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Retro-Diels-Alder decomposition of norbornadiene mediated by a cationic magnesium complex[†]

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First evidence for the coordination of norbornadiene (nbd) and dicyclopentadiene (dcpd) with the main group metal Mg is provided by the crystal structures of adducts with cationic β -diketiminate (BDI) Mg complexes. While the dcpd complex is thermally stable, [(BDI)Mg⁺.nbd][B(C₆F₅)₄⁻] shows slow room temperature *retro*-Diels-Alder decomposition to give a complex with the cation (BDI)Mg(C₅H₅)Mg(BDI)⁺.

First observations of Diels–Alder (DA) reactivity were reported by Albrecht as early as 1906.¹ The product of the reaction between quinone and cyclopentadiene had been wrongly formulated and it was more than 20 years later that Otto Diels and Kurt Alder correctly interpreted this as a [4+2]cycloaddition reaction between dienes and dienophiles.² This powerful transformation was subsequently a topic of intense research activities.³ Nowadays, DA reactions are widely used as a powerful synthetic tool for designing 6membered ring systems.⁴

The *retro*-Diels–Alder reaction (*r*DA), *i.e.*, the reverse of the Diels–Alder reaction, was already described in Albrecht's original publication.¹ Due to its highly endothermic character this transformation needs to be enforced under harsh reaction conditions and therefore it never found broad applications in synthesis. Despite limited popularity, it is today a useful tool for the preparation of unstable molecules.⁵ Since *r*DA is also an attractive method for preparing bioactive natural products such as terpenes and steroids,⁶ great efforts have been made to find milder reaction conditions for this synthetic tool.^{5–7} This has been

accomplished by the introduction of substituents or ring strain⁸ and by the addition of Brønsted or Lewis acid catalysts.⁹



We recently introduced cationic β -diketiminate complexes of Mg and Ca that are free of stabilizing Lewis bases (*e.g.* I).¹⁰ The B(C₆F₅)₄⁻ anion in complex I is only weakly bound to the metal and can partially be replaced by arene ligands (II).^{10,11} Increasing the bulk of the β -diketiminate ligand led to complete cation–anion charge separation (III).¹² Hill and coworkers demonstrated that similar cationic Mg and Ca arene complexes can also be isolated using Krossing's even less coordinating anion, Al[OC(CF₃)₃]₄⁻.¹³ It has been shown that the "naked" Mg complexes exhibit exceptional Lewis acidity that even exceeds that of the benchmark Lewis acid B(C₆F₅)₃.¹⁰ This allowed for Mg–alkyne bonding^{10,14} and the isolation of the first metal-complex of (Me₃Si)₂O, a silyl ether that so far had been reluctant to any metal coordination.¹⁵ Also, the full series of Mg–halobenzene complexes (IV) have been isolated and their

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Scheme 1 Formation and decomposition of cationic Mg complexes of norbornadiene and dicyclopentadiene (Ar = 2,6-diisopropylphenyl).

structures were discussed in the context of the halogen σ -hole.^{12,16} Most recently, we showed that these highly Lewisacidic cationic Mg complexes are also able to bind unsupported alkene ligands. Not only coordination complexes of dienes, typically used to stabilize low-valent transition metals (*e.g.* 1, 5-cyclooctadiene, 1,3,5-cycloheptatriene, 1,3-divinyltetramethyldisiloxane or 2,3-dimethyl-1,3-butadiene), but also alkene complexes with cyclooctene or 2-ethyl-1-butene have been isolated.¹⁷ Herein we



Fig. 1 Crystal structures of cationic Mg alkene complexes (H atoms not shown, except for H at double bonds, and the anion is only partially shown, or in case of (d) not shown) with selected bond lengths (Å). (a) $[(BDI)Mg^+ \cdot nbd][B(C_6F_5)_4^-]$ (**1**): Mg–N1 1.987(1), Mg–N2 1.988(1), Mg–F2 2.158(1), Mg–C1 2.523(2), Mg–C2 2.534(2), Mg–C4 2.701(2), Mg–C5 2.675(2), C1–C2 1.328(3), and C4–C5 1.325(3). (b) $[(BDI)Mg^+ \cdot dcpd][B(C_6F_5)_4^-]$ (**2**): Mg–N1 1.992(2), Mg–N2 1.992(2), Mg–F2 2.074(1), Mg–C30 2.555(2), Mg–C31 2.444(2), and C30–C31 1.334(3). (c) $[(BDI)Mg(Cp)Mg(BDI)^+][B(C_6F_5)_4^-]$ (**4**): Mg–N 2.000(2)–2.021(2) (average: 2.009), Mg–F 2.210(2)–2.361(2) (average: 2.291), and Mg–C 2.2291(2)–2.620(2) (average: 2.469). (d) Cationic unit of $[(BDI)Mg(Cp)Mg(BDI)^+][A(CC(CF_3)_3)_4^-]$: Mg–N 1.984(3)–1.998(3) (average: 1.991) and Mg–C 2.424(4)–2.515(4) (average: 2.453).

report Mg complexation of the dienes 2,5-norbornadiene and dicyclopentadiene and present a unique example of a Mg-mediated *retro*-Diels–Alder reaction.

The addition of 2,5-norbornadiene to a colorless solution of $[(BDI)Mg^+][B(C_6F_5)_4^-]$ in chlorobenzene, which was formed *in situ* by the reaction of (BDI)Mg*n*Bu with $[Ph_3C^+][B(C_6F_5)_4^-]$,¹⁰ led to an immediate color change to an intense yellow (Scheme 1; BDI = HC[C(Me)N-DIPP]_2, DIPP = 2,6-di*iso*propyl-phenyl). Layering with hexane gave the product $[(BDI)Mg^+$. nbd] $[B(C_6F_5)_4^-]$ (1) as an off-white solid in 85% yield. Using a similar procedure, the dicyclopentadiene complex $[(BDI)Mg^+ \cdot dcpd][B(C_6F_5)_4^-]$ (2) was obtained in 45% yield (the low yield is because of difficulty in crystallization due to clathrate formation).

Crystal structure determination shows that the nbd ligand is bound to Mg as an η^4 -chelating ligand but one of the alkenes (C1=C2) is signifantly closer to the metal than the other (C4=C5); see Fig. 1a. The asymmetry in Mg-nbd bonding is likely related to the additional Mg···F-C contact with B(C₆F₅)₄⁻. Indeed, the same complex with a more weakly coordinating Krossing's anion Al[OC(CF₃)₃]₄⁻ shows a completely free, undisturbed (BDI)Mg⁺·nbd cation with two similar Mg-alkene bonds (see Fig. S44, ESI⁺). The average Mg-C bond length in the latter (2.553 Å) is shorter than that in the borate complex 1 (2.608 Å).

In contrast, the crystal structure of 2 shows a dcpd ligand that is bound to Mg only in η^2 -fashion (Fig. 1b). Although the dcpd complex 2 was prepared using a mixture of exo- and endodcpd, 2 crystallized selectively only with the endo-isomer. This isomer has the potential to act as a chelating ligand, e.g., in (endo-dcpd)PtCl₂¹⁸ but the bulk of the BDI ligand apparently prevents the encapsulation of Mg by endo-dcpd and only a single Mg--alkene interaction is observed. Noteworthy is the asymmetry in Mg--alkene coordination. In agreement with previous observations of either intramolecular¹⁹ or intermolecular¹⁷ Mg-alkene complexes, a shorter Mg-C(alkene) bond is accompanied by a longer Mg-C(alkene) bond. This asymmetry leads to the polarization of π -electron density in the C=C bond, supporting an electrostatic bonding model in which the C=C bond elongation is negligible.^{17,19} In both, the nbd and dcpd complexes, the Mg coordination sphere is completed by a single Mg···F-C contact with $B(C_6F_5)_4^{-}$.

Although weakly bound Mg···alkene complexes cannot always be detected in solution,¹⁷ the ¹H NMR spectra of **1** and **2** in bromobenzene- d_5 give a clear indication that Mg-alkene bonding is preserved in solution. In both cases the signals for the alkene ligands are broadened and shifted with respect to those for free alkenes (Fig. S1 and S2, ESI†). In agreement with earlier observations, signals for the alkene protons shift slightly downfield upon metal coordination (nbd: 6.67 \rightarrow 6.73 ppm; dcpd: 5.91 \rightarrow 5.94 ppm). Signal broadening is caused by a dynamic dissociation–association equilibrium: (BDI)Mg⁺(alkene) \rightleftharpoons (BDI)Mg⁺ + alkene. High temperature NMR (60 °C) led to signal sharpening and a shift of the signals for the alkene protons to the values for the free alkene.

The high temperature ¹H NMR studies on the nbd complex 1 revealed that the nbd signals disappeared completely and a well-defined BDI complex with a sharp singlet at 5.62 ppm was formed. The same decomposition product also slowly formed at room temperature, reaching full conversion after two weeks (Fig. S31, ESI[†]). Although slow, this decomposition complicated the crystallization of $[(BDI)Mg^+ hbd][B(C_6F_5)_4^-]$ 1. During many attempts we isolated crystals of the decomposition product (4, isolated yield: 38%), which had a much lower solubility than the nbd complex 1. Its crystal structure revealed a cationic dinuclear Mg complex in which a Cp anion bridges two (BDI)Mg⁺ cations (Fig. 1c). The Mg-C(Cp) bonds (average: 2.469 Å) are due to the bridging nature of the Cp ligand, somewhat longer than those in Cp₂Mg (average: 2.304 Å).²⁰ The $B(C_6F_5)_4^-$ anions bridge between dinuclear cations by forming Mg ··· F-C contacts, resulting in a linear coordination polymer, but crystallization from fluorobenzene led to complete charge separation and formation of a dinuclear cation with $Mg \cdots FC_6H_5$ solvent interactions (Fig. S37, ESI[†]). The use of a weaker coordinating Krossing anion $Al[OC(CF_3)_3]_4^-$ and chlorobenzene as the solvent gave a solvent-free, undisturbed cation (BDI)Mg(Cp)Mg(BDI)⁺ (Fig. 1d). The average Mg-C bond in the latter (2.453 Å) is only slightly shorter than that in the borate complex (2.469 Å). A similar dinuclear Ni^{II} complex with the cation (BDI)Ni(Cp)Ni(BDI)⁺ was reported by Stephan and coworkers.21

Although decomposition of nbd in cyclopentadiene (CpH) and acetylene is contrathermodynamic, the interception of CpH by the deprotonation and precipitation of the poorly soluble product enabled full conversion. The acetylene sideproduct has not been detected and the fate of this side-product is hitherto unclear. Complex [(BDI)Mg(Cp)Mg(BDI)⁺][B(C₆F₅)₄⁻] 4 could alternatively be obtained in 77% yield by the reaction of [(BDI)Mg⁺·C₆H₆][B(C₆F₅)₄⁻] with (BDI)MgCp (see ESI[†] for full characterization) and was also successfully isolated in a one-pot reaction between (BDI)Mg*n*Bu, [Ph₃C⁺][B(C₆F₅)₄⁻] and CpH. While the *r*DA reaction for the nbd complex starts already at room temperature (and is fast at 60 °C), the dcpd complex 2 is essentially inert to *r*DA decomposition and even stays intact at 60 °C.

The contrathermodynamic decomposition of nbd needs temperatures well over 300 °C and is not fully selective (cycloheptatriene and toluene are also formed).²² Flash vacuum pyrolysis at high temperatures supplies the energy needed to overcome the kinetic barrier, while diene and dienophile are separated from each other by vacuum. The presence of (BDI)Mg⁺ results in the selective formation of the cation $(BDI)Mg(Cp)Mg(BDI)^+$ and apparently lowers the barrier for the rDA reaction allowing for conversion at room temperature. As activation barriers for DA can be decreased by Lewis acids,²³ the reverse rDA of nbd should also be facilitated by Lewis acids. Although there are some data for Lewis acid promoted rDA of activated substrates, 5,24 the challenging *r*DA decomposition of norbornadiene catalyzed by Fe⁺ has been so far only investigated by mass spectrometry²⁵ and comprehensive calculations which show that metal oxidation state changes are essential.²⁶ In contrast, the Mg-mediated rDA reaction of nbd cannot resort to redox reactions. There is, however, evidence for the noninnocence of the BDI ligand. While studying the thermal decomposition of $[(BDI)Mg^+ \cdot nbd][B(C_6F_5)_4^-]$ 1, crystals of an intermediate in which the BDI ligand is protonated have been isolated: $[(BDI-H)Mg^{+}(Cp)][B(C_{6}F_{5})_{4}^{-}]$ (3) (Fig. S39, ESI⁺). Although this complex could not be isolated in large quantities, it suggests a possible decomposition pathway (Scheme 1). It is known that the deprotonation of norbornene in the bridgehead C7-position allows for room temperature rDA.²⁷ On a similar note, intramolecular deprotonation of norbornadiene leads to a Mg-norbornadienyl intermediate which eliminates acetylene to give (BDI-H)Mg⁺(Cp) 3 which after reaction with (BDI)Mg⁺ forms the final dinuclear product (BDI)Mg(Cp)Mg(BDI)⁺ 4. The rDA reaction of the nbd-anion to Cp⁻ and acetylene is driven by aromaticity. Given the high pK_a value for the bridgehead CH_2 group in nbd (estimated >45), it is questionable, but not unlikely, that nbd deprotonation proceeds before rDA.²⁸ Alternatively, the CpH formed during decomposition is deprotonated by the BDI anion. Preliminary DFT calculations on a model system, $HC[C(Me)N(Ph)]_2Mg^+$, which for simplicity does not include the weakly coordinating anion $B(C_6F_5)_4^-$, are inconclusive (Scheme S2, ESI⁺) and more comprehensive studies by calculating the full system, including the influence of anion and solvent and considering the non-concerted radical routes as well as quadricyclene intermediates, are needed.

We here report the first crystal structural evidence for the main group metal complexes of nbd and dcpd. NMR data give a clear indication that these complexes are retained in a bromobenzene solution. While the Mg–dcpd complex 2 is thermally stable, Mg–nbd bonding in 1 can accelerate the *r*DA decomposition tremendously and the slow formation of a Cp complex 4 is observed already at room temperature. Although Lewis-acid mediated DA and *r*DA reactions of activated substrates have been reported, this is the first example of a Lewis-acid controlled room temperature *r*DA reaction of norbornadiene, a substrate that normally decomposes well over 300 °C. Conversion of the degradation product CpH into the Cp anion is key to this contrathermodynamic process. The precise mechanism of this transformation is not fully understood and currently under investigation.

Conflicts of interest

There are no conflicts to declare.

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