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Cyclohexa-1,4-dienes in transition-metal-free ionic transfer processes

Sebastian Keess and Martin Oestreich *

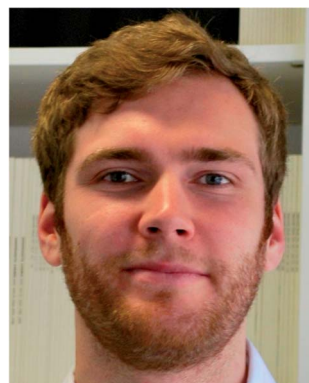
Safe- and convenient-to-handle surrogates of hazardous chemicals are always in demand. Recently introduced cyclohexa-1,4-dienes with adequate substitution fulfil this role as El^+/H^- equivalents in $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed transfer reactions of $\text{El}-\text{H}$ to π - and σ -donors ($\text{C}=\text{C}/\text{C}\equiv\text{C}$ and $\text{C}=\text{O}/\text{C}=\text{N}$). Surrogates of $\text{Si}-\text{H}/\text{Ge}-\text{H}$, $\text{H}-\text{H}$ and even $\text{C}-\text{H}$ bonds have been designed and successfully applied to ionic transfer hydrosilylation/hydrogermylation, hydrogenation and hydro-*tert*-butylation, respectively. These processes and their basic principles are summarised in this Minireview. The similarities and differences between these transfer reactions as well as the challenges associated with these transformations are discussed.

Concept

Transfer processes represent a practical strategy for performing challenging bond formations or avoiding handling hazardous reagents. Limited mainly to transfer hydrogenation¹ for a long time, this technique has recently emerged as a powerful approach for the application of various toxic, flammable/explosive and/or gaseous chemicals that have otherwise only been rarely used in synthetic chemistry.²

The aptitude of adequately substituted cyclohexa-1,4-dienes **I** to engage in ionic transfer reactions as synthetic equivalents

of El^+/H^- ($\text{El} = \text{Si},^3 \text{Ge},^4 \text{H},^5 t\text{Bu}^6$) was demonstrated by our laboratory during the last years (Scheme 1). The underlying concept relies on the ability of diene **I** to transiently form ion pair $\text{III}^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ by $\text{B}(\text{C}_6\text{F}_5)_3$ -mediated hydride abstraction from the bisallylic methylene group ($\text{I} \rightarrow \text{III}^+$)⁷ and subsequently release electrofuge El^+ ; aromatisation to furnish the respective arene is exploited as the driving force (Scheme 1, top). The fate of Wheland complex III^+ was shown to be dependent on the nature of the attached El group, following divergent pathways: $\text{El}-\text{H}$ release and subsequent activation by $\text{B}(\text{C}_6\text{F}_5)_3$ or direct delivery of electrofuge El^+ to substrate **V** (Scheme 1, bottom, grey pathways). Transfer hydrosilylation ($\text{El} = \text{Si}$)³ or hydrogermylation ($\text{El} = \text{Ge}$)⁴ were shown to pass through two interdependent catalytic cycles, liberating the



Sebastian Keess (born in 1988 in Wuppertal/Germany) studied chemistry at the RWTH Aachen University (2008–2013), including a research internship at the University of York (2012). He obtained his bachelor's degree with Dieter Enders (2011) and his master's degree with Magnus Rueping (2013). His education was funded by a Deutschlandstipendium supported by the Bayer Science &

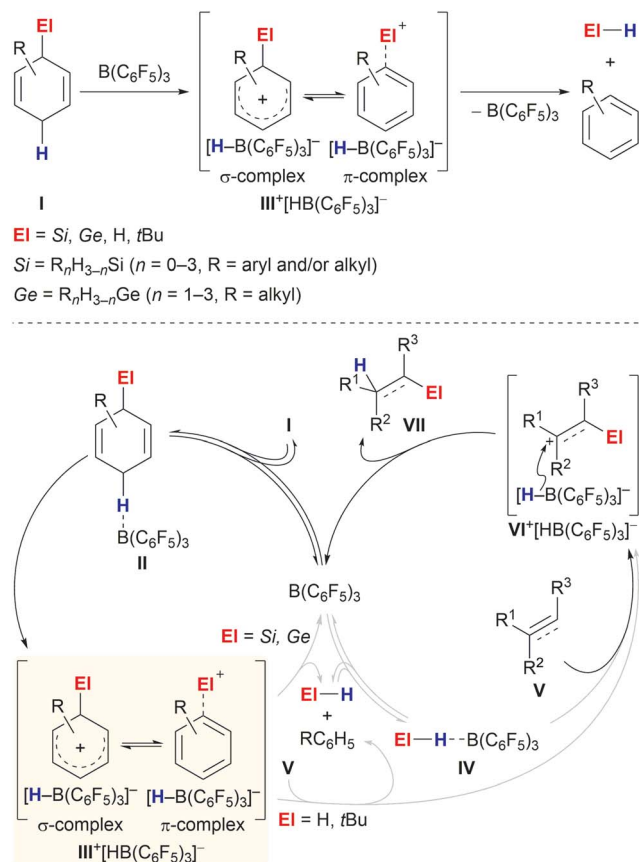
Education Foundation (2012–2013). After a five-month internship at Bayer Pharma AG (Wuppertal/Germany), he moved to Berlin where he currently pursues graduate research in the group of Martin Oestreich at the Technische Universität Berlin.



Martin Oestreich (born in 1971 in Pforzheim/Germany) is Professor of Organic Chemistry at the Technische Universität Berlin. He received his diploma degree with Paul Knochel (Marburg, 1996) and his doctoral degree with Dieter Hoppe (Münster, 1999). After a two-year postdoctoral stint with Larry E. Overman (Irvine, 1999–2001), he completed his habilitation with Reinhard Brückner

(Freiburg, 2001–2005) and was appointed as Professor of Organic Chemistry at the Westfälische Wilhelms-Universität Münster (2006–2011). He also held visiting positions at Cardiff University in Wales (2005) and at The Australian National University in Canberra (2010).





Scheme 1 Reaction of cyclohexa-1,4-dienes with $\text{B}(\text{C}_6\text{F}_5)_3$ in the absence (top) and presence (bottom) of π -basic substrates.

hydrosilane and hydrogermane, respectively ($\text{III}^+ \rightarrow \text{EI-H} + \text{RC}_6\text{H}_5$, left cycle), followed by $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed EI-H bond activation. The thus-formed η^1 -adduct **IV**⁸ then participates in the reduction of C–C multiple bonds (right cycle).^{9,10} Conversely, transfer hydrogenation⁵ and hydro-*tert*-butylation⁶ proceed by direct transfer of the electrofuge EI^+ from Wheland intermediate III^+ onto substrate **V** to eventually furnish adduct **VII** after hydride reduction by $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ ($\text{III}^+ + \text{V} \rightarrow \text{VI}^+ \rightarrow \text{VII}).¹¹ Consistent with this dichotomy, liberation of the EI-H functionality from **I** occurs even in the absence of a Lewis-basic substrate for hydrosilanes/hydrogermanes ($\text{EI} = \text{Si}$ and Ge)^{3,4} while degradation of the H–H and C–H surrogates ($\text{EI} = \text{H}$ and $t\text{Bu}$) proceeds only slowly at room temperature.^{5,6}$

The illustrated concept forms the foundation for all developed transition-metal-free ionic transfer processes using cyclohexa-1,4-dienes **I** as transfer reagents. This Minireview summarises the recent advances in these transformations. It outlines and discusses the challenges and limitations as well as the differences and similarities of the individual transfer processes.

Transfer reagents

The successful implementation of cyclohexa-1,4-dienes **I** in the different transfer reactions, *i.e.*, transfer hydrosilylation/

hydrogermylation, transfer hydrogenation and transfer hydro-*tert*-butylation, required deliberate modification of the substitution pattern of the cyclohexa-2,5-dien-1-yl unit (Fig. 1).

Unsubstituted cyclohexa-2,5-dien-1-ylsilanes **1** and -germanes **2** cleanly transform into the corresponding hydrosilane or hydrogermane and benzene at room temperature when treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (Fig. 1, top).^{3,4} Essential for this transformation to proceed is sufficient hydridic character of the bisallylic $\text{C}(\text{sp}^3)\text{-H}$ bond in **1** due to hyperconjugation with the $\text{C}(\text{sp}^3)\text{-Si}$ bond and the associated stabilisation of the resulting low-energy Wheland complex $\text{III}^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (*cf.* Scheme 1),¹² as supported by computational studies by Sakata and Fujimoto.⁹ Comparable stabilisation from the $\text{C}(\text{sp}^3)\text{-Ge}$ bond is expected to facilitate the release of hydrogermanes from surrogates **2**. Conversely, dihydrogen surrogates **3** are devoid of this stabilisation and require electron-donating substituents at C1/C5 (**3a**, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$)^{5a} or C1/C3/C5 (**3b**, $\text{R}^1 = \text{R}^2 = \text{Me}$)^{5b} to lend stabilisation to the resulting high-energy Wheland intermediates $\text{III}^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (middle), as well as to suppress undesired reaction pathways, *e.g.*, dihydrogen release or cationic heterodimerisation of reactants. While unsubstituted cyclohexa-1,4-diene (**3c**) favoured side reactions in the transfer hydrogenation of alkenes catalysed by the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$,^{5b} Brønsted acids such as Tf_2NH were shown to selectively mediate transfer hydrogenation from this surrogate.^{5c,13} Likewise, adjustment of the substitution pattern at the cyclohexa-2,5-dien-1-yl core was necessary for the design of the transfer reagents **4** for the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed transfer hydro-*tert*-butylation (bottom).⁶ Another substituent “*ipso*” to the *tert*-butyl group in **4** had to be introduced to avoid competing proton release from that position.

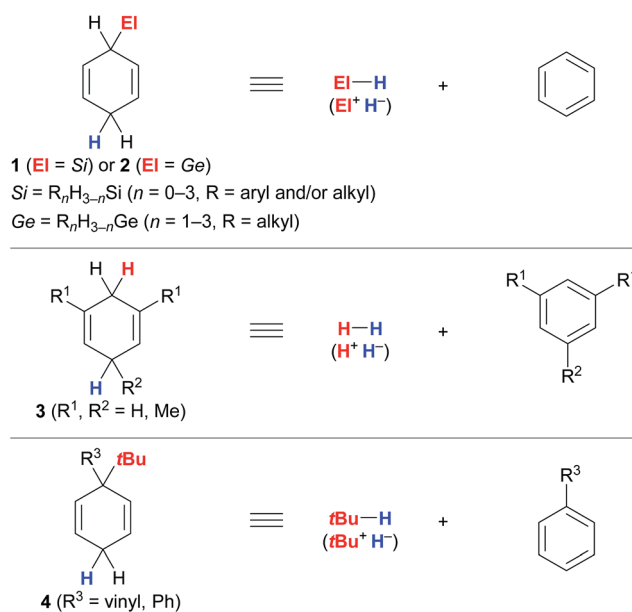


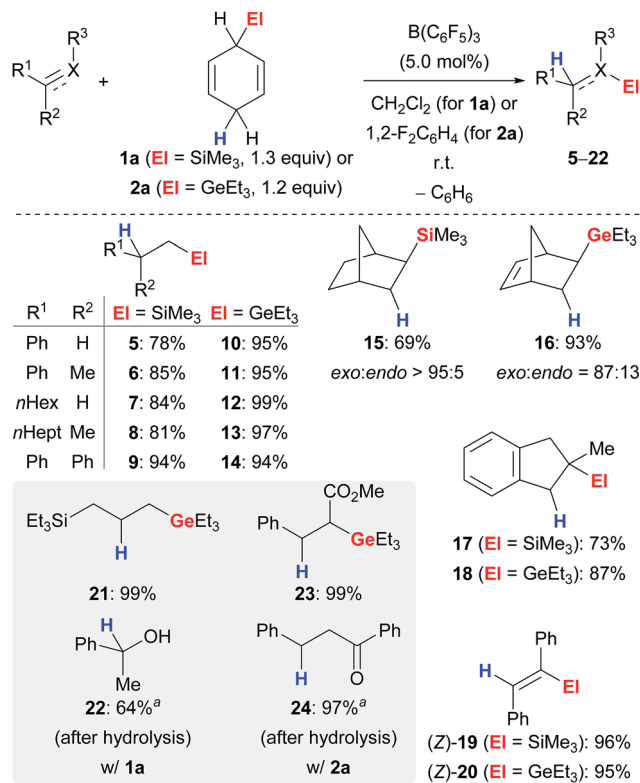
Fig. 1 Substituted cyclohexa-1,4-dienes as synthetic equivalents of hydrosilanes/hydrogermanes (top), dihydrogen (middle) and isobutane (bottom).



Transfer hydrosilylation/hydrogermylation

Simonneau and Oestreich introduced cyclohexa-1,4-dienes as reagents in ionic transfer processes¹⁴ and provided the proof-of-principle for the concept outlined above by employing the surrogate **1a** as an equivalent of gaseous Me₃SiH (Fig. 2, left).^{3b} Surrogates of various other hydrosilanes, *e.g.*, functionalised (EtO)₃SiH,^{3d} were prepared and successfully tested in B(C₆F₅)₃-catalysed ionic transfer hydrosilylations (not shown).^{3a} The development of solid **1b** as an easy-to-handle surrogate of pyrophoric and explosive SiH₄ disclosed a rare strategy for the use of monosilane in organic synthesis.^{3e,15} Likewise, related **2a** and **2b** are surrogates of Et₃GeH and gaseous MeGeH₃ (Fig. 2, right) that enabled the first examples of transfer hydrogermylation.⁴

The ionic transfer hydrosilylation and hydrogermylation of π -basic substrates, *i.e.*, alkenes and alkynes,¹⁶ proved to be applicable to a wide range of unfunctionalised derivatives (Scheme 2).^{3b,d,4} Both transfer processes proceeded at room temperature using catalytic amounts of the Lewis acid and a slight excess of surrogate **1a** or **2a** in CH₂Cl₂ or 1,2-F₂C₆H₄, respectively. Terminal (\rightarrow 5–14), *i.e.*, mono- and 1,1-disubstituted, as well as 1,2-disubstituted (\rightarrow 15–16) and trisubstituted (\rightarrow 17–18) alkenes were compatible with the transfer protocols and furnished tetraorganosilanes and -germanes in high yields. Reduction of an internal electronically unbiased alkyne selectively yielded the product of *trans*-addition (\rightarrow (Z)-19–(Z)-20) whereas transfer hydrogermylation of electronically biased ethyl 3-phenylpropionate proceeded selectively with *cis* addition, and the ester group was perfectly compatible (not shown).^{16b} The *exo* selectivity in the reduction of norbornene (\rightarrow 15) and norborna-2,5-diene (\rightarrow 16) and predominant *cis* diastereoselectivity in the hydrosilylation of 1-methylcyclohexene (not shown) as well as the absence of products of radical cyclisation in the hydrogermylation of an acyclic 1,6-diene (not shown) confirmed the ionic nature of the mechanism for both transfer reactions.^{4,9} The regioselective formation of **17** and **18** emphasises the favoured formation of a benzylic (secondary) carbocation over a tertiary. A discrepancy in the performance of both surrogates **1a** and **2a** was observed in the reduction of functionalised substrates (grey box). Allyltriethylsilane reacted cleanly in the transfer hydrogermylation (\rightarrow 21) whereas only decomposition was observed when subjected to the setup of the transfer hydrosilylation (not shown). Acetophenone yielded alcohol **22** as product of hydrosilylation,¹⁷ but hydrogermylation of α,β -unsaturated esters and ketones furnished products with



Scheme 2 Transfer hydrosilylation and hydrogermylation of C–X multiple bonds using surrogates of Me₃SiH and Et₃GeH. ^aPerformed at 90 °C.

untouched carboxyl (\rightarrow 23) and carbonyl (\rightarrow 24) groups, respectively.

A systematic study was recently reported by Oestreich and co-workers that provides comprehensive insight into the parameters that govern the transfer hydrosilylation.^{3d} The analysis includes surrogates **1** with modified electronic and steric properties, fully or partially fluorinated triarylboranes as well as representative π - and σ -basic substrates.¹⁸ Selected data of this study are summarised in Fig. 3. Cyclohexa-1,4-diene **1a** reacts readily with π -donor **25** at room temperature while elevated

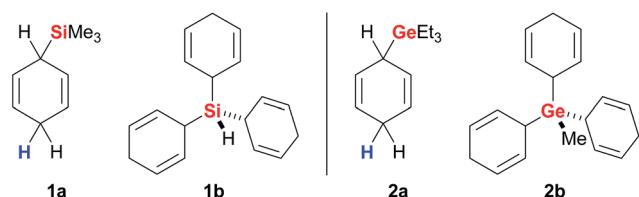


Fig. 2 Representative cyclohexa-1,4-dienes as surrogates of hydrosilanes (left) and hydrogermanes (right).

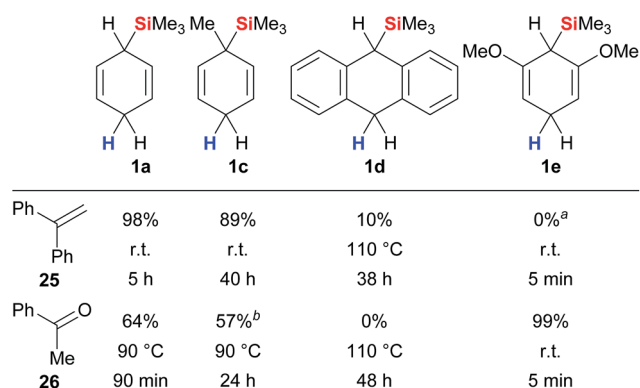


Fig. 3 Interplay between surrogate structure and reactivity. ^aSurrogate **1e** fully consumed. ^bPartial deoxygenation to styrene.

temperatures are required to split the Lewis acid/base adduct of σ -donor **26** and the borane catalyst (column 1). Derivative **1c** with a methyl group *ipso* to the departing silicon group was less reactive than parent **1a** (column 2), as was surrogate **1d** bearing an extended π system (column 3). Introduction of +M substituents as in **1e** significantly increased the reactivity due to an enhanced hydricity of the bisallylic methylene group, yielding quantitative conversion of σ -basic acetophenone (**26**) at room temperature within minutes (column 4). Conversely, the σ -donating methoxy substituents in resorcinol-derived **1e** outcompete π -basic 1,1-diphenylethylene (**25**) for the transfer of the silicon electrophile, and only cleavage of the ether groups of **1e** was observed (column 4).

Simonneau and Oestreich were able to further advance this strategy by introducing **1b** as a surrogate of SiH_4 , a silane that is rarely used by synthetic chemists due to the associated safety issues.^{3e} Later, this approach was unsuccessfully tested to access the related monogermane GeH_4 , and surrogate **2b** as equivalent of MeGeH_3 was prepared instead.⁴ Both surrogates **1b** and **2b** were shown to liberate SiH_4 and MeGeH_3 , respectively, upon treatment with catalytic amounts of $\text{B}(\text{C}_6\text{F}_5)_3$ followed by n -fold hydrosilylation or 3-fold hydrogermylation of typical alkenes (Scheme 3). Monohydro- (\rightarrow **27,30,31**), dihydro- (\rightarrow **28,32**) and tetraalkyl-substituted silanes (\rightarrow **29**) became accessible dependent on the steric demand of the alkene; the degree of substitution at the silicon atom can usually not be controlled by the stoichiometry of the reagents. However, for 1,1-diphenylethylene

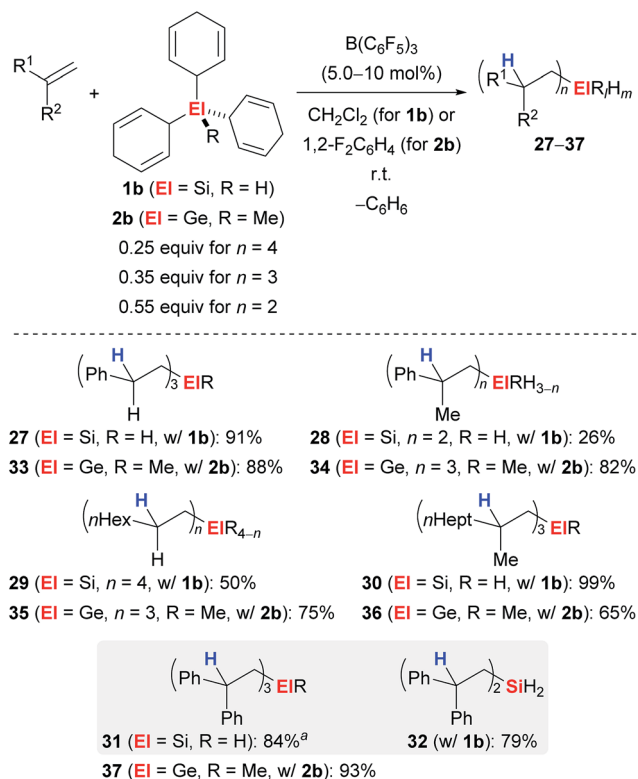
(**25**), reversal of the chemoselectivity, that is the formation of **31** over **32**, was achieved by adjustment of the stoichiometry and the use of di(cyclohexa-2,5-dien-1-yl)silane instead of **1b** (grey box). Also, this method allowed for the mild preparation of tetraalkyl-substituted germanes (\rightarrow **33–37**).

Transfer hydrogenation

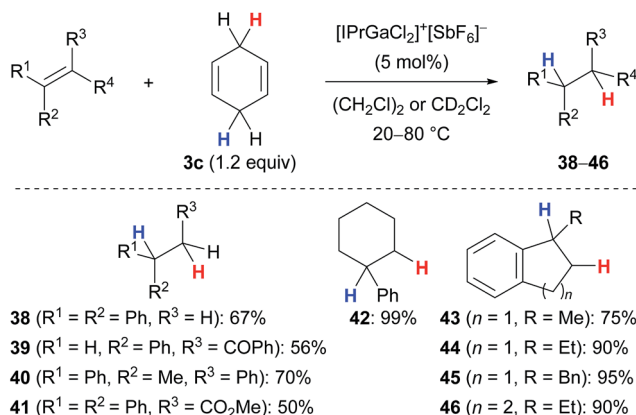
Kihara and co-workers introduced cyclohexa-1,4-diene (**3c**) as the dihydrogen source in the Lewis acid-catalysed reduction of dithioacetals to the corresponding sulfides (not shown).^{19,20} Later, the research group of Gandon reported a gallium(III)-assisted transfer hydrogenation of alkenes using the same hydrogen donor **3c** (Scheme 4).^{13,21} Their protocol was applicable to 1,1-disubstituted (\rightarrow **38**), 1,2-disubstituted (\rightarrow **39**) as well as trisubstituted acyclic (\rightarrow **40–41**) and cyclic (\rightarrow **42–46**) alkenes and tolerated ketone (\rightarrow **39**) or ester (\rightarrow **41**) functionalities. Tetrasubstituted alkenes or those without an aryl substituent were unreactive (not shown).

Aryl-substituted alkynes participated in a cascade hydroarylation/transfer hydrogenation sequence catalysed by the same gallium(III) complex with cyclohexa-1,4-diene (**3c**) as reductant to afford dicyclic (\rightarrow **47–49**) as well as tricyclic (\rightarrow **50**) products in high yields (Scheme 5).¹³ The formation of pentacyclic **51** gave a significantly lower yield. Although the mechanism of the gallium(III)-assisted transfer hydrogenation has not been studied in detail yet, an ionic process was proposed for the dihydrogen transfer (not shown).^{13a} Later, it was demonstrated that the transformations depicted in Schemes 4 and 5 work equally well with an indium(III) complex (not shown).^{13b}

Chatterjee and Oestreich disclosed the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed ionic transfer hydrogenation of imines and related heteroarenes employing substituted cyclohexa-1,4-dienes **3a** or **3b** as the dihydrogen source.^{5a} Later, Grimme and Oestreich showed that this transfer process also works with alkenes and confirmed the mechanism by quantum-chemical calculations.^{5b} The catalytic cycle commences with rate-limiting Lewis acid-mediated hydride abstraction from surrogate **3a** or **3b** to give ion pair $\text{VIII}^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ in low concentration (Scheme 6, left cycle). High-energy Wheland intermediate VIII^+ acts as a strong

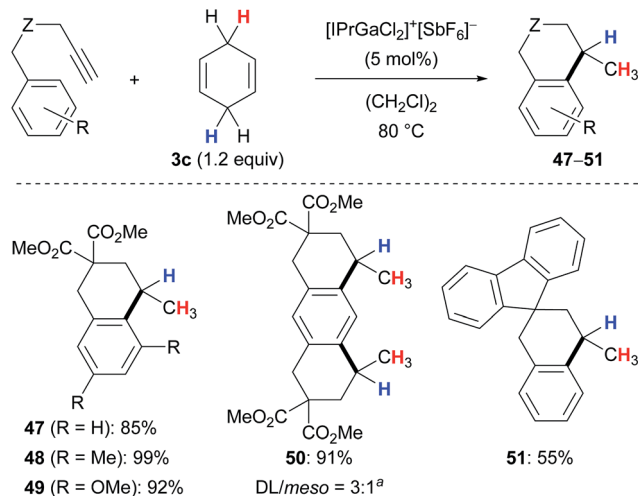


Scheme 3 Transfer hydrosilylation/hydrogermylation of alkenes with surrogates of monosilane or methylgermane. ^aDicyclohexa-2,5-dien-1-ylsilane was used as the surrogate.

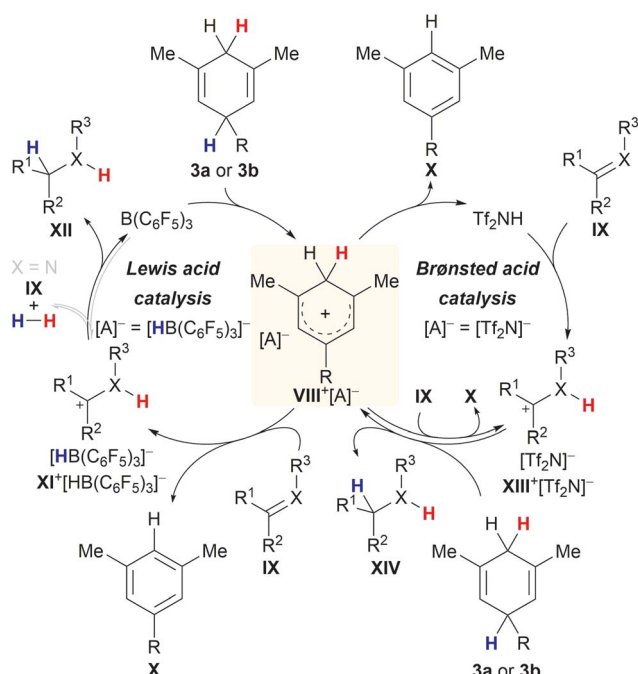


Scheme 4 Gallium(III)-assisted transfer hydrogenation of alkenes.





Scheme 5 Gallium(III)-assisted hydrogenative cyclisation of alkynes. ^a2.4 equiv. of **3c** used.

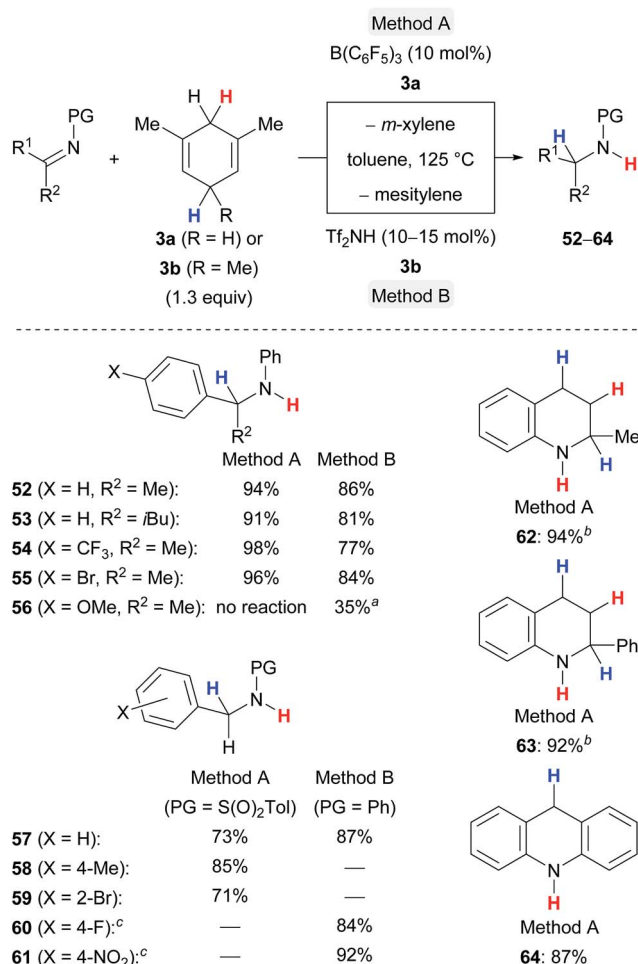


Scheme 6 Catalytic cycles for Lewis and Brønsted acid-catalysed transfer hydrogenation of imines (X = NPG) and alkenes (X = CH).

Brønsted acid protonates σ - or π -basic substrate **IX** to furnish ion pair **XI**⁺[HB(C₆F₅)₃][−] together with stoichiometric arene **X**. Dihydrogen release from **VIII**⁺ in the presence of a Lewis-basic substrate was excluded. Conversely, subsequent hydride transfer from [HB(C₆F₅)₃][−] to the carbenium ion in **XI**⁺ to regenerate B(C₆F₅)₃ concomitant with the formation of product **XII** was proposed to compete with reversible dihydrogen liberation in the case of imines (grey pathway).²² The preference of either pathway depends on the electrophilicity of the carbon atom of the iminium ion intermediate as well as the basicity of the imine nitrogen atom. The formation of highly Brønsted-

acidic Wheland intermediate **VIII**⁺ in the course of the Lewis acid-mediated transfer hydrogenation inspired Chatterjee and Oestreich to investigate potentially competing Brønsted-acid catalysis. As part of these studies, these authors successfully showed that reasonably strong Brønsted acids such as Tf₂NH are equally able to initiate transfer hydrogenation²³ from cyclohexa-1,4-dienes **3a** or **3b** by catalytically generating the same Wheland intermediate **VIII**⁺ (right cycle).^{5c} It seems plausible that protonation of substrate **IX** occurs from either Brønsted acids **VIII**⁺ or Tf₂NH to furnish intermediate **XIII**⁺[Tf₂N][−]. In the absence of the borohydride [HB(C₆F₅)₃][−], cyclohexa-1,4-diene **3a** or **3b** steps in as the hydride donor for the reduction of **XIII**⁺[HB(C₆F₅)₃][−], thereby closing the catalytic cycle.^{20g}

The transfer hydrogenation of imines requires forcing reaction conditions, *i.e.*, 125 °C and 10 to 15 mol% of the catalyst, and is limited to certain protecting groups at the nitrogen atom to secure optimal steric shielding, sufficient Lewis basicity and stability (Scheme 7).^{5a,c} The protocol is compatible with differently functionalised ketimines (\rightarrow **52–55**) and aldimines (\rightarrow **57–61**) and tolerated electron-withdrawing substituents (\rightarrow **54,55,59–61**) and even *ortho* substitution (\rightarrow **59**). A



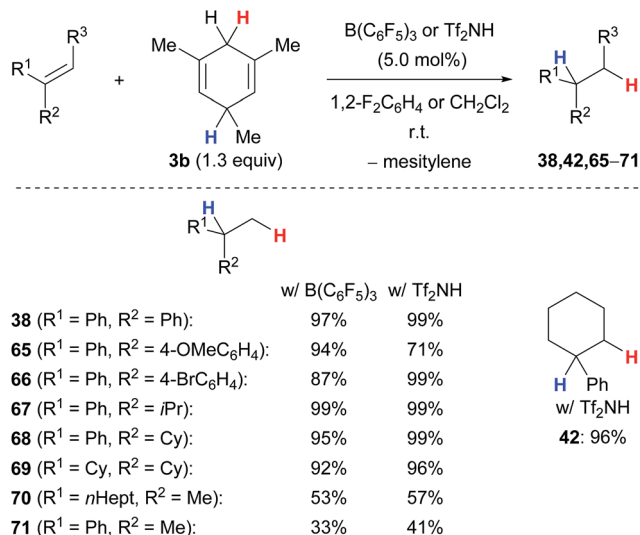
Scheme 7 Lewis and Brønsted acid-catalysed transfer hydrogenation of imines and nitrogen-containing heteroarenes. ^aMessy reaction. ^b2.6 equiv. of surrogate **3a** used. ^cPrepared by reductive amination.



The transfer hydrogenation of π -basic alkenes proceeds equally well with $\text{B}(\text{C}_6\text{F}_5)_3$ or TF_2NH under mild reaction conditions using 5.0 mol% of the catalyst at room temperature (Scheme 8).^{5b,c} The transfer process, however, requires an additional methyl group in the bisallylic position of the cyclohexadienyl group where the hydride abstraction occurs to prevent undesired side reactions, that is liberation of dihydrogen and heterodimerisation of cationic intermediates. The method can be applied to a wide range of 1,1-disubstituted alkenes (\rightarrow **38**, **65**–**71**) and works also with trisubstituted derivatives (\rightarrow **42**). 1,1-Diarylalkenes furnished the corresponding alkanes **38**, **65** and **66** in high yields, irrespective of the electronic properties of the arene. α -Alkyl-substituted styrenes as well as 1,1-dialkylalkenes required sterically demanding substituents, *e.g.*, an isopropyl (\rightarrow **67**) or a cyclohexyl group (\rightarrow **68**–**69**), to prevent thermoneutral cationic dimerisation as observed for **70** and **71**.

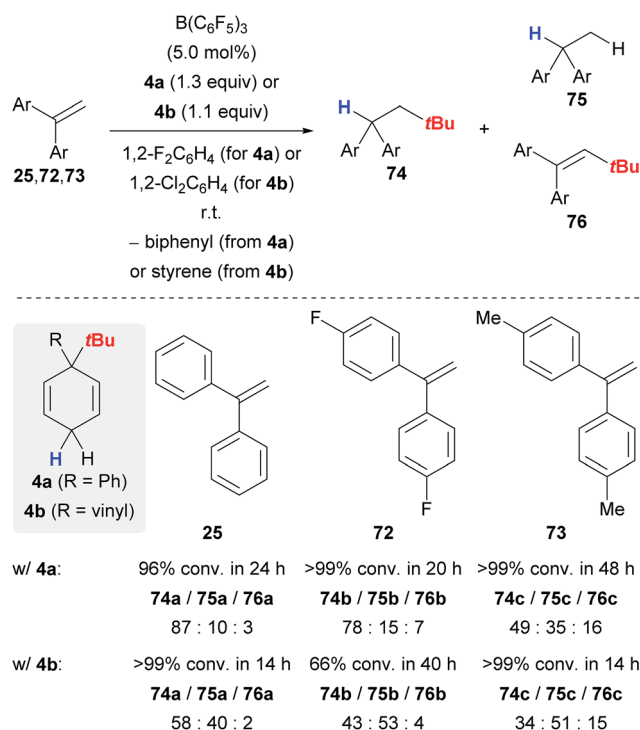
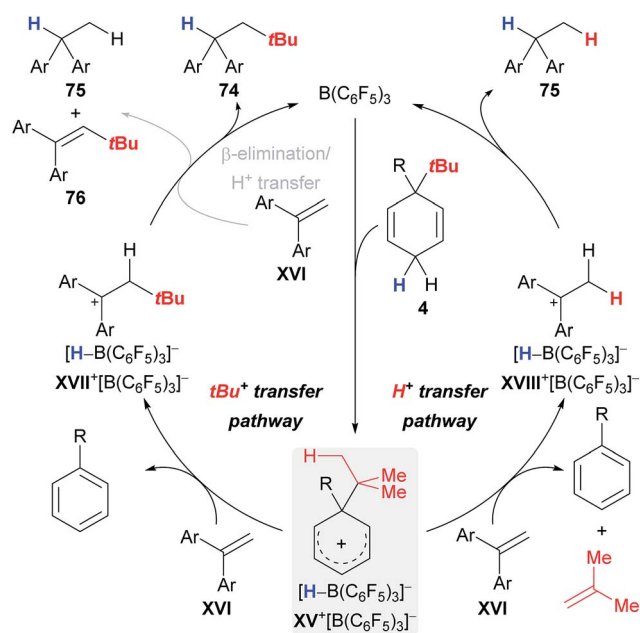
Keess and Oestreich introduced 3-*tert*-butyl-substituted cyclohexa-1,4-dienes **4** as transfer reagents in the transfer hydro-*tert*-butylation of alkenes.⁶ This methodology represents an unprecedented approach to install tertiary alkyl groups at carbon frameworks²⁴ but competing reaction channels that could not be completely suppressed still limit its synthetic utility.

The transfer of the *tert*-butyl group proceeds smoothly at room temperature with only little excess of transfer reagent **4**,



Scheme 8 Lewis acid- and Brønsted acid-catalysed transfer hydrogenation of alkenes.

yielding quantitative conversion of the alkene (Scheme 9).⁶ Extensive optimization of the reaction conditions using 1,1-diphenylethylene (**25**) as model substrate could not fully prevent the formation of byproducts **75a** and **76a** (column 1). Electronically modified 1,1-diarylethenes **72** and **73** were also tested but favoured the formation of the byproducts **75** and **76** to an

Scheme 9 Transfer hydro-*tert*-butylation of 1,1-diaryllalkenes.

Scheme 10 Proposed catalytic cycle for the transfer hydro-*tert*-butylation.

even greater extent (columns 2 and 3). The influence of the surrogate structure, namely the substituent “*ipso*” to the *tert*-butyl group, is profound, resulting in superior selectivities for surrogate **4a** (R = Ph) compared to **4b** (R = vinyl). In the latter case, separation of the stoichiometrically formed arene byproduct is conveniently achieved as styrene polymerises under the reaction conditions.

The proposed catalytic cycle that rationalises the pathways for byproduct formation commences with the $\text{B}(\text{C}_6\text{F}_5)_3$ -triggered abstraction of a bisallylic hydride from surrogate **4** to furnish Wheland complex $\text{XV}^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (Scheme 10), followed by transfer of either the *tert*-butyl cation ($\text{XV}^+ \rightarrow \text{XVII}^+$, left cycle) or a distal proton ($\text{XV}^+ \rightarrow \text{XVIII}^+$, right cycle) to alkene **XVI**; stoichiometric liberation of gaseous isobutene likely accounts for the latter pathway. The carbenium ion in XVIII^+ is eventually reduced by borohydride $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ to afford byproduct **75**, thereby closing the catalytic cycle. Likewise, intermediate XVII^+ can either directly collapse and form the desired alkane **74** or first transfer a proton from the β position in XVII^+ to another molecule of alkene **XVI** and form byproducts **75** and **76** after hydride transfer from $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (grey pathway).

Outlook

The recent advances in transition-metal-free ionic transfer processes using substituted cyclohexa-1,4-dienes as transfer reagents hint its great promise. While still at the early stages of development, we believe that these transformations are about to emerge as useful synthetic tools. Particularly, unleashing small reactive molecules such as SiH_4 from cyclohexa-1,4-dienes by straightforward treatment with a Lewis-acid catalyst could also prove valuable for inorganic chemists.

Transfer hydrosilylation is feasible for several π - and σ -donors with a variety of hydrosilane surrogates, particularly of SiH_4 and $(\text{EtO})_3\text{SiH}$. Lack of chemoselectivity and, hence, functional-group tolerance is the obvious limitation of this method. That problem is less pronounced in the related transfer hydrogermylation. Issues in the transfer hydrogenation such as hetero- and homodimerisation of the reactants have been successfully addressed by judicious choice of the substituents at cyclohexa-1,4-diene core. The substrate scope for both $\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds is however still relatively narrow. The transfer of a *tert*-butyl group is currently the biggest challenge. While it represents promising precedence for the transfer of carbon electrofuges, the surrogate synthesis still remains unsolved. The design of new (short) synthetic routes and extension to other stabilised carbenium ions as departing groups will hopefully allow for more efficient transfer hydroalkylation reactions in the future.

On the basis of the knowledge gained from these efforts, we will continue improving the existing procedures and devise new E^+/H^- equivalents. We also hope that our findings serve as an inspiration for others in the field.

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