ChemComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

View Article Online
DOI: 10.1039/C7CC06195A

ChemComm

COMMUNICATION

Cyclohexa-1,3-diene-based dihydrogen and hydrosilane surrogates in $B(C_6F_5)_3$-catalysed transfer processes†

Received 00th January 20xx,
Accepted 00th January 20xx

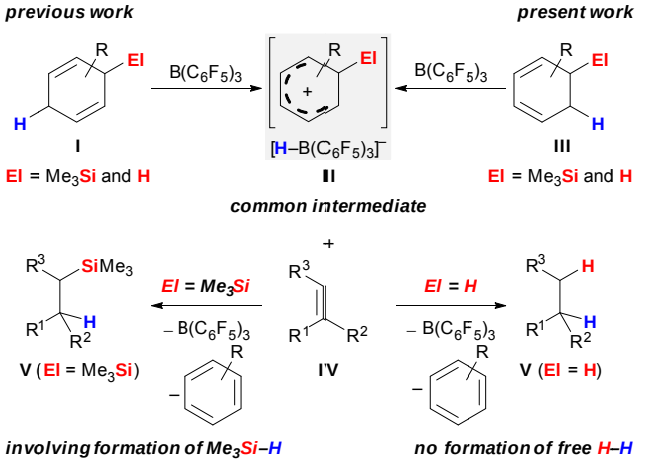
DOI: 10.1039/x0xx00000x

www.rsc.org/

Weiming Yuan,‡ Patrizio Orecchia‡ and Martin Oestreich*

The cyclohexa-1,3-diene motif is introduced as an equally effective alternative to the cyclohexa-1,4-diene platform in $B(C_6F_5)_3$-catalysed transfer processes. The transfer hydrogenation of alkenes is realised with α-terpinene and the related transfer hydrosilylation is achieved with 5-trimethylsilyl-substituted cyclohexa-1,3-diene. Both yields and substrate scope are comparable with the prior systems.

The (formal) transfer of a gaseous molecule from one compound to another is an old technique in synthetic chemistry. Transfer hydrogenation in all its facets is probably the classic example.[1] The area of transfer reactions recently gained new momentum when Morandi and co-workers as well as ourselves disclosed novel approaches. Morandi's transition-metal-catalysed *shuttle catalysis*[2] enabled potentially reversible transfer hydrocyanation[3] (HCN) and transfer hydrochlorocarbonylation[4] (CO and HCl). Our contributions make use of adequately substituted cyclohexa-1,4-dienes[5] that, *e.g.*, release hydrosilanes[6,7] (R_3SiH and even SiH_4) and transfer dihydrogen[8,9] (H_2) by treatment with the strong Lewis acid tris(pentafluorophenyl)borane [$B(C_6F_5)_3$]. These ionic transfer reactions are initiated by hydride abstraction from cyclohexa-1,4-dienes **I**,[8b,10] either forming silicon-stabilised low-energy[10] or high-energy[8b] Wheland complexes with the borohydride as counteranion (**I** → **II**, Scheme 1, left). The fate of intermediates **II** depends on the electrofuge: **II** (El = Me_3Si) recombines to yield the hydrosilane and the arene prior to $B(C_6F_5)_3$-mediated Si–H bond activation[11] followed by alkene hydrosilylation[12] (**II** → **V** for El = Me_3Si).[10] The situation changes for **II** (El = H). It directly protonates alkene **IV**, and the resulting carbenium ion is then reduced by the borohydride (**II** → **V** for El = H).[8b]



Scheme 1 Cyclohexa-1,4-dienes (known) and cyclohexa-1,3-dienes (planned) as dihydrogen and hydrosilane surrogates in $B(C_6F_5)_3$-catalysed transfer processes to alkenes. El = electrofuge.

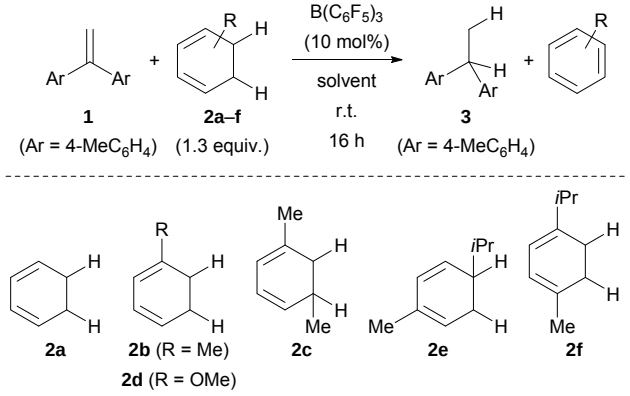
The success with the $B(C_6F_5)_3$-promoted degradation of cyclohexa-1,4-dienes[5] led us to the question whether cyclohexa-1,3-dienes with the double bonds in conjugation would also be suitable hydrosilane and dihydrogen surrogates. The conversion of cyclohexa-1,3-diene to benzene and dihydrogen is exothermic but just a few reports employ substituted cyclohexa-1,3-dienes as a dihydrogen sources.[13] We envisioned that $B(C_6F_5)_3$ could also abstract hydride from cyclohexa-1,3-dienes to arrive at the Wheland complex as the common intermediate (**III** → **II**, Scheme 1, right). We describe here transfer hydrogenation as well as hydrosilylation of alkenes using cyclohexa-1,3-diene-based surrogates.

To test the feasibility of our plan, we chose 1,1-diarylalkene **1** as the model substrate (**1** → **3**, Table 1). The parent surrogate, cyclohexa-1,3-diene (**2a**), was fully consumed but the yield was low (entry 1). That outcome made us remember the problems arising from hetero- and homodimerisation of the reactants in our previous study with cyclohexa-1,4-diene (**4a**).[8b] We therefore subjected methyl-substituted cyclohexa-1,4-dienes **2b** and **2c** to the standard setup and found little improvement (entries 2 and 3). These results are not fully

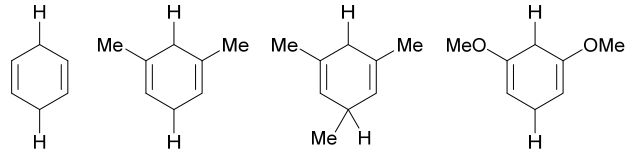
Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 115, 10623 Berlin, Germany. E-mail: martin.oestreich@tu-berlin.de
† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x
‡ These authors contributed equally.

consistent with what was observed with methyl-substituted cyclohexa-1,4-dienes **4b** and **4c** where yields were substantially higher.[8b] The more electron-donating methoxy group in **2d** suppressed the reaction completely because of interaction with the Lewis-acid catalyst (entry 4); this is in agreement with **4d** in the cyclohexa-1,4-diene series. We then examined the commercially available terpenes α-phellandrene (**2e**) and α-terpinene (**2f**). The yield with **2e** was in the same range as before (entry 5) but cheap **2f** afforded excellent 86% yield (entry 6). Screening of various solvents did not bring about higher yields (entries 7–10). Also, an increased amount of reagent **2f** (2.0 vs 1.3 equiv.) did not change the yield (entry 11). A slightly better yield was obtained at higher concentration, furnishing 88% isolated yield (entry 12). The reactions were routinely run inside a glovebox but worked without any relevant loss in yield outside the glovebox, even with exposure to air (entries 13 and 14). When exposed to moisture, proton catalysis could be also operative as a result of Lewis adduct formation between $B(C_6F_5)_3$ and water.[14] We had shown before that this transfer process is catalysed by Brønsted acids, and Tf_2NH had emerged as broadly applicable to cyclohexa-1,4-dienes **4a–c**.[8c] However, α-terpinene (**2f**) converted **1** into **3** in only 45% yield (entry 15).

Table 1 Optimisation of the transfer hydrogenation of alkenes with different cyclohexa-1,3-dienes (with published results[8b] for related cyclohexa-1,4-dienes at the bottom)[a]



Entry	Cyclohexa-1,3-diene **2**	Solvent	Yield of **3** (%)[b]
1	**2a**	CH_2Cl_2	30
2	**2b**	CH_2Cl_2	35
3	**2c**	CH_2Cl_2	52
4	**2d**	CH_2Cl_2	n.r.
5	**2e**	CH_2Cl_2	33
6	**2f**	CH_2Cl_2	86
7	**2f**	Toluene	74
8	**2f**	$1,2\text{-}F_2C_6H_4$	84
9	**2f**	$1,2\text{-}Cl_2C_6H_4$	78
10	**2f**	*n*-Hexane	67
11[c]	**2f**	CH_2Cl_2	85
12[d]	**2f**	CH_2Cl_2	92 (88)[e]
13[f]	**2f**	CH_2Cl_2	89
14[g]	**2f**	CH_2Cl_2	84
15[h]	**2f**	$1,2\text{-}F_2C_6H_4$	45

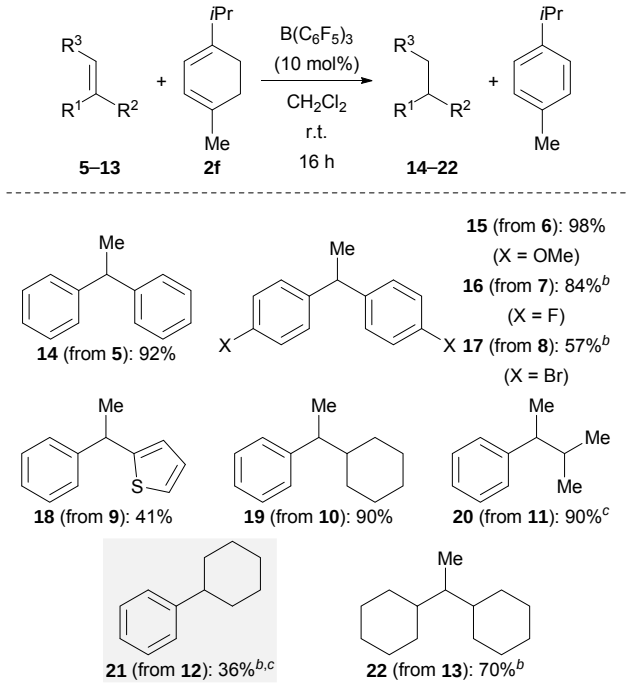


4a: 38% **4b**: 64% **4c**: 97% **4d**: n.r.

[a] Unless otherwise noted, all reactions were performed inside a glovebox with 0.1 mmol of **1**, 1.3 equiv. of **2** and 10 mol% of $B(C_6F_5)_3$ in CH_2Cl_2 (0.3 mL) at room temperature. [b] Determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard. [c] 2.0 equiv. of **2f** used. [d] 0.1 mL CH_2Cl_2 (1.0 M) used. [e] Isolated yield after purification by flash chromatography on silica gel. [f] Performed under inert atmosphere outside the glovebox. [g] Performed exposed to air and, hence, moisture. [h] 10 mol% of Tf_2NH (10 mol%) used as catalyst in $1,2\text{-}F_2C_6H_4$ at 80 °C. n.r. = no reaction.

With the optimised reaction conditions in hand, we assessed the substrate scope (Scheme 2). 1,2-Diphenylethylene reacted with comparable yield (**5** → **14**), and electron-donating as well as electron-withdrawing groups were tolerated (**6–8** → **15–17**); the halogenated substrates were less reactive, and the reaction had to be performed in $1,2\text{-}F_2C_6H_4$ at 50 °C. A thien-2-yl group was also compatible (**9** → **18**). Besides of 1,1-diarylalkenes, 1-alkyl-1-arylalkenes participated equally well (**10/11** → **19/20**), and even a trisubstituted alkene was converted in moderate yield (**12** → **21**, grey box). A 1,1-dialkylalkene was also shown to react in good yield (**13** → **22**).

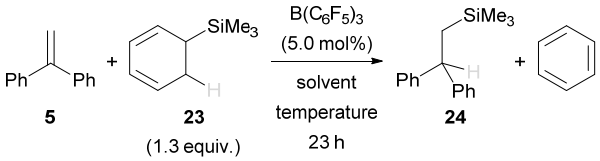
View Article Online DOI: 10.1039/C7CC06195A



Scheme 2 Substrate scope of the transfer hydrogenation of alkenes.[a] [a] Unless otherwise noted, all reactions were performed with 0.2 mmol of the indicated alkene, 1.3 equiv. of **2f** and 10 mol% of $B(C_6F_5)_3$ in CH_2Cl_2 (0.2 mL) at room temperature. [b] The solvent was 1,2-$F_2C_6H_4$ and the temperature was 50 °C. [c] Determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

We had recently established ionic transfer hydrosilylation as a safe way to engage highly flammable hydrosilanes such as Me_3SiH or SiH_4 in alkene hydrosilylation reactions.[6] To complement our earlier method with 3-silylated cyclohexa-1,4-dienes as surrogates,[6] we anticipated that 5-silylated cyclohexa-1,3-dienes could also serve as hydrosilane sources. To verify this, we prepared 5-trimethylsilyl-substituted cyclohexa-1,3-diene **23** according to a procedure by Sarlah and co-workers.[15] We were then pleased to see that the $B(C_6F_5)_3$-catalysed transfer hydrosilylation of 1,1-diphenylethylene with **23** proceeded smoothly in toluene at room temperature (**5** → **24**, Table 2, entry 1). The reaction temperature had only little effect, and yields did not improve significantly at 50 °C and 80 °C, respectively (entries 2 and 3). Running the reaction under air led to a decrease in yield (entry 4). Other commonly used solvents were screened but yet again without success (entries 5–8).

Table 2 Optimisation of the transfer hydrosilylation of alkenes with a 5-silylated cyclohexa-1,3-diene[a]



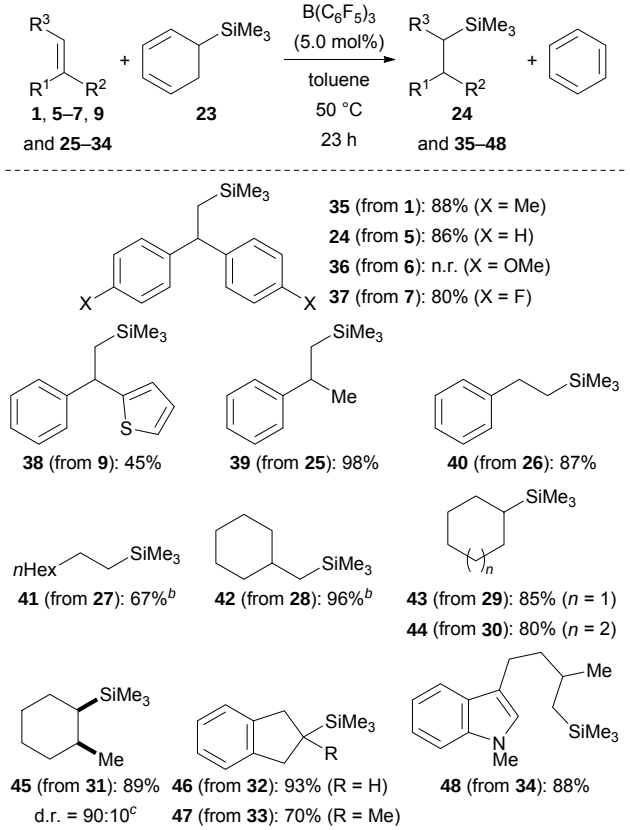
Entry	Solvent	Temperature (°C)	Yield of **24** (%)
1	Toluene	r.t.	82
2	Toluene	50	86
3	Toluene	80	85
4[b]	Toluene	50	52
5	CH_2Cl_2	r.t.	65 (5)[c]
6	*n*-Pentane	r.t.	24 (53)[c]
7	1,2-$Cl_2C_6H_4$	r.t.	66 (33)[c]
8	1,2-$F_2C_6H_4$	r.t.	82 (16)[c]

[a] Unless otherwise noted, all reactions were performed with 0.1 mmol of **5**, 1.3 equiv. of **23** and 5.0 mol% of $B(C_6F_5)_3$ in the indicated solvent (0.1 mL) at room temperature. [b] Performed exposed to air and, hence, moisture. [c] Yield of recovered alkene in parentheses.

View Article Online DOI: 10.1039/C7CC06195A

Monitoring the transfer hydrosilylation by ^{1}H NMR spectroscopy exhibited that Me_3SiH is rapidly liberated, *i.e.*, within a few minutes. Subsequent addition of the alkene to the reaction mixture then revealed that the hydrosilylation is markedly slower (see the Electronic Supplementary Information for details†). These findings agree with the two-step reaction sequence established for the transfer hydrosilylation with 3-silylated cyclohexa-1,4-dienes[6b,d] (cf. Scheme 1, left).

We then applied the above protocol to different types of alkenes with mono-, di- and trisubstituted double bonds (Scheme 3). 1,1-Diarylalkenes with substitution in the *para* position reacted cleanly. No reaction was seen with methoxy groups as substituents (as in **6**); this alkene had reacted in quantitative yield in the related transfer hydrogenation (**6** → **15**, Scheme 2), and we attribute its failure to react to silicon's strong affinity to oxygen. The thien-2-yl group was again tolerated (**9** → **38**). Unlike in the transfer hydrogenation, styrenes reacted cleanly in the transfer hydrosilylation (**25**/**26** → **39**/**40**) as did an α-olefin (**27** → **41**). Likewise, both exocyclic 1,1- and endocyclic 1,2-disubstituted alkenes showed good to excellent reactivity (**28** → **42** and **29**/**30** → **43**/**44**). Trisubstituted 1-methylcyclohexene reacted with good *cis* selectivity[6b] (**31** → **45**). As observed with the cyclohexa-1,4-diene-based surrogate,[6b] indenes with or without substitution at C2 transformed into the corresponding indanes with the trimethylsilyl group in the homobenzylic position (**32**/**33** → **46**/**47**). Finally, an indole-containing alkene underwent the transfer hydrosilylation as well (**34** → **48**).



Scheme 3 Substrate scope of the transfer hydrosilylation of alkenes.[a] [a] Unless otherwise noted, all reactions were performed with 0.1 mmol of the indicated alkene, 1.3 equiv. of **23** and 5.0 mol% of $B(C_6F_5)_3$ in toluene (0.1 mL) at 50 °C. [b] The solvent was CH_2Cl_2 and the temperature was 40 °C. [c] Determined by ^1H NMR spectroscopy.

Herein, we disclosed the $B(C_6F_5)_3$-catalysed transfer hydrogenation and hydrosilylation of alkenes employing cyclohexa-1,3-diene-based dihydrogen (H_2) and trimethylsilane (Me_3SiH) surrogates. The present work complements the prior art with cyclohexa-1,4-dienes and extends the range of reagents for these transfer reactions. While the substrate scope is largely the same as before,[6,8] the advantage lies in the availability of α-terpinene for the transfer hydrogenation. Conversely, Sarlah's 5-trimethylsilyl-substituted cyclohexa-1,3-diene is not yet accessible in useful quantities compared to the easy-to-make 1,4-regioisomer. Nevertheless, both transformations are rare examples of cyclohexa-1,3-dienes as transfer reagents.

This research was supported by the Cluster of Excellence *Unifying Concepts in Catalysis* of the Deutsche Forschungsgemeinschaft (EXC 314/2) and the Berlin Graduate School of Natural Sciences and Engineering (predoctoral fellowship to P.O., 2016–2019). M.O. is indebted to the Einstein Foundation (Berlin) for an endowed professorship.

There are no conflicts to declare

References

1 For a review, see: D. Wang and D. Astruc, *Chem. Rev.*, 2015, **115**, 6621–6686.

2 For recent overviews of transition-metal-catalysed transfer processes, see: (*a*) B. N. Bhawal and B. Morandi, *Chem. – Eur. J.*, 2017, **23**, DOI: 10.1002/chem.201605325; (*b*) B. N. Bhawal and B. Morandi, *ACS Catal.*, 2016, **6**, 7528–7535.

3 X. Fang, P. Yu and B. Morandi, *Science*, 2016, **351**, 832–836.

4 X. Fang, B. Cacherat and B. Morandi, *Nat. Chem.*, 2017, **9**, DOI: 10.1038/nchem.2798.

5 For a recent overview, see: S. Keess and M. Oestreich, *Chem. Sci.* 2017, **8**, 4688–4695.

6 For a review of transfer hydrosilylation, see: (*a*) M. Oestreich, *Angew. Chem., Int. Ed.*, 2016, **55**, 494–499; (*b*) A. Simonneau and M. Oestreich, *Angew. Chem., Int. Ed.*, 2013, **52**, 11905–11907; (*c*) A. Simonneau, J. Friebel and M. Oestreich, *Eur. J. Org. Chem.*, 2014, 2077–2083; (*d*) S. Keess, A. Simonneau and M. Oestreich, *Organometallics*, 2015, **34**, 790–799; (*e*) A. Simonneau and M. Oestreich, *Nat. Chem.*, 2015, **7**, 816–822; for the related transfer hydrogermylation, see: (*f*) S. Keess and M. Oestreich, *Org. Lett.*, 2017, **19**, 1898–1901.

7 For other approaches to transfer hydrosilylation, see: (*a*) S. Amrein, A. Timmermann and A. Studer, *Org. Lett.*, 2001, **3**, 2357–2360; (*b*) C. Chauvier, P. Thuéry and T. Cantat, *Angew. Chem., Int. Ed.*, 2016, **55**, 14096–14100.

8 (*a*) I. Chatterjee and M. Oestreich, *Angew. Chem., Int. Ed.*, 2015, **54**, 1965–1968; (*b*) I. Chatterjee, Z.-W. Qu, S. Grimme and M. Oestreich, *Angew. Chem., Int. Ed.*, 2015, **54**, 12158–12162; (*c*) I. Chatterjee and M. Oestreich, *Org. Lett.*, 2016, **18**, 2463–2466.

9 For another example of an alkene transfer hydrogenation using cyclohexa-1,4-diene, see: B. Michelet, C. Bour and V. Gandon, *Chem.–Eur. J.*, 2014, **20**, 14488–14492.

10 For the quantum-chemical analysis of the transfer hydrosilylation of alkenes, see: K. Sakata and H. Fujimoto, *Organometallics*, 2015, **34**, 236–241.

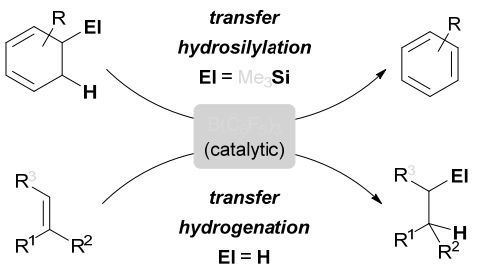
11 (*a*) S. Rendler and M. Oestreich, *Angew. Chem., Int. Ed.*, 2008, **47**, 5997–6000; (*b*) K. Sakata and H. Fujimoto, *J. Org. Chem.*, 2013, **78**, 12505–12512. For a comprehensive review of $B(C_6F_5)_3$-catalysed Si–H and H–H bond activation, see: (*c*) M. Oestreich, J. Hermeke and J. Mohr, *Chem. Soc. Rev.*, 2015, **44**, 2202–2220.

12 M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.*, 2002, **67**, 1936–1940

13 Examples include: (*a*) E. N. Frankel, *J. Org. Chem.* 1972, **37**, 1549–1552; (*b*) D. C. Tabor, F. H. White, L. W. Collier, IV and S. A. Evans, Jr., *J. Org. Chem.* 1983, **48**, 1638–1643; (*c*) H. Shima and T. Yamaguchi, *J. Catal.* 1984, **90**, 160–164; (*d*) N. A. Eddy, J. J. Richardson and G. Fenteany, *Eur. J. Org. Chem.*, 2013, 5041–5044.

14 A. A. Danopoulos, J. R. Galsworthy, M. L. H. Green, S. Cafferkey, L. H. Doerrer and M. B. Hursthouse, *Chem. Commun.*, 1998, 2529–2530.

15 M. Okumura, S. M. N. Huynh, J. Pospech and D. Sarlah, *Angew. Chem., Int. Ed.*, 2016, **55**, 15910–15914.



Transition-metal-free transfer hydrogenation and transfer hydrosilylation of alkenes are achieved with cyclohexa-1,3-diene-based surrogates.

