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Gallium-Assisted Transfer Hydrogenation of Alkenes

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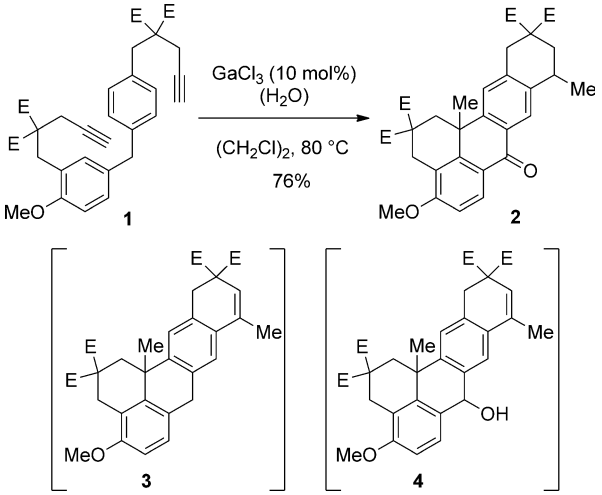
Abstract: We report a rare case of alkene transfer hydrogenation using a main-group compound instead of a transition-metal complex as catalyst. We disclosed that 1,4-cyclohexadiene can be used as H_2 surrogate towards olefin reduction in the presence of $[IPrGaCl_2][SbF_6]$. Hydrogenative cyclizations have also been carried out because this cationic gallium complex is also a potent hydroarylation catalyst.

Introduction

Catalytic transfer hydrogenation is a practical synthetic method that avoids the hazardous handling of gaseous molecular hydrogen.[1,2] Whereas various procedures have been developed for the reduction of heterofunctional groups such as ketones and imines,[3] catalytic transfer hydrogenation of alkenes has been less often studied.[4] The most versatile approaches involve late transition metals such as Ru, Rh, Ir, Pd, and Pt.[1] Methods employing catalysts based on abundant 1st row transition metals[5] and organocatalysts[6] have also been developed. As for main-group heteroelements, whereas the use of frustrated Lewis pairs[7] or calcium complexes as catalysts for the reduction of alkenes with H_2 has become a thriving area of research,[8,9,10] examples of transfer hydrogenations are exceedingly rare.[11,12] Styrene has been reduced into ethylbenzene by using a large excess of 1,4-cyclohexadiene and 25 mol% iodine as nonchemoselective catalyst.[13] By using 15 mol% $InCl_3$, highly activated electron-deficient alkenes undergo reduction with $NaBH_4$ as nonchemoselective hydrogen donor.[14]

To our knowledge, no alkene transfer hydrogenation catalyzed by a main-group compound and using a simple organic molecule as H_2 surrogate has been described.[15,16] We have tested a series of Group 13 Lewis acids and organic donors towards alkene reduction, among which the cationic NHC gallium complex $IPrGaCl_2^+$ and 1,4-cyclohexadiene emerged as the best candidates.[17,18,19] Furthermore, because gallium complexes efficiently catalyze the carbocyclization of arenynes into styrene derivatives,[20] the procedure has been extended to a new type of transfer hydrogenative cyclization process akin to those using transition metals.[21,22]



Scheme 1. Cyclization of **1** (E = CO_2Me) in the presence of $GaCl_3$.

The triggering factor of this study was the surprising outcome of the gallium-assisted carbocyclization of arenyne **1** (Scheme 1).[20b] Instead of the expected product **3**, ketone **2** was isolated in 76% yield. To explain the oxidation of the diphenyl methane fragment and concomitant reduction of the alkene moiety of **3**, we postulate the formation of alcohol **4** after hydride abstraction[23] and addition of adventitious water. Catalytic transfer hydrogenation then takes place to give **2**.[24]

Results and Discussion

Cyclohexenylbenzene was used to probe reaction conditions applicable to simple alkenes (Table 1). With 5 mol% $GaCl_3$, the classical hydrogen transfer agent *i*PrOH did not promote the reduction (entry 1). In contrast, exposure of the substrate to 1,4-cyclohexadiene resulted in efficient reduction at room temperature (entry 2). The gallium salt proved to be the only suitable catalyst among the MCl_3 (M = Al, Ga, In) triad (entries 3 and 4). Gallium(III) chloride is a hygroscopic salt that is difficult to handle, but we have previously reported that it can be advan-

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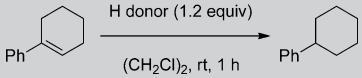
Table 1. Catalytic transfer hydrogenation of cyclohexenylbenzene.



Entry	Cat.	H Donor	Conv. [%][a]
1	$GaCl_3$	*i*PrOH	0
2	$GaCl_3$	1,4-CHD[b]	87
3	$AlCl_3$	1,4-CHD	0
4	$InCl_3$	1,4-CHD	9
5	$[IPrGaCl_2][SbF_6]$[c]	1,4-CHD	99
6	$[IPrGaCl_2$·(2,4,6-trifluorobenzonitrile)$][SbF_6]$	1,4-CHD	87
7	$[IPrGaCl_2][AlCl_4]$[d]	1,4-CHD	87
8	$[IPrGaCl_2][SbF_6]$[c]	2,4,6-trimethylphenol	30
9	$[IPrGaCl_2][SbF_6]$[c]	BHT[e]	–[f]
10	$[IPrGaCl_2][SbF_6]$[c]	*i*PrOH	0
11	$[IPrGaCl_2][SbF_6]$[c]	Hantzsch ester[g]	0
12	$[IPrGaCl_2][SbF_6]$[c]	Et_3SiH	<5
13	$[IPrGaCl_2][SbF_6]$[c]	H_2[h]	0

[a] Conversion was determined by GLC analysis. [b] 1,4-Cyclohexadiene. [c] Generated in situ by using $IPrGaCl_3$ (5 mol%) and $AgSbF_6$ (7 mol%); see ref. [18d] for the solid-state structure of $[IPrGaCl_2][SbF_6]$. [d] Generated in situ by using $IPrGaCl_3$ (5 mol%) and $AlCl_3$ (50 mol%). [e] Butylhydroxytoluene. [f] Complex mixture. [g] Diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate. [h] 1 atm.

tageously replaced by the bench-stable $IPrGaCl_3$[25] used jointly with $AgSbF_6$ to generate $[IPrGaCl_2][SbF_6]$.[18a,d] With this catalyst, the conversion reached 99% (entry 5).[26] The use of silver could be avoided by employing either the isolated cationic gallium complex $[IPrGaCl_2$(2,4,6-trifluorobenzonitrile)$][SbF_6]$[18a] (entry 6) or a catalytic mixture of $IPrGaCl_3$ and $AlCl_3$ (entry 7). With $[IPrGaCl_2][SbF_6]$, a low conversion was monitored with 2,4,6-trimethylphenol (entry 8). The use of butylhydroxytoluene (BHT) and *i*PrOH as H-donor proved inefficient (entries 9 and 10). Although oxidation of Hantzsch ester occurred to give Hantzsch pyridine in 70% yield, no hydrogen transfer was observed (entry 11). It is possible that Hantzsch pyridine traps the catalyst in the form of a stable donor–acceptor adduct,[27] or that it quenches an elementary step of the catalytic cycle for which a proton is required (see mechanistic discussion below). With Et_3SiH, the product was observed in trace amounts (entry 12). Lastly, with molecular hydrogen, no reaction took place (entry 13).

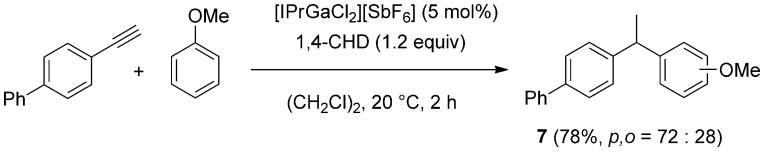
By using 1,4-cyclohexadiene as hydrogen donor, the reduction of other simple or activated alkenes was then carried out (Table 2). The *gem*-disubstituted alkene 1,1-diphenylethylene was fully converted within one hour at 20 °C to give 1,1-diphenylethane (entry 1). With the trisubstituted alkene (*Z*)-1,2-diphenyl-1-methylethene, the reaction took place at 40 °C (entry 2). On the other hand, tetraphenylethene remained unchanged, even at 80 °C (entry 3). The presence of ester or ketone functionalities was perfectly tolerated. Selective reduction of the alkene moiety occurred with benzylidenemalonates (entries 4 and 5) or phenylbutenoates (entries 6 and 7). *Trans*-chalcone was also selectively reduced into 1,3-diphenylpropanone (entry 8). In the absence of an aryl substituent, only traces of product were observed (entry 9).

The reduction of endocyclic alkenes was performed at 25 °C (Table 3). Indenes substituted at the 3-position (entries 1–3), as well as 4-ethyl-1,2-dihydronaphthalene (entry 4), gave rise to the expected products in good to excellent yields. In contrast, the use of indene and dihydronaphthalene themselves (R = H) led to polymers.

Owing to the ability of Ga(III) complexes to catalyze hydroarylation of alkynes to give phenyl-substituted alkenes,[28] a formal three-component coupling between 4-ethynylbiphenyl, anisole, and H_2 was attempted (Scheme 2). Gratifyingly, the expected product **7** was isolated in 78% yield.

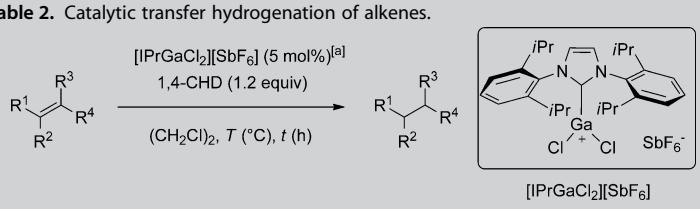
The dihydronaphthalene derivative **8** transformed very cleanly into **9** in 1 h at 80 °C with 91% yield (Scheme 3). Again, the formation of **9** can be envisaged by hydroarylation of arenyne **10**.[29] The reaction of the latter with 1,4-cyclohexadiene eventually furnished **9** in 85% yield.

The generality of this tandem process was validated further by using arenynes **11a–f** (Table 4). The desired bicyclic products were isolated in good to excellent yields even in the case



Scheme 2. Trimolecular hydroarylation/transfer hydrogenation tandem reaction.

Table 2. Catalytic transfer hydrogenation of alkenes.



Entry	R^1	R^2	R^3 [b]	R^4 [b]	*T* [°C]	*t* [h]	Yield [%][c]
1	Ph	Ph	H	H	20	1	67
2	Ph	Me	Ph	H	40	2	70
3	Ph	Ph	Ph	Ph	80	4	0
4	Ph	H	E^1	E^1	80	16	72
5	4-$MeOC_6H_4$	H	E^2	E^2	40	4	75[d]
6	Ph	Ph	E^2	H	80	4	50
7	Ph	Me	H	E^2	80	4	50
8	Ph	H	H	COPh	80	4	56
9	Me	Me	E^2	H	80	16	<5

[a] Generated in situ by using $IPrGaCl_3$ (5 mol%) and $AgSbF_6$ (7 mol%); see ref. [18d] for the solid-state structure of $[IPrGaCl_2][SbF_6]$. [b] $E^1 = CO_2Et$; $E^2 = CO_2Me$. [c] Yield determined by ^1H NMR spectroscopic analysis by using *p*-anisaldehyde as internal standard. [d] Isolated yield.

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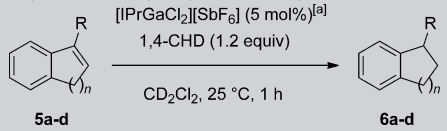
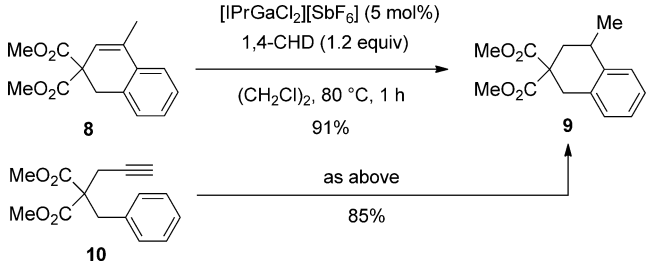
Table 3. Catalytic transfer hydrogenation of cycloalkenes.



5a-d 6a-d

Entry	Substrate	*n*	R	Yield [%][b]
1	**5a**	1	Me	75
2	**5b**	1	Et	90
3	**5c**	1	Bn	95
4	**5d**	2	Et	90

[a] Generated in situ by using $IPrGaCl_3$ (5 mol%) and $AgSbF_6$ (7 mol%). [b] Yield was determined by ^1H NMR spectroscopic analysis by using *p*-anisaldehyde as internal standard.



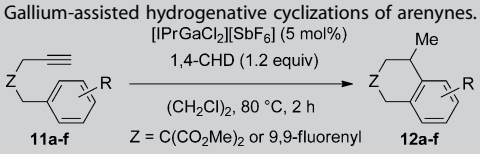
Scheme 3. Bimolecular hydroarylation/transfer hydrogenation tandem reaction.

of a double tandem reaction, which gave rise to tricyclic product **12 f** in 91% isolated yield (entry 6).

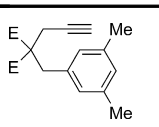
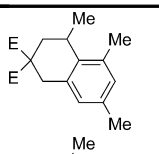
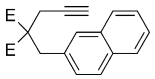
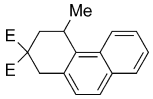
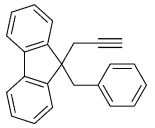
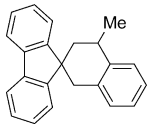
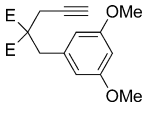
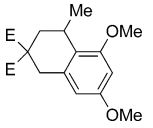
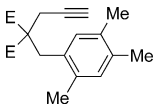
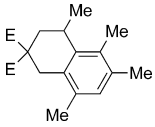
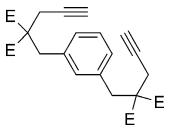
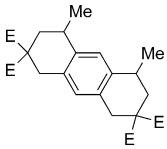
A catalytic cycle that accounts for both the carbocyclization of arenyne **I** and the transfer hydrogenation is shown in Scheme 4. Various activation processes can be envisaged because the mechanism of the transfer hydrogenation likely involves a relatively stable benzylic carbocation such as **IV**. Whereas Ga^+ could be the actual catalyst, it is also possible that the highly electrophilic gallium complex generates an active Brønsted acid in the reaction mixture.[30] For instance, the coordination of adventitious water to $IPrGaCl_2^+$ could form $IPrGaCl_2(OH_2)^+$ as proton source. Thus, the cyclization of **I** could be due to the coordination of $[Ga]^+$ to the triple bond or its protonation to give **II**. Nucleophilic attack of the arene moiety would give rise to the Wheland intermediate **III**. A 1,3-proton shift would then lead to the stabilized carbocation **IV**. A hydride would then be transferred from 1,4-cyclohexadiene to **IV** to give **V**. If [X] = Ga, a protodegallation step would finish the cycle. If [X] = H, E^1-elimination would regenerate the active species.

Additional experiments were carried out to gain more insight into this mechanistic ambiguity (Table 5). Considering that the gallium complex can possibly deliver three equivalents of protons, the transfer hydrogenation of cyclohexenylbenzene was carried out in the presence of a three-fold excess of powdered K_2CO_3, proton sponge, or 2,6-(tBu)$_2$-pyridine relative to gallium (entries 1–3). Whereas the conversion was 99% without the base, it dropped to 10% with K_2CO_3 and 0% with the other two. With a 1:2 or a 1:1 ratio of gallium vs. 2,6-(tBu)$_2$-pyri-

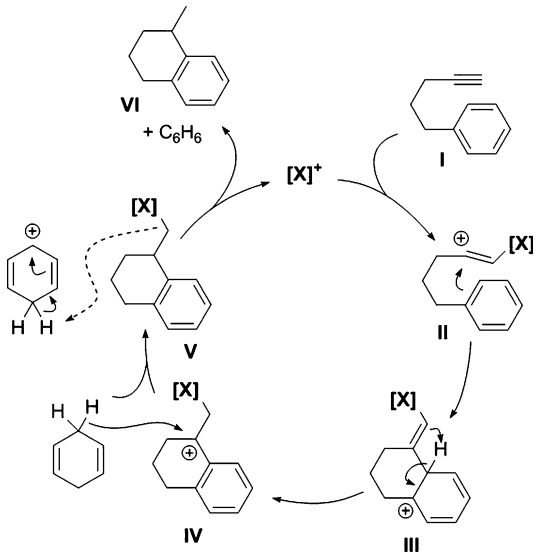
Table 4. Gallium-assisted hydrogenative cyclizations of arenynes.



11a-f 12a-f

Entry	Substrate[a]		Product[a]		Yield [%][b]
1		**11 a**		**12 a**	99
2		**11 b**		**12 b**	88
3		**11 c**		**12 c**	55
4		**11 d**		**12 d**	92
5		**11 e**		**12 e**	97
6		**11 f**		**12 f**	91[c]

[a] E = CO_2Me. [b] Isolated product. [c] DL/*meso* ratio 3:1; 2.4 equiv of 1,4-CHD.



Scheme 4. Mechanistic proposal, [X] = Ga or H (the dashed arrow is only valid for [X] = Ga).

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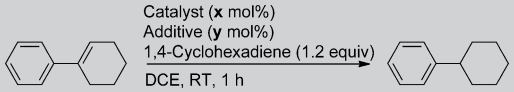
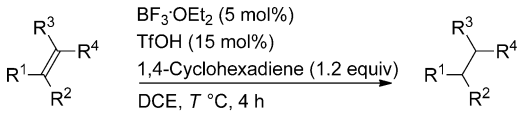
Table 5. Effect of acids and bases in the transfer hydrogenation of cyclohexenylbenzene.



Entry	Catalyst	Additive	*x*	*y*	Conv. [%][a]
1	$[IPrGaCl_2][SbF_6]$[b]	K_2CO_3	5	15	10
2	$[IPrGaCl_2][SbF_6]$[b]	proton sponge	5	15	0
3	$[IPrGaCl_2][SbF_6]$[b]	2,6-(*t*Bu)$_2$-pyridine	5	15	0
4	$[IPrGaCl_2][SbF_6]$[b]	2,6-(*t*Bu)$_2$-pyridine	5	10	0
5	$[IPrGaCl_2][SbF_6]$[b]	2,6-(*t*Bu)$_2$-pyridine	5	5	0
6	–	$HBF_4{\cdot}OEt_2$	–	15	4
7	–	TfOH	–	15	22
8	–	$HCl{\cdot}OEt_2$	–	15	0
9	$BF_3{\cdot}OEt_2$	–	5	–	0
10	$BF_3{\cdot}OEt_2$	TfOH	5	15	91
11	$BF_3{\cdot}OEt_2$	$HCl{\cdot}OEt_2$	5	15	0
12	$AlCl_3$	TfOH	5	15	99
13	$AlCl_3$	$HCl{\cdot}OEt_2$	5	15	0
14	$GaCl_3$	TfOH	5	15	99
15	$GaCl_3$	$HCl{\cdot}OEt_2$	5	15	12
16	$InCl_3$	TfOH	5	15	99
17	$InCl_3$	$HCl{\cdot}OEt_2$	5	15	17
18	$[IPrGaCl_2][SbF_6]$[b]	TfOH	5	15	72

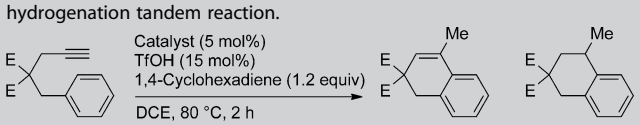
[a] Conversion was determined by GC analysis. [b] Generated in situ by using $IPrGaCl_3$ (5 mol%) and $AgSbF_6$ (7 mol%).



R^1 = *p*-MeO-C_6H_4; R^2 = H; R^3 = R^4 = CO_2Me; T = 40 °C; 24%
R^1 = Ph; R^2 = Ph; R^3 = CO_2Me; R^4 = H; T = 80 °C; 24%

Scheme 5. Lewis-acid-assisted Brønsted-acid-catalyzed transfer hydrogenation of alkenes.

Table 6. Lewis-acid-assisted Brønsted-acid-catalyzed cyclization/transfer hydrogenation tandem reaction.



Entry	Catalyst	Product	Conv. [%][a]
1	$BF_3{\cdot}OEt_2$	–	0
2	$AlCl_3$	–	0
3	$GaCl_3$	**9′**/**9** (46:54)	94[b]
4	$InCl_3$	–	0

[a] Conversion was determined by ^1H NMR spectroscopic analysis. [b] Isolated yield.

dine, no reaction took place (entries 4 and 5). Brønsted acids were then tested as catalysts (entries 6–8). Low conversions of 4 and 22% were obtained with $HBF_4{\cdot}OEt_2$ and TfOH, respectively. With $HCl{\cdot}OEt_2$, no reduction product was formed. We then tested the possibility of a Lewis-acid-assisted Brønsted-acid-catalyzed event. Whereas $BF_3{\cdot}OEt_2$ is an inactive complex (entry 9), a mixture of $BF_3{\cdot}OEt_2$ and TfOH gave rise to the expected product in 91% conversion (entry 10). Again, $HCl{\cdot}OEt_2$ proved to be inefficient, even in the presence of $BF_3{\cdot}OEt_2$ (entry 11). Similar results could be obtained by using $AlCl_3$, $GaCl_3$, or $InCl_3$ instead of $BF_3{\cdot}OEt_2$ (entries 12–17).

The finding that boron, aluminum, and indium salts were not efficient catalysts by themselves (see Table 5, entry 9, and Table 1, entries 3 and 4) indicates a Lewis-acid-assisted Brønsted-acid-catalyzed event with such species. The case of $GaCl_3$ and $[IPrGaCl_2][SbF_6]$ remains unclear because these complexes are very active by themselves and the use of a base could also quench the protodegallation step.[31] It is also notable that the use of TfOH together with $[IPrGaCl_2][SbF_6]$ reduced the conversion from 99 (see Table 1, entry 5) to 72% (Table 5, entry 18).

Although conversions of over 90% could be reached with MX_3/TfOH systems, the use of $[IPrGaCl_2][SbF_6]$ remains the best choice because, as stated above, it is more robust than simple Group 13 MX_3 salts and, furthermore, it is more versatile for transfer hydrogenation, as shown in Scheme 5. These alkenes were reduced in moderate yield (24%) with the $BF_3{\cdot}OEt_2$/TfOH system. For the same substrates, $[IPrGaCl_2][SbF_6]$ gave rise to the desired products in 75 and 50% yield, respectively (see Table 2, entries 5 and 6).

The superiority of the $[IPrGaCl_2][SbF_6]$ complex was also demonstrated in the tandem process (Table 6). With $BF_3{\cdot}OEt_2$/TfOH (entry 1), $AlCl_3$/TfOH (entry 2), and $InCl_3$/TfOH (entry 4), the cyclized products **9′** and **9** were not observed. With $GaCl_3$/TfOH (entry 3), the cyclization took place but the selectivity towards **14** was moderate.

Thus, transfer hydrogenation of alkenes is possible through Lewis-acid-assisted Brønsted-acid catalysis. However, with gallium complexes, a direct Lewis-acid activation cannot be ruled out.

Conclusions

This study has shown that chemoselective alkene transfer hydrogenations can be promoted by a main-group compound instead of a transition metal complex. At this time, our efforts have focused on styrene derivatives using $[IPrGaCl_2][SbF_6]$ as catalyst. We expect that a more electrophilic species will increase the scope of alkenes, as is the case for frustrated Lewis pairs/H_2 systems. Nevertheless, styrene derivatives can be rapidly constructed by gallium-catalyzed hydroarylation of alkynes, which allowed the development of an unprecedented hydrogenative cyclization process.

Experimental Section

General procedure for the hydrogenative cyclization of arenynes (Scheme 3 and Table 4): A solution of $[IPrGaCl_2][SbF_6]$ was prepared by adding $IPrGaCl_3$ (5 mol%, 7 mg) and $AgSbF_6$ (7 mol%, 6 mg) to dichloroethane (DCE) (1 mL) in a screw-cap vial under argon. Arenyne **10** or **11a–f** (0.25 mmol) and 1,4-cyclohexadiene (1.2 equiv, 29 μL) were subsequently added and the mixture was stirred at 80 °C for 2 h. The solution was cooled to RT and filtered

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through a pad of Celite. The volatiles were removed under reduced pressure and the crude product was purified by chromatography over silica gel (cyclohexane–ethyl acetate mixture) to afford the product **9** or **12a–f**.

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Keywords: alkenes · cyclization · gallium · homogeneous catalysis · hydrogenation

[1] a) G. Brieger, T. J. Nestrick, *Chem. Rev.* **1974**, *74*, 567–580; b) R. A. W. Johnstone, A. H. Wilby, *Chem. Rev.* **1985**, *85*, 129–170; c) H. Berke, *ChemPhysChem* **2010**, *11*, 1837–1849.

[2] S. Gücemal, A. G. Gökçe, B. Çetinkaya, *Inorg. Chem.* **2013**, *52*, 10601–10609, and references therein.

[3] a) T. Ikariya, K. Murata, R. Noyori *Org. Biomol. Chem.* **2006**, *4*, 393–406; b) S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226–236.

[4] S. Horn, M. Albrecht, *Chem. Commun.* **2011**, *47*, 8802–8804, and references therein.

[5] See Ref. [1b] and for selected examples: a) Fe: B. A. F. Le Bailly, S. P. Thomas, *RSC Adv.* **2011**, *1*, 1435–1445; b) Co: T.-P. Lin, J. C. Peters, *J. Am. Chem. Soc.* **2013**, *135*, 15310–15313; c) S. M. King, X. Ma, S. B. Herzon, *J. Am. Chem. Soc.* **2014**, *136*, 6884–6887; d) Ni: F. Alonso, P. Riente, M. Yus, *Tetrahedron* **2009**, *65*, 10637–10643; e) Cu: T. Subramanian, K. Pitchuman, *Catal. Sci. Technol.* **2012**, *2*, 296–300.

[6] a) D. B. Ramachary, R. Sakthidevi, P. S. Reddy, *RSC Adv.* **2013**, *3*, 13497–13506; b) C. Zheng, S.-L. You, *Chem. Soc. Rev.* **2012**, *41*, 2498–2518.

[7] a) D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; *Angew. Chem. Int. Ed.* **2010**, *49*, 49–76; b) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740–5746; c) D. W. Stephan, G. Erker, *Top. Curr. Chem.* **2013**, *332*, 85–110; d) J. Paradies, *Angew. Chem.* **2014**, *126*, 3624–3629; *Angew. Chem.* **2014**, *126*, 3624–3629; *Angew. Chem. Int. Ed.* **2014**, *53*, 3552–3557; e) L. J. Hounjet, D. W. Stephan, *Org. Process Res. Dev.* **2014**, *18*, 385–391.

[8] For metal-free catalytic hydrogenation reactions of electron-deficient alkenes, see: a) G. Erős, H. Mehdi, I. Pápai, T. A. Rokob, P. Király, G. Tárkányi, T. Soós, *Angew. Chem.* **2010**, *122*, 6709–6713; *Angew. Chem.* **2010**, *122*, 6709–6713; *Angew. Chem. Int. Ed.* **2010**, *49*, 6559–6563; b) J. S. Reddy, B.-H Xu, T. Mahdi, R. Frölich, G. Kehr, D. W. Stephan, G. Erker, *Organometallics* **2012**, *31*, 5638–5649; c) B. Inés, D. Palomas, S. Holle, S. Steinberg, J. A. Nicasio, M. Alcarazo, *Angew. Chem.* **2012**, *124*, 12533–12536; *Angew. Chem.* **2012**, *124*, 12533–12536; *Angew. Chem. Int. Ed.* **2012**, *51*, 12367–12369; d) L. Greb, C.-G. Daniliuc, K. Bergander, J. Paradies, *Angew. Chem.* **2013**, *125*, 5989–5992; *Angew. Chem.* **2013**, *125*, 5989–5992; *Angew. Chem. Int. Ed.* **2013**, *52*, 5876–5879.

[9] For metal-free catalytic hydrogenation reactions of simple olefins, see: a) L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem.* **2012**, *124*, 10311–10315; *Angew. Chem.* **2012**, *124*, 10311–10315; *Angew. Chem. Int. Ed.* **2012**, *51*, 10164–10168; b) G. Ménard, L. Tran, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 13685–13691; c) Y. Wang, W. Chen, Z. Lu, Z. H. Li, H. Wang, *Angew. Chem.* **2013**, *125*, 7644–7647; *Angew. Chem.* **2013**, *125*, 7644–7647; *Angew. Chem. Int. Ed.* **2013**, *52*, 7496–7499.

[10] For calcium-catalyzed hydrogenation reactions of alkenes, see: a) J. Spielmann, F. Buch, S. Harder, *Angew. Chem.* **2008**, *120*, 9576–9580; *Angew. Chem.* **2008**, *120*, 9576–9580; *Angew. Chem. Int. Ed.* **2008**, *47*, 9434–9438; b) G. Zheng, S. Li, *Inorg. Chem.* **2010**, *49*, 3361–3369; c) P. Jochmann, J. P. Davin, T. P. Spanoil, L. Maron, J. Okuda, *Angew. Chem.* **2012**, *124*, 4528–4531; *Angew. Chem. Int. Ed.* **2012**, *51*, 4452–4455.

[11] For transfer hydrogenation catalysis by $B(C_6F_5)_3$ by using iPr_2NH as the source of hydrogen, see: J. M. Farrell, Z. M. Heiden, D. W. Stephan, *Organometallics*, **2011**, *30*, 4497–4500.

[12] For $B(C_6F_5)_3$-catalyzed transfer hydrosilylation of alkenes, see: A. Simmoneau, M. Ostreich, *Angew. Chem.* **2013**, *125*, 12121–12124; *Angew. Chem. Int. Ed.* **2013**, *52*, 11905–11907.

[13] M. K. Eberhardt, *Tetrahedron* **1967**, *23*, 3029–3031.

[14] a) B. C. Ranu, S. Samanta, *J. Org. Chem.* **2003**, *68*, 7130–7132; b) B. C. Ranu, S. Samanta, *Tetrahedron* **2003**, *59*, 7901–7906.

[15] For phosphane-catalyzed transfer hydrogenation of the N=N bond of azobenzene, see: N. L. Dunn, M. Ha, A. T. Radosevich, *J. Am. Chem. Soc.* **2012**, *134*, 11330–11333.

[16] For zinc-catalyzed transfer hydrogenation of imines by using Hantzsch ester, see: S. Werkmeister, S. Fleischer, K. Junge, M. Beller, *Chem. Asian. J.* **2012**, *7*, 2562–2568.

[17] IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

[18] For the synthesis, stability, and catalytic activity of complexes of type $(NHC)\cdot GaX_2^+$, see: a) S. Tang, J. Monot, A. El-Hellani, B. Michelet, R. Guillot, C. Bour, V. Gandon, *Chem. Eur. J.* **2012**, *18*, 10239–10243; b) A. El-Hellani, J. Monot, R. Guillot, C. Bour, V. Gandon, *Inorg. Chem.* **2013**, *52*, 506–514; c) A. El-Hellani, J. Monot, S. Tang, R. Guillot, C. Bour, V. Gandon, *Inorg. Chem.* **2013**, *52*, 11493–11502; d) C. Bour, J. Monot, S. Tang, R. Guillot, J. Farjon, V. Gandon, *Organometallics*, **2014**, *33*, 594–599.

[19] For Group 13 Lewis-acid-catalyzed reduction of dithioacetals by 1,4-cyclohexadiene, see: K.-i. Ikeshita, N. Kihara, M. Sonoda, A. Ogawa, *Tetrahedron Lett.* **2007**, *48*, 3025–3028.

[20] See Ref. [18a] and: a) V. Mamane, P. Hannen, A. Fürstner, *Chem. Eur. J.* **2004**, *10*, 4556–4575; b) H.-J. Li, R. Guillot, V. Gandon, *J. Org. Chem.* **2010**, *75*, 8435–8449; c) S. Pascual, C. Bour, P. De Mendoza, A. M. Echavarren, *Beilstein J. Org. Chem.* **2011**, *7*, 1520–1525.

[21] For transition-metal-catalyzed transfer hydrogenative cyclizations, see: Y. Yamamoto, S. Mori, M. Shibuya, *Chem. Eur. J.* **2013**, *19*, 12034–12041, and the references therein.

[22] For seminal reports on Rh-catalyzed reductive cyclizations through hydrogenation and transfer hydrogenation, see: a) H.-Y. Jang, M. J. Krische, *J. Am. Chem. Soc.* **2004**, *126*, 7875–7880; b) H.-Y. Jang, F. W. Hughes, H. Gong, J. Zhang, J. S. Brodbelt, M. J. Krische, *J. Am. Chem. Soc.* **2005**, *127*, 6174–6175; c) J. U. Rhee, M. J. Krische, *J. Am. Chem. Soc.* **2006**, *128*, 10674–10675; d) R. L. Patman, M. R. Chaulagain, V. M. Williams, M. J. Krische, *J. Am. Chem. Soc.* **2009**, *131*, 2066–2067.

[23] a) F. Yonehara, Y. Kido, H. Sugimoto, S. Morita, M. Yamaguchi, *J. Org. Chem.* **2003**, *68*, 6752–6759; b) M. Oshita, N. Chatani, *Org. Lett.* **2004**, *6*, 4323–4325.

[24] For In-catalyzed Meerwein–Ponndorf–Verley reduction of aldehydes, see: J. Lee, T. Ryu, S. Park, P. H. Lee, *J. Org. Chem.* **2012**, *77*, 4821–4825.

[25] N. Marion, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, L. Fensterbank, M. Malacria, S. P. Nolan, *Organometallics* **2007**, *26*, 3256–3259.

[26] No reaction took place when using either $IPrGaCl_3$ or $AgSbF_6$ as catalyst.

[27] S. Nogai, H. Schmidbaur, *Dalton Trans.* **2003**, 3165–3171.

[28] M. K. Gupta, T. P. O'Sullivan, *RSC Adv.* **2013**, *3*, 25498–25522.

[29] H. Inoue, N. Chatani, S. Murai, *J. Org. Chem.* **2002**, *67*, 1414–1417.

[30] a) J. U. Rhee, M. J. Krische, *Org. Lett.* **2005**, *7*, 2493–2495; b) O. Kanno, W. Kuriyama, Z. J. Wang, F. D. Toste, *Angew. Chem.* **2011**, *123*, 10093–10096; *Angew. Chem. Int. Ed.* **2011**, *50*, 9919–9922; c) G. Lemière, B. Cacciuttolo, E. Belhassen, E. Duñach, *Org. Lett.* **2012**, *14*, 2750–2753.

[31] Addition of an exogenous base can prevent protodemetallation. See, for example: R. L. LaLonde, W. E. Brenzovich Jr., D. Benitez, E. Tkatchouk, K. Kelley, W. A. Goddard III, F. D. Toste, *Chem. Sci.* **2010**, *1*, 226–233.

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FULL PAPER

Gallium

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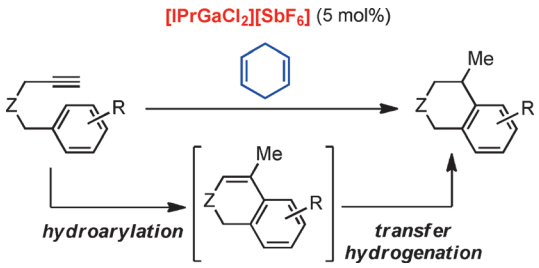
Gallium-Assisted Transfer Hydrogenation of Alkenes



Not just transition metals: A rare case of alkene transfer hydrogenation is reported using a main-group compound instead of a transition-metal complex as catalyst (see scheme). 1,4-Cyclohexadiene can be used as H_2 surrogate towards olefin reduction in the presence of $[IPrGaCl_2][SbF_6]$. Because this cationic gallium complex is also a potent hydroarylation catalyst, unprecedented hydrogenative cyclizations can also be carried out.

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