







# **Triazenido Complexes of Titanocene(III)**

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Abstract: Triazenido metal complexes have been extensively investigated for more than a century, especially transition metal complexes. However, in each of the known examples for titanium, the oxidation state of the metal is +4. Therefore, we sought to prepare a complex containing titanium(III). To achieve this goal, triazenes RNNN(H)R' (1R, with R = R' = Ph; Dipp; Ter; R = Mes\*, R' = *m*-Tol) and triazenido salts Li[RNNNR'] (R = R' = Ter; R = Ter, R' = m-Tol) were prepared. These were reacted with suitable titanium precursors either from reaction with the alkyne complex Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) or in a salt metathesis with [Cp<sub>2</sub>TiCl]<sub>2</sub> to give chelate complexes of the type Cp<sub>2</sub>Ti[RNNNR'] (**2**R, with R = R' = Ph; Dipp; R = Ter; R' = *m*-Tol). The synthesis, reactivity, and bonding of the titanocene triazenides were studied.

# Introduction

Bidentate anionic bases with nitrogen donor sites such as triazenides are able to stabilise coordination compounds and shield the coordination sphere of the metal centre. Therefore they are can be regarded as beneficial chelating ligands in coordination chemistry. <sup>1</sup> Triazenido ligands show a broad structural chemistry due to their two- or four-electron donor character, thus being able to bind as chelates or non-chelating. Also, formation of dinuclear complexes, *e.g.* Cu<sub>2</sub>[PhNNNPh],<sup>2</sup> as well as mononuclear complexes (Figure 1) is possible.

While many triazenido complexes are known, in particular for transition metals,<sup>3</sup> examples of titanium triazenido complexes are still rare.<sup>4-7</sup> In 1964 Brinckman et al.<sup>4</sup> reported on a tetrakis(1,3-dimethyltriazenido) titanium complex (**A**, Scheme 1), which was obtained in the reaction of MgI[MeNNMe] with TiCl<sub>4</sub>. Compund **A** was identified by elemental analysis and <sup>1</sup>H NMR spectroscopy. Later another example was published by Latham and Leigh who treated lithium diphenyltriazenide with CpTiCl<sub>3</sub> affording Cl<sub>2</sub>Ti(Cp)[PhNNNPh] (**B**).<sup>5</sup> The first full characterisation (including crystal structure analysis) was done by Winter et al., who investigated the chelate complexes Ti(NMe<sub>3</sub>)<sub>2</sub>[PhNNNPh]<sub>2</sub> and Ti(NEt<sub>2</sub>)<sub>2</sub>[PhNNNPh]<sub>2</sub> (**C**).<sup>6</sup> Recently, Beckhaus and co-workers

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presented titanium(IV) triazenides as isolable intermediates in the reaction of bis( $\eta^5$ : $\eta^1$ -pentafulvene)titanium complexes with azides yielding titanium imides (**D**).<sup>7</sup> It is worth noting the  $\eta^1$ -coordination of the triazenide which makes **D** the only known titanium complexes containing a monodentate triazenido ligand. All triazenido species **A** - **D** show well-resolved NMR spectra thus representing formal Ti(IV) species.



Figure 1. Known triazenido titanium complexes.

As shown on several occasions,  $Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)^8$ represents a titanocene species with a disguised [Cp<sub>2</sub>Ti(II)] fragment. The bis(trimethylsilyl)acetylene ligand is known to serve as a spectator ligand and can easily be released under mild reaction conditions to in situ generate the reactive 14 electron fragment [Cp2Ti(II)], which can be utilised to trap reactive fragments and stabilise unusual coordination geometries and ligand motifs.8a By this approach, some of us succeeded in isolating several pnictogen containing metallacycles featuring the general structural motifs Cp<sub>2</sub>Ti[RNENR] and Cp<sub>2</sub>Ti[R<sub>2</sub>PNPR<sub>2</sub>] with E = C, P, S as illustrated in Figure 2.9-12 Except for  $Cp_2Ti[Me_3SiNSNSiMe_3]$  (F), this approach mostly led to the formation of Ti(III) compounds. While compound E was formed by reaction of  $Cp_2Ti(II)(\eta^2-Me_3SiC_2SiMe_3)$  with a carbodiimide Me<sub>3</sub>SiNCNSiMe<sub>3</sub>, complex G could be isolated from the reaction of the titanocene alkyne complex with the corresponding 1,3dichloro-cyclo-1,3-diphospha(III)-2,4-diazane. Compound H was formed by hydrogen release from Ph<sub>2</sub>PN(H)PPh<sub>2</sub> and coordination of the anionic PNP ligand. Here we report on the synthesis of different titanium triazenido complexes of the type  $Cp_2Ti(III)[RNNNR']$  utilizing  $Cp_2Ti(II)(\eta^2-Me_3SiC_2SiMe_3)$  and  $[Cp_2Ti(III)CI]_2$  as the titanocene source.





**Figure 2.** Generation of nitrogen containing four-membered titanacycles starting from Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) and **E**: SiMe<sub>3</sub>NCNSiMe<sub>3</sub>, <sup>9</sup> **F**: Me<sub>3</sub>SiNSNSiMe<sub>3</sub>, <sup>10</sup> **G**: [DippNPCI]<sub>2</sub> (Dipp = 2,6-<sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), <sup>11</sup> **H**: [Ph<sub>2</sub>PN(H)PPh<sub>2</sub>].<sup>12</sup>

# **Results and Discussion**

#### Synthesis of the starting materials

To access Ti(III) triazenido species Cp2Ti[RNNNR'] we envisioned deprotonation of triazenes of the type RNNN(H)R' and subsequent coordination to titanocene as it was reported before for related PNP metallacycles.12 To examine the influence of different substituents at the triazene on the reaction sequence and its products, both symmetrically and unsymmetrically substituted triazenes RNNN(H)R' were utilised. The triazenes were generated by an adaption of different literature known protocols (Scheme 1). This includes the nucleophilic attack of aniline on aryldiazonium salts in pH-buffered aqueous solutions (1Ph)<sup>13</sup> as well as the treatment of the amine DippNH<sub>2</sub> (Dipp = 2,6- $Pr_2C_6H_3$ ) with isoamyl nitrite (1Dipp) 14 Unfortunately, in case of DippNNN(H)Dipp, only a mixture of unreacted DippNH<sub>2</sub> and the triazene 1Dipp,<sup>14b</sup> was isolated and it was impossible to obtain the desired compound in pure form by crystallisation. These two strategies were applicable for symmetrical triazenes while the unsymmetrical triazenes were synthesised via generation and hydrolysis of triazenide salts. For example, nucleophilic attack of an aryl Grignard reagent *m*-TolMgBr on the aryl azide, Mes\*N<sub>3</sub>  $(Mes^* = 2, 4, 6^{-t}BuC_6H_2)$ , and subsequent hydrolysis led to the formation of 1Mes\*Tol.<sup>15</sup> This method did not provide access to the analogous terphenyl substituted triazene, TerNNN(H)m-Tol  $(Ter = 2,6-(2,4,6-Me_3C_6H_2)_2C_6H_3)$ . However, treatment of Ter-N<sub>3</sub> with Lim-Tol resulted in the formation of the lithium triazenide salt, Li[TerNNNm-Tol] (LiTerTol). Hydrolysis of LiTerTol led to the formation of a mixture of the isomeric triazenes TerNNN(H) m-Tol and TerN(H)NNm-Tol, which unfortunately could not be separated by crystallisation. However, by this approach we were able to obtain the symmetrically substituted compond 1Ter.<sup>16,17</sup>

# Synthesis of Cp<sub>2</sub>Ti[RNNNR'] (R = R' = Ph; Dipp; R = Ter,

#### R' = *m*-Tol)

Similarly as observed before for the Ti(III) PNP metallacycles<sup>12</sup>, treatment of Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) with one equivalent of the acid **1**Ph in benzene at ambient temperature led to the formation of dark red complex **2**Ph (Scheme 2, left). The reaction was finished after two hours according to <sup>1</sup>H NMR studies which only showed the resonance of free bis(trimethylsilyl)acetylene ( $\delta$  = 0.16 ppm in C<sub>6</sub>D<sub>6</sub>). Therefore, the formation of a paramagnetic Ti(III) species was assumed. If the experiment is

done in a Young NMR tube a sharp singlet can be observed at 4.47 ppm (in  $C_6D_6$ ) as evidence for the formation of  $H_2$  (Figure S5 in supporting file). After removal of the solvent *in vacuo* dark red crystals of **2**Ph were isolated from Et<sub>2</sub>O via vapor diffusion using *n*-pentane (74% yield). Single crystal X-ray studies unequivocally proved the presence of **2**Ph (vide infra).

10.1002/ejic.201801

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Although it was impossible to obtain pure 1Dipp (always in a mixture with DippNH<sub>2</sub> vide supra), we treated such a mixture of 1Dipp / DippNH<sub>2</sub> with Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) in benzene. Overnight the brown reaction mixture turned dark green. Individual green crystals of 2Dipp suitable for single crystal structure analysis were picked after recrystallisation from THF at 5 °C. Interestingly, according to the <sup>1</sup>H NMR studies the reaction was not complete after 12 h and even after stirring for three weeks, signals of the starting materials 1Dipp, DippNH<sub>2</sub> and Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) could still be observed.



**Scheme 1.** Synthesis of triazenes 1Ph, 1Dipp, 1Mes\*Tol, 1Ter and Li[TerNNN*m*-Tol] (\* isomers TerNNN(H)*m*-Tol and TerN(H)NN*m*-Tol could not be separated from each other).

The reaction of Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) with one equivalent of 1Mes\*Tol and 1Ter, respectively, did not lead to conversion of the starting materials, even after stirring for 10 days at 70 °C. Presumably, steric strain of the Mes\* and Ter substituents impeded the formation of a triazene species. Therefore, we decided to use a salt metathesis method to generate triazenido titanocene heterocycles with larger substituents starting from [Cp<sub>2</sub>TiCl]<sub>2</sub> and a lithium triazenide species (Scheme 2, right). When triazenide Li[TerNNN*m*-Tol]·2 Et<sub>2</sub>O was added to a solution of [Cp<sub>2</sub>TiCl]<sub>2</sub> in benzene, the immediate formation of **2**TerTol was observed, while in case of the reaction with triazenide Li[TerNNNTer]·Et<sub>2</sub>O no reaction was observed due to the larger steric hindrance of two Ter groups, neither after heating nor stirring for several days. Yellow crystals of **2**TerTol were obtained from THF at 5 °C in good yields (73%).





Scheme 2. Synthesis of symmetrical and unsymmetrical triazenido titanocene heterocycles 2.

### Characterization of Cp<sub>2</sub>Ti(RNNNR') (R = R' = Ph; Dipp;

#### R = Ter, R' = m-Tol)

Due to the existence of a paramagnetic Ti(III) centre, NMR spectra of all herein studied triazenido titanocene complexes were not informative for structural characterisation. X-ray analysis however unequivocally proved the existence of Cp<sub>2</sub>Ti[RNNNR'] (R = R' = Ph; Dipp; R = Ter, R' = m-Tol) species, all of which featuring a planar TiN<sub>3</sub> four-membered heterocycle (Figure 3, deviation from planarity: -1.0(2) 2Ph, 0.9(1) 2Dipp, -1.8(1)° 2TerTol). The titanium centre is embedded in a strongly distorted tetrahedral coordination environment with rather small bite angles of the triazenido ligands of around 57° (Table 1) that are those in related Ti(IV) comparable to complexes Ti(NEt<sub>2</sub>)<sub>2</sub>[PhNNNPh]<sub>2</sub> (57.65(8)°) and Ti(NMe<sub>3</sub>)<sub>2</sub>[PhNNNPh]<sub>2</sub> (58.00(6)°).<sup>6</sup> No significant intermolecular interactions were found.



Figure 3. ORTEP drawing of the molecular structures of 2Ph, 2Dipp and 2TerTol in the crystal. Hydrogen atoms are omitted and Cp ligands as well as nitrogen substituents shown as wireframe representation for clarity. Thermal ellipsoids are shown with 50% probability at 173 K. Selected bond lengths [Å] and angles [°] are summarised in Table 1.

As expected both Ti-N distances are identical in the symmetrically substituted compounds 2Ph and 2Dipp but are slightly elongated in 2Dipp compared to 2Ph due to the larger steric demand of the (*cf.* **2**Ph: 2.164(3)/2.171(2) Dipp moietv VS. 2Dipp: 2.215(2)/2.200(2) Å). In the asymmetrically substituted species 2TerTol two significantly different Ti-N distances were observed. As expected a longer Ti-N1 distance (2.273(3) Å) can be observed in proximity to the bulkier terphenyl group, while the shorter Ti-N3 (2.145(2) Å) is linked to the tolyl substituent. These Ti-N bond lengths are in agreement with those found in similar Cp<sub>2</sub>Ti(III) complexes E and G (Figure 2, E: Ti1-N1 2.196(2), Ti1-N2 2.193(1) Å, G: Ti1-N1 2.296(2), Ti1-N2 2.265(2) Å) and slightly longer than in the Cp<sub>2</sub>Ti(IV) complex F (Figure 2, Ti-N 2.051-2.064



Å), indicating that the oxidation state at the titanium centre affects the molecular structure. However, similar Ti-N distances in (R<sub>2</sub>N)<sub>2</sub>Ti(IV) complexes **C** (Figure 1, 2.128(2)–2.238(2) Å)<sup>6</sup> which contains the same triazenido ligand show the influence of the anionic ligands on these structures. The N-N distances were found in the range between 1.309(3) and 1.320(2) Å, displaying some double bond character (cf.  $\sum r_{cov}(N-N) = 1.42$  and  $\sum r_{cov}(N=N) = 1.20$  Å),<sup>18</sup> which is typical for chelate complexes containing triazenido ligands.<sup>3</sup> Interestingly, the N1-Ti-N3 angles are identical within the standard deviation (approximately 57°) in all three species, the N1-N2-N3 angles slightly increase along the series 2Ph (105.7°) < 2Dipp (107.3°) ≤ 2TerTol (107.5°) in accord with the corresponding angles in related transition metal compounds with  $\eta^2$ -coordinated triazenido ligands (99–109.2°).<sup>3</sup> However, they differ from those found in the  $\eta^1$ -coordinated monodentate (D) (cf. 113.6(3)°)7 or bridging complexes,3 emphasising the strained nature of four membered Ti triazenido heterocycles.

**Table 1** Selected experimental and computed structural parameters of  $Cp_2Ti(RNNNR')$  (R = R' = Ph; Dipp; R = Ter, R' = m-Tol; distances in Å, angles in °).

	<b>2</b> Ph	<b>2</b> Dipp	2TerTol
N1 N2 oxp	1 217(2)	1 217(2)	4 220(2)
n = n z exp.	1.317(3)	1.317(2)	1.320(2)
pbe1pbe/dof2tzyp	1.297	1.299	1.300
	1.230	1.231	1.293
DI 00/12 VI /LANEZDZ	1.515	1.517	1.515
N2–N3 exp.	1.309(3)	1.316(2)	1.310(2)
pbe1pbe/6-31g(d,p)	1.297	1.299	1.295
pbe1pbe/def2tzvp	1.290	1.291	1.288
BP86/TZVP/LANL2DZ	1.315	1.317	1.313
Ti1–N1 exp.	2.164(3)	2.215(2)	2.273(3)
pbe1pbe/6-31g(d,p)	2.178	2.238	2.302
pbe1pbe/def2tzvp	2.179	2.233	2.297
BP86/TZVP/LANL2DZ	2.179	2.238	2.292
		/ - >	
Ti1–N3 exp.	2.171(2)	2.200(2)	2.145(2)
pbe1pbe/6-31g(d,p)	2.178	2.238	2.149
pbe1pbe/def2tzvp	2.180	2.233	2.150
BP86/TZVP/LANL2DZ	2.179	2.239	2.154
N1–Ti1–N3 exp.	57.74(9)	57.40(5)	57.28(6)
pbe1pbe/6-31g(d,p)	57.19	56.53	56.42
pbe1pbe/def2tzvp	57.09	56.55	56.38
BP86/TZVP/LANL2DZ	57.72	57.13	57.06
N1–N2–N3 exp.	105.7(2)	107.3(1)	107.5(2)
pbe1pbe/6-31g(d,p)	107.01	109.38	108.64
pbe1pbe/def2tzvp	107.69	109.99	109.24
BP86/TZVP/LANL2DZ	106.19	108.69	107.84

In order to gain a better and deeper understanding of the bonding situation in **2R** complexes, we have decided to perform quantum chemical bond analyses. To find a suitable method and basis set combination for a good description of the complexes, we performed optimizations and frequency analysis at three different levels of theory and compared the resulting gas phase structures with the experimental molecular structures (Table 1). For this



reason, we used the hybrid density functional pbe1pbe<sup>19</sup> in combination with 6-31g(d,p)<sup>20</sup> or def2tzvp<sup>21</sup> basis set, thirdly, a pure density functional BP86<sup>22</sup> in combination with the LANL2DZ basis set and corresponding effective core potential (ECP) at Ti<sup>23</sup> and the TZVP basis set <sup>24</sup> on all other atoms (notation BP86/TZVP/LANL2DZ). The latter turned out to be the most suitable model with respect to the best description of bond length and angles in these three complexes **2R** (Table 1). Therefore we used the BP86/TZVP/LANL2DZ level of theory for all following calculations.

#### **Vibrational Spectroscopy**

The FTIR and Raman spectra of LiTerTol, 2Ph and 2Ter have been detected and the experimental data have been interpreted by density functional theory (DFT). The harmonic vibrational frequencies, infrared intensities and Raman scattering activities have been calculated at the BP86/TZVP/LANL2DZ level of theory. The results of quantum-chemical calculations are in excellent agreement with all details of the experimental spectra (Table 2). The asymmetrical stretching formation of the triazenide moiety displays an infrared absorptions at 1263 cm<sup>-1</sup> (2Ph) and 1243 cm<sup>-1</sup> (2TerTol), respectively, while the absorption in the Raman experiment at 1356 cm<sup>-1</sup> (2Ph) and 1309 cm<sup>-1</sup> (2TerTol) arose from the symmetrical stretching formation of the triazenide moiety (Figure S10-S16 in supporting file). This data corresponds well with the typical range of the characteristic vibrations for triazenido complexes<sup>3</sup> along with lithium triazenide complex LiTerTol.

**Table 2** Selected experimental and calculated frequencies of Li(TerNNN*m*-Tol) and Cp<sub>2</sub>Ti(RNNNR') (R = R' = Ph; Dipp; R = Ter, R' = m-Tol; in cm<sup>-1</sup>).

	LiTerTol	<b>2</b> Ph	<b>2</b> Dipp	2TerTol
vas exp.	1257	1263	-	1243
$ u_{as}$ theor.	1265	1278	1251	1254
<b>v</b> ₅ exp.	1335	1356	-	1332
$\nu_{s}$ theor.	1335	1334,1344	1311	1319

### Charge transfer and bonding in Cp2Ti[PhNNNPh]

Further computations were carried out to shed some light into the bonding and radical character of Ti triazenido heterocycles. (Table 1). Cp<sub>2</sub>Ti[PhNNNPh] (2Ph) was used as model species. MO theory (MO = molecular orbital) and NBO theory (NBO = natural bond orbital)<sup>25,26</sup> computations revealed the existence of a formal Ti(III) species with spin densities localised at the Ti centre (Table 3 SD-M: 1.048 and SD-NBO: 0.970e). Natural charge considerations (Table 3) feature a positive charge (Q) of 0.50e for the Ti centre in accord with an overall charge transfer of 2.50e onto the formal Ti<sup>3+</sup> ion (see below). Moreover, the total charge of -0.35e for the Ph-NNN-Ph fragment (if a formal charge of -1 is assumed) indicates a charge transfer of 0.65e and the charge of -0.075e for the formal Cp<sup>-</sup> ion hints at a charge transfer of 0.925e for each Cp unit. Therefore, the overall charge transfer  $Q_{CT}(Ti) =$ 2.50e for the Ti centre is composed of 2\*0.925e (Q<sub>CT</sub>, Cp<sup>-</sup>) and 0.65e (Q<sub>CT</sub>, [Ph-NNN-Ph]<sup>-</sup>). Interestingly, NBO theory indicates a



highly ionic bond situation between titanium and the two nitrogen donor atoms of the [Ph-NNN-Ph]-ligand as manifested by >83% percentage localization of the Ti-N bonds at the N atoms and >14% at the Ti atom. Hence, the best Lewis presentation for **2**Ph displays two Cp<sub>2</sub>Ti(III)—N donor-acceptor bonds of the triazenide ligand as displayed in Scheme 2 for all compounds **2** in accord with the computed electron localisation function of **2**Ph (ELF, Figure 4).<sup>27</sup>

#### Table 3. Computed natural charges (e) and spin densities (e) of 2Ph.

	Q	SD-M	SD-NBO		
Ti	0.502 <sup>[b]</sup>	1.048	0.970		
N1	-0.254	-0.001	-0.010		
N2	-0.016	-0.012	0.013		
N3	-0.254	-0.001	-0.010		
PhNNNPh	-0.350	-0.031	-0.002		
Ср	-0.076	-0.008	0.016		
Cp₂Ti	0.350	1.031	1.002		

<sup>[a]</sup> SD-M = Mulliken spin density, SD-NBO natural spin density from NBO analysis; <sup>[b]</sup> Natural Electron Configuration at Ti: 4s(0.21) 3d(3.21) 4p(0.01) 4d(0.08).



Figure 4. Left: ELF isosurface @ 0.90 of 2Ph. Right: 2D contour plot of ELF (LP = lone pair).

### Reactivity of Cp2Ti[PhNNNPh] (2Ph)

It should be noted that all titanocene triazenido complexes are highly air- and moisture-sensitive compounds. Therefore, we were motivated to study further reactivity of these new Ti(III) complexes. Treatment of 2Ph with H<sub>2</sub> gas led to the formation of PhNNN(H)Ph besides a product mixture containing different titanocene species. Insertion of small unsaturated substrates is a well-known reaction motif in the chemistry of group 4 metallacycles.<sup>28</sup> For this reason, we attempted reactions with CO<sub>2</sub>,  $CS_2$  or DmpNC (Dmp-2,6-Me<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>)), but found no reaction, even after prolonged heating for several days. We believe that the oxidation state of the titanium centre has a considerable impact on reactivity, as titanocene species with Ti(II)<sup>8-10</sup> and Ti(IV)<sup>29</sup> centres are known to display high reactivity towards molecules containing multiple bonds. Also, comparably few examples for well-defined reactions of Ti(III) compounds with the above mentioned substrates are known.<sup>30</sup> We have thus envisioned using the stable Ag salt Ag[CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>] for oxidation of the Ti(III)



center to a Ti(IV) species which might be more interested in follow-up chemistry. Therefore, redox behavior of these TiN<sub>3</sub> species was investigated by adding Ag[CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>] to a solution of 2Ph in benzene, which resulted in the formation of a red solution and a black precipitate, presumably elemental Ag. Recrystallisation from toluene afforded red crystals, which were examined by means of single-crystal X-ray diffraction, revealing a diazenium salt of the type [1-{NN(H)Ph}-4- $NH_2(C_6H_4)$ ][CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>] (**3**, Figure 5). Even though the yield of **3** is relatively small (17%), according to NMR studies it seems to be the major product. In the common range of Cp protons multiple unknown signals could be detected. Those multiple unknown species may inhibit further crystallisation. The additional protons found in the diazenium salt could originate from a ring-slippageinduced C-H activation at titanocene<sup>31</sup> or from the solvent. Since the main reaction product did not exhibited a metallocene fragment, we did not perform further redox experiments.



Figure 5. ORTEP drawing of the molecular structure of 3 in the crystal. Thermal ellipsoids with 50% probability at 173 K. Selected bond lengths [Å]: N1–N2 1.257(8), H1–Br1 2.6(8).

# Conclusions

We have presented the synthesis of a series of triazenide compounds and its coordination chemistry at titanocene. In all cases, formation of titanium(III) complexes occurs, which is further corroborated by computational analysis of its electronic structure. As major results of the natural bond orbital analysis (NBO) and the analysis of the electron localisation function (ELF) the bond situation can be best described as an electrostatic interaction between a Cp<sub>2</sub>Ti(III) cation and the chelating anionic triazenido ligand. These complexes show an unexpectedly poor reactivity with common small unsaturated molecules. Ligand insertion or displacement reactions were not observed. Evaluation of metallacycle transfer chemistry of these new titanium(III) heterometallacycles will however be part of future studies on this type of complexes.



# **Experimental Section**

General Information. All manipulations were carried out under oxygenand moisture-free conditions under argon using standard Schlenk or dry box techniques. All solvents were obtained from commercial sources and dried according to standard procedures. NMR spectra of <sup>1</sup>H were obtained on a Bruker AVANCE 300 MHz spectrometer and were referenced internally to protic impurities in the deuterated solvent (1H: C6HD5  $\delta_{ref} = 7.16 \text{ ppm}, \text{ THF-} d_7 \delta_{ref,1} = 1.73 \text{ ppm}, \delta_{ref,2} = 3.58 \text{ ppm}).$  <sup>11</sup>B spectra were referenced externally ( $(BF_3:OEt_2) = 0$  ppm). All measurements were carried at room temperature. IR spectra of crystalline samples were recorded on a Nicolet 380 FT-IR spectrometer with a Smart Orbit ATR unit at ambient temperature. Raman spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by a red laser (633 nm, 17 mW) or a blue laser (473 nm, 25 mW). All measurements were carried out at ambient temperature. Elemental analyses were obtained using an Elementar vario Micro cube CHNS analyser or a LECO TruSpec Micro CHNS analyser. Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 20 °C/min. DSC analyses were carried out at a heating rate of 5 °C/min usig a Mettler-Toledo DSC 823e. Mass spectra were recorded on a Thermo Electron MAT 95-XP sector field mass spectrometer using crystalline samples. Xray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 173(2) K or 123(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer or a Bruker D8 Quest Eco DMOS diffractometer using graphite monochromated Mo-Ka radiation  $(\lambda = 0.71073 \text{ Å}).$ 

10.1002/ejic.201801

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Details of the synthesised products, crystallographic data, and NMR spectra are given in the Supporting Information.

Compound 2Ph:To a stirred solution of PhNNN(H)Ph (200 mg, 1.01 mmol) in benzene (6 mL), a solution of  $Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)$ (353 mg, 1.01 mmol) in benzene (6 mL) is added. The brown solution is stirred for two hours turning reddish-brown. Subsequently, the solvent is removed in vacuo and the solid residue is dissolved in Et<sub>2</sub>O (2 mL). Via vapour diffusion using *n*-pentane (5 mL) dark red crystals of 2Ph can be obtained (278 mg, 0.74 mmol, 74 %). Mp: 299 °C (dec.). EA for C<sub>22</sub>H<sub>20</sub>N<sub>3</sub>Ti found (calc.): C 70.62 (70.60), H 4.90 (5.39), N 10.94 (11.23). IR (ATR, 25°C, 16 scans cm<sup>-1</sup>): 3940 (w), 3285 (w), 3061 (w), 2956 (w), 2723 (w), 2594 (w), 2505 (w), 2325 (w), 2279 (w), 1940 (w), 1708 (w), 1601 (m), 1591 (m), 1504 (m), 1479 (s), 1466 (m), 1447 (m), 1415 (m), 1358 (w),  $% \left( {m_{1}} \right) = 0$ 1324 (w), 1297 (m), 1242 (s), 1196 (s), 1169 (m), 1070 (m), 996 (m), 892 (w), 790 (s), 750 (s). Raman (473 nm, cm<sup>-1</sup>): 3496 (1), 1593 (6), 1487 (3), 1459 (1), 1438 (1), 1414 (1), 1356 (10), 1328 (3), 1271 (1), 1238 (1), 1168 (2), 1134 (2), 1124 (1), 1000 (2), 975 (3), 616 (1), 500 (2), 378 (1), 349 (1), 268 (1). MS (CI, pos., m/z (%): 374 (100) [Cp<sub>2</sub>TiN<sub>3</sub>Ph<sub>2</sub>]+.

**Compound 2Dipp:** To a stirred solution of DippNNN(H)Dipp (200 mg, 0.58 mmol) in benzene (6 mL), a solution of Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) (202 mg, 0.58 mmol) in benzene (6 mL) is added. The orange solution is stirred for six days turning into a dark green suspension overnight. After filtration, the solvent is removed *in vacuo* and the solid residue is dissolved in THF (2 mL). Subsequently the solution is concentrated and stored at 5 °C, resulting in formation of small green crystals of **2**Dipp, which are suitable for structural analysis. According to the <sup>1</sup>H NMR spectra the reaction is not complete. Even after stirring for three weeks, still signals of the starting materials could be detected and the experiment was stopped. <sup>1</sup>H NMR (25 °C, CD<sub>2</sub>Cl<sub>2</sub>, 300.13 MHz):  $\delta$  = -0.32 (s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>{ $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>}), 0.16 (s, 18 H,

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Compound 2TerTol: To a stirred solution of TerNNN(H)m-Tol (200 mg, 0.44 mmol) in benzene (6 mL), a solution of [Cp<sub>2</sub>TiCl]<sub>2</sub> (88 mg, 0.22 mmol) in benzene (6 mL) is added. The dark vellow solution is stirred overnight turning brown. Subsequently, the solvent is removed in vacuo and the solid residue is dissolved in THF (2 mL). The solution is concentrated and stored at 5 °C, resulting in formation of small yellow needle-shaped crystals of 2TerTol (204 mg, 0.33 mmol, 73 %). Mp: 166 °C. EA for C41H42N3Ti found (calc.): C 78.60 (78.83), H 6.54 (6.78), N 6.38 (6.73). IR (ATR, 25°C, 16 scans cm<sup>-1</sup>):2968 (w), 2945 (w), 2912 (w), 2855 (w), 1597 (m), 1583 (w), 1481 (w), 1441 (w), 1404 (w), 1372 (w), 1332 (w), 1307, (w), 1243 (s), 1231 (s), 1185 (m), 1158 (s), 1125 (m), 1088 (m), 1066 (m), 1014 (m), 983 (m), 905 (w), 895 (w), 872 (w), 862 (w), 849 (m) 814 (m), 804 (m), 781 (s), 759 (s), 742 (m), 694 (m), 678 (m), 663 (m), 616 (w), 604 (w), 592 (m), 573  $(w),\,557\ (w),\,542\ (m),\,517\ (w),\,507\ (m),\,478\ (w),\,447\ (w),\,429\ (m),\,404\ (w).$ Raman (632 nm, cm<sup>-1</sup>): 995 (1), 1246 (2), 1288 (2), 1332 (10), 1403 (3), 1582 (2), 1597 (1). MS (CI, pos., m/z (%): 624 (100) [Cp<sub>2</sub>TiN<sub>3</sub>Ter/m-Tol]<sup>+</sup>.

**Compound 3:** A solution of **2**Ph (0.103 g, 0.28 mmol) in benzene (5 mL) is added to a solution of Ag[CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>] (0.200 g, 0.28 mmol) in benzene (10 mL). The solution turns immediately dark red and a black precipitate is formed. The suspension is stirred for one hour at room temperature and subsequently filtered. After removal of the solvent *in vacuo* the red solid is dissolved in toluene (8 mL). The dark red brown suspension is filtered; the solution is concentrated and stored at 5 °C, resulting in formation of small red crystals of **3**, which are suitable for structural analysis (38 mg, 204 mg, 0.05 mmol, 17 %). 1H NMR (25 °C, [D8]THF, 300.13 MHz): 0.63-3.43 (m, vb [CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>]), 7.02-7.64 (m, 9H, CH), 8.29 (b, 3H, NH); 11B NMR (25 °C, [D8]THF, 96.29 MHz): -22.09 (d, B7-11,<sup>2</sup>J(11B1H) = 163 Hz), -11.54 (b, B2-6), -3.59 (b, B1).

CCDC 1859067-1859071 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Keywords:** Titanium • Triazenides • N Ligands • Triazenes • Structure

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