



An Aluminum Hydride That Functions like a Transition-Metal Catalyst**

Zhi Yang,* Mingdong Zhong, Xiaoli Ma, Susmita De, Chakkittakandiyil Anusha, Pattiyil Parameswaran,* and Herbert W. Roesky*

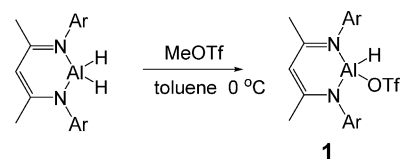
Dedicated to Professor Jean-Marie Lehn on the occasion of his 75th birthday

Abstract: The reaction of $[LAlH_2]$ ($L = HC(CMeNAr)_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$) with $MeOTf$ ($Tf = SO_2CF_3$) resulted in the formation of $[LAlH(OTf)]$ (**1**) in high yield. The triflate substituent in **1** increases the positive charge at the aluminum center, which implies that **1** has a strong Lewis acidic character. The excellent catalytic activity of **1** for the hydroboration of organic compounds with carbonyl groups was investigated. Furthermore, it was shown that **1** effectively initiates the addition reaction of trimethylsilyl cyanide (TMSCN) to both aldehydes and ketones. Quantum mechanical calculations were carried out to explore the reaction mechanism.

Group 13 hydrides have been studied for hydrogen storage,^[1] and used for various organic transformations.^[2] The chemistry of the aluminum hydrides is well-developed for the reduction of various polar functional and unsaturated substrates.^[3] Considering the distinct reactivity of $[LAlH_2]$ ($L = HC(CMeNAr)_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$), it can be used for the activation of nonpolar sulfur–sulfur bonds.^[4] Moreover, the β -diketiminato substituent has found widespread application as a supporting ligand for metal-mediated catalysis.^[5] Consequently, functionalized $[LAlH_2]$ can be a viable alternative to transition-metal compounds for catalysis through rational ligand design. Recently, Driess and co-workers reported on the activation of C–H and C–O bonds mediated by the hydrido-Al(I)→Fe complex.^[6] In contrast to the reported

bimetallic system, where alkaline bases are crucial for the activation of inert C–H bonds,^[7] the THF coordinate anion is stabilized in this complex only by the Al center. This observation prompted us to investigate aluminum(III) hydride as a main-group catalyst based on the principles of transition-metal catalysts.^[8] Previous examples of single-site main-group metal catalysts require a strong Lewis acid cocatalyst.^[9] One consideration to increase the reactivity of aluminum hydride species is the opening of the coordination site for substrate binding and activation. This feature is made possible by conferring a higher positive charge to the Al center, while concurrently retaining its requisite hydridic character of the Al–H bond.

The electrophilic $MeOTf$ ($Tf = SO_2CF_3$) was treated with $[LAlH_2]$ resulting in **1** in high yield (Scheme 1). Compound



Scheme 1. Synthesis of aluminum monohydride complex **1**. $Ar = 2,6\text{-}iPr_2C_6H_3$, $Tf = SO_2CF_3$.

1 was characterized by multinuclear NMR spectroscopy, single-crystal X-ray studies, and elemental analysis. The 1H NMR spectrum of **1** shows splitting of the isopropyl group signals. The infrared spectrum of **1** shows only one absorption band (1797 cm^{-1}) in contrast to that of $[LAlH_2]$ (1832 and 1795 cm^{-1}),^[10] thus confirming the existence of only one Al–H bond. The calculated gas-phase reaction energy for the formation of **1** from $[LAlH_2]$ ($-67.9\text{ kcal mol}^{-1}$), indicates the thermodynamic feasibility of the reaction (Scheme S1).^[11] Single crystals of X-ray quality were obtained from a toluene solution of **1** at low temperature. The molecular structure as well as the selected bond lengths and angles are shown in the caption of Figure S1 (see the Supporting Information). The Al–N bond length (average $1.8674\text{ \AA}$) of **1** is shorter than that of $[LAlH_2]$ (average $1.8989\text{ \AA}$).^[10] This observation suggests that the OTf substituent in **1** increases the positive charge at the aluminum center, which implies a strong Lewis acidic character of **1**.^[12] This behavior is consistent with the NBO charge on Al, which is $1.41e$ in $[LAlH_2]$ and $1.81e$ in compound **1** (Table S3).

[*] Prof. Z. Yang, Dr. M. Zhong, Dr. X. Ma
School of Chemical Engineering and Environment
Beijing Institute of Technology
100081 Beijing (P.R. China)
E-mail: zhiyang@bit.edu.cn

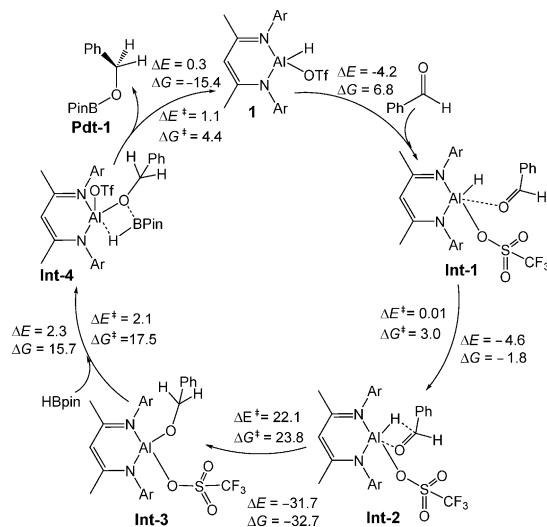
Prof. H. W. Roesky
Institut für Anorganische Chemie, Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
E-mail: hroesky@gwdg.de

Dr. S. De, M. Sc. C. Anusha, Dr. P. Parameswaran
Department of Chemistry,
National Institute of Technology Calicut
NIT Campus P.O., Calicut, Kerala, 673 601 (India)
E-mail: param@nitc.ac.in

[**] We are grateful to the Beijing Natural Science Foundation (2132044) and Beijing Higher Education Young Elite Teacher Project (YETP1191). Support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201503304>.

Jones and co-workers recently reported on the catalytic hydroboration of ketones and aldehydes using Group 14 metal(II) hydrides with two-coordinate metal atoms.^[13] In order to compare the results of the well-defined *p*-block metals in this catalysis, we used **1** as an active catalyst for hydroboration of organic carbonyl groups. As shown in Scheme 2, the reaction of **1** with one equivalent of benzaldehyde



Scheme 2. Reaction mechanism for the hydroboration of benzaldehyde calculated at the M06/def2-TZVPP/BP86/def2-SVP level of theory.^[11b]

hyde (PhCHO) is rapid at ambient temperature and affords the hydrometalation product [LAl(OCH₂Ph)(OTf)] (**Int-3**), in essentially quantitative yield (as determined by ¹H NMR spectroscopic analyses of the reaction mixture). Finally, **Int-3** was reacted with a stoichiometric amount of pinacolborane (HBpin) at room temperature in C₆D₆. The formation of the desired molecule PhCH₂OBpin (**Pdt-1**) was monitored by ¹H NMR spectroscopy, and shows that σ-bond exchange occurs between the Al–O bond of the catalyst with the B–H bond of pinacolborane. To the best of our knowledge, this is the first example of an organoaluminum hydride acting as a catalyst for the hydroboration of organic carbonyl groups. In contrast, the uncatalyzed hydroboration of benzaldehyde showed little reactivity (Table 1, entry **2a**), while the addition of only 1 mol % of **1** led to full conversion to [PhCH₂OBpin] within 1 h at room temperature (Table 1, entry **2b**).

We have carried out quantum-mechanical calculations at the M06/def2-TZVPP/BP86/def2-SVP level of theory to explore the reaction mechanism (Scheme 2 and Figure S2).^[11] The first step of the reaction can be considered as the formation of a weakly bound complex (**Int-1**), where the incoming substrate PhCHO approaches the tetrahedral Al center from the side opposite to one of the Al–N bonds (Al–O_{CHPh} distance is 3.581 Å). The reaction energy (Δ*E*) and Gibbs free energy (Δ*G*) for this step are –4.2 and 6.8 kcal mol^{–1}, respectively.^[11b] The nucleophilic attack of the carbonyl oxygen atom of PhCHO to the electrophilic tetrahedral Al center (NBO charge on Al = 1.81 *e*) results in the complex **Int-2** (Al–O_{PhCHO} = 2.090 Å), which has a distorted trigonal-

Table 1: Hydroboration of aldehydes and ketones catalyzed by **1**.^[a]

Entry	Substrate	Cat. [mol %]	<i>t</i> [h]	Yield [%] ^[b]
2a		0	1	trace
2b		1	1	99%
2c		1	1	99%
2d		1	1	99%
2e		1	1.5	99%
2f		1	1	99%
2g		1	1.5	99%
2h		1	1.5	71%
2i		1	6	99%
2j		2	6	51%
2k		2	6	58%
2l		1	1	99%

[a] All reactions carried out in [D₆]benzene at room temperature using 1 equiv of HBpin. [b] Conversion was determined by NMR spectroscopy on the basis of the consumption of the aldehyde/ketone, and the identity of the product was confirmed by RCH₂OBpin or RR'¹CHOBpin resonances.

bipyramidal geometry at the Al center, which has PhCHO and one of the N atoms of the β-diketiminato ligand at the axial positions. The elongated Al–H bond (1.608 Å) in **Int-2** compared to the Al–H bond (1.585 Å) in catalyst **1** indicates a weak bonding interaction of the nucleophilic hydrogen atom (NBO charge = –0.48 *e*) with the carbonyl carbon atom (NBO charge = 0.50 *e*). The increase in the coordination number at the Al center from four in **1** to five in **Int-2** also contributes to the elongation of the Al–H bond. However, the large distance between the hydrogen atom at the aluminum and the carbonyl carbon atom is significant (2.839 Å). The Δ*E* (–4.6 kcal mol^{–1}) and Δ*G* (–1.8 kcal mol^{–1}) values for the formation of **Int-2** from **Int-1** are slightly negative and the corresponding barriers (Δ*E*[‡] and Δ*G*[‡]) are quite low. The next step is the formation of the tetrahedral Al benzyloxide

complex (**Int-3**) by a hydride shift to the carbonyl carbon atom through a four-membered transition state (**TS-Int-2_Int-3**; Figure S2). The ΔE (-31.7 kcal mol $^{-1}$) and ΔG (-32.7 kcal mol $^{-1}$) values for this step are large and negative and the corresponding kinetic barrier is also very high ($\Delta E^\ddagger = 22.1$ and $\Delta G^\ddagger = 23.8$ kcal mol $^{-1}$). Hence, this step can be considered as the overall rate-determining step of the hydroboration reaction (Figure S2). Here, the Al center in catalyst **1** acts as a hydride donor to the electrophilic carbonyl carbon atom. In the next step, the addition of the B–H bond of pinacolborane across the Al–O_{CH₂Ph} bond of **Int-3** results in intermediate **Int-4** having a four-membered Al–O–B–H ring. The reaction proceeds through a four-membered transition state (**TS-Int-3_Int-4**), which is similar to that of σ -bond metathesis reactions. The B center in this intermediate is tetrahedral and shows significant B–H bond activation (1.308 Å) as compared to the B–H bond (1.209 Å) in pinacolborane. The Al–H bond length in **Int-4** is also significantly longer (1.898 Å) than those in **1** and **Int-2**. The reaction energy and Gibbs free energy for this step are positive. Hence, **Int-4** undergoes rapid ring opening by the breakage of Al–O and B–H bonds to result in the hydroboration product and regeneration of the catalyst **1**. The ΔG value for this step is -15.4 kcal mol $^{-1}$ and the kinetic barrier (**TS-Int-4_Pdt-1**) is significantly low ($\Delta G^\ddagger = 4.4$ kcal mol $^{-1}$). In this step, the catalyst **1** is regenerated by the addition of hydride from pinacolborane and the subsequent release of **Pdt-1**.

We have also calculated the energetics for the pathways involving ionic intermediates (Schemes S3 and S4 in the Supporting Information). Since the dissociation of OTf $^-$ from the catalyst is a highly endothermic process ($\Delta E = 116.5$ kcal mol $^{-1}$), we have not considered reaction pathways involving ionic intermediates for further discussion.

Encouraged by this result, the scope of the catalytic reaction with a variety of aldehydes was briefly examined. Aliphatic aldehydes (Table 1, entries **2c, 2d**) were investigated for hydroboration activity with HBpin at room temperature using catalyst loadings of 1 mol %, which afforded the borate esters in essentially quantitative yield. Excellent yields were also obtained when aldehydes with electron-withdrawing or electron-donating aromatic groups were investigated (Table 1, entries **2e, 2f**). The analogous reaction with substrates including heterocycles was also found to be effective for the hydroboration reaction (Table 1, entries **2g, 2h**). This compound underwent hydroboration with a catalyst loading of 0.5 mol % in 6 h (Table 1, entry **2i**). It is obvious from the results presented (Table 1, entries **2j, 2k**) that the hydroboration of ketones is significantly less efficient than those of aldehydes. The ketone substituent (R^1) reduces the Lewis basicity of the O center of [LAIOC(R) R^1]. In order to investigate if the rate was affected by bulky aldehydes, the reaction of trimethylacetaldehyde with HBpin was also investigated (Table 1, entry 2l).

Recently, Takagi and Sakaki reported on a computational investigation and predicted that hydrosilylation of the activated ketone is viable when taking advantage of kinetic and thermodynamic stabilization of germylene hydride with three-coordinate germanium.^[14] Thus we investigated **1** as the catalyst for the hydrosilylation of aldehydes. Mild

temperature (ca. 23 °C) and catalyst loading of 3 mol % was used. The addition of *p*-tolylaldehyde (1.0 mmol) and PhSiH₃ (1.6 mmol) to **1** in C₆D₆ results in 60 % yield of **3e** (see the Supporting Information) within 6 h. We found that butyraldehyde reacts with (EtO)₃SiH under similar conditions to form the desired product **3j** in a comparable yield of 60 %. Further products of the hydrosilylation reaction with aldehydes are given in the Supporting Information. However, the results of hydrosilylation are so far not optimized.

The addition reaction of trimethylsilyl cyanide (TMSCN) to either an aldehyde or a ketone to form cyanohydrin trimethylsilyl ethers (*O*-trimethylsilyl cyanohydrins) can be catalyzed by a variety of Lewis acids and bases.^[15,16] We found that **1** is an effective catalyst for the addition reaction of TMSCN to either aldehydes or ketones. The reaction of TMSCN with benzaldehyde gives an almost quantitative yield of product within 1 h with 0.5 mol % loading of the catalyst at ambient temperature in C₆D₆ (Table 2, entry **4a**). When the loading of the catalyst is reduced to 0.1 mol % the reaction is completed within 5 h (Table 2, entry **4b**). This reaction does not proceed without the catalyst.

Quantum mechanical calculations indicate that the initial nucleophilic attack by PhCHO to give **Int-2** ($\Delta E = -8.8$ and $\Delta G = 5.0$ kcal mol $^{-1}$; Scheme 2) and by TMSCN to give **Int-B** ($\Delta E = -6.1$ and $\Delta G = 6.2$ kcal mol $^{-1}$, Scheme S2) are com-

Table 2: Addition reaction of TMSCN to aldehydes and ketones catalyzed by **1**.^[a]

$\text{R}-\text{C}(=\text{O})-\text{R}^1 + \text{TMSCN} \xrightarrow[\text{C}_6\text{D}_6, \text{rt}]{\text{1, 0.1-2 mol \%}} \text{R}-\text{C}(\text{OTMS})(\text{R}^1)-\text{CN}$					
R=alkyl or aryl group R ¹ =alkyl or H					
Entry	Substrate	Product	Cat. [mol %]	t [h]	Yield [%] ^[b]
4a			0.5	1	99%
4b			0.1	5	99%
4c			0.5	1	99%
4d			0.5	1	99%
4e			0.5	1	99%
4f			0.5	1	99%
4g			0.5	1	99%
4h			2	1	99%
4i			2	1	99%

[a] Aldehyde or ketone, 2 mmol; TMSCN, 3 mmol; at ambient temperature. [b] Yield was obtained according to ¹H and ¹³C NMR spectroscopic analysis.

table. However, the formation of **Int-5** by the reaction of TMSCN with **Int-2** is less favorable (Scheme S3) as compared to the formation of **Int-C** by the reaction of PhCHO with **Int-B** (Scheme S2). Moreover, the activation of the Si–C bond and the addition of the bulky Si(CH₃)₃ group to the Al–O bond of the pentacoordinate Al (**Int-6**, Scheme S3) are practically unfeasible from the geometrical point of view.^[11b] Hence, we have considered the reaction pathway for the initial attack of TMSCN. The nucleophilic group (TMSCN) attacks from the side opposite to that of the Al–O bond to result in a weakly bound intermediate (**Int-A**) that rearranges to **Int-B** (Figure S4). **Int-B** possesses a trigonal bipyramidal geometry at the Al center, where OTf and TMSCN occupy the axial positions. The longer Si–C (1.904 Å) bond as compared to TMSCN (1.886 Å) indicates that the Si–C bond is activated in **Int-B**. The reaction is exothermic by 3.0 kcal mol^{−1} for this step and the Δ*G* value is close to zero (0.04 kcal mol^{−1}) at 298.15 K. The addition of PhCHO to this intermediate results in another weakly bound complex **Int-C**. The cycloaddition of the Si–C σ bond of the TMSCN fragment to the O=C bond of PhCHO fragment in **Int-C** proceeds through a concerted cyclic four-membered transition state and results in the formation of cyanohydrin aluminum complex **Int-D** (Figure S4). The Δ*E* and Δ*G* values for this step are negative (−13.8 and −12.0 kcal mol^{−1}, respectively) and the corresponding Δ*E*[‡] and Δ*G*[‡] values are 29.4 and 32.0 kcal mol^{−1}, respectively. This step can be considered as the rate-determining step for the catalytic formation of cyanohydrin. The Δ*G*[‡] value for the release of the product is only 2.1 kcal mol^{−1}, and the Δ*G* value of the reaction is −3.6 kcal mol^{−1}. In contrast to the hydroboration reaction, the catalyst **1** activates the Si–C bond in TMSCN, which subsequently facilitates the cycloaddition reaction with PhCHO.

We investigated the catalytic properties of **1** in the reaction of TMSCN with a number of aldehydes and ketones. The results shown in Table 2 indicate that the reaction involving a variety of aryl aldehydes worked well with **1** as a catalyst. Thus, reaction of *p*-tolylaldehyde or phenylacrolein led to the corresponding cyanohydrin trimethylsilylether in 99% yield (Table 2, entries **4c**, **4d**, respectively). Even the reaction of sterically hindered 2-fluorobenzaldehyde afforded the desired product in 99% yield (Table 2, entry **4e**). We also screened a variety of heterocyclic aldehydes by using catalyst **1**. Furfural and 2-thenaldehyde functioned well in our protocol, giving both the corresponding products in 99% yield (Table 2, entries **4f**, **4g**). Even the reaction of acetophenone and 1-(4-methylphenyl)ethanone with trimethylsilyl cyanide also provided desired products in excellent yields (Table 2, entries **4h**, **4i**).

In conclusion, [LAH(OSO₂CF₃)] can be used as a catalyst for hydroboration under mild conditions of organic compounds containing carbonyl groups and therefore serves as a catalyst for industrially important reactions. Interestingly, the activation process proceeds at room temperature, when usually elevated temperature or pressure is needed. The theoretical calculations indicate that during the hydroboration reaction catalyst **1** initially acts as a hydride donor to PhCHO. The Al–O bond of the resulting Al alkoxide

complex undergoes a σ bond metathesis reaction with the B–H bond of pinacolborane. As a result, catalyst **1** is finally regenerated by hydride addition. In contrast to the hydroboration reaction, catalyst **1** plays a significant role in activating the Si–C bond in TMSCN and subsequently facilitates the cycloaddition reaction with PhCHO.

Experimental Section

Synthesis of 1: A solution of [LAH₂] (0.446 g, 1.0 mmol) in toluene (15 mL) was added dropwise to MeOTf (0.164 g, 1 mmol) in toluene (15 mL) at 0°C with elimination of CH₄. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued overnight. The solvent was removed in vacuo, and the crude product was crystallized from toluene to afford colorless crystals of **1** (0.512 g, 86%); mp 240–242°C; IR (KBr): $\tilde{\nu}$ = 1797 cm^{−1} (s, Al–H); ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 7.35–7.25 (m, 6H, Ar–H), 5.35 (s, 1H, γ–H), 3.14 (sept, ³*J*_{H–H} = 6.8 Hz, 2H, CHMe₂), 3.01 (sept, ³*J*_{H–H} = 6.8 Hz, 2H, CHMe₂), 1.96 (s, 3H, Me), 1.94 (s, 3H, Me), 1.29 (d, ³*J*_{H–H} = 6.8 Hz, 6H, CHMe₂), 1.19 (d, ³*J*_{H–H} = 6.8 Hz, 6H, CHMe₂); elemental analysis calculated for C₃₀H₃₂AlF₃N₂O₃S: C 60.48, H 7.03, N 4.69. Found: C 60.80, H 7.16, N 4.51.

Keywords: aluminum · homogeneous catalysis · hydrides · hydroboration · hydrosilylation

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10225–10229
Angew. Chem. **2015**, *127*, 10363–10367

- [1] Aluminum hydride systems: a) B. Bogdanović, M. J. Schwickardi, *J. Alloys Compd.* **1997**, *253*, 1–9; b) X. Lui, H. W. Langmi, S. D. Beattie, F. F. Azenwi, G. S. McGrady, C. M. Jensen, *J. Am. Chem. Soc.* **2011**, *133*, 15593–15597.
- [2] For selected reviews, see: a) J. A. B. Abdalla, I. M. Riddlesone, R. Tirfoin, S. Aldridge, *Angew. Chem. Int. Ed.* **2015**, *54*, 5098–5102; *Angew. Chem.* **2015**, *127*, 5187–5191; b) L. A. Berben, *Chem. Eur. J.* **2015**, *21*, 2734–2742; c) A. J. Blake, A. Cunningham, A. Ford, S. J. Teat, S. Woodward, *Chem. Eur. J.* **2000**, *6*, 3586–3594; d) A. Ford, S. Woodward, *Angew. Chem. Int. Ed.* **1999**, *38*, 335–336; *Angew. Chem.* **1999**, *111*, 347–348; e) T. W. Myers, L. A. Berben, *J. Am. Chem. Soc.* **2013**, *135*, 9988–9990; f) T. W. Myers, L. A. Berben, *Chem. Sci.* **2014**, *5*, 2771–2777.
- [3] For selected reviews, see: a) J. C. Fetting, P. A. Gray, C. E. Melton, P. P. Power, *Organometallics* **2014**, *33*, 6232–6240; b) W. Uhl, C. Appelt, J. Backs, H. Westenberg, A. Wollschläger, J. Tannert, *Organometallics* **2014**, *33*, 1212–1217; c) W. Uhl, J. Grunenberg, A. Hepp, M. Matar, A. Vinogradov, *Angew. Chem. Int. Ed.* **2006**, *45*, 4358–4361; *Angew. Chem.* **2006**, *118*, 4465–4468; d) C. Y. Lin, C. F. Tsai, H. J. Chen, C. H. Hung, R.-C. Yu, P.-C. Kuo, H. M. Lee, J.-H. Huang, *Chem. Eur. J.* **2006**, *12*, 3067–3073.
- [4] a) V. Jancik, Y. Peng, H. W. Roesky, J. Li, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *J. Am. Chem. Soc.* **2003**, *125*, 1452–1453; b) V. Jancik, M. M. Moya Cabrera, H. W. Roesky, R. Herbst-Irmer, D. Neculai, A. M. Neculai, M. Noltemeyer, H.-G. Schmidt, *Eur. J. Inorg. Chem.* **2004**, 3508–3512.
- [5] For selected reviews, see: a) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Oviatt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238; b) F. Basuli, H. Aneetha, J. C. Huffman, D. J. Mindiola, *J. Am. Chem. Soc.* **2005**, *127*, 17992–17993; c) T. L. Gianetti, N. C. Tomson, J. Arnold, R. G. Bergman, *J. Am. Chem. Soc.* **2011**, *133*, 14904–14907.
- [6] G. Tan, T. Szilvási, S. Inoue, B. Blom, M. Driess, *J. Am. Chem. Soc.* **2014**, *136*, 9732–9742.

- [7] D. R. Armstrong, E. Crosbie, E. Hevia, R. E. Mulvey, D. L. Ramsay, S. D. Robertson, *Chem. Sci.* **2014**, 5, 3031–3045.
- [8] a) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, 2, 389–399; b) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, 111, 354–396; c) P. P. Power, *Nature* **2010**, 463, 171–177; d) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, 49, 46–76; *Angew. Chem.* **2010**, 122, 50–81.
- [9] M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. Kociok-Kohn, D. J. Liptrot, M. F. Mahon, C. Weetman, *Chem. Sci.* **2014**, 5, 2826–2830.
- [10] C. Cui, H. W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem. Int. Ed.* **2000**, 39, 1815–1817; *Angew. Chem.* **2000**, 112, 1885–1887.
- [11] a) See the Supporting Information for the details of computational methodology and related references; b) we could not locate a transition state for rearrangement of **Int5** to **Int6** or directly to the product and the catalyst **1** (Scheme S3).
- [12] D. Franz, E. Irran, S. Inoue, *Dalton Trans.* **2014**, 43, 4451–4461.
- [13] T. J. Hadlington, M. Hermann, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2014**, 136, 3028–3031.
- [14] N. Takagi, S. Sakaki, *J. Am. Chem. Soc.* **2013**, 135, 8955–8965.
- [15] a) D. A. Evans, L. K. Truesdale, G. L. Carroll, *J. Chem. Soc. Chem. Commun.* **1973**, 55–56; b) D. A. Evans, L. K. Truesdale, *Tetrahedron Lett.* **1973**, 14, 4929–4932; c) D. A. Evans, J. M. Hoffman, L. K. Truesdale, *J. Am. Chem. Soc.* **1973**, 95, 5822–5823.
- [16] M. Takamura, Y. Hamashima, H. Usuda, M. Kanai, M. Shibasaki, *Angew. Chem. Int. Ed.* **2000**, 39, 1650–1652; *Angew. Chem.* **2000**, 112, 1716–1718.

Received: April 12, 2015

Revised: May 28, 2015

Published online: June 18, 2015