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Redox-disproportionation of a decamethyltitanocene(III) isonitrile alkinyl complex

Fabian Reiß,[a] Kai Altenburger,[a] Dirk Hollmann,[a] Anke Spannenberg,[a] Haijun Jiao,[a] Perdita Arndt,[a] Uwe Rosenthal,[a] Torsten Beweries*[a]

Dedicated to Karel Mach on the occasion of his 80th birthday.

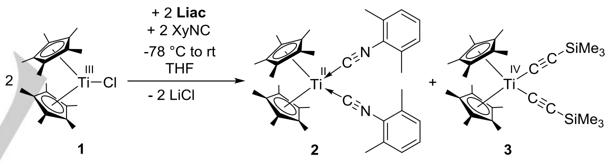
Abstract: A mixed decamethyltitanocene(III) isonitrile alkinyl complex (**7**) was synthesised via sequential introduction of the isonitrile and alkinyl ligands. Direct synthesis results in the formation of the diamagnetic decamethyltitanocene bis(isonitrile) (**2**) and bis(alkinyl) (**3**) complexes. Compound **7** undergoes disproportionation at room temperature to give **2** and **3**. All complexes were fully characterised by IR, MS as well as by NMR and EPR, respectively. Molecular structures for complexes **2** and **7** are reported. The stability and reactivity of these complexes are rationalised by DFT computations.

Introduction

The formation of metallacycles by intermolecular coupling of unsaturated substrates or intramolecular coupling of ligands is known in organometallic chemistry and has allowed for the synthesis of highly strained and exotic structures.[1] Heterometallacycles as well as all-C metallacycles with exocyclic heteroatoms can be accessed by using substrates and/or ligands such as CO_2 [2], phosphaalkynes[3], nitriles[4], isonitriles[5], etc. The versatility of isonitriles as ligands was thoroughly reviewed only recently.[6] We have demonstrated that isonitriles are versatile ligands for the realisation of a variety of coordination as well as C-C and C-N coupling products at zirconocene and hafnocene fragments.[5a] Depending on the ratio of metallocene precursor and isonitrile, complexes showing different unusual structural motifs were identified and interconversion reactions were investigated. In general, exocyclic N substitution was predicted to be favourable for the realisation of small, highly strained metallacycles.[7] We thus considered combination of an isonitrile fragment with an alkyne or alkinyl complex as a promising approach to access these. In this contribution, we report the synthesis and characterisation of a mixed decamethyltitanocene isonitrile alkinyl complex. In solution this complex shows an equilibrium with the corresponding bis(isonitrile) and bis(alkinyl)complexes via disproportionation. These complexes can be regarded as potential precursors for the design of small, highly strained and exotic four membered (hetero)metallacycles.

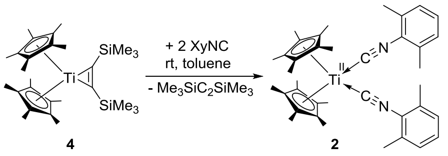
Results and Discussion

In order to evaluate the possibility of a direct synthesis of a mixed titanocene(III) isonitrile alkinyl, we performed a reaction of Cp^*_2TiCl (**1**) with 2,6-dimethylphenylisonitrile (XyNC) and lithium alkinyl compound LiC_2SiMe_3 (**Liac**) (Scheme 1). The latter was prepared by lithiation of trimethylsilylacetylene, isolated as a colourless solid in good yield and unequivocally identified based on its NMR (^{29}Si: δ -30.3 ppm) and Raman data (1985 cm^{-1}).[8]
After workup in *n*-hexane we observed precipitation of a mixture of two different crystalline compounds, which could not be isolated by fractional crystallisation but were successfully separated by crystal picking. The ^1H NMR spectrum of this mixture clearly reveals the presence of two different diamagnetic decamethyltitanocene complexes (C_5Me_5 resonances at δ 1.88 and 1.95 ppm, respectively, Figure 2a).



Scheme 1. Reaction of complex **1** with **Liac** and XyNC.

As we considered the formation of the bis(isonitrile) complex **2** and the bis(alkinyl) complex **3**, we next aimed for the synthesis and characterisation of both complexes individually. Reaction of the alkyne complex $Cp^*_2Ti(Me_3SiC_2SiMe_3)$ with XyNC in toluene cleanly yields the bis(isonitrile) complex **2**[9] in good yield (Scheme 2). Indeed, ^1H NMR analysis shows that **2** matches one of the species mentioned before (singlets at δ 1.88 and 2.44 ppm, respectively). This reaction is computed to be exergonic by 29.36 kcal/mol, indicating the easy formation and high stability of complex **2**.



Scheme 2. Synthesis of **2**.

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Single crystals suitable for an X-ray analysis were obtained from saturated *n*-hexane solution at -78 °C. In the solid state two inequivalent isonitrile ligands coordinate to the titanium center (Figure 1). The C-N bond distances (C1-N1 1.196(2) and C2-N2 1.183(2) Å) are in the same range and are slightly elongated due to complexation (*c.f.* C-N 1.160(3)/1.161(2) Å in the free isonitrile XyNC).[10] Both isonitrile fragments in **2** display a significant deviation from linearity of the C≡N-C(Xy) unit [C1-N1-C3 149.23(16), C2-N2-C11 171.08(17)°]. This observation was reported before for the complex [$Cp^*_2Ti(\eta^1\text{-CNMes})_2$] [C-N-C(Mes) 142.4(2)/176.1(2)°; Mes = 2,4,6-trimethylphenyl].[11] A possible explanation was given by Filippou *et al.*, who reported that a very strong back donation from the metallocene fragment to the isonitrile ligand induced the bending.[12] The cyclopentadienyl ligand seems to have a strong influence as on one hand the complex [$\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Ti(\eta^1\text{-CNXy})_2$][13] shows only small deviations from linearity [C-N-C(Xy) 176.3(5)/170.3(5)8] on the other hand the complex *rac*-(ebthi)Ti(η^1-CNXy)$_2$][5a] exhibits two bent isonitrile units [C-N-C(Xy) 154.14/155.24°]. The optimised gas-phase structure of complex **2** has C_2 symmetry and two equivalent isonitrile ligands. It also shows the deviation of the linear C≡N-C moiety in the free ligand to the bent complexed ligand by 156.3°; and the C-N triple bond is slightly elongated from 1.185 Å in the free ligand to 1.214 Å in **2**, revealing the strong back donation from the formal d^2 Ti(II) center to ligands.

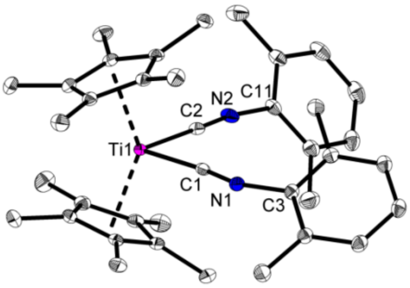
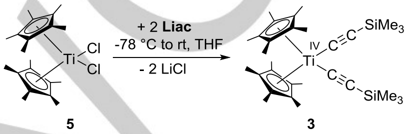


Figure 1. Molecular structure of **2** in the solid state. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

ATR-IR spectra of complex **2** shows the expected sharp signal at 2115 cm^{-1} due to the C≡N vibration, which is in good agreement with the observed signal in *rac*-(ebthi)Ti(η^1-CN-Xy)$_2$. In addition, broad signals at 3367 and 1813 cm^{-1} were observed, which point towards extreme moisture sensitivity of these complexes.

Next, we prepared the proposed bis(alkinyl) complex **3**, which – to our surprise – was not isolated in pure form to date. However, it should be noted that such complexes were investigated before by the groups of Rosenthal and Mach.[14] Indeed, Mach and co-workers identified **3** as an intermediate by means of IR spectroscopy.[14a] Reaction of $Cp^*_2TiCl_2$ with **Liac** at low temperature furnishes the desired product in moderate yield (Scheme 3). To avoid the quantum chemical problem of LiCl formation/solvation, we computed the exchange of two chlorides by two alkinyl anions resulting in complex **3**; and this exchange reaction is exergonic by 12.02 kcal/mol, indicating a thermodynamically very favoured reaction.

ATR-IR data for the triple bond in **3** resemble those reported before by Mach (2016 cm^{-1}). Also, the NMR data are in the expected range with the signal for the α-C atom showing a ^{13}C resonance at δ 182.7 ppm. In the ^{29}Si NMR spectrum a slight downfield shift is found compared to **Liac** (δ -25.3 ppm). The optimised structure of complex **3** has C_2 symmetry and two equivalent alkinyl ligands. In contrast to complex **2**, the C-C-Si moiety in complex **3** is only slightly bent (178.4°). This is in line with the d^0 Ti(IV) center, which does not have free valance electrons to donate back to the ligands.



Scheme 3. Synthesis of **3**.

A comparison of ^1H NMR spectra of isolated **2** and **3** with the ^1H NMR spectrum of the mixture as obtained from the reaction shown in Scheme 1 shows that – as assumed – the proposed Ti(II) bis(isonitrile) and Ti(IV) bis(alkinyl) complex were indeed formed in a redox disproportionation reaction of the Ti(III) precursor Cp^*_2TiCl (Figure 2). Similar reactions were described before for titanocenes, e.g. by Bercaw for the system [Cp^*_2TiH]/[Cp^*_2Ti]/[$Cp^*_2TiH_2$][15]; however, well-defined examples are rare. Ti(III) halides are known to undergo disproportionation reactions to Ti(II) and Ti(IV) species under drastic conditions.[16]

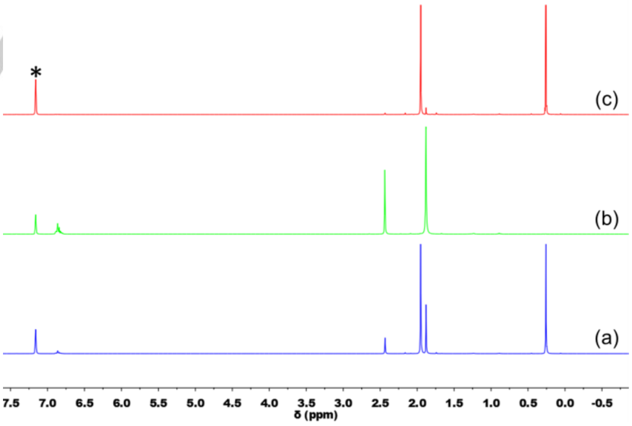
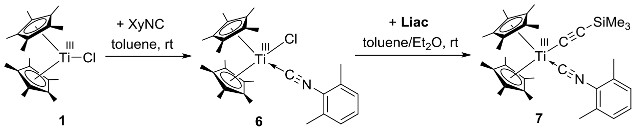


Figure 2. ^1H NMR spectra of crystal mixture (a) as obtained from the reaction shown in Scheme 1 and isolated complexes **2** (b) and **3** (c) (*: [D6]benzene).

For this reason, we changed our strategy to prepare a mixed Ti isonitrile-alkinyl complex. Addition of one equivalent of XyNC to Cp^*_2TiCl gives the Ti(III) coordination product **6**, which can be isolated as a brownish solid in good yields (Scheme 4). As in complex **2**, the optimised structure of complex **6** has the bent C-C-N moiety (168.9°). Under stoichiometric condition, the formation of complex **6** from complex **1** via isonitrile coordination is only slightly endergonic by 1.88 kcal/mol, indicating a ligand mediated equilibrium between complexes **1** and **6**.



Scheme 4. Synthesis of complex **7** via **6**.

The paramagnetic nature of **6** was investigated by EPR spectroscopy. **6** shows an EPR signal of an isolated Ti(III) centre with a g value (g = 1.9911) comparable with previously isolated [Cp*$_2$Ti(III)] complexes (Figure 3).[17] Furthermore the signal shows the typical hyperfine structure (hfs) splitting (A_{Ti} = 10.3 G) which results from the coupling of the single electron of Ti(III) to the nuclear spin of the isotopes ^{47}Ti (I = 5/2, 7.44 % natural abundance) and ^{49}Ti (I = 7/2, 5.41 % natural abundance).

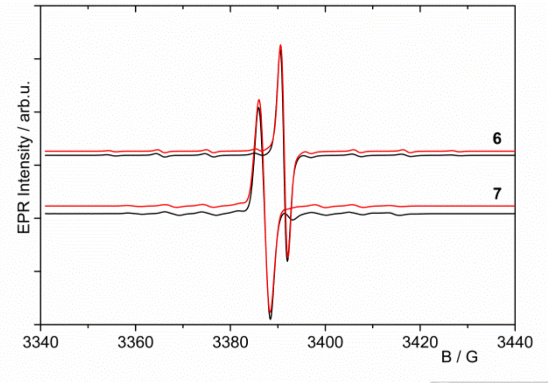


Figure 3. Comparison of EPR spectra of **6** and **7** at *T* = 300 K in toluene (black: experimental spectrum, red: simulation).

However, the reaction from complex **6** to complex **7** via chloride exchange by alkinyl anion is exergonic by 3.34 kcal/mol. Reaction of **6** with **Liac** results in the formation of the Ti(III) complex **7**, which can be obtained in yield up to 73% after workup using *n*-hexane. Again EPR spectroscopy revealed the paramagnetic nature of an isolated Ti(III) complex (Figure 3, g = 1.9941, A_{Ti} = 7.9 G).

The molecular structure (Figure 4) shows the titanium centre in distorted tetrahedral coordination environment with two Cp* ligands and the alkinyl and the isonitrile moieties. Bond lengths are in the expected range (C1-C2 1.209(2), C6-N1 1.162(2)), however, also in this case, the C-N-C(Xy) fragment is slightly bent (C6-N1-N7 175.03(18)°). The C-N bond in **7** is significantly shorter compared to those in **2,** on the other hand the C-Ti bonds in **7** (C1-Ti1 2.135(2), C6-Ti1 2.130(2) Å) are significant longer compared to those in **2** (C1-Ti1 2.025(2), C2-Ti1 2.071(2) Å). To the best of our knowledge, **7** represent the first structurally characterised mixed metallocene isonitrile alkinyl complex. The optimised structure of complex **7** has bent C-N-C (168.4°) and C-C-Si (175.2°) moieties. As found experimentally, the C-N bond in **7** is shorter than in **2** (1.195 vs. 1.214 Å). However, both C-N bonds in **2** and **7** are longer than that in the free ligand (1.185 Å). Indeed, such structural changes in C-N as well as C-Ti bond lengths and C-N-C bond angle from complexes **2** to **7** is associated with the formal oxidation state of the Ti center. The Ti(II) in **2** with d^2 configuration can have stronger back donation than Ti(III) in **7** with d^1 configuration.

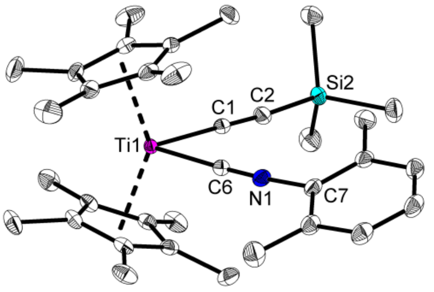


Figure 4. Molecular structure of **7** in the solid state. Hydrogen atoms and co-crystallised *n*-hexane are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

NMR spectra of the isolated crystals of **7** show apart from a broad paramagnetic resonance due to the compound (δ 2.5 - 7.5 ppm) signals that can be assigned to complexes **2** and **3** which points towards redox equilibrium between **7** and **2**/**3**. (Figure S3) Similarly, when NMR samples of a mixture of **2** and **3** were heated to *T* = 60 °C for two days, a significant decay of the signals of the diamagnetic species **2** and **3** was observed (Figure 5) due to the formation of the paramagnetic species **7** which unambiguously was confirmed by EPR spectroscopy (Figure S4).

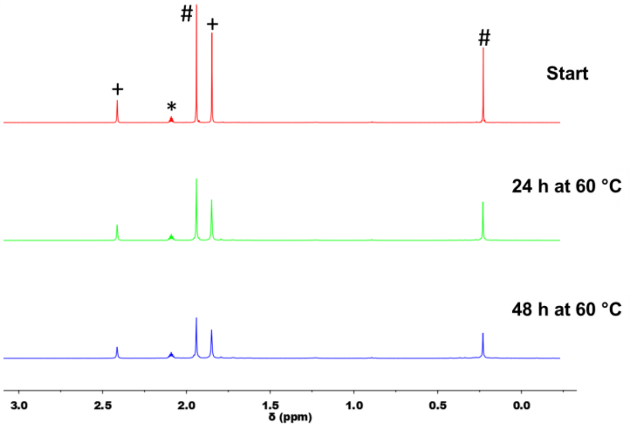
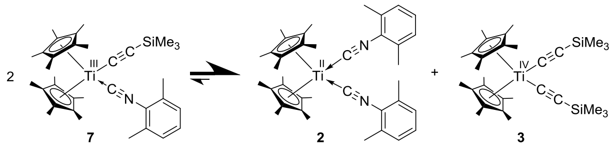


Figure 5. ^{1}H NMR spectra of the synproportionation reaction of complexes **2** (+) and **3** (#) to yield the paramagnetic complex **7** (*: [D8]toluene).

Indeed, such equilibrated redox property has been confirmed by computation. The disproportionation of the mixed isonitrile alkinyl complex **7** into complexes **2** and **3** is exergonic by 0.70

kcal/mol and has an equilibrium constant of 3.26 in favour of the formation of **2** and **3**. In turn, this can also explain the observed synproportionation from complexes **2** and **3** to complex **7** at elevated temperature and elongated reaction time.



Scheme 5. Disproportion of complex **7** into **2** and **3**.

In previous studies, light-induced intramolecular coupling of bis(alkinyl) compounds gave unusual five-membered metallacyclopentatri-2,3,4-ene (i.e. metallacyclocumulene)[2a] structures. In order to evaluate if this is also possible for the novel isonitrile alkinyl complex **7** we irradiated using UV and visible light. However, apart from the aforementioned disproportionation reaction, no further reactions were observed. Further studies on the reactivity of **7** and related compounds are ongoing in our group.

Conclusions

We have reported the synthesis of a mixed isonitrile alkinyl complex (**7**). Direct reaction of the isonitrile and the alkinyl ligands with the Ti(III) precursor results in the formation of two diamagnetic species which were identified as decamethyltitanocene(II) bis(isonitrile) (**2**) and decamethyltitanocene(IV) bis(alkinyl) complex (**3**). The formation can be explained by a rare example of disproportionation of the paramagnetic Ti(III) complex. The mixed isonitrile alkinyl complex **7** can, however, be accessed by sequential addition of the ligands starting from Cp^*_2TiCl by coordination of one XyNC ligand, followed by an addition of the alkinyl precursor LiC_2SiMe_3. Interestingly mixed isonitrile alkinyl complex **7** undergoes a redox disproportionation under comparable mild conditions to give the bis(isonitrile) complex **2** and the bis(alkinyl) complex **3**. The redox relationship between these complexes was examined by NMR and EPR experiments as well as in a computational study. Regarding structures, stability and reactivity of the compounds full interplay between theory and experiment has been clearly demonstrated.

Acknowledgements

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Keywords: titanium • metallocenes • X-ray diffraction • EPR spectroscopy • DFT calculations

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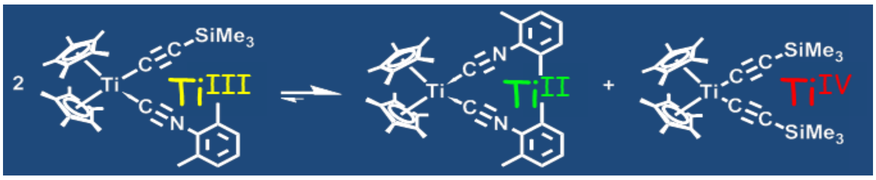

Stepwise introduction of isonitrile and alkinyl ligand gives a mixed decamethyltitanocene(III) isonitrile alkinyl complex, which undergoes redox disproportionation at room temperature to yield two well-defined diamagnetic Ti complexes.

Titanocenes*

*F. Reiß, K. Altenburger, D. Hollmann, A. Spannenberg, H. Jiao, P. Arndt, U. Rosenthal, T. Beweries**

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Redox-disproportionation of a decamethyltitanocene(III) isonitrile alkinyl complex