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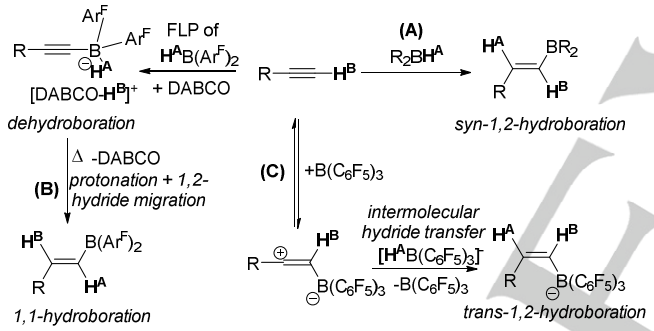
Frustrated Lewis Pair Mediated 1,2-Hydrocarbation of Alkynes

V. Fasano,[a] L. D. Curless,[a] J. E. Radcliffe[a] and M. J. Ingleson[a]*

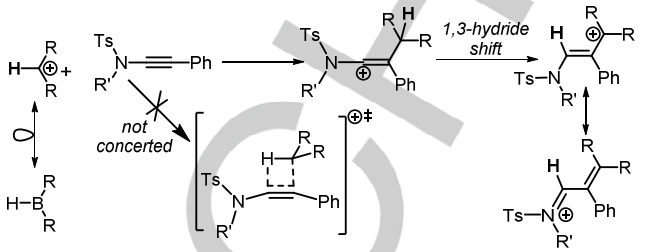
Abstract: Frustrated Lewis pair (FLP) chemistry enables a rare example of alkyne 1,2-hydrocarbation to be achieved using *N*-Me-acridinium salts as the carbon Lewis acid. This 1,2-hydrocarbation process does not proceed via a concerted mechanism as per alkyne *syn*-hydroboration, or via an intramolecular 1,3-hydride migration as operating in the only other reported alkyne 1,2-hydrocarbation reaction. Instead, in this work alkyne 1,2-hydrocarbation proceeds by a novel mechanism involving alkyne dehydrocarbation using a carbon Lewis acid based FLP to form the new C-C bond. Subsequently, intermolecular hydride transfer proceeds, with the Lewis acid component of the FLP acting as a hydride shuttle that enables alkyne 1,2-hydrocarbation.

The functionalisation of alkynes using borane Lewis acids is ubiquitous and best exemplified by the alkyne *syn*-1,2-hydroboration reaction (route **A**, scheme 1).[1] More recent work has led to the development of other metal free alkyne hydroboration reactions (e.g. 1,1-hydroboration, route **B**, and *trans*-1,2-hydroboration reactions, route **C**).[2-5]



Scheme 1. Metal free alkyne hydroborations. Ar^F = (2,4,6-$(CF_3)_3$-C_6H_2).

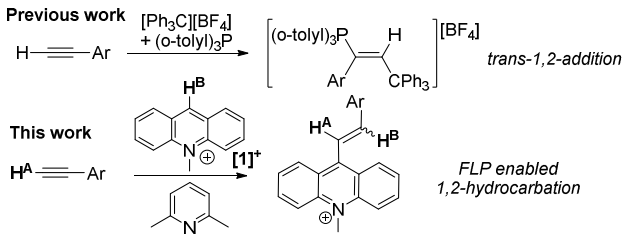
Carbenium ions are isoelectronic to boranes; however, the metal catalyst free hydrocarbation of alkynes remains extremely rare in contrast to alkyne hydroboration for reasons discussed in detail by Mayr and co-workers.[6] 1,2-hydrocarbation involves the addition of a C-H of a $[R_2CH]^+$ electrophile across a triple bond and thus is distinct to the more common Lewis acid activation of an alkyne for a subsequent S_EAr reaction.[7] To the best of our knowledge there is only one previous report of alkyne 1,2-hydrocarbation, specifically the addition of benzhydrylium cations to ynamides (Scheme 2).[6] This previous study



Scheme 2. Stepwise 1,2-hydrocarbation of ynamides by Mayr and co-workers.

determined that: (a) alkyne 1,2-hydrocarbation is a stepwise process, (b) that only highly nucleophilic alkynes were amenable and (c) that hydrocarbation only occurs when the carbocation formed post 1,3-hydride transfer is significantly stabilized. Therefore alkyne hydrocarbation reactions are currently limited and new mechanistic pathways for achieving this conversion are highly desirable as breakthroughs in this area will help realise a new way of creating C-C and C-H bonds in one step.

One approach to access novel products from alkynes and Lewis acids is to react alkynes with Lewis acid / Lewis base mixtures that form frustrated Lewis pairs (FLPs).[8] This approach has led to alkyne dehydroelementation (e.g. dehydroboration, scheme 1 top left) and 1,2-*trans*-addition of the FLP components to the alkyne (e.g. scheme 3, top).[9-12] Whilst most FLPs utilise boron based Lewis acids cationic carbon Lewis acids can be effective in FLPs.[13] Of specific relevance to this work is the reaction of alkynes with $[Ph_3C][BF_4]$ in a FLP with $(o\text{-tolyl})_3P$ that resulted in either intramolecular Friedel-Crafts reactivity or 1,2-addition to the alkyne (Scheme 3).[14] In these cases, the absence of a C-H functionality at the electrophilic carbon centre precludes hydrocarbation reactivity. As part of our studies into carbon Lewis acid based FLPs[15] we were interested in determining the reaction outcome(s) from combining the carbon Lewis acid *N*-methyl-acridinium ([**1**]$^+$) with alkynes with and without additional Lewis bases. This has led to the discovery of a new FLP mediated route to achieve the 1,2-hydrocarbation of alkynes. This is distinct to the mechanisms reported by Mayr et al. and those established in alkyne hydroboration chemistry.



Scheme 3. 1,2-addition *vs.* 1,2-hydrocarbation using carbon Lewis acids.

For alkyne 1,2-hydrocarbation via an analogous stepwise route to that reported by Mayr and co-workers to be feasible the cation formed post the 1,3-hydride shift (the hydrocarbation product, [**2**]$^+$) has to be more stable than the vinyl cation initially formed from the interaction of the carbon Lewis acid and the

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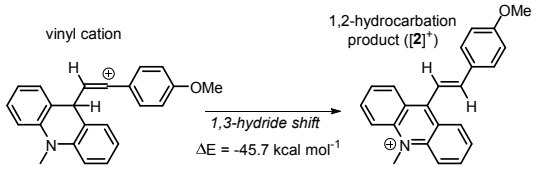
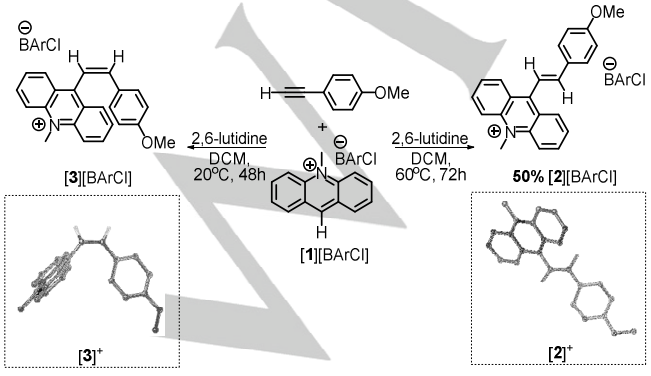
alkyne. Calculations at the M06-2X-6-311G(d,p) level (with PCM (DCM)) confirmed that this was indeed the case for the combination of the *N*-Me-acridinium cation ([**1**]$^+$) with 4-ethynylanisole with the 1,2-hydrocarbation product, [**2**]$^+$, being energetically favoured over the vinyl cation (Scheme 4).



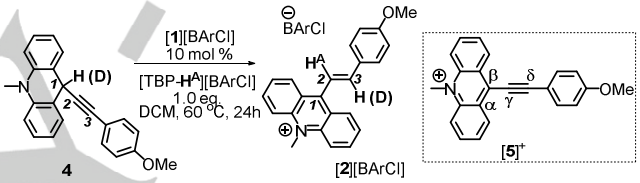
Scheme 4. Energy difference between the vinyl cation (from reaction of [**1**]$^+$ with 4-ethynyl anisole) and the 1,2-hydrocarbation product [**2**]$^+$.

However, the combination of [**1**][BArCl] ([BArCl] = [B(3,5-Cl_2-C_6H_3)$_4$]$^-$ this anion was chosen as it was an effective counterion in previous FLP chemistry using [**1**]$^+$)[15] and 4-ethynylanisole led to no reaction in dichloromethane (DCM) at 20 °C or on heating at 60 °C (in a sealed tube). This is in contrast to the reactivity of benzhydrylium salts and ynamides (which proceeds at 20 °C) and is presumably due to the lower electrophilicity of [**1**]$^+$ (relative to benzhydrylium salts) and the lower nucleophilicity of 4-ethynyl anisole (relative to ynamides) resulting in a larger kinetic barrier which prevents hydride migration in this case despite the favourable thermodynamics.[16] Furthermore, an attempt to achieve *trans*-hydrocarbation using mixtures of [**1**]$^+$ and *N*-Me-acridane (as a hydride source) and 4-ethynylanisole (analogous to pathway **C**, scheme 1) led to complex mixtures with minimal hydrocarbation product observed. In contrast, an equimolar mixture of [**1**][BArCl], 2,6-lutidine (which forms an FLP)[15a] and 4-ethynylanisole resulted in a slow reaction. After 48 hours at 20 °C in DCM only partial consumption of [**1**][BArCl] had occurred; nevertheless, crystallisation (by layering the sample with pentane) and X-ray diffraction studies revealed formation of the *Z*-1,2-hydrocarbation product [**3**][BArCl] (Scheme 5). Repeating the reaction at higher temperature (60 °C, 72 hours) accelerated the reaction but led to a different product being observed in the ^{1}H NMR spectrum consistent with the trans isomer, [**2**]$^+$ (which has two diagnostic vinylic doublets with a $^3J_{HH}$ of 16 Hz). The formation of the *E*-1,2-hydrocarbation product [**2**][BArCl] was confirmed by NMR and mass spectroscopy and X-ray diffraction studies. It should be noted that: (i) identical outcomes were observed performing reactions in the dark, and (ii) during these reactions *N*-Me-acridane (**1-H**) plus a new acridinium species were observed as intermediates.



Scheme 5. Synthesis of the alkyne 1,2-hydrocarbation products [**2**][BArCl] and [**3**][BArCl]. Inset the solid-state structures of [**2**]$^+$ and [**3**]$^+$.

As no hydrocarbation reaction proceeds in the absence of 2,6-lutidine a concerted mechanism (analogous to *syn*-1,2-hydroboration of alkynes with R_2BH) and a stepwise mechanism (analogous to the 1,2-hydrocarbation of ynamides with benzhydrylium salts) are precluded. The FLP of [**1**]$^+$ / 2,6-lutidine conceivably can react with alkynes by a number of pathways including dehydrocarbation or 1,2-addition. In order to preclude the 1,2-addition pathway a non-nucleophilic Lewis base was utilised instead of 2,6-lutidine. On replacing 2,6-lutidine with the hindered base 2,4,6-tri-tert-butylpyridine (TBP), [**2**][BArCl] was again formed *in situ* as the major product from [**1**][BArCl] / 4-ethynylanisole (after 72 h at 60 °C). The formation of [**2**][BArCl] using TBP indicates that a deprotonation (dehydrocarbation) pathway is most likely as alkyne 1,2-addition products are precluded using this extremely hindered base. The most probable proton source is the Lewis acid activated alkyne (the vinyl cation, Scheme 4, left) which on deprotonation would yield the dehydrocarbation product **4** (Scheme 6) containing a new C-C bond, along with an equivalent of protonated base. Direct deprotonation of the alkyne by these two pyridines is not feasible due to the large difference in pK_a values of the pyridiniums and terminal alkyne (~ 6 and ~25 in water, respectively).



Scheme 6. Synthesis of the 1,2-hydrocarbation product [**2**][BArCl] from **4**.

To determine if **4** is indeed a possible intermediate on the hydrocarbation pathway an equimolar mixture of independently synthesized **4** and [TBP-H][BArCl] was dissolved in DCM, both in the presence and absence of 10 mol % [**1**][BArCl]. The latter variable was explored as the FLP mediated production of [**2**]$^+$/[**3**]$^+$ is slow therefore any intermediates formed during alkyne hydrocarbation (such as **4**) will exist in solution in the presence of [**1**]$^+$. Upon mixing **4,** [TBP-H][BArCl] and 10 mol % [**1**][BArCl] an immediate colour change was noted, with [**1**][BArCl] completely converted to **1-H**, along with ~ 10 mol % formation of a new *N*-methyl-acridinium species, proposed to be [**5**]$^+$ (inset, Scheme 6) which was confirmed by subsequent independent synthesis. Upon heating this reaction at 60 °C, [**2**][BArCl] was detected as the major product. Upon repeating the reaction in the absence of [**1**][BArCl] conversion to [**2**][BArCl] still proceeds although it is notably slower. Therefore, these results are consistent with the 1,2-hydrocarbation reaction proceeding via initial dehydrocarbation of the terminal alkyne by the FLP combination of [**1**]$^+$ / pyridyl base to form **4**. Compound **4** is then converted by reaction with the hydridophilic Lewis acid [**1**]$^+$ ultimately to form [**2**]$^+$. To preclude any hydride transfer processes mediated by Lewis acidic boranes derived from decomposition of [BArCl],[17] a different anion was utilised. An equimolar mixture of **4** and [TBP-H][$AlCl_4$] also led to the formation of the hydrocarbation product [**2**][$AlCl_4$] after heating at 60 °C confirming these conversions are not borane mediated.

With **4** being identified as a viable intermediate on the hydrocarbation pathway we focused our attention on the details of the hydride transfer / protonation steps that convert **4** to [**2**]$^+$.

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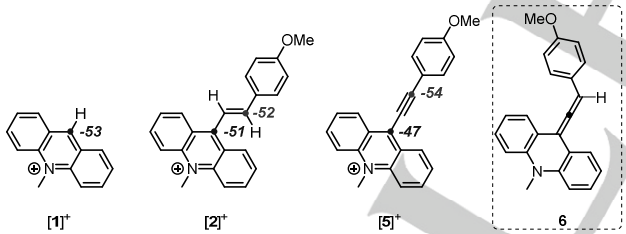
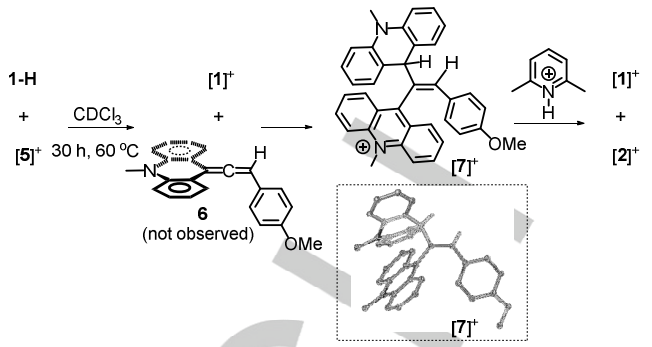
The formation of $[\mathbf{2}]^+$ could proceed from **4** by concerted protonation / 1,2-hydride transfer (analogous to pathway **B**, scheme 1). However, when the migrating hydrogen in **4** was replaced with deuterium (Scheme 6), the deuterium was transferred from position *1* to position *3* precluding a 1,2-hydride transfer mechanism. Furthermore, a related mechanism involving protonation at position *2* and an intramolecular 1,3-hydride shift is disfavoured as this would proceed via the original vinyl cation formed on combination of $[\mathbf{1}]^+$ and the alkyne (Scheme 4, left) and thus would be expected to proceed in the absence of pyridyl base which is not observed. Compound **4** is not observed *in situ* on reacting 4-ethynylanisole with the FLP 2,6-lutidine / $[\mathbf{1}]^+$ indicating it is rapidly consumed, presumably by reaction with $[\mathbf{1}]^+$ as discussed above. This would generate an equivalent of $[\mathbf{5}]^+$ and **1-H**. The chemical structure of $[\mathbf{5}]^+$ contains an α,β,γ,δ-unsaturated system and is a Michael acceptor. Therefore it is feasible that **1-H** will transfer a hydride to the δ position of $[\mathbf{5}]^+$ which would be consistent with the deuterium labelling studies and represent an intermolecular hydride shuttle route to achieve the 1,3-hydride migration. To gain insight into this hypothesis, the hydride ion affinity (HIA) of $[\mathbf{5}]^+$ (relative to Et_3B) was computationally determined (at the M06-2X/6–311G(d,p) level (DCM solvation (PCM)). The HIA of $[\mathbf{5}]^+$ at the β position (-47 kcal mol^{-1}) is lower than that of $[\mathbf{1}]^+$ (-53 kcal mol^{-1}) confirming the intermolecular hydride transfer from **4** to $[\mathbf{1}]^+$ is favoured, consistent with the formation of **1-H** observed during the FLP reaction. More notably, the HIA of $[\mathbf{5}]^+$ at the δ position is higher than that at the β position and higher than that of $[\mathbf{1}]^+$. This indicates that the hydride maybe transferred from **4** to the δ position of **5** (yielding allene tautomer **6**, inset Scheme 7) in a process mediated by $[\mathbf{1}]^+$ (as the direct conversion of **4** to **6** does not proceed). An analogous transformation is reported in the acid catalyzed rearrangement of tertiary propargyl alcohols to allenenols (known as Meyer–Schuster rearrangement).[18] Protonation of **6** would then lead to the observed product, $[\mathbf{2}]^+$.



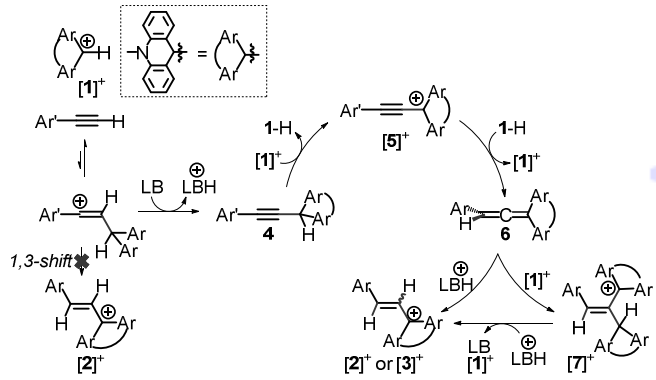
Scheme 7. Hydride ion affinities of $[\mathbf{1}]^+$, $[\mathbf{2}]^+$ and $[\mathbf{5}]^+$, inset compound **6**.

In order to assess experimentally the reactivity of $[\mathbf{5}]^+$ equimolar amounts of $[\mathbf{5}][\mathrm{I}]$ and *N*-methyl-acridane (**1-H**), both independently synthesized, were heated in solution at 60 °C. Interestingly, no formation of the expected product from hydride transfer, **6**, was detected. Instead after 30 hours, the major product observed was the alkene $[\mathbf{7}]^+$ (confirmed crystallographically) presumably formed by reaction between allene **6** and the by-product from hydride transfer $[\mathbf{1}]^+$ (Scheme 8). Characterisation of $[\mathbf{7}]^+$ enabled the minor species observed in the formation of $[\mathbf{2}]^+/[\mathbf{3}]^+$ from the reaction of $[\mathbf{1}]^+$ / 2,6-lutidine / 4-ethynylanisole to be identified as $[\mathbf{7}]^+$. This supports the intermediacy of allene **6** in the FLP reaction to form $[\mathbf{2}]^+/[\mathbf{3}]^+$ and also indicates that protonation of **6** is favoured over its alkylation. The latter was confirmed by the fact that adding one equivalent of [2,6-lutidinium][$AlCl_4$] to $[\mathbf{7}][\mathrm{I}]$ led to the hydrocarbation product $[\mathbf{2}]^+$ and $[\mathbf{1}]^+$. The conversion of $[\mathbf{7}]^+$ to $[\mathbf{2}]^+$ also suggests reversibility of the C-C bond formation involving allene **6** and $[\mathbf{1}]^+$.



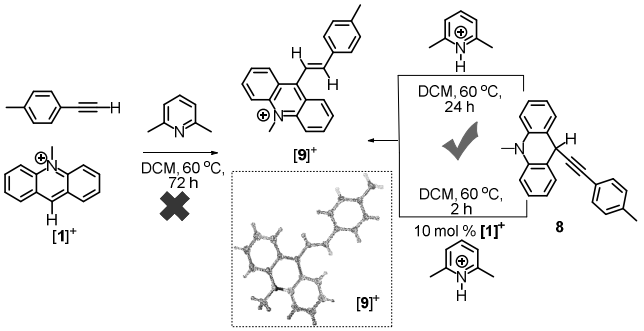
Scheme 8. Synthesis of the 1,2-hydrocarbation product [**7**][BArCl], inset the solid-state structure of $[\mathbf{7}]^+$.

It should be noted that the hydrocarbation product $[\mathbf{2}]^+$ is also a Michael acceptor so could undergo further reduction initiated by hydride transfer from **1-H**. However, this was not observed in any reaction which is potentially due to the fact that $[\mathbf{1}]^+$ has a higher HIA than $[\mathbf{3}]^+$ (HIA = -51 kcal mol^{-1} in the β and -52 kcal mol^{-1} in the δ–position). The lower electrophilicity in the δ–position of $[\mathbf{2}]^+$ relative to that in $[\mathbf{5}]^+$ is attributed to the reduced conjugation between the γ,δ-system and the acridinyl moiety (in the solid state structure of $[\mathbf{2}]^+$ the torsion angle Cα,Cβ,Cγ,Cδ = 46.0° whereas it will be 0° in $[\mathbf{5}]^+$). Combined, the data indicate that this 1,2-hydrocarbation reaction is the result of an initial FLP-type process: Lewis acid activation of the alkyne / deprotonation (dehydrocarbation) to form **4**, followed by stepwise intermolecular hydride transfer / protonation steps to yield the final products $[\mathbf{2}]^+$ or $[\mathbf{3}]^+$ with $[\mathbf{1}]^+$ acting as an exogenous Lewis acid to facilitate hydride shuttling (Scheme 9). The computationally optimized structure of allene **6** reveals that the least hindered face of the allene would lead, on protonation, to the *Z*-isomer $[\mathbf{3}]^+$, which is consistent with this being the kinetic product observed at 20°C. We hypothesize that due to greater unfavourable steric interactions of the substituents in the *Z*-isomer $[\mathbf{3}]^+$, heating is sufficient to form predominately the thermodynamic *E*-isomer $[\mathbf{2}]^+$ (possibly by reversible protonation/deprotonation of $[\mathbf{3}]^+$. Similar reactivity has been observed for the protonation of allenolates, with the *Z*-isomer being the kinetic product and the *E*-isomer the thermodynamic one.[19]



Scheme 9. Proposed mechanism for the formation of the 1,2-hydrocarbation products $[\mathbf{2}]^+/[\mathbf{3}]^+/[\mathbf{7}]^+$.

The rate determining step of the overall reaction appears to be the dehydrocarbation of the alkyne with the Lewis acid / Lewis base FLP. This was supported by the fact that on replacing 4-ethynylanisole with the less nucleophilic alkyne 4-ethynyltoluene, minimal reactivity was observed with the carbon Lewis acid based FLP combination after 72 h at 60 °C (Scheme 10, left). However, starting with independently synthesized **8**, the hydrocarbation product [**9**]$^+$ was observed as the major product on heating in the presence of the 2,6-lutidinium cation and 10 mol % [**1**]$^+$ to facilitate hydride transfer. Notably, the conversion from **8** to [**9**]$^+$ is significantly quicker when using [**1**]$^+$ as an exogenous hydridophilic Lewis acid to mediate the 1,3-hydride migration than in the absence of [**1**]$^+$ as observed in the formation of [**2**]$^+$ from **4**.



Scheme 10. Synthesis of the 1,2-hydrocarbation product [**9**]$^+$ from **8** and [2,6-lutidinium]. Inset, crystal structure of [**9**][$AlCl_4$] (thermal ellipsoids at 50% probability; [$AlCl_4$]$^-$ is omitted for clarity).

In summary, the first example of alkyne 1,2-hydrocarbation enabled by FLP chemistry has been presented. It is based on extending a well-established FLP reaction involving alkyne activation / deprotonation to carbon Lewis acid based FLPs which in this case results in dehydrocarbation. This is then followed by hydride transfer, which is an intermolecular process enabled by the Lewis acidic component of the FLP acting as a hydride shuttle. Finally, protonation delivers the hydrocarbation product. A series of control experiments has disfavoured a mechanism based on an intramolecular 1,3-hydride migration, thus this work represent a new alkyne 1,2-hydrocarbation mechanism that requires a Lewis base and a free Lewis acid. The ability to circumvent the intramolecular 1,3-hydride migration step in this hydrocarbation mechanism is particularly important as 1,3-hydride migrations are slow (even when highly exothermic) as highlighted by Mayr and co-workers.[6] Therefore, in previous work slow intramolecular 1,3-hydride migration led to the carbocation derived from addition of [R_2CH]$^+$ to an alkyne/olefin reacting with an external nucleophile and not undergoing hydrocarbation.[20] The intermolecular hydride shuttle mechanism disclosed herein offers the potential to circumvent the intramolecular 1,3-hydride migration step and make hydrocarbations more general.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: 1,2-hydrocarbation • Frustrated Lewis Pairs • hydride transfer • alkynes • carbocations

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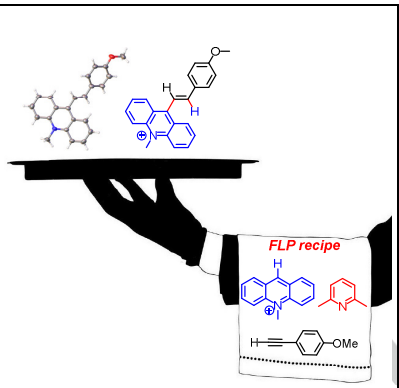
COMMUNICATION

1,2-hydrocarbation? Yes, please! : Frustrated Lewis pair (FLP) chemistry has been employed to achieve a rare example of alkyne 1,2-hydrocarbation. The reaction proceeds via a novel mechanism involving FLP mediated alkyne dehydrocarbation, followed by hydride transfer enabled by an intermolecular hydride shuttle, and finally protonation.



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Frustrated Lewis Pair mediated 1,2-hydrocarbation of alkynes