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ARTICLE

1,4-Dihydropyridyl complexes of magnesium: synthesis by pyridine insertion into the magnesium-silicon bond of triphenylsilyls and catalytic pyridine hydrofunctionalization

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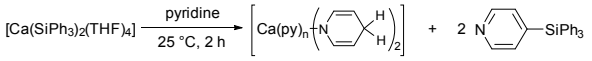
Magnesium bis(triphenylsilyl) $[Mg(SiPh_3)_2(THF)_2]\cdot THF$ (**1**) reacted with stochiometric amount of pyridine to give the magnesium 4-(triphenylsilyl)dihydropyridyl complex $[Mg(NC_5H_5\text{-}4\text{-}SiPh_3)_2(THF)_3]$ (**2**). Using an excess of pyridine, a mixture of magnesium dihydropyridyl $[Mg(NC_5H_6)_2(py)_4]$ (**3**) and 4-(triphenylsilyl)pyridine was formed. Complex **3** underwent exchange with pyridine-d_5 at 25 °C to give $[Mg(NC_5D_5H\text{-}4)_2(py\text{-}d_5)_4]$ (**3-HD**). Analogous reactions with Me_3TACD-supported magnesium triphenylsilyls $[(Me_3TACD)Mg(SiPh_3)]$ (**4**) and $[(Me_3TACD\cdot AlEt_3)Mg(SiPh_3)]$ (**6**) ($(Me_3TACD)H = Me_3[12]aneN_4$: 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) with pyridine gave $[(Me_3TACD)Mg(NC_5H_5\text{-}4\text{-}SiPh_3)]$ (**5**), $[(Me_3TACD\cdot AlEt_3)\text{-}Mg(NC_5H_5\text{-}4\text{-}SiPh_3)]$) (**7**) and a mixture of $[(Me_3TACD)Mg(NC_5H_6)]$ (**8**) and 4-(triphenylsilyl)pyridine. Complex **8** is also formed by reacting **3** with $(Me_3TACD)H$ and underwent exchange with pyridine-d_5 at higher temperatures. The activation energy for the exchange is about 25 $kJ\cdot mol^{-1}$ higher than for the exchange reaction of **3** to **3-HD**. Complexes **2**, **3**, **3-HD**, **5**, **7** and **8** were characterized by NMR spectroscopy and by single crystal structure analysis for **3**, **5** and **8**. Complex **3** was found to be slightly active in the hydrosilylation of pyridine using phenylsilane, whereas complex **8** showed no activity. Both complexes **3** and **8** were active in the hydroboration of pyridine with pinacolborane.

Introduction

In the context of bio-inspired hydride transfer reagents, dihydropyridines such as Hantzsch ester have been studied quite intensively.[1-4] Hydrofunctionalization of pyridine is useful for the synthesis of nitrogen-containing heterocycles and a number of transition metal catalysts have been reported which are active in the hydrosilylation[5-13] and hydroboration[12, 14-19] of pyridine. More recently, some main group metal complexes have been reported to hydrosilylate[20, 21] and hydroborate[20, 22-27] pyridine. Magnesium dihydropyridyl complexes have been known for decades.[20, 23, 25, 28-35] $[Mg(NC_5H_6)_2(py)_2]$, obtained from the reaction of activated MgH_2 with pyridine by Ashby et al. and De Koning et al. was found to reduce aldehydes, ketones, enols and imines.[28-31, 36] Lansbury's reagent $Li^+[Al(1,4\text{-}NC_5H_6)_4]^-$[37-39] formed starting from $LiAlH_4$ with excess pyridine is thought to contain a mixture of 1,2- and 1,4-isomers, depending on the reaction conditions and can also be used as highly selective stoichiometric reducing agent.

Snaith and Mulvey were able to isolate $[2\text{-}(^n BuC_5H_5N)Li\cdot(py)_2]$ from the reaction of ^{n}BuLi with excess pyridine which acted as a lithium hydride source.[40-42] More recently, lithium, sodium and potassium *tert*-butyl-dihydropyridyls were prepared[43-46] and the hydrocarbon soluble lithium *tert*-butyl-dihydropyridyl was found to catalyze the hydroboration of aldehydes and ketones with pinacolborane.[47]

When the molecular calcium silyl $[Ca(SiPh_3)_2(THF)_4]$ was treated with excess pyridine, calcium 1,4-dihydropyridyl $[Ca(NC_5H_6)_2(py)_n]$ (py = pyridine) was obtained along with stoichiometric amount of 4-(triphenylsilyl)pyridine (Scheme 1).[48]



Scheme 1. Reaction of $[Ca(SiPh_3)_2(THF)_4]$ with an excess of pyridine.

This reaction can be regarded as a regioselective hydrosilylation of pyridine, followed by hydride transfer from the intermediate 1,4-dihydropyridyl $[Ca(NC_5H_5\text{-}4\text{-}SiPh_3)_2(L)_n]$ (L = THF, py). Mechanistically, this reaction probably involves insertion of pyridine into both metal-silyl and metal-hydride bond. Pyridine insertion into metal-silyl[49] and metal-hydride bonds[17, 20, 21, 23, 25, 28-31, 34, 35, 37, 50] are known and the formation of a metal-hydride intermediate is regarded to be crucial in the hydrofuctionalization of pyridine.[15-17, 19, 21-24, 51]

We report here on the results of the reaction of two magnesium triphenylsilyls with pyridine to give 1,4-dihydropyridyls along with their catalytic activity in the hydrosilylation and hydroboration of pyridine.

Results and discussion

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Electronic Supplementary Information (ESI) available: [NMR spectra of the complexes **2**, **3**, **3-HD**, **5**, **7** and **8** and X-ray crystallographic details for **3**, **5** und **8**]. See DOI: 10.1039/x0xx00000x

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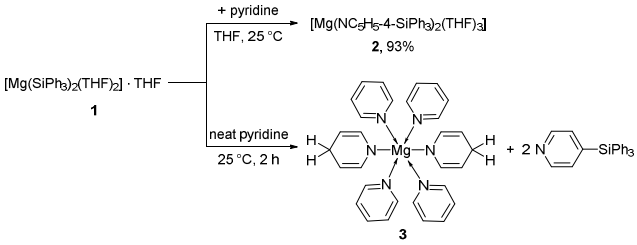
Reaction of magnesium bis(triphenylsilyl)

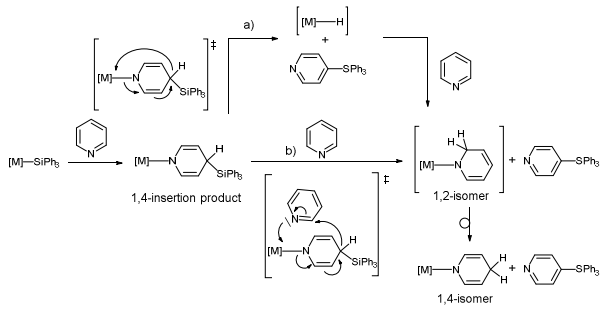
The reaction of the magnesium triphenylsilyl $[Mg(SiPh_3)_2(THF)_2]\cdot THF$ (**1**)[52] with one equivalent of pyridine (Scheme 2) gave $[Mg(NC_5H_5\text{-}4\text{-}SiPh_3)_2(THF)_3]$ (**2**) isolated as a yellow powder in excellent yields.



Scheme 2. Synthesis of $[Mg(NC_5H_5\text{-}4\text{-}SiPh_3)_2(THF)_3]$ (**2**) and $[Mg(NC_5H_6)_2(py)_4]$ (**3**) and 4-(triphenylsilyl)pyridine.

Analogous insertion of pyridine into metal-silicon bonds are known in the literature.[48, 49] The reaction of **1** with an excess of pyridine gave $[Mg(NC_5H_6)_2(py)_4]$ (**3**) and 4-(triphenylsilyl)-pyridine which precipitated from the reaction mixture as pale yellow solid and was identified by NMR spectroscopy. Complete separation of **3** from 4-(triphenylsilyl)pyridine was not possible. Upon repeated crystallizations from pyridine/*n*-hexane, **3** was obtained in 70% yield still containing 6 mol% of 4-(triphenylsilyl)pyridine. Complexes **2** and **3** are derived from 1,4-insertion of pyridine into the Mg–Si bond. No indication for the formation of the 1,2-insertion products was found. Nevertheless, the formation of 1,2-insertion products as intermediates cannot be unequivocally ruled out. The ^{1}H NMR spectroscopic data for **2** and **3** are summarized in Table S1 (see Electronic Supplementary Information). The ^{1}H NMR spectroscopic data in pyridine-d_5 of **3** is comparable to that of the bis(pyridine) complex $[Mg(NC_5H_6)_2(py)_2]$ in pyridine-d_5.[29, 30]

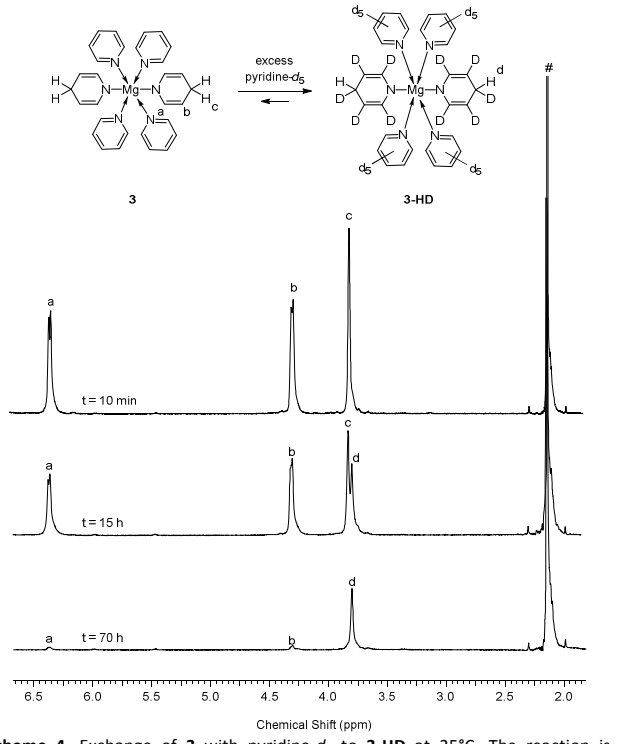
A mechanism for the formation of $[Mg(NC_5H_5\text{-}4\text{-}SiPh_3)_2(THF)_3]$ (**2**) and $[Mg(NC_5H_6)_2(py)_4]$ (**3**) was proposed in analogy to the formation of $[Ca(NC_5H_6)_2(py)_n]$[48] (Scheme 3).



Scheme 3. Proposed mechanisms for the formation of group 2 metal 1,4-dihydropyridyl complexes: a) formation of a metal hydride intermediate or b) hydride transfer to a coordinated pyridine molecule and re-aromatization.

Formation of a magnesium hydride intermediate or a mechanism through re-aromatization initiated by the coordination of a second pyridine followed by hydride transfer are conceivable (Scheme 3). A hydride transfer to an incoming pyridine molecule was also reported for $[Li(NC_5H_5{}^n\text{Bu-}2)(py)_2]$ to give 2-(*n*-butyl)pyridine and $[Li(NC_5H_6)_2(py)_2]_2$.[42] The formation of $[Mg(NC_5H_6)_2(py)_4]$ (**3**) could only be observed with an excess of pyridine, suggesting that the second mechanism is more probable (Scheme 3 b). The formation of a magnesium hydride intermediate was postulated by Hill et al. for the reaction of [(DIPPnacnac)Mg^{n}Bu] (DIPPnacnac = HC[C(Me)N(2,6-^{i}Pr$_2$-C$_6$H$_3$)]$_2$) with phenylsilane in the presence of pyridine giving the dihydropyridyl complex [(DIPPnacnac)Mg(NC_5H_6)(py)].[32]

Pure $[Mg(NC_5H_6)_2(py)_4]$ (**3**) without 4-(triphenylsilyl)pyridine contamination was isolated following the method of De Koning:[29, 30] Activated MgH_2[53] was stirred in the presence of an excess of pyridine at room temperature for 18 h to give only the 1,4-dihydropyridyl complex in 69% yield after recrystallization from pyridine/*n*-hexane. De Koning et al. reported the formation of the 1,2-dihydropyridyl species at shorter reaction times. The ^{1}H NMR spectra in THF-d_8 and benzene-d_6 are identical with that of $[Mg(NC_5H_6)_2(py)_4]$ (**3**) obtained from the reaction of $[Mg(SiPh_3)_2(THF)_2]\cdot THF$ (**1**) with an excess of pyridine. The ^{1}H NMR spectrum of **3** shows signals for free pyridine which indicate that the coordination of pyridine in **3** is labile.



Scheme 4. Exchange of **3** with pyridine-d_5 to **3-HD** at 25°C. The reaction is monitored by ^{1}H NMR spectroscopy (t = 10 min; t = 15 h; t = 70 h).

Complex **3** undergoes an exchange with pyridine-d_5 to give $[Mg(NC_5D_5H\text{-}4)_2(py\text{-}d_5)_4]$ (**3-HD**) (Scheme 4). The exchange is reversible as **3-HD** reacts with protio-pyridine to **3** as monitored by ^{1}H NMR spectroscopy in THF-d_8 (See Electronic Supplementary Information). The exchange follows pseudo-first order kinetics and the reaction rates at 298 K, 313 K and 333 K were obtained: k_1(298 K) = (1.29±0.01)·10^{-5} s^{-1}; k_1(313 K)

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= (7.12±0.08)·10^{-5} s^{-1}; k_1(333 K) = (5.59±0.10)·10^{-4} s^{-1}. The activation energy for the exchange of **3** to **3-HD** was determined as E_A = (70.1±0.6)·kJ·mol^{-1} (See Electronic Supplementary Information). A possible mechanism for the exchange of **3** to **3-HD** consist of two steps. After exchange of the labile pyridine ligands by pyridine-d_5, hydride transfer from dihydropyridyl to pyridine-d_5 occurs to generate **3-HD**. Such an exchange between dihydropyridyl and pyridine was also found for NN-{[Mg(NC$_5$H$_6$)(py)]$_2$} (NN = [(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)–CHC(Me)N–]$_2$) and [Li(NC$_5$H$_5$-^{n}Bu-2)(py)$_2$].[23, 42] Over a period of 15 days a very slow reaction of **3-HD** in pyridine-d_5 to the completely deuterated species [Mg(NC$_5$D$_6$)$_2$(py-d_5)$_4$] (**3-D**) was observed at 25 °C. This may be due to the primary kinetic isotopic effect.[54] Allyl complexes [K(NC$_5$H$_5$-4-η^1-C$_3$H$_5$)] and [K([18]crown-6)]$_2$[Zn(η^1-C$_3$H$_5$)$_4$] were reported also to undergo a reversible exchange reaction with pyridine-d_5.[55]

[Mg(NC$_5$D$_5$H)$_2$(py-d_5)$_4$] (**3-HD**) was independently obtained in 82% yield from the reaction of activated MgH_2 with an excess of pyridine-d_5 and characterized by NMR spectroscopy. Highly temperature sensitive single crystals of [Mg(NC$_5$H$_6$)$_2$(py)$_4$] (**3**) were obtained from pyridine/*n*-hexane at −30 °C over a period of 48 h. Complex **3** crystallizes with three additional molecules of pyridine per formula unit of **3**.

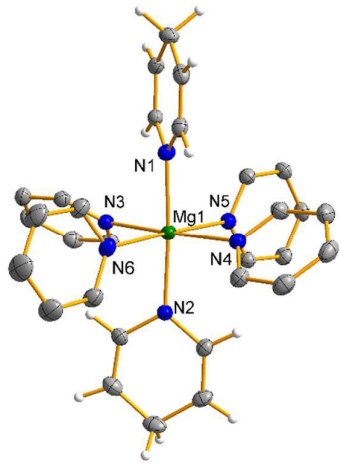
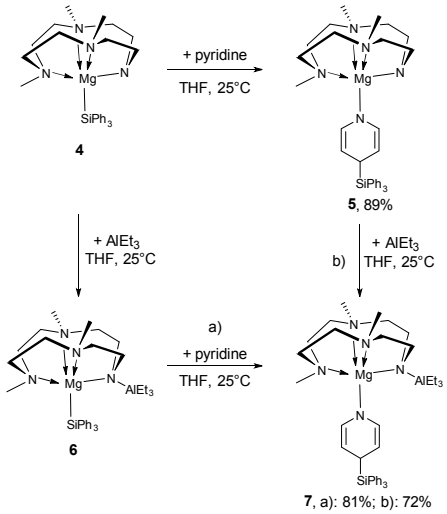


Figure 1. Molecular structure of [Mg(NC$_5$H$_6$)$_2$(py)$_4$] (**3**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, except for the dihydropyridyl rings, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N1 2.1186(13), Mg1–N2 2.1396(13), Mg1–N3 2.2538(13), Mg1-N4 2.2509(13), Mg1–N5 2.3861(13), Mg1–N6 2.3799(13), N1-Mg1-N2 176.21(5), N3-Mg1-N4 176.15(5) N5-Mg1-N6 177.56(5).

[Mg(NC$_5$H$_6$)$_2$(py)$_4$] (**3**) shows an octahedral coordination geometry for magnesium ligated to four pyridine and two 1,4-dihydropyridyl ligands. The four pyridine rings form a square plane around the magnesium center whereas the apical positions are occupied by the two 1,4-dihydropyridyl ligands. The 1,4-dihydropyridyl ligands are rotated by 37° relative to each other. The Mg-N1 and Mg-N2 distances of 2.1186(13) Å and 2.1396(13) Å are slightly longer compared to distances in other magnesium 1,4-dihydropyridyl complexes ([(DIPPnacnac)Mg(NC$_5$H$_6$)(py)][32] (1.993(2) Å); {NN-[Mg(NC$_5$H$_6$)]$_2$·(py)$_2$}[23] (2.0035(9) Å); {PARA-[Mg(NC$_5$H$_6$)]$_2$·(py)$_2$}[23] (PARA = [(2,6-iPr$_2$C$_6$H$_3$)NC(Me)C(H)C(Me)N]$_2$-(p-C$_6$H$_4$)) (1.9893(15)-1.9986(15) Å); [(PIA)Mg(NC$_5$H$_6$)(py)][34] (PIA = (2,6-iPr$_2$-C$_6$H$_3$)NC(Me)]CHP(Cy$_2$)]N(2,6-Me$_2$-C6H$_3$)) (1.999(6) Å).

Triphenylsilyl Complex with a Me$_3$TACD ligand

In analogy to the reaction of **1** with pyridine, reactions of the Me$_3$TACD-containing magnesium triphenylsilyls [(Me$_3$TACD)Mg(SiPh$_3$)] (**4**) and [(Me$_3$TACD·AlEt$_3$)Mg(SiPh$_3$)] (**6**)[52] ((Me$_3$TACD)H = Me$_3$[12]aneN$_4$: 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane)[56] with pyridine were performed (Scheme 5).



Scheme 5 Synthesis of [(Me$_3$TACD)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**5**) and [(Me$_3$TACD·AlEt$_3$)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**7**).

Complexes [(Me$_3$TACD)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**5**) and [(Me$_3$TACD·AlEt$_3$)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**7**) were isolated in good yields. Complex **7** can also be obtained in 72% yield by adding $AlEt_3$ to a solution of **5** in THF (Scheme 5b). The products **5** and **7** are derived from 1,4-insertion of pyridine into the magnesium-silicon bond. Again, no indication for the formation of the 1,2-insertion products was found which might be attributed to the high steric demands of the Me$_3$TACD ligand as well as the triphenylsilyl group. The formation of 1,2-insertion products as intermediates cannot be completely ruled out. An analogous reaction was observed when the allyl complex [(Me$_3$TACD)Mg(η^1-C$_3$H$_5$)] was treated with one equivalent of pyridine.[57]

Complex **5** is soluble in THF and benzene, whereas complex **7** is soluble in THF but decomposes in benzene at r.t over a period of 24 h. The ^{1}H NMR spectroscopic data for the 1,4-dihydropyridyl ring in **5** and **7** are given in Table S1 (See Electronic Supplementary Information).

Single crystals of **5** were obtained by layering *n*-hexane on a toluene solution at −30 °C. Complex **5** crystallizes with one additional molecule of toluene per formula unit of **5**. [(Me$_3$TACD)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**5**) is monomeric with a square pyramidal coordination geometry for magnesium (Figure 2). The 4-(triphenylsilyl)pyridyl group and four nitrogen atoms of the monoanionic Me$_3$TACD ligand are coordinated to the

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magnesium center (structural parameter τ = 0.16). The Mg-N5 distance of 2.022(2) Å lies in the range of known magnesium pyridyl complexes.[23, 32, 34] The L_3X-type ligand Me_3TACD displays the usual bonding parameters.

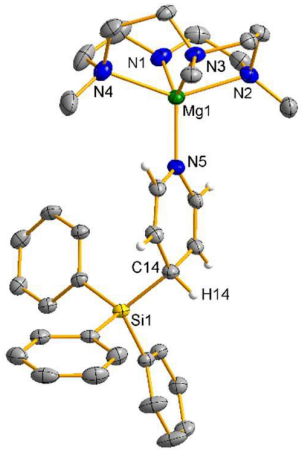
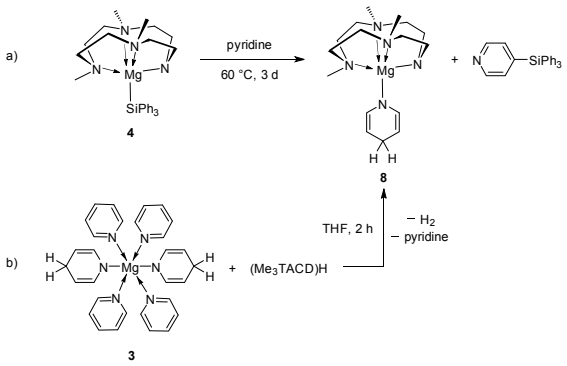


Figure 2. Molecular structure of [(Me_3TACD)Mg(NC_5H_5-4-$SiPh_3$)] (**5**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, except for the pyridyl ring, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N1 1.993(3), Mg1–N2 2.284(2), Mg1–N3 2.1866(17), Mg1-N4 2.294(3), Mg1–N5 2.022(2), C14-H14 1.00(4), C14-Si1 1.892(2), N1-Mg1-N3 111.38(8), N2-Mg1-N4 144.53(8).

To investigate whether the formation of the 1,4-insertion products **5** and **7** proceeds via intermediate 1,2-insertion products, the reaction of [(Me_3TACD)Mg($SiPh_3$)] (**4**) with different pyridine derivatives was performed in THF-d_8. Complex **4** reacted with 3-picoline to give the 1,4-insertion product, whereas the reaction with 2-picoline proceeded slowly. After 7 days about 50% of **4** was converted into the 1,4-insertion product and the residual 50% underwent C-H bond activation to form [(Me_3TACD)Mg($CH_2NC_5H_4$)] and triphenylsilane. The C-H bond activation or metalation of the methyl group as competition to the insertion reaction was reported for the reaction of bis(allyl)calcium with pyridine derivatives.[58] With 4-picoline and 2,6-lutidine exclusive C-H bond activation was observed without any formation of 1,2 insertion products. The reaction with 2,6-lutidine was slow and after 11 days only 50% of **4** were consumed. With 2,6-di-*tert*-butylpyridine no reaction occurred after 3 days at 60 °C.

When [(Me_3TACD)Mg($SiPh_3$)] (**4**) was stirred in pyridine for 3 days at room temperature, the formation of only **5** was observed. Heating this reaction mixture to 60 °C for 3 days gave [(Me_3TACD)Mg(NC_5H_6)] (**8**) and 4-(triphenylsilyl)pyridine (Scheme 6a).



Scheme 6. Formation of [(Me_3TACD)Mg(NC_5H_6)] (**8**).

Again, the separation of 4-(triphenylsilyl)pyridine was difficult. The ^{1}H NMR spectrum of the product mixture contains besides signals for 4-(triphenylsilyl)pyridine, signals characteristic for [(Me_3TACD)Mg(NC_5H_6)] (**8**) including the dihydropyridyl protons in *2*-, *3*- and *4*-position δ 4.05, 4.57 and 6.38 ppm, respectively. Complex **8** was obtained without the by-product 4-(triphenylsilyl)pyridine by reacting [Mg(NC_5H_6)$_2$(py)$_4$] (**3**) with one equivalent of (Me_3TACD)H (Scheme 6b).

The formation of [(Me_3TACD·$AlEt_3$)Mg(NC_5H_6)] was not possible starting from **6** in pyridine due to decomposition of **6** at 60 °C. A similar complex [(Me_3TACD·Al^iBu_3)Mg(NC_5H_6)] was obtained from the reaction of [(Me_3TACD·Al^iBu_3)MgH] with pyridine in 53% yield.[35]

[(Me_3TACD)Mg(NC_5H_6)] (**8**) showed no exchange with pyridine-d_5 to give [(Me_3TACD)Mg(NC_5D_5H)] (**8-HD**) at 25 °C but at 60 °C exchange was observed and follows pseudo-first order kinetics. The reaction rates at different temperatures were determined for 333 K, 343 K and 353 K: k_1(333 K) = (2.48±0.06)·10^{-5} s^{-1}; k_1(343 K) = (7.30±0.13)·10^{-5} s^{-1}; k_1(353 K) = (1.72±0.02)·10^{-4} s^{-1} (see Electronic Supplementary Information). The exchange reaction of **8** with pyridine-d_5 is slower than that of complex **3**. The activation energy for the exchange of **8** to **8-HD** was determined as E_A = (94.7±1.9)·kJ·mol^{-1} and can be seen to be about 25 kJ·mol^{-1} higher than that for the exchange of complex **3** with E_A = (70.1±0.6)·kJ·mol^{-1}.

Single crystals of [(Me_3TACD)Mg(NC_5H_6)] (**8**) were obtained from toluene/*n*-hexane at −30 °C over a period of 24 h.

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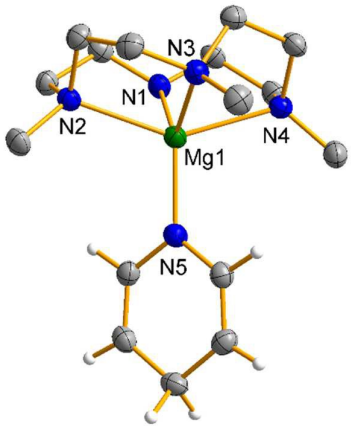


Figure 3. Molecular structure of [(Me$_3$TACD)Mg(NC$_5$H$_6$)] (**8**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, except for the dihydropyridyl ring, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N1 1.986(2), Mg1–N2 2.297(2), Mg1–N3 2.180(2), Mg1-N4 2.285(2), Mg1–N5 2.017(2), N1-Mg1-N3 112.20(9), N2-Mg1-N4 145.07(8).

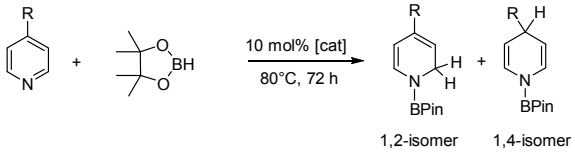
[(Me$_3$TACD)Mg(NC$_5$H$_6$)] (**8**) is monomeric with a distorted square pyramidal coordination geometry for magnesium (τ = 0.25). The magnesium center is coordinated by one 1,4-dihydropyridyl ligand and four nitrogen atoms of the monoanionic Me$_3$TACD ligand. The Mg-N5 distance of 2.017(2) Å is slightly shorter when compared to the Mg-N distances of the 1,4-dihydropyridyl ligand in complex **3** and lies in the range of other magnesium1,4-dihydropyridyl complexes reported in the literature.[23, 32, 34]

Hydrofunctionalization of pyridine

[Mg(NC$_5$H$_6$)$_2$(py)$_4$] (**3**), [(Me$_3$TACD)Mg(NC$_5$H$_6$)] (**8**) and [(Me$_3$TACD·Al^{i}Bu$_3$)Mg(NC$_5$H$_6$)][25] were tested as catalysts for the hydrosilylation of pyridine. At a catalyst loading of 10 mol% [(Me$_3$TACD)Mg(NC$_5$H$_6$)] (**8**) and [(Me$_3$TACD·Al^{i}Bu$_3$)Mg(NC$_5$H$_6$)][25] showed no activity at 80 °C in the hydrosilylation of pyridine using phenylsilane after 72 h. β-Diketiminato-supported magnesium dihydropyridyls were also not active.[22, 33] Hill et al. assumed that the presence of additional strongly coordinating pyridine ligands prevented the interaction of phenylsilane with the magnesium center. [Mg(NC$_5$H$_6$)$_2$(py)$_4$] (**3**) was found to be active at 80°C in the hydrosilylation of pyridine with phenylsilane and after 72 h a mixture consisting of [(1,4-NC$_5$H$_6$)$_2$PhSiH] (12%), [(1,2-NC$_5$H$_6$)$_2$PhSiH] (9%) and [(1,4-NC$_5$H$_6$)PhSiH$_2$] (14%) was obtained. These results are comparable to those using {[(DipNHPPh$_2$)MgH]$_4$} (Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$) which produced a mixture of [(1,4-NC$_5$H$_6$)$_2$PhSiH], [(1,2-NC$_5$H$_6$)$_2$PhSiH] and [(1,2-NC$_5$H$_6$)(1,4-NC$_5$H$_6$)PhSiH] at 80 °C after 48 h with a total conversion of 52%.[20]

Furthermore, [Mg(NC$_5$H$_6$)$_2$(py)$_4$] (**3**), [(Me$_3$TACD)Mg(NC$_5$H$_6$)] (**8**) and [(Me$_3$TACD·Al^{i}Bu$_3$)Mg(NC$_5$H$_6$)][25] were tested as catalysts for the hydroboration of pyridine. For pyridine hydroboration with pinacolborane (HBpin) 10 mol% of the complexes were used and the conversions were monitored by ^{1}H NMR spectroscopy (Table 1).

Table 1. Hydroboration of pyridine derivatives with HBpin catalyzed by **3**, **8** and [(Me$_3$TACD·Al^{i}Bu$_3$)Mg(NC$_5$H$_6$)][25].



1,2-isomer 1,4-isomer

Entry	Complex	R	1,2-:1,4-isomers [%]	Conversion[a] [%]
1	**3**	H	3:97	52
2	**8**	H	4:96	74
3[b]	**8**	H	10:90	68
4	**8**	^{t}Bu	27:73	75
5[b,c]	**8**	^{t}Bu	47:53	75
6[d]	[LMg(DHP)][25]	H	3:97	70

Relative to hexamethylbenzene as internal standard in THF-d_8. [a] Determined by ^{1}H NMR spectroscopy. [b] In benzene-d_6. [c] pinB-1,4-DHP is also detected due to release of pyridine by **8**. [d] [LMg(DHP)]= [(Me$_3$TACD·Al^{i}Bu$_3$)Mg(NC$_5$H$_6$)].

[Mg(NC$_5$H$_6$)$_2$(py)$_4$] (**3**), [(Me$_3$TACD)Mg(NC$_5$H$_6$)] (**8**) and [(Me$_3$TACD·Al^{i}Bu$_3$)Mg(NC$_5$H$_6$)][25] are active in the hydroboration of pyridine using HBpin. Complex **8** and [(Me$_3$TACD·Al^{i}Bu$_3$)Mg(NC$_5$H$_6$)][25] are slightly more active than complex **3** and their results in the hydroboration of pinacolborane are comparable to those of the magnesium complexes [(DipNHPPh$_2$)MgH)$_4$][20], [(DIPPnacnac)Mg^{n}Bu][22] and NN-{[Mg(NC$_5$H$_6$)(py)]$_2$} (NN = [(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)-CHC(Me)N−]$_2$),[23] whereas [Mg(THF)$_6$][HBPh$_3$]$_2$[26] is considerably more active. Finally, 4-*tert*-butylpyridine was hydroborated in THF-d_8 or benzene-d_6 at 80°C with 75% conversion using 10 mol% of complex **8** as catalyst over a period of 72 h. In THF-d_8 a higher selectivity towards the 1,4-isomer was observed (Entry 2/3 and 4/5).

Conclusion

Pyridine was found to insert into the Mg–Si bond of the molecular magnesium triphenylsilyl **1**, **4** and **6**[52] to give the magnesium 4-(triphenylsilyl)pyridyls **2, 5** and **7**, respectively. Products of 1,2-insertion were not detected. With an excess of pyridine, magnesium 1,4-dihydropyridyl complexes **3** and **8** along with 4-(triphenylsilyl)pyridine were formed. The facile hydride transfer from the 1,4-(triphenylsilyl)dihydropyridyl to pyridine may be accounted for by stabilizing effect by a silyl substituent in the re-aromatized pyridine. In the literature the triphenylsilyl group is described to have an electron withdrawing effect when substituted in the *para*-position of an aromatic ring.[59]

As expected, the introduction of the macrocyclic ligand Me$_3$TACD resulted in significant stabilization of the 1,4-dihydropyridyl complexes. The presence of a Lewis acid at the amido nitrogen had no effect, as observed previously in other Me$_3$TACD magnesium complexes.[52]

Whilst complex **8** was not active in the hydrosilylation of pyridine using phenylsilane, a mixture of hydrosilylated

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dihydropyridines were obtained with complex **3**. It was also active in the hydroboration of pyridine using pinacolborane, whereas complex **8** showed activity comparable to that of catalysts reported in the literature.[20, 22, 23, 26]

Experimental

General considerations

All operations were performed under inert atmosphere of dry argon using standard Schlenk techniques or glovebox techniques. THF, *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. The starting materials activated MgH_2,[53] $[Mg(SiPh_3)(THF)_2]\cdot THF$ (**1**), $[(Me_3TACD)Mg(SiPh_3)]$ (**4**) and $[(Me_3TACD\cdot AlEt_3)Mg(SiPh_3)]$ (**6**)[52] were prepared according to literature procedures. 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, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ 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, HMBC). Combustion analyses were performed with an Elementar Vario EL. The low carbon content for **2**, **3** and **8** may be ascribed to incomplete combustion due to possible formation of incombustible magnesium carbide or carbonate. Similar problems are reported for earth alkaline metal complexes in the literature.[52, 60] The magnesium contents of **2**, **3** and **5** were determined by complexometric titrations and were carried out according to the published procedure.[61] Metal contents of **7** and **8** were determined by inductively coupled plasma mass spectrometry using a Spectro ICP Spectroflame D instrument. A defined amount of sample was dissolved in 8 mL of 40% hydrofluoric acid, 2 mL of concentrated sulfuric acid, and 40 mL of water.

$[Mg(NC_5H_5\text{-}4\text{-}SiPh_3)_2(THF)_3]$ (2)

A solution of pyridine (63 mg; 0.8 mmol) in THF (2 mL) was added to a solution of $[Mg(SiPh_3)_2(THF)_2]\cdot THF$ (**1**) (304 mg; 0.4 mmol) in THF (2 mL). The reaction mixture turned orange and was stirred for 3 h at room temperature. The solvent was removed under reduced pressure and the orange oil washed with *n*-pentane (3 x 3mL) until it became a solid. $[Mg(NC_5H_5\text{-}4\text{-}SiPh_3)_2(THF)_3]$ (**2**) (343 mg; 0.37 mmol) was obtained as a yellow powder; yield 93%.

^1H NMR (C_6D_6; 400.1 MHz):δ = 1.34 (THF), 3.53 (THF), 4.00 (br. s, 1H, $N(CH)_2(CH)_2CH$), 4.56 (br. s, 2H, $N(CH)_2(CH)_2CH$), 5.95 (br. s, 2H, $N(CH)_2(CH)_2CH$), 7.20-7.23 (m, 18H, *meta*-/*para*-Ph), 7.88-7.89 (m, 12H, *ortho*-Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6; 100.6 MHz): δ = 25.3 ($N(CH)_2(CH)_2CH$), 26.0 (THF), 69.1 (THF), 98.5 ($N(CH)_2(CH)_2CH$), 128.2 (*meta*-Ph, overlapped by the signal of benzene-d_6 but identified by HSQC), 129.7 (*para*-Ph), 136.2 (*ipso*-Ph), 137.1 (br., $N(CH)_2(CH)_2CH$), 137.4 (*ortho*-Ph) ppm. ^1H NMR (THF-d_8; 400.1 MHz): δ = 3.71-3.74 (m, 2H, $N(CH)_2(CH)_2CH$), 3.81 (m, 1H, $N(CH)_2(CH)_2CH$), 5.57 (m, 2H, $N(CH)_2(CH)_2CH$), 7.22-7.30 (m, 18H, *meta*-/*para*-Ph), 7.67-7.69 (m, 12H, *ortho*-Ph) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8; 100.6 MHz): δ = 26.6 ($N(CH)_2(CH)_2CH$), 98.5 ($N(CH)_2(CH)_2CH$), 128.1 (*meta*-Ph), 129.4 (*para*-Ph), 137.5 (*ipso*-Ph), 137.7 (*ortho*-Ph), 140.3 ($N(CH)_2(CH)_2CH$) ppm. $^{29}Si\{^1H\}$ NMR (THF-d_8; 79.5 MHz): δ = 23.0 ppm. Anal. calc. for $C_{58}H_{64}N_2O_3Si_2Mg$ (917.64 g·mol-1): C, 75.92; H, 7.03; N, 3.05; Mg, 2.65. Found: C, 74.51; H, 6.94; N, 3.23; Mg, 2.67%.

$[Mg(NC_5H_6)_2(py)_4]$ (3)

Method A. $[Mg(SiPh_3)_2(THF)_2]\cdot THF$ (**1**) (380 mg; 0.5 mmol) was dissolved in pyridine (4 mL). After 2 h, a slightly yellow solid precipitated from the red solution. The solid, which was identified as 4-(triphenylsilyl)pyridine, was filtered off and the red filtrate was reduced to a volume of 2 mL. The filtrate was cooled to −30 °C and more of the byproduct precipitated. The reaction solution was filtered again and cooled down to −30°C. $[Mg(NC_5H_6)_2(py)_4]$ (**3**) (174 mg; 0.35 mmol) crystallized from the solution at −30 °C as orange crystals over a period of 48 h in a yield of 70%. The product still contained 6 mol% of 4-(triphenylsilyl)pyridine as impurity. Thermally highly sensitive crystals suitable for X-ray analysis were obtained from pyridine/*n*-hexane over a period of 48 h at −30 °C.

Method B.[29, 30] Activated MgH_2 (33 mg, 1.25 mmol) was stirred in pyridine (2 mL) at room temperature for 18 h. The reaction solution was reduced and cooled at −30 °C for 24 h. $[Mg(NC_5H_6)_2(py)_4]$ (**3**) (470 mg; 0.94 mmol) was obtained as orange-brown crystals in 75% yield.

^1H NMR (THF-d_8; 400.1 MHz): δ = 3.21 (m, 4H, $N(CH)_2(CH)_2CH_2$), 3.75 (m, 4H, $N(CH)_2(CH)_2CH_2$), 5.84 (m, 4H, $N(CH)_2(CH)_2CH_2$), 7.28 (pyridine), 7.69 (pyridine), 8.55 (pyridine) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8, 100.6 MHz): δ = 26.2 ($N(CH)_2(CH)_2CH_2$), 92.2 ($N(CH)_2(CH)_2CH_2$), 124.6 (pyridine), 136.8 (pyridine), 139.9 ($N(CH)_2(CH)_2CH_2$), 150.9 (pyridine) ppm. ^1H NMR (benzene-d_6; 400.1 MHz): δ = 3.81 (m, 4H, $N(CH)_2(CH)_2CH_2$), 4.54 (m, 4H, $N(CH)_2(CH)_2CH_2$), 6.44 (m, 4H, $N(CH)_2(CH)_2CH_2$), 6.66 (pyridine), 6.96 (pyridine), 8.57 (pyridine) ppm. ^1H NMR (pyridine-d_5; 400.1 MHz): δ = 3.83 (m, 4H, $N(CH)_2(CH)_2CH_2$), 4.32 (m, 4H, $N(CH)_2(CH)_2CH_2$), 6.38 (m, 4H, $N(CH)_2(CH)_2CH_2$), 7.23 (pyridine), 7.59 (pyridine), 8.74 (pyridine) ppm. $^{13}C\{^1H\}$ NMR (pyridine-d_5, 100.6 MHz): δ = 26.8 ($N(CH)_2(CH)_2CH_2$), 92.6 ($N(CH)_2(CH)_2CH_2$), 124.5 (pyridine), 136.5 (pyridine), 141.3 ($N(CH)_2(CH)_2CH_2$), 150.8 (pyridine) ppm. Anal. calc. for $C_{30}H_{32}N_6Mg$ (500,93 g·mol^{-1}): C, 71.93; H, 6.44; N, 16.78; Mg, 4.85. Found: C, 70.39; H, 6.47; N, 16.70; Mg, 4.77%.

$[Mg(NC_5D_5H)_2(py\text{-}d_5)_4]$ (3-HD)

Activated MgH_2 (33 mg, 1.25 mmol) was stirred in pyridine-d_5 (2 mL) at room temperature for 8 h. The reaction solution was concentrated and cooled to −30°C for 24 h. $[Mg(NC_5D_5H)_2(py\text{-}d_5)_4]$ (**3-HD**) (545 mg; 1.03 mmol) was obtained as orange-red crystals in 82% yield. The crystals melt at room temperature.

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^{1}H NMR (THF-d_8; 400.1 MHz): δ = 3.18 (m, 2H, N(CD)$_2$(CD)$_2$CD*H*) ppm. ^{13}C{^{1}H} NMR (THF-d_8; 100.6 MHz): δ = 25.5 (N(CD)$_2$(CD)$_2$*C*DH, overlapped by the signal of THF-d_8 but identified by HSQC) ppm. ^{1}H NMR (pyridine-d_5; 400.1 MHz): δ = 3.80 (m, 2H, N(CD)$_2$(CD)$_2$CD*H*) ppm. ^{13}C{^{1}H} NMR (pyridine-d_8; 100.6 MHz): δ = 25.5 (N(CD)$_2$(CD)$_2$*C*DH, just identified by HSQC) ppm. ^{1}H NMR (benzene-d_6; 400.1 MHz): δ = 3.89 (m, 2H, N(CD)$_2$(CD)$_2$CD*H*) ppm. ^{2}D NMR (THF; 400.1 MHz): δ = 3.00 (br. s, N(CD)$_2$(CD)$_2$*C*D*H*), 3.60 (br. s, N(CD)$_2$(C*D*)$_2$CDH), 5.70 (br. s, N(C*D*)$_2$(CD)$_2$CDH) ppm.

[(Me$_3$TACD)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (5)

A solution of pyridine (20 mg; 0.25 mmol) in THF (2 mL) was added to a solution of [(Me$_3$TACD)Mg(SiPh$_3$)](**4**) (124 mg; 0.25 mmol) in THF (2 mL). The color of the reaction mixture turned yellow and the reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the solid residue was washed with *n*-pentane (3 x 3 mL). [(Me$_3$TACD)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**5**) (128 mg; 0.22 mmol) was obtained in 89% yield as a yellow powder.

^{1}H NMR (THF-d_8, 400.1 MHz): δ = 2.24-2.28 (m, 2H, C*H*$_2$), 2.37-2.46 (m, 4H, C*H*$_2$), 2.40 (s, 3H, Me), 2.41 (s, 6H, Me), 2.53-2.55 (m, 2H, C*H*$_2$), 2.70-2.78 (m, 4H, C*H*$_2$), 2.86-2.94 (m, 4H, C*H*$_2$), 3.69-3.71 (m, 2H, N(CH)$_2$(C*H*)$_2$CH), 3.75-3.77 (m, 1H, N(CH)$_2$(CH)$_2$C*H*), 5.72-5.74 (m, 2H, N(C*H*)$_2$(CH)$_2$CH), 7.23-7.30 (m, 9H, *meta*-/*para*-Ph), 7.71-7.73 (m, 6H, *ortho*-Ph) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ = 26.8 (N(CH)$_2$(CH)$_2$*C*H), 43.8 (Me), 46.9 (Me), 51.2 (CH$_2$), 53.0 (*C*H$_2$), 55.8 (*C*H$_2$), 63.8 (*C*H$_2$), 92.0 (N(CH)$_2$(*C*H)$_2$CH), 128.1 (*meta*-Ph), 129.3 (*para*-Ph), 137.7 (*ortho*-Ph), 137.7 (*ipso*-Ph), 140.5 (N(*C*H)$_2$(CH)$_2$CH) ppm. ^{29}Si{^{1}H} NMR (THF-d_8, 79.5 MHZ): δ = −27.4 ppm. ^{1}H NMR (benzene-d_6, 400.1 MHz): δ = 1.38-1.48 (m, 4H, C*H*$_2$), 1.65 (s, 3H, Me) 1.74-1.80 (m, 2H, C*H*$_2$), 2.04 (s, 6H, Me), 2.09-2.17 (m, 4H, C*H*$_2$), 2.75-2.90 (m, 4H, C*H*$_2$), 3.26-3.30 (m, 2H, C*H*$_2$), 4.43-4.44 (m, 3H, N(CH)$_2$(C*H*)$_2$C*H*), 6.02-6.03 (m, 2H, N(C*H*)$_2$(CH)$_2$CH), 7.23-7.26 (m, 9H, *meta*-/*para*-Ph), 8.09-8.12 (m, 6H, *ortho*-Ph), ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 100.6 MHz): δ = 26.8 (N(CH)$_2$(CH)$_2$*C*H), 43.3 (Me), 46.6 (Me), 50.4 (*C*H$_2$), 52.6 (*C*H$_2$), 54.9 (*C*H$_2$), 63.2 (*C*H$_2$), 92.8 (N(CH)$_2$(*C*H)$_2$CH), 128.2 (*meta*-Ph), 129.3 (*para*-Ph), 137.7 (*ortho*-Ph), 137.5 (*ipso*-Ph), 140.4 (N(*C*H)$_2$(CH)$_2$CH) ppm. ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHZ): δ = −25.7 ppm. Anal. calc. for $C_{34}H_{45}N_5SiMg$ (576,16 g·mol^{-1}): C, 70.88; H, 7.87; N, 12.16; Mg, 4.22. Found: C, 70.09; H, 7.85; N, 11.68; Mg, 4.05%.

[(Me$_3$TACD·AlEt$_3$)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (7)

Method A. A solution of pyridine (16 mg; 0.2 mmol) in THF (2 mL) was added to a solution of [(Me$_3$TACD·AlEt$_3$)Mg(SiPh$_3$)] (**6**) (122 mg; 0.2 mmol) in THF (2 mL). The color of the reaction mixture turned yellow. The reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the solid residue was washed with *n*-pentane (3 x 3 mL). [(Me$_3$TACD·AlEt$_3$)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**7**) (112 mg; 0.16 mmol) was obtained in 81% yield as a yellow powder.

Method B. A solution of AlEt$_3$ (11.5 mg; 0.1 mmol) in THF (2 mL) was added to a solution of [(Me$_3$TACD)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**2**) (58 mg; 0.1 mmol) in THF (2 mL). The reaction solution was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the oily residue was washed with *n*-pentane (3 x 3mL). [(Me$_3$TACD·AlEt$_3$)Mg(NC$_5$H$_5$-4-SiPh$_3$)] (**7**) (50 mg; 0.07 mmol) was obtained in 72% yield as a yellow powder.

^{1}H NMR (THF-d_8, 400.1 MHz): δ = −0.17 (q, $^3J_{HH}$ = 8.03 Hz, 6H, Al(CH$_2$C*H*$_3$)$_2$), 1.07 (t, $^3J_{HH}$ = 8.03 Hz, 9H, Al(C*H*$_2$CH$_3$)$_2$), 2.35 (s, 3H, Me), 2.39 (s, 6H, Me), 2.42-2.56 (m, 8H, C*H*$_2$), 2.70-2.81 (m, 6H, C*H*$_2$), 2.97-3.03 (m, 2H, C*H*$_2$), 3.77-3.80 (m, 3H, N(CH)$_2$(C*H*)$_2$C*H*), 5.76-5.78 (m, 2H, N(C*H*)$_2$(CH)$_2$CH), 7.25-7.30 (m, 9H, *meta*-/*para*-Ph), 7.69-7.71 (m, 6H, *ortho*-Ph) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ = 2.1 (Al(*C*H$_2$CH$_3$)$_2$), 12.1 (Al(CH$_2$*C*H$_3$)$_2$), 26.0 (N(CH)$_2$(CH)$_2$*C*H), 44.1 (Me), 45.5 (Me), 47.8 (*C*H$_2$), 54.1 (*C*H$_2$), 54.3 (*C*H$_2$), 56.8 (*C*H$_2$), 92.3 (N(CH)$_2$(*C*H)$_2$CH), 128.2 (*meta*-Ph), 129.2 (*ipso*-Ph), 129.4 (*para*-Ph), 137.7 (*ortho*-Ph), 140.7 (N(*C*H)$_2$(CH)$_2$CH) ppm. ^{29}Si{^{1}H} NMR (THF-d_8, 79.5 MHZ): δ = −27.2 ppm. Anal. calc. for $C_{40}H_{60}N_5SiMgAl$ (690.30 g·mol^{-1}): C, 69.60; H, 8.76; N, 10.15; Mg, 3.52; Al, 3.91. Found: C, 69.56; H, 8.61; N, 9.79; Mg, 3.52; Al, 3.66%.

[(Me$_3$TACD)Mg(NC$_5$H$_6$)] (8)

Method A. [(Me$_3$TACD)Mg(SiPh$_3$)] (**4**) was dissolved in pyridine (2 mL) and stirred at 60 °C for 3 days. The color of the solution turned from orange to red-brown. The solvent was removed under reduced pressure and the red-brown solid residue was washed with *n*-pentane (3 x 3 mL) and dried under vacuum. The product mixture of [(Me$_3$TACD)Mg(NC$_5$H$_6$)] (**8**) and 4-(triphenylsilyl)pyridine could not be separated.

Method B. (Me$_3$TACD)H (140 mg; 0.65 mmol) in THF (1 mL) was added to a solution of [Mg(NC$_5$H$_6$)$_2$(py)$_4$] (**3**) (328 mg; 0.65 mmol) in THF (2 mL) and stirred at room temperature for 2 h. A color change of the solution from red to pale red-orange was observed. The solvent was removed under reduced pressure and the red-brown oily residue was washed with *n*-pentane (3x 3mL) until it became a solid. The solid was dried under vacuum to give [(Me$_3$TACD)Mg(NC$_5$H$_6$)] (**8**) (192 mg; 0.60 mmol) as a pale brown powder in 92% yield.

^{1}H NMR (benzene-d_6, 400.1 MHz): δ = 1.37-1.48 (m, 4H, C*H*$_2$), 1.69 (s, 3H, Me) 1.73-1.79 (m, 2H, C*H*$_2$), 2.07 (s, 6H, Me), 2.08-2.17 (m, 4H, C*H*$_2$), 2.76-2.83 (m, 2H, C*H*$_2$), 2.86-2.93 (m, 2H, C*H*$_2$), 3.29-3.33 (m, 2H, C*H*$_2$), 4.04-4.05 (m, 2H, N(CH)$_2$(CH)$_2$C*H*$_2$), 4.55-4.59 (m, 2H, N(CH)$_2$(C*H*)$_2$CH$_2$), 6.37-6.39 (m, 2H, N(C*H*)$_2$(CH)$_2$CH$_2$) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 100.6 MHz): δ = 26.6 (N(CH)$_2$(CH)$_2$*C*H$_2$), 43.4 (Me), 46.6 (Me), 50.3 (*C*H$_2$), 52.6 (*C*H$_2$), 54.9 (*C*H$_2$), 63.2 (*C*H$_2$), 92.9 (N(CH)$_2$(*C*H)$_2$CH$_2$), 140.2 (N(*C*H)$_2$(CH)$_2$CH$_2$) ppm. ^{1}H NMR (THF-d_8, 400.1 MHz): δ = 2.23-2.30 (m, 2H, C*H*$_2$), 2.40-2.48 (m, 4H, C*H*$_2$), 2.44 (s, 9H, Me), 2.53-2.59 (m, 2H, C*H*$_2$), 2.71-2.79 (m, 4H, C*H*$_2$), 2.86-2.95 (m, 4H, C*H*$_2$), 3.19-3.21 (m, 2H, N(CH)$_2$(CH)$_2$C*H*$_2$), 3.67-3.99 (m, 2H, N(CH)$_2$(C*H*)$_2$CH$_2$), 5.90-5.92 (m, 2H, N(C*H*)$_2$(CH)$_2$CH$_2$) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ = 26.3 (N(CH)$_2$(CH)$_2$*C*H$_2$), 43.8 (Me), 46.7 (Me), 51.2 (*C*H$_2$), 53.1 (*C*H$_2$), 55.8 (*C*H$_2$), 63.8 (*C*H$_2$), 91.7 (N(CH)$_2$(*C*H)$_2$CH$_2$), 140.2 (N(*C*H)$_2$(CH)$_2$CH$_2$) ppm. Anal. calc. for $C_{16}H_{31}N_5Mg$ (317,76 g·mol^{-1}): C, 60.48; H, 9.83; N, 22.04; Mg, 7.65. Found: C, 60.55; H, 9.90; N, 21.35; Mg, 7,01%.

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4-(Triphenylsilyl)pyridine

^{1}H NMR (benzene-d_6, 400.1 MHz): δ = 7.12-7.14 (m, 6H, *meta*-Ph), 7.18-7.22 (m, 3H, *para*-Ph), 7.26-7.27 (m, 2H, $N(CH)_2(CH)_2$), 7.52-7.54 (m, 6H, *ortho*-Ph), 8.56-8.58 (m, 2H, $N(CH)_2(CH)_2$) ppm. $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ = 128.8 (*meta*-Ph), 130.6 (*para*-Ph), 131.3 ($N(CH)_2(CH)_2$), 133.5 (*ipso*-Ph), 137.1 (*ortho*-Ph), 144.4 (*ipso*-Ph), 150.0 ($N(CH)_2(CH)_2$) ppm. $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.5 MHZ): δ = 14.3 ppm. Anal. calc. for $C_{23}H_{19}NSi$ (337,50 g·mol^{-1}): C, 81.85; H, 5.67; N, 4.15. Found: C, 80.48; H, 5.67; N, 4.33%.

Conflicts of interest

There are no conflicts to declare.

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TOC

1,4-Dihydropyridyl Complexes of Magnesium: Synthesis by Pyridine Insertion into the Magnesium-Silicon Bond of Triphenylsilyls and Catalytic Pyridine Hydrofunctionalization

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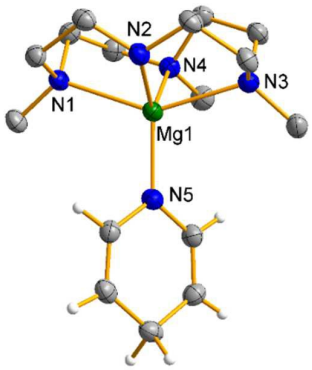

Magnesium triphenylsilyl complexes $[Mg(SiPh_3)_2(THF)_2]$ and $[(Me_3TACD)Mg(SiPh_3)]$ ($(Me_3TACD)H = Me_3[12]aneN_4$: 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) serve as precursors for 1.4-dihydropyridyl complexes of magnesium which are active in the hydroboration of pyridine using pinacolborane.