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Group 4 metallocene complexes with pendant nitrile groups

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ABSTRACT

The preparation of a new functionalized cyclopentadienyl ligand bearing a nitrile pendant substituent, $(C_5H_4CMe_2CH_2CN)^-$ is reported. The corresponding lithium salt of this ligand (**1**) was prepared by the reaction of *in situ* lithiated acetonitrile with 6,6-dimethylfulvene. The ligand was subsequently utilized for the synthesis of group 4 metal complexes $[(\eta^5{-}C_5H_4CMe_2CH_2CN)_2MCl_2]$ (M = Ti, **2**; M = Zr, **3**; M = Hf, **4**), $[(\eta^5{-}C_5H_5)(\eta^5{-}C_5H_4CMe_2CH_2CN)MCl_2]$ (M = Ti, **7**; M = Zr, **8**), and $[(\eta^5\text{-}C_5Me_5)(\eta^5\ C_5H_4CMe_2CH_2CN)_2ZrCl_2]$ (**9**). Alternative route to **2** comprised the preparation of half-sandwich complex $[(\eta^5{-}C_5H_4CMe_2CH_2CN)TiCl_3]$ (**6**). The prepared compounds were characterized by common spectroscopic methods and the solid state structures of complexes **2**, **3**, **4**, **7**, and **9** were determined by the single-crystal X-ray diffraction analysis. In addition, compound **7** was converted to the corresponding dimethyl derivative $[(\eta^5{-}C_5H_5)(\eta^5{-}C_5H_4CMe_2CH_2CN)TiMe_2]$ (**10**) and also treated with the chloride anion abstractor $Li[B(C_6F_5)_4]$ to generate the cationic complex with the coordinated nitrile group, as suggested by the NMR spectroscopy. A formation of yet another cationic complex was observed upon treating compound **10** with $(Ph_3C)[B(C_6F_5)_4]$.

1. Introduction

Cyclopentadienyl ligands occupy a prominent position in the coordination chemistry of group 4 elements. Metallocene complexes of these metals were found to act as effective catalysts for various processes, polymerization of olefins being among the most important examples, and found applications also as reagents in organic synthesis [1]. Such findings have been continuously prompting vigorous research activity in this area during past decades. However, new derivatives of the discussed complexes, especially those bearing additional functional groups, are still demanded. Pendant moieties attached to the η^5-cyclopentadienyl ligand could alter chemical and/or catalytic properties of such complexes [2]. Furthermore, reactive groups could be further modified or used to attach other molecular building blocks [3]. Nevertheless, the range of synthetic methods to modify group 4 metallocenes is significantly limited, mainly due to their incompatibility with nucleophilic reagents common in organic synthesis. The functional groups are therefore often introduced to the ligand before the transmetalation step [4]. Future efforts must be undoubtedly directed toward broadening the range of synthetic approaches providing a convenient access to variously substituted compounds.

In contrast to the variety of pendant substituents utilized in group 4 metallocene complexes, examples of compounds having a $C{\equiv}N$ functionality in the sidearm are obviously missing [5,6]. The nitrile group represents an unsaturated, yet relatively robust *N*-donor group, which has a potential for further synthetic modification. We therefore decided to prepare such derivatives. In this contribution, we report the synthesis of a new functionalized cyclopentadienyl ligand possessing the nitrile group by a straightforward and high-yielding method and its utilization for the preparation of group 4 metal complexes.

2. Results and discussion

2.1. Synthesis of the new ligand and its complexes

The introduction of nitrile group to the cyclopentadienyl moiety was carried out by the nucleophilic addition of *in situ* formed $LiCH_2CN$ to 6,6-dimethylfulvene (Scheme 1). Such approach starting with fulvenes is well precedented, even involving functionalization with polar moieties [7]. The organyllithium reagent was conveniently obtained by lithiation of acetonitrile by 1 M equivalent of *n*-butyllithium in THF at low temperature [8]. The reaction with fulvene afforded the lithium salt of the substituted cyclopentadienyl

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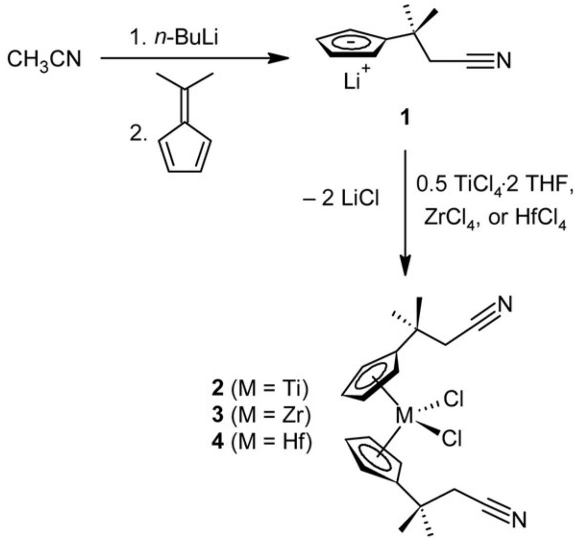
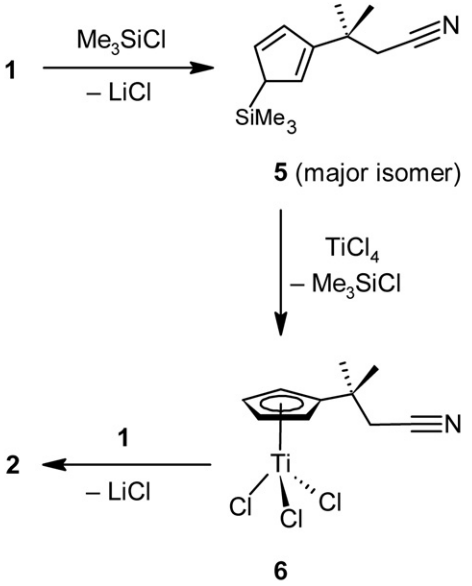


Scheme 1. Preparation of lithium salt **1** and complexes **2**–**4**.

(**1**) in almost quantitative yield. NMR spectroscopy of **1** revealed the expected set of signals for the CMe_2 and CH_2 groups, and signals for two mutually interacting pairs of protons of the monosubstituted cyclopentadienyl moiety in ^1H and the corresponding resonances in ^{13}C spectra. Additionally, the nitrile carbon resonance was found at δ_C 120.2 ppm, which lies in a usual range for this group.

Lithium salt **1** was subsequently transmetalated with 0.5 M equivalents of group 4 metal tetrachlorides [9]. In the case of titanium, the preformed adduct $TiCl_4 \cdot 2THF$ was used in order to decrease Lewis acidity of the metal center. The reactions were performed in THF at −78 °C and afforded the corresponding bent metallocene complexes $[(\eta^5{-}C_5H_4CMe_2CH_2CN)_2MCl_2]$ (M = Ti, **2**; M = Zr, **3**; M = Hf, **4**) in low (Ti) to moderate (Zr, Hf) yields as crystalline solids (Scheme 1). With the aim to increase the yield of compound **2**, another route was tested utilizing $TiCl_3 \cdot 3THF$ and a subsequent oxidative work-up with aqueous HCl [9b]. Unfortunately, this approach failed to produce **2** in sufficient yields, while significant decomposition was observed. Another route via the preparation of half-sandwich complex **6** succeeded better (Scheme 2). In the first step, **1** was converted to the silylated derivative **5** (>90% of the depicted isomer as observed by NMR), which was then reacted with $TiCl_4$ in toluene to produce the trichloride $[(\eta^5{-}C_5H_4CMe_2CH_2CN)TiCl_3]$ (**6**). This complex could be further converted to **2** by the reaction with 1 M equivalent of **1**. The overall yield of **2** using this route was 59%.

In another series of reactions, mixed metallocene dichlorides were synthesized from equimolar amounts of monocyclopentadienyl precursors and lithium salt **1** under similar conditions as for previous syntheses (Scheme 3). Thus, complexes $[(\eta^5{-}C_5H_5)(\eta^5{-}C_5H_4CMe_2CH_2CN)MCl_2]$ (M = Ti, **7**; M = Zr, **8**) were prepared starting from $[(\eta^5{-}C_5H_5)MCl_3]$ in good yields. Since for the zirconium compound **8** it was not possible to obtain good quality crystals for X-ray analysis, we also prepared an analog with the permethylated cyclopentadienyl ligand $[(\eta^5{-}C_5Me_5)(\eta^5{-}C_5H_4CMe_2CH_2CN)_2ZrCl_2]$ (**9**) starting from $[(\eta^5{-}C_5Me_5)ZrCl_3]$. In the case of hafnium, we attempted the synthesis of analogous complex $[(\eta^5{-}C_5H_5)(\eta^5{-}C_5H_4CMe_2CH_2CN)HfCl_2]$, but we encountered problems with low reaction rate. When the mixture was heated to accomplish the reaction, a mixture of products was obtained containing the desired product, but also symmetrically substituted complexes $[(\eta^5{-}C_5H_5)_2HfCl_2]$ and **4**. Isolation of the mixed hafnocene dichloride from the mixture was unsuccessful.

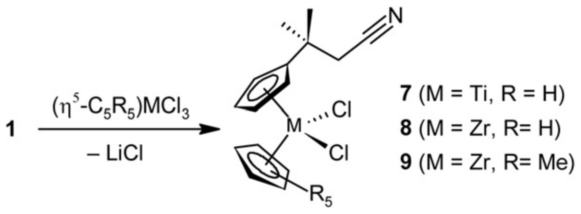


Scheme 2. Preparation of complex **6**; alternative route to **2**.

All newly prepared compounds were characterized by conventional spectral methods. The NMR spectra showed an expected pattern for all metal complexes. In comparison to lithium salt **1**, complexes of the ligand exhibited a downfield shift of the resonances for the cyclopentadienyl moiety. In ^{13}C spectra, the nitrile carbon signal was observed with δ_C in the range 118.3–119.0 ppm for all compounds **2**–**4**, **6**, and **7**–**9**, indicating that the pendant functionality remained uncoordinated in solution. It became evident from IR spectra that the nitrile group is not significantly influenced also in the solid state. For all above mentioned complexes the band corresponding to the C≡N stretching vibration appeared in the region typical for the free nitrile group (2237–2250 cm^{-1}). Electron impact (EI) mass spectra confirmed the formulation of compounds **2**–**4**, **6**, and **7**–**9** displaying molecular ions ($[M^{+\bullet}]$) and ions resulting from simple fragmentation (e.g., $[M{-}Cl]^+$, $[M{-}(C_5H_4CMe_2CH_2CN)]^+$, $[M{-}(C_5H_5)/(C_5Me_5)]^+$, $[C_5H_4CMe_2CH_2CN]^+$). In addition, combustion elemental analyses were performed for all complexes.

2.2. Crystal structure analyses

In addition to the spectral characterization, molecular structures of compounds **2**, **3**, **4**, **7**, and **9** were determined by the single-crystal X-ray diffraction analysis. The structures of compounds **2**–**4** are isomorphous (a view of the structure is shown for **2** in Fig. 1; for **3** and **4**, see the Supplementary material). These complexes crystallized in the chiral orthorhombic space group $P2_12_12_1$ with one C_2-symmetric molecule in the asymmetric unit. Selected geometric data are given in Table 1. The compounds exhibit the expected bent metallocene structure with the pendant substituents both oriented



Scheme 3. Preparation of complexes **7**–**9**.

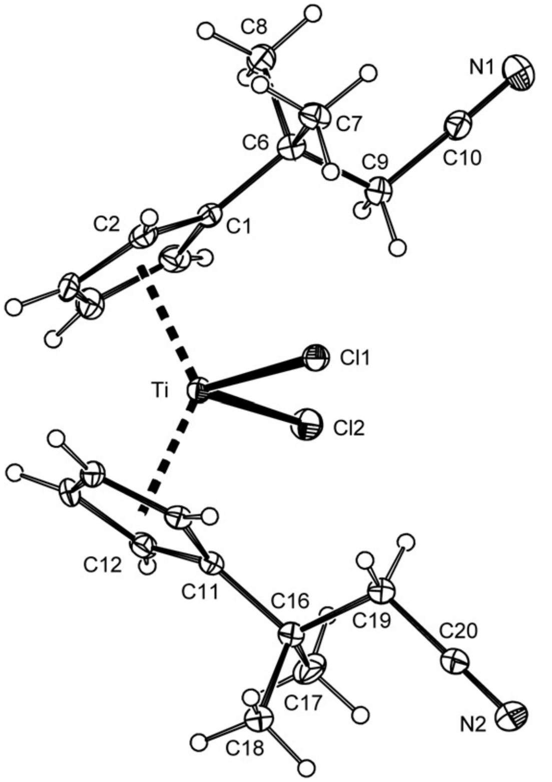


Fig. 1. A view of the molecular structure of **2** showing the atom labeling scheme and displacement ellipsoids at the 30% probability level. Complexes **3** and **4** are isostructural; for their graphical representations, see the Supplementary material.

toward the opened side of the metallocene wedge, which is manifested by the dihedral angle C1–Cg(1)–Cg(2)–C11 (denoted as θ) found for complexes **2**–**4** in the range 28.0–29.5° (absolute value). This is in contrast with similar structures of substituted bent metallocenes with more sterically demanding substituents [9a,10]. Nitrile groups at the end of each arm are pointing away from the metallocene core precluding any coordination to the metal center. Likewise, no intermolecular interactions were found in the discussed structures.

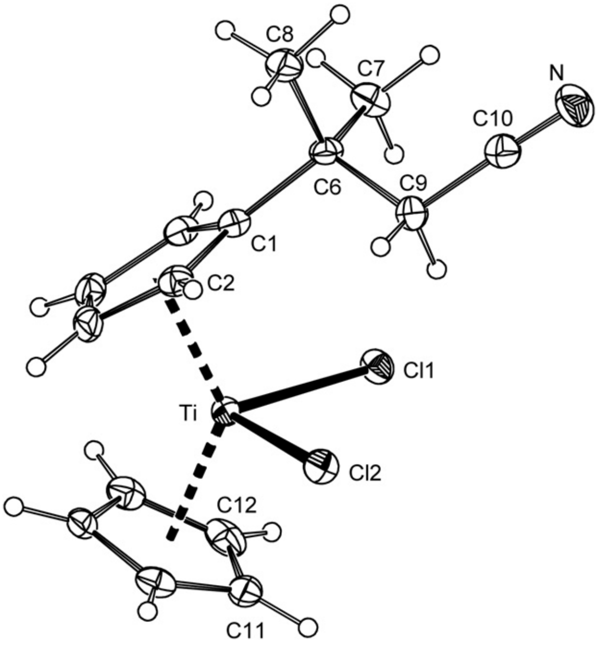


Fig. 2. A view of the molecular structure of **7** showing the atom labeling scheme and displacement ellipsoids at the 30% probability level.

Molecular structures of mixed metallocene dichlorides **7** and **9** are depicted in Figs. 2 and 3, respectively. Selected geometric data are summarized in Table 2. Complex **7** crystallized in the chiral monoclinic space group $P2_1$ with one molecule in the asymmetric unit, while complex **9** crystallized as a racemate in the centrosymmetric monoclinic space group $P2_1/n$ with two molecules in the asymmetric unit, which differ slightly in the conformation of pendant group and in the mutual rotation of the substituted cyclopentadienyl rings. Both structures **7** and **9** are similar to the previously discussed complexes concerning the conformation of the nitrile substituted cyclopentadienyl ligand, while the other cyclopentadienyl is obviously replaced by the unsubstituted or permethylated one.

Table 1
Selected distances and angles [in Å and °] for **2**, **3**, and **4**.[a]

Compound	**2** (M = Ti)	**3** (M = Zr)	**4** (M = Hf)
M–Cg1	2.0991(12)	2.2116(13)	2.191(3)
M–Cg2	2.0819(11)	2.2287(14)	2.206(4)
M–C (1–15; range)	2.323(2)–2.519(2)	2.446(3)–2.610(3)	2.422(6)–2.600(7)
M–Cl1	2.3457(7)	2.4337(8)	2.409(2)
M–Cl2	2.3585(8)	2.4446(7)	2.419(2)
C1/11–C6/16	1.519(3)/1.525(3)	1.527(4)/1.529(4)	1.510(10)/1.523(11)
C6/16–C9/19	1.543(3)/1.551(4)	1.543(4)/1.540(4)	1.545(11)/1.553(10)
C9/19–C10/20	1.467(4)/1.466(4)	1.462(4)/1.468(4)	1.451(11)/1.452(11)
C10/20–N1/2	1.140(3)/1.144(3)	1.142(4)/1.137(4)	1.161(10)/1.159(11)
∠Cp(1),Cp(2)	58.1(2)	58.4(2)	58.4(5)
Cl1–M–Cl2	94.62(3)	96.75(3)	95.90(7)
Cg(1)–M–Cg(2)	131.03(5)	129.07(5)	129.70(14)
C1/11–C6/16–C9/19	109.7(2)/109.5(2)	109.7(2)/109.8(2)	109.8(7)/108.4(6)
C6/16–C9/19–C10/20	111.8(2)/112.4(2)	112.2(2)/112.4(2)	113.7(7)/111.8(6)
C9/19–C10/20–N1/2	178.4(3)/178.1(3)	178.5(4)/177.8(4)	178.2(9)/176.8(10)
C2/12–C1/11–C6/16-C9/19	138.1(2)/139.4(2)	54.3(4)/53.9(4)	54.7(9)/54.0(9)
C1/11–C6/16–C9/19–C10/20	176.3(2)/167.8(2)	−169.1(3)/−176.2(2)	−168.6(6)/−175.6(6)
θ[b]	−29.5	28.6	28.0

[a] The ring planes are defined as follows: Cp(1) = C(1–5), Cp(2) = C(11–15) and Cg(1,2) are the respective ring centroids.

[b] θ denotes the dihedral angle C1–Cg(1)–Cg(2)–C11.

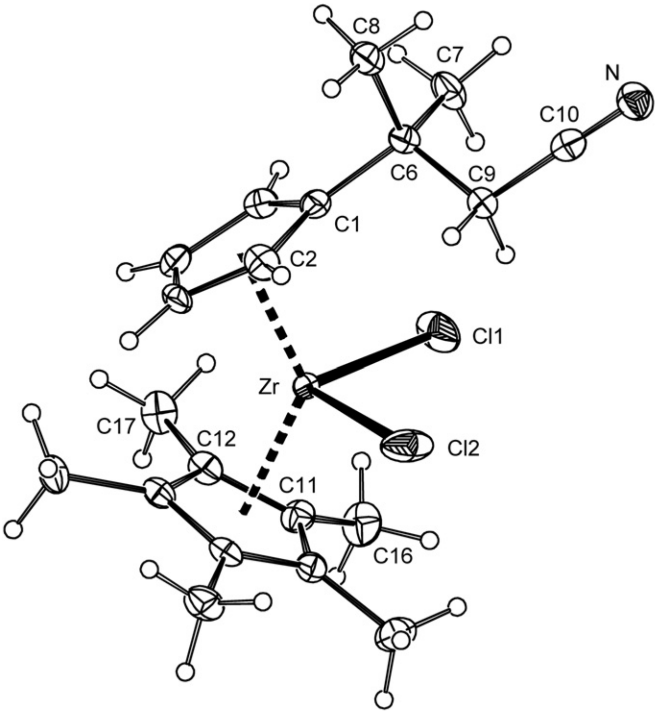
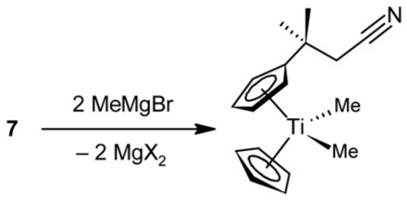


Fig. 3. A view of the molecular structure of **9** (molecule 1) showing the atom labeling scheme and displacement ellipsoids at the 30% probability level.

2.3. *Reactivity of compounds **7** and **10***

To investigate the reactivity of prepared metallocene dichlorides, we tested alkylation reactions of compound **7** as a selected example. First attempts to utilize two equivalents of methyllithium failed, since it led to partial reduction of the titanium center and intractable mixture of products was obtained. In contrast to these disappointing results, methylation with methylmagnesium bromide in THF resulted in a clean conversion of the dichloride to the dimethyl derivative [(η^5–C_5H_5) (η^5–$C_5H_4CMe_2CH_2CN$)$TiMe_2$] (**10**, Scheme 4). This compound was isolated as an amorphous solid, reluctant to crystallization, sensitive to light, which decomposed slowly over few days at room temperature in the solid state as well as in solution. NMR spectra revealed the presence of methyl groups σ-bonded to titanium, manifested by the signals at δ_H −0.18 ppm and δ_C 45.6 ppm, respectively. In the IR spectrum, the C≡N stretching band was found at slightly higher energies (2287 cm^{-1}) compared to the parent complex. EI-mass spectrometry did not provide satisfactory results, probably due to decomposition of compound **10** at relatively low temperatures.



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Scheme 4. Methylation of dichloride **7** yielding compound **10**.

Table 2
Selected distances and angles [in Å and °] for **7** and **9** (two symmetrically independent molecules).[a]

Compound	**7** (M = Ti)	**9** (M = Zr; mol. 1)	**9** (M = Zr; mol. 2)
M–Cg(1)	2.088(2)	2.231(2)	2.237(2)
M–Cg(2)	2.062(2)	2.217(2)	2.214(2)
M–C (1–15; range)	2.321(4)–2.514(3)	2.445(4)–2.639(5)	2.465(4)–2.628(4)
M–Cl1	2.3568(10)	2.4368(13)	2.4472(14)
M–Cl2	2.3626(12)	2.436(2)	2.431(2)
C1–C6	1.528(5)	1.530(6)	1.524(6)
C6–C9	1.531(5)	1.536(7)	1.557(6)
C9–C10	1.471(6)	1.481(7)	1.489(7)
C10–N	1.138(5)	1.135(6)	1.123(6)
∠Cp(1),Cp(2)	54.9(2)	55.1(3)	56.3(2)
Cl1–M–Cl2	94.05(4)	98.76(7)	99.03(6)
Cg(1)–M–Cg(2)	131.41(7)	131.41(9)	130.05(8)
C1–C6–C9	109.6(3)	108.8(4)	109.2(4)
C6–C9–C10	114.8(3)	112.9(4)	113.6(4)
C9–C10–N	178.0(4)	179.2(5)	178.2(5)
C2–C1–C6–C9	58.1(4)	54.3(6)	46.3(6)
C1–C6–C9–C10	−176.9(3)	−175.5(4)	179.7(4)
θ[b]	25.8	−45.0	−35.7

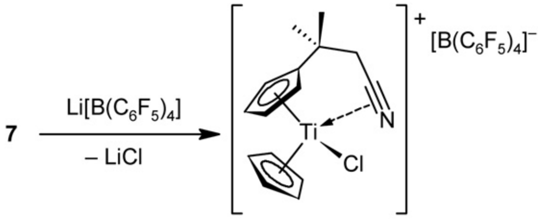
[a] The ring planes are defined as follows: Cp(1) = C(1–5), Cp(2) = C(11–15) and Cg(1,2) are the respective ring centroids.

[b] θ denotes the dihedral angle C1–Cg(1)–Cg(2)–C11.

Motivated by known intermolecular reactions of the unsubstituted dimethyltitanocene with nitriles under thermal conditions [11], we made attempts to perform a controlled thermolysis of **10** in toluene-d_8 at 80 °C. Unfortunately, an intractable mixture of products was observed by the NMR spectroscopy. However, methane could be identified as one of the products, indicating the expected route of thermolysis starting with CH_4 elimination.

Group 4 bent metallocene complexes are also known to generate stable cationic species e.g., by an abstraction of chloride anion [12]. We tested this possibility by performing the reaction of complex **7** with Li[B(C_6F_5)$_4$] in CD_2Cl_2 (Scheme 5), which was monitored *in situ* by the NMR spectroscopy. Very slow formation of a supposed cationic complex **11** over few weeks was observed. A set of signals attributable to an unsymmetrical compound appeared, in which the resonances for both methyls of the CMe_2 group, protons of the methylene, and all four protons of the cyclopentadienyl moiety are nonequivalent. Also a dramatic change in the shift of the nitrile carbon to δ_C 180.5 ppm suggested an intramolecular coordination of the pendant arm in a η^2-*C*,*N*-fashion [13]. ESI-MS analysis of the mixture supported the formulation of **11** showing abundant fragment of the complex cation, for which the observed isotopic distribution corresponded to the calculated one.

Another route to cationic complexes was probed starting with complex **10**. A methyl group abstraction using (Ph_3C)[B(C_6F_5)$_4$] [14] yielded a new compound, which has been tentatively assigned to structure **12** (Scheme 6). According to the NMR spectroscopy, the nitrile group in **12** is not intramolecularly coordinated to the metal ion (the *C*N resonance at δ_C 119.5 ppm). Also for **12** the ESI-MS analysis confirmed the suggested ionic nature of the complex showing fragments of the complex cation (either free or with one water molecule, which was likely formed during the measurement



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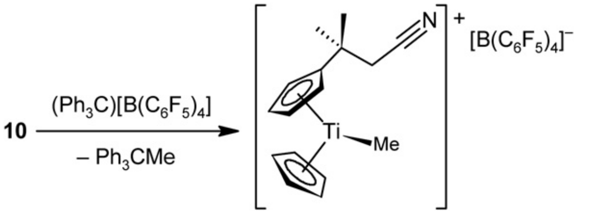
Scheme 5. Proposed reaction pathway for the chloride anion abstraction by Li[B(C_6F_5)$_4$] in complex **7**.



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Scheme 6. Proposed reaction pathway for the methyl group abstraction by $(Ph_3C)[B(C_6F_5)_4]$ in complex **10**.

in contact with moisture). Unfortunately, in cases of both cationic species **11** and **12**, attempts to isolate these compounds have been so far unsuccessful.

3. Conclusion

A new nitrile-functionalized cyclopentadienyl ligand was prepared in a straightforward manner by the fulvene route in the form of its lithium salt. Its coordination to group 4 metals yielded bent metallocene dichlorides, in which the pendant arms did not interact with the metal center. Lower yields of titanium complex **2**, caused by the reducing ability of the lithium salt were overcome by the sequential preparation of monocyclopentadienyl complex **6**, which was then converted to **2**. Titanocene dichloride **7** was alkylated by the Grignard reagent to afford the corresponding dimethyl derivative **10**, while the nitrile functional group remained unaffected. The reaction of **7** with $Li[B(C_6F_5)_4]$ provided a preliminary evidence of formation of the cationic species with the intramolecularly coordinated nitrile group. A methyl group abstraction in **10** using $(Ph_3C)[B(C_6F_5)_4]$ also led to the formation of the corresponding cationic complex, but in this case, the nitrile group did not exhibit the intramolecular coordination according to the spectral data. Further investigations into the reactivity of functionalized metallocene complexes involving transformations of the pendant group are currently in progress.

4. Experimental

4.1. Materials and methods

All syntheses and manipulations with air- and moisture-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox Labmaster 130 (mBraun) under purified nitrogen. All solvents (including deuterated) were appropriately dried: THF, diethyl ether, toluene, *n*-hexane by refluxing with Na/benzophenone ketyl until blue color persisted, then distilled under argon and stored over sodium mirror; chloroform, dichloromethane by refluxing with CaH_2, acetonitrile by refluxing with P_2O_5, then distilled under argon and stored over 4 Å molecular sieves. 6,6-dimethylfulvene was prepared as described in the literature [15]. Other chemicals were used as received from commercial sources (Aldrich, Strem).

NMR spectra were measured on a Varian Unity 300 spectrometer at 293 K. Chemical shifts (δ/ppm) are given relative to solvent signals ($CDCl_3$: δ_H 7.26, δ_C 77.16; CD_2Cl_2: δ_H 5.32, δ_C 53.84; THF-d_8 δ_H 3.58, δ_C 67.21). The assignment of NMR signals is based on 1D-NOESY, gCOSY, gHSQC, and gHMBC experiments. EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Electrospray (ESI) mass spectra were measured with a Bruker Esquire 3000 instrument on dichloromethane/acetonitrile solutions. GC–MS was performed on a Thermo Focus DSQ machine using the capillary column Thermo TR-5MS (15 m × 0.25 mm ID × 0.25 μm). IR spectra were measured on a Nicolet Avatar FTIR spectrometer on Nujol suspensions between KBr plates (prepared in a glovebox) in the range of 400–4000 cm^{-1}. Elemental analyses were performed on a FLASH 2000 CHN elemental analyzer (Thermo Scientific). Melting points were determined on a Kofler apparatus, the values are uncorrected; samples were sealed in glass capillaries under nitrogen.

4.2. Preparation of $(C_5H_4CMe_2CH_2CN)Li$ (**1**)

n-Butyllithium (10.0 mL of 2.5 M solution in hexanes, 25.0 mmol) was added dropwise to a stirred solution of acetonitrile (1.31 mL, 25.0 mmol) in THF (30 mL) at −78 °C. While the cooling was maintained, the mixture was stirred for 15 min. Subsequently, neat 6,6-dimethylfulvene (2.65 g, 25.0 mmol) was added dropwise. The yellow-orange color of the added fulvene quickly changed to pale yellow, indicating a formation of the product. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for 2 h. The solution was concentrated in vacuo to ca. 5 mL and *n*-hexane (30 mL) was added, which led to a formation of a brownish precipitate. The liquid phase was removed and the solids were washed with *n*-hexane (10 mL), and dried in vacuo. After ca 1 h at low pressure (5×10^{-2} Torr), the precipitate turned into an oily residue (as the solvating THF was being released) that later solidified to a brownish waxy solid, identified as the lithium salt **1** by NMR spectroscopy. The air- and moisture-sensitive product retained various amounts of THF, which proved to be difficult to remove, but was of a sufficient purity to be used for further reactions. Yield: 3.75 g (98%).

NMR (THF-d_8) ^{1}H: δ 1.34 (s, 6 H, C*Me*$_2$), 2.49 (s, 2 H, C*H*$_2$CN), 5.34 (m, 2 H, C_5*H*$_4$ *distal*), 5.39 (m, 2 H, C_5*H*$_4$ *proximal*). $^{13}C\{^1H\}$: δ 29.8 (C*Me*$_2$), 34.0 (*C*H$_2$CN), 34.6 (*C*Me$_2$), 100.3 (C_5H_4 *CH dist.*), 103.0 (C_5H_4 *CH prox.*), 120.2 (*C*N), 125.6 (C_5H_4 C_{ipso}).

4.3. Preparation of $[(\eta^5-C_5H_4CMe_2CH_2CN)_2TiCl_2]$ (**2**)

A 1 M solution of $TiCl_4$ in toluene (1.0 mL, 1.0 mmol) was added to 10 mL of THF at −78 °C, forming a bright yellow precipitate of $TiCl_4 \cdot 2THF$. To the stirred suspension, a solution of lithium salt **1** (306 mg, 2.0 mmol) in THF (10 mL) was slowly introduced. The color of the mixture immediately changed to deep red. After 15 min at −78 °C, the mixture was allowed to warm slowly to room temperature and stirred for further 16 h. All volatiles were removed under vacuum and the dark residue was extracted with toluene/dichloromethane mixture (2:1 v/v, 3 × 10 mL). The combined extracts were evaporated, redissolved in dichloromethane (5 mL), filtered, and allowed to stand at −30 °C overnight, affording deep red crystals, which were separated from the solution, washed with cold diethyl ether, and dried in vacuo. The mother liquor afforded another crop of the product upon reducing the volume. Total yield of **2**: 107 mg (26%). Repeated runs gave similar results.

M.p. 162 °C. NMR ($CDCl_3$) ^{1}H: δ 1.54 (s, 6 H, C*Me*$_2$), 2.90 (s, 2 H, C*H*$_2$CN), 6.46 (m, 2 H, C_5*H*$_4$ *dist.*), 6.55 (m, 2 H, C_5*H*$_4$ *prox.*). $^{13}C\{^1H\}$: δ 28.5 (C*Me*$_2$), 31.5 (*C*H$_2$CN), 36.4 (*C*Me$_2$), 114.8 (C_5H_4 *CH dist.*), 118.6 (*C*N), 122.2 (C_5H_4 *CH prox.*), 143.9 (C_5H_4 C_{ipso}). IR (Nujol): 3107 (m), 3100 (w), 2241 (w, ν_{CN}), 1492 (m), 1427 (w), 1418 (w), 1415 (w), 1395 (w), 1369 (m), 1319 (w), 1258 (w), 1141 (m), 1056 (w), 944 (w), 872 (s), 850 (s), 842 (m), 731 (w) cm^{-1}. EI-MS, *m/z* (relative abundance): 410 (6; $[M]^{+\bullet}$), 375 (38; $[M-Cl]^+$), 146 (85; $[C_5H_4CMe_2CH_2CN]^+$), 106 (100; $[C_5H_4CMe_2]^+$). Anal. calc. for $C_{20}H_{24}Cl_2N_2Ti$ (411.21): C 58.41, H 5.88, N 6.81%. Found: C 58.29, H 5.91, N 6.88%.

4.4. Preparation of $[(\eta^5-C_5H_4CMe_2CH_2CN)_2ZrCl_2]$ (**3**)

Lithium salt **1** (306 mg, 2.0 mmol) and $ZrCl_4$ (233 mg, 1.0 mmol) were placed in a Schlenk flask under argon and after cooling the solids to −78 °C, THF (30 mL) was slowly introduced. The suspension was stirred, gradually warmed to room temperature over a period of 30 min. A clear yellow solution was obtained, which was further stirred for 3 h. All volatiles were removed and the residue was extracted with dichloromethane (3 × 10 mL), filtered, and evaporated under vacuum. The crude product was recrystallized from THF/diethyl ether at −30 °C giving pale yellow crystals. Yield of **3**: 236 mg (52%).

M.p. 154 °C. NMR ($CDCl_3$) ^{1}H: δ 1.53 (s, 6 H, C*Me*$_2$), 2.74 (s, 2 H, C*H*$_2$CN), 6.37 (m, 2 H, C_5*H*$_4$ *dist.*), 6.48 (m, 2 H, C_5*H*$_4$ *prox.*). $^{13}C\{^1H\}$: δ 28.3 (C*Me*$_2$), 32.6 (*C*H$_2$CN), 35.7 (*C*Me$_2$), 111.4 (C_5H_4 *C*H *dist.*), 117.5 (C_5H_4 *C*H *prox.*), 118.4 (*C*N), 139.2 (C_5H_4 C_{ipso}). IR (Nujol): 3100 (m), 2242 (w, ν_{CN}), 1488 (w), 1422 (w), 1416 (w), 1394 (w), 1388 (w), 1370 (m), 1319 (w), 1139 (m), 1045 (w), 945 (w), 860 (m), 835 (s), 820 (w), 665 (w) cm^{-1}. EI-MS, *m*/*z* (relative abundance): 452 (76; $[M]^{+\bullet}$), 417 (37; $[M-Cl]^+$), 306 (95; $[M-C_5H_4CMe_2CH_2CN]^+$), 265 (100). Anal. calc. for $C_{20}H_{24}Cl_2N_2Zr$ (454.53): C 52.85, H 5.32, N 6.16%. Found: C 52.72, H 5.38, N 6.22%.

4.5. Preparation of $[(\eta^5-C_5H_4CMe_2CH_2CN)_2HfCl_2]$ (**4**)

Lithium salt **1** (306 mg, 2.0 mmol) and $HfCl_4$ (320 mg, 1.0 mmol) were placed in a Schlenk flask under argon and THF (30 mL) was slowly introduced while cooling the reaction vessel to −78 °C. The suspension was stirred, gradually warmed to room temperature over a period of 30 min. A clear orange solution was obtained, which was further stirred for 4 h. All volatiles were removed and the residue was extracted with toluene/dichloromethane mixture (1:1 v/v, 3 × 10 mL), filtered, and concentrated under vacuum to ca. 10 mL. The product crystallized from the solution at 4 °C giving pale yellow crystals, which were dried in vacuo. Yield of **4**: 303 mg (56%).

M.p. 135–140 °C. NMR ($CDCl_3$) ^{1}H: δ 1.53 (s, 6 H, C*Me*$_2$), 2.72 (s, 2 H, C*H*$_2$CN), 6.26 (m, 2 H, C_5*H*$_4$ *dist.*), 6.39 (m, 2 H, C_5*H*$_4$ *prox.*). $^{13}C\{^1H\}$: δ 28.3 (C*Me*$_2$), 32.8 (*C*H$_2$CN), 35.6 (*C*Me$_2$), 110.2 (C_5H_4 *C*H *dist.*), 116.0 (C_5H_4 *C*H *prox.*), 118.4 (*C*N), 137.1 (C_5H_4 C_{ipso}). IR (Nujol): 3102 (m), 2242 (w, ν_{CN}), 1489 (w), 1422 (w), 1416 (w), 1388 (m), 1319 (w), 1139 (m), 1045 (w), 945 (w), 862 (m), 837 (s), 821 (w), 665 (w) cm^{-1}. EI-MS, *m*/*z* (relative abundance): 542 (7; $[M]^{+\bullet}$), 396 (100; $[M-C_5H_4CMe_2CH_2CN]^+$), 355 (99). Anal. calc. for $C_{20}H_{24}Cl_2N_2Hf$ (541.80): C 44.33, H 4.47, N 5.17%. Found: C 44.26, H 4.56, N 5.20%.

4.6. Preparation of $[(\eta^5-C_5H_4CMe_2CH_2CN)TiCl_3]$ (**6**)

Me_3SiCl (230 mg, 2.12 mmol) was added dropwise to a stirred solution of lithium salt **1** (306 mg, 2.0 mmol) in THF (30 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred for 18 h. The solvents were removed in vacuo and the resulting pale yellow oil was dissolved in toluene (15 mL) and filtered to another flask leaving a white precipitate of LiCl. According to the NMR spectroscopy and GC–MS analysis, the oil contained predominantly the silylated cyclopentadiene, $Me_3SiC_5H_4CMe_2CH_2CN$ (**5**, >90% of this particular isomer), which was directly used in the next step.

5: NMR ($CDCl_3$): ^{1}H: δ −0.03 (s, 9 H, Si*Me*$_3$), 1.36 (s, 6 H, C*Me*$_2$), 2.51 (s, 2 H, C*H*$_2$CN), 3.32 (m, 1 H, Me_3SiC*H*), 6.18, 6.50, 6.57 (3× m, 1 H, C=C*H*). $^{13}C\{^1H\}$: δ −1.93 (Si*Me*$_3$), 28.0 (C*Me*$_2$), 31.6 (*C*H$_2$CN), 34.7 (*C*Me$_2$), 51.4 (Me_3Si*C*), 118.6 (*C*N), 126.2, 128.7, 135.1 (3 × C=*C*H), 150.6 ($Me_3SiC_5H_4$ C_{ipso}). GC–MS, *m*/*z* (relative abundance): 219 (3; $[M]^{+\bullet}$), 163 (6), 113 (36), 73 (100; $[SiMe_3]^+$).

The toluene solution of **5** (prepared as described above) was slowly added to a stirred solution of $TiCl_4$ in the same solvent (2.0 mL of 1 M solution, 2.0 mmol) with cooling to −30 °C. After warming to room temperature, the mixture was stirred for 16 h and subsequently evaporated under vacuum. The residue was extracted with toluene (3 × 10 mL). The extracts afforded, upon removal of the solvent, amber amorphous solid, which was triturated with *n*-hexane to remove soluble impurities. The crude product thus obtained was sufficiently pure according to the NMR spectroscopy. Yield of **6**: 523 mg (87%). Analytically pure sample was obtained by sublimation (5 × 10^{-2} Torr, 150 °C) as an orange solid, but significant loss due to decomposition was observed.

6: M.p. 78 °C. NMR ($CDCl_3$) ^{1}H: δ 1.64 (s, 6 H, C*Me*$_2$), 2.83 (s, 2 H, C*H*$_2$CN), 6.97 (m, 2 H, C_5*H*$_4$ *dist.*), 7.14 (s, 6 H, C_5*H*$_4$ *prox.*). $^{13}C\{^1H\}$: δ 28.0 (C*Me*$_2$), 32.9 (*C*H$_2$CN), 36.5 (*C*Me$_2$), 118.3 (*C*N), 121.1 (C_5H_4 *C*H *dist.*), 123.8 (C_5H_4 *C*H *prox.*), 148.4 (C_5H_4 C_{ipso}). IR (Nujol): 3111 (m), 3093 (w), 2250 (w, ν_{CN}), 1482 (m), 1419 (m), 1397 (w), 1307 (m), 1293 (m), 1242 (m), 1056 (w), 984 (w), 851 (s), 844 (m) cm^{-1}. EI-MS, *m*/*z* (relative abundance): 299 (25; $[M]^{+\bullet}$), 264 (8; $[M-Cl]^+$), 146 (91; $[C_5H_4CMe_2CH_2CN]^+$), 106 (100; $[C_5H_4CMe_2]^+$). Anal. calc. for $C_{10}H_{12}Cl_3NTi$ (300.46): C 39.97, H 4.03, N 4.66%. Found: C 39.86, H 4.13, N 4.69%.

4.7. Preparation of **2** from **6**

Lithium salt **1** (118 mg, 0.78 mmol) and complex **6** (233 mg, 0.78 mmol) were placed in a Schlenk flask under argon, cooled to −78 °C, and THF (15 mL) was slowly introduced with vigorous stirring. The color of the mixture changed immediately to deep red. After 10 min at −78 °C, the mixture was allowed to warm slowly to room temperature and stirred for further 4 h. Following the same work-up procedure as described in the Section 4.3, complex **2** was obtained. Yield: 218 mg (68%). Analytical data same as above.

4.8. Preparation of $[(\eta^5-C_5H_5)(\eta^5-C_5H_4CMe_2CH_2CN)TiCl_2]$ (**7**)

Lithium salt **1** (306 mg, 2.0 mmol) and $[(\eta^5-C_5H_5)TiCl_3]$ (439 mg, 2.0 mmol) were placed in a Schlenk flask under argon, cooled to −78 °C, and THF (30 mL) was slowly introduced with stirring. The suspension, which immediately turned red, was gradually warmed to room temperature over a period of 30 min. The resulting clear red solution was further stirred for 3 h. All volatiles were removed under vacuum and the solid residue was extracted with toluene/dichloromethane mixture (2:1 v/v, 3 × 10 mL). The combined extracts were concentrated to ca. 5 mL and the product was allowed to crystallize at −30 °C overnight. Red crystals were separated from the solution, washed with diethyl ether, and dried in vacuo. The mother liquor afforded another crop of the product upon reducing the volume. Combined yield: 541 mg (82%).

M.p. 168 °C. NMR ($CDCl_3$) ^{1}H: δ 1.52 (s, 6 H, C*Me*$_2$), 2.91 (s, 2 H, C*H*$_2$CN), 6.47 (m, 2 H, C_5*H*$_4$ *dist.*), 6.58 (overlapping signals: m, 2 H, C_5*H*$_4$ *prox.* and s, 5 H, C_5*H*$_5$). $^{13}C\{^1H\}$: δ 28.6 (C*Me*$_2$), 31.5 (*C*H$_2$CN), 36.3 (*C*Me$_2$), 115.1 (C_5H_4 *C*H *dist.*), 118.7 (*C*N), 120.6 (*C*$_5$H$_5$), 121.6 (C_5H_4 *C*H *prox.*), 143.8 (C_5H_4 C_{ipso}). IR (Nujol): 3105 (m), 2237 (w, ν_{CN}), 1488 (m), 1448 (s), 1421 (m), 1382 (m), 1366 (m), 1316 (w), 1258 (w), 1139 (m), 1028 (m), 1017 (m), 947 (w), 873 (m), 860 (m), 830 (vs), 737 (w), 661 (w) cm^{-1}. EI-MS, *m*/*z* (relative abundance): 329 (40; $[M]^{+\bullet}$), 294 (58; $[M-Cl]^+$), 264 (68; $[M-(C_5H_5)]^+$), 146 (92; $[C_5H_4CMe_2CH_2CN]^+$), 106 (90; $[C_5H_4CMe_2]^+$), 65 (100, $[C_5H_5]^+$). Anal. calc. for $C_{15}H_{17}Cl_2NTi$ (330.10): C 54.58, H 5.19, N 4.24%. Found: C 54.39, H 5.23, N 4.25%.

4.9. Preparation of $[(\eta^5-C_5H_5)(\eta^5-C_5H_4CMe_2CH_2CN)ZrCl_2]$ (**8**)

In a similar manner as in the previous case, lithium salt **1** (153 mg, 1.0 mmol) and $[(\eta^5-C_5H_5)ZrCl_3]$ (263 mg, 1.0 mmol) were reacted at −78 °C in THF (15 mL). The mixture was gradually warmed to room temperature over a period of 30 min and the resulting clear pale yellow solution was further stirred for 3 h. All volatiles were removed under vacuum and the oily residue was extracted with dichloromethane (3 × 10 mL). Evaporation of the extracts afforded the crude product as a colorless oil that solidified after standing at 4 °C overnight. Recrystallization from dichloromethane/diethyl ether at −30 °C afforded a colorless powder. Yield: 280 mg (75%).

M.p. 109–110 °C. NMR ($CDCl_3$) ^{1}H: δ 1.53 (s, 6 H, CMe_2), 2.78 (s, 2 H, CH_2CN), 6.38 (m, 2 H, C_5H_4 *dist.*), 6.49 (s, 5 H, C_5H_5), 6.50 (m, 2 H, C_5H_4 *prox.*). ^{13}C{^{1}H}: δ 28.3 (CMe_2), 32.5 (CH_2CN), 35.7 (CMe_2), 111.6 (C_5H_4 *CH dist.*), 116.3 (C_5H_5), 117.0 (C_5H_4 *CH prox.*), 119.0 (*C*N), 139.0 (C_5H_4 C_{ipso}). IR (Nujol): 3110 (m), 3101 (m), 2239 (w, ν_{CN}), 1487 (m), 1442 (s), 1415 (m), 1384 (m), 1369 (m), 1315 (w), 1137 (w), 1023 (m), 1016 (m), 946 (w), 857 (m), 838 (s), 823 (vs), 664 (w) cm^{-1}. EI-MS, *m/z* (relative abundance): 371 (25; $[M]^{+\bullet}$), 336 (16; $[M-Cl]^+$), 306 (90; $[M-(C_5H_5)]^+$), 265 (100), 225 (90, $[M-(C_5H_4CMe_2CH_2CN)]^+$). Anal. calc. for $C_{15}H_{17}Cl_2NZr$ (373.42): C 48.24, H 4.59, N 3.75%. Found: C 48.12, H 4.62, N 3.81%.

4.10. Attempted preparation of $[(\eta^5-C_5H_5)(\eta^5-C_5H_4CMe_2CH_2CN)HfCl_2]$

A similar procedure as for complex **7** (Section 4.8) was applied starting from **1** (153 mg, 1.0 mmol) and $[(\eta^5-C_5H_5)HfCl_3]$ (350 mg, 1.0 mmol). After 16 h, still about half of the trichloride remained unreacted, therefore heating to 60 °C was applied for additional 18 h. NMR spectroscopy revealed a mixture of complexes $[(\eta^5-C_5H_5)_2HfCl_2]$, $[(\eta^5-C_5H_5)(C_5H_4CMe_2CH_2CN)HfCl_2]$, and **4** in ca. 2:2:1 ratio (because of an extensive overlap of the signals, it was difficult to exactly determine the molar ratio). Colorless crystals of $[(\eta^5-C_5H_5)_2HfCl_2]$ were isolated by crystallization from dichloromethane, further attempts to separate the mixture failed.

$[(\eta^5-C_5H_5)(C_5H_4CMe_2CH_2CN)HfCl_2]$: NMR ($CDCl_3$) ^{1}H: δ 1.54 (s, 6 H, CMe_2), 2.73 (s, 2 H, CH_2CN), 6.27 (m, 2 H, C_5H_4 *dist.*), 6.39 (overlapping signals: m, 2 H, C_5H_4 *prox.* and s, 5 H, C_5H_5).

4.11. Preparation of $[(\eta^5-C_5Me_5)(\eta^5-C_5H_4CMe_2CH_2CN)_2ZrCl_2]$ (**9**)

Following the same procedure as for the preparation of **7** (Section 4.8), lithium salt **1** (306 mg, 2.0 mmol) and $[(\eta^5-C_5Me_5)ZrCl_3]$ (666 mg, 2.0 mmol) were mixed at −78 °C with THF (30 mL) and stirred for 3 h at room temperature. After removing the solvents under vacuum, the orange residue was extracted with toluene (3 × 10 mL). The combined extracts were concentrated to ca. 5 mL and the product was allowed to crystallize at −30 °C overnight. Light yellow crystals were separated, washed with diethyl ether, and dried in vacuo. The mother liquor afforded another crop of the product upon reducing its volume. Combined yield: 754 mg (85%).

M.p. 176–178 °C. NMR ($CDCl_3$) ^{1}H: δ 1.53 (s, 6 H, CMe_2), 2.02 (s, 15 H, C_5Me_5), 2.82 (s, 2 H, CH_2CN), 5.87 (m, 2 H, C_5H_4 *dist.*), 6.31 (m, 2 H, C_5H_4 *prox.*). ^{13}C{^{1}H}: δ 12.6 (C_5Me_5), 28.4 (CMe_2), 32.2 (CH_2CN), 35.6 (CMe_2), 110.4 (C_5H_4 *CH dist.*), 118.0 (C_5H_4 *CH prox.*), 118.7 (*C*N), 124.8 (C_5Me_5), 139.0 (C_5H_4 C_{ipso}). IR (Nujol): 3105 (w), 2237 (w, ν_{CN}), 1490 (m), 1414 (w), 1383 (m), 1319 (w), 1140 (m), 1025 (w), 946 (w), 872 (w), 814 (vs), 682 (w), 664 (w) cm^{-1}. EI-MS, *m/z* (relative abundance): 441 (50; $[M]^{+\bullet}$), 406 (11; $[M-Cl]^+$), 306 (100; $[M-(C_{10}H_{15})]^+$), 295 (83; $[M-(C_5H_4CMe_2CH_2CN)]^+$), 265 (94). Anal. calc. for $C_{20}H_{27}Cl_2NZr$ (443.55): C 54.15, H 6.14, N 3.16%. Found: C 54.07, H 6.22, N 3.18%.

4.12. Preparation of $[(\eta^5-C_5H_5)(\eta^5-C_5H_4CMe_2CH_2CN)TiMe_2]$ (**10**)

The following synthesis was performed in the dark. Methylmagnesium bromide (0.9 mL of 1 M solution in dibutyl ether, 0.9 mmol) was added dropwise to a stirred solution of compound **7** (149 mg, 0.45 mmol) in THF (10 mL) at −78 °C. The mixture was gradually warmed to room temperature, while the color slowly changed from deep red to orange, and the stirring was maintained for 3 h. All volatiles were removed in vacuo and the yellow residue was extracted with toluene/*n*-hexane mixture (3:2 v/v, 5 × 5 mL) in order to thoroughly separate the product from inorganic salts. The combined extracts were evaporated to leave a yellow amorphous solid. Yield: 116 mg (89%). NOTE: The compound seems to be light sensitive. It gradually decomposes even in dark in a few days at room temperature when in the solid state and even faster in solution, but can be stored at −30 °C at least for weeks.

NMR (THF-d_8) ^{1}H: δ −0.18 (s, 6 H, $TiMe_2$), 1.22 (s, 6 H, CMe_2), 2.48 (s, 2 H, CH_2CN), 5.97 (m, 2 H, C_5H_4 *dist.*), 6.06 (s, 5 H, C_5H_5), 6.21 (m, 2 H, C_5H_4 *prox.*). ^{13}C{^{1}H}: δ 27.7 (CMe_2), 33.2 (CH_2CN), 35.5 (CMe_2), 45.6 ($TiMe_2$), 111.3 (C_5H_4 *CH dist.*), 114.5 (C_5H_5), 114.9 (C_5H_4 *CH prox.*), 118.3 (*C*N), 135.4 (C_5H_4 C_{ipso}). IR (Nujol): 3091 (w), 2287 (w, ν_{CN}), 1487 (w), 1418 (w), 1306 (w), 1180 (m), 1140 (m), 1023 (m), 879 (w), 820 (vs), 723 (w) cm^{-1}. Anal. calc. for $C_{17}H_{23}NTi$ (289.26): C 70.58, H 8.01, N 4.84%. Found: C 69.53, H 8.32, N 4.64%.

4.13. Reaction of **7** with $Li[B(C_6F_5)_4]$

Complex **7** (16 mg, 0.05 mmol) and $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$ (44 mg, 0.05 mmol) were placed into a Schlenk tube under argon and

Table 3
Selected crystallographic data for **2**, **3**, **4**, **7**, and **9**.

Compound	**2**	**3**	**4**	**7**	**9**
Formula	$C_{20}H_{24}Cl_2N_2Ti$	$C_{20}H_{24}Cl_2N_2Zr$	$C_{20}H_{24}Cl_2N_2Hf$	$C_{15}H_{17}Cl_2NTi$	$C_{20}H_{27}Cl_2NZr$
M (g mol^{-1})	411.21	454.53	541.80	330.10	443.55
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)
a (Å)	7.3411(2)	7.43860(10)	7.4293(4)	6.6785(6)	18.2406(8)
b(Å)	14.9654(3)	15.0201(3)	15.0096(7)	11.4021(9)	12.1165(4)
c (Å)	17.7994(5)	18.0693(4)	18.0116(5)	10.1469(5)	18.3373(7)
β (°)	90	90	90	107.524(5)	96.919(2)
V (Å^3)	1955.49(9)	2018.86(7)	2008.49(15)	736.82(10)	4023.3(3)
Z	4	4	4	2	8
D_{calc} (g mL^{-1})	1.397	1.495	1.792	1.488	1.465
Diffractions total	28700	37016	14391	10970	32650
Unique/observed[a] diffractions	4472/3436	4623/3866	4579/3336	3341/2694	9047/6115
R_{int} (%)[b]	6.6	5.7	9.1	7.4	3.7
R (observed data) (%)[c]	3.58	3.22	4.19	4.35	4.65
R, wR (all data) (%)[c]	6.09, 7.63	4.73, 7.02	7.96, 7.73	6.14, 10.05	8.38, 12.31
Flack's parameter	−0.03(3)	−0.02(4)	−0.027(13)	−0.01(3)	–
$\Delta\rho$ (e Å^{-3})	0.30, −0.32	0.69, −0.53	2.03, −1.99	0.37, −0.71	1.11, −0.89

[a] Diffractions with $I_o > 2\sigma(I_o)$.
[b] $R_{int} = \Sigma|F_o^2 - F_o^2(\mathrm{mean})|/\Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions.
[c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$.

CD_2Cl_2 (ca. 0.6 mL) was condensed into the tube at liquid nitrogen temperature under vacuum. After warming the mixture to room temperature, a clear red solution was formed, which was transferred into the NMR tube, cooled to liquid nitrogen temperature and flame-sealed under vacuum. The reaction was *in situ* periodically monitored by NMR. Over several days, a set of signals started to appear in the spectrum, while the starting compound was being consumed. Simultaneously, a small amount of white precipitate (LiCl) appeared in the tube. After one month, approximately 1:1 M ratio was reached. The new compound was tentatively assigned to structure **11**. Attempts to isolate this compound have been so far unsuccessful.

NMR (CD_2Cl_2) ^{1}H: δ 1.17, 1.34 (2× s, 3 H, CMe_2), 2.42, 2.82 (2× d, $^2J = 15.3$ Hz, 1 H, CH_2CN), 6.02, 6.25 (2× m, 1 H, C_5H_4), 6.65 (s, 5 H, C_5H_5), 6.77, 7.14 (2× m, 1 H, C_5H_4). ^{13}C{^{1}H}: δ 27.9, 28.5 (2× CMe_2), 34.2 (CMe$_2$), 46.2 (CH$_2$CN), 108.9, 117.6, 120.8 (3× C_5H_4 CH), 122.2 (C_5H_5), 126.9 (C_5H_4 CH), 148.3 (C_5H_4 C_{ipso}), 180.5 (CN); signals for the free $[B(C_6F_5)_4]^-$ anion: 136.6 (dm, $J_{C,F} = 246$ Hz, m-C_6F_5), 138.6 (dm, $J_{C,F} = 246$ Hz, p-C_6F_5), 148.4 (dm, $J_{C,F} = 241$ Hz, o-C_6F_5) ppm, C_{ipso} of C_6F_5 not observed. MS, m/z (ESI+): 312 ($[M_{cation}+H_2O]^+$), 294 ($[M_{cation}]^+$); (ESI−): 679 ($[B(C_6F_5)_4]^-$).

4.14. *Reaction of **10** with $(Ph_3C)[B(C_6F_5)_4]$*

Complex **10** (30 mg, 0.10 mmol) and $(Ph_3C)[B(C_6F_5)_4]$ (96 mg, 0.10 mmol) were placed into a Schlenk tube under argon and C_6D_6 (1.0 mL) was added at room temperature with stirring. Amber oil separated from a yellowish solution after several minutes. The solution was removed and analyzed by the NMR spectroscopy, which revealed the presence of Ph_3CMe (δ_H 2.10 (s, 3 H, CMe), 7.05–7.20 (m, 15 H, Ph_3C)). The oil was washed once with toluene and redissolved in THF-d_8. The identity of cationic complex **12** was proposed based on NMR and MS data. Attempts to crystallize the complex failed. The compound gradually decomposed at room temperature in chlorinated solvents.

NMR (THF-d_8) ^{1}H: δ 0.50 (s, 3 H, TiMe), 1.36, 1.37 (2× s, 3 H, CMe_2), 2.92, 2.99 (2× d, $^2J = 16.5$ Hz, 1 H, CH_2CN), 5.63, 6.01 (2× m, 1 H, C_5H_4), 6.35 (s, 5 H, C_5H_5), 6.81, 7.04 (2× m, 1 H, C_5H_4). ^{13}C{^{1}H}: δ 27.8, 29.2 (2× CMe_2), 31.4 (CH$_2$CN), 35.8 (CMe$_2$), 51.4 (TiMe), 107.5, 111.1 (2× C_5H_4 CH), 117.3 (C_5H_5), 119.2 (C_5H_4 CH), 119.5 (CN), 123.8 (C_5H_4 CH), 140.0 (C_5H_4 C_{ipso}); signals for the free $[B(C_6F_5)_4]^-$ anion: 136.7 (dm, $J_{C,F} = 244$ Hz, m-C_6F_5), 138.8 (dm, $J_{C,F} = 245$ Hz, p-C_6F_5), 148.9 (dm, $J_{C,F} = 242$ Hz, o-C_6F_5) ppm, C_{ipso} of C_6F_5 not observed. MS, m/z (ESI+): 534 ($[(M_{cation}-Me)_2 + O]^+$), 292 ($[M_{cation}+H_2O]^+$), 274 ($[M_{cation}]^+$); (ESI−): 679 ($[B(C_6F_5)_4]^-$).

4.15. *X-ray crystallography*

Crystals suitable for single-crystal X-ray diffraction analysis were obtained by crystallization from $CDCl_3/Et_2O$ (**2**; red-brown plate, 0.33 × 0.30 × 0.08 mm^3), THF/Et_2O (**3**; pale yellow–green prism, 0.45 × 0.12 × 0.05 mm^3), toluene/CH_2Cl_2 (**4**; colorless prism, 0.20 × 0.05 × 0.05 mm^3. **7**; red plate, 0.58 × 0.35 × 0.08 mm^3), and toluene (**9**; pale yellow prism, 0.60 × 0.15 × 0.12 mm^3). Full-set diffraction data ($\pm h \pm k \pm l$; $2\theta \leq 55^\circ$ for all crystals) were collected on a Nonius KappaCCD diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) at 150(1) K using graphite monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å) and analyzed with the HKL program package [16]. The data for **7** were corrected for absorption (absorption coefficient $\mu = 0.928$ mm^{-1}, range of transmission coefficients was 0.731–0.931) using a gaussian method based on the indexed crystal shape, which is incorporated in the diffractometer software.

The structures were solved by direct methods (SIR97, Ref. [17]) and refined by full-matrix least-squares routine based on F^2 (SHELXL97, Ref. [18]). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their calculated positions and treated as riding atoms with U_{iso}(H) assigned to a multiple of U_{eq} of their bonding carbon atom. Selected crystallographic data are given in Table 3. Geometric parameters and structural drawings were obtained with a recent version of the Platon program [19].

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Appendix. Supplementary material

Views of the molecular structures of compounds **3** and **4** are enclosed. CCDC-807693 (for compound **2**), -807694 (**3**), -807695 (**4**), -807696 (**7**), and -807697 (**9**), respectively, contain the supplementary crystallographic data in cif format. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.02.032.

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