Group 13 Metal Catalysis | Hot Paper

International Edition: DOI: 10.1002/anie.201500570
German Edition: DOI: 10.1002/ange.201500570

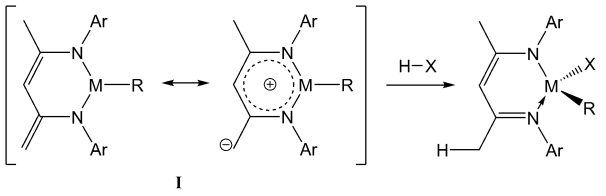
Cooperative Bond Activation and Catalytic Reduction of Carbon Dioxide at a Group 13 Metal Center**

*Joseph A. B. Abdalla, Ian M. Riddlestone, Rémi Tirfoin, and Simon Aldridge**

Abstract: *A single-component ambiphilic system capable of the cooperative activation of protic, hydridic and apolar H–X bonds across a Group 13 metal/activated β-diketiminato (Nacnac) ligand framework is reported. The hydride complex derived from the activation of H_2 is shown to be a competent catalyst for the highly selective reduction of CO_2 to a methanol derivative. To our knowledge, this process represents the first example of a reduction process of this type catalyzed by a molecular gallium complex.*

H–X bond activation processes represent key mechanistic steps in numerous catalytic reactions of critical industrial importance.[1] Classically such activation is brought about by oxidative addition utilizing the readily accessible $n/n+2$ redox states of "noble" transition metals.[1] Recently however, economic and environmental imperatives have driven the development of alternative catalyst systems, including a number based on cooperative metal–ligand activation processes.[2–4] The implication of metal centers in a single fixed oxidation state, for example in the pincer systems of Milstein,[4] suggests that such bond activation processes might also be viable using complexes of the lighter main group metals.

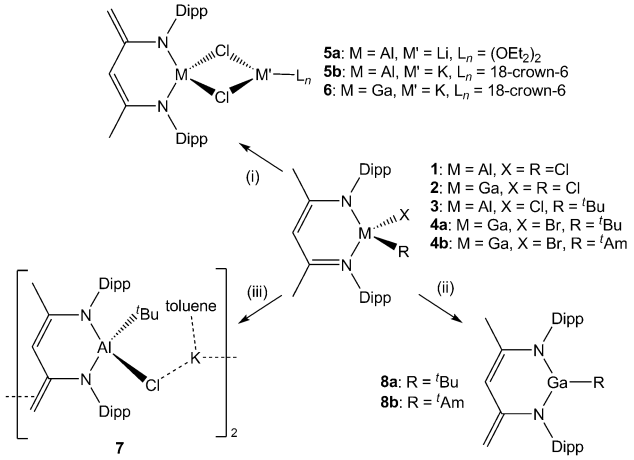
A key feature of many complexes capable of such cooperative H–X bond activation is the availability of a ligand site with appreciable Lewis basicity.[4] As such, H–X cleavage takes place by ligand (re)protonation, with the formally anionic X^- component sequestered by the metal center. β-Diketiminato ("Nacnac") ligand systems have proved to be highly effective in the stabilization of a range of low-valent/low-coordinate main group metal centers.[5] Moreover, the backbone methyl groups of such ligands are amenable to deprotonation, thereby generating a pendant alkene function (with appreciable nucleophilic character at the terminal carbon), and converting the monoanionic iminoamide ligand into a dianionic diamide.[6–9] With this in mind, we wondered if such a backbone activated system might be partnered with a Lewis acidic three-coordinate Group 13 center to generate an ambiphilic system (e.g. **I**, Scheme 1) capable of the cooperative activation of H–X bonds.



I

Scheme 1. Cooperative H–X bond activation using target ambiphilic systems I (M = group 13 metal).

The deprotonation of an aluminium-bound Nacnac ligand at the backbone methyl position has previously been accomplished by the use of an amide base in THF.[8] The use of a donor solvent, however, necessarily generates a tetracoordinate, base-stabilized metal center. In order to circumvent this problem we envisaged carrying out deprotonation in more weakly coordinating media. However, in either diethyl ether or benzene the reactions of the dichloroaluminum and -gallium systems [(Dipp$_2$Nacnac)MCl$_2$] (**1**: M = Al; **2**: M = Ga)[10] with lithium or potassium alkyls exclusively generate "ate" complexes (Scheme 2). ^{1}H and ^{13}C NMR data for the products **5a/b** and **6** reveal the characteristic patterns of the deprotonated diene (Nacnac′) backbone,[6–9] but X-ray crystallography shows that the alkali metal chloride is retained



Scheme 2. Reactions of β-diketiminato (Nacnac)-stabilized aluminium and gallium halides with strong Brønsted bases: formation of "ate" complexes and halide-free systems. Key reagents and conditions: i) (for **5a**) *t*BuLi (1.5 equiv), Et_2O, −78 °C to RT, 12 h 39%, (for **5b**, **6**) K[CH(SiMe$_3$)$_2$] (1.1 equiv), benzene, RT, 12 h, then 18-crown-6, 87% (for **5b**), 46% (for **6**); ii) K[CH(SiMe$_3$)$_2$] (1.3 equiv), benzene, 30 min, RT, >95% conversion by NMR (the 10% isolated yield of **8b** reflects very high solubility in hydrocarbon media); iii) K[CH(SiMe$_3$)$_2$] (1.5 equiv), benzene, 30 min, RT, 45%.

[*] J. A. B. Abdalla, Dr. I. M. Riddlestone, R. Tirfoin, Prof. S. Aldridge
Inorganic Chemistry Laboratory, Department of Chemistry
University of Oxford, South Parks Road, Oxford, OX1 3QR (UK)
E-mail: Simon.Aldridge@chem.ox.ac.uk

[**] EPSRC (studentship: J.A.B.A.; NMSF, Swansea University; EP/L025000/1 and EP/K014714/1).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500570.

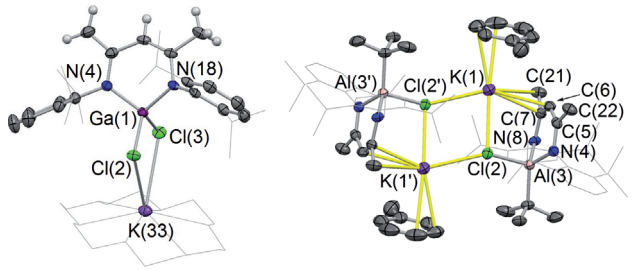


Figure 1. Molecular structures of **6** (left) and **7** (right) determined by X-ray crystallography. Most H atoms omitted, and selected C atoms shown in wireframe format for clarity; thermal ellipsoids at 50% probability level. Key bond lengths [Å] and angles [°]: (for **6**) Ga(1)–N(4) 1.874(3), Ga(1)–N(18) 1.871(3), Ga(1)–Cl(2) 2.198(1), Ga(1)–Cl(3) 2.210(1), Cl(2)–K(33) 3.285(1), Cl(3)–K(33) 3.425(1); (for **7**) Al(3)–N(4) 1.869(3), Al(3)–N(8) 1.856(3), Al(3)–Cl(2) 2.292(1), K(1)–Cl(2) 3.160(2), K(1′)–Cl(2) 3.292(1).

even when a potassium base is used (Figure 1 and Supporting Information). The Group 13 metal center therefore remains 4-coordinate, with minimal M–Cl elongation, and with the lithium/potassium cation bridging the two chloride substituents of the dichloroaluminate/gallate fragment.

With this in mind, we hypothesized that replacement of one of the aluminium/gallium-bound chlorides with a sterically bulky, weakly bridging substituent (e.g. *t*Bu) might promote KCl loss. Accordingly, the reaction of [(Dipp$_2$Nacnac)Al(*t*Bu)Cl] (**3**) with K[CH(SiMe$_3$)$_2$] was investigated; the product so generated (after recrystallization from toluene) also shows the desired backbone deprotonation, but KCl is again retained within an overall dimeric structure, [{(Dipp$_2$NacNac′)Al(*t*Bu)ClK(toluene)}$_2$] (**7**, Figure 1). **7** nonetheless features a markedly lengthened Al–Cl contact compared to **3** [2.292(1) Å vs. 2.168(1) Å], and the less halophilic nature of gallium (vs. aluminum)[11] suggested to us that similar chemistry might be successful with gallium, especially if carried out in conjunction with a weaker metal–halogen bond. Thus, the deprotonation of [(Dipp$_2$Nacnac)Ga(*t*Bu)Br] (**4a**) with K[CH(SiMe$_3$)$_2$] was investigated (Scheme 2). In this case, the ^{1}H and ^{13}C NMR spectra are also consistent with backbone deprotonation [for example, signals at $\delta_H = 1.52$, 3.23/3.93 and 5.29 ppm, corresponding to the CH_3, two distinct alkene CH, and γ-CH protons, respectively],[8] but in contrast to **7**, the pattern of resonances for the Dipp groups (two methine septets, four methyl doublets) is indicative of a plane of symmetry within the molecule. While the oily nature of this compound (**8a**) prevented definitive structural characterization, analogous chemistry using the *tert*-amyl substituent (*t*Am, -CMe$_2$Et) allowed for crystallization of [(Dipp$_2$Nacnac′)Ga(*t*Am)] (**8b**). With the exception of the *t*Am/*t*Bu signals, the ^{1}H and ^{13}C NMR spectra of **8a** and **8b** are essentially indistinguishable, and in the latter case the formation of a three-coordinate gallium center could be confirmed crystallographically (Figure 2).

The molecular structure of **8b** features disparate endocyclic [1.372(3), 1.440(3) Å] and exocyclic C–C distances [1.375(3), 1.484(4) Å], consistent with the presence of localized C=C double and C–C single bonds across the Nacnac′ backbone. In addition, the C–N [1.397(3), 1.409(3) Å] and Ga–N contacts [1.849(2), 1.854(2) Å] are consistent with a diamido ligand description,[8] and the sum of the N-Ga-N and N-Ga-C angles [360.0(3)°] confirms the presence of a trigonal planar gallium center.

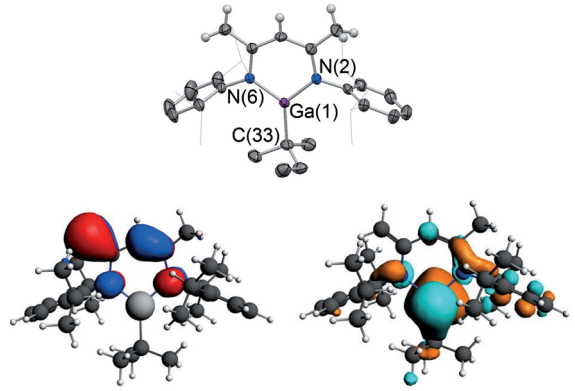
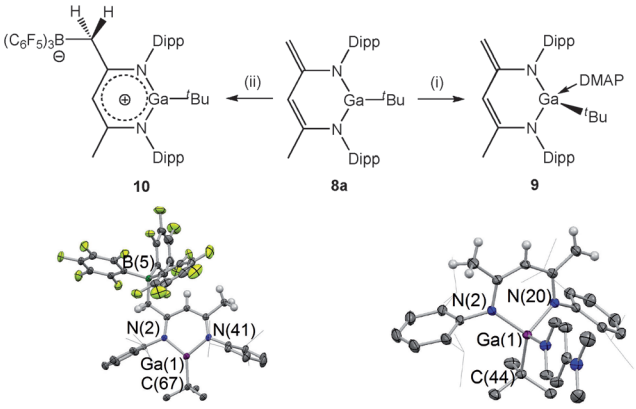


Figure 2. Molecular structure of **8b** determined by X-ray crystallography. Most H atoms omitted, and selected C atoms shown in wireframe format for clarity; thermal ellipsoids at 50% probability level. Key bond lengths [Å] and angles [°]: Ga(1)–N(2) 1.854(2), Ga(1)–N(6) 1.849(2), Ga(1)–C(33) 1.988(2), N(2)–C(3) 1.397(3), N(6)–C(5) 1.409(3), C(3)–C(4) 1.372(3), C(4)–C(5) 1.440(3), C(3)–C(20) 1.484(4), C(5)–C(19) 1.375(3); N(2)-Ga(1)-N(6) 104.5(1), N(2)-Ga(1)-C(33) 126.5(1), N(6)-Ga(1)-C(33) 129.0(1). DFT calculated HOMO (left, −3.72 eV) and LUMO (right, −1.59 eV) for **8a**.

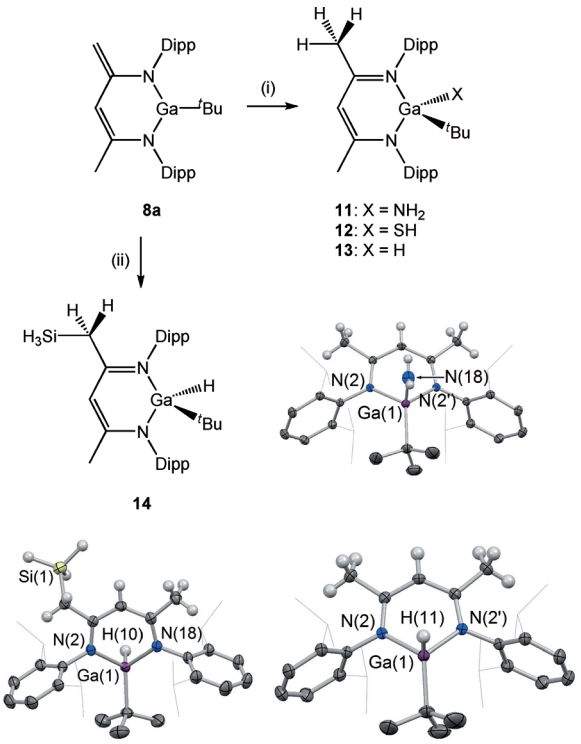
The fundamental basis for ambiphilic reactivity in **8a**/**8b** was probed by a combination of experimental and quantum chemical studies. DFT calculations (Figure 2 and Supporting Information) accurately reproduce the key geometric parameters and reveal a HOMO which has significant amplitude at the terminal carbon of the exocyclic alkene function, and a LUMO which is dominated by Ga 4p$_z$ character. Such observations are also borne out experimentally: **8a** reacts with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) through coordination at gallium, and with B(C$_6$F$_5$)$_3$ to give a zwitterionic system featuring a borate-appended Nacnac ligand (Scheme 3



Scheme 3. Reactivity of **8a** towards external Lewis acids/bases. Key reagents and conditions: i) DMAP (1.0 equiv), benzene, RT, 15 min, 66%; ii) B(C$_6$F$_5$)$_3$ (1.0 equiv), benzene, RT, 1 h, 71%. Molecular structures of **9** (right) and **10** (left) determined by X-ray crystallography. Most H atoms omitted, and selected C atoms shown in wireframe format for clarity; thermal ellipsoids at 50% probability level.

and Supporting Information). **8a** therefore possesses both Lewis basic *and* Lewis acidic character, and the fact that it does not undergo intermolecular aggregation is attributed to the high steric loading around the gallane center.

Confirmation that this system might be regarded as single-component frustrated Lewis pair,[12] led us to investigate its reactivity towards a range of H–X bonds. Thus, protic H–X bonds, such as those found in ammonia and hydrogen sulfide are cleaved rapidly at room temperature,[13] leading to protonation of the Nacnac′ backbone and to the assimilation of the NH_2^-/SH^- conjugate base at the gallium center (Scheme 4 and Supporting Information). In each case, regeneration of the β-diketiminato backbone is reflected in



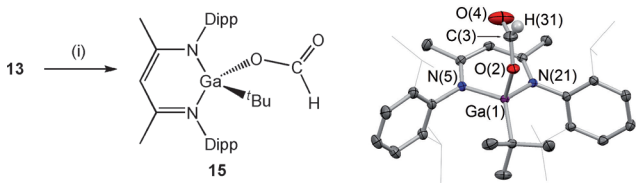
Scheme 4. Differing regioselectivities in the activation of protic and hydridic H–X bonds by **8a**. Key reagents and conditions: i) (for **11**/**12**) excess NH_3/H_2S gas, benzene, RT, 30 min (decolorization in < 2 min), 60–75%; (for **13**) H_2 (ca. 4 atm), benzene, 70 °C, 7 h, 54%; ii) SiH_4 (1 atm), benzene, RT, 1 h, 62%. Molecular structures of **11** (upper), **13** (lower right) and **14** (lower left) determined by X-ray crystallography (see Supporting Information for **12**). Most H atoms omitted, and selected C atoms shown in wireframe format for clarity; thermal ellipsoids at 50% probability level.

a heterocycle geometry featuring equivalent internal C–C distances [1.400(1) Å for **11**], and C–N bonds which are shortened compared to the formal single bonds found in the diamido Nacnac′ ligand in **8b** [1.332(1) Å for **11** cf. 1.397(3), 1.409(3) Å]. Activation of hydridic H–X bonds proceeds in the opposite sense, with SiH_4, for example, giving rise to a backbone appended SiH_3 moiety and a gallium bound hydride (Scheme 4). The latter is signaled in the ^{1}H NMR spectrum of **14** by a broad resonance at $\delta_H = 5.43$ ppm and is visible in the crystallographic difference Fourier map at a Ga–H distance of 1.44(3) Å.

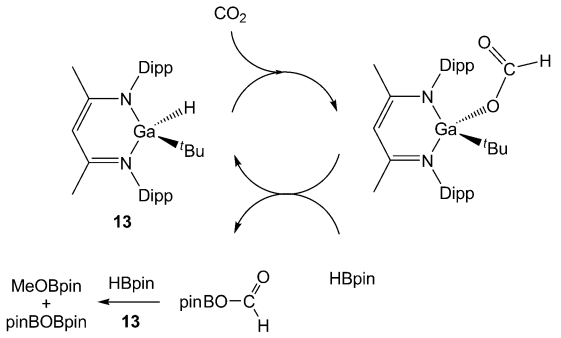
While the ready reactivity of **8a** towards both acidic and hydridic H–X bonds can be rationalized on the basis of the strongly polarized electron distribution in **8a**, this system remarkably also possesses the ability to heterolytically cleave non-polar molecules such as dihydrogen. In this case, the reaction requires more forcing conditions (12 h at 70 °C), but the product so generated [(Dipp$_2$Nacnac)Ga(*t*Bu)H] (**13**; Scheme 4) has been unambiguously characterized both spectroscopically and crystallographically, and synthesized independently from **4a** and K[BEt_3H] (Supporting Information).

In the case of protic substrates such as ammonia, it can be shown that pre-coordination at gallium, followed by intermolecular deprotonation is a feasible reaction pathway.[14,15] In the case of H_2, however, we hypothesized that concerted activation was more likely: Sicilia and co-workers, for example, have examined computationally the possibility for direct 1,4-addition of an H–X bond across a single (Nacnac′)E molecule (E = Si, Ge).[16] Monitoring the conversion of **8a** to **13** (and the corresponding reaction of **8a** with D_2) by in situ ^{1}H NMR spectroscopy, however, reveals 1) the formation of several long-lived intermediate species characterized by Nacnac γ-CH signals in the region $\delta_H = 4.89$-5.27 ppm; 2) the appearance of a broad Ga–H resonance at $\delta_H = 5.44$ ppm showing similar concentration–time behavior. These observations imply that a simple concerted bimolecular process is unlikely, a finding in line with the crystallographically determined 1,4 Ga···C separation of ca. 4.14 Å for **8b**.[17] By contrast, the observation of discrete GaH-containing intermediates is not inconsistent with initial activation of H_2 by **8a** in 1,2 fashion across the Ga–N bond(s), and computational evaluation of the regioisomeric Ga–N/H–H activation products is energetically consistent with their potential intermediacy in the **8a**/H_2 reaction.[18,19] Moreover, precedent for 1,2-activation of H_2 within a strongly Lewis acidic Group 13 heterocycle comes from the work of Piers and co-workers on pentaarylboroles.[20]

Ga–H bonds have previously been shown 1) to be capable of inserting unsaturated substrates featuring C=E multiple bonds, and 2) to be generated from Ga–X bonds by metathesis reactions utilizing silanes or boranes as the hydride source.[21] Thus, we hypothesized that the *catalytic* reduction of C=O double bonds might be possible using either **8a** or **13** as an entry point into an appropriate cycle. In particular, we were interested in the catalytic reduction of CO_2, since such chemistry has little precedent among single-site main group systems. In the event, although CO_2 reacts with **8a** to give an intractable mixture of products, the corresponding reaction with **13** cleanly yields the formate complex [(Dipp$_2$Nacnac)Ga(*t*Bu){κ^1-OC(O)H}] (**15**) which has been characterized by standard spectroscopic and crystallographic techniques (Scheme 5 and Supporting Information).[22] Moreover, **15** can be shown to react with pinacolborane (HBpin, pin = $OCMe_2CMe_2O$) in benzene to yield **13** and MeOBpin.[23] Such observations imply that **13** could act as a catalyst for the reduction of CO_2 to MeOBpin using HBpin. Thus, in benzene solution at 60 °C, (using excess CO_2) complete (highly selective) conversion of HBpin to MeOBpin (and pinBOBpin) occurs over 4 h at 10 mol% loading (Scheme 6). Catalytic reduction of CO_2 in this fashion by non-transition



Scheme 5. Stoichiometric uptake of CO_2 by [(Nacnac^{Dipp})Ga(*t*Bu)H] (**13**). Key reagents and conditions: i) CO_2 gas (ca. 1 atm), toluene, RT, 12 h, 66%. Molecular structure of **15** determined by X-ray crystallography. Most H atoms omitted, and selected C atoms shown in wireframe format for clarity; thermal ellipsoids set at the 50% probability level.



Scheme 6. Reduction of CO_2 to MeOBpin by HBpin catalyzed by gallium hydride **13**.

metal systems is very rare,[24] with previous examples of single-site main group metal catalysts requiring the use of a strong Lewis acid co-catalyst. The activity of **13** can thus be compared to $B(C_6F_5)_3$-activated magnesium and calcium hydride systems reported by Hill and co-workers (complete conversion over 6 d (Mg) or 4 d (Ca) at 60 °C using 10 mol% loading).[24h] The derived turnover frequencies (2.5 vs. 0.07/0.1 h^{-1}) therefore imply that **13** is 1–2 orders of magnitude more active for this selective reduction process.

In conclusion, we report the synthesis of a single-component ambiphilic system capable of the cooperative activation of protic, hydridic and apolar H–X bonds across a gallium/activated Nacnac ligand framework. Moreover, the hydride complex derived from the activation of H_2 is a competent catalyst for the selective reduction of CO_2 to a methoxy derivative using HBpin. Although gallium hydrides have previously been reported to act a radical initiators in a similar fashion to Bu_3SnH,[25] the process we describe represents, to our knowledge the first example of such a reduction process catalyzed by a molecular gallium species. Further studies aimed at extension to the corresponding alanes are ongoing.

Experimental Section

Synthetic, spectroscopic and crystallographic data for all new compounds, details of the DFT calculations (including run files), and all CIFs are included in the Supporting Information. CCDC 1038748–1038762 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Keywords: β-diketiminate · bond activation · carbon dioxide · cooperative reactivity · gallium

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 5098–5102
Angew. Chem. **2015**, *127*, 5187–5191

[1] See, for example: *Organotransition Metal Chemistry: From Bonding to Catalysis* (Ed.: J. F. Hartwig), University Science Books, Sausalito, **2010**.
[2] Main group systems in small-molecule activation: a) P. P. Power, *Nature* **2010**, *463*, 171–177; b) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389–399.
[3] See, for example: a) P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794–795. For approaches to hydrogenation using "non-precious" transition metals see: b) R. M. Bullock, *Science* **2013**, *342*, 1054–1055.
[4] a) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588–602; b) C. Gunanathan, D. Milstein, *Chem. Rev.* **2014**, *114*, 12024–12087.
[5] For a review of Group 13 systems, see: M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354–396.
[6] M. Driess, S. Yao, M. Brym, C. van Wüllen, *Angew. Chem. Int. Ed.* **2006**, *45*, 4349–4352; *Angew. Chem.* **2006**, *118*, 4455–4458.
[7] a) M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz, *J. Am. Chem. Soc.* **2006**, *128*, 9628–9629; b) S. Yao, Y. Xiong, M. Driess, *Organometallics* **2011**, *30*, 1748–1767.
[8] a) S. P. Sarish, H. Roesky, M. John, A. Ringe, J. Magull, *Chem. Commun.* **2009**, 2390–2392; b) S. P. Sarish, B. Nekoueishahraki, A. Jana, H. Roesky, T. Schulz, D. Stalke, *Chem. Eur. J.* **2011**, *17*, 890–894.
[9] M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon, I. Mallov, *Inorg. Chem.* **2012**, *51*, 13408–13418.
[10] M. Stender, B. E. Eichler, N. J. Hardman, P. P. Power, J. Prust, M. Noltemeyer, H. W. Roesky, *Inorg. Chem.* **2001**, *40*, 2794–2799.
[11] *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Petterns and Peculiarities* (Eds.: S. Aldridge, A. J. Downs), Wiley, Chichester, **2011**.
[12] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81.
[13] Previous examples of 1,4-activation of ammonia and hydrogen sulfide by Group 14 Nacnac′ systems: a) A. Jana, I. Objartel, H. W. Roesky, D. Stalke, *Inorg. Chem.* **2009**, *48*, 798–800; b) A. Meltzer, S. Inoue, C. Präsang, M. Driess, *J. Am. Chem. Soc.* **2010**, *132*, 3038–3046. For the oxidative activation of NH_3 at gallium, see: c) Z. Zhu, X. Wang, Y. Peng, H. Lei, J. C. Fettinger, E. Rivard, P. P. Power, *Angew. Chem. Int. Ed.* **2009**, *48*, 2031–2034; *Angew. Chem.* **2009**, *121*, 2065–2068.
[14] The 1:1 ammonia adduct of **10** has been synthesized by direct combination with NH_3 (and structurally characterized, see the Supporting Information) and its reaction with **8a** shown to proceed through a proton transfer to the alkenic backbone function of the latter to generate [(Nacnac)Ga(*t*Bu)]$^+$.
[15] For an example of the coordination of a less polar E–H bond at a Group 13 center see: A. Y. Houghton, J. Hurmalainen, A. Mansikkamäki, W. E. Piers, H. M. Tuononen, *Nat. Chem.* **2014**, *6*, 983–988.
[16] M. E. Alberto, N. Russo, E. Sicilia, *Chem. Eur. J.* **2013**, *19*, 7835–7846.
[17] A termolecular process involving the concerted activation of H_2, with one molecule of **8a** acting as a Lewis acid and a second acting as a Lewis base (as is postulated for certain FLP systems)[12] is also conceivable. However, the γ-CH ^{1}H NMR resonance for [(Nacnac) Ga(*t*Bu)]$^+$ (as would be generated in such a reaction by protonation of **8a**) is found at very low field ($\delta_H = 6.41$ ppm in C_6D_5Br). As such, it is unlikely that [(Nacnac)Ga(*t*Bu)]$^+$ corresponds to one of the intermediate

species found in the **8a**/H_2 reaction by in situ ^{1}H NMR monitoring.

[18] The presence in the reaction mixture of appreciable concentrations of the regioisomeric products resulting from addition of H_2 across either of the Ga–N bonds in **8a** is consistent with preliminary DFT calculations which show that these two systems lie within 1.0 kcal mol^{-1} energetically of **8a** + H_2 (see Supporting Information).

[19] For an example of E–H bond activation across an Al–N bond see: T. W. Myers, L. A. Berben, *J. Am. Chem. Soc.* **2013**, *135*, 9988 – 9990.

[20] a) C. Fan, L. G. Mercier, W. E. Piers, H. M. Tuononen, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 9604 – 9608.

[21] a) A. J. Downs, C. R. Pulham, *Chem. Soc. Rev.* **1994**, *23*, 175 – 184; b) S. Aldridge, A. J. Downs, *Chem. Rev.* **2001**, *101*, 3305 – 3366.

[22] For insertion of CO_2 into a Nacnac-stabilized Ge hydride, see: A. Jana, G. Tavčar, H. W. Roesky, M. John, *Dalton Trans.* **2010**, *39*, 9487 – 9489. For related insertion into an Al–H bond, see: b) T. W. Myers, L. A. Berben, *Chem. Sci.* **2014**, *5*, 2771 – 2777.

[23] MeOBpin has previously been shown to result from the further reaction of the formate ester HC(O)OBpin with excess HBpin under catalytic conditions.[24h] If the reduction of CO_2 by HBpin catalyzed by 10 mol% **13** is carried out in THF, the reaction proceeds more slowly and the predominant reduction product after 16 h is HC(O)OBpin.

[24] For catalytic CO_2 reduction by non-transition metal systems, see: a) L. Gu, Y. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 914 – 915; b) S. N. Riduan, Y. Zhang, J. Y. Ying, *Angew. Chem. Int. Ed.* **2009**, *48*, 3322 – 3325; *Angew. Chem.* **2009**, *121*, 3372 – 3375; c) A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem. Int. Ed.* **2009**, *48*, 9839 – 9843; *Angew. Chem.* **2009**, *121*, 10023 – 10027; d) A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660 – 10661; e) M. J. Sgro, D. W. Stephan, *Angew. Chem. Int. Ed.* **2012**, *51*, 11343 – 11345; *Angew. Chem.* **2012**, *124*, 11505 – 11507; f) R. Dobrovetsky, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 2516 – 2519; *Angew. Chem.* **2013**, *125*, 2576 – 2579; g) M.-A. Courtemanche, M.-A. Légaré, L. Maron, F.-G. Fontaine, *J. Am. Chem. Soc.* **2013**, *135*, 9326 – 9329; h) M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. Kociok-Köhn, D. J. Liptrot, M. F. Mahon, C. Weetman, *Chem. Sci.* **2014**, *5*, 2826 – 2830; i) T. Wang, D. W. Stephan, *Chem. Eur. J.* **2014**, *20*, 3036 – 3039.

[25] See, for example: M. Satoshi, K. Fujita, T. Nakamira, H. Yorimitsu, H. Shinokubo, S. Matsubara, K. Oshima, *Org. Lett.* **2001**, *3*, 1853 – 1855.

Received: January 20, 2015
Published online: February 27, 2015

