

Reactivity of the molecular magnesium hydride cation $[MgH]^+$ supported by an NNNN macrocycle



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ABSTRACT

The reactivity of the molecular magnesium hydride cation in $[(Me_4TACD)_2Mg_2(\mu-H)_2][B(3,5-Me_2-C_6H_3)_4]_2$ ($Me_4TACD = 1,4,7,10$ -tetramethyl-1,4,7,10-tetraazacyclododecane) toward Brønsted acids, the mild oxidant diphenyldisulfide as well as heterocumulenes CO₂, phenyl isocyanate, and carbodiimide has been investigated. While the hydridic character of the Mg–H bond is evident in reactions with Brønsted acids or an oxidant to give dihydrogen, hydrometallation of double bonds occurred smoothly to give insertion (hydromagnesiation) products.

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1. Introduction

Organometallic and catalytic chemistry of structurally well-characterized scandium alkyl and hydride complexes has been pioneered by Bercaw et al. using bis(η^5 -pentamethylcyclopentadienyl) [1–5] and related ligand systems including the commercially successful CpSiNR (“constrained geometry”) ligand [6,7]. Given the so-called diagonal relationship of scandium to magnesium, similar reactivity of discrete magnesium alkyl and hydride complexes could be anticipated. However, due to the divalent state and, most importantly, due to the higher ionicity of the metal–ligand bonds (Schlenk equilibrium) the search for a kinetically inert ancillary ligand for magnesium can be challenging [8]. Recently we introduced a cationic magnesium hydride $[MgH]^+$ that is supported by the NNNN macrocycle Me_4TACD and that was isolated as a dimer in the compound $[(Me_4TACD)_2Mg_2(\mu-H)_2][B(3,5-Me_2-C_6H_3)_4]_2$ [9]. While hydromagnesiation of double bond substrates was sluggish, polar substrates such as carbonyls and pyridine were found to insert smoothly into the magnesium–hydride bond. We report here that other polar substrates including weak Brønsted acids, mild oxidants and heterocumulenes also undergo reactions with $[MgH]^+$.

2. Results and discussion

Protonolysis of $[(Me_4TACD)_2Mg_2(\mu-H)_2][B(3,5-Me_2-C_6H_3)_4]_2$ (**1**) with the weak Brønsted acids $[NEt_3H]Cl$ and $PhC\equiv CH$ gave the

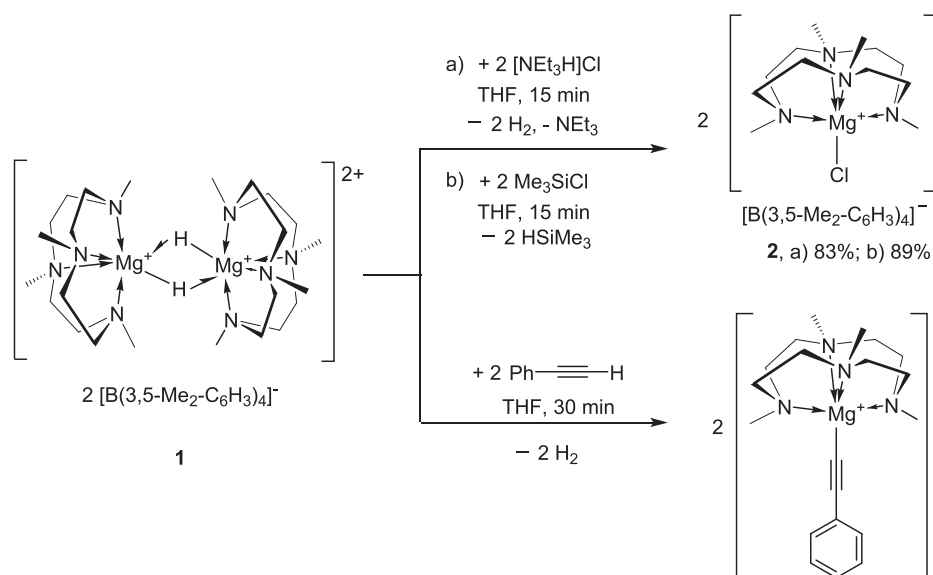
monomeric compounds $[(Me_4TACD)MgX][B(3,5-Me_2-C_6H_3)_4]$ (**2**: X = Cl, **3**: X = C≡CPh) under release of dihydrogen in 83 and 85% isolated yield, respectively (Scheme 1).

Both reactions can also be classified as σ -bond metathesis. If **2** was formed by treating **1** with Me_3SiCl , trimethylsilane was generated in a nucleophilic substitution reaction at silicon. Both compounds **2** and **3** are soluble in THF, THP and DME, but insoluble in aromatic and aliphatic hydrocarbons. The characteristic ¹³C NMR signals at δ 111.3 ppm (C≡CPh) of **3** can be compared with those of the related Me_3TACD stabilized magnesium phenylacetylide complexes $[(Me_3TACD)Mg(C\equiv CPh)]$ (δ 110.4 ppm [10] and $[(Mg(Me_3TACD-Al^iBu_3)(C\equiv CPh)]$ (δ 110.0 ppm [11], as well as that in related terminal alkyne complexes of magnesium such as $[Tism^{iPr^tBenz}MgC\equiv CPh]$ (Tism = tris[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]) (δ 112.2) [12]. Single crystals of **2** were obtained from a THF/*n*-hexane mixture at -30 °C over a period of 48 h. The packing of the chlorido complex **2** contains two crystallographically independent molecules of similar geometry within the asymmetric unit (Fig. 1).

The magnesium center in the monomeric molecular cation is coordinated by one chloride and four nitrogen atoms of the Me_4TACD ligand, showing almost perfect square pyramidal coordination geometry (structural parameter $\tau = 0.02$) [13]. The Mg–Cl distances (Mg1–Cl1: 2.278(3) Å; Mg2–Cl2: 2.266(3) Å) are comparable to those in $\{\eta^3\text{-HB}(3\text{-}t\text{Bu}^t\text{pz})_3\}MgCl$ (2.262(2) Å) [14,15], $[(Tp^{tBu,Me})MgCl]$ ($Tp^{tBu,Me} = \text{tris}(3\text{-}t\text{ert-butyl-5-pyrazolyl})\text{hydroborato}$) (2.2701(15) Å and 2.2677(15) Å) [16], as well as in $[\{(TerN)_2P\}MgCl]$ ($\{(TerN)_2P\} = \text{bis}(\text{terphenylimino})\text{phosphide}$) (2.269(2) Å) [17]. The coordination of the alkyne ligand in **3** could

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Scheme 1. Protonolysis of **1** with $[\text{NEt}_3\text{H}]\text{Cl}$ and $\text{PhC}\equiv\text{CH}$.

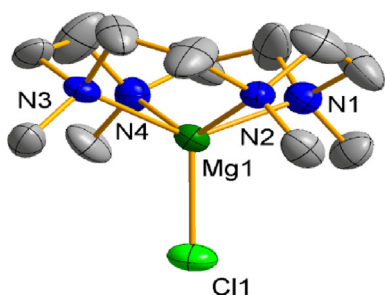


Fig. 1. Structure of one of the two crystallographically independent molecular cations in $[(\text{Me}_4\text{TACD})\text{MgCl}][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]^-$ (**2**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Mg1–Cl1 2.278(3), Mg1–N1 2.192(6), Mg1–N2 2.191(6), Mg1–N3 2.188(6), Mg1–N4 2.186(6), N1–Mg1–N3 134.4(2), N2–Mg1–N4 135.5(2), Mg2–Cl2 2.266(3), Mg2–N5 2.166(7), Mg2–N6 2.193(6), Mg2–N7 2.166(7), Mg2–N8 2.198(7), N5–Mg2–N7 133.4(3), N6–Mg2–N8 134.6(3).

also be confirmed by X-ray diffraction of a single crystal obtained from THF/*n*-hexane at -30°C (see supporting information). Most likely due to the co-crystallization of an unidentified minor impurity, the crystallographic refinement had to be carried out with isotropic parameters for both carbon atoms of the $\text{C}\equiv\text{C}$ fragment. This impurity might be the hydroxide formed from the adventitious reaction with a trace amount (ca. 10%) water, but this cannot be proved because the resolution of the X-ray data is not high enough. Details of the molecular structure obtained by X-ray diffraction are not discussed (see Fig. S20).

The reaction of **1** with the mild oxidant diphenyl disulfide PhSSPh gave the thiophenolate complex $[(\text{Me}_4\text{TACD})\text{Mg}(\text{SPh})][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]^-$ (**4**) under release of dihydrogen. This reaction may involve an electron transfer from a $\mu\text{-H}$ ligand to diphenyl disulfide, [18] leading to oxidation of the hydride ligands to give H_2 and to the reduction of PhSSPh under cleavage of the S–S bond (Scheme 2). Nucleophilic attack at the sulfur by the magnesium hydride cation to give thiophenol and $[(\text{Me}_4\text{TACD})\text{Mg}(\text{SPh})]$ may be another plausible pathway [18b], whereby the thiophenol is deprotonated by the magnesium hydride to give dihydrogen.

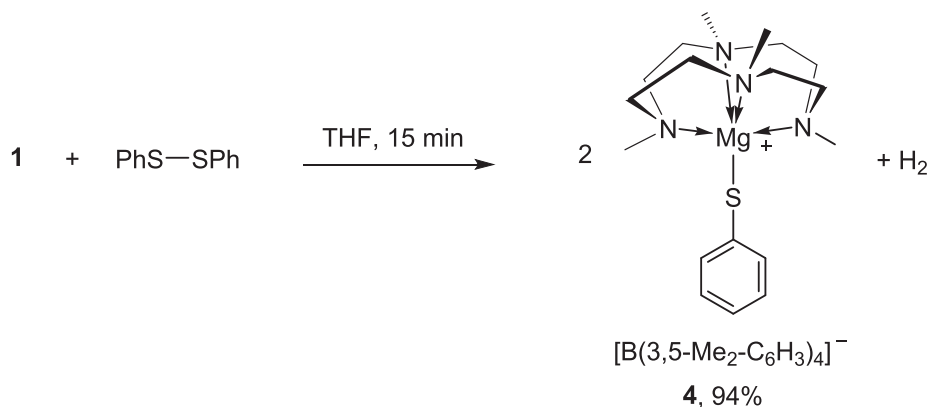
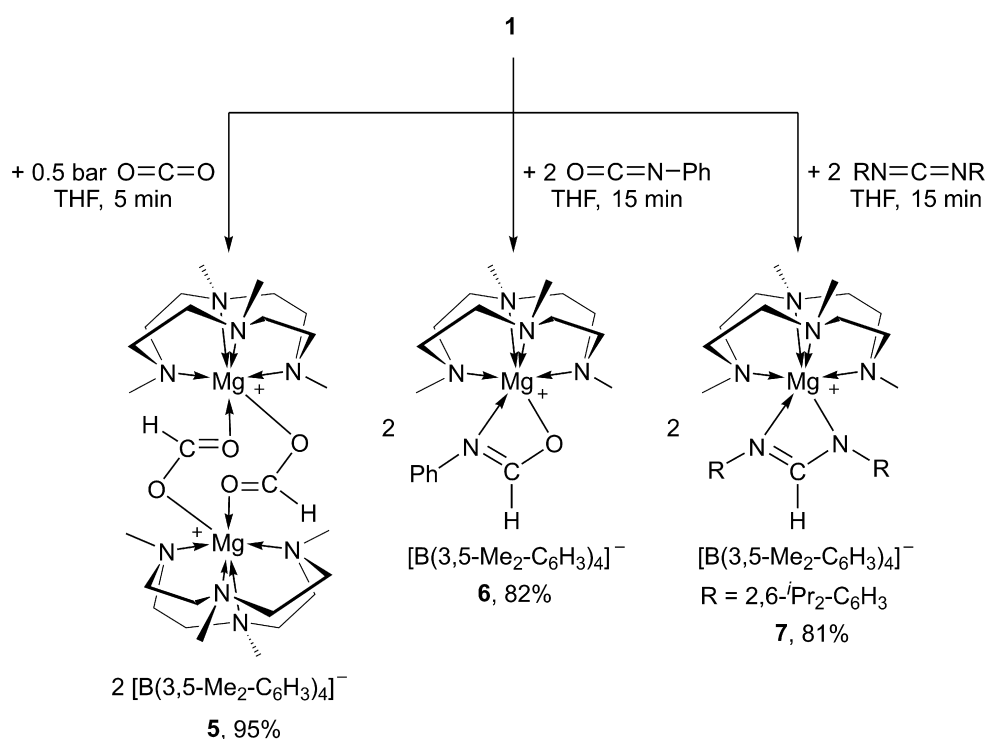
The ^1H NMR spectrum of **4** shows the signals for the coordinated Me_4TACD ligand, the borate anion, as well as the phenyl groups with resonances for the protons in *ortho*-, *meta*- and *para* position at δ 7.33, 6.96 and 6.86 ppm, respectively (see Fig. S7).

Reaction of **1** with the heterocumulenes CO_2 (0.5 bar), $\text{PhN}=\text{C}=\text{O}$ and bis(2,6-di-isopropylphenyl)carbodiimide gave $[(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu\text{-O}_2\text{CH}_2)][\text{A}]_2$ (**5**), $[(\text{Me}_4\text{TACD})\text{Mg}(\text{OCHNPh})][\text{A}]$ (**6**) and $[(\text{Me}_4\text{TACD})\text{Mg}(\{\text{DippN}\}_2\text{CH})][\text{A}]$ (Dipp = 2,6- $^i\text{Pr}_2\text{-C}_6\text{H}_3$) (**7**) in 95, 82, and 80% yield, respectively ($[\text{A}] = [\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]^-$) (Scheme 3).

All these compounds are soluble in THF, but not in aromatic or aliphatic hydrocarbons. Single crystals of the formate complex $[(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu\text{-O}_2\text{CH}_2)][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]_2$ (**5**) were obtained from a THF/*n*-pentane/ Et_2O mixture at 25°C over a period of 48 h. The molecular structure of the cation in **2** shows a dimeric structure with crystallographic $\bar{1}$ symmetry relating both magnesium centers that are bridged by two HCO_2 ligands (Fig. 2).

Each metal center is coordinated by two oxygen atoms of the formate units and by four nitrogen atoms of the Me_4TACD ligand, leading to distorted octahedral coordination geometry. The Mg1–O1 and Mg1–O2' distances with 2.023(2) and 2.0124(19) Å are longer than those in the dimeric magnesium formate complex $[(\text{C}_6\text{F}_5)_3\text{BOC}(\text{H})\text{OC}(\text{H})\{(\text{Me})\text{CNDipp}\}_2\text{Mg}(\mu\text{-O}_2\text{CH})_2]$ (1.979(4) and 1.935(3) Å) [19], but shorter than in the monomeric complexes $[(\text{Me}_3\text{TACD-Al}^i\text{Bu}_3)_2\text{Mg}_2(\kappa^2\text{-O}_2\text{CH})]$ (2.120(2) and 2.121(2) Å) [11] as well as in $[(\text{Tism}^{i\text{PrBenz}})\text{Mg}(\kappa^2\text{-O}_2\text{CH})]$ ($\text{Tism}^{i\text{PrBenz}} = \text{tris}[(1\text{-isopropylbenzimidazol-2-yl})\text{dimethylsilyl}]\text{methyl}$) (2.1746(16) and 2.1419(15) Å) [20]. The O1–Mg1–O2 bond angle of $87.63(8)^\circ$ is significantly smaller than in $[(\text{C}_6\text{F}_5)_3\text{BOC}(\text{H})\text{OC}(\text{H})\{(\text{Me})\text{CNDipp}\}_2\text{Mg}(\mu\text{-O}_2\text{CH})_2]$ ($99.55(16)^\circ$) [19]. One of the Me_4TACD ligands is disordered, but could be refined with split positions. In the major isomer, all four methyl groups of the ring ligand are pointing to the metal center, as usually observed for metal complexes of the Me_4TACD ligand; the main difference of the minor isomer is that one methyl group is directed away from the metal (Fig. 3).

The high symmetry is retained in solution, as revealed by the presence of only one signal at δ 8.27 ppm for the formate unit in the ^1H NMR spectrum (Fig. S10, see supporting information) and a signal at δ 175.9 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (Fig. S11).

Scheme 2. Reaction of **1** with diphenyl disulfide.Scheme 3. Reaction of **1** with heterocumulenes.

These signals are comparable to those of the magnesium formate complexes [(Me₃TACD·AlⁱBu₃)Mg(κ²O₂CH)] (¹H NMR: δ 8.25 ppm, ¹³C{¹H} NMR: δ 174.5 ppm) [11] and [(C₆F₅)₃BOC(H)OC(H){(Me)CNAr}₂Mg(OHCO)]₂ (¹H NMR: δ 8.31 ppm; ¹³C{¹H} NMR: δ 182.7) [19].

In contrast to the reaction of the hydride **1** with CO₂, treatment with the sterically more demanding PhN=C=O leads to the monomeric compound **6**. Single crystals of [(Me₄TACD)Mg(OCHNPh)][B(3,5-Me₂-C₆H₃)₄]⁻ (**6**) were obtained from a THF/*n*-pentane mixture at 25 °C over a period of 24 h. The structure obtained by single-crystal X-ray diffraction shows the magnesium center coordinated by the oxygen and nitrogen atom of the formamidato unit, as well as by the four nitrogen atoms of the Me₄TACD ligand, leading to a distorted trigonal prismatic coordination geometry (Fig. 4). The distances Mg1–O1 (2.043(6)) and Mg1–N5 (2.191(5)) Å are longer than those in [HC{(Me)CN(Dipp)}₂Mg(OCHNDipp)] (Mg–O: 2.0118 (10) Å; Mg–N: 2.0983(11) Å), but the angle O1–Mg1–N5 (63.7(2)°)

is comparable with that in [HC{(Me)CN(Dipp)}₂Mg(OCHNDipp)] (65.86(4)°) [21].

The ¹H NMR spectrum in THF-*d*₈ shows one singlet at δ 8.21 ppm for the formamidate ligand (Fig. S13, see supporting information), which agrees with the signal of [HC{(Me)CN(Dipp)}₂Mg(OCHNDipp)] (7.92 ppm) [21]. The aromatic protons in *ortho*-, *meta*- and *para* position of the phenyl ring appear as three multiplets at δ 6.89–7.23 ppm. At 25 °C, the resonances for the Me₄TACD ligand show an unusual pattern with two singlets at δ 2.48 and 2.31 ppm, indicating that the Me₄TACD ligand is dissociated from the metal. At –90 °C, the ¹H NMR spectrum reveals one singlet for the CH₃ groups and broad multiplets for the CH₂ groups that is characteristic of a coordinated Me₄TACD ligand. Thus, the labile nature of the Me₄TACD ligand in **6** is established. A labile coordination is also revealed in the ¹³C{¹H} NMR spectrum that shows one signal for the carbon atom of the formamidate ligand at δ 172.8 ppm in agreement with that in [HC{(Me)CN(Dipp)}₂Mg

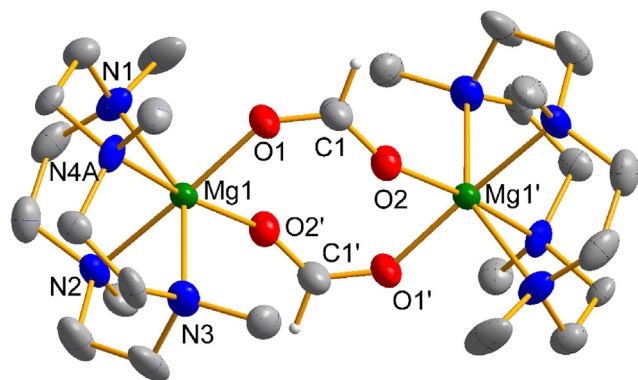


Fig. 2. Structure of the molecular cation of $[(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu\text{-OCHO})_2][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]_2$ (**5**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, except for these of the formate ligands, are omitted for clarity. Disordered atoms are shown with the split position of the major isomer. Primed and unprimed atoms are related by the symmetry operation $-x, -y, 2 - z$. Selected interatomic distances [Å] and angles [°]: Mg1–O1 2.023(2), Mg1–O2' 2.0124(19), C1–O1 1.241(3), C1–O2 1.235(3), Mg1–N1 2.224(2), Mg1–N2 2.262(2), Mg1–N3 2.235(2), Mg1–N4A 2.283(14), Mg1–N4B 2.49(3), O1–Mg1–O2 87.63(8), O1–C1–O2 128.6(3), N1–Mg1–N3 147.10(9).

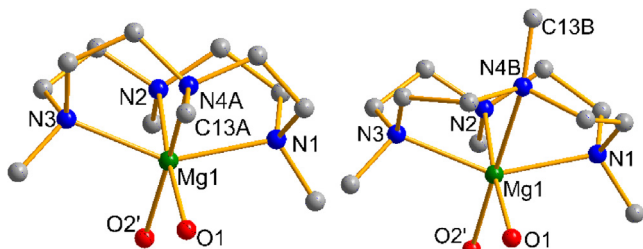


Fig. 3. Representations of the two conformers in the solid state of **5**. Left: major isomer with all four methyl groups pointing towards the metal center; right: minor isomer with one methyl group pointing away from the metal.

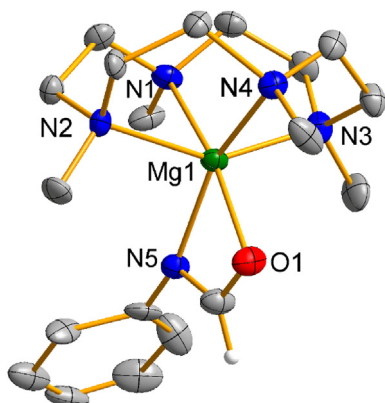


Fig. 4. Molecular structure of $[(\text{Me}_4\text{TACD})\text{Mg}(\text{OCHNPh})][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$ (**6**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, except for these of the formamidate ligand, are omitted for clarity. The borate anion is not shown. Selected interatomic distances [Å] and angles [°]: Mg1–O1 2.043(6), Mg1–N1 2.238(7), Mg1–N2 2.297(10), Mg1–N3 2.169(10), Mg1–N4 2.204(6), Mg1–N5 2.191(5), O1–Mg1–N5 63.7(2), N2–Mg1–N3 148.6(4), N1–Mg1–N4 103.5(3).

(OCHNDipp) (175.0 ppm) [21]. The ^1H NMR spectrum of the imidoforamidate complex **7** that was obtained from reaction with bis(2,6-di-isopropylphenyl)carbodiimide in THF- d_8 contains a singlet at δ 7.53 ppm for the proton of the $(\text{RN})_2\text{CH}$ ligand that correlates to the signal at δ 7.23 ppm in $[(\text{DippN})_2\text{CH}]\text{Mg}(\mu\text{-Cl})(\text{THF})_2$. [22]

In analogy to **6** where the structure in the solid state has been established, we assume a monomeric structure for compound **7**.

3. Conclusion

The molecular cationic hydride $[\text{MgH}]^+$ in $[(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu\text{-H})_2][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]_2$ (**1**) reacts with the Brønsted acids $[\text{NEt}_3\text{H}]\text{Cl}$ and $\text{PhC}\equiv\text{CH}$ to give the monomeric coordination compounds $[(\text{Me}_4\text{TACD})\text{MgCl}]$ and $[(\text{Me}_4\text{TACD})\text{Mg}(\text{C}\equiv\text{CPh})]$, respectively. **1** is oxidized by PhSSPh leading to $[(\text{Me}_4\text{TACD})\text{Mg}(\text{SPh})]$. Double bonds in the heteroallenes CO_2 , phenyl isocyanate, and a carbodiimide are smoothly hydrometallated by **1** to form hydro-magnesium products as the result of the insertion into the magnesium-hydride bond.

4. Experimental

4.1. General considerations

All operations were performed under inert atmosphere of dry argon using standard Schlenk or glovebox techniques THF, THP, Et_2O , n -pentane, n -hexane and toluene were purified using a MB SPS-800 solvent purification system or distilled under argon from sodium/benzophenone ketyl prior to use. Pyridine was dried over CaH_2 and distilled under argon prior to use. Deuterated solvents (THF- d_8 , benzene d_6) were distilled under argon from sodium/benzophenone ketyl prior to use. NMR spectra were recorded on a Bruker Avance II 400 or a Bruker Avance III HD 400 spectrometer at 25 °C in J. Young-type NMR tubes. Chemical shifts (δ in ppm) in the ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. The resonances in the ^1H and ^{13}C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBSC). Combustion analyses were performed with an Elementar Vario EL. Consistently low carbon contents for compounds **3**, **4**, **6** and **7** are ascribed to incomplete combustion [23]. The magnesium contents were determined by complexometric titrations and were carried out according to the published procedure [24] or were determined by inductively coupled plasma mass spectrometry using a Spectro ICP Spectroflame D instrument. X-ray data of **2**, **3**, **5** and **6** were collected at 100 K with a Bruker SMART APEX CCD detector in ω -scan mode (MoK α radiation, $\lambda = 0.71073$, multilayer optics, see supporting information).

4.1.1. $[(\text{Me}_4\text{TACD})\text{MgCl}][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$ (**2**)

Method A: A solution of $[\text{NEt}_3\text{H}]\text{Cl}$ (14 mg, 0.1 mmol) in THF (1 mL) was added to a solution of $[(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu\text{-H})_2][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]_2$ (68 mg, 0.05 mmol) in THF (3 mL) and the reaction solution was stirred for 15 min. The solvent was removed under reduced pressure and the colorless solid was washed with n -pentane (3 mL). The solid was dried under vacuum and $[(\text{Me}_4\text{TACD})\text{MgCl}][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$ (**2**) (60 mg, 0.04 mmol) was obtained in 83% yield.

Method B: To a solution of $[(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu\text{-H})_2][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]_2$ (68 mg, 0.05 mmol) in THF (3 mL), SiMe_3Cl (13 μL , 10 mg, 0.1 mmol) was added and the solution was stirred for 15 min. The solvent was removed under reduced pressure and the colorless solid was washed with n -pentane (3 mL). The solid was dried under vacuum and $[(\text{Me}_4\text{TACD})\text{MgCl}][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$ (**2**) (64 mg, 0.04 mmol) was obtained in 89% yield.

^1H NMR (THF- d_8 ; 400.1 MHz): δ 2.11 (s, 24H, $\text{CH}_3\text{-}[\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$), 2.28–2.42 (m, 16H, $\text{CH}_2\text{-Me}_4\text{TACD}$), 2.31 (s, 12H, $\text{CH}_3\text{-Me}_4\text{TACD}$), 6.39 (m, 4H, *para*-CH- $[\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$), 7.01 (m, 8H, *ortho*-CH- $[\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 ;

100.6 MHz): δ 22.5 (s, 24H, $\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 43.8 ($\text{CH}_3\text{-Me}_4\text{TACD}$), 53.4 ($\text{CH}_2\text{-Me}_4\text{TACD}$), 123.9 (*para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 133.3 (q, $^3J_{\text{BC}} = 2.9$ Hz, *meta*-C-[B(3,5-Me₂-C₆H₃)₄]), 135.7 (*ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 165.9 (q, $^1J_{\text{BC}} = 49.2$ Hz, *ipso*-C-[B(3,5-Me₂-C₆H₃)₄]) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF-*d*₈; 128.4 MHz): δ -7.00 ppm. Anal. calc. for $\text{C}_{44}\text{H}_{64}\text{N}_4\text{BClMg}$ (719.59 g·mol⁻¹): C, 73.44; H, 8.97; N, 7.79; Mg, 3.38%. Found: C, 73.76; H, 9.32; N, 7.73; Mg, 3.46%.

4.1.2. [(Me₄TACD)Mg(C≡CPh)][B(3,5-Me₂-C₆H₃)₄] (3)

A solution of phenylacetylene (10 mg, 0.1 mmol) was added to a solution of [(Me₄TACD)₂Mg₂(μ-H)₂][B(3,5-Me₂-C₆H₃)₄]₂ (68 mg, 0.05 mmol) in THF (3 mL) and the solution was stirred for 30 min. The solvent was removed under reduced pressure and the colorless solid was washed with *n*-pentane (3 mL). The solid was dried under vacuum and [(Me₄TACD)Mg(C≡CPh)][B(3,5-Me₂-C₆H₃)₄] (3) (67 mg, 0.09 mmol) was obtained in 85% yield. ^1H NMR (THF-*d*₈; 400.1 MHz): δ 2.11 (s, 24H, $\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 2.31–2.45 (m, 16H, $\text{CH}_2\text{-Me}_4\text{TACD}$), 2.39 (s, 12H, $\text{CH}_3\text{-Me}_4\text{TACD}$), 6.39 (m, 4H, *para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 7.01 (m, 8H, *ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 7.07 (m, 1H, *para*-CH-Ph), 7.12 (m, 1H, *meta*-CH-Ph), 7.21 (m, 1H, *ortho*-CH-Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-*d*₈; 100.6 MHz): δ 22.5 ($\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 43.7 ($\text{CH}_3\text{-Me}_4\text{TACD}$), 53.6 ($\text{CH}_2\text{-Me}_4\text{TACD}$), 111.3 (C≡CPh), 118.4 (C≡CPh), 123.8 (*para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 126.5 (*para*-CH-Ph), 128.6 (*meta*-CH-Ph), 128.9 (*ipso*-C-Ph), 132.3 (*ortho*-CH-Ph), 133.3 (q, $^3J_{\text{BC}} = 2.9$ Hz, *meta*-C-[B(3,5-Me₂-C₆H₃)₄]), 135.7 (*ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 165.9 (q, $^1J_{\text{BC}} = 49.2$ Hz, *ipso*-C-[B(3,5-Me₂-C₆H₃)₄]) ppm. ^{11}B NMR (THF-*d*₈; 128.4 MHz): δ -8.85 ppm. Anal. calc. for $\text{C}_{52}\text{H}_{69}\text{N}_4\text{BMg}$ (785.27 g·mol⁻¹): C, 79.54; H, 8.86; N, 7.13; Mg, 3.10%. Found: C, 75.76; H, 8.64; N, 6.46; Mg, 3.03%.

4.1.3. [(Me₄TACD)Mg(SPh)][B(3,5-Me₂-C₆H₃)₄] (4)

To a solution of [(Me₄TACD)₂Mg₂(μ-H)₂][B(3,5-Me₂-C₆H₃)₄]₂ (68 mg, 0.05 mmol) in THF (3 mL) a solution of diphenyl disulfide (11 mg, 0.05 mmol) in THF (1 mL) was added and the evolution of gas was observed while the reaction solution was stirred for 15 min. The solvent was removed under reduced pressure and the colorless oil was washed with *n*-pentane (3 mL) until it became solid. The solid was dried under vacuum and [(Me₄TACD)Mg(SPh)][B(3,5-Me₂-C₆H₃)₄] (4) (75 mg, 0.09 mmol) was obtained in 94% yield. ^1H NMR (THF-*d*₈; 400.1 MHz): δ 2.10 (s, 24H, $\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 2.22 (s, 12H, $\text{CH}_3\text{-Me}_4\text{TACD}$), 2.24–2.41 (m, 16H, $\text{CH}_2\text{-Me}_4\text{TACD}$), 6.38 (m, 4H, *para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 6.86 (m, 1H, *para*-CH-Ph), 6.96 (m, 2H, *meta*-CH-Ph), 7.00 (m, 8H, *ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 7.33 (m, 2H, *ortho*-CH-Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-*d*₈; 100.6 MHz): δ 22.5 ($\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 44.3 ($\text{CH}_3\text{-Me}_4\text{TACD}$), 53.6 ($\text{CH}_2\text{-Me}_4\text{TACD}$), 123.6 (*para*-CH-Ph), 123.9 (*para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 128.7 (*meta*-CH-Ph), 133.3 (q, $^3J_{\text{BC}} = 2.9$ Hz, *meta*-C-[B(3,5-Me₂-C₆H₃)₄]), 135.7 (*ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 135.8 (*ortho*-CH-Ph), 143.0 (*ipso*-C-Ph; identified by HSQC NMR), 165.9 (q, $^1J_{\text{BC}} = 49.2$ Hz, *ipso*-C-[B(3,5-Me₂-C₆H₃)₄]) ppm. ^{11}B NMR (THF-*d*₈; 128.4 MHz): δ -7.02 ppm. Anal. calc. for $\text{C}_{50}\text{H}_{69}\text{N}_4\text{BSMg}$ (793.31 g·mol⁻¹): C, 75.70; H, 8.77; N, 7.06; Mg, 3.06%. Found: C, 73.48; H, 8.74; N, 6.95; Mg, 2.90%.

4.1.4. [(Me₄TACD)₂Mg₂(μ-OCHO)₂][B(3,5-Me₂-C₆H₃)₄]₂ (5)

A solution of [(Me₄TACD)₂Mg₂(μ-H)₂][B(3,5-Me₂-C₆H₃)₄]₂ (68 mg, 0.05 mmol) in THF (3 mL) was pressurized with CO₂ (0.5 bar) and the reaction solution was stirred for 5 min. The solvent was removed under reduced pressure and the colorless solid was washed with *n*-pentane (6 mL). The solid was dried under vacuum and [(Me₄TACD)₂Mg₂(μ-OCHO)₂][B(3,5-Me₂-C₆H₃)₄]₂ (5) (69 mg, 0.05 mmol) was obtained as slightly yellow powder in 95% yield. ^1H NMR (THF-*d*₈; 400.1 MHz): δ 2.10 (s, 48H, $\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 2.24 (s, 24H, $\text{CH}_3\text{-Me}_4\text{TACD}$), 2.33–2.47 (m,

32H, $\text{CH}_2\text{-Me}_4\text{TACD}$), 6.37 (m, 8H, *para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 7.00 (m, 16H, *ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 8.27 (s, 2H, OCHO) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-*d*₈; 100.6 MHz): δ 22.5 ($\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 44.6 ($\text{CH}_3\text{-Me}_4\text{TACD}$), 55.1 ($\text{CH}_2\text{-Me}_4\text{TACD}$), 123.8 (*para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 133.2 (q, $^3J_{\text{BC}} = 2.9$ Hz, *meta*-C-[B(3,5-Me₂-C₆H₃)₄]), 135.7 (*ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 165.9 (q, $^1J_{\text{BC}} = 49.2$ Hz, *ipso*-C-[B(3,5-Me₂-C₆H₃)₄]), 175.9 (OCHO) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF-*d*₈; 128.4 MHz): δ -6.99 ppm. Anal. calc. for $\text{C}_{90}\text{H}_{130}\text{N}_8\text{B}_2\text{Mg}_2$ (1458.31 g·mol⁻¹): C, 74.13; H, 8.99; N, 7.68; Mg, 3.33%. Found: C, 73.94; H, 8.97; N, 7.68; Mg, 3.20%.

4.1.5. [(Me₄TACD)Mg(OCHNPh)][B(3,5-Me₂-C₆H₃)₄] (6)

To a solution of [(Me₄TACD)₂Mg₂(μ-H)₂][B(3,5-Me₂-C₆H₃)₄]₂ (68 mg, 0.05 mmol) in THF (3 mL) phenylisocyanate was added dropwise (12 mg, 0.1 mmol) and the reaction solution was stirred for 15 min at 25 °C. The solvent was removed under reduced pressure and the colorless solid was washed with *n*-pentane (6 mL). The solid was dried under vacuum and [(Me₄TACD)Mg(OCHNPh)][B(3,5-Me₂-C₆H₃)₄] (6) (66 mg, 0.08 mmol) was obtained as colorless powder in 82% yield. ^1H NMR (THF-*d*₈; 400.1 MHz): δ 2.09 (s, 24H, $\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 2.30 (m, 8H, $\text{CH}_2\text{-Me}_4\text{TACD}$), 2.31 (s, 6H, $\text{CH}_3\text{-Me}_4\text{TACD}$), 2.47 (m, 8H, $\text{CH}_2\text{-Me}_4\text{TACD}$), 2.48 (s, 6H, $\text{CH}_3\text{-Me}_4\text{TACD}$), 6.37 (m, 4H, *para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 6.89 (m, 2H, *ortho*-CH-Ph), 6.99 (m, 9H, *ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), *para*-CH-Ph), 7.23 (m, 2H, *meta*-CH-Ph), 8.21 (OCHN) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-*d*₈; 100.6 MHz): δ 22.5 ($\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 44.5 ($\text{CH}_3\text{-Me}_4\text{TACD}$), 56.7 ($\text{CH}_2\text{-Me}_4\text{TACD}$), 123.8 (*para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 124.1 (*ortho*-CH-Ph), 124.4 (*para*-CH-Ph), 130.0 (*meta*-CH-Ph), 133.2 (q, $^3J_{\text{BC}} = 2.9$ Hz, *meta*-C-[B(3,5-Me₂-C₆H₃)₄]), 135.7 (*ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 149.0 (OCHN), 165.9 (q, $^1J_{\text{BC}} = 49.2$ Hz, *ipso*-C-[B(3,5-Me₂-C₆H₃)₄]), 175.9 (OCHO) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF-*d*₈; 128.4 MHz): δ -6.99 ppm. Anal. calc. for $\text{C}_{51}\text{H}_{70}\text{N}_5\text{BMg}$ (804.27 g·mol⁻¹): C, 76.16; H, 8.77; N, 8.71; Mg, 3.02%. Found: C, 74.37; H, 8.68; N, 8.45; Mg, 2.56%.

4.1.6. [(Me₄TACD)Mg({N(2,6-ⁱPr₂-C₆H₃)₂CH})][B(3,5-Me₂-C₆H₃)₄] (7)

To a solution of [(Me₄TACD)₂Mg₂(μ-H)₂][B(3,5-Me₂-C₆H₃)₄]₂ (68 mg, 0.05 mmol) in THF (3 mL) a solution of bis(2,6-diisopropylphenyl)carbodiimide (36 mg, 0.1 mmol) in THF (1 mL) was added and the reaction solution was stirred for 15 min at 25 °C. The solvent was removed under reduced pressure and the waxy colorless solid was washed with *n*-pentane (2 × 3 mL). The solid was dried under vacuum and [(Me₄TACD)Mg({N(2,6-ⁱPr₂-C₆H₃)₂CH})][B(3,5-Me₂-C₆H₃)₄] (7) (84 mg, 0.08 mmol) was obtained as colorless powder in 80% yield. ^1H NMR (THF-*d*₈; 400.1 MHz): δ 1.10 (d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}_3\text{-}^i\text{Pr}$), 1.28 (d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}_3\text{-}^i\text{Pr}$), 2.09 (s, 24H, $\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 2.19 (s, 12H, $\text{CH}_3\text{-Me}_4\text{TACD}$), 2.23–2.30 (m, 8H, $\text{CH}_2\text{-Me}_4\text{TACD}$), 2.37–2.46 (m, 8H, $\text{CH}_2\text{-Me}_4\text{TACD}$), 3.41 (sept., 4H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH-}^i\text{Pr}$), 6.37 (m, 4H, *para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 7.01 (m, 10H, *ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), *para*-CH-N(2,6-ⁱPr₂-C₆H₃)), 7.07 (d, 4H, $^3J_{\text{HH}} = 6.8$ Hz, *meta*-CH-N(2,6-ⁱPr₂-C₆H₃)), 7.53 (s, 1H, NCHN) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-*d*₈; 100.6 MHz): δ 22.5 ($\text{CH}_3\text{-[B(3,5-Me}_2\text{-C}_6\text{H}_3)_4]$), 24.0 ($\text{CH}_3\text{-}^i\text{Pr}$), 26.9 ($\text{CH}_3\text{-}^i\text{Pr}$), 28.4 ($\text{CH-}^i\text{Pr}$), 46.4 ($\text{CH}_3\text{-Me}_4\text{TACD}$), 55.2 ($\text{CH}_2\text{-Me}_4\text{TACD}$), 123.8 (*para*-CH-[B(3,5-Me₂-C₆H₃)₄]), 124.4 (*meta*-CH-N(2,6-ⁱPr₂-C₆H₃)), 125.3 (*para*-CH-N(2,6-ⁱPr₂-C₆H₃)), 133.2 (q, $^3J_{\text{BC}} = 2.9$ Hz, *meta*-C-[B(3,5-Me₂-C₆H₃)₄]), 135.6 (*ortho*-CH-[B(3,5-Me₂-C₆H₃)₄]), 144.6 (*ortho*-CH-N(2,6-ⁱPr₂-C₆H₃)), 146.9 (*ipso*-C-N(2,6-ⁱPr₂-C₆H₃)), 165.9 (q, $^1J_{\text{BC}} = 49.2$ Hz, *ipso*-C-[B(3,5-Me₂-C₆H₃)₄]), 171.1 (NCHN) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF-*d*₈; 128.4 MHz): δ -8.88 ppm. Anal. calc. for $\text{C}_{69}\text{H}_{99}\text{N}_6\text{BMg}$ (1047.71 g·mol⁻¹): C, 79.10; H, 9.52; N, 8.02; Mg, 2.32%. Found: C, 76.88; H, 9.34; N, 8.10; Mg, 2.03%.

CRediT authorship contribution statement

Lara E. Lemmerz: Investigation. **Anthony Wong:** Investigation. **Gabriel Ménard:** Resources. **Thomas P. Spaniol:** Writing - original draft. **Jun Okuda:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC 1964869–1964872 contain the supplementary crystallographic data for **2**, **3**, **5** and **6**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2019.114331>.

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