Angewandte International Edition Chemie

Metallacycles

International Edition: DOI: 10.1002/anie.201500109
German Edition: DOI: 10.1002/ange.201500109

Formation of Tri- and Tetranuclear Titanacycles through Decamethyltitanocene-Mediated Intermolecular C–C Coupling of Dinitriles**

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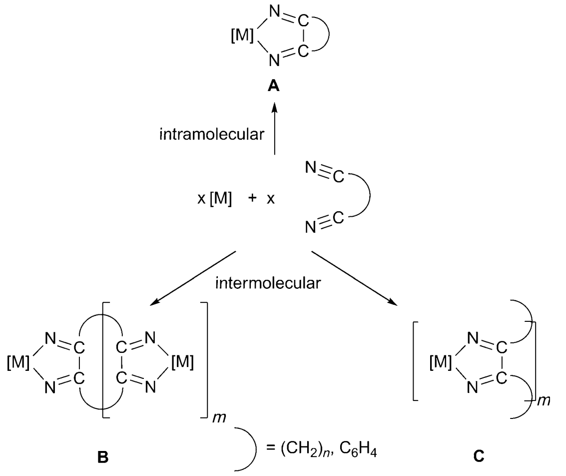
Dedicated to Professor Günther Wilke on the occasion of his 90th birthday

Abstract: *The reactions of [$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) with various dicyano compounds were investigated. Nitrile–nitrile C–C couplings result in multinuclear complexes owing to the bifunctionality of the substrates. Applying 1,3- or 1,4-dicyanobenzene led to tri- and tetranuclear complexes of the rare 1-metalla-2,5-diaza-cyclopenta-2,4-dienes. These are potential catalysts and were tested in the ring-opening polymerization of ε-caprolactone. The reaction with adiponitrile as alkyl dinitrile afforded a trinuclear 1-metalla-2,5-diaza-cyclopent-3-ene through additional protonation of the nitrogen atoms. The structure and bonding of the products were investigated by X-ray crystallography and DFT analysis to understand the molecular organization in the macrocycles.*

The options for the synthesis of macromolecules based on the early transition metals titanium and zirconium are few in number. For example Beckhaus et al. described the complexation of [Cp_2Ti] and [$(t\text{Bu}Cp)_2Ti$] by neutral bi- or multifunctional N-heterocyclic bridging ligands.[1] Furthermore, the same authors described a procedure that involved dehydroaromatization followed by a selective C–C coupling.[2] As an extension of the coupling of monoynes at metal complexes to metallacyclopentadienes, Tilley et al. investigated an oxidative coupling of diynes $R{-}C{\equiv}C{-}(X){-}C{\equiv}C{-}R$ ($X = (C_6H_4)_n$ ($n = 1, 2$), 2,2′-bipyridyl, etc.) as bifunctional substrates.[3] We have described the formation of ring-strained heterometallacycles[4] (1-metalla-2,5-diaza-cyclopenta-2,4-dienes) for group 4 metallocenes through nitrile–nitrile C–C coupling reactions of aryl nitriles.[5] Such systems were previously only known for aluminum,[6] antimony, and bismuth.[7] Additionally, these species were reported based on silylenes[8] and evidence for the existence of corresponding zirconium complexes was found.[9]

Regarding these results, the reactions of the in situ formed [Cp^*_2Ti] with dinitriles ($N{\equiv}C{-}X{-}C{\equiv}N$, $X = (CH_2)_n$ ($n = 1, 2, \ldots$), o-/m-/p-C_6H_4) are of considerable interest. Depending on the linking moiety X, three different types of reactions are expected: *intra*molecular coupling (**A**; Scheme 1) and *inter*molecular coupling to give rings (**B**) or chains (**C**).



Scheme 1. Coupling options for dicyano compounds.

Some reactions of 1,2-dicyanobenzene with group 4 metals have already been studied. In case of a Lewis acid activated [Cp_2TiCl_2], the end-on coordination of two substrate molecules via one nitrile function to the metal led to ionic complexes.[10] Coupling reactions at $TiCl_4$ produced phthalocyanine complexes.[11] Unfortunately, the reaction of [$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (**1**, $Cp^* = \eta^5$-pentamethylcyclopentadienyl)[12] with 1,2-dicyanobenzene afforded a mixture which could not be separated. However, there were no indications for the formation of the aforementioned product types, probably due to the sterically demanding Cp* ligand.

The addition of 1,3-dicyanobenzene (**2a**) to [$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (**1**) resulted in an *inter*molecular nitrile-nitrile C–C coupling to give **3a** (Scheme 2). A similar behavior has already been described for **1** in reactions with aryl nitriles.[5a,b] Owing to the bifunctionality of **2a**, the product is a highly symmetrical macrocycle. This resembles the reactions with alkynes and diynes as mentioned above.[3]

As can be seen in the molecular structure, **3a** consists of three {Cp^*_2Ti} moieties and three former molecules of **2a** (Figure 1). The preference for the trinuclear structure is

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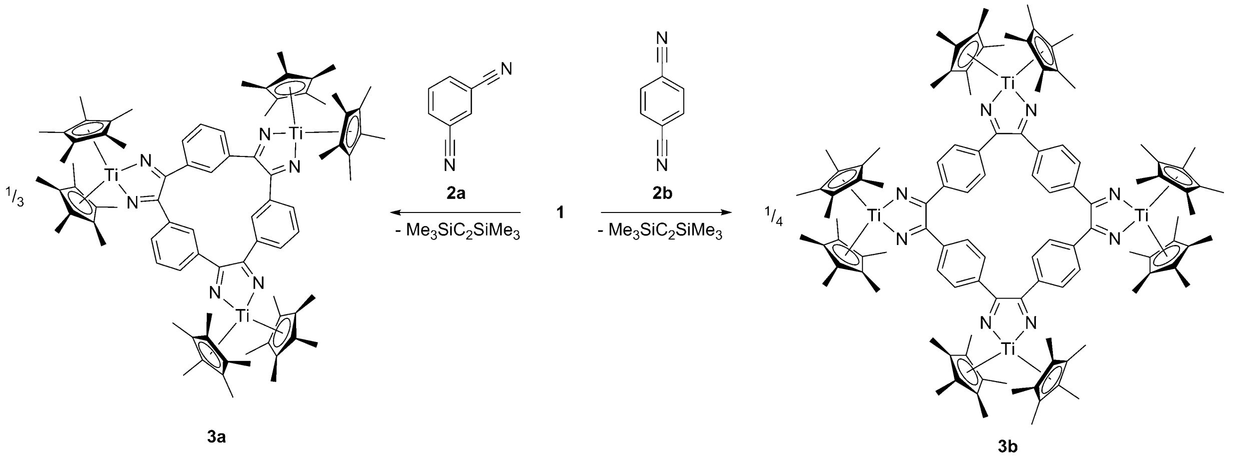
[**] We thank our technical and analytical staff for assistance. Financial support by the DFG (RO 1269/9-1) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500109.



Scheme 2. Reactions of **1** with **2a** and **2b** to give **3a** and **3b**, respectively.

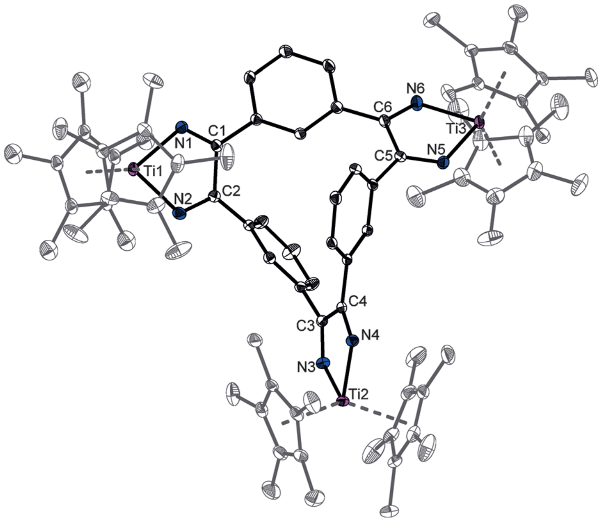


Figure 1. Molecular structure of **3a** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 30% probability. Selected bond lengths [Å]: C1–N1 1.286(3), C2–N2 1.282(3), C3–N3 1.278(3), C4–N4 1.283(2), C5–N5 1.290(3), C6–N6 1.298(3), C1–C2 1.513(3), C3–C4 1.523(3), C5–C6 1.509(3).

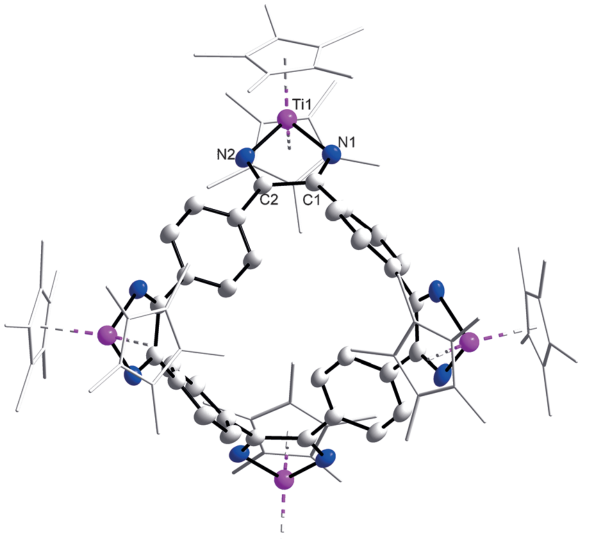


Figure 2. Structural motif of **3b** (ball-and-stick model, Cp* drawn as wire models). Hydrogen atoms are omitted for clarity.

remarkable. In accordance with the mononuclear complexes [Cp*$_2$Ti(−N=C(*R*)−C(R)=N−)] (R = Ph, *p*Tol, *o*Tol, Fc)[5a,b] the C–N distances are in the range of double bonds. The newly formed C−C bonds are elongated C_{sp2}−C_{sp2} single bonds. In comparison to the mononuclear complexes, the elongation is less pronounced. Another difference to these compounds is that **3a** starts to decompose after two months.

When applying 1,4-dicyanobenzene (**2b**) in the reaction with **1**, a highly symmetric macrocycle (**3b**) is formed as well (Scheme 2). In contrast to **3a**, **3b** consists of four {Cp*$_2$Ti} moieties and four coupled dicyano compounds. The structural motif of this complex was confirmed by X-ray crystallography (Figure 2). Owing to the low solubility of **3b** and its instability—the decomposition starts after some days—our attempts of recrystallization failed (see the Supporting Information).

For a better understanding of the structure and the stability of **3a** and **3b**, we computed the energetic changes during the reactions at the BP86 level with the SVP basis set for nonmetal elements and the effective core potential LANL2DZ basis set for Ti. For the calculations, we used the analogous complexes **1′**, **3a′**, and **3b′** with Cp (η^5-cyclopentadienyl) ligands instead of Cp*. The computational details are given in the Supporting Information.

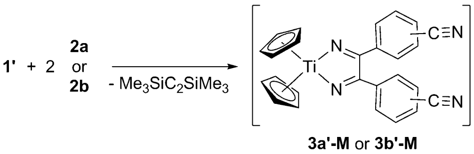
We showed in previous work that nitrile couplings to five-membered cycles have low activation barriers and are reversible.[5a] Therefore, we focused on the thermodynamic stability of **3a′** and **3b′** in the context of the substitution reaction of the alkyne in **1′** by 1,3-dicyanobenzene (**2a**) or 1,4-dicyanobenzene (**2b**) [Eq. (1) and (2)]. The formation of **3a′** and **3b′** is exergonic by −50.4 and −68.2 kcal mol^{-1} (−16.8 and −17.0 kcal mol^{-1} per Ti unit), respectively, which indicates this process is thermodynamically possible.

$$3 \times \mathbf{1'} + 3 \times \mathbf{2a} \rightarrow \mathbf{3a'} + 3 \times \mathrm{Me_3SiC_2SiMe_3} \qquad \Delta G = -50.4\ \mathrm{kcal\,mol^{-1}} \tag{1}$$

$$4 \times \mathbf{1'} + 4 \times \mathbf{2b} \rightarrow \mathbf{3b'} + 4 \times \mathrm{Me_3SiC_2SiMe_3} \qquad \Delta G = -68.2\ \mathrm{kcal\,mol^{-1}} \tag{2}$$

Due to the geometric constraints of **2a** (C_{2v}) and **2b** (D_{2h}), both complexes are highly symmetrical; **3a′** is twisted and has a C_2 axis through one Ti center and the remote benzene ring, and **3b′** shows S_4 symmetry.

In addition, we were interested in the formation pathway of **3a′** and **3b′**. In a concerted mechanism, the intermolecular C–C couplings should take place simultaneously, while in a stepwise sequence, the monomeric intermediates **3a′-M** and **3b′-M** (Scheme 3) should be formed first, followed by a reversible nitrile exchange and the formation of the macrocycle.



Scheme 3. Formation of the calculated monomeric intermediates.

To decide which pathway is more likely, we computed the formation energy of **3a′-M** and **3b′-M**. The substitution of the alkyne in **1′** by **2a** or **2b** is exergonic by −20.05 and −21.58 kcal mol^{-1}, respectively. These values are close to the reported data for reactions with other nitriles.[5a] Starting from the mononuclear intermediates **3a′-M** and **3b′-M**, we computed the formation free energy values for **3a′** and **3b′**, which were endergonic by 9.78 and 18.17 kcal mol^{-1}, respectively [Eq. (3) and (4)]. This illustrates that the concerted mechanism is more likely to take place.

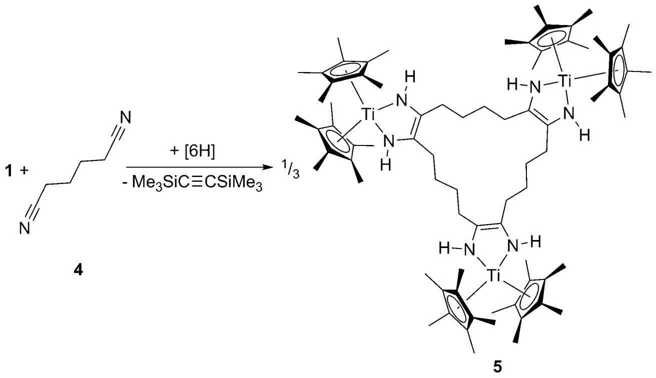
$$3 \times \mathbf{3a'\text{-}M} \rightarrow \mathbf{3a'} + 3 \times \mathbf{2a} \qquad \Delta G = +9.78\ \mathrm{kcal\,mol^{-1}} \tag{3}$$

$$4 \times \mathbf{3b'\text{-}M} \rightarrow \mathbf{3b'} + 4 \times \mathbf{2b} \qquad \Delta G = +18.17\ \mathrm{kcal\,mol^{-1}} \tag{4}$$

In addition to the structure and bonding of **3a** and **3b**, we were interested in the reactivity of these compounds, especially towards small molecules. However, we observed the formation of ill-defined mixtures in the reactions with CO_2, H_2, or HCl.

Despite these results, we consider **3a** and **3b** to be potential catalysts. Both compounds were therefore tested in the ring-opening polymerization of ε-caprolactone, which was monitored by NMR spectroscopy (spectra in the Supporting Information). Both complexes showed catalytic activity and a detailed study on the applicability of **3a** and **3b** in this and other catalytic reactions are currently under investigation and will be published in due course.

In contrast to the aforementioned reactions of **1** with aryl mono- and dinitriles, the alkyl dinitrile adiponitrile (**4**) led to a trinuclear 1-metalla-2,5-diaza-cyclopent-3-ene (**5**, a 1,4-diazabuta-1,3-diene complex; Scheme 4) and not to a 1-metalla-2,5-diaza-cyclopenta-2,4-diene.[13] This was determined by X-ray crystallography (Figure 3). The C–N distances are in the range of single bonds and the newly formed C–C bonds are C_{sp2}–C_{sp2} double bonds. In contrast to **3a** and **3b**, **5** does not decompose rapidly at ambient temperature.



Scheme 4. Reaction of **1** with **4** to give **5**.

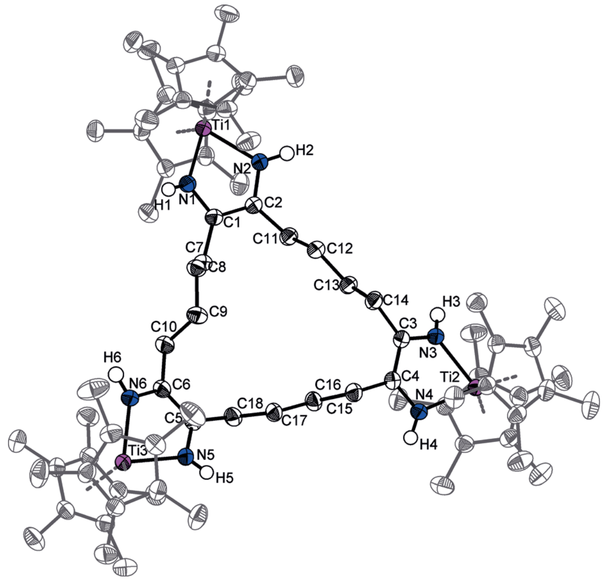


Figure 3. Molecular structure of **5** in the solid state. Hydrogen atoms (except for H1–H6) are omitted for clarity. Thermal ellipsoids are shown at 30% probability. Selected bond lengths [Å]: C1–N1 1.355(3), C2–N2 1.357(3), C3–N3 1.363(3), C4–N4 1.356(3), C5–N5 1.359(3), C6–N6 1.357(3), C1–C2 1.396(3), C3–C4 1.392(3), C5–C6 1.387(4).

The formation of corresponding mononuclear 1,4-diazabuta-1,3-diene complexes of titanium has mostly been observed in the coupling of isonitriles[14] or the coordination of 1,4-diazadienes.[15] Examples for the coupling of nitriles to such complexes are rare.[5b,16]

Of considerable interest is the origin of the additional hydrogen atoms required for the protonation of the nitrogen atoms. The source is most likely the solvent or deprotonation of the nitrile, which is a common reaction for alkyl nitriles.[17] Investigating the conversion of **1** with **4** by NMR-spectroscopy revealed that the solvent remains intact, whereas additional signals are observed that are assigned to a potential deprotonation product.

In conclusion, the addition of dicyano compounds as bifunctional substrates to **1** resulted in selective intermolecular nitrile–nitrile C–C couplings with formation of remarkable new macrocycles. In case of dicyanobenzenes, tri- and tetranuclear 1-metalla-2,5-diaza-cyclopenta-2,4-dienes were established, which are potential catalysts. For adiponitrile as alkyl dinitrile, a trinuclear 1-metalla-2,5-diaza-cyclopent-3-ene was formed.

Keywords: C–C coupling · macrocycles · metallacycles · nitriles · titanocene

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 5523–5526
Angew. Chem. **2015**, *127*, 5614–5617

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Received: January 6, 2015