, $C_{q,C6H4}C{=}NH$), 148.6 ($C_{q,ipso}$), 148.7 (dm, $^{1}J_{C,F}$ = 233.1 Hz, $C_{q,Ar}F$), 166.0 (TiC), 216.2 (C=NH) ppm. * = overlap with residue of toluene. ** = assignment by $^{1}H/^{13}C$ HMQC/HMBC spectra. $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 300 K): δ −14.9 ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, CD_2Cl_2, 300 K): δ −167.9 (m, 6F, *m*-$F_{Ar}B$), −165.3 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.1 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 300 K): δ −13.2 ppm. ^{15}N NMR (51 MHz, CD_2Cl_2, 300 K): δ 282.6 ppm. HR/MS: calculated *m*/*z* 770.3395 [M^+]; measured (ESI) *m*/*z* 770.3400.

Synthesis of ***6b***. Complex **4b** (0.100 g, 0.089 mmol) was suspended in 8 mL of toluene. Phenylacetylene (0.01 mL, 0.089 mmol) was added, and the reaction mixture was stirred for 16 h at room temperature. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane (3 × 5 mL). The residue was dried under vacuum to give complex **6b** as a reddish solid.

Data for **6b** are as follows. Yield: 0.073 g (82%). Mp: 68−70 °C dec. IR (ATR): $\tilde{\nu}$ 2961, 2913, 2867, 2062, 1640, 1554, 1509, 1486, 1454, 1382, 1263, 1081, 1024, 994, 978, 965, 952, 935, 869, 829, 802, 757, 691, 659, 642, 604 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 305 K): δ 0.50 (s, 3H, BCH_3), 0.62 (d, $^{3}J_{H,H}$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 0.64 (dd, $^{3}J_{P,H}$ = 2.8 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.12 (dd, $^{3}J_{P,H}$ = 14.8 Hz, $^{3}J_{H,H}$ = 7.2 Hz, 3H, $CH(CH_3)_2$), 1.23 (dd, $^{3}J_{P,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.60−1.76 (m, 11H, $CH(CH_3)_2$, 10 × $CH_{Ad}/CH_{2,Ad}$), 2.06 (s, 15H, C_5Me_5), 2.23−2.35 (m, 3H, $CH(CH_3)_2$, 2 × $CH_{Ad}/CH_{2,Ad}$), 2.54−2.61 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.33−3.38 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 5.84−5.87 (m, 1H, C_5H_4), 6.32−6.35 (m, 1H, C_5H_4), 6.37−6.40 (m, 1H, C_5H_4), 6.99−7.03 (m, 1H, C_6H_4), 7.34−7.38 (m, 3H, 3 × CH_{Aryl}), 7.43−7.53 (m, 5H, C_5H_4, 4 × CH_{Aryl}), 7.60−7.63 (m, 1H, C_6H_4), 8.28 (s, 1H, NH) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 305 K): δ 9.8 (BCH_3)*, 13.4 (C_5Me_5), 18.9 (d, $^{2}J_{C,P}$ = 6.6 Hz, $CH(CH_3)_2$), 19.9 (d, $^{2}J_{C,P}$ = 15.9 Hz, $CH(CH_3)_2$), 20.2 (d, $^{2}J_{C,P}$ = 15.0 Hz, $CH(CH_3)_2$), 22.0 (d, $^{2}J_{C,P}$ = 15.7 Hz, $CH(CH_3)_2$), 24.6 (d, $^{1}J_{C,P}$ = 12.5 Hz, $CH(CH_3)_2$), 27.0 (CH_{Ad}), 27.49 (CH_{Ad}), 27.5 (d, $^{1}J_{C,P}$ = 13.1 Hz, $CH(CH_3)_2$), 33.1 ($CH_{2,Ad}$), 33.6 ($CH_{2,Ad}$), 34.5 (CH_{Ad}), 34.8 ($CH_{2,Ad}$), 36.3 ($CH_{2,Ad}$), 36.7 (CH_{Ad}), 38.3 ($CH_{2,Ad}$), 60.0 ($C_{q,exo}$), 112.4 (C_5H_4), 115.2 (C_5H_4), 119.6 (d, $^{TS}J_{C,P}$ = 4.9 Hz, C_5H_4), 120.1 (C_5H_4), 124.2 (TiCC), 126.4 (d, $J_{C,P}$ = 8.5 Hz, C_6H_4), 128.0 (C_5Me_5), 128.9 ($C_{q,Ar}B$)*, 129.0 (2 × CH_{Ph}), 129.5 (CH_{Ph}), 130.0 (C_6H_4), 130.7 (C_6H_4), 132.4 (2 × CH_{Ph}), 134.0 (C_6H_4), 136.1 (d, $^{1}J_{C,P}$ = 23.1 Hz, $C_{q,C6H4}P$), 136.8 (dm, $^{1}J_{C,F}$ = 243.3 Hz, $C_{q,Ar}F$), 138.0 (dm, $^{1}J_{C,F}$ = 241.7 Hz, $C_{q,Ar}F$), 142.8 ($C_{q,Ph}$), 148.9 (dm, $^{1}J_{C,F}$ = 240.0 Hz, $C_{q,Ar}F$), 149.2 (d, $^{2}J_{C,P}$ = 33.5 Hz, $C_{q,C6H4}C{=}NH$), 149.7 ($C_{q,ipso}$), 165.3 (TiC), 219.4 (C=NH) ppm. * = assignment by $^{1}H/^{13}C$ HMQC/HMBC spectra. $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 305 K): δ −14.9 ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, CD_2Cl_2, 305 K): δ −167.9 (m, 6F, *m*-$F_{Ar}B$), −165.3 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.1 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 305 K): δ 0.7 ppm. ^{15}N NMR (51 MHz, CD_2Cl_2, 305 K) δ 284.2 ppm. Anal. Calcd for $C_{65}H_{60}BF_{15}NPTi$: C, 63.48; H, 4.92; N, 1.14. Found: C, 63.84; H, 4.70; N, 0.72. HR/MS: calculated *m*/*z* 702.3708 [M^+]; measured (ESI) *m*/*z* 702.3716.

Synthesis of ***7b***. Complex **4b** (0.200 g, 0.177 mmol) was suspended in 8 mL of toluene. The Schlenk tube was connected to a Schlenk line and filled with 1.1 bar of H2 at room temperature and stirred overnight resulting in a slight color change. All volatiles were removed in vacuum and the residue was washed with *n*-hexane (3 × 8 mL). The residue was dried under vacuum to give complex **7b** as a yellow solid.

Data for **7b** are as follows. Yield: 0.135 g (68%). Mp: 90−92 °C. IR (ATR): $\tilde{\nu}$ 2912, 2865, 1640, 1509, 1450, 1266, 1081, 1036, 965, 951, 935, 888, 803, 766, 755, 735, 681, 659, 649 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ −0.13 (dd, $^{3}J_{P,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 6.8 Hz, 3H, $CH(CH_3)_2$), 0.49 (s, 3H, BCH_3), 1.08 (dd, $^{3}J_{P,H}$ = 11.1 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.16 (dd, $^{3}J_{P,H}$ = 19.0 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.62 (dd, $^{3}J_{P,H}$ = 11.2 Hz, $^{3}J_{H,H}$ = 7.4 Hz, 3H, $CH(CH_3)_2$), 1.68−1.72 (m, 3H, 3 × $CH_{Ad}/CH_{2,Ad}$), 1.88−1.96 (m, 8H, 8 × $CH_{Ad}/CH_{2,Ad}$), 2.04 (s, 15H, C_5Me_5), 2.37−2.53 (m, 4H, $CH(CH_3)_2$, 3 × $CH_{Ad}/CH_{2,Ad}$), 3.13−3.24 (m, 1H, $CH(CH_3)_2$), 5.38−5.43 (m, 2H, 2 × C_5H_4), 5.67−5.70 (m, 1H, NHC*H*), 6.04−6.05 (m, 1H, C_5H_4), 6.57−6.60 (m, 1H, C_5H_4), 7.45−7.52 (m, 3H, 3 × C_6H_4), 7.58−7.64 (m, 1H, C_6H_4), 9.62−9.63 (m, 1H, NH) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 300 K): δ 10.2 (BCH_3)*, 17.1 (d, $^{2}J_{C,P}$ = 7.6 Hz, $CH(CH_3)_2$), 20.0 (d, $^{2}J_{C,P}$ = 13.9 Hz, $CH(CH_3)_2$), 20.7 (d, $^{2}J_{C,P}$ = 14.9 Hz, $CH(CH_3)_2$), 24.8 (d, $^{1}J_{C,P}$ = 8.8 Hz, $CH(CH_3)_2$), 27.4 (CH_{Ad}), 27.8 (d, $^{1}J_{C,P}$ = 10.1 Hz, $CH(CH_3)_2$), 28.0 (CH_{Ad}), 33.1 (CH_{Ad}), 33.6 ($CH_{2,Ad}$), 34.06 (CH_{Ad}), 34.1 ($CH_{2,Ad}$), 34.5 ($CH_{2,Ad}$), 36.2 ($CH_{2,Ad}$), 38.6 ($CH_{2,Ad}$), 51.8 (d, $^{4}J_{C,P}$ = 1.3 Hz, $C_{q,exo}$), 93.1 (d, $^{3}J_{C,P}$ = 2.1 Hz, NHCH), 103.9 (C_5H_4), 109.3 (C_5H_4), 109.5 (d, $^{TS}J_{C,P}$ = 1.9 Hz, C_5H_4), 114.3 (C_5H_4), 121.8 (C_5Me_5), 126.2 (d, $^{1}J_{C,P}$ = 28.0 Hz, $C_{q,C6H4}P$), 128.7 (d, $J_{C,P}$ = 5.5 Hz, C_6H_4), 128.9 ($C_{q,Ar}B$)*, 129.9 (d, $J_{C,P}$ = 2.2 Hz, C_6H_4), 132.0 (d, $J_{C,P}$ = 2.9 Hz, C_6H_4), 133.1 (d, $J_{C,P}$ = 8.6 Hz, C_6H_4), 136.8 (dm, $^{1}J_{C,F}$ = 237.9 Hz, $C_{q,Ar}F$), 137.9 (dm, $^{1}J_{C,F}$ = 242.5 Hz, $C_{q,Ar}F$), 147.5 ($C_{q,C6H4}CHNH$), 148.7 ($C_{q,ipso}$), 148.72 (dm, $^{1}J_{C,F}$ = 242.8 Hz, $C_{q,Ar}F$) ppm. * = assignment by $^{1}H/^{13}C$ HMQC/HMBC spectra. $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 300 K): δ −14.9 ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, CD_2Cl_2, 300 K): δ −167.8 (m, 6F, *m*-$F_{Ar}B$), −165.3 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.1 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 300 K): δ 58.4 ppm. ^{15}N NMR (51 MHz, CD_2Cl_2, 300 K): δ 324.8 ppm. HR/MS: calculated *m*/*z* 602.3395 [M^+]; measured (ESI) *m*/*z* 602.3383.

Synthesis of ***8***. Complex **1** (1.028 g, 2.466 mmol) and 4-chlorobenzonitrile (0.339 g, 2.466 mmol) were dissolved in 12 mL of *n*-hexane, resulting in a red suspension. The solvent was removed under vacuum to yield complex **8** as a red solid. No further purification steps were required.

Data for **8** are as follows. Yield: 1.212 g (89%). Mp: 104−106 °C dec. IR (ATR): $\tilde{\nu}$ 2904, 2854, 1592, 1449, 1375, 1354, 1220, 1099, 1087, 1065, 1043, 1014, 992, 945, 927, 848, 837, 820, 806, 791, 772, 737, 713, 678, 661, 633, 624, 610 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 1.07−1.11 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 1.38−1.65 (m, 9H, (m, 9H, 9 × $CH_{Ad}/CH_{2,Ad}$), 1.81 (s, 15H, C_5Me_5), 1.95−1.96 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.17−2.20 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.44−2.48 (m, 2H, 2 × $CH_{Ad}/CH_{2,Ad}$), 5.16−5.17 (m, 1H, C_5H_4), 5.34−5.36 (m, 1H, C_5H_4), 6.18−6.20 (m, 1H, C_5H_4), 6.49−6.51 (m, 1H, C_5H_4), 6.97−7.05 (m(br), 4H, 4 × CH_{Aryl}) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 300 K): δ 12.8 (C_5Me_5), 27.5 (CH_{Ad}), 27.7 (CH_{Ad}), 33.0 ($CH_{2,Ad}$), 33.5 (CH_{Ad}), 33.9 ($CH_{2,Ad}$), 34.6 ($CH_{2,Ad}$), 35.8 ($CH_{2,Ad}$), 36.6 (CH_{Ad}), 38.7 ($CH_{2,Ad}$), 59.9 ($C_{q,exo}$), 105.4 (C_5H_4), 109.2 (C_5H_4), 116.1 (C_5H_4), 117.5 (C_5H_4), 123.4 (C_5Me_5) 132.9 ($C_{q,Aryl}$), 141.9 ($C_{q,Aryl}$), 149.1 ($C_{q,ipso}$), 198.0 (CN) ppm. CH_{Aryl} signals masked by C_6D_6 signal.

Synthesis of ***9***. To a solution of complex **8** (1.000 g, 1.804 mmol) in 15 mL of tetrahydrofuran was added a methyllithium solution (1.1 mL, 1.804 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 10 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 10 mL). All volatiles were removed under vacuum to give complex **9** as a pale red solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at −4 °C.

Data for **9** are as follows. Yield: 0.842 g (87%). Mp: 198−200 °C dec. IR (ATR): $\tilde{\nu}$ 2907, 2878, 2858, 1589, 1485, 1471, 1449, 1384, 1371, 1352, 1310, 1261, 1240, 1217, 1099, 1088, 1065, 1040, 1014, 989, 943, 924, 903, 854, 833, 813, 793, 733, 714, 694, 675, 660, 635, 625, 609 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 305 K): δ 0.14 (s, 3H, $TiCH_3$), 1.17−1.20 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 1.49−1.69 (m, 8H, 8 × $CH_{Ad}/CH_{2,Ad}$), 1.75 (s, 15H, C_5Me_5), 1.99−2.00 (m, 2H, 2 × $CH_{Ad}/CH_{2,Ad}$), 2.15−2.17 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.46−2.47 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.68−2.70 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 4.91−4.93 (m, 1H, C_5H_4), 5.36−5.37 (m, 1H, C_5H_4), 5.77−5.79 (m, 1H, C_5H_4), 6.21−6.23 (m, 1H, C_5H_4), 6.89−6.91 (m, 2H, 2 × CH_{Aryl}), 7.01−7.09 (m(br), 2H, 2 × CH_{Aryl}) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 305 K): δ 12.2 (C_5Me_5), 27.8 (CH_{Ad}), 27.9 (CH_{Ad}), 33.4 ($CH_{2,Ad}$), 33.7

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(CH_{Ad}), 34.2 ($CH_{2,Ad}$), 34.9 ($TiCH_3$), 35.0 ($CH_{2,Ad}$), 35.8 ($CH_{2,Ad}$), 36.9 (CH_{Ad}), 38.9 ($CH_{2,Ad}$), 60.2 ($C_{q,exo}$), 104.9 (C_5H_4), 106.8 (C_5H_4), 112.4 (C_5H_4), 114.6 (C_5H_4), 119.0 (C_5Me_5), 132.5 ($C_{q,Aryl}$), 143.7 ($C_{q,Aryl}$), 144.7 ($C_{q,ipso}$), 196.8 (CN) ppm. CH_{Aryl} signals masked by C_6D_6 signal. Anal. Calcd for $C_{33}H_{40}ClNTi$: C, 74.22; H, 7.55; N, 2.62. Found: C, 72.76; H, 7.62; N, 2.56.

Synthesis of ***10***. A mixture of complex **9** (0.400 g, 0.749 mmol) and $B(C_6F_5)_3$ (0.383 g, 0.749 mmol) was stirred in 12 mL of toluene. When the stirring process is stopped after a few minutes, the development of two phases can be observed due to the formation of the cationic complex **10**. The solvent was removed under vacuum, and the residue was washed with *n*-hexane (3 × 10 mL) and dried under vacuum to give complex **10** as a reddish solid.

Data for **10** are as follows. Yield: 0.682 g (87%). Mp: 69−71 °C. IR (ATR): $\tilde{\nu}$ 2913, 2862, 1834, 1643, 1593, 1571, 1513, 1455, 1385, 1293, 1271, 1220, 1159, 1092, 1016, 1001, 972, 891, 834, 809, 792, 769, 738, 711, 681, 607 cm^{-1}. ^1H NMR (500 MHz, THF-d_8, 305 K): δ 0.50 (s, 3H, BCH_3), 1.57−1.71 (m, 8H, 8 × $CH_{Ad}/CH_{2,Ad}$), 1.91 (s, 15H, C_5Me_5), 1.97−2.05 (m, 3H, 3 × $CH_{Ad}/CH_{2,Ad}$), 2.21−2.24 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.51−2.53 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.75−2.76 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 5.38−5.39 (m, 1H, C_5H_4), 5.67−5.68 (m, 1H, C_5H_4), 5.97−5.98 (m, 1H, C_5H_4), 6.39−6.40 (s, 1H, C_5H_4), 7.11−7.13 (m, 2H, 2 × CH_{Aryl}), 7.22−7.28 (m, 2H, 2 × CH_{Aryl}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, THF-d_8, 305 K): δ 8.9 (BCH_3)*, 12.6 (C_5Me_5), 28.1 (CH_{Ad}), 28.3 (CH_{Ad}), 33.6 ($CH_{2,Ad}$), 34.0 (CH_{Ad}), 34.2 ($CH_{2,Ad}$), 35.0 ($CH_{2,Ad}$), 36.2 ($CH_{2,Ad}$), 37.0 (CH_{Ad}), 39.1 ($CH_{2,Ad}$), 60.3 ($C_{q,exo}$), 106.2 (C_5H_4), 109.9 (C_5H_4), 116.3 (C_5H_4), 117.8 (C_5H_4), 123.6 (C_5Me_5), 128.1 (2 × CH_{Aryl}), 128.7 (2 × CH_{Aryl}), 129.0 ($C_{q,Ar}B$)*, 132.8 ($C_{q,Aryl}$), 136.9 (dm, $^1J_{C,F}$ = 243.2 Hz, $C_{q,Ar}F$), 138.1 (dm, $^1J_{C,F}$ = 248.6 Hz, $C_{q,Ar}F$), 142.6 ($C_{q,Aryl}$), 149.0 (dm, $^1J_{C,F}$ = 236.8 Hz, $C_{q,Ar}F$), 149.5 ($C_{q,ipso}$), 198.4 (CN) ppm. * = assignment by $^1H/^{13}C$ HMQC/HMBC spectra. $^{11}B\{^1H\}$ NMR (160 MHz, THF-d_8, 305 K): δ −15.5 ppm. $^{19}F\{^1H\}$ NMR (470 MHz, THF-d_8, 305 K): δ −169.1 (m, 6F, *m*-$F_{Ar}B$), −167.0 (t, $^3J_{F,F}$ = 20.2 Hz, 3F, *p*-$F_{Ar}B$), −132.8 (m, 6F, *o*-$F_{Ar}B$) ppm. HR/MS: calculated *m*/*z* 518.2094 [M^+]; measured (ESI) *m*/*z* 518.2093.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00283.

Crystallographic parameters for compounds **L2**, **2a**, **3a**, and **9** and ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, $^{19}F\{^1H\}$, $^{15}N/^1H$ HMBC, and $^{31}P\{^1H\}$ NMR spectra of all compounds (PDF)

Accession Codes

CCDC 1839587−1839590 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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