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C–C Coupling

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Nitrile–Nitrile C–C Coupling at Group 4 Metallocenes to Form 1-Metalla-2,5-diaza-cyclopenta-2,4-dienes: Synthesis and Reactivity**

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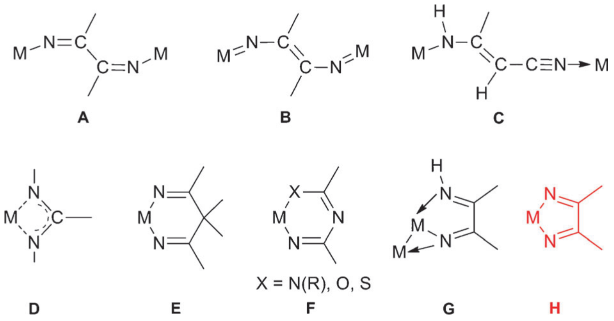
During the last decades, the synthesis and reactivity of small metallacycles of Group 4 metallocenes have been of great interest. The focus lies on all-carbon three- and five-membered cycles, namely metallacyclopropenes, 1-metallacyclopent-3-ynes (metallacyclopentynes), 1-metalla-cyclopenta-2,3,4-trienes (metallacyclocumulenes), and 1-metalla-cyclopenta-2,3-dienes (metallacycloallenes).[1]

Metallacyclopropenes are prepared by reduction of metallocene dichlorides in the presence of the alkynes.[2] In many cases, an excess of the alkyne yields the 1-metallacyclopenta-2,4-dienes by a coupling of two alkynes.[2] Owing to these results with all-carbon species, we switched to heterometallacycles[3] and investigated the formation of the corresponding 1-metalla-2,5-diaza-cyclopenta-2,4-dienes by a coupling of two nitriles at Group 4 metallocenes. Nitriles are one of the most common and versatile building blocks and have attracted considerable attention for the development of new synthetic strategies.

Only few nitrile–nitrile coupling reactions were observed before, producing several kinds of complexes (Scheme 1). Bridging ligands of type **A**, as a result of such a coupling, were observed for metals such as molybdenum,[4] tantalum,[5] niobium,[6] tungsten,[7] zirconium,[8] germanium,[9] and iridium.[10] Similar products are possible for titanium; this is always accompanied by an oxidation of the metal from Ti^{III} to Ti^{IV}.[11] Enediimido ligands $[N{-}C(R){=}C(R){-}N]^{4-}$ (**B**) are obtained in four-electron reductive coupling of nitriles at Ti^{II} compounds.[12]



Scheme 1. Products of nitrile–nitrile coupling reactions.

Another possibility for a nitrile–nitrile coupling product is a complex with a five-membered bridge (as in **C**), which was established in the reaction of $[Sr(dpp\text{-}bian)(thf)_4]$ (dpp-bian = 1,2-bis[(2,6)-diisopropylphenyl)imino]acenaphthene) with acetonitrile.[13] In contrast to the aforementioned coupling reaction, the coordination of the first nitrile was followed by a deprotonation, yielding a keteneiminate. Subsequently, a new bond formed between the α-carbon atom of the second CH_3CN and the β-carbon atom of the keteneiminate unit. Furthermore, four-, five-, and six-membered metallacycles are possible products of nitrile–nitrile coupling reactions. These are mostly generated by an additional interaction with ligands or stabilizing transformations. Four-membered cycles of type **D** as result of an N–C coupling of nitriles were obtained for an yttrium[14] and a titanium[15] complex.

The reactions of $(CH_3)_3M$ (M = Al, Ga, In) with acetonitrile lead by trimerization to the six-membered cycles (**E**).[16] Such a complex can also be obtained by a dimerization of nitriles.[17] The first step in these reactions is always an insertion of the N–C moiety into the M–C bond. The resulting C–C coupling with a second nitrile does therefore not always take place between the nitriles. Such six-membered cycles as formal products of a nitrile–nitrile coupling were established with a tin[17b] and a scandium[17c] complex. The six-membered cycles (**F**) with X=N(R) can be either formed in stepwise coupling reactions of three nitriles[18] or of $[Cp^*Ti\{MeC(N\mathit{i}Pr)_2\}\{NNCPh_2\}]$ with two nitriles (Cp^* = pentamethylcyclopentadienyl).[19] Additionally, the conversions of the intermediates $[Cp^*_2Zr{=}X]$ with two nitriles yields the complexes of type **F** with X = O, S.[20]

Five-membered cycles of type **G** as a result of a nitrile–nitrile coupling are very rare, but they are known for tungsten[7b,21] and rhenium.[22] These special structures are stabilized by an additional coordination of a metal to one of the N atoms and an H atom as substituent at the other N atom. Such a stabilization by H-transfer was already observed for alkyne–nitrile coupling products at Group 4 metallocene complexes with 1-metalla-2-aza-cyclopenta-2,4-dienes as intermediates.[23]

All of these selected examples **A**–**G** clearly demonstrate how sophisticated the coupling reactions of nitriles are. It strongly depends on the metal, the ligands, and the structure of the nitrile whether the first step of the reaction is a coordination, a reduction, a deprotonation, or an insertion. The desired C–C coupling takes place in the second step and therefore yields so many different products. Nonetheless, the stable 1-metalla-2,5-diaza-cyclopenta-2,4-dienes (**H**) as

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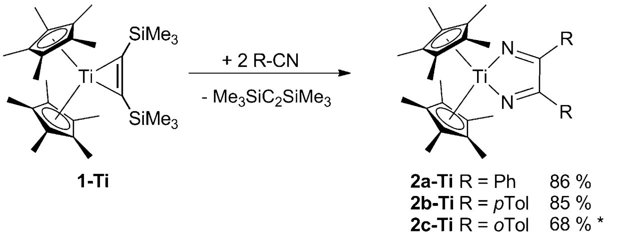
a result of a nitrile–nitrile coupling are rare and to the best of our knowledge there are only two hints for this reaction. Such compounds were briefly mentioned for aluminum[24] and zirconium[25] but without X-ray crystal structure analysis of the products and only characterization by elemental analysis and IR and NMR spectroscopy. The zirconium compound reacted with hydrogen to the bis(iminyl) complex [$Cp^*_2Zr(N{=}CHp\text{Tol})_2$] (most likely via [$Cp^*_2ZrH_2$] and a free nitrile). Additionally, a mixture of two different pure 1-zircona-2,5-diaza-cyclopenta-2,4-dienes gave a near-statistical mixture of the cross-coupled metallacycles by an exchange of the nitriles, indicating the reversibility of the coupling reaction. None of these results were published and only briefly cited in a paper.[17c]

The lack of information regarding the nitrile–nitrile C–C coupling to 1-metalla-2,5-diaza-cyclopenta-2,4-dienes motivated us to investigate the reactions of nitriles with Group 4 metallocene complexes in detail. Very recently, our group published first results in this direction with the mono- and diphenylated acetonitriles $PhCH_2CN$ and Ph_2CHCN, which led (depending on the metals and Cp ligands) to different products.[15] All of these investigations about elemental steps of substrate coupling are important for synthetic and catalytic applications of nitriles. Herein, we report on the synthesis, structural and energetic properties, and the reaction behavior of the complexes **2a-Ti**–**2c-Ti** and **2a-Zr**–**2c-Zr**. These were obtained by reactions of [$Cp^*_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (**1-Ti**: M = Ti; **1-Zr**: M = Zr) with two equivalents of the appropriate aryl nitriles. The analogous complexes with Cp (Cp = cyclopentadienyl) instead of Cp* do not form similar products with these substrates.[26]

Treatment of a toluene solution of [$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (**1-Ti**)[27] with two equivalents of nitriles at elevated temperatures led to a nitrile–nitrile C–C coupling and the formation of the 1-titana-2,5-diaza-cyclopenta-2,4-dienes **2-Ti** (Scheme 2), which were isolated as red crystals in high yields. For **2a-Ti** and **2b-Ti**, crystals suitable for X-ray crystal structure analysis could be obtained. One example is shown in Figure 1 (**2a-Ti**) with C–N double bonds of C1–N1 1.274(2), C2–N2 1.276(2) Å, and a C1–C2 single bond of 1.540(2) Å in the metallacycle.



Scheme 2. Synthesis of 1-titana-2,5-diaza-cyclopenta-2,4-dienes (* = yield determined by NMR spectroscopy).

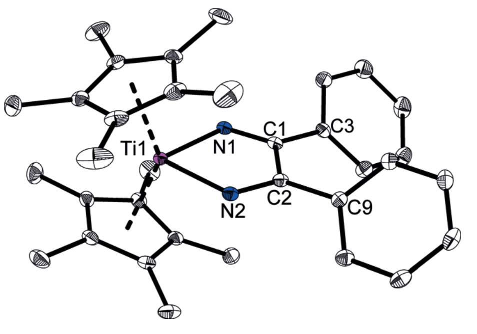


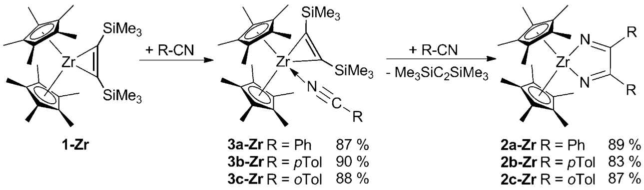
Figure 1. Molecular structure of **2a-Ti** in the solid state. Hydrogen atoms are omitted for clarity; ellipsoids are set to 30% probability. Selected bond lengths [Å] and angles [°]: C1–C2 1.540(2), C1–N1 1.274(2), C2–N2 1.276(2), Ti1–N1 2.006(1), Ti1–N2 2.006(1); C1-N1-Ti1 115.54(9), C2-N2-Ti1 115.60(9), N1-C1-C2 114.28(11), N2-C2-C1 114.10(11).

Table 1: Comparison of selected bond lengths [Å] and angles [°] of the diazacyclopentadiene complex **2a-Ti** and the diazacyclopentene complex $Cp_2Ti({-}N(H){-}C(Ph){=}C(Ph){-}N(H){-})$.[28]

	2a-Ti[a]	[$Cp_2Ti(N(H)C(Ph)C(Ph)N(H))$]
N–M	2.006(1)	2.036(2)
	2.006(1)	2.005(2)
C–N	1.274(2)	1.360(3)
	1.276(2)	1.357(3)
C1–C2	1.540(2)	1.400(4)
C-N-M	115.54(9)	108.9(2)
	115.60(9)	111.6(2)

A comparison of the main structural parameters in the diazacyclopentadiene complex **2a-Ti** and the diazacyclopentene complex [$Cp_2Ti({-}N(H){-}C(Ph){=}C(Ph){-}N(H){-})$] is given in Table 1, and reveals significant differences in the geometry of the metallacycle.[28] The five-membered cycle in the latter compound is folded at the N1–N2 axis by 32.1°, whereas it is nearly planar in **2a-Ti** (angle between the planes defined by Ti1, N1, N2 and N1, C1, C2, N2: 0.81°).

For the similar reaction of the zirconium complex $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1-Zr**),[29] we found, in contrast to **1-Ti**, a coordination of the nitriles at room temperature in the first step (Scheme 3, **3-Zr**), and no further reaction with a second equivalent of the nitriles was observed. Warming the solution of the coordination products **3-Zr** for several days led to the elimination of the alkyne and a nitrile–nitrile C–C coupling yielded the desired products **2-Zr** (Scheme 3). The described reactions show, as often observed, the preference of a dissociative reaction by titanium and of an associative pathway by zirconium complexes, which is determined by the size of the metals.[1d]



Scheme 3. Synthesis of 1-zircona-2,5-diaza-cyclopenta-2,4-dienes.

Yellow crystals were obtained in high yields for **2a-Zr**, which are isostructural to those of **2-Ti**. Additionally, the conversion of **3-Zr** to **2-Zr** was monitored by ^{1}H NMR spectroscopy. Such a reaction behavior of **1-Zr** was recently described by us in its reaction with Ph_2CHCN. Owing to the acidic proton neighboring to the nitrile function, the second step was a H shift instead of the remarkable coupling that we describe here.[15] The complexes **3-Zr** were isolated as dark blue crystals and for **3a-Zr**, which were suitable for X-ray crystal-structure analysis (Figure 2), showing the same structural motif as the already described [$Cp^*_2Zr(\eta^2$-$Me_3SiC_2SiMe_3)(NCCHPh_2)$].[15]

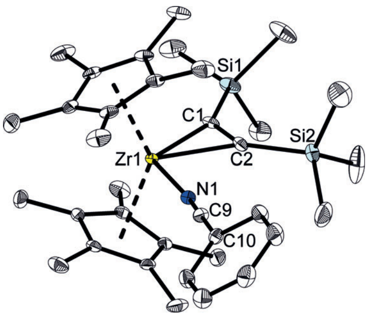
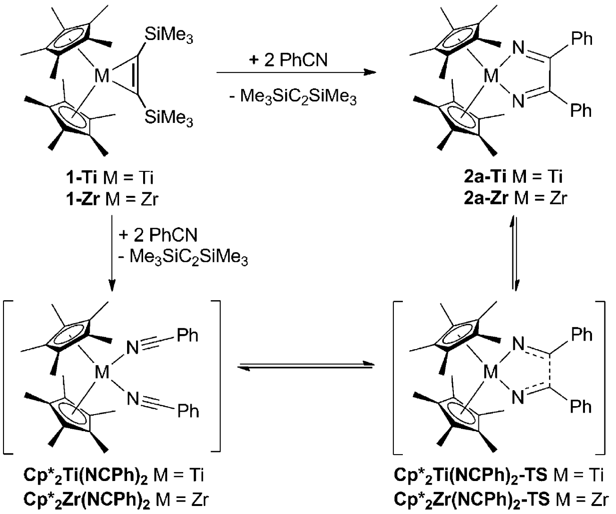


Figure 2. Molecular structure of **3a-Zr** in the solid state. Hydrogen atoms and the second molecule of the asymmetric unit are omitted for clarity; ellipsoids are set to 30% probability. Selected bond lengths [Å] and angles [°], corresponding values of the second molecule in the asymmetric unit are given in square brackets: C1–C2 1.314(3) [1.306(3)], Zr1–N1 2.269(2) [2.281(2)], N1–C9 1.152(3) [1.143(3)]; C2-C1-Zr1 73.80(12) [73.87(12)], N1-C9-C10 178.7(2) [176.5(2)].

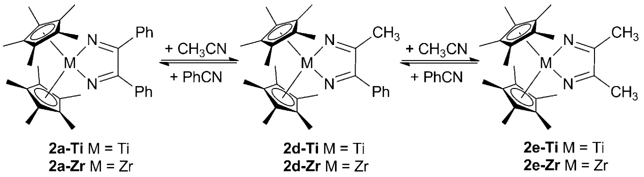
To understand the reaction behavior of **1-Ti** and **1-Zr** with nitriles, we have computed the energetic changes during the reactions. In our calculations, we have used the real-size molecules **1-Ti** and **1-Zr** as well as PhCN and CH_3CN at the BP86 level with the TZVP basis set for non-metal elements and the effective core potential LANL2DZ basis set for Ti and Zr. It is firstly noted that the computed structural parameters for **1-Ti** and **1-Zr** are in excellent agreement with those determined by X-ray crystal structure analysis. The computational details are given in the Supporting Information.

For the substitution of the alkyne ligand in **1-Ti** and **1-Zr** by two PhCN molecules to [$Cp^*_2Ti(NCPh)_2$] and [$Cp^*_2Zr(NCPh)_2$] (Scheme 4), the computed reaction energy is highly exergonic by 20.9 and 18.2 kcal mol^{-1}, respectively, indicating their thermodynamic probability. For the C–C coupling of two nitrile units in [$Cp^*_2M(NCPh)_2$], we have located the authentic transition states [($Cp^*_2M(NCPh)_2$]-TS), and the computed free energy barrier is 10.3 for M = Ti and 9.6 kcal mol^{-1} for M = Zr. The formation of **2a-Ti** (−1.6) and **2a-Zr** (−3.6 kcal mol^{-1}) is exergonic. These very low exergonic energy shows the thermodynamic probability of the reverse reaction from **2a-M** back to [$Cp^*_2M(NCPh)_2$] (the barrier of the reverse reaction is 11.9 and 12.2 kcal mol^{-1} for **2a-Ti** and **2a-Zr**, respectively), and also a possible equilibrium between **2a-M** and [$Cp^*_2M(NCPh)_2$]. The total reaction free energy from **1-Ti** to **2a-Ti** is −22.5 and from **1-Zr** to **2a-Zr** −21.8 kcal mol^{-1}.



Scheme 4. Calculated reaction path from **1-Ti/1-Zr** to **2a-Ti/2a-Zr**.

Investigating the reactions of **2a-Ti** and **2a-Zr** with CH_3CN shows that in addition to **2a-Ti** and **2a-Zr**, two new complexes are formed: the 1-metalla-2,5-diaza-cyclopenta-2,4-dienes with two substituents R = CH_3 (**2e-Ti** and **2e-Zr**), and the mixed compounds with one R = CH_3 and the other R = Ph (**2d-Ti** and **2d-Zr**; Scheme 5).

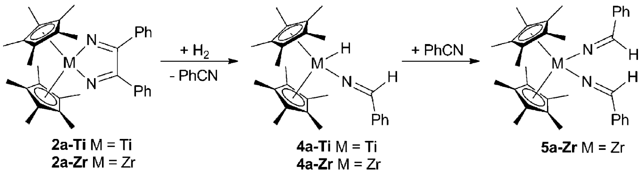


Scheme 5. Exchange of the nitriles.

Indeed, our calculations show that the free energy change is only −1.5 kcal mol^{-1} from **2a-Ti** to **2d-Ti**, and −2.2 kcal mol^{-1} from **2d-Ti** to **2e-Ti**. The corresponding free energy change from **2a-Zr** to **2d-Zr** is −1.4 kcal mol^{-1}, and that from **2d-Zr** to **2e-Zr** is −0.9 kcal mol^{-1}. These rather small free energy changes from R = Ph to CH_3 have their steric origin between the two R substituents on the one hand, and reveal their possible equilibrium as found experimentally on the other.

The coupling reaction of CH_3CN with **1-Ti** and **1-Zr** was also computed, and structure optimization led directly to **2e-Ti** and **2e-Zr** without any barriers, but the experiment did not yield the expected products. Therefore, the nitrile-exchange reaction is important for the possible isolation of these compounds. In some aspects this resembles the Group 4 1-metallacyclopenta-2,4-dienes, which can undergo ring opening reactions to the bis(alkyne) complexes and subsequently eliminate one alkyne.[22a,30]

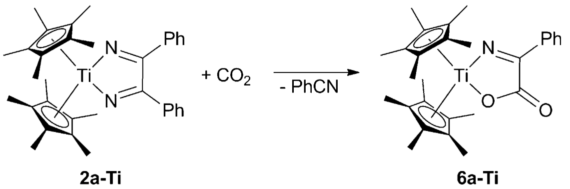
Furthermore, the reaction behavior of the very unusual 1-metalla-2,5-diaza-cyclopenta-2,4-dienes was investigated in the reactions with H_2, CO_2, and HCl. The reaction of the zirconium complex **2a-Zr** with H_2 at room temperature, giving compound **4a-Zr** and free PhCN, was investigated by



Scheme 6. Reaction of **2a-Ti** and **2a-Zr** with H_2.

^{1}H- and ^{13}C NMR spectroscopy (Scheme 6). Further warming of these products led to the formation of **5a-Zr** by insertion of PhCN. Insertion reactions of nitriles into M–H bonds are well known.[17c,31] In contrast to this, **2a-Ti** did not react with H_2 at room temperature. Warming the mixture to 65 °C for three days yielded the desired product **4a-Ti** in quantitative yield. A nitrile insertion does not occur as a result of further heating.

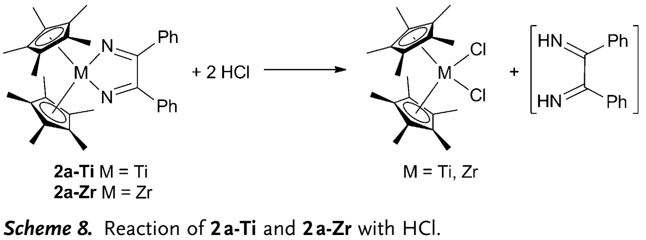
An exchange of one nitrile is also observed in the reaction of **2a-Ti** with CO_2. The formation of **6a-Ti** (Scheme 7) is the result of a C–C coupling between the CO_2 and the mono-nitrile complex. This underlines the existence of the equilibrium of the metallacycle **2a-Ti** and a bis(nitrile) complex in solution (Scheme 4). In contrast, the corresponding zirconium compound **2a-Zr** forms complex mixtures in the reaction with CO_2 at room temperature. The coupling reaction of CO_2 with nitriles was rarely observed,[32] and to the best of our knowledge was never described for Group 4 metals in this way.



Scheme 7. Reaction of **2a-Ti** with CO_2.

In comparison to these exchange reactions, the release of a diimine can be accomplished in the reaction with HCl. Unfortunately, these diimines are not stable at room temperature,[33] but the corresponding metallocene dichlorides can be isolated (Scheme 8).

In summary, we were able to accomplish a remarkable C–C coupling between two nitriles to form unusual ring-strained 1-metalla-2,5-diazacyclopenta-2,4-dienes. In the case of the reactions of [Cp*$_2$Zr(η^2-Me$_3$SiC$_2$SiMe$_3$)] (**1-Zr**), we could isolate **3-Zr** as an intermediate as well. We investigated the structural and energetic properties of the five-membered metallacycles and their reaction behavior. This shows that the new C–C bond between the nitriles is relatively labile and can be easily cleaved. This leads to the release of one nitrile and its replacement by different co-substrates, giving a high potential for synthetic strategies which are currently under investigation.



Scheme 8. Reaction of **2a-Ti** and **2a-Zr** with HCl.

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