



BIAN-Aluminium-Catalysed Imine Hydrogenation

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On the occasion of the 60th birthday of Matthias Beller

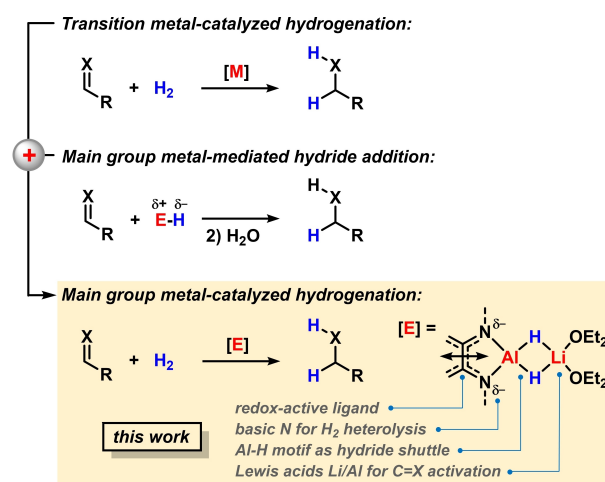
Hydrogenations have been dominated by transition metal catalysis, while the use of more abundant and inexpensive main group metal catalysts has remained a great challenge. Here, a bimetallic Li/Al dihydride was successfully applied to catalytic

hydrogenations of imines. The catalyst $[(\text{DippBIAN})\text{Al}(\mu\text{-H})_2\text{Li}(\text{OEt})_2]$ was easily prepared from the 2e-reduced BIAN derivative and LiAlH_4 .

Introduction

Catalytic hydrogenations are among the most important synthetic processes in the production of technical, pharmaceutical, and fine chemicals. These transformations commonly employ catalysts based on late transition metals (Rh, Pd, Pt, Fe, Co, Ni) that enable great efficiencies and broad applications.^[1] Hydride additions are an alternative class of reduction reactions that mostly utilize main group metal hydrides based on B, Al, Si for the transfer of a formal hydride anion to an electrophilic function.^[2] Upon sequential combination with a protolytic work-up in acidic or aqueous media, an overall 1,2-dihydrogen addition to unsaturated C=C or C=X bonds can be effected, albeit with generally lower chemoselectivity. These reactions require stoichiometric amounts of a metal hydride which prohibits applications on larger scales. The development of main group metal-catalysed hydrogenations aims at a merger of both synthetic concepts that would benefit from the use of inexpensive H_2 gas as stoichiometric reductant and H atom source and the replacement of rare and toxic metal catalysts by more abundant main group elements (Scheme 1).

Aluminium is the most abundant metal in the earth's crust, it is inexpensive and much less toxic than most heavier metals. Covalent aluminium hydride derivatives – such as lithium



Scheme 1. Merging the mechanistic concepts of transition metal-catalysed hydrogenations and metal-mediated hydride additions into the development of main group metal-catalysed hydrogenation reactions. This report involves the synthesis of a modular amidoaluminium hydride complex and its application to catalytic imine hydrogenations.

aluminium hydride (LiAlH_4) and diisobutylaluminium hydride (DiBAL-H) – find wide use as stoichiometric reductants of polar single (C–X) and double bonds (C=X).^[3] Catalytic applications of aluminium compounds include the employment of alkylaluminium co-catalysts in technical Ziegler-type Aufbau reactions^[4] and Lewis acidic Al(III) complexes in polar addition reactions on lab-scales.^[5] The potential of aluminium hydride catalysts was only recently untapped in hydrofunctionalization and hydrogenation reactions.^[1a,6–9] The reactions most likely operate via heterolytic activation of dihydrogen at a metal ion and a basic ligand.^[7] From recent literature reports and our own studies into the development of active aluminium catalysts for hydrogenations,^[1a,6–9] we reasoned that an effective yet operationally simple protocol would fulfil the following criteria: i) the catalyst can be rapidly assembled from a commercial Al(III) precursor; ii) the catalyst contains an electron-rich ligand that imparts basic properties on the donor atoms to enable heterolytic H_2 activation and to prevent unwanted aggregation; iii) the catalyst contains Lewis acidic metal ions that may

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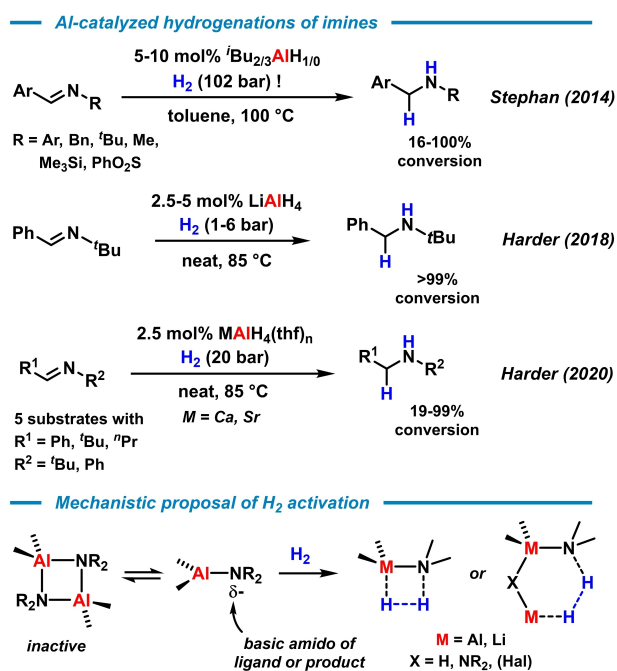
activate Lewis basic substrates by coordination; and *iv*) the catalyst structure can accommodate active hydride ligands at the Al centre. With these framework conditions, we have developed an easily accessible modular diamidoaluminium- μ_2 -dihydrido lithium complex that exhibited high activity in catalytic imine hydrogenations (Scheme 1, bottom).

The hydrogenation of imines is a key strategy in technical and lab-scale preparations of secondary amines that is based on the facile access to the starting materials from condensation reactions, the availability of inexpensive H_2 , and the high activity of transition metal catalysts. Commonly, late transition metals (Ru, Ir, Pd) are being employed.^[10] Fewer examples of alternative catalysts (Zn, Ti, Mn, Fe, Co, Ni, Zr, U, Sm, Ca, Sr, Ba,^[11,12] and organo-catalysts^[13]) have been reported. Despite the numerous applications of stoichiometric aluminium hydride reagents to imine reductions, the development of Al-catalysed hydrogenation protocols has remained an unresolved challenge (Scheme 2). Stephan *et al.* reported the first catalytic application of *i*-butyl-aluminium hydrides to hydrogenations of benzaldimines at harsh conditions (102 bar H_2 , 100 °C). The absence of ligands favoured the formation of an inactive dimer.^[6] Harder and co-workers adopted milder conditions (1 bar H_2 , 85 °C) when employing the more basic hydride complex $LiAlH_4$ but at the expense of a very narrow substrate scope.^[7] A theoretical study suggested that the catalytically active species may contain active hydrides coordinated to Li or Al ions and two amido ligands (*i.e.* deprotonated product).^[7] The authors proposed a mechanism that involves H_2 -heterolysis by the amide and Li ion (Scheme 2, bottom). Such autocatalytic mechanism by incorporation of the amine products in the active catalyst species, however, should exhibit a strong correlation of catalytic turnover with the stereo-electronic

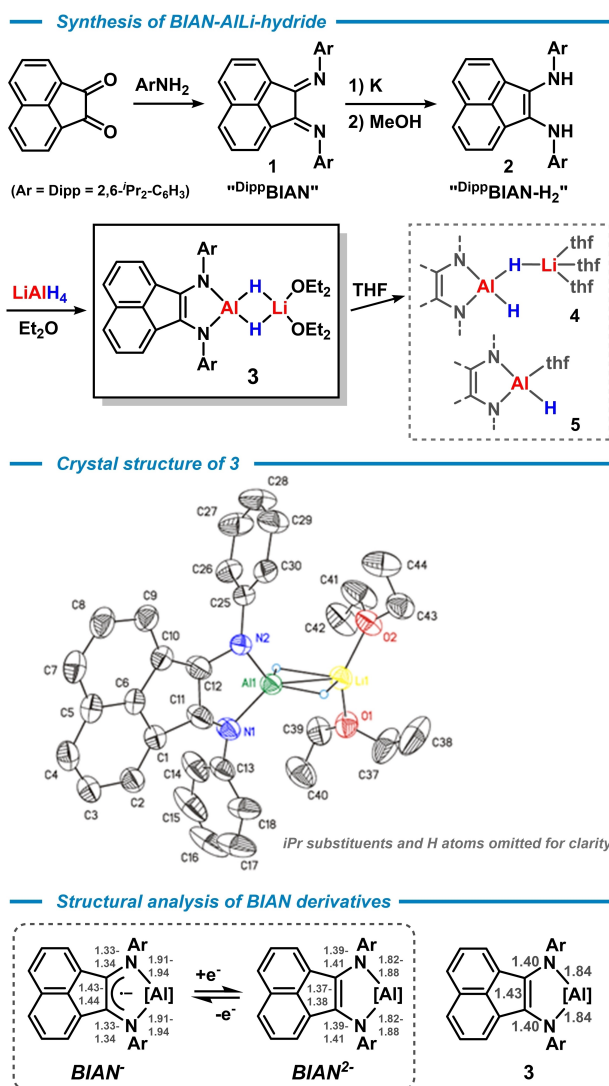
properties of the produced amines which ultimately limits broad applications. Indeed, high activities were only observed for *N*-*tert*-butyl imines. Later, an improved protocol was reported with bimetallic alkaline earth metal (Ae = Ca, Sr) aluminates.^[8] Building upon the few literature precedents and the postulated notion of a bifunctional H_2 -activation mechanism,^[6–8] we considered the implementation of a chelating, Brønsted basic and redox-active *N,N*-ligand that may exhibit enhanced thermodynamic stability (even after formal *N*-protonation by H_2 heterolysis) and impart steric and electronic stabilization of the Al centre in various steps of the catalytic mechanism. We aimed at an easily accessible heterobimetallic catalyst structure that harbours ample opportunities for both metals to act as Lewis acids in substrate activation and as hydride shuttles (Scheme 1, bottom).

Results and Discussion

We commenced our study with the identification of a suitable ligand backbone that accommodates Al in a chelating coordination geometry and with flexible stereo-electronic properties. Several examples of aluminium complexes bearing Brønsted basic and redox-active ligands were recently reported. Berben *et al.* reported Al(III)-amido complexes based on pyridyl imine ligands that mediate proton/electron transfer steps.^[4,14] Fedushkin and co-workers prepared complexes of aluminium with bis(imino)acenaphthene (BIAN) ligands and studied their structure-activity relationships under various conditions and with diverse sets of low-molecular weight substrates (alkynes, ketones, amines, alcohols, or pyridines).^[5,15] The BIAN ligand family displays great advantages by virtue of *i*) their modular synthesis from acenaphthenedione and various amines; *ii*) the stable aromatic backbone and chelating 1,2-diimine motif; *iii*) the ability to engage in stabilizing or directing arene- π -interactions between the arene backbone or the peripheral anilines with aromatic substrates; *iv*) their high capacity as electron reservoir (up to 6e-reduction) and facile redox-activity, and *v*) the rich coordination chemistry with many main group^[16] and transition metal ions.^[17] A significant body of research on BIAN-complexes has been documented by Fedushkin and co-workers over the past years.^[3,5,15] We adopted a two-step protocol starting from the easily accessible diimine ^{Dipp}BIAN (1, Dipp = 2,6-diisopropylphenyl): Reaction of 1 with 2 equiv. K and protolysis cleanly afforded the enediamine 2 (BIAN- H_2). Subsequent addition of $LiAlH_4$ in diethyl ether (Et_2O) resulted in rapid colour change to green and formation of a single aluminium hydride complex (Scheme 3).^[3b] D-2ark green single crystals were obtained by recrystallization from diethyl ether at -20 °C. Complex 3 is thermally stable and showed only minimal evolution of H_2 at 100 °C for 24 h (~5%). The crystal structure of 3 displayed the desired reduced BIAN-Al motif and a central Al(μ - H) $_2$ Li tetragon. Contrary to related aluminium hydride complexes 4 and 5 from Fedushkin *et al.*,^[3b] both hydrides adopt μ^2 -bridging modes, possibly due to the lower coordination ability of Et_2O vs. THF. IR spectra of 3 showed an Al-H band in solution and solid state, so that the integrity of the hydride



Scheme 2. Literature reports of Al-catalysed hydrogenations of imines.^[6–9]



Scheme 3. Top: Synthesis of the LiAl- μ_2 -dihydride **3** by sequential reduction, hydrolysis, reduction. Structurally related complexes **4** and **5**.^[3b] Centre: ORTEP plot (50% probability) of the molecular structure of **3**. Selected bond lengths (Å): C(11)–C(12) 1.429(4), C(11)–N(1) 1.397(3), C(13)–N(1) 1.418(3), N(1)–Al(1) 1.842(2), Al(1)–H(Al) 1.56(3), Li(1)–H(Al) 2.01(3), Li(1)–Al(1) 2.608(5), O(1)–Li(1) 1.898(5). Bottom: Average literature data of bond distances in Al(III)–BIAN complexes.^[3b,18]

motifs could be concluded (solid: 1685 cm^{-1} , in Et_2O : 1753 cm^{-1}). Complex **4** gave bands at 1737, 1677 cm^{-1} (solid state) and 1750, 1667 cm^{-1} (in THF).^[18] The electronic state of the BIAN ligand in **3** can be derived from the bond distances (Scheme 3, bottom). Coordination of both H atoms to the Li ion resulted in reduced electron density and longer bond distance of the central C1–C2 bond than in the related aluminium hydride complex **4** (1.429(4) in **3** vs. 1.372(3) in **4**; cf. 1.441(3)–1.424(4) of dialkylaluminium complexes with BIAN[−] ligand states, all in Å).^{[3b][19]} The C–N bond lengths indicate the presence of the dianionic BIAN^{2−} state (1.397(3), 1.418(3) Å in **3** vs. 1.387(2), 1.394(2) Å in **4**).^[3b] The radical monoanionic BIAN^{•−} display typical C–N bond lengths of 1.32–1.34 Å.^[19] NMR (Evans method) and EPR spectra were not indicative of radical species.

Complex **3** was further characterized by LIFDI-MS and elemental analysis. Rapid conversion of **3** to **4** was observed in THF solution (XRD, EA, NMR, IR).^[3b] A distinct behaviour of **3** in the presence of unsaturated C=C bonds was first observed when dissolving **3** in aromatic solvents (benzene-*d*₆, toluene-*d*₈): deep blue solutions formed that gave broad ¹H-NMR signals, possibly as consequence of a highly flexible or oligomeric structure.^[20] In contrast, benzene solutions of **4** gave sharp ¹H-NMR resonances.

The catalytic activity of complex **3** in the hydrogenation of imines was initially explored with the model substrate *N*-phenyl benzalimine (Table 1).^[6–8] Clean hydrogenation to *N*-phenyl benzyl-amine was observed at lower catalyst loading and lower H₂ pressure than the literature precedents.^[6] Near-quantitative yields of amine formation were obtained with 10 mol% of pre-catalyst **3** at 50 bar H₂ and 100 °C in 1.7 M toluene solution (entry 2). Alternative aluminium hydrides and *i*Bu₃Al gave significantly lower conversions (entries 6–10). The lithium alkoxyaluminium hydride **6** and the Li-free BIAN complex **5** were inactive (entries 8–9).^[3b] Importantly, the mixture of LiAlH₄ and ligand **2** (with 30 mol% Et₂O) was an equally competent catalyst as **3** whereas LiAlH₄ alone gave much lower yield (entries 10–11).^[7] Change of the alkali ion by using catalytic NaAlH₄ and ligand **2** afforded only 42% yield (entry 12). All reactions operated at high substrate concentrations in toluene.^[6]

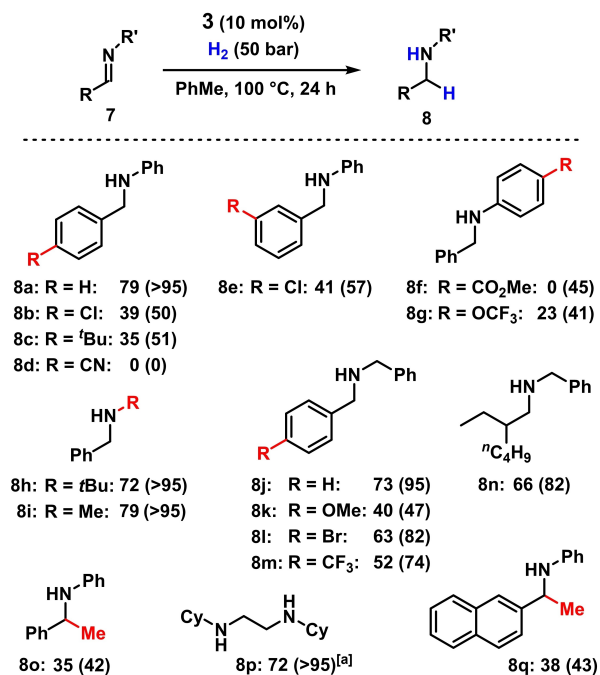
The optimized conditions were applied to hydrogenations of a diverse set of *N*-aryl and *N*-alkyl imines (Scheme 4). The reaction proceeded with high conversions of most substrates.^[21] The discrepancies between GC-conversions and isolated yields are due to product losses during work-up. No side reactions were observed (GC, MS, NMR). The reaction tolerated Cl, Br, CF₃, OCF₃, and methoxy substituents. Electrophilic groups such as

Table 1. Selected optimizations of the Al-catalysed imine hydrogenation.

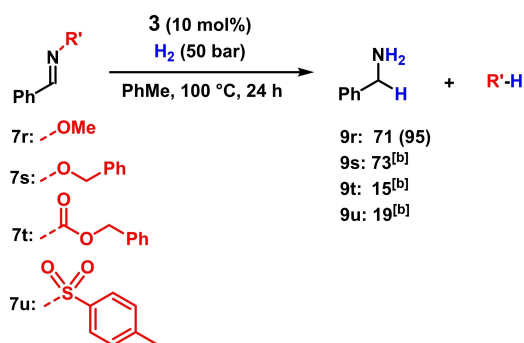
Entry	Deviations from conditions above ^[a]	Yield [%] ^[a]
1	100 bar H ₂	> 95
2	–	> 95; 65 ^[b]
3	5 mol% 3 , 100 bar H ₂	73
4	25 bar H ₂ , 85 °C	78; 39 ^[b]
5	25 °C	18
6	10 mol% <i>i</i> Bu ₂ AlH	36
7	10 mol% <i>i</i> Bu ₃ Al	19
8	10 mol% Li[<i>t</i> BuO) ₃ AlH] (6)	9
9	10 mol% 5	10
10	10 mol% LiAlH ₄	50
11	10 mol% [LiAlH ₄ + 2] ^[c]	> 95
12	10 mol% [NaAlH ₄ + 2] ^[c]	42
13	10 mol% [LiAlH ₄ + 1]	29
14	10 mol% LiAlH ₄ ^[c]	56
15	10 mol% <i>i</i> Bu ₂ AlH, 100 bar H ₂	94 ^[b,d]

[a] For experimental details, see the Supporting Information. GC yields vs. internal *n*-pentadecane. [b] Neat conditions (solvent-free). [c] 30 mol% Et₂O. [d] Conditions from ref. [6].

Hydrogenations of imines



Tandem hydrogenation-deprotection

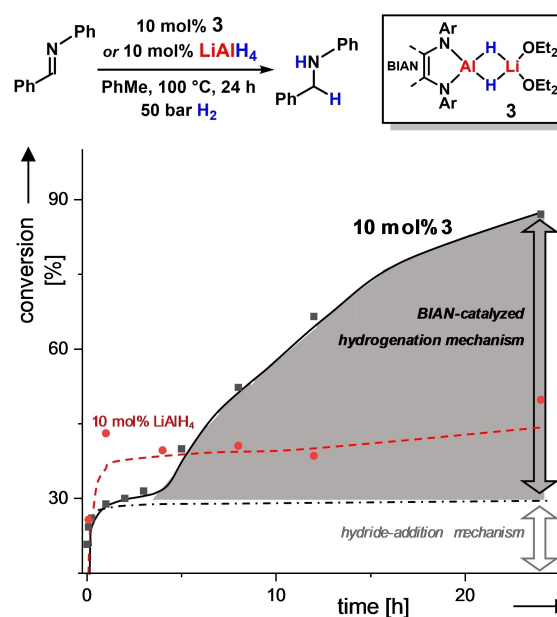


Scheme 4. Substrate scope of the **3**-catalyzed imine hydrogenation. Isolated yields (conversions from GC-FID in parentheses). [a] 20 mol% **3**. [b] ¹H NMR yield with 1,3,5-trimethoxybenzene as internal standard.

CN and CO₂Me underwent competing reductions to give complex product mixtures that were not isolated. Hydrogenations of various imines bearing *N*-aryl, *N*-alkyl, and *N*-benzyl substitutions were successfully performed. Ketimines were challenging substrates that gave moderate hydrogenation yields (**8o**, **8q**). Tandem hydrogenation-defunctionalisation reactions could be achieved with bifunctional substrates: Oximes enabled dual hydrogenations of both the N–O and C=N functions and cleanly afforded the primary amines (**7r**, **7s**, Scheme 4, bottom). Carbamate and sulfonamide functions underwent competing reductions at much lower rates (**7t**, **7u**).

Detailed reaction progress analyses of the imine hydrogenations were performed at 50 bar H₂ and 100 °C with catalytic LiAlH₄ and **3**, respectively (Scheme 5). Two distinct mechanistic scenarios can be concluded: Fast amine formation operates at short reaction times (~30 min) which most likely involves direct

Reaction progress analyses



Scheme 5. Reaction progress analyses of LiAlH₄-mediated reduction and Al/BIAN-catalysed hydrogenation reveal the operation of a fast stoichiometric hydride addition mechanism (with transfer of four hydrides from LiAlH₄ and two hydrides from **3**; dashed lines) and a slower BIAN-catalysed hydrogenation mechanism (solid line along grey area). No (significant) hydrogenation mechanism proceeds in the absence of the ^DIPPBIAN ligand.

hydride addition to the imine. After consumption of all active hydrides of the pre-catalysts and a significant induction period, the slower hydrogenation mechanism commences. Comparison of reaction rates clearly supported the notion of a ligand-accelerated catalytic hydrogenation pathway in the presence of the BIAN ligand. LiAlH₄ showed almost no (at best a very slow) operation of a hydrogenation mechanism, whereas rapid amine formation was observed when employing pre-catalyst **3** (or a mixture of **2** and LiAlH₄). After the active hydrides of the pre-catalysts are consumed, the catalytic hydrogenation mechanism must involve effective H₂ activation at the catalyst via heterolytic H₂ splitting.

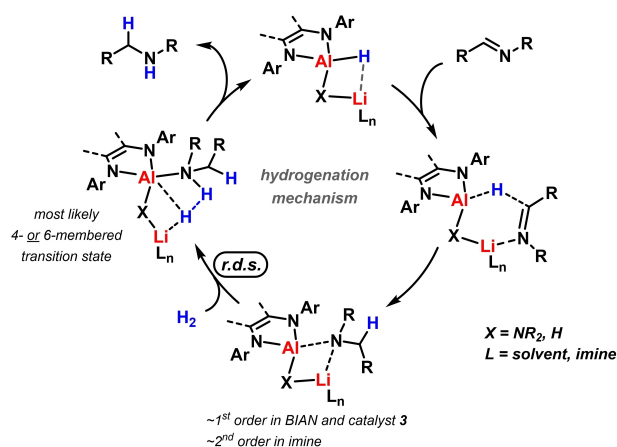
We have studied the kinetic aspects specifically in the regime of this new hydrogenation mechanism that followed the faster hydride-addition regime. The partial reaction orders of the **3**-catalyzed hydrogenation (after initial hydrides were consumed) at standard conditions were: ~1.3 (pre-catalyst **3**), ~2.0 (imine), and >1 (H₂, from the linear relation of rate vs. p(H₂)). The mixture of [LiAlH₄, **2**, Et₂O] gave an identical reaction progress curvature and the same partial reaction order in ligand **2** (~1.3).

The fractional orders of ligand **2** and complex **3** match well (and may indicate a complex mechanism); the rate-limiting step appears to involve two imines. From these data, the following conclusions can be drawn: Imine hydrogenation is catalysed by the BIAN ligand. Higher catalyst-substrate aggregates may be involved in the rate-determining step of the mechanism. The high partial order in imine concentration documents the crucial

role of effective imine coordination to the catalyst which is governed by the stereo-electronic effects of substituents. No reversibility of the reaction mechanism was observed when combining an electron-rich amine and an electron-deficient imine in the presence of catalyst **3** and in the absence of H₂ (see ESI). Steric bulkiness of the catalyst appears to be determining: Catalyst deactivation by the formation of dimers in the absence of ligand was reported by Stephan *et al.*^[6] The addition of the bulky ^{Dipp}BIAN most likely prevents the formation of inactive higher aggregates. A related observation was made with simple lithium amide catalysts: The model reaction gave 56% yield with 10 mol% lithium diisopropylamide (LDA) while the bulkier lithium bis(hexamethyldisilazide) (Lihmds) afforded 87% benzylamine.^[22] Based on the collected key mechanistic data and the literature precedents,^[6–9] we postulate a hydrogenation mechanism that involves ligand-accelerated Li–Al catalysis and heterolytic H₂ activation. The rate-determining step most likely operates at an active catalyst species that contains two amido ligands (2nd order rate in imine, ligand X in Scheme 6). H₂ splitting was postulated to proceed at Li–N linkages.^[7,22,23] Li ions are key to high catalytic activity: the Li-free complex **5** and the mixture NaAlH₄/2 gave poor catalytic activities (10% and 40% yield, respectively, Table 1).

Summary and Conclusions

Main group complexes have only recently been demonstrated to exhibit good activities in catalytic hydrogenations, an area of synthesis methods that hitherto has been entertained by transition metal catalysts. The μ_2 -dihydrido complex [(^{Dipp}BIAN)Al(H)₂Li(OEt)₂] (**3**) was prepared from the 2e-reduced BIAN derivative and LiAlH₄. **3** showed good activity in catalytic hydrogenations of *N*-aryl and *N*-alkyl imines and oximes. Optimized reaction conditions and a broader substrate scope were realized. Mechanistic studies documented an initial rapid hydride transfer mechanism and a slower hydrogenation mechanism. The rate-determining H₂ heterolysis may be



Scheme 6. Proposed mechanism of the BIAN-LiAl-catalysed imine hydrogenation (that operates after completion of the preceding and faster hydride-addition mechanism).

operative at Li–N linkages of amido-bridged LiAl complexes. The combination of a strongly electron-rich, stable ligand with two Lewis acidic metal ions and a heterolytic H₂ activation at highly polar metal-amide bonds appeared to be key to the observed catalyst activity. Implementation of these structural requirements into related main group metal complexes may pave the way to the development of more active catalysts that complement or even rival the existing arsenal of transition metal catalysts. The wide availability of diverse sets of amine ligands and main group hydride reagents provides ample opportunities for catalyst design.

Experimental Section

Synthesis of complex 3. LiAlH₄ (38 mg, 1.00 mmol) was slowly added to a solution of ^{Dipp}BIANH₂ (**2**, 0.50 g, 0.99 mmol) in diethyl ether (15 mL). The mixture was stirred at room temperature for 12 h, after which all volatiles were removed under reduced pressure. The solid residue was washed with heptane (20 mL) to afford complex **3** as green solid (555 mg, 0.81 mmol, 81%). Single crystals were obtained by recrystallization from diethyl ether at –20 °C (CCDC no. 2145612). EA: Calcd (%) for C₄₄H₆₂AlLiN₂O₂: C, 77.16; H, 9.12; N, 4.09; found: C, 77.13; H, 8.75; N, 4.06. LIFDI-MS (m/z): Calcd for C₃₆H₄₂AlLiN₂ [3 – 2 OEt₂]: 536.33; found: 536.41 [M]⁺. IR (ATR, cm^{–1}): $\nu = 3782, 3628, 3508, 3427, 3227, 2956, 2863, 2348, 2124, 1921, 1685, 1430, 1338, 1177, 1060, 924, 760$. IR (ATR in Et₂O, cm^{–1}): $\nu = 3818, 3713, 3630, 3568, 3521, 3460, 3315, 3053, 2955, 2762, 2707, 2598, 2501, 2349, 2266, 2211, 2157, 1975, 1903, 1753, 1662, 1589, 1506, 1425, 1336, 1176, 1056, 999, 924, 862, 805, 761$.

General procedure of imine hydrogenation. Under an atmosphere of argon, a glass vial was charged with a stir bar, the imine (0.25 mmol), complex **3** (10 mol%), and toluene (0.15 mL). The vial was sealed with a rubber septum, the septum punctured with a needle, and the vial placed into an argon-flushed stainless steel 200 mL high-pressure reactor (Parr Instr. Co.TM). Hydrogen gas was purged through the reactor, 47 bar H₂ were applied, and the reactor heated to 100 °C at which 50 bar H₂ pressure were reached. The reactor was stirred with an external magnetic stir plate. After 24 h at 100 °C internal temperature, the gas was released, the vial retrieved, water was added (1 mL), the organic phase extracted (3 × 1 mL diethyl ether) and dried (Na₂SO₄). The mixture was filtered and the filtrate treated with HCl (1 mL, 1 M in Et₂O) to give the ammonium salts upon filtration.

CCDC-2145612 contain(s) the supplementary crystallographic data for this paper (3). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aluminium · hydrides · main group metal catalysis · hydrogenation · imines

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