Title

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

Permalink

https://escholarship.org/uc/item/1b18v7ht

Authors

Lemmerz, Lara E
Wong, Anthony
Ménard, Gabriel
et al.

Publication Date

2020-03-01

DOI

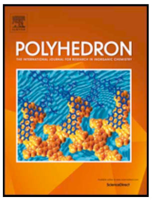
10.1016/j.poly.2019.114331

Peer reviewed

Contents lists available at ScienceDirect

Polyhedron

journal homepage: http://ees.elsevier.com



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

Lara E. Lemmerz [a], Anthony Wong [b], Gabriel Ménard [b], Thomas P. Spaniol [a], Jun Okuda [a]

[a] *Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany*
[b] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA*

ARTICLE INFO

Article history:
Received 13 November 2019
Accepted 22 December 2019
Available online xxx

Keywords
Magnesium
Hydride
Hydrometallation
CO_2
Heterocumulene

ABSTRACT

The reactivity of the molecular magnesium hydride cation in $[(Me_4TACD)_2Mg_2(\mu\text{-}H)_2][B(3,5\text{-}Me_2\text{-}C_6H_3)_4]_2$ (Me_4TACD = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) toward Brønsted acids, the mild oxidant diphenyldisulfide as well as heterocumulenes CO_2, 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.

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 $[(Me_4TACD)_2Mg_2(\mu\text{-}H)_2][B(3,5\text{-}Me_2\text{-}C_6H_3)_4]_2$ [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 $[MgH]^+$.

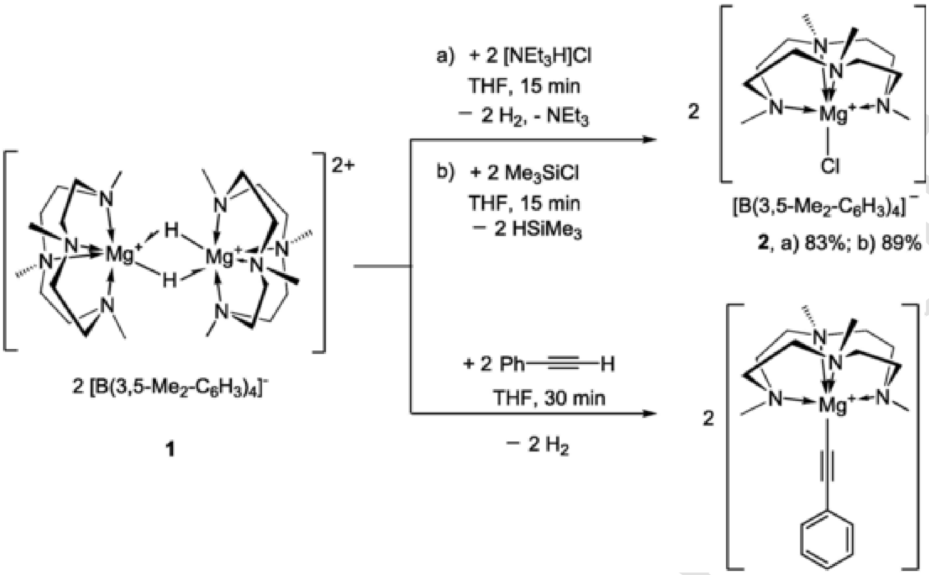
2. Results and discussion

Protonolysis of $[(Me_4TACD)_2Mg_2(\mu\text{-}H)_2][B(3,5\text{-}Me_2\text{-}C_6H_3)_4]_2$ (**1**) with the weak Brønsted acids $[NEt_3H]Cl$ and $PhC\equiv CH$ gave the monomeric compounds $[(Me_4TACD)MgX][B(3,5\text{-}Me_2\text{-}C_6H_3)_4]$ (**2**: X = Cl, **3**: X = $C\equiv CPh$) 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 ^{13}C NMR signals at δ 111.3 ppm ($C\equiv CPh$) 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 $[[Mg(Me_3TACD{\cdot}Al^iBu_3)(C\equiv CPh)]$ (δ 110.0) ppm [11], as well as that in related terminal alkyne complexes of magnesium such as $[Tism^{iPrBenz}MgC\equiv CPh]$ (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 τ = 0.02) [13]. The Mg–Cl distances (Mg1–Cl1: 2.278(3) Å; Mg2–Cl2: 2.266(3) Å) are comparable to those in $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}MgC1$ (2.262(2) Å) [14,15], $[(Tp^{tBu,Me})MgCl]$ ($Tp^{tBu,Me}$ = tris(3-*tert*-butyl-5-pyrazolyl)hydroborato) (2.2701(15) Å and 2.2677(15) Å) [16], as well as in $[\{(TerN)_2P\}MgCl]$

https://doi.org/10.1016/j.poly.2019.114331
0277-5387/© 2019.



Scheme 1. Protonolysis of **1** with $[NEt_3H]Cl$ and $PhC\equiv CH$.

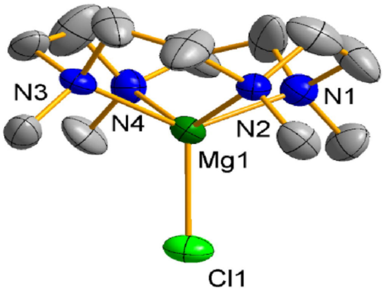


Fig. 1. Structure of one of the two crystallographically independent molecular cations in $[(Me_4TACD)MgCl][B(3,5\text{-}Me_2\text{-}C_6H_3)_4]$ (**2**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Mg1–Cl1 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).

($(TerN)_2P$ = bis(terphenylimino)phosphide) (2.269(2) Å) [17]. The coordination of the alkyne ligand in **3** could 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 $C\equiv C$ 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. 2).

The reaction of **1** with the mild oxidant diphenyldisulfide PhSSPh gave the thiophenolate complex $[(Me_4TACD)Mg(SPh)][B(3,5\text{-}Me_2\text{-}C_6H_3)_4]$ (**4**) under release of dihydrogen. This reaction may involve an electron transfer from a μ-H ligand to diphenyl disulfide [18a], 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 $[(Me_4TACD)Mg(SPh)]$ 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

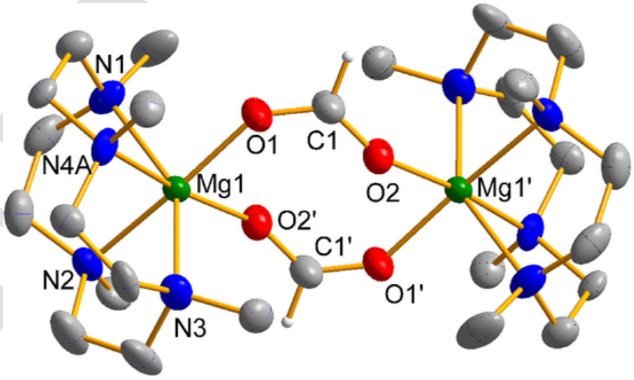


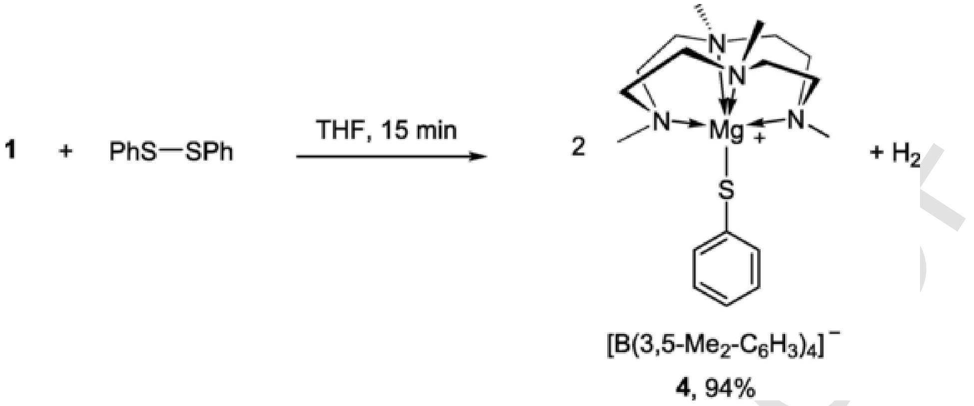
Fig. 2. Structure of the molecular cation of $[(Me_4TACD)_2Mg_2(\mu\text{-}OCHO)_2][B(3,5\text{-}Me_2\text{-}C_6H_3)_4]_2$ (**5**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, except for these of the formate ligands, are omitted for clarity. Disordered atoms are shown 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).

resonances for the protons in *ortho*-, *meta*- and *para* position at *δ* 7.33, 6.96 and 6.86 ppm, respectively (see Scheme 3).

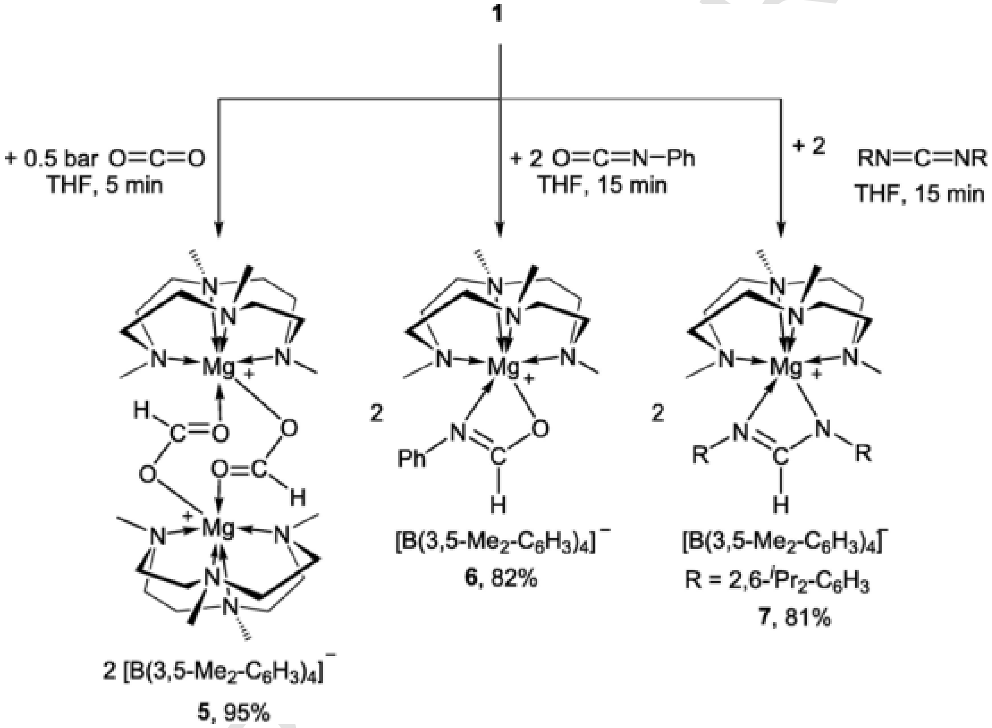
Reaction of **1** with the heterocumulenes CO_2 (0.5 bar), PhN = C ═O and bis(2,6-di-isopropylphenyl)carbodiimide gave $[(Me_4TACD)_2Mg_2(\mu\text{-}O_2CH)_2][A]_2$ (**5**), $[(Me_4TACD)Mg(OCHNPh)][A]$ (**6**) and $[(Me_4TACD)Mg(\{DippN\}_2CH)][A]$ (Dipp = $2,6\text{-}{}^iPr_2\text{-}C_6H_3$) (**7**) in 95, 82, and 80% yield, respectively ($[A] = [B(3,5\text{-}Me_2\text{-}C_6H_3)_4]$).

All these compounds are soluble in THF, but not in aromatic or aliphatic hydrocarbons. Single crystals of the formato complex $[(Me_4TACD)_2Mg_2(\mu\text{-}O_2CH)_2][B(3,5\text{-}Me_2\text{-}C_6H_3)_4]_2$ (**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.

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 formato complex $[(C_6F_5)_3$



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



Scheme 3. Reaction of **1** with heterocumulenes.

BOC(H)OC(H){(Me)CNDipp}$_2$Mg(μ-O$_2$CH)]$_2$ (1.979(4) and 1.935(3) Å) [19], but shorter than in the monomeric complexes [(Me$_3$TACD·Al^{i}Bu$_3$)$_2$Mg$_2$(κ^2-O$_2$CH)] (2.120(2) and 2.121(2) Å) [11] as well as in [(Tism^{iPrBenz})Mg(κ^2-O$_2$CH)] (Tism^{iPrBenz} = tris[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl) (2.1746(16) and 2.1419(15) Å) [20]. The O1–Mg1–O2 bond angle of 87.63(8)° is significantly smaller than in [(C$_6$F$_5$)$_3$BOC(H)OC(H){(Me)CNDipp}$_2$Mg(μ-O$_2$CH)]$_2$ (99.55(16)°) [19]. One of the Me$_4$TACD 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$_4$TACD 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 ^{1}H NMR spectrum (Fig. S10, see supporting information) and a signal at δ 175.9 ppm in the ^{13}C{^{1}H} NMR spectrum (Fig. S11). These signals are comparable to those of the magnesium formate complexes [(Me$_3$TACD·Al^{i}Bu$_3$)Mg(κ^{2}O$_2$CH)] (^{1}H NMR: δ 8.25 ppm, ^{13}C{^{1}H} NMR: δ 174.5 ppm) [11] and [(C$_6$F$_5$)$_3$BOC(H)OC(H){(Me)CNAr}$_2$Mg(OHCO)]$_2$ (^{1}H NMR: δ 8.31 ppm; ^{13}C{^{1}H} NMR: δ 182.7) [19].

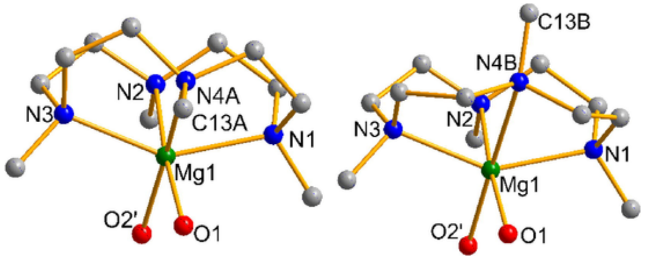


Fig. 3. Representations of the two conformers in the solid state of **5**. Left: major isomer with all four methyl groups pointing towards the metal center; right: minor isomer with one methyl group pointing away from the metal.

In contrast to the reaction of the hydride **1** with CO$_2$, treatment with the sterically more demanding PhN = C═O leads to the monomeric compound **6**. Single crystals of [(Me$_4$TACD)Mg(OCHNPh)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (**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 Me$_4$TACD 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)}$_2$Mg(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)}$_2$Mg(OCHNDipp)] (65.86(4)°) [21].

The ^{1}H 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)}$_2$Mg(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 Me$_4$TACD ligand show an unusual pattern with two singlets at δ 2.48 and 2.31 ppm, indicating that the Me$_4$TACD ligand is dissociated from the metal. At –90 °C, the ^{1}H NMR spectrum reveals one singlet for the CH$_3$ groups and broad multiplets for the CH$_2$ groups that is characteristic of a coordinated Me$_4$TACD ligand. Thus, the labile nature of the Me$_4$TACD ligand in **6** is established. A labile coordination is also revealed in the ^{13}C{^{1}H} 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)}$_2$Mg(OCHNDipp)] (175.0 ppm) [21]. The ^{1}H NMR spectrum of the imidoformamide 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 (RN)$_2$C*H* ligand that correlates to the signal at δ 7.23 ppm in [({DippN}$_2$CH)Mg(μ-Cl)(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 [MgH]$^+$ in [(Me$_4$TACD)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (**1**) reacts with the Brønsted acids [NEt$_3$H]Cl and PhC$\equiv$CH to give the monomeric coordination compounds [(Me$_4$TACD)MgCl] and [(Me$_4$TACD)Mg(C$\equiv$CPh)], respectively. **1** is oxidized by PhSSPh leading to [(Me$_4$TACD)Mg(SPh)]. Double bonds in the heteroallenes CO$_2$, phenyl isocyanate, and a carbodiimide are smoothly hydrometallated by **1** to form hydromagnesiation products as the result of the insertion into the magnesium-hydride bond.

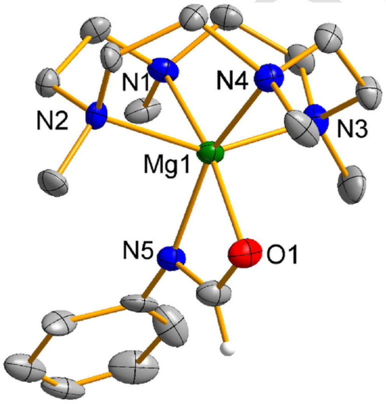


Fig. 4. Molecular structure of [(Me$_4$TACD)Mg(OCHNPh)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (**6**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, except for these of the formamidate ligand, are omitted for clarity. The borate anion is not shown. Selected interatomic distances [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).

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$_2$O, *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 ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. The resonances in the ^{1}H and ^{13}C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBC). 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 (MoKα radiation, λ = 0.71073, multilayer optics, see supporting information).

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

Method A: A solution of [NEt$_3$H]Cl (14 mg, 0.1 mmol) in THF (1 mL) was added to a solution of [(Me$_4$TACD)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$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 [(Me$_4$TACD)MgCl][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (**2**) (60 mg, 0.04 mmol) was obtained in 83% yield.

Method B: To a solution of [(Me$_4$TACD)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (68 mg, 0.05 mmol) in THF (3 mL), SiMe$_3$Cl (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 [(Me$_4$TACD)MgCl][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (**2**) (64 mg, 0.04 mmol) was obtained in 89% yield.

^{1}H NMR (THF-d_8; 400.1 MHz): δ 2.11 (s, 24H, C*H*$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 2.28–2.42 (m, 16H, C*H*$_2$-Me$_4$TACD), 2.31 (s, 12H, C*H*$_3$-Me$_4$TACD), 6.39 (m, 4H, *para*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 7.01 (m, 8H, *ortho*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]) ppm. ^{13}C{^{1}H} NMR (THF-d_8; 100.6 MHz): δ 22.5 (s, 24H, *C*H$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 43.8 (*C*H$_3$-Me$_4$TACD), 53.4 (*C*H$_2$-Me$_4$TACD), 123.9 (*para*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 133.3 (q, $^3J_{BC}$ = 2.9 Hz, *meta*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 135.7 (*ortho*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 165.9 (q, $^1J_{BC}$ = 49.2 Hz, *ipso*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]) ppm. ^{11}B{^{1}H} NMR (THF-d_8; 128.4 MHz): δ –7.00 ppm. Anal. calc. for C$_{44}$H$_{64}$N$_4$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. [(Me$_4$TACD)Mg(C$\equiv$CPh)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (3)

A solution of phenylacetylene (10 mg, 0.1 mmol) was added to a solution of [(Me$_4$TACD)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (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 [(Me$_4$TACD)Mg(C$\equiv$CPh)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (**3**) (67 mg, 0.09 mmol) was obtained in 85% yield. ^{1}H NMR (THF-*d*$_8$; 400.1 MHz): *δ* 2.11 (s, 24H, C*H*$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 2.31–2.45 (m, 16H, C*H*$_2$-Me$_4$TACD), 2.39 (s, 12H, C*H*$_3$-Me$_4$TACD), 6.39 (m, 4H, *para*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 7.01 (m, 8H, *ortho*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 7.07 (m, 1H, *para*-C*H*-Ph), 7.12 (m, 1H, *meta*-C*H*-Ph), 7.21 (m, 1H, *ortho*-C*H*-Ph) ppm. ^{13}C{^{1}H} NMR (THF-*d*$_8$; 100.6 MHz): *δ* 22.5 (*C*H$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 43.7 (*C*H$_3$-Me$_4$TACD), 53.6 (*C*H$_2$-Me$_4$TACD), 111.3 (C≡*C*Ph), 118.4 (*C*≡CPh), 123.8 (*para*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 126.5 (*para*-*C*H-Ph), 128.6 (*meta*-*C*H-Ph), 128.9 (*ipso*-*C*-Ph), 132.3 (*ortho*-*C*H-Ph), 133.3 (q, $^3J_{BC}$ = 2.9 Hz, *meta*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 135.7 (*ortho*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 165.9 (q, $^1J_{BC}$ = 49.2 Hz, *ipso*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]) ppm. ^{11}B NMR (THF-*d*$_8$; 128.4 MHz): δ −8.85 ppm. Anal. calc. for $C_{52}H_{69}N_4BMg$ (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. [(Me$_4$TACD)Mg(SPh)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (4)

To a solution of [(Me$_4$TACD)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (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 [(Me$_4$TACD)Mg(SPh)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (**4**) (75 mg, 0.09 mmol) was obtained in 94% yield. ^{1}H NMR (THF-*d*$_8$; 400.1 MHz): *δ* 2.10 (s, 24H, C*H*$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 2.22 (s, 12H, C*H*$_3$-Me$_4$TACD), 2.24–2.41 (m, 16H, C*H*$_2$-Me$_4$TACD), 6.38 (m, 4H, *para*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 6.86 (m, 1H, *para*-C*H*-Ph), 6.96 (m, 2H, *meta*-C*H*-Ph), 7.00 (m, 8H, *ortho*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 7.33 (m, 2H, *ortho*-C*H*-Ph) ppm. ^{13}C{^{1}H} NMR (THF-*d*$_8$; 100.6 MHz): *δ* 22.5 (*C*H$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 44.3 (*C*H$_3$-Me$_4$TACD), 53.6 (*C*H$_2$-Me$_4$TACD), 123.6 (*para*-*C*H-Ph), 123.9 (*para*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 128.7 (*meta*-*C*H-Ph), 133.3 (q, $^3J_{BC}$ = 2.9 Hz, *meta*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 135.7 (*ortho*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 135.8 (*ortho*-*C*H-Ph), 143.0 (*ipso*-*C*-Ph; identified by HSQC NMR), 165.9 (q, $^1J_{BC}$ = 49.2 Hz, *ipso*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]) ppm. ^{11}B NMR (THF-*d*$_8$; 128.4 MHz): δ −7.02 ppm. Anal. calc. for $C_{50}H_{69}N_4BSMg$ (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. [(Me$_4$TACD)$_2$Mg$_2$(μ-OCHO)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (5)

A solution of [(Me$_4$TACD)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (68 mg, 0.05 mmol) in THF (3 mL) was pressurized with CO_2 (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 [(Me$_4$TACD)$_2$Mg$_2$(μ-OCHO)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (**5**) (69 mg, 0.05 mmol) was obtained as slightly yellow powder in 95% yield. ^{1}H NMR (THF-*d*$_8$; 400.1 MHz): *δ* 2.10 (s, 48H, C*H*$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 2.24 (s, 24H, C*H*$_3$-Me$_4$TACD), 2.33–2.47 (m, 32H, C*H*$_2$-Me$_4$TACD), 6.37 (m, 8H, *para*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 7.00 (m, 16H, *ortho*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 8.27 (s, 2H, OC*H*O) ppm. ^{13}C{^{1}H} NMR (THF-*d*$_8$; 100.6 MHz): *δ* 22.5 (*C*H$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 44.6 (*C*H$_3$-Me$_4$TACD), 55.1 (*C*H$_2$-Me$_4$TACD), 123.8 (*para*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 133.2 (q, $^3J_{BC}$ = 2.9 Hz, *meta*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 135.7 (*ortho*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 165.9 (q, $^1J_{BC}$ = 49.2 Hz, *ipso*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 175.9 (O*C*HO) ppm. ^{11}B{^{1}H} NMR (THF-*d*$_8$; 128.4 MHz): δ −6.99 ppm. Anal. calc. for $C_{90}H_{130}N_8B_2Mg_2$ (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. [(Me$_4$TACD)Mg(OCHNPh)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (6)

To a solution of [(Me$_4$TACD)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (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 [(Me$_4$TACD)Mg(OCHNPh)][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (**6**) (66 mg, 0.08 mmol) was obtained as colorless powder in 82% yield. ^{1}H NMR (THF-*d*$_8$; 400.1 MHz): *δ* 2.09 (s, 24H, C*H*$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 2.30 (m, 8H, C*H*$_2$-Me$_4$TACD), 2.31 (s, 6H, C*H*$_3$-Me$_4$TACD), 2.47 (m, 8H, C*H*$_2$-Me$_4$TACD), 2.48 (s, 6H, C*H*$_3$-Me$_4$TACD), 6.37 (m, 4H, *para*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 6.89 (m, 2H, *ortho*-C*H*-Ph), 6.99 (m, 9H, *ortho*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$], *para*-C*H*-Ph), 7.23 (m, 2H, *meta*-C*H*-Ph), 8.21 (OC*H*N) ppm. ^{13}C{^{1}H} NMR (THF-*d*$_8$; 100.6 MHz): *δ* 22.5 (*C*H$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 44.5 (*C*H$_3$-Me$_4$TACD), 56.7 (*C*H$_2$-Me$_4$TACD), 123.8 (*para*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 124.1 (*ortho*-*C*H-Ph), 124.4 (*para*-*C*H-Ph), 130.0 (*meta*-*C*H-Ph), 133.2 (q, $^3J_{BC}$ = 2.9 Hz, *meta*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 135.7 (*ortho*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 149.0 (O*C*HN), 165.9 (q, $^1J_{BC}$ = 49.2 Hz, *ipso*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 175.9 (O*C*HO) ppm. ^{11}B{^{1}H} NMR (THF-*d*$_8$; 128.4 MHz): δ −6.99 ppm. Anal. calc. for $C_{51}H_{70}N_5BMg$ (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. [(Me$_4$TACD)Mg({N(2,6-^{i}Pr$_2$-C$_6$H$_3$)$_2$}$_2$CH][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (7)

To a solution of [(Me$_4$TACD)$_2$Mg$_2$(μ-H)$_2$][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (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 [(Me$_4$TACD)Mg({N(2,6-^{i}Pr$_2$-C$_6$H$_3$)$_2$}$_2$CH][B(3,5-Me$_2$-C$_6$H$_3$)$_4$] (**7**) (84 mg, 0.08 mmol) was obtained as colorless powder in 80% yield. ^{1}H NMR (THF-*d*$_8$; 400.1 MHz): *δ* 1.10 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C*H*$_3$-^{i}Pr), 1.28 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C*H*$_3$-^{i}Pr), 2.09 (s, 24H, C*H*$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 2.19 (s, 12H, C*H*$_3$-Me$_4$TACD), 2.23–2.30 (m, 8H, C*H*$_2$-Me$_4$TACD), 2.37–2.46 (m, 8H, C*H*$_2$-Me$_4$TACD), 3.41 (sept., 4H, $^3J_{HH}$ = 6.8 Hz, C*H*-^{i}Pr), 6.37 (m, 4H, *para*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 7.01 (m, 10*H*, *ortho*-C*H*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$], *para*-C*H*-N(2,6-^{i}Pr$_2$-C$_6$H$_3$)), 7.07 (d, 4H, $^3J_{HH}$ = 6.8 Hz, *meta*-C*H*-N(2,6-^{i}Pr$_2$-C$_6$H$_3$)), 7.53 (s, 1H, NC*H*N) ppm. ^{13}C{^{1}H} NMR (THF-*d*$_8$; 100.6 MHz): *δ* 22.5 (*C*H$_3$-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 24.0 (*C*H$_3$-^{i}Pr), 26.9 (*C*H$_3$-^{i}Pr), 28.4 (*C*H-^{i}Pr), 46.4 (*C*H$_3$-Me$_4$TACD), 55.2 (*C*H$_2$-Me$_4$TACD), 123.8 (*para*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 124.4 (*meta*-*C*H-N(2,6-^{i}Pr$_2$-C$_6$H$_3$)), 125.3 (*para*-*C*H-N(2,6-^{i}Pr$_2$-C$_6$H$_3$)), 133.2 (q, $^3J_{BC}$ = 2.9 Hz, *meta*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 135.6 (*ortho*-*C*H-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 144.6 (*ortho*-*C*H-N(2,6-^{i}Pr$_2$-C$_6$H$_3$)), 146.9 (*ipso*—*C*—N(2,6-^{i}Pr$_2$-C$_6$H$_3$)), 165.9 (q, $^1J_{BC}$ = 49.2 Hz, *ipso*-*C*-[B(3,5-Me$_2$-C$_6$H$_3$)$_4$]), 171.1 (N*C*HN) ppm. ^{11}B{^{1}H} NMR (THF-*d*$_8$; 128.4 MHz): δ −8.88 ppm. Anal. calc. for $C_{69}H_{99}N_6BMg$ (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.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft through the International Research Training Group “Selectivity in Chemo- and Biocatalysis” for financial support. A.W. acknowledges the National Science

Foundation OISE through “IRES: Training Next Generation Researchers in Advanced Magnetic Resonance at Chemistry Interfaces” (#1658652) for financial support.

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.

References

[1] M.E. Thompson, J.E. Bercaw, Pure Appl. Chem. 56 (1984) 1.

[2] J.E. Bercaw, D.L. Davies, P.T. Wolczanski, Organometallics 5 (1986) 443.

[3] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.

[4] E. Bunel, B.J. Burger, J.E. Bercaw, J. Am. Chem. Soc. 110 (1988) 976.

[5] B.J. Burger, M.E. Thompson, W.D. Cotter, J.E. Bercaw, J. Am. Chem. Soc. 112 (1990) 1566.

[6] P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867.

[7] W.E. Piers, P.J. Shapiro, E.E. Bunel, J.E. Bercaw, Synlett (1990) 74.

[8] M. Rauch, S. Ruccolo, G. Parkin, J. Am. Chem. Soc. 139 (2017) 13264.

[9] L.E. Lemmerz, D. Mukherjee, T.P. Spaniol, A. Wong, G. Ménard, L. Maron, J. Okuda, Chem. Commun. 55 (2019) 3199.

[10] L.E. Lemmerz, V. Leich, D. Martin, T.P. Spaniol, J. Okuda, Inorg. Chem. 57 (2017) 14979.

[11] S. Schnitzler, T.P. Spaniol, J. Okuda, Inorg. Chem. 55 (2016) 12997.

[12] M. Rauch, R.C. Roberts, G. Parkin, Inorg. Chim. Acta 494 (2019) 271.

[13] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans (1984) 1349.

[14] R. Han, M. Bachrach, G. Parkin, Polyhedron 9 (1990) 1775.

[15] R. Han, G. Parkin, J. Am. Chem. Soc. 114 (1992) 748.

[16] M. Rauch, S. Ruccolo, J.P. Mester, Y. Rong, G. Parkin, Chem. Sci. 7 (2016) 142.

[17] A. Hinz, J. Rothe, A. Schulz, A. Villinger, Dalton Trans. 45 (2016) 6044.

[18] (a) KrishnamurthyS. AiminoD. J. Org. Chem.541989 4458
(b) LaRochelleR.W. TrostB.M. J. Am. Chem. Soc.931971 6077.

[19] M.D. Anker, M. Arrowsmith, P. Bellham, M.S. Hill, G. Kociok-Köhn, D.J. Liptrot, M.F. Mahon, C. Weetman, Chem. Sci. 5 (2014) 2826.

[20] M. Rauch, G. Parkin, J. Am. Chem. Soc. 139 (2017) 18162.

[21] Y. Yang, M.D. Anker, J. Fang, M.F. Mahon, L. Maron, C. Weetman, M.S. Hill, Chem. Sci. 8 (2017) 3529.

[22] P.C. Andrews, M. Brym, C. Jones, P.C. Junk, M. Kloth, Inorg. Chim. Acta 359 (2006) 355.

[23] A. Marcó, R. Compañó, R. Rubio, I. Casals, Microchim. Acta 142 (2003) 13.

[24] E. Merck, Komplexometrische Bestimmungsmethoden mit Titriplex, Merck, Darmstadt, 1975.