Journal of Fluorine Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

A closer look at the reactivity between *N*-heterocyclic carbenes and fluoroalkenes

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A B S T R A C T

The fundamental reactivity leading to *N*-heterocyclic fluoroalkene adducts is explored in detail, featuring a total of 15 *N*-heterocyclic carbenes (NHCs) with various electronic and steric environments. The activity of these carbenes towards tetrafluoroethylene (TFE), hexafluoropropene (HFP), trifluoroethylene (HTFE) and vinylidene fluoride (VDF) is assessed in THF and toluene. Attempts were made to correlate the observed reactivity with electronic (Tolman Electronic Parameters) and steric (% buried volume) parameters unique to each NHC, but a trend has yet to be fully determined. However, the unique steric constraints of a cyclic (alkyl)(amino)carbene (CAAC) were shown to modify the initial point of nucleophilic attack on HTFE, providing selective transformation to a different adduct than has been observed to date with all reactions involving this fluoroalkene.

1. Introduction

The incredible diversity of isolable carbenes available to researchers has contributed to these molecules becoming mainstays of transition metal catalysis as ancillary ligands and in main-group chemistry as potent stabilizers for low-valent species [1,2]. More recently, *N*-heterocyclic carbenes (NHCs) and thiazol-2-ylidenes have also been featured prominently as organocatalysts, with most examples of such reactivity proceeding via the Breslow intermediate and involving a formal umpolung of the carbon in the initially electrophilic substrate [3–5].

Since the pioneering work of Bertrand et al. [6] and the seminal isolation of the first persistent carbene by Arduengo et al. in 1991 [7], there has been a significant push towards the synthesis of an ever-increasing amount of derivatives and analogues, many of which exhibit marked differences in reactivity from one another. The design of such molecules was greatly aided when it became apparent that the stability of free carbenes was not necessarily governed by sterics, but rather by important σ and π electronic effects, as evidenced by the stability of **IMe$_4$** (1,3,4,5-tetramethylimidazol-2-ylidene) [8]. The field is largely dominated by *N*-heterocyclic carbenes, with the possibility of a saturated or unsaturated two-carbon backbone for systems based on imidazoline or imidazole fragments, respectively. The nitrogen atoms in these types of carbenes can possess both aryl or alkyl substituents, and the backbone can also be functionalized. Furthermore, six- and seven-membered expanded ring NHCs are known to be more basic than their five-membered analogues, with the seven-membered species featuring a very twisted ring, which can lead to desirable orientation of the *N*-substituents upon coordination [9,10]. A unique class of carbenes termed cyclic (alkyl)(amino)carbenes (CAACs), introduced by Bertrand et al., has been shown to possess unique steric environments and electronic parameters [11–13].

As powerful nucleophiles, it is somewhat surprising that the reactivity between NHCs and electrophilic alkenes remains relatively unexplored. Arduengo and coworkers reported on the reactivity of cyanocarbons with imidazole-2-ylidene carbenes, which includes the very electrophilic tetracyanoethylene (TCNE) [14]. Following up on this study, they chose to focus on the reactivity between imidazolin-2-ylidenes and fluoroalkenes [15]. Closely following the publication of this manuscript, we published our own report examining the formation of NHC fluoroalkene adducts [16]. More recently, we have demonstrated that NHCs can promote facile C—F bond activation from NHC fluoroalkene adducts and polyfluoroalkenyl imidazolium salts to form a variety of C—E (E = C, N, O, S) and C-M bonds (M = Mn, Mo) [17]. Recently, several reports have emerged demonstrating the ability of NHCs and CAACs to affect C—F bond activation in various aryl fluorides, further demonstrating the affinity of these systems towards these types of activations [18–24]. Due to the difficulties associated with the formation and manipulation of C—F bonds, the selectivity and ease of activation observed in these systems is somewhat surprising, and herein we aim to gain a better understanding of the fundamental reactivity between various carbenes and fluoroalkenes.

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http://dx.doi.org/10.1016/j.jfluchem.2017.05.012
Received 27 April 2017; Received in revised form 24 May 2017; Accepted 26 May 2017

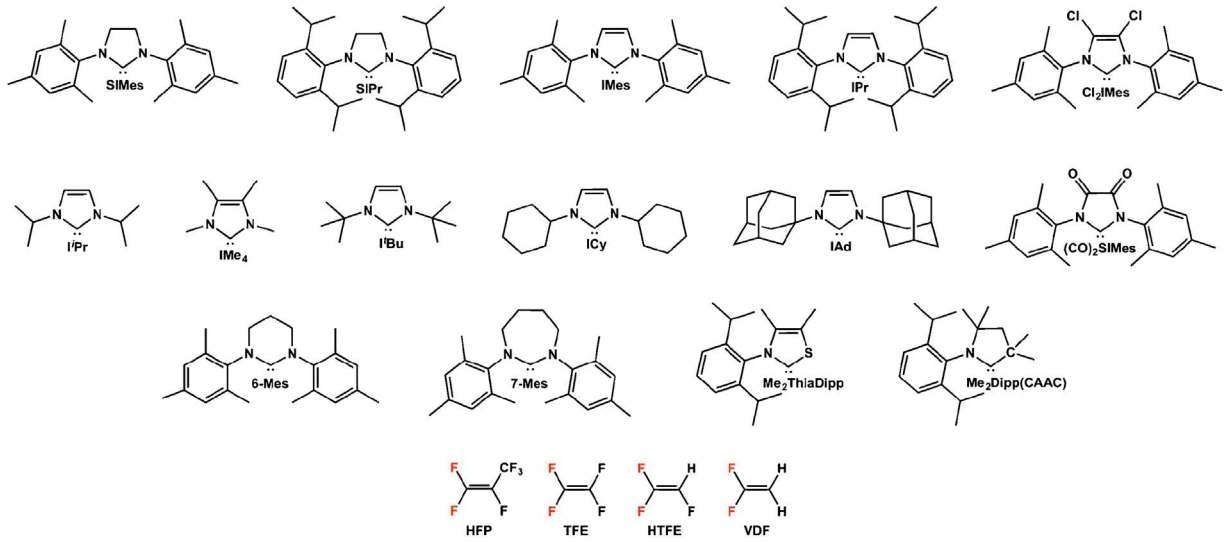


Fig. 1. Various NHCs (top) and fluoroalkenes (bottom) studied in this work. Terminal $=CF_2$ fragments on fluoroalkenes are highlighted in red, indicating principal point of nucleophilic attack by the carbene. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Results and discussion

To probe the limitations and requirements of the reactivity between NHCs and fluoroalkenes, a total of 15 relatively common NHCs (Fig. 1) were explored. Their reactivity with tetrafluoroethylene (TFE), hexafluoropropene (HFP), trifluoroethylene (HTFE) and vinylidene fluoride (VDF) was examined. Owing to the element's large electronegativity, the presence of more fluorine substituents on an alkene might appear to render it more electrophilic, but the π-donor abilities of fluorine must also be considered as a factor that mitigates electrophilicity in these systems. Consequently, the reactivity observed in this work must take both effects into account.

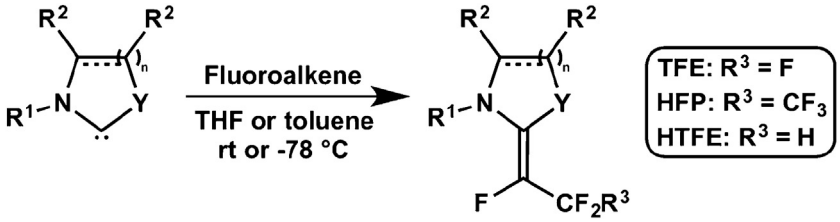
We have previously demonstrated the importance of a sufficiently electron deficient sp^2 carbon center for reactivity with an NHC to occur [16]. Specifically, it was found that *cis*-1,2-difluoroethylene offered no reactivity whatsoever, while seemingly every other fluoroalkene with a terminal $=CF_2$ fragment reacts in some way. The proposed mechanistic pathway for this reaction involves initial attack of the carbene at the $=CF_2$ position of the fluoroalkene, leading to a transient zwitterionic intermediate [15,16]. Expulsion of a fluoride then leads to a polyfluoroalkenyl imidazolium fluoride species, which will rearrange via formal 1,2-F shift to form the observed NHC fluoroalkene adduct. Our previous isolation and characterization of the proposed imidazolium fluoride salt lends support for this pathway.

The general reaction studied in this work is presented in Scheme 1, and the products shown are those expected from the different fluoroalkenes based on previous work. Due to the extreme reactivity observed between most carbenes and fluoroalkenes in this work, every reaction was performed a minimum of two times, in both polar THF and non-polar toluene. When many different products were observed, the reactions were repeated at −78 °C.

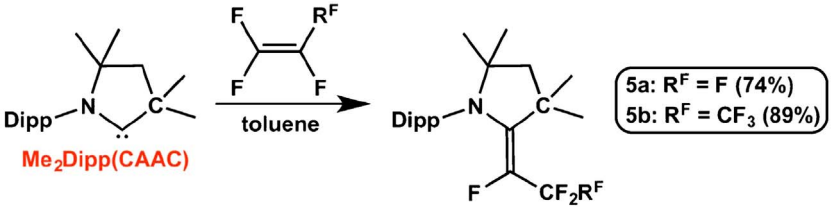
2.1. Reactivity with N,N'-diaryl NHCs

As we have previously reported [16], both **SIMes** and **SIPr** react cleanly with TFE, HFP and HTFE in THF at room temperature within seconds to afford NHC fluoroalkene adducts, including the **SIMes** adduct with TFE also reported by Arduengo et al. [15]. The reaction of **IPr** with TFE in C_6D_6 was reported by Ogoshi et al. in the Supporting information of their work as a by-product to their reactions [25]. In our hands, **IPr** was shown to react unfavourably with HFP and HTFE, providing a multitude of unidentified products, even at −78 °C. Additionally, less sterically demanding **IMes** was found to require low temperatures to afford a clean adduct with TFE, and did not provide identifiable products with HFP. When a solution of **IMes** in THF was exposed to HTFE at room temperature, several unidentified products were observed and separation proved difficult. However, when the reaction was performed in toluene or C_6D_6 and HTFE was allowed to slowly diffuse into the solution a colour change to pale yellow was observed, along with clean formation of **1** (IMes = $CF(CF_2H)$). Monitoring the reaction by ^{19}F NMR revealed that the reaction is over within less than 2 min, but the product is not stable for more than 10 min in solution, decomposing to a mixture of dark brown, almost black products. Attempts to isolate **1** promptly led to decomposition.

Substitution of the backbone hydrogen atoms with electron withdrawing chlorine atoms lowers the basicity of **IMes** by an appreciable degree [26]. Indeed, **Cl_2IMes** forms **2a** (Cl_2IMes = $CF(CF_3)$) cleanly with TFE without the need for low temperature reaction conditions. Product **2a** can be isolated in very good yield (83%) as a bright yellow crystalline solid. Unfortunately, HFP still proved too reactive at room temperature; however, the expected adduct could be observed via ^{19}F NMR if the reaction was performed at −78 °C. Unfortunately, this product was one of several and was thus not fully characterized. The reactivity between **Cl_2IMes** and HTFE to give **2b** (Cl_2IMes = $CF(CF_2H)$) is analogous with **IMes**. The formation of **2b** is noticeably slower, however the stability of the product is only marginally increased. In this



Scheme 1. General reaction scheme for the transformation studied in this work.



Scheme 2. Synthetic scheme for 5a and 5b.

case, the reaction is shown to be complete within 5 min, and **2b** is stable in solution for approximately 15 min, upon which decomposition to dark orange products is observed.

Due to the positive effect of backbone substitution with chloride, we chose to examine **(CO)$_2$SIMes**. This carbene requires deprotonation at low temperatures and immediate *in situ* reactivity due to its thermally accessible triplet state, which leads it to readily dimerize [27]. Unfortunately, generation of the free carbene and injection of fluoroalkenes at low temperature did not provide any reactivity. When the solution was slowly warmed up to room temperature, immediate dimerization was observed and only unreacted fluoroalkene was observed by ^{19}F NMR.

2.2. Reactivity with N,N'-dialkyl NHCs

We have previously noted that smaller NHCs, **IMe$_4$** and **I^{i}Pr**, do not react cleanly with the fluoroalkenes in our work [16]. Here, we have tried to isolate clean products by performing reactions at −78 °C but no change in reactivity was observed, prompting us to believe that the adducts formed in these reactions are inherently unstable. Attempts to limit further reactivity between the theoretically formed adducts and excess gas by instead utilizing an excess of NHC led to no change in the product distribution. Conversely, **I^{t}Bu** was reported to not react with our studied fluoroalkenes, even upon heating. Unfortunately, we failed to specify that this only applies to TFE and HTFE. Indeed, **I^{t}Bu** reacts with HFP to form a multitude of products, the ^{19}F NMR spectra of which are difficult to interpret. When reactions with IAd were attempted, analogous reactivity was obtained. A detailed inspection of the ^{19}F NMR spectra obtained using **I^{t}Bu** and **IAd** with HFP reveals that although both reactions are messy, there is very little overlap between the products that are formed with the two NHCs. Analogously, **ICy** failed to provide any clean or identifiable products with the fluoroalkenes studied herein.

2.3. Reactivity with ring-expanded NHCs and a thiazol-2-ylidene

Most NHCs feature five-membered core structures, but examples of ring-expanded structures have been reported [9,10]. Due to our lack of success with alkyl-substituted NHCs, we chose to utilize aryl-substituted carbenes **6-Mes** and **7-Mes**. When **6-Mes** is allowed to react with TFE, clean transformation to **3** (6-Mes = CF(CF$_3$)) is observed within seconds at room temperature, and can be isolated in excellent yield (94%) as a pale beige crystalline solid (Scheme 4). Conversely, the reactivity with HFP was messy and no distinguishable products were observed.

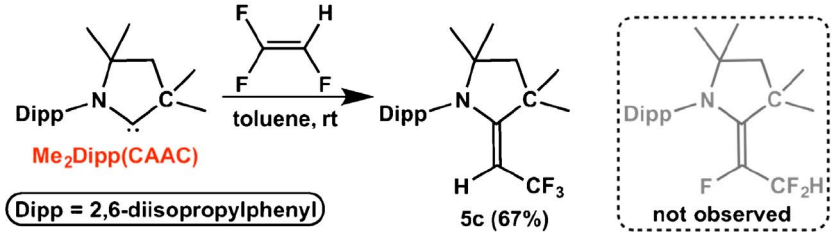
We have previously noted that most of these reactions undergo a vivid, and very short-lived (*ca.* 1–2 s), colour change when exposed to fluoroalkenes [16]. This has been proposed to arise from the transient zwitterion and is especially noticeable with TFE and HFP. However, we have been unable to trap this proposed intermediate despite exploring a large variety of substrates and reaction conditions. When **6-Mes** is exposed to TFE or HFP, an immediate change from colourless to a very bright yellow is observed. Curiously, this colour change persists for approximately 15 s before settling on a paler yellow for TFE and a deep red mixture of decomposition products for HFP. When these reactions are performed at −78 °C, the brightly-coloured intermediate could be observed and maintained for approximately 2 h before eventually giving rise to the light yellow or deep red colors of the final reaction mixtures. Unfortunately, limitations pertaining to the introduction of a fluorinated gas into a cooled NMR tube in an NMR probe has prohibited us from visualizing this proposed zwitterionic intermediate by ^{19}F NMR. Attempts to inject the gas and immediately lower the NMR tube into a pre-cooled probe (−50 °C) also proved unsuccessful. Finally, **6-Mes** did not provide clean reactivity with HTFE. The reactivity observed with **7-Mes** was analogous to that of **6-Mes**, giving rise to **4** (7-Mes = CF(CF$_3$)) in very similar yield (92%).

A thiazol-2-ylidene, which we've termed **Me$_2$ThiaDipp**, failed to provide any adducts with the fluoroalkenes studied in this work. With TFE and HFP, an immediate colour change to deep red was observed, which is indicative of dimerization for this carbene [28]. This was confirmed by ^{1}H NMR and the values matched those reported in the literature. This carbene is known to undergo immediate dimerization in the presence of trace amounts of protic acids, and it is currently unclear what catalyzes this dimerization in the presence of TFE and HFP. No reactivity was observed when HTFE was introduced to **Me$_2$ThiaDipp**.

2.4. Reactivity with CAACs

The unique steric constraints imposed by **Me$_2$Dipp(CAAC)**, wherein the methyl groups on carbon are relatively near the carbene centre and are also in and out of the plane of the heterocyclic fragment, implies these CAACs might react in unique ways with fluoroalkenes. Reactivity with TFE and HFP afforded the expected adducts **5a** ({Me$_2$Dipp(CAAC)} = CF(CF$_3$)) and **5b** ({Me$_2$Dipp(CAAC)} = CF(CF$_2$CF$_3$)), respectively (Scheme 2). The products are formed in high yields and can be isolated as a pale yellow free-flowing solid (**5a**) or a pale pink-red crystalline solid (**5b**). Although **5b** is stable indefinitely at room temperature in the solid state, it is not stable in solution for more than a few hours.

When HTFE was slowly diffused into a solution of **Me$_2$Dipp(CAAC)** in toluene, a color change from nearly colorless to dark red and then a very dark green occurred. Surprisingly, a new isomer was identified (**5c**, **(Me$_2$Dipp(CAAC))** = **CH(CF$_3$)**) and characterized for the first time (Scheme 3). As opposed to the expected =CF(CF$_2$H) isomer that has been observed thus far in successful reactions, the =CH(CF$_3$) isomer is



Scheme 3. Synthetic scheme for 5c.

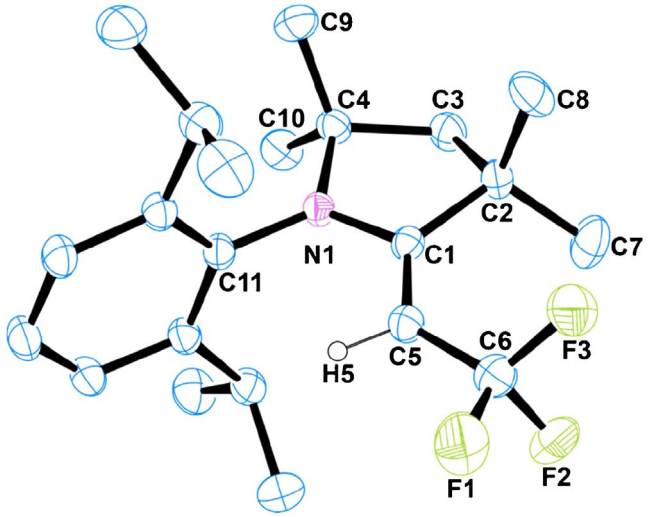


Fig. 2. Crystallographic representation of **5c** with 30% probability thermal ellipsoids. H atoms (except H5) are omitted for clarity. Selected bond lengths and angles are presented in Table S1 in the Supporting information.

obtained in this case. In fact, this is the only isomer present and there is no evidence for the formation of the $=CF(CF_2H)$ product. The products can be distinguished with ease from their ^1H and ^{19}F NMR spectra, due to the different coupling patterns. Thus far, this represents the only isolated example of a fluoroalkene affording a regioisomeric adduct in a clean fashion. The isolation of **5c** proceeds in decent yield (67%) and affords bright green-yellow needles. It is probable that this change in reactivity is encouraged by the unique steric environment present in **Me_2Dipp(CAAC)**, wherein the nucleophilic attack proceeds at the less sterically demanding $=CH(F)$ carbon instead of the bulkier, more electrophilic $=CF_2$ carbon. Following this initial attack, the same rearrangement that forms the other NHC fluoroalkene adducts would lead to **5c**. As TFE is symmetrical it cannot offer a less hindered site of attack, while the reactivity with HFP already proceeds via the less encumbered site.

Single crystals of **5c** were grown by cooling (−35 °C) a concentrated solution in pure hexanes, and the proposed structure was confirmed crystallographically (Fig. 2). The data confirm the orientation of the H and CF_3 substituents with respect to the carbene, wherein H is located closer to the Dipp substituent (Dipp = 2,6-diisopropylphenyl) and CF_3 is oriented towards the side of the two methyl substituents. Analogous to crystallographic data we have previously reported, the Dipp fragment is rotated perpendicular to the plane of the heterocycle. At this time, we do not have any evidence for the formation of the isomer where H and CF_3 would be switched.

2.5. Reactivity summary

A summary of the reactivity observed between NHCs and fluoroalkenes studied in this work is presented in Table 1. Although not discussed until now, VDF has not yet provided any clean or identifiable products. In fact, it leads to decomposition and unstable product mixtures in most cases, except with **I^{t}Bu**, **IAd** and **Me_2ThiaDipp**, where no reactivity was observed. It bears mentioning that the ^{19}F NMR shift of the fluorine atom bound directly to the alkene in TFE adducts is very sensitive to the electronic nature of the NHC. Considering data from the **IPr** adduct by Ogoshi et al. [25] and our own previous reports with **SIPr** and **SIMes** [16], as well as the examples with **Cl_2IMes**, **6-Mes**, **7-Mes** and **Me_2Dipp(CAAC)** reported in this work, this shift was shown to vary between *ca.* $\delta(^{19}F) = -170$ to -218 ppm.

To attempt and correlate the reactivity observed between the various NHCs and fluoroalkenes with certain structural or electronic characteristics, we have chosen to focus on a few key steric and electronic parameters. The Tolman cone angle [29] is still the most common way of evaluating the steric impact of a wide variety of phosphines and phosphites, but this model was shown to be an inefficient metric to evaluate NHCs and related carbenes. Instead, the percent buried volume ($\%V_{bur}$) is commonly employed as a more accurate representation of this effect [30–34]. A recent review by Nolan et al. explores this subject in depth, and offers an extensive collection of values reported to date [35]. Defining the electronic parameters of an NHC is somewhat less straightforward than its steric effects. However, the Tolman electronic parameter (TEP) [29] remains the most widely utilized method to accomplish this, as elaborated upon in another useful review by Nolan et al. [36].

Although the values between different systems do vary slightly for both $\%V_{bur}$ and the TEP, there is sufficient work supporting the general trends observed for these series of values to feel confident in comparing these relative values [35,36]. Finally, it is important to note that TEP values fail to provide any accurate information about the π-acidity of NHCs. For many years, these species were viewed solely as σ-donors, but it is now known that a more accurate depiction of NHC bonding must involve at least some amount of π-backbonding [37–41]. The two primary methods of establishing or quantifying the degree of π-acidity of NHCs involve the formation of carbene-phosphinidene [37,39] and carbene-selenium [38,40] complexes.

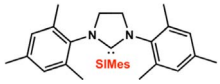
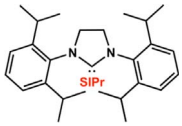
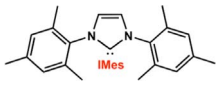
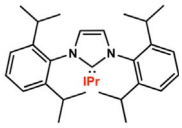
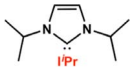
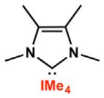
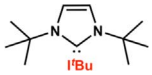
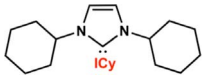
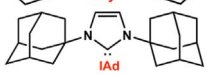
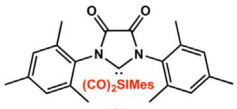
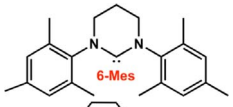
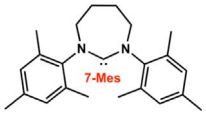
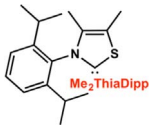
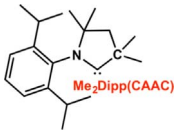
As evidenced in Table 1, **SIPr** and **SIMes** remain the best candidates for reactivity with electrophilic fluoroalkenes. They are the only NHCs thus far that have proven capable of affording clean adducts, at room temperature and in various solvents, with TFE, HFP and HTFE. Generally, HFP has proven to be too reactive, while HTFE appears to often give rise to unstable products that are prone to decomposition. The cleaner reactivity obtained with TFE when utilizing **Cl_2IMes** as opposed to **IMes**, and the complete lack of reactivity observed with **$(CO)_2$SIMes**, does appear to be indicative of a system that is sensitive to the electronic parameters of the NHC. However, the isolation of clean adducts with carbenes that are more nucleophilic than **IMes**, i.e., **Me_2Dipp(CAAC)**, **6-Mes** and **7-Mes**, suggests that there are several other factors at play. To correlate the reactivity presented in this work with key electronic and steric parameters of NHCs, the relative TEP and $\%V_{bur}$ values of these carbenes were plotted and are presented in Fig. S22.

Although it would be appealing to draw sweeping conclusions from these data, it is still unclear if a correlation can be made between the observed reactivity and the NHC parameters presented in this work. In particular, **I^{t}Bu** and **IAd** stand out as exceptions. It is thus somewhat curious that no clean reactivity with these carbenes has been observed yet, with various solvents and reaction conditions. Finally, attempts to incorporate the relative π-acidity of these carbenes when looking at the TEP values to perhaps obtain a more complete picture of the electronic effects of these carbenes have been inconclusive. In fact, **IAd** has been shown to be a significant π-acceptor, along with **I^{t}Bu**. As with the other factors, it appears that the desired NHCs are spread out over the π-acidity scale and it is difficult to draw any significant conclusions from these values. It does appear, however, that a moderate amount of steric bulk is required for the successful formation and isolation of NHC fluoroalkene adducts. Thus far, no adducts have been isolated with carbenes having a $\%V_{bur}$ below *ca.* 32%. However, it is important to note that although a generous cross-section of carbenes have been studied herein, the incredible number and variety of these species having been reported in the literature means that there may be other classes that could provide clean adducts. Indeed, the isolation of **5c** should encourage studies involving the use of carbenes with unique or atypical steric arrangements, perhaps aiming towards the formation of other novel isomers or of more labile systems, perhaps capable of effecting organocatalysis or controlled fluoroalkene polymerization.

3. Conclusions

In summary, a combination of 15 NHCs with various electronic and

Table 1
Summary of the reactivity observed between NHCs and fluoroalkenes, as well as TEP (cm^{-1}) and%V_{bur} values.

NHC	TFE	HFP	HTFE	VDF	TEP (cm^{-1})[a]	%V_{bur}[b]
 SIMes	✓	✓	✓	decomp.	2050.8 [36]	36.9 [35]
 SIPr	✓	✓	✓	decomp.	2051.1 [36]	47.0 [35]
 IMes	✓ (−78 °C)	decomp.	✓ (unstable)	decomp.	2049.6 [36]	36.5 [35]
 IPr	✓	decomp.	decomp.	decomp.	2050.2 [36]	45.4 [35]
 Cl_2IMes	✓	decomp.	✓ (unstable)	decomp.	2054.2 [42]	32.7[d] [43]
 I^{i}Pr	decomp.	decomp.	decomp.	decomp.	2050.3 [36]	27.5 [35]
 IMe_4	decomp.	decomp.	decomp.	decomp.	2051.7[c] [44]	26.2 [35]
 I^{t}Bu	n/r	decomp.	n/r	n/r	2048.9 [36]	39.6 [35]
 ICy	decomp.	decomp.	decomp.	decomp.	2049.5 [36]	27.5 [35]
 IAd	n/r	decomp.	n/r	n/r	2048.3 [36]	39.8 [35]
 $(CO)_2$SIMes	dimerization	dimerization	dimerization	dimerization	2069.0 [36]	34.7 [45]
 6-Mes	✓	decomp.	✓ (unstable)	decomp.	2042.6[d] [36]	42.2 [10]
 7-Mes	✓	decomp.	✓ (unstable)	decomp.	2041.9[d] [36]	42.9 [10]
 Me_2ThiaDipp	dimerization	dimerization	n/r	n/r	2053.6 [36]	32.4[f] [4]
 Me_2Dipp(CAAC)	✓	✓	✓ (alternate isomer)	decomp.	2046.0[e] [46]	38.0[e] [46]

[a] Obtained from $Ir(Cl)(CO)_2$(NHC) complexes.
[b] Obtained (NHC)AuCl complexes.
[c] Obtained from DFT calculations.
[d] Obtained from $Rh(Cl)(CO)_2$(NHC) complexes.
[e] Obtained from $Ni(CO)_3$(NHC) complexes.
[f] Obtained from the corresponding $HClO_4$ salt.

steric environments and 4 fluoroalkenes were studied to obtain a better understanding of their reactivity to form NHC fluoroalkene adducts. To date, a stable adduct with VDF has not been isolated. Reactivity between a cyclic (alkyl)(amino)carbene and HTFE provided an alternate isomer than is typically observed with this fluoroalkene, the first time this switch in reactivity has been demonstrated. Unfortunately, we were unable to discern any clear correlations between electronic (TEP) or steric ($\%V_{bur}$) factors, and carbenes providing positive reactivity. However, the unexpected result obtained by using **Me_2Dipp(CAAC)** is encouraging, and should prompt further studies into carbenes featuring atypical steric demands. By employing flexible steric bulk and varying the initial point of attack of the carbene on a fluoroalkene, it is interesting to envision forming novel adducts that could potentially be involved in exciting umpolung chemistry or polymerization reactions with other fluoroalkenes.

3.1. Experimental section

3.1.1. General considerations

All manipulations were carried out using standard Schlenk techniques or in an MBraun glove box. All glassware was oven-dried at > 150 °C for a minimum of 2 h prior to use, or flame-dried using a torch. Toluene, tetrahydrofuran (THF), diethyl ether (Et_2O) and hexanes were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour®) solvent purification system. Dichloromethane (DCM), chloroform ($CHCl_3$), chloroform-d ($CDCl_3$) and acetonitrile (MeCN) were dried by refluxing over calcium hydride under a nitrogen flow, followed by distillation and filtration through a column of activated alumina (ca. 10 wt.%). Methanol (MeOH) and ethanol (EtOH) were dried by refluxing over Mg/I_2 under nitrogen, followed by distillation. Benzene-d_6 (C_6D_6) was dried by standing over activated alumina (ca. 10 wt.%) overnight, followed by filtration. All solvents were stored over activated (heated at 250 °C for > 6 h under vacuum) 4 Å molecular sieves, except EtOH (stored over activated 3 Å molecular sieves). Acetone (Sigma Aldrich, 99.5 +%) and dimethylsulfoxide (DMSO) (Sigma Aldrich, 99.9 +%) were used as purchased, without further drying. The following chemicals were used as purchased, without further purification: 2,6-diisopropylaniline (Alfa Aesar, 90 +%), 2,4,6-trimethylaniline (Alfa Aesar, 98%), triethyl orthoformate (Alfa Aesar, 98%), glacial acetic acid (Alfa Aesar, 99 +%), *N,N*-diisopropylethylamine (Alfa Aesar, 99%), formic acid (Alfa Aesar, 97%), ethyl acetate (Alfa Aesar, 99 +%), trimethylsilyl chloride (Sigma Aldrich, 99 +%), sodium tetrafluoroborate (Strem Chemicals, 98%), potassium bis(trimethylsilyl)amide (Sigma Aldrich, 95%), carbon tetrachloride (Sigma Aldrich, anhydrous, 99,5 +%), 1,3-diisopropylimidazolium chloride (**I^iPr**) (Strem Chemicals, 97%), 1,3-di-*tert*-butylimidazol-2-ylidene (**I^tBu**) (Strem Chemicals, 98%), 1-hexanol (Sigma Aldrich, 98%), 3-hydroxy-2-butanone (Sigma Aldrich, 98 +%), *N,N*'-dimethylthiourea (Sigma Aldrich, 99%), potassium (Sigma Aldrich, 98%), cyclohexylamine (Alfa Aesar, 98 +%), tetrafluoroboric acid (Strem Chemicals, 48% aqueous solution), oxalyl chloride (Sigma Aldrich, 98%), sodium bis(trimethylsilyl)amide (Sigma Aldrich, 95%), potassium carbonate (Sigma Aldrich, 99 +%), 1,3-dibromopropane (Alfa Aesar, 98%), 1,4-diiodobutane (Alfa Aesar, 99%), sodium hydroxide (Sigma Aldrich, 97 +%), carbon disulfide (Sigma Aldrich, anhydrous, 99 +%), 3-chlorobutan-2-one (Sigma Aldrich, 97%), sodium perchlorate (Sigma Aldrich, 98 +%), isobutyraldehyde (Oakwood Chemicals, 99%), lithium diisopropylamide (Sigma Aldrich, 1.0 M in THF/hexanes), isobutylene oxide (Oakwood Chemicals, 97%), trifluoromethanesulfonic anhydride (Oakwood Chemicals, 98%), sodium hydride (Strem Chemicals, 60% in oil), hexafluoropropene (HFP) (SynQuest Labs, 98.5%), trifluoroethylene (HTFE) (SynQuest Labs, 98%) and 1,1-difluoroethylene (VDF) (SynQuest Labs, 99%). Tetrafluoroethylene (TFE) was made by pyrolysis of polytetrafluoroethylene (PTFE) (Scientific Polymer Products, powdered) under vacuum, using a slightly modified literature procedure [10–20 mTorr, 650 °C, 15 g scale, product stabilized with (*R*)-(+)-limonene (Aldrich, 97%), giving TFE of ≥97% purity] [47]. The synthesis of [SIMes][HCl] [48], [SIPr][HCl] [49], [IMes][HBF_4] [50], [IPr][HBF_4] [50], **Cl_2IMes** [26], **IMe_4** [49], [ICy][HBF_4] [50], [IAd][HBF_4] [51], ($(CO)_2$)SIMes(H)(Cl) [27], [6-Mes][HBF_4] [9], [7-Mes][HBF_4] [9], [Me_2ThiaDipp][$HClO_4$] [28] and [Me_2Dipp(CAAC)][HOTf] [11] have been previously described. Free **SIMes**, **SIPr** and **Me_2ThiaDipp** carbenes were synthesized from the appropriate imidazolium chloride salts by reaction with sodium hydride (2 equiv.) and catalytic potassium *tert*-butoxide (5 mol %) in THF overnight with vigorous stirring. The resulting solution was filtered through Celite with THF washings and the solvent removed *in vacuo* to afford flaky white solid of pure free N-heterocyclic carbene. Following an analogous procedure, but using KHMDS as the base, free **IMes**, **IPr**, **$(CO)_2$SIMes** (at −78 °C), **6-Mes** and **7-Mes** carbenes were prepared from their respective salts. Free **ICy** and **IAd** carbenes were similarly prepared by using KO^{t}Bu as the base. Finally, free **Me_2Dipp(CAAC)** carbene was prepared by deprotonation with LDA at −78 °C. All the carbenes utilized in this work were recrystallized according to their respective literature procedures prior to being screened for reactivity and stored in the freezer at −35 °C. ^{1}H, ^{19}F and ^{19}F{^{1}H} NMR spectra were recorded on either a Bruker Avance 300 or Bruker Avance II 300 spectrometer at room temperature. ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature. ^{1}H NMR spectra were referenced to the residual proton peaks associated with the deuterated solvents (C_6D_6 = 7.16 ppm, $CDCl_3$ = 7.26 ppm). ^{13}C NMR spectra were referenced to the signal associated with $CDCl_3$ (77.16 ppm). It is important to note that ^{13}C NMR signals coupled to ^{19}F nuclei are broadened out significantly, and although coupling constant values and multiplicity can sometimes be extracted it is often impossible to do so. As such, the data is presented to the best of our ability and all efforts are made to avoid any ambiguity in the presentation of the data. ^{19}F and ^{19}F{^{1}H} NMR spectra were referenced to internal 1,3-bis(trifluoromethyl)benzene (BTB) (Aldrich, 99%, deoxygenated by purging with nitrogen and stored over 4 Å molecular sieves), set to −63.5 ppm. ^{1}H NMR data for BTB: (300 MHz, C_6D_6) δ 6.60 (m, 1H, Ar-5-H), 7.12 (m, 2H, Ar-4,6-H), 7.76 (m, 1H, Ar-2-H). A Micromass Q-ToF 1 (positive mode) was used for electrospray ionization (ESI), with samples diluted to *ca.* 5 μg/mL in acetonitrile. A Mel-Temp II was used for the determination of melting points.

3.1.2. Synthesis of IMes = CF(CF$_2$H) (1)

In a glove box, **IMes** (20 mg, 0.07 mmol) was placed in a vial with a stir bar and dissolved in C_6D_6 (~ 0.6 mL). The solution was transferred to a screw-cap septum NMR tube. Outside of the glove box, a 3 mL plastic syringe was filled with HTFE and purged, before an additional 3 mL were added and slowly injected into the NMR tube. The gas was allowed to slowly diffuse through the solution to avoid the formation of unwanted, unidentified products. A color change from nearly colorless to pale yellow could be observed within a few minutes of gas addition. The product is formed quickly and decomposes to a mixture of dark brown, almost black products within *ca.* 10 min if left in solution or if attempts are made to isolate it (see main text for more details). The product was thus not isolated, and characterized to the best of our ability using ^{19}F NMR spectroscopy. ^{19}F NMR (282 MHz, C_6D_6) δ −107.6 (dd, $^2J_{FH} \approx 52$ Hz, $^3J_{FF} \approx 15$ Hz, 1F, IMes = CF(C*F*$_2$H)), −221.1 (dt, $^3J_{FH} \approx 22$ Hz, $^3J_{FF} \approx 16$ Hz, 1F, IMes = C*F*(CF$_2$H)). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6) δ −107.6 (d, $^3J_{FF} \approx 15$ Hz, 1F, IMes = CF(C*F*$_2$H)), −221.1 (t, $^3J_{FF} \approx 16$ Hz, 1F, IMes = C*F*(CF$_2$H)).

3.1.3. Synthesis of Cl$_2$IMes = CF(CF$_3$) (2a)

In a glove box, **Cl_2IMes** (100 mg, 0.27 mmol) was placed in a 50 mL round bottom Schlenk flask with a stir bar and dissolved in THF (~ 4 mL). The flask was sealed with a septum and hooked up to a Schlenk line outside of the glove box. A 10 mL plastic syringe was filled with nitrogen and purged, before being filled with 10 mL of TFE. The gas was quickly injected into the flask, and an additional 5 mL were

added immediately after. Immediately upon addition of TFE, a color change from nearly colorless to bright yellow could be observed. After stirring for 30 min, the septum was replaced with a glass stopper, and all volatiles were removed *in vacuo*, affording an off-white residue. The flask was returned to the glove box, and the product was extracted with hexanes (~ 4 mL) and filtered through Celite® with hexanes washings (2 × 1 mL). The solution was concentrated under reduced pressure until the formation of solid could be observed, and then recrystallized from this cloudy solution at −35 °C. The product was isolated by filtration on a frit and dried under vacuum, affording bright yellow crystalline solid. Yield: 105 mg, 83% based on Cl_2IMes. mp: 162–163 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22 (br s, 12H, Ar-CH_3), 2.32 (s, 6H, Ar-CH_3), 6.94 (br, 4H, Ar-*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 17.86, 21.31, 112.94 (ov s), 118.79 (dq, $^1J_{CF}$ ≈ 48 Hz, $^2J_{CF}$ ≈ 196 Hz, Cl_2IMes = CF(*C*F_3)), 123.90 (dq, $^1J_{CF}$ ≈ 264 Hz, Cl_2IMes = *C*F(CF_3)), 129.06, 129.39, 131.38, 132.33, 137.20, 137.83, 139.20, 139.60, 139.86 (dq, $^2J_{CF}$ ≈ 20 Hz, $^3J_{CF}$ ≈ 2 Hz, Cl_2IMes(*C*) = CF(CF_3)). ^{19}F NMR (282 MHz, $CDCl_3$) δ −60.1 (d, $^3J_{FF}$ ≈ 16 Hz, 3F, Cl_2IMes = CF(CF_3)), −213.1 (q, $^3J_{FF}$ ≈ 16 Hz, 1F, Cl_2IMes = C*F*(CF_3)). MS [ESI (positive mode), solvent: MeCN] Calc. *m/z* (% intensity) for [Cl_2IMes = CF(CF_3) + H^+, $C_{23}H_{23}Cl_2F_4N_2^+$]: 473.12 (100), 475.11 (64), 476.12 (16). Found *m/z* (% intensity): 473.1174 (100), 475.1247 (60), 476.1349 (14).

3.1.4. Synthesis of Cl_2IMes = CF(CF_2H) (2b)

In a glove box, **Cl_2IMes** (20 mg, 0.05 mmol) was placed in a vial with a stir bar and dissolved in C_6D_6 (~ 0.6 mL). The solution was transferred to a screw-cap septum NMR tube. Outside of the glove box, a 3 mL plastic syringe was filled with HTFE and purged, before an additional 3 mL were added and slowly injected into the NMR tube. The gas was allowed to slowly diffuse through the solution to avoid the formation of unwanted, unidentified products. A color change from nearly colorless to pale yellow could be observed within a few minutes of gas addition. The product is formed quickly and decomposes to a mixture of dark orange products within *ca*. 15 min if left in solution or if attempts are made to isolate it (see main text for more details). The product was thus not isolated, and characterized to the best of our ability using ^{19}F NMR spectroscopy. ^{19}F NMR (282 MHz, C_6D_6) δ −111.1 (dd, $^2J_{FH}$ ≈ 52 Hz, $^3J_{FF}$ ≈ 17 Hz, 1F, Cl_2IMes = CF(CF_2H)), −215.8 (dt, $^3J_{FH}$ ≈ 21 Hz, $^3J_{FF}$ ≈ 17 Hz, 1F, Cl_2IMes = C*F*(CF_2H)). ^{19}F {^{1}H} NMR (282 MHz, C_6D_6) δ −111.1 (d, $^3J_{FF}$ ≈ 17 Hz, 1F, Cl_2IMes = CF(CF_2H)), −215.8 (t, $^3J_{FF}$ ≈ 17 Hz, 1F, Cl_2IMes = C*F*(CF_2H)).

3.1.5. Synthesis of 6-Mes = CF(CF_3) (3)

In a glove box, **6-Mes** (100 mg, 0.31 mmol) was placed in a 50 mL round bottom Schlenk flask with a stir bar and dissolved in THF (~4 mL). The flask was sealed with a septum and hooked up to a Schlenk line outside of the glove box. A 10 mL plastic syringe was filled with nitrogen and purged, before being filled with 10 mL of TFE. The gas was quickly injected into the flask, and an additional 5 mL were added immediately after. Immediately upon addition of TFE, a color change from nearly colorless to very bright yellow could be observed, which persisted for a few seconds before settling on yellow-orange. After stirring for 30 min, the septum was replaced with a glass stopper, and all volatiles were removed *in vacuo*, affording an off-white residue. The flask was returned to the glove box, and the product was extracted with THF (~4 mL) and filtered through Celite® with THF washings (2 × 1 mL). The solution was concentrated under reduced pressure until the formation of solid could be observed, and then recrystallized from this cloudy solution at −35 °C. The product was isolated by filtration on a frit and dried under vacuum, affording a pale beige crystalline solid. Yield: 123 mg, 94% based on 6-Mes. mp: 175–177 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 1.41 (ov m, 2H, N−CH_2CH_2CH_2−N), 2.11 (s, 6H, Ar-CH_3), 2.12 (s, 6H, Ar-CH_3), 2.29 (s, 6H, Ar-CH_3), 2.99 (ov m, 4H, N−CH_2CH_2CH_2−N), 6.78 (ov m, 4H, Ar-*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 18.66, 19.26, 20.86, 21.03, 25.28, 47.67, 48.42, 119.55 (dq, $^1J_{FC}$ ≈ 42 Hz, $^2J_{FC}$ ≈ 202 Hz, 6-Mes = CF(*C*F_3)), 123.52 (dq, $^1J_{FC}$ ≈ 263 Hz, $^2J_{FC}$ ≈ 34 Hz, 6-Mes = *C*F(CF_3)), 129.82, 130.02, 133.84, 134.77, 134.80, 134.96, 136.12, 141.78, 141.82, 142.64, 143.62 (dq, $^2J_{CF}$ ≈ 15 Hz, $^3J_{CF}$ ≈ 2 Hz, 6-Mes(*C*) = CF(CF_3)). ^{19}F NMR (282 MHz, C_6D_6) δ −63.4 (d, $^3J_{FF}$ ≈ 16 Hz, 3F, 6-Mes = CF(CF_3)), −198.0 (q, $^3J_{FF}$ ≈ 16 Hz, 1F, 6-Mes = C*F*(CF_3)). MS [ESI (positive mode), solvent: MeCN] Calc. *m/z* (% intensity) for [6-Mes = CF(CF_3) + H^+, $C_{24}H_{29}F_4N_2^+$]: 421.23 (100), 422.23 (26), 423.23 (3). Found *m/z* (% intensity): 421.2201 (100), 422.2305 (26), 423.2442 (3).

3.1.6. Synthesis of 7-Mes = CF(CF_3) (4)

In a glove box, **7-Mes** (100 mg, 0.30 mmol) was placed in a 50 mL round bottom Schlenk flask with a stir bar and dissolved in THF (~ 4 mL). The flask was sealed with a septum and hooked up to a Schlenk line outside of the glove box. A 10 mL plastic syringe was filled with nitrogen and purged, before being filled with 10 mL of TFE. The gas was quickly injected into the flask, and an additional 5 mL were added immediately after. Immediately upon addition of TFE, a color change from nearly colorless to yellow could be observed. After stirring for 30 min, the septum was replaced with a glass stopper, and all volatiles were removed *in vacuo*, affording an off-white residue. The flask was returned to the glove box, and the product was extracted with THF (~ 4 mL) and filtered through Celite® with THF washings (2 × 1 mL). The solution was concentrated under reduced pressure until the formation of solid could be observed, and then recrystallized from this cloudy solution at −35 °C. The product was isolated by filtration on a frit and dried under vacuum, affording a pale beige crystalline solid. Yield: 120 mg, 92% based on 7-Mes. mp: 150–153 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 1.03 (ov m, 4H, N-CH_2CH_2CH_2-N), 2.11 (s, 6H, Ar-CH_3), 2.12 (s, 6H, Ar-CH_3), 2.30 (s, 6H, Ar-CH_3), 3.12-3.66 (ov m, 4H, N-CH_2CH_2CH_2-N), 6.80 (ov m, 4H, Ar-*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 18.42, 19.92, 20.67, 20.75, 20.89, 21.16, 28.58, 28.68 (br), 30.51, 54.03, 55.07, 101.03, 118.83, 121.32 (m), 123.69 (m), 126.44, 129.71 (ov s), 130.38 (ov m), 134.72, 135.20, 142.30, 143.45 (ov s), 143.53, 144.00. ^{19}F NMR (282 MHz, C_6D_6) δ −63.7 (d, $^3J_{FF}$ ≈ 14 Hz, 3F, 7-Mes = CF(CF_3)), −184.4 (q, $^3J_{FF}$ ≈ 14 Hz, 1F, 7-Mes = C*F*(CF_3)). MS [ESI (positive mode), solvent: MeCN] Calc. *m/z* (% intensity) for [7-Mes = CF(CF_3) + H^+, $C_{25}H_{31}F_4N_2^+$]: 435.24 (100), 436.25 (27), 437.25 (3). Found *m/z* (% intensity): 435.2572 (100), 436.2694 (11), 437.2495 (6).

3.1.7. Synthesis of (Me_2Dipp(CAAC)) = CF(CF_3) (5a)

In a glove box, **Me_2Dipp(CAAC)** (100 mg, 0.35 mmol) was placed in a 50 mL round bottom Schlenk flask without a stir bar and dissolved in toluene (~4 mL). The flask was sealed with a septum and hooked up to a Schlenk line outside of the glove box. A 10 mL plastic syringe was filled with nitrogen and purged, before being half-filled with 5 mL of TFE. The gas was slowly injected into the flask, and allowed to slowly diffuse through the solution to avoid the formation of unwanted, unidentified products. This process was repeated twice with 5 mL portions of TFE. Soon after the addition of TFE, a color change from nearly colorless to yellow-green could be observed. Following the final gas addition, and after allowing the gas to diffuse through the solution for 1 h, the septum was replaced with a glass stopper, and all volatiles were removed *in vacuo*, affording a pale yellow residue. The flask was returned to the glove box, and the product was extracted with hexanes (~4 mL) and filtered through Celite® with hexanes washings (2 × 1 mL). The solution was concentrated under reduced pressure until the formation of solid could be observed, and then recrystallized from this cloudy solution at −35 °C. The product was isolated by filtration on a frit and dried under vacuum, affording a pale yellow, free-flowing solid. Yield: 99 mg, 74% based on Me_2Dipp(CAAC). mp: 87–90 °C (decomposition). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, $^3J_{HH}$ ≈ 6.6 Hz, 6H, CH(CH_3)$_2$), 1.17 (s, 6H, C(CH_3)$_2$), 1.28 (d, $^3J_{HH}$ ≈ 6.6 Hz, 6H, CH(CH_3)$_2$), 1.51 (s, 6H, C(CH_3)$_2$), 2.12 (s, 2H, CH_2),

3.13 (sept, $^3J_{HH} \approx 6.6$ Hz, 2H, C*H*(CH_3)$_2$), 7.09-7.29 (ov m, 3H, Ar-*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 23.93, 25.19, 25.22, 28.94, 29.22, 29.80 (br m), 57.80, 65.37, 123.86, 127.83, 148.51 (d, $^2J_{CF} \approx 4$ Hz, Me_2Dipp(CAAC)(*C*) = CF(CF_3)). ^{19}F NMR (282 MHz, $CDCl_3$) δ −60.9 (d, $^3J_{FF} \approx 13$ Hz, 3F, Me_2Dipp(CAAC) = CF(C*F*$_3$)), −170.98 (q, $^3J_{FF} \approx 13$ Hz, 1F, Me_2Dipp(CAAC) = C*F*(CF_3)). MS [ESI (positive mode), solvent: MeCN] Calc. *m/z* (% intensity) for [Me_2Dipp(CAAC) = CF(CF_3) + H^+, $C_{22}H_{32}F_4N^+$]: 386.25 (100), 387.25 (24), 388.25 (3). Found *m/z* (% intensity): 386.2356 (100), 387.2316 (35), 388.2249 (5).

3.1.8. Synthesis of (Me_2Dipp(CAAC)) = CF(CF_2CF_3) (5b)

In a glove box, **Me_2Dipp(CAAC)** (100 mg, 0.35 mmol) was placed in a 50 mL round bottom Schlenk flask without a stir bar and dissolved in toluene (~4 mL). The flask was sealed with a septum and hooked up to a Schlenk line outside of the glove box. A 10 mL plastic syringe was filled with nitrogen and purged, before being half-filled with 5 mL of HFP. The gas was slowly injected into the flask, and allowed to slowly diffuse through the solution to avoid the formation of unwanted, unidentified products. This process was repeated twice with 5 mL portions of HFP. Soon after the addition of HFP, a color change from nearly colorless to pale pink could be observed. Following the final gas addition, and after allowing the gas to diffuse through the solution for 1 h, the septum was replaced with a glass stopper, and all volatiles were removed *in vacuo*, affording a pale pink, almost white residue. The flask was returned to the glove box, and the product was extracted with hexanes (~ 4 mL) and filtered through Celite® with hexanes washings (2 × 1 mL). The solution was concentrated under reduced pressure until the formation of solid could be observed, and then recrystallized from this cloudy solution at −35 °C. The product was isolated by filtration on a frit and dried under vacuum, affording a pale pink-red crystalline solid. The product is stable in the solid state, but decomposes in solution over several hours, and we were thus unable to characterize it cleanly by $^{13}C\{^1H\}$ NMR. Yield: 135 mg, 89% based on Me_2Dipp (CAAC). mp: 82–83 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 1.10 (d, $^3J_{HH} \approx 6.7$ Hz, 6H, CH(CH_3)$_2$), 1.17 (s, 6H, C(CH_3)$_2$), 1.29 (d, $^3J_{HH} \approx 6.7$ Hz, 6H, CH(CH_3)$_2$), 1.52 (s, 6H, C(CH_3)$_2$), 2.12 (s, 2H, CH_2), 3.12 (sept, $^3J_{HH} \approx 6.7$ Hz, 2H, C*H*(CH_3)$_2$), 7.07-7.30 (ov m, 3H, Ar-*H*). ^{19}F NMR (282 MHz, $CDCl_3$) δ −83.0 (dt, $^3J_{FF} \approx 3$ Hz, $^4J_{FF} \approx 13$ Hz, 3F, Me_2Dipp(CAAC) = CF(CF_2C*F*$_3$)), −108.6 (dq, $^3J_{FF} \approx 13$ Hz, $^3J_{FF} \approx 18$ Hz, 2F, Me_2Dipp(CAAC) = CF(C*F*$_2$CF$_3$)), −171.8 (tq, $^3J_{FF} \approx 18$ Hz, $^4J_{FF} \approx 13$ Hz, 1F, Me_2Dipp(CAAC) = C*F*(CF_2CF_3)). MS [ESI (positive mode), solvent: MeCN] Calc. *m/z* (% intensity) for [Me_2Dipp(CAAC) = CF(CF_2CF_3) + H^+, $C_{23}H_{32}F_6N^+$]: 436.24 (100), 437.25 (25), 438.25 (3). Found *m/z* (% intensity): 436.2459 (100), 437.2626 (33), 438.2620 (6).

3.1.9. Synthesis of (Me_2Dipp(CAAC)) = CH(CF_3) (5c)

In a glove box, **Me_2Dipp(CAAC)** (100 mg, 0.35 mmol) was placed in a 50 mL round bottom Schlenk flask without a stir bar and dissolved in toluene (~4 mL). The flask was sealed with a septum and hooked up to a Schlenk line outside of the glove box. A 10 mL plastic syringe was filled with nitrogen and purged, before being half-filled with 5 mL of HTFE. The gas was slowly injected into the flask, and allowed to slowly diffuse through the solution to avoid the formation of unwanted, unidentified products. This process was repeated twice with 5 mL portions of HTFE. Soon after the addition of TFE, a color change from nearly colorless to dark red could be observed, which eventually turned into a very dark green. Following the final gas addition, and after allowing the gas to diffuse through the solution for 1 h, the septum was replaced with a glass stopper, and all volatiles were removed *in vacuo*, affording a dark red-green residue. The flask was returned to the glove box, and the product was extracted with hexanes (~ 12 mL) and filtered through Celite® with hexanes washings (2 × 3 mL), leaving behind the dark red-green residue and affording a bright green-yellow solution. The solution was concentrated under reduced pressure until the formation of solid could be observed, and then recrystallized from this cloudy solution at −35 °C. The product was isolated by filtration on a frit and dried under vacuum, affording bright green-yellow needles. Yield: 86 mg, 67% based on Me_2Dipp(CAAC). mp: 92–93 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (d, $^3J_{HH} \approx 6.7$ Hz, 6H, CH(CH_3)$_2$), 1.22 (s, 6H, C(CH_3)$_2$), 1.28 (d, $^3J_{HH} \approx 6.7$ Hz, 6H, CH(CH_3)$_2$), 1.55 (m, 6H, C(CH_3)$_2$), 2.10 (s, 2H, CH_2), 2.99 (sept, $^3J_{HH} \approx 6.7$ Hz, 2H, C*H*(CH_3)$_2$), 3.44 (q, $^3J_{HF} \approx 10$ Hz, 1H, Me_2Dipp(CAAC) = C*H*(CF_3)), 7.22-7.40 (ov m, 3H, Ar-*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 23.74, 26.33, 28.67, 29.47 (br m), 42.39, 56.39, 64.36, 79.36 (q, $^3J_{CF} \approx 38$ Hz, Me_2Dipp(CAAC) = CH(C*F*$_3$)), 124.99, 128.76, 132.58, 149.48, 165.53 (q, $^3J_{CF} \approx 5$ Hz, Me_2Dipp (CAAC)(*C*) = CH(CF_3)). ^{19}F NMR (282 MHz, C_6D_6) δ −46.9 (d, $^3J_{FH} \approx 10$ Hz, 3F, Me_2Dipp(CAAC) = CH(C*F*$_3$)). $^{19}F\{^1H\}$ NMR (282 MHz, C_6D_6) δ −46.9 (s, 3F, Me_2Dipp(CAAC) = CH(C*F*$_3$)).MSCH (C*F*$_3$))·MS [ESI (positive mode), solvent: MeCN] Calc. *m/z* (% intensity) for [Me_2Dipp(CAAC) = CH(CF_3) + H^+, $C_{22}H_{33}F_3N^+$]: 368.26 (100), 369.26 (24), 370.26 (3). Found *m/z* (% intensity): 368.2135 (100), 369.2284 (27), 370.2165 (5).

Acknowledgements

We thank the NSERC for generous financial support and the University of Ottawa, Canada Foundation for Innovation and Ontario Ministry of Economic Development and Innovation for essential infrastructure. M.C.L. gratefully acknowledges support from the NSERC.

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