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ARTICLE

Pursuing the active species in an aluminium-based Lewis acid system for catalytic Diels-Alder cycloadditions

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Several Al-based complexes supported by a bis(imino)aryl NCN pincer ligand have been prepared. Systematic structural and experimental evidence identified a cationic species, supported by a THF molecule, as the best Lewis acid precatalyst for a range of Diels-Alder cycloadditions. This highlighted the importance of fully isolating and characterizing the active species in any catalytic process especially when Lewis acids are used due to presence of hidden Brønsted acids (HBAs). Lastly, the control experiments conducted in order to eliminate HBA activity that involve a bulky pyridine base should be performed with caution as the corresponding protonated pyridinium salt could also serve as a proton source.

Introduction

The examples of organic reactions catalysed by electron deficient species or Lewis acids (LA) appear to be quite extensive according to the numerous published reports.[1] However, in recent years there is growing evidence that a vast majority of these processes are in fact catalysed by hidden Brønsted acids (HBA).[2] One of the major issues is manifested by *in-situ* formation of the active species without any spectroscopic or structural evidence for their existence. Also, the lack of experimental steps suggested by Hintermann *et al.* that could distinguish between LA vs HBA catalysis denotes another problem in reporting organic transformations as being catalysed by an LA system.[2e] The most prominent approaches to gather evidence against HBA catalysis are (i) addition of a hindered base (e.g. 2,6-di-*tert*butylpyridine, dbpy) to the examined catalytic system and (ii) investigation of the same transformations using a soluble source of triflic acid (HOTf; Tf = O_2SCF_3) by mixing AgOTf and ^{t}BuCl.[2e] Therefore, rigorous steps have to be undertaken in order to minimize the possibility of the presence and subsequent catalytic activity of an HBA. This was certainly the case for recently reported ferrocenyl-stabilized silylium cation[3] and β-diketiminate supported Al-based[4] systems that have been shown to act as Lewis acids for various Diels-Alder transformations. Herein we report on a detailed pursuit of a bis(imino)phenyl-stabilized Al-containing system that is acting as a very effective LA catalyst for Diels-Alder cycloadditions. We also emphasize the importance of identify the active species in the reaction medium, as well as the issues associated with the use of dbpy for the control experiments.

Results and discussion

After identifying a well-defined β-diketiminate-stabilized aluminium bis(triflate) system to be capable of catalysing several difficult Diels-Alder transformations[3d,4] we decided to investigate the role of the ligand on the overall catalytic activity. We decided to use bis(imino)aryl NCN pincer ligand L (L = 2,6-(DipNC)$_2$-C$_6$H$_3$, Dip = 2,6-^{i}Pr$_2$-C$_6$H$_3$, Scheme 1) as these types of ligand have been shown to support both main group[5a,b] and transition metal[5c,d] complexes. With respect to the aluminium chemistry, there is only a single report describing the preparation of diethylaluminium complexes stabilized by these NCN ligands and their role as L-lactide polymerization catalysts.[6] Our initial synthetic procedure involved bromine-lithium-exchange of the free ligand (**1**, Scheme 1) with ^{n}BuLi in THF followed by addition of $AlCl_3$. After removing all volatiles under reduced pressure and extraction with toluene the target dichloride compound **2** was isolated (Scheme 1). THF-free analogue **3** could be obtained if **2** was subjected to extensive drying under reduced pressure. The identity of **2** and **3** were established by multinuclear NMR spectroscopy as well as by single crystal X-ray diffraction in the case of **3** (Figure 1). Even though the two Al-N bond distances (2.132(2) and 2.498(2) Å) for **3** are significantly different, solution state NMR spectroscopy strongly suggest that the Al-N distances are equivalent in solution. The Al-C (1.945(2) Å) and Al-Cl (2.1208(8) and 2.1382(7) Å) bond lengths are virtually identical to the same bond distances observed for similar compounds.[4,6] It is also worth mentioning that according to ^{1}H NMR spectroscopy only(VT) ^{1}H NMR spectroscopy the broad signal split into two distinct peaks at around – 50°C.[7] Considering that

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Electronic Supplementary Information (ESI) available: Copies of multinuclear NMR as well as the crystallographic details. See DOI: 10.1039/x0xx00000x

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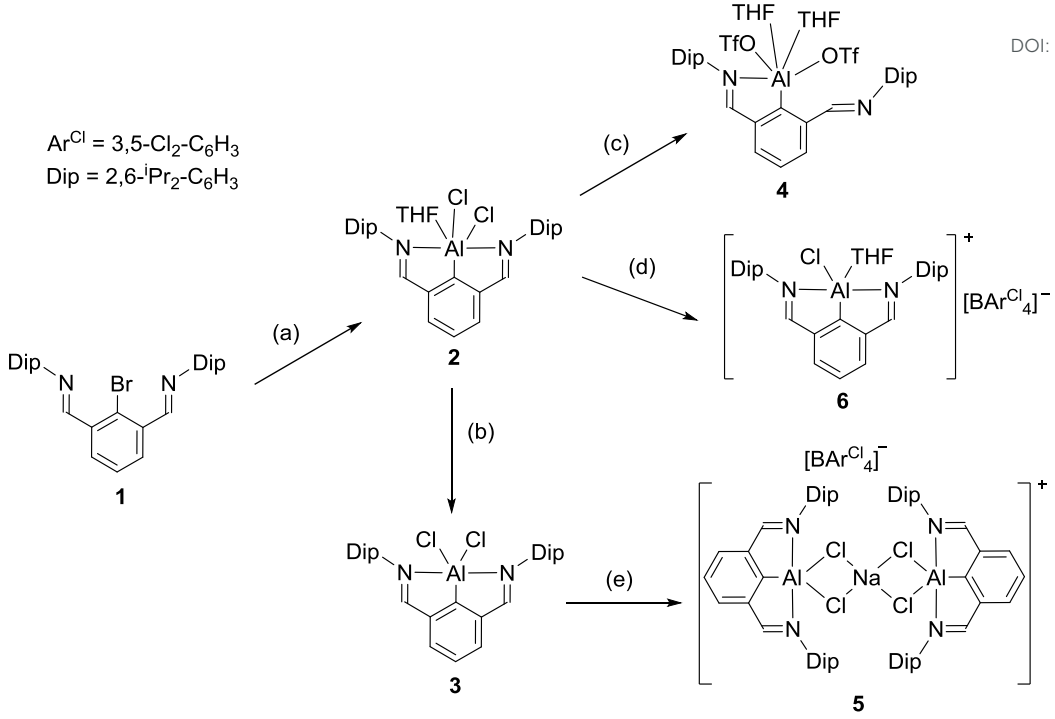

Scheme 1. Reaction conditions: (a) 1.05 equiv of ^{n}BuLi, 1 equiv $AlCl_3$, THF; (b) reduced pressure, 12 h; (c) preparation of 2 in THF (step (a)) was followed by addition of 3 equiv of AgOTf and layering with *n*-hexane; (d) 3, 1 equiv $Na[BAr^{Cl}_4]$, CH_2Cl_2; (e) 2, 1 equiv $Na[BAr^{Cl}_4]$, CH_2Cl_2.

there was no evidence of broadening of any other signals, in particular the vinylic signal at around δ_H 8.3 ppm, it can be assumed the room temperature broadening of the ^{i}Pr signal is due to loss of symmetry of these groups with respect to the central phenyl ring i.e. ligand backbone.

Our next aim was to replace the Cl ligands with OTf in order to prepare **4** (Scheme 1) as this ligand exchange was shown to enhance the Lewis acidic properties of the aluminium center.[4] However, even after numerous attempts we could not obtain a clean sample of our target compound. According to ^{1}H NMR spectroscopy numerous species were present in the reaction mixture and it was very difficult to determine whether **4** has actually formed. Fortunately, on one occasion we managed to isolate few crystals suitable for single crystal X-ray diffraction by layering the resulting THF solution with *n*-hexane. This analysis (Figure 1) showed that the target species was indeed present in the overall reaction mixture. Interestingly, one of the N-Dip arms of the pincer ligand is pointing away from the Al centre. This type of ligand behaviour has been observed for Cu,[8a] Sn,[8b] Pb[8c] and Ge[8d] complexes stabilized by this particular ligand. In our case this behaviour could be possibly explained by the fact that the Al centre is already six-coordinate and that it prefers oxygen- over nitrogen-based ligands i.e. aluminium is quite oxophilic. Nevertheless, compound **4** appear to be extremely air/moisture sensitive as we never managed to isolate it in pure form impeding our efforts to investigate its catalytic activity for various Diels-Alder transformations.

We then focused our attention to **2**/**3** as potential catalytic systems for a Diels-Alder reaction between 2,3-dimethylbutadiene (**7**) and 1,3-diphenyl-2-propenone (**8**, Table 1). These substrates were chosen because diene **7** is 250 times less reactive than cyclopentadiene,[9] dienophile **8** is rarely used in Diels-Alder cycloadditions[3d] and this overall transformation is poorly catalysed (conversion ~ 30 %) by HOTf even after extended reaction times (24 h).[4] Unfortunately, **2** or **3** (i.e. regardless of THF amount) was not able to catalyse the target cycloaddition as no evidence for the formation of **9** was observed (entry 1, Table 1). In our experience the catalytic activity could be increased by introducing $Na[BAr^{Cl}_4]$ (Ar^{Cl} = 3,5-Cl_2-C_6H_3) in the reaction mixture. Indeed, the addition of 1 equiv of this weakly coordinating anion to a CD_2Cl_2 solution containing **3** resulted in 22 % conversion in about 3 h (entry 3, Table1). However, when this reaction was repeated using **2** a complete substrate conversion was observed in 3 h (entry 2, Table1). This suggested that the presence of THF was crucial for enhancing the reaction rate and, consequently, it was of paramount importance to identify the major components of the two catalytic systems. However, addition of 1 equiv of THF to a solution containing **3** does not result in THF coordination and formation of **2** (via ^{1}H NMR spectroscopy) i.e. no evidence that **2** and **3** exist in an equilibrium at room temperature. This is also evident by the fact that addition of 1 equiv of THF followed by 1 equiv of $Na[BAr^{Cl}_4]$ into a CD_2Cl_2 solution containing **3** does not improve the catalytic activity in comparison to the **3**/$Na[BAr^{Cl}_4]$ (i.e. THF-free) system. In fact, it is necessary to heat **3**/THF mixture for about 6 h at 60°C, followed by the addition of $Na[BAr^{Cl}_4]$ to mimic the initial reaction rate established for the **2**/$Na[BAr^{Cl}_4]$ system (entry 6, Table 1). These observations might suggest, even without another piece of spectroscopic evidence that one of the N-Dip arms for **2** is not coordinated to the central Al as already observed for **4**. However, due to lack of structural data, **2** is still depicted in Scheme 1 as having both N atoms coordinated to the Al centre. It should also be noted that

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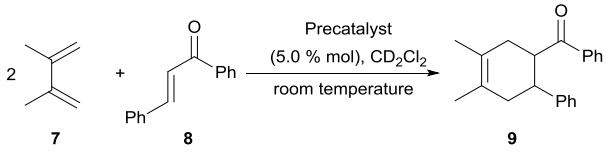
Table 1. Screening of potential (pre)catalysts for Diels-Alder cyclization between 3-dimethylbutadiene and 1,3-diphenyl-2-propenone.



7 **8** **9**

#	Precatalyst	Time Yield (isolated) Trans/cis ratio
1	**2** or **3**	-
2	**2**/Na[BAr^{Cl}_4]	3 h 99% 99:1
3	**3**/Na[BAr^{Cl}_4]	3 h 22 % 99:1
4	**3**/Na[BAr^{Cl}_4] + THF[a]	3 h 99 % 99:1
5	**3**/Na[BAr^{Cl}_4] + OEt_2[b]	3 h 99 % 99:1
6	**5**	4 h 11 % 99:1
7[c]	**6**	3 h 99 % 99:1
8	Na[BAr^{Cl}_4]	-

[a]**3** was preheated with THF at 60°C for 6h before the addition of Na[BAr^{Cl}_4]. [b]**3** was preheated with OEt_2 at 60°C for 6h before the addition of Na[BAr^{Cl}_4]. [c]in the presence or absence of dbpy.

using only Na[BAr^{Cl}_4] showed no catalytic activity for the examined transformation (entry 8, Table 1).

Stirring **3** and Na[BAr^{Cl}_4] in DCM for about 5 min and layering the resulting solution with *n*-hexane produced a crop of colourless crystals, suitable for solid state analysis, which were identified as compound **5** (Scheme 1 and Figure 1). This compound is essentially a dimer of **3** supported by a sodium cation. As the sodium cation for **5** is surrounded by the chloride ligands it is not surprising to witness Al-Cl bond distance (2.150(2) and 2.158(2) Å) elongation in comparison to **3** (2.1208(8) and 2.1382(7) Å). This would then shift the electron density away from the Al centre for **5** resulting in shortening of the Al-C (**3**: (1.945(2) Å; **5**: 1.936(3) Å) and the average Al-N (**3**: (2.316(2) Å; **5**: 2.210(4) Å) bond distances. After isolating it, **5** was tested as a catalyst in the initial Diels-Alder reaction resulting in a very slow reaction progress (~ 11% conversion after 4h; entry 6, Table 1). This suggested that either **5** was not the active species that produced high reaction rates or it is a very poor precatalyst. On the other hand, when **2** was reacted with Na[BAr^{Cl}_4] in CH_2Cl_2 it was possible to identify a mononuclear cationic aluminium complex **6** in which one of the Cl ligands was replaced by a THF molecule. When compound **6**

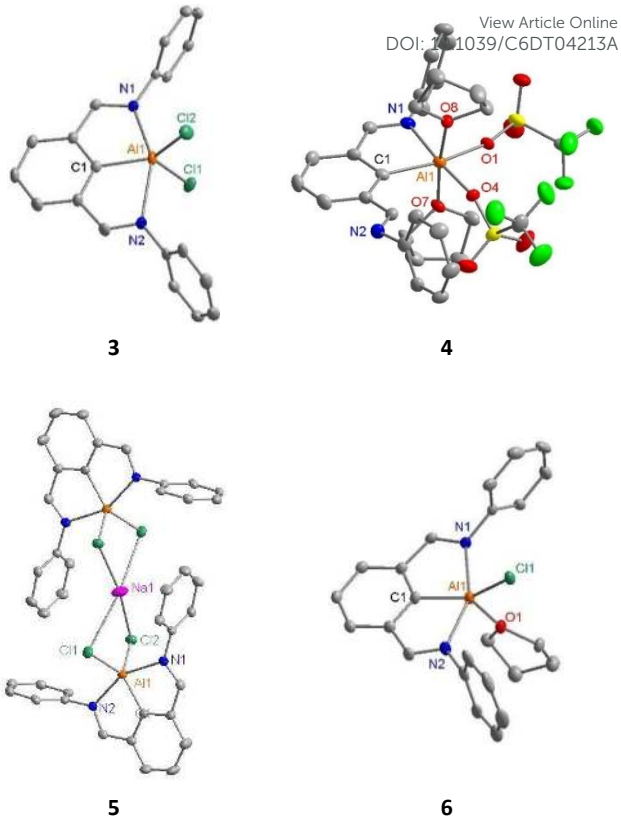


Fig 1. Molecular structures for **3**, **4**, **5** and **6** drawn at 30% probability. All hydrogen atoms, the ^{i}Pr groups of the Dip substituents, the counter ions (for **5** and **6**) and solvent molecules have been removed for clarity. Selected bond distances (Å): **3**: Al1-C1 1.9446(19), Al1-N1 2.1317(16), Al1-N2 2.498(2); **5**: Al1-C1 1.933(3), Al1-N1 2.238(2), Al1-N2 2.180(2). **6**: Al1-C1 1.932(3), Al1-N1 2.181(2), Al1-N2 2.213(2)

was tested as a catalyst complete substrate conversion occurred within 3 h, which is the same time frame observed when the **2**/Na[BAr^{Cl}_4] system was used. This suggested that we formed a more Lewis acidic system, in comparison to **2**/**3**. This is further supported by the solid state analysis as the formation of cation **6** was manifested not only by shortening of the Al1-C1 (**3**: 1.945(2) Å; **6**: 1.932(3) Å), Al-Cl (**3**: 2.130(2) Å; **6**: 2.119(2) Å) and the average Al1-N (**3**: 2.316(2) Å; **6**: 2.197(3) Å) bond distances but also by diminished discrepancy with respect to the two Al-N-bond distances in **6** (2.181(2) and 2.213(2) Å) in comparison to **3** (2.132(2) and 2.498(2) Å). It also should be noted that according to VT ^{1}H NMR spectroscopy the ^{i}Pr groups of the Dip substituents for **5** and **6** show the same behaviour as already described for **3**.

Apart from stabilizing the cationic species it was also important to understand whether the coordinated THF molecule had any role in the overall catalytic process. Addition of 5 equiv of dienophile **8** to a CD_2Cl_2 solution containing **6** resulted in complete de-coordination of THF and coordination of the dienophile, through the oxygen atom of the carbonyl group, as observed by ^{1}H NMR spectroscopy.[8] Addition of diene **7** to this newly formed cationic species ([LAlCl]$^{+}$ cation stabilized by **8**) resulted in complete conversion with virtually identical reaction

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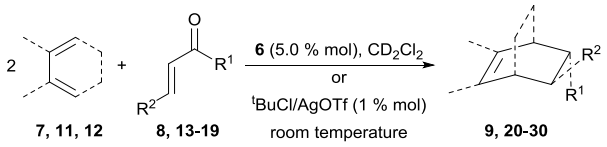
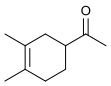
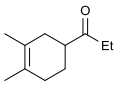
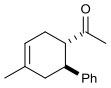
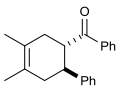
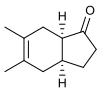
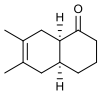
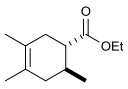
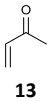
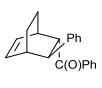
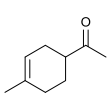
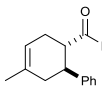
Table 2. **6** or ^{t}BuCl/AgOTf (HBA) catalysed Diels-Alder reactions of dienophiles 8 and 13-19 with 2,3-dimethyl-1,3-butadiene (7), 2-methyl-1,3-butadiene (12) or cyclohexadiene (11). The results are listed as: time (h), isolated yield (%), *trans*/*cis* or endo:exo, and/or *para*:*meta* ratios for each run.



7, 11, 12 **8, 13-19** **9, 20-30**

#	Diene	Dienophile	Adduct	**6**	HBA
1	 **7**	 **13**	 **20**	1 h 96 % - -	1 h[a] 90 % - -
2	 **7**	 **14**	 **21**	1 h 98 % - -	1 h[a] 89 % - -
3	 **7**	 **15**	 **22**	24 h 72 % 99:1 -	24 h[a] 58 % 99:1 -
4	 **7**	 **8**	 **9**	3 h 98 % 99:1 -	24 h[a,c] 33 % 99:1 -
5	 **7**	 **16**	 **23**	-	1 h[a,b]
6	 **7**	 **17**	 **24**	24 h 41 % 99:1 -	1 h[a,b]
7	 **7**	 **18**	 **25**	12 h 96 % 91:9 -	24 h[a] 60 % 91:9 -
8	 **7**	 **19**	 **26**	40 h[d] 89 % 99:1 -	1 h[a,b]
9	 **11**	 **13**	 **27**	1 h 97 % 99:1 -	1 h[a] 92 % 99:1 -
10	 **11**	 **8**	 **28**	12 h 99 % 99:1 -	24 h[c] 16 % 99:1 -
11	 **12**	 **13**	 **29**	1 h 97 % - 99:1	2 h[a] 83 % - 97:3
12	 **12**	 **8**	 **30**	10 h 99 % 99:1 99:1	10 h[c] 29 % 99:1 88:12

[a]See reference 4. [b]Diene polymerization occurred within the first hour with no evidence for the formation of the product. [c]% conversion as estimated by ^{1}H NMR spectroscopy. [d]4 equiv of the diene used.

rates observed when using **6**. Furthermore, heating **3** in DCM-d_2 solution containing 2 equiv OEt_2, followed by the addition of $Na[BAr^{Cl}{}_4]$ did result in the formation of the active catalyst as quantitative cycloaddition between **7** and **8** was observed (entry 7, Table 1). This collective evidence clearly indicated that the active species was, in fact, free cation $[LAlCl]^+$ (**10**) and that the role of THF in **6** (precatalyst for **10**) was only for stabilization purposes. Furthermore, considering that **2** and **3** were shown to be inactive, it is then believed that the observed catalytic activities for **3**/$Na[BAr^{Cl}{}_4]$ (i.e. **5**) was due to the ability of this systems to form, but not as efficiently as **2**/$Na[BAr^{Cl}{}_4]$ (i.e. **6**), the active species in the presence of dienophile **8**.

After determining that **6** was the most prominent precatalyst several other Diels-Alder transformations were investigated as summarized in Table 2. Almost all dienophiles, including the difficult ones[3d] such as **8**, **15**, **17** and **19**, were quite suitable for the targeted cycloadditions with **7** resulting in isolated yields of 41 to 99% and selectivities > 91:9. The only exception is cyclopentenone (**16**) which showed no activity under the investigated reaction conditions. For ethylcrotonate (**19**) extra amounts of the diene and extended reaction times were required. Additionally, using the less active dienes (**11** and **12**) expectedly resulted in slower reaction rates but isolated yields of > 97% (entries 9-12, Table 2) were achieved. Considering these observations the catalytic activity of cation **10** is comparable with those for the β-diketiminate supported Al-based systems with respect to the attempted Diels-Alder cycloadditions.[4] In particular, the cycloadditions between diene **7** and dienophiles **13**, **14** and **19** as well as between **11** and **13** were virtually identical for both Al-containing systems with respect to isolated yields and reaction rates. Catalyst **6** did outperform its β-diketiminate counterpart for the reactions involving **7** and **8**/**18**, and **12** and **13** but showed slower reaction rates involving **7** and **15**/**16**/**17**.

Even though detailed investigations on the nature of the catalytic species were undertaken it still did not rule out the presence of an HBA. However, when the abovementioned catalytic cycloadditions were repeated with a source of an HBA (AgOTf/^{t}BuCl generating HOTf[2e]) more evidence was gathered to suggest the absence of HBA activity. For example, HBA catalysed reactions between **7**/**11**/**12** and **8** resulted in poor yields while for the same cycloadditions excellent yields were achieved when catalysed by **2**/$Na[BAr^{Cl}{}_4]$ (entries 4, 10, 12; Table 2). Also, no reactivity or substrate decomposition were observed in the presence of HOTf for transformations involving cyclic dienophiles (**16** and **17**) and **19** while the use of our system resulted in substrate conversions (entries 6 and 8; Table 2) or absence of substrate decomposition (entry 5, Table 2). Additionally, when **7** and **8** (entry 7, Table 1) were cyclized by **10**

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in the presence of dbpy there was absolutely no loss of catalytic activity which was not the case when the AgOTf/^{t}BuCl system was used. In fact, the addition of dbpy in the reaction mixtures that are catalysed by this source of HOTf and involving dienophiles **8**, **13** and **14** completely quenched the target Diels-Alder transformations while, as already pointed out, the use of dbpy could not prevent the aluminium system from performing the same cycloadditions.[4] Thus, the aforementioned observations that are catalysed by this source of HOTf and involving dienophiles **8**, **13** and **14** completely quenched the target Diels-Alder transformations while, as already pointed out, the use of dbpy could not prevent the aluminium system from performing the same cycloadditions.[4] Thus, the aforementioned observations strongly suggested that the investigated cycloadditions were most likely catalysed by Lewis acidic complex **10**.

When **6** and equimolar amounts of dbpy were mixed in CD_2Cl_2 solution the formation of the corresponding pyridinium cation ([dbpy-H]$^+$), presumably due to the presence of residual moisture, was limited to less than 10 % (^{1}H NMR spectroscopy), which would translate in less than 0.5% with respect to the attempted dienophiles.[8] This is important because if large amounts of the [dbpy-H]$^+$ are produced, especially if excess (with respect to catalyst) quantities of dbpy are used,[10] then [dbpy-H]$^+$ could actually act as a proton source because the pKa value for [dbpy-H]$^+$ varies from 0.9 (DMSO) to 5 (H_2O) suggesting that this pyridinium cation could be a quite potent proton donor. Indeed, the Diels-Alder cycloaddition between diene **7** and dienophile **14** (2:1 mole ratio) achieved 50% conversion in 6 h when 0.5 equiv of [dbpy-H][OTf] was introduced and quantitative conversion in 12 h when 1 equiv of this salt was used. Thus, we believe that when using dbpy to potentially gather evidence against an HBA activity it is crucial to determine the amount of [dbpy-H]$^+$ that has been produced under the established reaction conditions as large quantities of this pyridinium cation appears to be a quite decent source of HBA activity.

Conclusions

We have synthesized and fully characterized several bis(imino)phenyl-stabilized aluminium complexes. The mononuclear compound **6** appears to be the most prominent pre-catalyst for the investigated Diels-Alder transformations. We have performed several control experiments to show that cation **10** is most likely responsible for the observed catalytic activity. We believe that in-situ preparation of potential Lewis acid systems used for catalysis should be avoided as well as performing the target transformations in wet reaction conditions. Lastly, the control experiment using dbpy should be carefully examined as the presence of large quantities of the corresponding pyridinium cation could serve as a proton source.

Experimental

General. All manipulations were carried out using standard Schlenk techniques and a dry-box. CH_2Cl_2, CD_2Cl_2 and $CDCl_3$ were distilled over CaH_2 while THF, toluene and *n*-hexane were distilled over sodium. All solvents were stored over 4 Å molecular sieves. Ligand **1**[11a] and Na[BAr$^{Cl}_4$][11b] were prepared according to reported synthetic procedures. Apart from **8** and **15** all other dienophiles and dienes used in this study were distilled and stored under argon. All other chemicals were purchased from commercial sources and used without further purification. The NMR spectra were recorded on **a** Bruker Avance III 400 or JEOL ECA400 (^{1}H NMR at 400 MHz; ^{13}C NMR at 100 MHz, ^{11}B NMR at 128 MHz and ^{27}Al NMR at 104 MHz) instrument. Tetramethysilane was used as reference for ^{1}H and ^{13}C NMR, while ^{11}B and ^{27}Al NMR spectra were recorded with respect to $Et_2O{\cdot}BF_3$, and $AlCl_3/D_2O$, respectively. Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using the electro spray ionization (ESI) mode. Elemental analysis has been attempted for all new compounds. However, acceptable results have been obtained only after numerous runs presumably due to high air/moisture sensitivity of these compounds. Therefore, these results are not included in the experimental sections as they might not be reliable and the purity of all compounds has been assess based on multinuclear NMR.

Synthesis of LAlCl$_2$(THF), 2. ^{n}BuLi (0.52 mL, 1.05 mmol, 2M in cyclohexane) was added dropwise to a THF (20 mL) solution of 2,6-(2,6-^{i}Pr$_2$-C$_6$H$_3$N=CH)$_2$-C$_6$H$_3$-1-Br (0.53 g, 1.00 mmol) at – 78 °C. The mixture was stirred for 30 min before $AlCl_3$ (0.13 g, 1.00 mmol) was added. The solution was allowed to warm to room temperature gradually and stir overnight. The solvent was removed under reduced pressure and the residue was extracted by dichloromethane. After evaporation of most of the dichloromethane, 10 mL *n*-hexane was added. The red powder formed was dried under vacuum for 5 min. Yield: 0.46g, (74%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.16 (d, $^3J_{H\text{-}H}$ = 6.50 Hz, 24H, CH(C*H*$_3$)$_2$), 1.89 (b, 4H, THF), 3.16 (sept, $^3J_{H\text{-}H}$ = 6.50 Hz, 4H, C*H*(CH$_3$)$_2$), 3.92 (b, 4H, THF), 7.19-7.24 (m, 6H, Ph), 7.60 (t, $^3J_{H\text{-}H}$ = 7.48 Hz, 1H, Ph), 7.74 (d, $^3J_{H\text{-}H}$ = 7.48 Hz, 2H, Ph), 8.34 (s, 2H, C*H*=N) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 24.5 (CH(*C*H$_3$)$_2$), 25.5 (THF), 28.2 (*C*H(CH$_3$)$_2$), 69.5 (THF), 123.7 (*p*-N-C$_6$H$_3$), 126.7 (*m*-N-C$_6$H$_3$), 131.0 (*p*-Al-C$_6$H$_3$), 132.3 (*m*-Al-C$_6$H$_3$), 139.7 (*o*-N-C$_6$H$_3$), 140.9 (C=N-*C*), 143.7 (*o*-Al-C$_6$H$_3$), 168.4 (*C*=N-C) ppm. ^{27}Al NMR (104.2 MHz, $CDCl_3$, 25 °C): δ 97.5 ppm. HRMS (ESI) calculated for $C_{36}H_{48}N_2OCl_2Al$ [M + H]: 621.2959; Found: 621.2927. MP: ~ 191°C (onset of decomposition)

Synthesis of LAlCl$_2$, 3. ^{n}BuLi (0.52 mL, 1.05 mmol, 2M in cyclohexane) was added dropwise to a THF (20 mL) solution of 2,6-(2,6-^{i}Pr$_2$-C$_6$H$_3$N=CH)$_2$-C$_6$H$_3$-1-Br (0.53 g, 1.00 mmol) at –78 °C. The mixture was stirred for 30 min before $AlCl_3$ (0.13 g, 1.00 mmol) was added. The solution was allowed to warm to room temperature gradually and stir overnight. The solvent was removed under reduced pressure and the residue was extracted by toluene. After evaporation of toluene, 10 mL *n*-hexane was added to wash the crude product. The red powder obtained was dried under vacuum for about 15h. Yield: 0.41g, (75%). Crystals

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were grown in toluene/*n*-hexane mixed solution. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.16 (d, $^3J_{H\text{-}H}$ = 6.52 Hz, 24H, CH(CH_3)$_2$), 3.16 (sept, $^3J_{H\text{-}H}$ = 6.52 Hz, 4H, CH(CH_3)$_2$), 7.19-7.23 (m, 6H, Ph), 7.60 (t, $^3J_{H\text{-}H}$ = 7.48 Hz, 1H, Ph), 7.74 (d, $^3J_{H\text{-}H}$ = 7.48 Hz, 2H, Ph), 8.34 (s, 2H, CH=N) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 25.5 (CH(CH_3)$_2$), 28.2 (*C*H(CH_3)$_2$), 123.7 (*p*-N-C_6H_3), 126.7 (*m*-N-C_6H_3), 131.0 (*p*-Al-C_6H_3), 132.3 (*m*-Al-C_6H_3), 139.8 (*o*-N-C_6H_3), 140.9 (C=N-*C*), 143.7 (*o*-Al-C_6H_3), 168.4 (*C*=N-C) ppm. ^{27}Al NMR (104.2 MHz, $CDCl_3$, 25 °C): δ 106 ppm. HRMS (ESI) calculated for $C_{32}H_{40}N_2Cl_2Al$ [M + H]: 549.2384; Found: 549.2371. MP: ~ 190°C (onset of decomposition)

Preparation of LAl(OTf)$_2$(THF)$_2$, 4. ^{n}BuLi (0.52 mL, 1.05 mmol, 2M in cyclohexane) was added dropwise to a 20 mL THF solution containing **1** (0.53 g, 1.00 mmol) at – 78 °C. The mixture was stirred for 30 min before $AlCl_3$ (0.13, 1.00 mmol) was added. The solution was gradually allowed to warm to room temperature and stir for 15h. This reaction mixture was then transferred to another flask that contained AgOTf (0.77 g, 3.0 mmol) and left to stir overnight in the absence of light. After filtration, the solution was concentrated and layered with *n*-hexane. Few yellow crystals were obtained at -15°C after 1 day. The product appeared to be generally unstable presumably due to high air/moisture sensitivity and, thus, it was possible only to obtain single crystal X-ray analysis.

Synthesis of [LAlCl$_2$NaCl$_2$AlL][NaBAr$^{Cl}_4$], 5. 3 (0.55g, 1.00 mmol) and NaBAr$^{Cl}_4$ (0.62g, 1.00 mmol) were dissolved in 5 mL of CH_2Cl_2 and left to stir for 5 min. After filtration, the solution was layered with 5 mL *n*-pentane. Colourless crystals were obtained after 1 day. Yield: 0.61g, 71%. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.12 (broad, 48H, CH(CH_3)$_2$), 2.99 (sept, $^3J_{H\text{-}H}$ = 6.84 Hz, 8H, CH(CH_3)$_2$), 6.97-7.21 (m, 24H, Ph), 7.64 (t, $^3J_{H\text{-}H}$ = 7.58 Hz, 2H, Ph), 7.83 (d, $^3J_{H\text{-}H}$ = 7.58 Hz, 4H, Ph), 8.42 (s, 4H, CH=N) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 25.5 (CH(CH_3)$_2$), 28.4 (*C*H(CH_3)$_2$), 123.1 (*p*-N-C_6H_3), 124.2 (*p*-C, Ar^{Cl}), 127.6 (*m*-N-C_6H_3), 132.1 (*m*-Al-C_6H_3), 132.9 (*m-C,* Ar^{Cl}), 133.0 (*o*-C, Ar^{Cl}), 133.1 (*p*-Al-C_6H_3), 139.2 (*o*-N-C_6H_3), 140.9 (C=N-*C*), 142.2 (o-Al-C_6H_3), 164.0 (q, $^1J_{BC}$ = 49 Hz, B-C), 170.0 (*C*=N-C) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C): δ -7.9 ppm. ^{27}Al NMR (104.2 MHz, CD_2Cl_2, 25 °C): no signal observed. HRMS (ESI): (the only signal observed was actually for $LAlCl_2$) calculated for $C_{32}H_{40}N_2Cl_2Al$ [M + H]: 549.2384; Found: 549.2372. MP: ~ 254°C (onset of decomposition)

Synthesis of [LAlCl(THF)][BAr$^{Cl}_4$], 6. A fresh sample of **2** (0.62g, 1.00 mmol) was dissolved in 5 mL of CH_2Cl_2 followed by the addition of NaBAr$^{Cl}_4$ (0.62g, 1 mmol). After it was left to stir for 6 h, the solution was filtered and layered with 5 mL pentane. Colourless crystals were obtained after 1 day. Yield: 0.73g, 62%. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.10 (broad, 24H, CH(CH_3)$_2$)), 2.10 (b, 4H, THF), 2.56 (sept, $^3J_{H\text{-}H}$ = 6.88 Hz, 4H, CH(CH_3)$_2$), 4.07 (b, 4H, THF), 6.94-7.34 (m, 18H, Ph), 7.71 (t, $^3J_{H\text{-}H}$ = 7.32 Hz, 1H, Ph), 7.91 (d, $^3J_{H\text{-}H}$ = 7.32 Hz, 2H, Ph), 8.59 (s, 2H, CH=N) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 25.2 (CH(CH_3)$_2$), 25.8 (THF), 29.1 (*C*H(CH_3)$_2$), 75.5 (THF), 123.0 (*p*-N-C_6H_3), 124.3 (*p*-C, Ar^{Cl}), 128.2 (*m*-N-C_6H_3), 132.9 (*m-C,* Ar^{Cl}), 133.1 (*o*-C, Ar^{Cl}), 134.0 (*m*-Al-C_6H_3), 134.4 (*p*-Al-C_6H_3), 139.0 (*o*-N-C_6H_3), 140.1 (*C*=N-C), 142.2 (o-Al-C_6H_3), 164.0 (q, $^1J_{BC}$ = 48 Hz, B-C), 173.3 (C=N-C) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C): δ -7.9 ppm. ^{27}Al NMR (104.2 MHz, CD_2Cl_2, 25 °C): no signal observed. HRMS (ESI): (the only signal observed was due to ligand L) calculated for $C_{32}H_{41}N_2$ [M + H]: 453.3270; Found: 453.3269. MP: ~ 156°C (onset of decomposition).

Synthesis of pyridinium triflate, [dbpy-H][OTf]. 300 mg HOTf was dissolved in 100 mL hexane in a 500 mL round-bottomed flask. To this solution, a mixture of 2,6-dibutylpyridine (0.43 mL, 2.0 mmol) in 5 mL hexane was added slowly while vigorous stirring. White precipitate formed immediately. After filtration and dry under vacuum, pure product was obtained as white solid. Yield: 510 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.16 (s, 18H, C(CH_3)$_3$), 7.77 (d, $^3J_{H\text{-}H}$ = 8.24 Hz, 2H, *m*-H), 8.39 (t, $^3J_{H\text{-}H}$ = 8.24 Hz, 1H, *p*-H), 12.46 (broad, 1H, N*H*) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 29.1 (C(*C*H$_3$)$_3$), 37.2 (*C*(CH_3)$_3$), 119.0 (*C*F$_3$), 122.1 (*C*H), 147.8 (*C*H), 164.9 (*C*) ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$, 25 °C): δ -78.08 ppm.

General procedure for Diels-Alder cycloadditions. A precatalyst, usually **6**, (0.017 mmol, 0.05 equiv) was dissolved in 1 mL CD_2Cl_2 in a J. Young NMR tube. To this solution a diene (0.68 mmol, 2 equiv) and a dienophile (0.34 mmol, 1 equiv) was added. The reaction mixture was left for the time indicated in Table 1 or 2. Then, the crude mixture was purified by flash column chromatography on silica gel using *n*-hexane/ethyl acetate solvent mixture affording the corresponding Diels-Alder products. The *endo*:*exo* ratio is determined by GLC analysis of the reaction mixture prior to workup. Copies of the ^{1}H and ^{13}C NMR of the prepared organic compounds are included in the supporting information.

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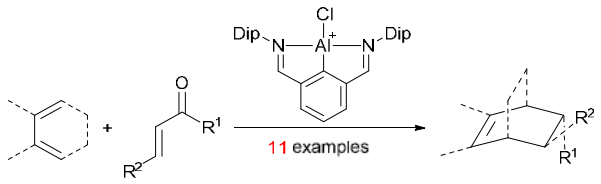
Detailed characterization of the catalytically active aluminium species supported by a bis(imino)aryl ligand has been reported.



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