1. Introduction

Hydrides of s-, p-, d- and f-block metals are insoluble solid state materials. Currently, hydrides of highly electropositive metals (electronegativity $< \approx 1.6$) such as MgH$_2$, Ca(BH$_4$)$_2$, and LaNi$_5$H$_6$ are being considered as hydrogen storage materials to allow reversible hydrogen uptake and release.$^1$

Metal hydrides could also become useful as inexpensive and non-toxic precursors for homogeneous catalysts, if they can be dissolved. By introducing ligands such as CO, phosphines, and N-heterocyclic carbenes (NHCs)$^2$ homogeneous hydride catalyst precursors based on late transition metals such as Wilkinson’s catalyst became widely available.$^3$

When early transition metals were considered, their more electropositive (oxophilic) character and large size required new types of more electron-rich ligands to saturate the low valence electron counts of these metals. Bis($\eta^5$-cyclopentadienyl) ligand systems tremendously contributed to the rapid development of early transition metal compounds,$^4$ including Brintzinger-type ansa-zirconocene catalysts for stereoselective olefin hydrogenation and polymerization.$^5$ Generally, when dealing with highly electropositive, large metal centers, the use of chelating ligands is preferred, to suppress intermolecular ligand exchange reactions during catalysis.

TACD ligands, derived from the NNNN macrocycle cyclen (1,4,7,10-tetraazacyclododecane or [12]aneN$_4$) were initially developed for group 3 metals as alternatives to the ubiquitous cyclopentadienyl ligand class (Fig. 1). Commercial success of gadolinium(III) complexes containing DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetoxy) ligands as MRI contrast agents$^6$ inspired us to study simpler derivatives such as (Me$_3$TACD)H, the N,N$'$,N$''$,N$'''$methylated ligand [12]aneN$_4$.$^7$ Me$_3$TACD acts as an amido triamine supporting ligand (7-electron L$_3$X or 9-electron L$_4$X-type ligand, depending on the presence of p-donation of the amido function). Originally, (Me$_3$TACD)H was conceived as a surrogate for the 5-electron L$_2$X-type cyclopentadienyl ligand to support large metal centers such as lanthanides.$^4b$

The neutral L$_4$-type ligand N,N$'$,N$''$,N$'''$methylated cyclen Me$_4$TACD (Me$_4$[12]aneN$_4$) is similar to the crown ether 12-crown-4 but acts as a more kinetically inert ancillary ligand for metal ions with different size of the s-, p-, d-, and f-block.

---

Fig. 1 NNNN macrocyclic ligands derived from cyclen.
As a model reaction for the reversible reaction of solid state hydrogen storage material, a lutetium hydrido complex of Me₄TACD was shown to undergo a relatively fast reaction with dihydrogen based on reversible σ-bond metathesis. The reaction of a relatively kinetically inert dihydrogen molecule is facilitated by heterolysis of the thermodynamically stable H-H bond (ΔH_diss = 436 kJ mol⁻¹) through the polar Lu–C bond and a low-lying empty orbital across the Lu–Lu vector (Scheme 1).

Building on work such as this, some efforts have been expended to study molecular group 2 metal hydrides, since magnesium dihydride MgH₂ is one of the early examples of a solid state hydrogen storage material (prepared from the organometallic precursor anthracenyl magnesium). We have prepared and structurally characterized new molecular hydrides of group 2 metals supported by the ligands Me₃TACD and Me₄TACD. Not only do they serve as models for hydrogen storage materials but show reactivity as efficient hydride nucleophiles and catalysts for various reactions.

2. Me₃TACD Complexes

2.1. Ligand Properties

As an amido triamine ligand, Me₃TACD acts as a versatile macrocyclic supporting ligand (Fig. 2). Originally it was designed to support large rare-earth metal centers with reactive ligands such as hydrides and hydrocarbyls. As a monoanionic ligand, it coordinates not only larger metals of groups 3 and 4 (resembling half-sandwich complexes), but also a wide range of main group metals encompassing group 1 to 13 metals.

In order to reduce steric repulsion, the four CH₂CH₂ bridges in Me₄TACD assume dissymmetric conformations in the solid state upon metal coordination. Solution NMR spectra at ambient temperature indicate structures of higher symmetry on the NMR timescale. The ¹³C{¹H} NMR spectra show four resonances assignable to the cycen ring carbons, as in the yttrium complex [(Me₃TACD)Y(CH₂SiMe₃)]. This complex undergoes a rapid exchange process between both enantiomers and appears to be Cₐ-symmetrical on the NMR timescale (Scheme 2). The exchange is caused by the ring flipping of the Me₃TACD macrocycle and twisting of the CH₂SiMe₃ groups through a transition state with a pseudo-mirror plane. According to IUPAC rules, these enantiomers are called Δ(λδδδ) and Δ(δλλλ), both of which are found in the crystal lattice. Related fast interconversion was observed in Lu₁⁴(DOTA) complexes.

2.2. Group 1 Metal Complexes

In order to learn about the general coordination properties of Me₃TACD ligand, alkali metal complexes were studied. They were prepared by metalation using alkyl or allyl reagents. Reaction of (Me₃TACD)H with n-butyllithium in a 1:1 ratio afforded [(Me₃TACD)Li]₂ (1) as a dimer in the solid state (Scheme 3). The lithium atoms in 1 are four-coordinate with a pseudo-tetrahedral geometry with Me₃TACD σ-bonded to lithium. According to ¹H NMR spectrum, this coordination mode is also retained in solution.

![Scheme 1](image)

**Scheme 1** Reversible dihydrogen activation at a dinuclear rare earth metal complex. Calculated energy profile for the hydrogenolysis.

![Scheme 2](image)

**Scheme 2** Interconversion of the enantiomers of [(Me₃TACD)Y(CH₂SiMe₃)].
Metalation using n-butylnium gave trimeric \([\text{Me}_3\text{TACD})\text{Na}_3\] (2), in which the sodium ions are bridged through the amide nitrogen atoms of Me3TACD in the crystal (Scheme 3).13 Metalation by potassium allyl \([\text{K}((\text{C}_3\text{H}_5))\text{]}\) in benzene gave \([(\text{Me}_3\text{TACD})\text{K}]_2(\text{C}_6\text{H}_6)_2\] (3) as benzene-soluble, light yellow crystals, consisting of benzene-bridged oligomers (Scheme 3).13 As well known in the literature, the nuclearity of \([(\text{Me}_3\text{TACD})\text{M}]_n\) (M = Li, Na, K) increases with the size of the alkali metal ion and the strong arene coordination becomes prominent for potassium.

The highly basic nature of the amido group is underscored by the observation that Lewis acid-base adducts \([(\text{Me}_3\text{TACD})\text{SiH}_2\text{Ph}_2\text{M(\text{thf})}_n]\) (M = Li, Na, K) were treated with Ph3SiH2. Complexes 4–6 formally contain a pendant hypervalent dihydridosilicate and in the potassium complex 6, a weak interaction between the metal and hydride substituent can be implied. The lithium complex 4 catalyzed the hydrosilylation of styrene derivatives under mild conditions with anti-Markovnikov regioselectivity.

Reactions of two equiv. of MgR2 with \((\text{Me}_3\text{TACD})\text{H}\) resulted in the tetranuclear complexes \([(\text{Me}_3\text{TACD})\text{Mg}_2\text{R}_3]_2\) (8, R = Et (a), "Bu (b), "Bu (c)) (Fig. 4). The X-ray crystal structure of 8a shows two \([(\text{Me}_3\text{TACD})\text{Mg}_2\text{R}_3]_2\) units being bridged by a central Mg2R4 moiety through the amide nitrogen atoms.17,18 The addition of trialkyl aluminum AlR3 to compounds 7 and 8 formed Lewis acid-base adducts \([(\text{Me}_3\text{TACD})\text{AlR}_3\text{MgR}]\) (9, R = Me (a), Et (b), "Bu (c)) (Fig. 4).17

In the case of calcium, \([\text{Ca}(\eta^1\text{-C}_3\text{H}_5)]_2\) and \([\text{Ca}(\text{CH}_2\text{Ph})_2\text{M(\text{thf})}_n]\) deprotonated \((\text{Me}_3\text{TACD})\text{H}\) to give the allyl and benzyl complexes \([(\text{Me}_3\text{TACD})\text{Ca}(\eta^1\text{-C}_3\text{H}_5)]_2\) (10a) and \([(\text{Me}_3\text{TACD})\text{Ca}(\text{CH}_2\text{Ph})_2]\) (10b), respectively.19 Unlike \(\eta^1\)-allyl magnesium 7d, 10a was characterized as a dimer, with the calcium centers bridged through the amido nitrogen atoms of Me3TACD and \(\eta^1\)-coordinated allyl ligands (Fig. 5).
Macrocyclic Ligands for Molecular Hydrides of s-Block Metals

**Fig. 6** Me₃TACD-supported neutral and cationic magnesium hydride clusters 11–13 and the molecular structure of the [(Me₃TACD)₆Mg₁₃H₁₈]²⁺ dication in 12a–c.

The tetranuclear magnesium alkyls 8a and 8b reacted with one equiv. of PhSiH₃ to give the mixed alkyl hydrides [(Me₃TACD)Mg₂(m-H)₂R]²⁺ (R = Et (11a), n-Bu (11b)) (Fig. 6). In the presence of ionic Mg₂A₂, both 11a and 11b reacted further with PhSiH₃ to give the dicationic cluster [(Me₃TACD)₆Mg₁₃(m₂-H)₁₂(m₃-H)₆][A]²⁺ (A = [AlEt₄] (12a), [Al(n-Bu)₄] (12b), [B{3,5-(CF₃)₂C₆H₃}₄] (12c)) with different counter anions (Fig. 6). This dication is the largest known molecular magnesium hydride cluster and formally contains a segment of MgH₂ as ”6 [Mg(NR₂H)₂][Mg²⁻]·6 [MgH₂]”.

It decomposes above 197 °C to give dihydrogen and an intractable material. Protonolysis of tetranuclear 11 with 2 equiv. of [NEt₃H][A] (A = B{3,5-(CF₃)₂C₆H₃}₄) in the presence of 1,2-dimethoxyethane (DME) gave the dicaticionic hydride cluster [(Me₃TACD)₅Mg₂(μ-H)₂(DME)]₂⁺[A]₂⁻ (13) (Fig. 6). The Mg₁₃ cluster 12 also gave 13 upon treatment with 6 equiv. of [NEt₃H][A].

When the amido function is blocked with Al(‘Bu)₃, the monomeric [(Me₃TACD)Al(‘Bu)₃]MgH (15) with a rare terminal Mg–H bond was obtained from the reaction of the isobutyl complex 9c with AlH(‘Bu)₃. The hydridoaluminate complex [[(Me₃TACD)Al(‘Bu)₃]Mg(μ-H)Al(‘Bu)₃] (14) (Scheme 4) acts as an intermediate.

Although DFT calculation of 15 indicates a highly ionic Mg–H bond with HOMO almost entirely (> 95%) located on the terminal hydride, reactivity studies suggest the importance of steric control, as expected for a more covalent Mg–H bond. Protonolysis of 15 with weak Brønsted acids AX gave the derivatives [[(Me₃TACD)Al(‘Bu)₃]MgX] (16, X = C≡CR, NHR, OSiR₃, Hal), while reaction with N₂O gave the μ-oxo complex [[(Me₃TACD)Al(‘Bu)₃]Mg(μ-O)] (17). 1,1-Diphenylethylene (1,1-DPE) led to a 3:1 mixture of regioisomers [[(Me₃TACD)Al(‘Bu)₃]MgMe(CMePh₂)] (18a) and [(Me₃TACD)Al(‘Bu)₃]Mg(CH₂CHPh₂)] (18b) as the result of both Markovnikov (2,1-) and anti-Markovnikov (1,2-) addition of Mg–H to the C=C bond (hydromagnesiation).

Insertion of CO₂ gave the magnesium formate [(Me₃TACD)Al(‘Bu)₃]Mg(κ¹-O₂CH) (19). Reaction of 15 with BH₃(THF) gave the borohydride complex [(Me₃TACD)Al(‘Bu)₃]Mg(BH₄) (20a), whereas BPh₃ resulted in the ion pair complex [[(Me₃TACD)Al(‘Bu)₃]Mg(thf)][HBPh₃] (20b) by hydride abstraction (Scheme 5).

**Scheme 4** Me₃TACD-supported hydridoaluminate 14 and the terminal magnesium hydride 15. Molecular structure of the hydride 15.

**Scheme 5** Reactivity of Me₃TACD-supported terminal magnesium hydride 15. Molecular structure of the formate complex 19.
Treating a calcium precursor such as allyl 10a with Ph3SiH2 led to the formation of the trinuclear cationic hydride cluster [(Me3TACD)3Ca(H-H)] [SiH3Ph2] (21a) in low yields and in a somewhat obscure reaction.19

Hydrogenolysis of the calcium triphenylsilanide [(Me3TACD)Ca(SiPh3)] (22) under mild conditions (1 bar, 25–60 °C) provided a more rational route to [(Me3TACD)3Ca3(H-H)] [SiPh3] (21b) which consists of the same trinuclear cation as 21a but with [SiPh3]⁻ as the counter anion.21 Similarly, the strontium triphenylsilyl complex gave the homologous cationic tristrontium dihydride cluster [(Me3TACD)3Sr3(H-H)] [SiPh3] (23) (Fig. 7).

Similarly, the strontium triphenylsilyl complex gave the homologous cationic tristrontium dihydride cluster [(Me3TACD)3Sr3(H-H)] [SiPh3] (23) (Fig. 7).

The C₃-symmetric trinuclear dihydride cations [(Me3TACD)3M3(H-H)]⁺ are isostructural for M = Ca and Sr. The [M₃(H-H)]⁴⁺ core is trigonal bipyramidal, the hydrides being equally shared by the three metal atoms, which are additionally bridged by the amido nitrogen atoms of Me₃TACD, resulting in an almost coplanar M₃N₃ ring. The cationic strontium hydride cluster 23 underwent a facile isotope exchange with D₂ (1 bar) under ambient conditions.22 The exchange in the calcium homolog 21b was slower and occurred only at 60 °C.22

### 3. Me₄TACD Complexes

#### 3.1. Ligand Properties

The macrocyclic tetraamine ligand, Me₄TACD (also called 12-TMC⁴⁻ or Me₄cyclen⁴⁻) has been used in coordination chemistry of 3d metals as a redox non-innocent supporting ligand. It was first developed in 1982 to study the effect of N-methylation of cyclic polyamines on the coordination number of late transition metals such as Ni and Cu.²³ and extensively used by Nam et al. to study O₂ activation at Cr, Mn, Fe, Co, Ni, and Cu centers.²³⁻²⁴

![Me₄TACD-supported cationic calcium and strontium hydride clusters 21a-b and 23 and the molecular structure of 23 showing the cation [(Me₄TACD)₃Sr(H₂)]⁺.](image)

The Me₄TACD ligand adopts a C₄-symmetric, boat-like conformation upon complexation to a metal fragment MLX (Fig. 8). The four nitrogen atoms of the ligand form a square planar core with the coordinated metal residing above the plane and all the four NMe groups pointing towards the metal.²⁴ To avoid steric congestion, the four CH₂CH₂ groups assume staggered conformation in the solid state, giving rise to two enantiomers (dddd, llll) for an achiral metal center. The CH₃ protons of the ligand are magnetically inequivalent, leading to AA′XX′-type signal sets for CH₂CH₂ groups in the ¹H NMR spectrum.

#### 3.2. Group 1 Metal Complexes

The alkali metal silanides [MSiH₃]ₙ (M = Li–Cs) have recently been studied as the hydrogenated form of the hydrogen storage material MSi, which is known to be a Zintl phase consisting of M⁺ and Si₄⁻.²⁵ Employing the macrocyclic Me₄TACD ligand a series of molecular alkali metal silanides [(Me₄TACD)M(SiH₃)]ₙ (M = Li (28), Na (29), K (30) and Rb (31); n = 1–2) have been obtained by treatment of the triphenylsilanides [(Me₄TACD)M(SiPh₃)]ₙ (M = Li (24), Na (25), K (26), Rb (27); n = 1 (Li–K), 2 (Rb)) with H₂.²⁶

![Scheme 6 Synthesis of Me₄TACD stabilized alkali metal silanides and the molecular structure of the potassium silanide 30.](image)

Remarkably, instead of the highly polar metal-silicon bond the covalent carbon-silicon bond is hydrogenolyzed to give benzene as the by-product (Scheme 6).²⁶b The triphenylsilanes 24–27 were prepared from the reaction of Me₄TACD, disilane Ph₃SiSiMe₃, and LiCH₂SiMe₃, or MO'Bu (M = Na–Rb) or by the ligand exchange reaction of...
[MSiPh(thf)] with Me₄TACD. The sodium trihydridosilanide 29 exists in monomeric form with square pyramidal coordination geometry around the sodium atom, and the potassium and rubidium analogues 30 and 31 form dimers in the solid state with SiH₃ anions binding the two [(Me₄TACD)-M] (M = K, Rb) fragments.

3.3. Group 2 Metal Complexes

Whilst Me₄TACD gave high nuclearity magnesium hydride clusters, reacting bis(hexamethyldisilazide) [Mg{N(SiMe₃)₂}(thf)] and Me₄TACD with PhSiH₃ in aromatic solvents provided the dinuclear complex [(Me₄TACD)Mg(μ-H₂)₂Mg{N(SiMe₃)₂}(thf)] (32). Alternately, compound 32 was also prepared by reacting magnesium dihydride [MgH₂] with [NEt₃H][A] (35). Compound 32 was also prepared by reacting magnesium dihydride [MgH₂(thf)] with [Mg{N(SiMe₃)₂}(thf)] and Me₄TACD. The dinuclear structure of 32 can be viewed as monomeric [(Me₄TACD)-MgH₂] stabilized by [Mg{N(SiMe₃)₂}]-. Partial protonolysis of 32 with [NEt₃H][A] (A⁺ = B(C₆H₄-3,5-Me₂)₄) afforded the dimeric cationic magnesium hydride [(Me₄TACD)₂Mg(μ-H₂)] [A]₂ (33) (Scheme 7). In the D₅h-symmetric structure of 33, two macrocyclic ligands bind the [Mg(μ-H₂)]³⁺ core in a κ¹-coordination mode and exist in a staggered conformation (Scheme 7), which differs from its calcium analogue that shows an eclipsed conformation (vide infra).

Hydridic nature of the Mg–H functionality in 33 was exploited in the reaction with the weak Brønsted acids [NET₃H] Cl and PhC≡CH, affording the monomeric magnesium complexes [(Me₄TACD)MgX][A] (X = Cl (34a), C≡CPh (34b)) (Scheme 8). In comparison, neutral magnesium halide and acetylide complexes supported by bidentate nacnac ligands are typically dimeric. Lewis acids such as BH₃(thf) and HBpin bind to 33 to give the mononuclear adducts [(Me₄TACD)-Mg(μ-H),BH][A] (35) and [(Me₄TACD)Mg(μ-H)BHpin][A] (36), respectively (Scheme 8). While insertion of CO₂ into the Mg–H bond gave the dimeric formato complex [(Me₄TACD)₂Mg₂(μ-O₂CH₂)][A]₂ (37), the reactions with RN=C=NR (R = 2,6-Pr₂-C₆H₄) afforded the monomeric compound [(Me₄TACD)Mg{(RN)₂CH}][A] (38), respectively (Scheme 8). Magnesium hydride 33 also reduces pyridine at slightly elevated temperature to give the 1,2-dihydridopyridyl complex [(Me₄TACD)Mg(1,2-DHP)][A] (39a), which isomerizes to the thermodynamically more stable 1,4-isomer [(Me₄TACD)Mg(1,4-DHP)][A] (39b) in the presence of [Mg(thf)₆][A] (Scheme 8). A series of Me₄TACD ligated neutral and cationic calcium silyl, benzyl and allyl complexes [(Me₄TACD)CaR₂](thf) (R = SiPh₃ (40a), CH₂Ph (40b)) and [(Me₄TACD)CaR(thf)][BAr₄] (R = CH₂Ph, Ar = C₆H₄-3,5-Me₂ (41a), Ar = C₆H₄-4-Bu (41b); R = η⁵-C₅H₄, Ar = C₆H₄-3,5-Me₃ (42)) were also synthesized as potential precursors for molecular calcium hydride starting with [CaR₂(thf)] (n = 4 (CH₂Ph), n = 0 (η⁵-C₅H₄)) and Me₄TACD or [(Me₄TACD)H][BAr₄], or [(Me₄TACD)CaR₂] and [NET₃H][BAr₄] (Fig. 9).

Hydrogenolysis of bis(triphenylsilyl)calcium [(Me₄TACD)-Ca(SiPh₃)₂] (40a) under mild conditions (1 bar of H₂, 25 °C) resulted in the calcium hydride [(Me₄TACD)₂CaH₂][SiPh₃]...
(43a), isolated as red crystals. The molecular structure of the cation revealed a monocapped trigonal-prismatic coordination geometry around the seven-coordinate calcium centers (Scheme 9). Complex 43a undergoes H/D exchange in solution when treated with D2.

The reaction of neutral dibenzyl calcium complex 40b with Ph3SiH produced the thermolabile dicationic calcium hydride [(Me4TACD)2CaH2][PhCHSiPh3]2 (44a). More stable dicationic calcium hydrides [(Me4TACD)2Ca2H2][BAr4]2 (Ar = C6H3-3,5-Me2 (44b), Ar = C6H3-4-tBu (44c)) were obtained with borate anions upon hydrogenolysis of the cationic mono(benzyl) complexes 41 under ambient conditions (Scheme 10). While the hydrogenolysis of 44a selectively gave the dicalcium trihydride [(Me4TACD)2Ca2H3][PhCHSiPh3]2 (43c), the dihydrides 44b and 44c with borate anions did not provide the corresponding trihydride when treated with H2.

The Brønsted basicity of the molecular calcium hydride 44b-thf was shown in the reactions with terminal alkynes RC≡CH (R = SiMe3, cyclopropyl) and 1,4-diphenylbutadiene, affording the dinuclear complexes [(Me4TACD)2Ca2(m-OCHO)]2[BAr4]2 (47) and [(Me4TACD)2Ca2(m-OCH=CHO)]2[BAr4]2·3.5 THF (48) (Scheme 11). While the reaction with BH3(thf) gave the tetrahydridoborate complex [(Me4TACD)Ca(BH4)(thf)]2[BAr4]2 (49), reaction with tris(dimethylsilyle)amine and (alkoxy)hydrosilane (MeO)2SiMeH afforded [(Me4TACD)2Ca{N(SiMe2H)2}]2[BAr4]2 (50) and [(Me4TACD)2Ca2(m-OMe)]2[BAr4]2 (51) after cleavage of silyl-amide and silyl-ether bonds, respectively (Scheme 11). The cationic difluorido complex [(Me4TACD)2Ca2(m-F)]2[BAr4]2 (52) was obtained from 44b-thf upon H/F exchange with fluorobenzene at 45a, isolated as red crystals. The molecular structure of the cation revealed a monocapped trigonal-prismatic coordination geometry around the seven-coordinate calcium centers (Scheme 9). Complex 43a undergoes H/D exchange in solution when treated with D2.

The reaction of neutral dibenzyl calcium complex 40b with Ph3SiH produced the thermolabile dicationic calcium hydride [(Me4TACD)2CaH2][PhCHSiPh3]2 (44a). More stable dicationic calcium hydrides [(Me4TACD)2Ca2H2][BAr4]2 (Ar = C6H3-3,5-Me2 (44b), Ar = C6H3-4-tBu (44c)) were obtained with borate anions upon hydrogenolysis of the cationic mono(benzyl) complexes 41 under ambient conditions (Scheme 10). While the hydrogenolysis of 44a selectively gave the dicalcium trihydride [(Me4TACD)2Ca2H3][PhCHSiPh3]2 (43c), the dihydrides 44b and 44c with borate anions did not provide the corresponding trihydride when treated with H2.

The Brønsted basicity of the molecular calcium hydride 44b-thf was shown in the reactions with terminal alkynes RC≡CH (R = SiMe3, cyclopropyl) and 1,4-diphenylbutadiene, affording the dinuclear complexes [(Me4TACD)2Ca2(m-OCHO)]2[BAr4]2 (47) and [(Me4TACD)2Ca2(m-OCH=CHO)]2[BAr4]2·3.5 THF (48) (Scheme 11). While the reaction with BH3(thf) gave the tetrahydridoborate complex [(Me4TACD)Ca(BH4)(thf)]2[BAr4]2 (49), reaction with tris(dimethylsilyle)amine and (alkoxy)hydrosilane (MeO)2SiMeH afforded [(Me4TACD)2Ca{N(SiMe2H)2}]2[BAr4]2 (50) and [(Me4TACD)2Ca2(m-OMe)]2[BAr4]2 (51) after cleavage of silyl-amide and silyl-ether bonds, respectively (Scheme 11). The cationic difluorido complex [(Me4TACD)2Ca2(m-F)]2[BAr4]2 (52) was obtained from 44b-thf upon H/F exchange with fluorobenzene at
elusive, while alkaline earth dihydride [(Me₄TACD)MH₂] as anti provide monodentate amido ligands are used. Related to the formation of even larger hydride clusters when MH²⁻ remain elusive, while alkaline earth dihydride [(Me₄TACD)MH₂] as well as monohydride [(Me₃TACD)MH] and [(Me₄TACD)MH⁻] were recognized as part of polymeric complexes. The general principle of de-aggregating solid metal ligands with a stable ionic lattice to obtain molecular complexes appears to be feasible using NNNN macrocyclic ligands.

As expected the ring size is of critical importance. When the 9-membered TACN derivatives were coordinated at group 2 metals Mg and Ca, larger hydride clusters resulted. This is related to the formation of even larger hydride clusters when monodentate amido ligands are used.

In conclusion, our detailed study of molecular hydrides undoubtedly allows to understand the inherent properties of s-block metal cations as well as the nature of the metal-hydride bond. While the application of such complexes as reagents and homogeneous catalysts has started to gain attention, whether s-block metals ever reach the activity and selectivity of transition metals remains to be seen.

Acknowledgment

Our work has been funded by the German Research Foundation (DFG), in particular in the years 2010 to 2019 through the International Research Training Group “Selectivity in Chemo- and Biocatalysis” that allowed us to establish cooperation with Profs. Kazushi Mashima and Takashi Hayashi of Osaka University. This article is dedicated to the memory of Prof. Malcolm L. H. Green (1936–2020).

References

1. N. A. A. Rusman, M. Dahari, Int. J. Hydrogen Energy 2016, 41, 12108–12126.
2. R. H. Crabtree, The Organometallic Chemistry of the Transition Metals, 7th Edition, Wiley, Hoboken, NJ, 2019.
3. a) W. N. M. van Leeuwen, Homogeneous Catalysis: Understanding the Art, Kluwer, Dordrecht, 2006. b) D. Steinborn, Fundamentals of Organometallic Catalysis, Wiley-VCH, Weinheim, 2012.
4. a) G. Wilkinson, J. M. Birmingham, J. Am. Chem. Soc. 1954, 76, 4281–4284. b) G. Wilkinson, J. M. Birmingham, J. Am. Chem. Soc., 1954, 76, 6210.
5. a) H. Brintzinger, I. E. Berzawa, J. Am. Chem. Soc., 1971, 93, 2045–2046. b) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, Angew. Chem. Int. Ed. Engl. 1995, 34, 1143–1170.
6. a) M. Ohashi, M. Konkol, I. D. Rosal, R. Poteau, L. Maron, J. Okuda, J. Am. Chem. Soc. 2008, 130, 6920–6921. b) D. Mukherjee, J. Okuda, Chem. Commun. 2018, 54, 2701–2714.
7. a) W. Fegler, A. Venugopal, T. P. Spaniol, L. Maron, J. Okuda, Angew. Chem. Int. Ed. 2013, 52, 7976–7980. b) A. Venugopal, W. Fegler, T. P. Spaniol, L. Maron, J. Okuda, J. Am. Chem. Soc. 2011, 133, 17574–17577. c) W. Fegler, A. Venugopal, M. Kramer, J. Okuda, Angew. Chem. Int. Ed. 2015, 54, 1724–1736. d) T. Shimamoto, Z. Hou, Recent Development in Clusters of Rare Earths and Actinides: Chemistry and Materials (Z. Zheng, Ed.), Springer, 2016, p. 315–336.
8. a) D. Mukherjee, J. Okuda, Angew. Chem. Int. Ed. 2018, 57, 1458–1473. b) D. Mukherjee, D. Schuhknecht, J. Okuda, Angew. Chem. Int. Ed. 2018, 57, 9590–9602.
9. S. Arndt, J. Okuda, Chem. Rev. 2002, 102, 1953–1976.
10. J. K. Beattie, Acc. Chem. Res. 1971, 4, 253–259.
11. a) S. Aime, M. Botta, G. Ermondi, Inorg. Chem. 1992, 31, 4291–4299. b) S. Aime, M. Botta, M. Fasano, M. P. M. Marques, C. F. G. C. Geraldes, D. Pubanz, A. E. Merbach, Inorg. Chem. 1997, 36, 2059–2068.
12. M. Lappert, A. Protchenko, P. Power, A. Seeber, Metal Amide Chemistry, Wiley, Hoboken, NJ, 2008.
13. S. Standfuss, T. P. Spaniol, J. Okuda, Eur. J. Inorg. Chem. 2010, 2987–2991.
14. D. Schuhknecht, V. Leich, T. P. Spaniol, J. Okuda, Chem.–Eur. J. 2018, 24, 13424–13427.
15. a) D. Mukherjee, T. P. Spaniol, J. Okuda, Dalton Trans. 2017, 46, 651–655. b) H. Osseili, K.-N. Truong, T. P. Spaniol, L. Maron, U. Englert, J. Okuda, Angew. Chem. Int. Ed. 2019, 58, 1833–1837.
16. D. Martin, Doctoral Dissertation, RWTH Aachen University, 2015.
17. D. Martin, K. Beckerle, S. Schnitzler, T. P. Spaniol, L. Maron, J. Okuda, Angew. Chem. Int. Ed. 2015, 54, 4115–4118.
18. P. Jochmann, J. M. Pavin, T. P. Spaniol, L. Maron, J. Okuda, Angew. Chem. Int. Ed. 2012, 51, 4452–4455.
19. a) S. Schnitzler, T. P. Spaniol, L. Maron, J. Okuda, Chem.–Eur. J. 2015, 21, 11330–11334. b) S. Schnitzler, T. P. Spaniol, J. Okuda, Inorg. Chem. 2016, 55, 12997–13006. c) L. E. Lemmerz, V. Leich, D. Martin, T. P. Spaniol, J. Okuda, Inorg. Chem. 2017, 56, 14979–14990.
20. V. Leich, T. P. Spaniol, J. Okuda, Inorg. Chem. 2015, 54, 4927–4933.
21. D. Mukherjee, T. Höfflerhage, V. Leich, T. P. Spaniol, U. Englert, L. Maron, J. Okuda, J. Am. Chem. Soc. 2018, 140, 3403–3411.
22. a) J. H. Coates, D. A. Hadi, S. F. Lincoln, Aust. J. Chem. 1982, 35, 903–909. b) J. Cho, R. Sarangi, J. Annaraj, S. Y. Kim, M. Kubo, T. Ogura, E. I. Solomon, W. Nam, Nat. Chem. 2009, 1, 568–572. c) J. Cho, R. Sarangi, W. Nam, Acc. Chem. Res. 2012, 45, 1321–1330.
Award Accounts

24 a) H. Bhakhoa, L. Rhyman, E. P. Lee, D. K. W. Mok, P. Ramasami, J. M. Dyke, 
*Dalton Trans.*, **2017**, 46, 15301–15310. b) H. Osseili, K.-N. Truong, T. P. Spaniol, D. Mukherjee, U. Englert, J. Okuda, 
*Chem. –Eur. J*. **2017**, 23, 17213–17216.

25 a) W. S. Tang, J.-N. Chotard, P. Raybaud, R. Janot, 
*Phys. Chem. Chem. Phys.* **2012**, 14, 13319–13324. b) A. Jain, T. Ichikawa, S. Yamaguchi, H. Miyaoka, Y. Kojima, 
*Phys. Chem. Chem. Phys.* **2014**, 16, 26163–26167.

26 a) D. Schuhknecht, V. Leich, T. P. Spaniol, I. Douair, L. Maron, J. Okuda, 
*Chem. –Eur. J.* **2020**, 26, 2821–2825. b) V. Leich, T. P. Spaniol, J. Okuda, 
*Chem. Commun.* **2015**, 51, 14772–14774.

27 L. E. Lemmerz, D. Mukherjee, T. P. Spaniol, A. Wong, G. Ménard, L. Maron, J. Okuda, 
*Chem. Commun.* **2019**, 55, 3199–3202.

28 L. E. Lemmerz, A. Wong, G. Ménard, T. P. Spaniol, J. Okuda, 
*Polyhedron* **2020**, 178, 114331.

29 a) M. Arrowsmith, M. R. Crimmin, M. S. Hill, S. L. Lomas, D. J. MacDougall, M. F. Mahon, 
*Organometallics* **2013**, 32, 4961–4962. b) J. Pahl, T. E. Stennett, M. Volland, D. M. Guldi, S. Harder, 
*Chem. –Eur. J.* **2019**, 25, 2025–2034.

30 V. Leich, T. P. Spaniol, L. Maron, J. Okuda, 
*Angew. Chem. Int. Ed.* **2016**, 55, 4794–4797.

31 D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron, J. Okuda, 
*Angew. Chem. Int. Ed.* **2017**, 56, 12367–12371.

32 D. Schuhknecht, T. P. Spaniol, L. Maron, J. Okuda, 
*Angew. Chem. Int. Ed.* **2020**, 59, 310–314.

33 D. Schuhknecht, T. P. Spaniol, Y. Yang, L. Maron, J. Okuda, 
*Inorg. Chem.* **2020**, 59, 9406–9415.

34 a) S. Schnitzler, T. P. Spaniol, J. Okuda, 
*Dalton Trans.* **2017**, 46, 1761–1765. b) D. Schuhknecht, T. P. Spaniol, I. Douair, L. Maron, J. Okuda, 
*Chem. Commun.* **2019**, 55, 14837–14839.

35 M. Wiesinger, B. Maitland, C. Färber, G. Ballmann, C. Fischer, H. Elsen, S. Harder, 
*Angew. Chem. Int. Ed.* **2017**, 56, 16654–16659.

36 P. P. Power, *Nature* **2010**, 463, 171–177.

Profile

Priyabrata Ghana

Priyabrata Ghana obtained his B.Sc. degree in Chemistry from the University of Calcutta in 2009, and M.Sc. degree from the Indian Institute of Technology, Kanpur in 2011. After his M.Sc., he moved to Germany and received his Dr. rer. nat. degree at the University of Bonn in 2017 under the supervision of Alexander C. Filippou at the interface between molecular transition metal and main group element chemistry. Currently, he is a postdoctoral fellow in the group of Jun Okuda at the RWTH Aachen University, working on small molecule activation using early transition metal complexes.

Jun Okuda

Jun Okuda, born in Osaka/Japan, received his Dr. rer. nat. degree at the RWTH Aachen University in 1984 with G. E. Herberich and was a postdoctoral associate at MIT with R. R. Schrock. After his habilitation at the Technical University Munich in 1991, he held academic positions at the State University of New York at Albany, the University of Marburg, and the University of Mainz before assuming the Chair of Organometallic Chemistry at the RWTH Aachen University in 2003. In 2013, he was elected a member of the North Rhine-Westphalian Academy of Sciences, Humanities and in 2018 was awarded an honorary degree from Osaka University. His research interest includes earth-abundant metal complexes for catalysis, artificial metalloenzymes, and energy applications.