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Dihydrogen activation by intermolecular rare-earth aryloxide/N-heterocyclic carbene Lewis pairs†

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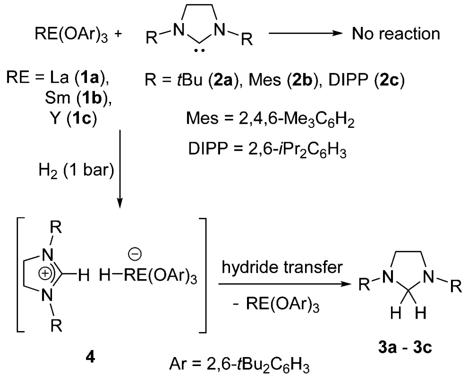
Dihydrogen was readily activated by combination of homoleptic rare-earth metal aryloxides, $RE(OAr)_3$ (RE = La, Sm, and Y) with N-heterocyclic carbenes (NHCs) under mild conditions. $RE(OAr)_3$ were found to be active catalysts for the reductive hydrogenation of NHCs to aminals under 1 bar of H_2. In addition, the La/NHC pair also exhibited frustrated Lewis pair (FLP)-like reactivity towards carbon dioxide and phenylacetylene, affording 1,2-addition and deprotonation products, respectively.

Transition-metal (TM) mediated dihydrogen (H_2) activation is of significant importance in organometallic chemistry and industrial hydrogenation catalysis.[1] Specifically, cleavage of the inert, nonpolar H–H bond by TM complexes plays a crucial role in the utilization of H_2. In this context, two-electron oxidative-addition provides an ideal pathway for homolytic H_2 splitting at a single TM center. However, this conventional strategy is not applicable to rare-earth (RE) metal complexes because RE metal ions are typically stable in the +3 oxidation state, and thus the activation of H_2 by RE metal complexes proceeds *via* a four-centered σ-bond metathesis mechanism.[2] Such species are often RE metal alkyl complexes containing RE–C bonds.[3] Chen and co-workers have shown that the highly reactive scandium imido or alkylidene complexes enable H_2 activation through 1,2-addition to Sc–N or Sc–C double bonds.[4] Recently, frustrated Lewis pair (FLP) chemistry has flourished for the main-group elements and the dipolar activation of H_2 represents a most prominent feature of FLP.[5,6] Inspired by this powerful strategy, Piers[7] and our group[8] have developed several intra- and intermolecular Lewis pair complexes based on RE metal Lewis acids that exhibit typical FLP-type reactivity towards a variety of unsaturated substrates. In the present work, both the activation of molecular H_2 and catalytic hydrogenation were successfully achieved using simple combinations of Lewis acidic RE metal tris-aryloxides $[RE(OAr)_3$, RE = Y, Sm and La, Ar = $2,6\text{-}{}^t\text{Bu}_2\text{-}C_6H_3]$[9] with Lewis basic N-heterocyclic carbenes (NHCs) under mild conditions. In addition, such Lewis pairs also underwent stoichiometric reactions with carbon dioxide and phenylacetylene, affording FLP-type reaction products.

NHCs are attractive ancillary ligands for supporting both TM and RE complexes.[10,11] Although commonly considered a spectator ligand, NHCs may participate in reactions at reactive carbene carbons. As an example, Arnold and co-workers have shown that RE metal complexes bearing tethered NHC ligands enable the cooperative activation of several polar bonds by RE/NHC.[12] In the work reported herein, we initially assessed the reactions of $RE(OAr)_3$ [RE = La (**1a**), Sm (**1b**), and Y (**1c**)] with one equivalent of 1,3-bis-(*t*-butyl)imidazolin-2-ylidene (**2a**), which has a saturated carbene backbone, in C_6D_6 solution at ambient temperature (Scheme 1). Both the ^1H and $^{13}C\{^1H\}$ NMR spectra showed no evidence for the formation of classical RE metal-carbene adducts in the solution (for details, see the ESI†), likely due to the use of a sterically hindered Lewis acid.[13] The same result was obtained from the reaction of the lanthanum complex **1a** with either 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene (**2b**) or 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene (**2c**).[14]



Scheme 1 Reactions of RE/NHC FLPs with dihydrogen.

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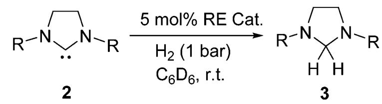
Subsequently, the reactivities of these frustrated RE/NHC Lewis pairs towards H_2 were investigated. Interestingly, the exposure of a 1 : 1 mixture (molar ratio) of **1a** and **2a** in C_6D_6 solution at room temperature to 1 bar of H_2 resulted in rapid and quantitative formation of aminal **3a** [^{1}H: δ 3.67 ppm (s, NCH_2N); ^{13}C: δ 63.3 ppm (NCH$_2$N)] and La complex **1a** remained intact in the solution after the reaction (Scheme 1). It should be noted that either of the RE complexes **1a** and NHC **2a** alone is inert towards dihydrogen under our typical conditions.[15] Apparently, during the course of the reaction, the intermolecular La/NHC FLP heterolytically splits the H_2 molecule to form a zwitterionic intermediate **4** in a typical FLP fashion.[16] This species subsequently underwent hydride transfer from the metal center to the C2-imidazolium atom to eventually give the NHC hydrogenation product **3a** while releasing the complex **1a**. A similar phenomenon was also observed for the main-group/NHC FLP system.[17] Attempts to trap **4** by adding unsaturated substrates (*e.g.*, 1-hexene, styrene, and benzaldehyde) to the reaction system failed, presumably due to the rapid intramolecular hydride transfer in this system. Other RE Lewis acids based on smaller metals, such as the Sm complex **1b** and the Y complex **1c**, were also examined with regard to H_2 activation in combination with equimolar amounts of NHC **2a** under analogous conditions. Both the reactions gave an identical NHC hydrogenation product **3a** within 1 h, with no zwitterionic species being observed. The NHC species **2b** and **2c** could also be employed to generate the corresponding aminals **3b** and **3c**, in conjunction with the La complex **1a**. However, the quantitative transformation of **2c** to **3c** required forcing conditions, involving an elevated temperature (80 °C) and a prolonged reaction time (24 h).

To obtain further insights into this H_2 activation reaction, a control experiment using deuterium gas was also carried out. Treatment of the frustrated **1a**/**2a** Lewis pair at 1 bar D_2 under the same conditions as applied previously resulted in quantitative formation of the corresponding deuterated congener **3a-D** (Scheme 2). The ^{2}H NMR spectrum of **3a-D** clearly showed a single resonance at δ 3.61 ppm that was attributed to the NCD_2N moiety.

Catalytic hydrogenation using substrates as Lewis bases has been achieved with many main-group FLP systems.[18] In the present work, because the RE Lewis acid component was recovered after the reaction with H_2, we subsequently investigated the hydrogenation of NHC compounds using a catalytic amount of RE complexes **1** and the results are summarized in Table 1. All three RE complexes were found to be effective catalysts for the conversion of NHC **2a** to the corresponding aminal **3a** with a 5 mol% catalyst loading under mild conditions (1 bar H_2, room temperature). The catalytic activities were found to be dependent on the ionic radii of the RE metals. The reactions were completed in 1 h when using the larger metals La and Sm (entries 1 and 2), whereas a 12 h time span was required for the Y catalyst (entry 3). Deuterated aminal **3a-D** was also obtained under catalytic conditions (entry 4). Employing 5 mol% of the La complex **1a** as the catalyst, the 2,6-di-mesityl substituted NHC compound **2b** was quantitatively hydrogenated in 1 h under our typical conditions (entry 5). Consistent with the result of the stoichiometric reaction, hydrogenation of the 2,6-di-isopropylphenyl substituted NHC **2c** required an elevated temperature (80 °C) even with a high catalyst loading (30 mol% of **1a**, entry 6). Further isolation of compounds **3a–3c** and **3a-D** was also conducted. After the reactions were complete, the volatiles were removed *in vacuo* and the residues were extracted using hexane to finally afford the desired products. Such aminals were conventionally obtained by condensation reactions of diamines with formaldehydes.[19] Our study thus provides an alternative method for their preparations.

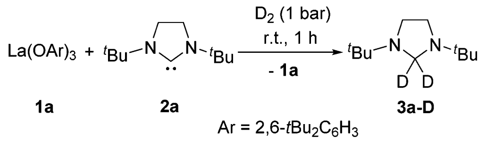
Table 1 Catalytic hydrogenation of NHCs with RE aryloxides[a]



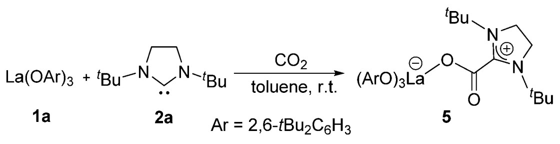
Entry	NHC	RE cat.	Time (h)	Yield (%)
1	**2a** (R = ^{t}Bu)	**1a** (La)	1	99 (79)[b]
2	**2a** (R = ^{t}Bu)	**1b** (Sm)	1	99
3	**2a** (R = ^{t}Bu)	**1c** (Y)	12	73
4[c]	**2a** (R = ^{t}Bu)	**1a** (La)	1	99 (84)[b]
5	**2b** (R = Mes)	**1a** (La)	1	99 (86)[b]
6[d]	**2c** (R = DIPP)	**1a** (La)	24	50 (46)[b]

[a] Conditions: hydrogenation reactions were conducted in C_6D_6 (0.5 mL) under 1 bar H_2 at room temperature, with 0.1 mmol of NHC and 0.005 mmol of the RE catalyst used. Yields were determined by ^{1}H NMR using mesitylene or ferrocene as an internal standard. [b] Isolated yields in parentheses. [c] Reaction was performed under 1 bar D_2 with 20 mol% catalyst loading. [d] Reaction was performed at 80 °C with 30 mol% catalyst loading.

Because the intermolecular combination **1a**/**2a** showed typical FLP reactivity towards H_2, we attempted to determine whether the La/NHC pair was capable of activating CO_2[20] as can be done using the main-group[21] or other organometallic FLPs.[22] Recent studies by Arnold[12d] and Roesky[23] have also shown that molecular CO_2 can insert into an internal RE-carbene bond. We conducted a three-component reaction by adding one equivalent of CO_2 to a 1 : 1 mixture of the La complex **1a** and the NHC **2a** at room temperature in toluene. The reaction proceeded rapidly and gave the expected La/NHC FLP-type 1,2-addition product **5** as a crystalline solid in 88% isolated yield (Scheme 3). Complex **5** was fully



Scheme 2 Reaction of FLP **1a**/**2a** with deuterium gas.



Scheme 3 Reaction of La/NHC FLP with CO_2.

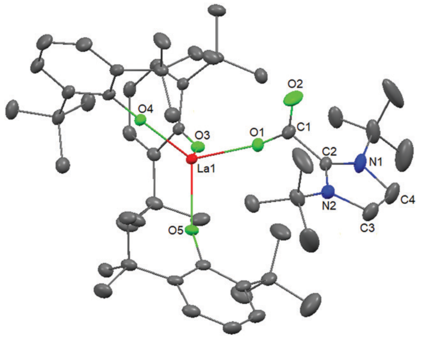


Fig. 1 Molecular structure of the complex **5**. Hydrogen atoms are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level.

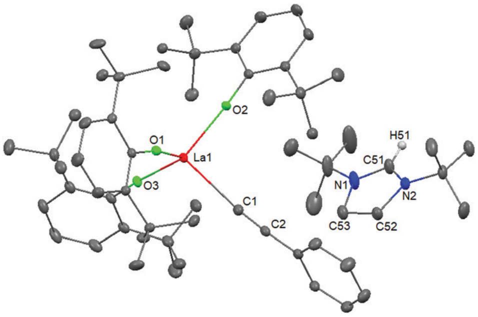
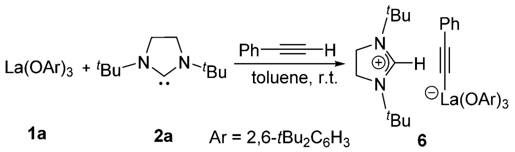


Fig. 2 Molecular structure of the complex **6**. Hydrogen atoms (except H51) are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level.

characterized by NMR spectroscopy, single crystal X-ray diffraction and C,H,N-elemental analysis, and its molecular structure is depicted in Fig. 1. This structure clearly shows that, during the reaction, the Lewis acidic La center attacked the oxygen atom of the CO_2 molecule to form a new La–O bond (La1–O1 2.372(2) Å), whereas the Lewis basic NHC attacked the carbonyl carbon atom to form a C–C bond (C1–C2 1.532(4) Å). The geometry at C1 is planar tricoordinate ($\Sigma C1^{OCO}$ = 360.0°) with different C–O bond lengths (C1–O1 1.270(4) Å, C1–O2 1.196(4) Å), precluding the bidentate chelating coordination mode of the carboxylate.[23] The product generated an infrared band at 1633 cm^{-1} that is attributed to the C–O double bond. It is also notable that complex **5** was found to be thermally stable up to 60 °C, up to which point no CO_2 liberation was observed, in contrast to the main-group B/P systems.[21a]

Finally, the reaction of the **1a**/**2a** FLP with the terminal alkyne phenylacetylene was performed in toluene at room temperature.[24] This reaction selectively afforded a deprotonated, zwitterionic complex **6** in a high isolated yield (90%, Scheme 4), despite the potential for phenylacetylene to undergo oxidative addition to NHC **2a** in the absence of **1a** (for details, see the ESI†). Single crystals of **6** were obtained from a layered toluene/hexane solution at room temperature. The X-ray crystal structure analysis of **6** (Fig. 2) showed a separated ion pair containing a heteroleptic La anion and an imidazolium cation. In solution, this complex produced a lower-field signal at δ 7.42 ppm in its ^1H NMR spectrum, attributed to the NC*H*N unit, with the corresponding ^{13}C NMR signal at δ 150.7 ppm.

In conclusion, stimulated by the flourishing field of FLP chemistry, cooperative H_2 activation was achieved based on a facile combination of homoleptic rare-earth aryloxides with N-heterocyclic carbenes under mild conditions. In these reactions, RE/NHC Lewis pairs heterolytically split H_2 molecules to form transient species **4**, followed by hydride transfer to give aminal **3**. Consequently, RE complexes **1** were able to serve as active catalysts for the hydrogenation of NHCs. The La/NHC Lewis pair also showed typical FLP reactivity toward CO_2 and phenylacetylene. This study demonstrates a new approach to rare-earth metal mediated H_2 activation and catalytic hydrogenation. The use of $RE(OAr)_3$ complexes as catalysts for other chemical transformations is currently the subject of ongoing research by our group.



Scheme 4 Reaction of La/NHC FLP with phenylacetylene.

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Conflicts of interest

There are no conflicts to declare.

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13 We conducted the reaction of NHC **2a** with sterically less encumbered La(OAr)$_3$ (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$) at room temperature. However, it seemed to be complicated, giving an NHC self-dehydrogenation compound and other unidentified complexes, rather than a simple NHC coordination.

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