

## C–C Bond Formation

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## Lewis Acid Catalyzed Transfer Hydromethallylation for the Construction of Quaternary Carbon Centers

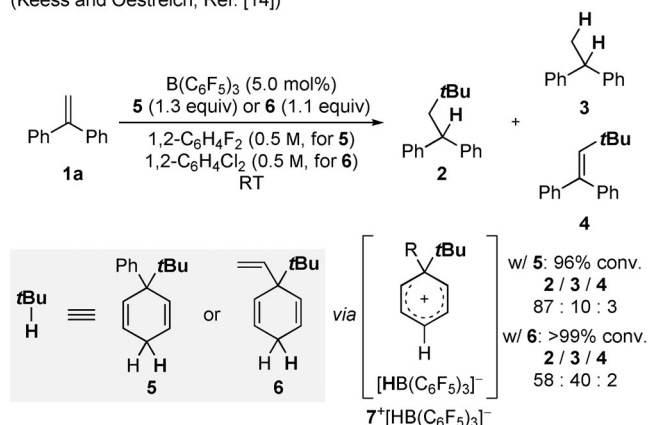
Johannes C. L. Walker and Martin Oestreich\*

**Abstract:** The design and gram-scale synthesis of a cyclohexa-1,4-diene-based surrogate of isobutene gas is reported. Using the highly electron-deficient Lewis acid  $B(C_6F_5)_3$ , application of this surrogate in the hydromethallylation of electron-rich styrene derivatives provided sterically congested quaternary carbon centers. The reaction proceeds by  $C(sp^3)-C(sp^3)$  bond formation at a tertiary carbenium ion that is generated by alkene protonation. The possibility of two concurrent mechanisms is proposed on the basis of mechanistic experiments using a deuterated surrogate.

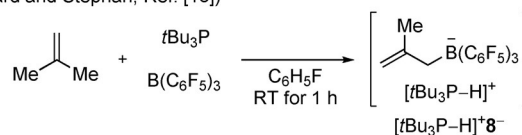
The catalytic preparation of quaternary carbon centers using  $C(sp^3)-C(sp^3)$  bond-forming reactions has been identified as a key challenge in organic synthesis.<sup>[1]</sup> Recent progress in this area has mainly centered on transition-metal-catalyzed transformations.<sup>[2–4]</sup> Metal-free approaches are less common.<sup>[5,6]</sup> One strategy to achieve  $C(sp^3)-C(sp^3)$  bond formation is the attack of a carbon nucleophile onto a tertiary carbenium ion.<sup>[7,8]</sup> Although this has been exploited in the context of carbenium ion generation by dehydration of tertiary alcohols with catalytic amounts of strong acid,<sup>[5,6,9]</sup> the complementary process by catalytic protonation of alkenes is far less well explored.<sup>[10,11]</sup>

Our laboratory has been investigating cyclohexa-1,4-diene-based surrogates of difficult-to-handle compounds for metal-free transfer reactions.<sup>[12–15]</sup> As part of this program we previously developed cyclohexa-1,4-dienes **5** and **6** as surrogates of isobutane gas and reported their use in the transfer hydro-*tert*-butylation of alkenes using the strong boron Lewis acid  $B(C_6F_5)_3$  (Scheme 1, top).<sup>[14,16]</sup> Hydride abstraction from the bisallylic position of the surrogates led to formation of the *tert*-butyl-substituted Wheland intermediates **7**<sup>+</sup> and transfer of the electrofugal *tert*-butyl group to the terminus of 1,1-diaryl-substituted alkenes. Borohydride addition to the resulting benzylic tertiary carbenium ion delivered formally anti-Markovnikov alkylation products such as **2**. However,

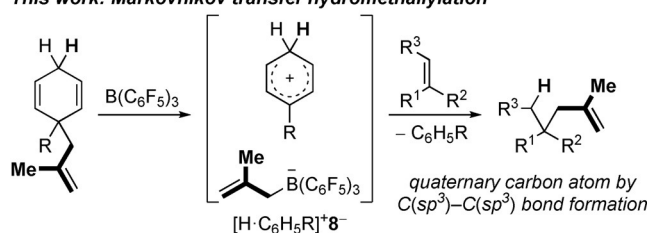
**Previous work:** anti-Markovnikov transfer hydro-*tert*-butylation (Keess and Oestreich, Ref. [14])



**C–H activation of isobutene by a frustrated Lewis pair** (Ménard and Stephan, Ref. [18])



**This work:** Markovnikov transfer hydromethallylation



**Scheme 1.** Cyclohexa-1,4-diene-based surrogates of isobutane and isobutene gas for metal-free transfer hydroalkylation and -allylation, respectively.

this process was hampered by side reactions to give **3** and **4**, and the substrate scope was quite limited.

We wondered whether an appropriately substituted cyclohexa-1,4-diene would facilitate abstraction of a nucleofugal hydrocarbon group and then lead to the complementary Markovnikov hydroalkylation.<sup>[17]</sup> In seeking a plausible hydrocarbon unit, we were interested in a report by Ménard and Stephan who had achieved the stoichiometric C–H activation of isobutene with the frustrated Lewis pair  $tBu_3P/B(C_6F_5)_3$  (Scheme 1, middle).<sup>[18]</sup> The methallyl borate **8**<sup>−</sup> formed represents a potential nucleophilic source of the methallyl group,<sup>[19,20]</sup> and we hoped that a cyclohexa-1,4-diene surrogate of isobutene gas could be developed to allow for the abstraction of the methallyl nucleofuge by  $B(C_6F_5)_3$  to give **8**<sup>−</sup> and a Brønsted acidic Wheland intermediate. Interception of this complex by an alkene might then allow for transfer

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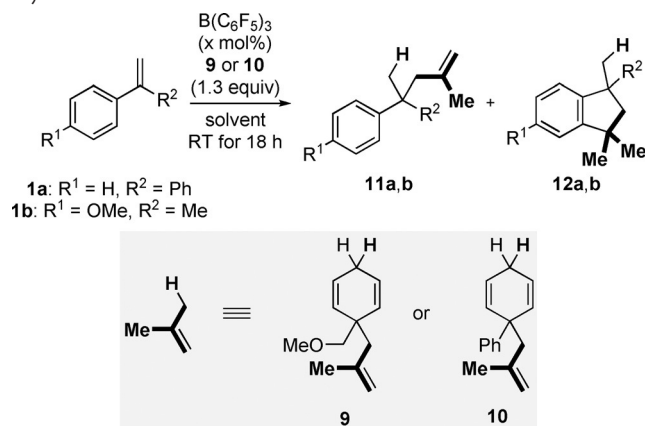
hydromethallylation and the formation of a quaternary carbon center by way of  $C(sp^3)-C(sp^3)$  bond formation (Scheme 1, bottom).<sup>[21–23]</sup>

The required surrogate would likely necessitate a quaternary center adjacent to the methallyl group to prevent undesired side reactions such as transfer hydrogenation,<sup>[24]</sup> as well as to help stabilize the positively charged Wheland intermediate. Surrogates **9** and **10** fulfill this requirement and were easily accessible by Birch alkylation from benzoic acid and biphenyl, respectively (see the Supporting Information for experimental details). We then subjected the surrogates to a model reaction with 1,1-diphenylethene (**1a**) and 10 mol %  $B(C_6F_5)_3$  in  $CH_2Cl_2$  (Table 1, entry 1). Benzyl ether based surrogate **9** did not give any of the desired hydromethallylation product **11a**, instead providing indane **12a** in 6% yield; **12a** presumably results from the intramolecular Friedel–Crafts alkylation of **11a**.<sup>[25]</sup> Biphenyl-based surrogate **10** was more reactive, forming the intended product **11a** in 3% and indane **12a** in 40% yield (entry 2). Switching the solvent to toluene improved the selectivity for **11a** (entry 3). We eventually established that electron-rich styrene derivatives allowed the reaction to proceed to full conversion, and we could suppress cyclization to indanes **12** by modifying the steric environment of the alkene. Using *para*-anisyl-substituted alkene **1b**, we were initially able to form **11b** in 82% yield with no indane **12b** observed (entry 4). The loading of

both surrogate **10** and  $B(C_6F_5)_3$  could be reduced with no detrimental impact on the yield, and **11b** was then isolated in 82% yield (entry 5). The reaction could also be scaled up to 1.00 mmol (entry 6). No reaction occurred in the absence of the catalyst (entry 7), but interestingly,  $B(C_6F_5)_3$  was able to partially decompose surrogate **10** to biphenyl in the absence of the alkene starting material (entry 8).

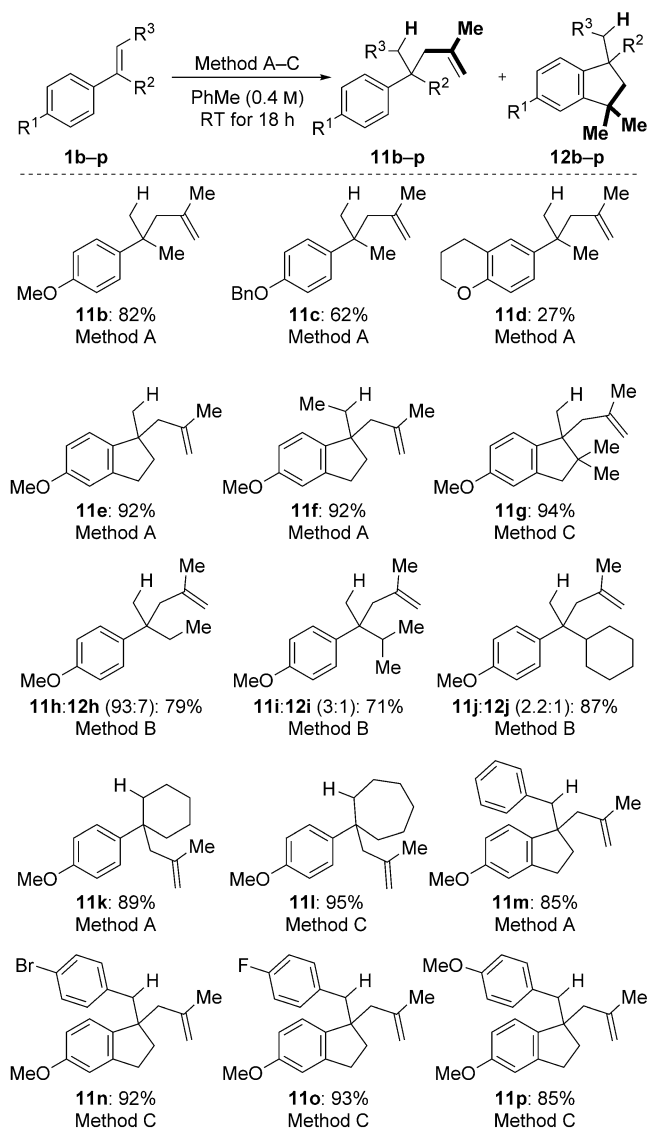
With optimized conditions in hand, we proceeded to investigate the substrate scope (Scheme 2). A range of electron-rich  $\alpha$ -substituted styrenes could be used, with benzyl ethers as in **11c** and cyclic ethers as in **11d** both tolerated. The indane-based alkene **11e** could be prepared in 92% yield and, using this framework, an exocyclic trisubstituted alkene could also be reacted to give **11f** in 92% yield. As previously observed in other transfer reactions, tetrasubstituted alkenes were unreactive.<sup>[12,13]</sup> Products bearing two contiguous quaternary carbon centers could be accessed, with

**Table 1:** Optimization of the  $B(C_6F_5)_3$ -catalyzed transfer hydromethallylation.<sup>[a]</sup>



Entry	Alkene	Surrogate	$B(C_6F_5)_3$ [mol %]	Solv.	Yield of <b>11</b> [%] <sup>[b]</sup>	Yield of <b>12</b> [%] <sup>[b]</sup>
1	<b>1a</b>	<b>9</b>	10	$CH_2Cl_2$	< 1	6
2	<b>1a</b>	<b>10</b>	10	$CH_2Cl_2$	3	40
3	<b>1a</b>	<b>10</b>	10	PhMe	32	11
4	<b>1b</b>	<b>10</b> <sup>[c]</sup>	10	PhMe	82	< 1
5	<b>1b</b>	<b>10</b>	5.0	PhMe	85 (82) <sup>[d]</sup>	< 1
6 <sup>[e]</sup>	<b>1b</b>	<b>10</b>	5.0	PhMe	74 <sup>[d]</sup>	< 1
7	<b>1b</b>	<b>10</b>	–	PhMe	< 1	< 1
8 <sup>[f]</sup>	<b>1b</b>	<b>10</b>	5.0	PhMe	< 1 <sup>[f]</sup>	< 1

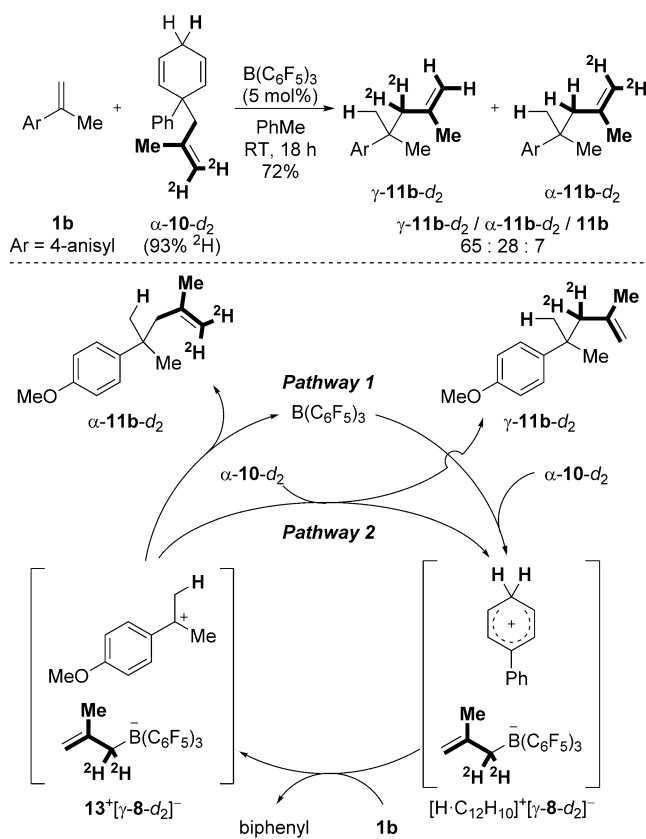
[a] Unless otherwise noted, reactions were performed on a 0.10 mmol scale with 1.3 equiv **9** or **10** in 0.25 mL (0.4 M) of the indicated solvent. [b] Determined by  $^1H$  NMR spectroscopy by the addition of 1,2-dibromomethane as an internal standard. [c] 1.5 equiv surrogate **10** used. [d] Yield of isolated product. [e] On a 1.0 mmol scale. [f] Alkene **1b** was not added. 22% conversion of surrogate **10** to biphenyl.



**Scheme 2.** Scope of the  $B(C_6F_5)_3$ -catalyzed transfer hydromethallylation of alkenes. Method A:  $B(C_6F_5)_3$  (5.0 mol %), surrogate **10** (1.3 equiv); Method B:  $B(C_6F_5)_3$  (5.0 mol %), surrogate **10** (2.0 equiv); Method C:  $B(C_6F_5)_3$  (7.5 mol %), surrogate **10** (2.0 equiv).

**11g** formed in 94% yield. Here, slightly higher loadings of  $B(C_6F_5)_3$  and surrogate **10** were required to push the reaction to completion. These conditions found further application with other less reactive substrates. Increased substitution at the  $\alpha$ -position of the styrene was also tolerated, as in **11h–j**, although in these cases cyclization to indanes **12h–j** could not be completely suppressed; the proportion of indanes **12h–j** increased with the size of the  $\alpha$ -substituent. Performing the reaction with two equivalents of surrogate **10** did help to reduce the extent of cyclization; **11h** and **12h** were, however, formed in a 3:1 mixture with 1.3 equiv surrogate **10**. A substrate bearing the bulky *tert*-butyl group in the  $\alpha$ -position was unreactive. Cyclic alkanes containing quaternary carbon centers could also be synthesized using this methodology, with cyclohexane **11k** and cycloheptane **11l** being formed in 89% and 95% yield, respectively. Finally, a series of compounds bearing pendant aryl groups was prepared. Phenyl-substituted **11m** was formed in 85% yield, and products with halogen substituents, as in **11n** and **11o**, as well as an electron-donating methoxy substituent, as in **11p**, could also be accessed. To illustrate the utility of these products, a selection of these compounds were further derivatized (see the Supporting Information for details).

To gain insight into the reaction mechanism, we prepared deuterated surrogate  $\alpha$ -**10-d<sub>2</sub>** (Scheme 3; see the Supporting Information for experimental details). Although this surrogate was deuterated solely at the allyl terminus ( $\gamma$ -position), its reaction with alkene **1b** produced **11b-d<sub>2</sub>** with deuterium



**Scheme 3.** Mechanistic experiment with deuterated surrogate and proposed mechanism.

incorporation in both the  $\alpha$ - and  $\gamma$ -positions. This suggests the presence of at least two concurrent mechanisms (see the Supporting Information for more elaborate catalytic cycles). First, based on the work of Ménard and Stephan,<sup>[18]</sup> we propose that alkene attack from surrogate  $\alpha$ -**10-d<sub>2</sub>** to  $B(C_6F_5)_3$  results in abstraction of the methallyl group and formation of  $\alpha$ -deuterated methallyl borate complex  $[\gamma$ -**8-d<sub>2</sub>**]<sup>-</sup> along with protonated biphenyl  $[H-C_{12}H_{10}]^+$  (Scheme 3, Pathway 1). Protonation of alkene **1b** by the Brønsted acidic Wheland complex yields the tertiary carbenium ion **13<sup>+</sup>** with concomitant aromatization of the surrogate core to biphenyl. Transfer of the methallyl group from methallyl borate  $[\gamma$ -**8-d<sub>2</sub>**]<sup>-</sup> to **13<sup>+</sup>** then provides  $\gamma$ -deuterated alkene  $\alpha$ -**11b-d<sub>2</sub>** with formation of a  $C(sp^3)$ – $C(sp^3)$  bond. Alternatively, direct transfer of the methallyl fragment from  $\alpha$ -**10-d<sub>2</sub>** to carbenium ion **13<sup>+</sup>** would result in the formation of the regioisomer  $\gamma$ -**11b-d<sub>2</sub>** with deuteration in the  $\alpha$ -position (Pathway 2). In this scenario,  $B(C_6F_5)_3$  operates as an initiator and methallyl borate  $[\gamma$ -**8-d<sub>2</sub>**]<sup>-</sup> as a spectator counteranion. The dual role of  $B(C_6F_5)_3$  as catalyst and initiator in transfer chemistry has previously been discussed on the basis of computational calculations.<sup>[26]</sup> Another pathway to arrive at  $\gamma$ -**11b-d<sub>2</sub>** is the transfer of the methallyl group between two boron centers (see Pathway 3 in the Supporting Information). This would lead to  $\gamma$ -deuterated  $\alpha$ -**8-d<sub>2</sub>**, and attack of the methallyl group onto carbenium ion **13<sup>+</sup>** then provides  $\gamma$ -**11b-d<sub>2</sub>**. It has not yet been possible to distinguish between the two possible pathways leading to  $\gamma$ -**11b-d<sub>2</sub>**.

To summarize, a cyclohexa-1,4-diene-based surrogate of isobutene gas has been developed and utilized in the transfer hydromethallylation of electron-rich styrene derivatives. The method enables the catalytic formation of sterically congested quaternary carbon atoms and represents a rare example of the formation of  $C(sp^3)$ – $C(sp^3)$  bonds from carbenium ions that have been formed by the protonation of an alkene. A range of different scaffolds could be incorporated, and the utility of the products was demonstrated by their derivatization.

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## Conflict of interest

The authors declare no conflict of interest.

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