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A Strongly Ambiphilic Ferrocene-Based Cyclic (Alkyl)(amino)carbene – Specific Decomposition to an Enamine by a 1,2-Phenyl Shift

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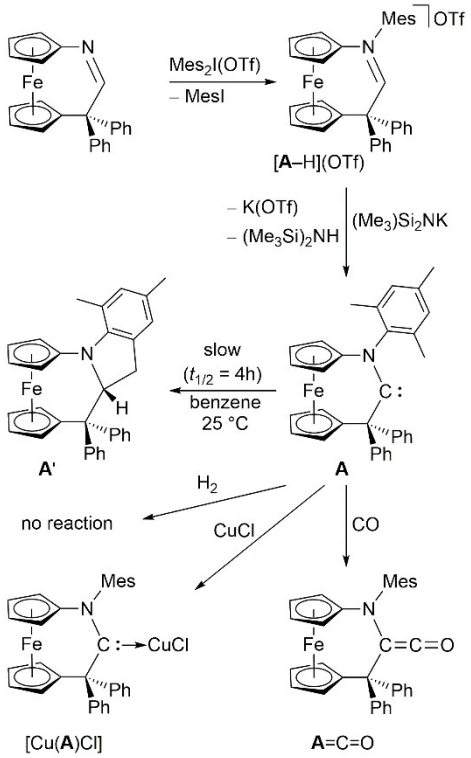
The recently described crystalline cyclic (alkyl)(amino)carbene with a 1,1′-ferrocenylene (fc) backbone fc(CPh_2–C–NMes) (**A**, Mes = mesityl) is highly reactive due to its particularly pronounced ambiphilicity and is thermally not stable in solution due to an intramolecular insertion of the divalent carbon atom into a methyl C–H bond of the Mes substituent. The closely related congener fc(CPh_2–C–N-*p*-C_6H_4-*t*Bu) (**1**) cannot undergo such an insertion reaction. Nevertheless, **1** is too short-lived for isolation due to a rapid 1,2-shift of a phenyl group, furnishing the isomeric cyclic enamine fc[C(Ph)=C(Ph)–N-*p*-C_6H_4-*t*Bu] (**1′**) in a specific decomposition process unprecedented for CAACs. Trapping of **1** was possible with carbon monoxide, elemental selenium and with [$CuBr(SMe_2)$], respectively affording the aminoketene **1**=C=O, the selenoamide **1**=Se and the homoleptic Cu^I complex [$Cu(\mathbf{1})_2$][$CuBr_2$]. **1** is an even stronger ambiphile than **A** according to NMR spectroscopic data. Similar to **A**, **1** does not react with H_2, because the experimentally observed intramolecular process is kinetically more favourable according to DFT results.

Introduction

N-heterocyclic carbenes (NHCs) are nucleophilic singlet carbenes, which are widely used in synthesis and catalysis.[1,2] Their divalent carbon atom is stabilised by the π-donor/σ-acceptor character of the two amino substituents. We have developed thermally stable N-heterocyclic carbenes with a 1,1′-ferrocenylene (fc) backbone (fcNHCs).[3] In contrast to conventional NHCs, these fcNHCs react readily with fundamentally important small molecules like CO and NH_3 under ambient conditions.[3c,4] The unusual reactivity of fcNHCs can be traced back to the large carbene bond angle caused by the fc backbone, leading to a pronounced ambiphilicity similar to that of cyclic (alkyl)(amino)carbenes (CAACs).[4,5] CAACs are strong ambiphiles because their $C_{carbene}$ atom is stabilised by only a single amino substituent.[6,7] We recently established cyclic (alkyl)(amino)carbenes with a 1,1′-ferrocenylene backbone (fcCAACs) as an original family by the preparation of the crystalline congener **A** (Scheme 1), whose carbene bond angle of 121.5(5)° is unprecedentedly wide for a CAAC, causing an exceptionally pronounced σ-donor strength in combination with an electrophilicity higher than that of any previously



Scheme 1. Synthesis and selected reactions of fcCAAC **A**.

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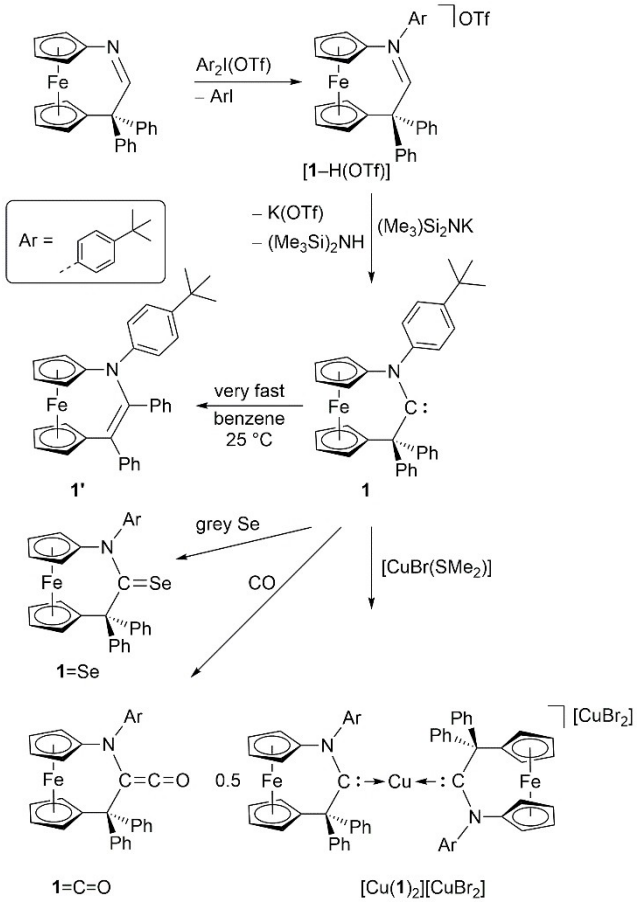
reported CAAC.[8] Not surprisingly, therefore, **A** is highly reactive and undergoes a carbonylation with CO even below room temperature, affording the stable aminoketene **A**=C=O. However, no reaction could be observed with H_2, because the intramolecular insertion of the divalent carbon atom into a methyl C–H bond is kinetically preferred, affording isomer **A'**. This prompted us to address homologues with *N*-aryl substituents not prone to undergo such C(sp^3)–H insertions, thus enabling H_2 addition. The aryl groups C_6F_5 and C_6H_3-3,5-$(CF_3)_2$ appeared particularly attractive for this purpose, since DFT results indicated that the respective fcCAAC will add H_2 under mild conditions, while barriers for potentially competing intramolecular insertions are prohibitively high.

Results and Discussion

The immediate precursor of **A** is the iminium salt [**A**–H](OTf), which is accessible by reaction of the [3]ferrocenophane-type cyclic imine fc(CPh_2CH=N) with the diaryliodonium compound Mes_2I(OTf).[8] Diaryliodonium salts are versatile electrophilic aryl sources.[9] Due to their popularity, synthetic protocols are available for the preparation of a broad variety of these reagents, including $(F_5C_6)_2I$(OTf)[10] and $[(F_3C)_2$-2,5-$C_6H_3]_2I[BF_4]$.[11] The seemingly simple protocol published by Naumann for the preparation of $(F_5C_6)_2I$(OTf) from $[F_3CC(O)O]_3I$ and F_5C_6H did not work in our hands.[10] We found, however, that $(F_5C_6)_2I$(OTf) may be conveniently prepared from F_5C_6I and $F_5C_6B(OH)_2$ following the protocol published by Han for the synthesis of (2,5-F_2-$H_3C_6)_2I$(OTf),[12] which is based on a seminal paper by Olofsson, describing the one-pot synthesis of diaryliodonium salts from aryl iodides and arylboronic acids.[13] Unfortunately, we have not been able to prepare the desired aryl-substituted iminium salts from fc(CPh_2CH=N) and $(F_5C_6)_2I$(OTf) or $[(F_3C)_2$-2,5-$C_6H_3]_2I[BF_4]$, despite many attempts. ^{1}H NMR spectroscopic monitoring of the reaction with $[(F_3C)_2$-2,5-$C_6H_3]_2I[BF_4]$ gave no indication for the formation of fc[CPh_2CH=NC_6H_3-3,5-$(CF_3)_2$] and the BF_3 adduct of the cyclic imine was identified as main product (see Section B of the Supporting Information and Figures S19–S21 for details; note that the corresponding iodonium triflate is not known). In the case of $(F_5C_6)_2I$(OTf) the results were compatible with initial formation of the target compound, followed, however, by its decomposition in C_6D_6 (see Figure S22 in the Supporting Information), affording intractable material.

We therefore turned our attention to less electron-poor aryl groups. Preliminary experiments were performed with Ph_2I(OTf) in order to introduce C_6H_5 as the simplest aryl substituent. However, these experiments were soon abandoned because fc(CPh_2CH=NPh)(OTf) could not be isolated in pure form due to unfavourable solubility behaviour. In contrast to the previously described *N*-mesityl congener [**A**–H](OTf), which could be purified by an extraction/precipitation sequence,[8] this iminium salt showed a solubility very similar to that of the impurities or side products, which prevented efficient purification. Gratifyingly, such purification problems were not encountered with the *p*-*t*Bu-C_6H_4 *N*-substituent thanks to the beneficial influence of the *tert*-butyl group. The reaction of fc(CPh_2CH=N) with (*p*-*t*Bu-$C_6H_4)_2I$(OTf) proceeded smoothly and swiftly at room temperature (Scheme 2) and the resulting iminium salt precipitated from the reaction solution. Pure fc(CPh_2CH=N-*p*-C_6H_4-*t*Bu)(OTf) ([**1**–H](OTf)) was obtained as dark purple crystals in 54% yield after recrystallization from a mixture of THF and diethyl ether.

The iminium proton of [**1**–H](OTf) gives rise to a diagnostic low-field signal at $\delta = 9.52$ ppm in CD_2Cl_2, close to the value of 9.76 ppm found for [**A**–H](OTf).[8] Likewise, the chemical shifts of the ^{13}C NMR signal due to the carbon atom of the iminium unit are similar for both compounds, viz. 187.1 and 195.4 ppm for [**1**–H](OTf) and [**A**–H](OTf), respectively. The $^1J_{CH}$ coupling constant determined for the iminium unit of [**1**–H](OTf) is 179 Hz, which is slightly lower than the value of 181 Hz obtained for [**A**–H](OTf).[8] Such $^1J_{CH}$ coupling constants of protonated carbenes are useful for estimating the σ-donor strength of carbenes.[14] The $^1J_{CH}$ coupling constant correlates with the amount of s-character of the carbon orbital involved in the C–H bond.[15] In turn, the σ-donor strength of carbenes correlates inversely with the $^1J_{CH}$ coupling constant, because a small coupling constant originates from a high p-character, and consequently high energy and directionality, of the carbon orbital which is involved in the C–H bond and contains the lone pair of electrons at the divalent carbon atom in the free carbene. Protonated standard NHCs exhibit $^1J_{CH}$ values



Scheme 2. Synthesis and chemical behaviour of fcCAAC **1**.

> 200 Hz.[16] For comparison, a value of 183 Hz has been reported for $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{CH}[\mathrm{PF}_6]$, whose deprotonation affords the iconic "Alder carbene".[17] Such acyclic diaminocarbenes have a nucleophilicity significantly higher than that of standard five-membered CAACs,[18] for which $^1J_{CH}$ values of ca. 190 Hz have been published.[8,19] The $^1J_{CH}$ value of 179 Hz determined for [**1**–H](OTf) indicates an exceptionally high σ-donor strength of fcCAAC **1**. [**1**–H](OTf) was structurally characterised by single-crystal X-ray diffraction (XRD). The molecular structure is shown in Figure 1.

The metric parameters of [**1**–H](OTf) are generally quite similar to those of [**A**–H](OTf). However, the comparatively large steric demand of the mesityl *N*-substituent present in the latter compound causes an almost perpendicular orientation of the *N*-aryl ring plane with respect to the iminium C1–N1–C8 plane with a dihedral angle of 77.8°, whereas the corresponding value of [**1**–H](OTf) is only 49.7°. The bulky mesityl group is also responsible for the rather acute Ph–C2–Ph angle of 107.5(2)° in [**A**–H](OTf) vs. 113.25(16)° in [**1**–H](OTf).

With the iminium salt [**1**–H](OTf) in hand, we next addressed the synthesis of the new fcCAAC **1**. In analogy to our previous work with [**A**–H](OTf),[8] deprotonation of the cation of [**1**–H](OTf) was performed with $(\mathrm{Me}_3\mathrm{Si})_2\mathrm{NK}$ in benzene. An immediate colour change from purple to orange was observed, indicating an instantaneous reaction. The product turned out to be not the target fcCAAC **1**, but its isomer **1′**, which was formed in at least 90% yield according to ^{1}H NMR spectroscopic analysis. **1′** plausibly forms from **1** by a 1,2-shift of a phenyl group, which is reminiscent of the Fritsch-Buttenberg-Wiechell (FBT) rearrangement of alkylidene carbenes or carbenoids to alkynes, where phenyl groups are known to exhibit a particularly high migratory aptitude.[20,21] This mechanistic scenario is strongly supported by DFT results (vide infra). Such a process is unprecedented for CAACs and closely related carbenes.[22] We note in this context that, although not directly observed so far, several five-membered CAACs containing phenyl groups at C_α are known.[23] **1′** was structurally characterised by XRD (Figure 2).

The N atom of **1′** is in an essentially trigonal-planar bonding environment (sum of bond angles 358.3°). The nitrogen bond lengths (1.42–1.43 Å) are indistinguishable within experimental error and typical of single bonds to C(sp^2) atoms. The C1–C2 distance of 1.36 Å is slightly elongated in comparison to standard alkenes,[24] compatible with a significant involvement of the amino group in π-conjugation with the alkene moiety, as is typical of enamines.[25]

While fcCAAC **A**, although unstable due to the slow intramolecular C(sp^3)–H insertion observed in solution, can be isolated in crystalline form, fcCAAC **1** is too short-lived for isolation due to rapid rearrangement to **1′**. However, indirect proof for the generation of **1** from [**1**–H](OTf) and $(\mathrm{Me}_3\mathrm{Si})_2\mathrm{NK}$ in solution is provided by trapping reactions, which were successfully performed with carbon monoxide, elemental selenium, and with [CuBr(SMe$_2$)], respectively affording **1**=C=O, **1**=Se and [Cu(**1**)$_2$][CuBr$_2$] (Scheme 2). The aminoketene **1**=C=O was obtained in 77% yield, when **1** was generated in situ at ca. −80 °C in toluene under an atmospheric pressure of CO. The other two trapping products were easily obtained from **1** generated at room temperature, albeit in moderate yields of ca. 45%. Attempts to trap **1** with H_2, which were performed in a way analogous to the trapping experiment with CO, furnished the rearrangement product **1′**. No indication for the formation of the H_2 addition product fc(CPh$_2$–CH$_2$–N-*p*-C$_6$H$_4$-*t*Bu) (**1**H$_2$) was obtained. **A** reacts smoothly with CuCl or [AuCl(THT)] (THT = tetrahydrothiophene) to afford [MCl(**A**)] (M = Cu, Au).[8] However, attempts to trap **1** with these reagents failed, leading only to the formation of **1′** or a gold mirror.

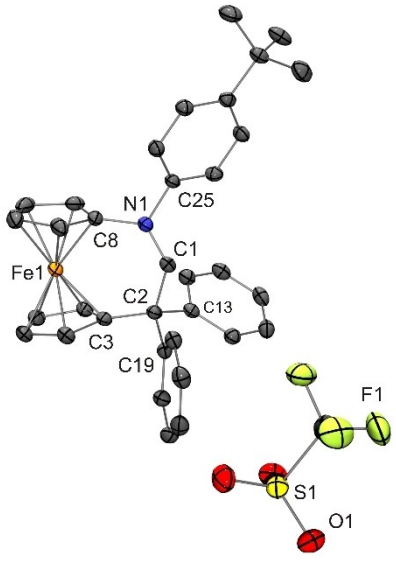


Figure 1. Molecular structure of [**1**–H](OTf) in the crystal (ORTEP with 30% probability ellipsoids, H atoms not shown). Selected bond lengths [Å] and angles [°]: N1–C1 1.292(3), N1–C8 1.444(3), N1–C25 1.453(2), C1–C2 1.513(3), C2–C3 1.525(3), C2–C13 1.555(3), C2–C19 1.529(3); C1–N1–C8 125.30(17), C1–N1–C25 118.36(17), C8–N1–C25 116.32(16), N1–C1–C2 131.70(18), C13–C2–C19 113.25(16).

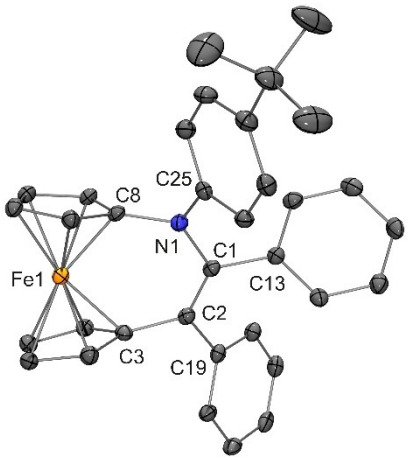


Figure 2. Molecular structure of **1′** in the crystal (ORTEP with 30% probability ellipsoids, H atoms not shown). Selected bond lengths [Å] and angles [°]: N1–C1 1.418(4), N1–C8 1.428(4), N1–C25 1.434(4), C1–C2 1.360(5), C1–C13 1.493(5), C2–C3 1.481(5), C2–C19 1.490(5); C1–N1–C8 123.4(3), C1–N1–C25 121.8(3), C8–N1–C25 113.1(3), N1–C1–C2 124.7(3).

The aminoketene **1**=C=O could not be structurally characterised by XRD, because all attempts to obtain single crystals unfortunately remained unsuccessful. However, the identity of this compound is clearly demonstrated by diagnostic spectroscopic features, which compare well with those published for the structurally characterised congener **A**=C=O.[8] The IR spectrum of **1**=C=O exhibits a characteristic ketene band at 2075 cm^{-1}, close to the value of 2084 cm^{-1} found for **A**=C=O. The ketene moiety of **1**=C=O gives rise to ^{13}C NMR signals at 211.9 (C=*C*=O) and 81.9 ppm (*C*=C=O), similar to the chemical shifts of 220.7 and 77.8 ppm observed for the corresponding signals of **A**=C=O. The ^{1}H NMR spectrum of **1**=C=O exhibits very broad aryl and cyclopentadienyl signals at room temperature. In the same vein, the ^{13}C NMR spectrum hardly shows signals due to aryl and cyclopentadienyl CH units. A variable-temperature ^{1}H NMR study revealed that line broadening becomes less and less severe upon increasing the temperature, suggesting a dynamic process with a coalescence temperature close to room temperature. The ^{1}H NMR spectrum recorded at 70 °C shows four well-resolved aryl signals (integrating for 4 + 4 + 4 + 2 protons) and four still slightly broadened cyclopentadienyl signals (each integrating for 2 protons), compatible with a time-averaged C_s symmetric structure.

1=Se was used to judge the electrophilicity of fcCAAC **1** by ^{77}Se NMR spectroscopy. This convenient method was established by Ganter and subsequently extended by Nolan, who confirmed that ^{77}Se NMR shifts of carbene–selenium adducts are suitable for quantifying the π-accepting capability of the parent carbenes.[26] The ^{77}Se NMR signal of **1**=Se is located at $\delta = 1082$ ppm in acetone-d_6, downfield-shifted in comparison to **A**=Se (1039 ppm) and thus indicative of an electrophilicity of **1** even higher than that of **A**. **1**=Se was structurally characterised by XRD (Figure 3). The bond lengths and angles are very similar to those of **A**=Se.

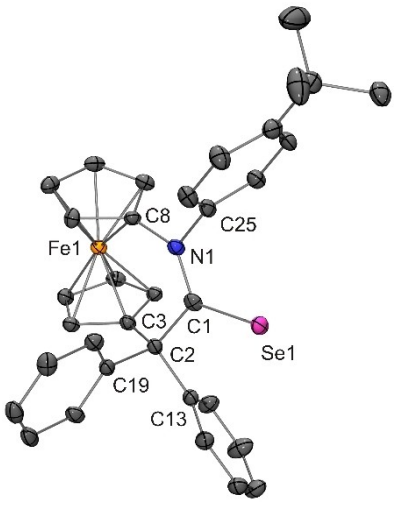


Figure 3. Molecular structure of **1**=Se in the crystal (ORTEP with 30% probability ellipsoids, H atoms not shown). Selected bond lengths [Å] and angles [°]: Se1–C1 1.816(3), N1–C1 1.356(4), N1–C8 1.436(3), N1–C25 1.450(4), C1–C2 1.572(4). C2–C3 1.528(4), C2–C13 1.552(4), C2–C19 1.557(4); C1–N1–C8 128.8(2), C1–N1–C25 120.1(2), C8–N1–C25 111.0(2), Se1–C1–N1 118.0(2), Se1–C1–C2 120.0(2), N1–C1–C2 121.6(3), C13–C2–C19 108.4(2).

The isolation of the homoleptic complex $[Cu(\mathbf{1})_2][CuBr_2]$ from the reaction of fcCAAC **1** with $[CuBr(SMe_2)]$ is interesting in view of the fact that the heteroleptic complex [Cu(**A**)Cl] had been obtained in an analogous reaction of the bulkier fcCAAC **A**, whose steric demand plausibly prevents the formation of $[Cu(\mathbf{A})_2]^+$. The different coordination behaviour of fcCAACs **A** and **1** is reminiscent of that of two recently described bicyclic (alkyl)(amino)carbenes (BICAACs) of different steric demand.[27] The reaction of the sterically less demanding $BICAAC^{Me}$ (Me at C_α) with $[CuBr(SMe_2)]$ afforded a homoleptic complex $[Cu(BICAAC^{Me})_2][CuBr_2]$, whereas the heteroleptic complex $[CuBr(BICAAC^{iPr})]$ was selectively obtained with the sterically more demanding $BICAAC^{iPr}$ (*i*Pr at C_α). In the same vein, formation of the homoleptic species $[Cu(CAAC)_2][CuCl_2]$ from the corresponding heteroleptic complex [CuCl(CAAC)] containing a standard five-membered CAAC of comparatively low steric demand has been observed in polar solvents.[28,29] $[Cu(\mathbf{1})_2][CuBr_2]$ was structurally characterised by XRD (Figure 4).

The result of the XRD study was compromised by the poor quality of the crystal. Atom connectivities have been established unequivocally. However, a discussion of metric parameters is not meaningful, except for the heavy atoms. The cation and the anion both contain Cu^{I} in an essentially linear dicoordinate environment. The copper bond lengths and angles are very similar to those published for $[Cu(BICAAC^{Me})_2][CuBr_2]$, whose linear-dicoordinate Cu^{I} atoms exhibit average Cu–Br and Cu–C bond lengths of 2.23 and 1.92 Å, respectively.[27] The heteroleptic complex $[CuBr(BICAAC^{iPr})]$ has a slightly shorter Cu–C bond length of 1.90 Å,[27] in line with observations made for analogous complexes of conventional five-membered CAACs.[29,30] The cation of $[Cu(\mathbf{1})_2][CuBr_2]$ exhibits a twist angle of 67° of the two "carbene planes" defined by the respective $N–C_{carbene}–C_\alpha$ units. This is unusual, because structurally characterised compounds of the type $[Cu(CAAC)_2]X$ invariably contain a centrosymmetric cation with a twist angle of 0°.[30,31] This is also the case for $[Cu(BICAAC^{Me})_2][CuBr_2]$.[27] Essentially the same holds true for analogous Ag^{I} and Au^{I} complexes.[32,33]

To rationalise the different reactivity observed for **1** and **A** we have performed quantum-chemical calculations on the full

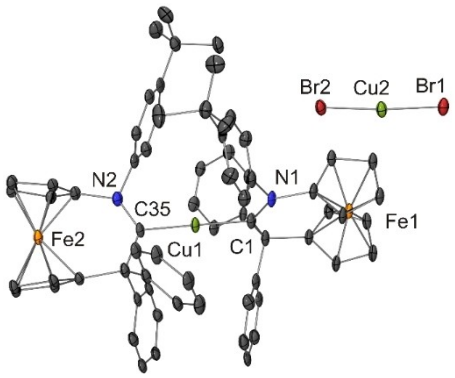


Figure 4. Molecular structure $[Cu(\mathbf{1})_2][CuBr_2]$·toluene in the crystal (ORTEP with 30% probability ellipsoids, H atoms and solvent molecule not shown). Selected bond lengths [Å] and angles [°]: Br1–Cu2 2.229(3), Br2–Cu2 2.226(3), Cu1–C1 1.974(16), Cu1–C35 1.920(15); C1–Cu1–C35 179.1(8), Br1–Cu2–Br2 175.78(16).

molecular systems (see Schemes S3 and S4 in the Supporting Information). The aryl migration in **1** has a lower kinetic barrier ($\Delta^{\ddagger}G^{298} = 20$ kcal mol^{-1}) than the activation of H_2 ($\Delta^{\ddagger}G^{298} = 23$ kcal mol^{-1}), which is consistent with the absence of any H_2 activation product in the experiments. The same migration in **A**, however, has a free energy barrier of 27 kcal mol^{-1}, while the mesityl C(sp^3)–H bond insertion has a barrier of 25 kcal mol^{-1}, which is also consistent with experiment.

Figure 5 schematically shows molecular orbitals involving the carbene environment (see Scheme S2 in the Supporting Information). In **A** we find the three orbitals characteristic for CAACs, i.e. bonding and antibonding π-orbitals of the C–N fragment as well as the carbene lone pair. In contrast to **A**, the optimised geometry of **1** features a coplanar orientation of the *N*-aryl substituent with the C–C–N plane (see Scheme S1 in the Supporting Information). This enables two additional orbital contributions arising from the bonding and antibonding combination of the π(C–N) and π*(C–N) orbitals with suitable orbitals of the aromatic π-system (only the C_{ipso} atomic p-orbital contributions are sketched in Figure 5). Quantification of the orbital interactions by perturbative analysis of donor/acceptor interactions between natural bond orbitals shows only moderately strong donation of the nitrogen lone pair into two σ*(C–C) orbitals (see Scheme S10 in the Supporting Information). With the coplanar *N*-aryl arrangement in **1**, much stronger donation into the aryl π-system is observed. This goes hand in hand with an increased double-bond character of the N–C_{ipso} bond in **1**, which is in line with a higher ellipticity obtained from QTAIM analysis (see Scheme S11 in the Supporting Information). With the nitrogen lone pair in **1** significantly engaged in interactions with the *N*-aryl substituent, the LP(N) to p($C_{carbene}$) donation is weakened. This interaction is replaced by an increased π-donation from the adjacent σ(C–C_{Ph}) bond. This specific interaction, which is substantially weaker in **A**, thus promotes the phenyl migration. This is further highlighted by a localised intrinsic bond orbital (IBO) analysis performed along the intrinsic reaction coordinate (IRC) path connecting **TS1** with the reactant **1** and the phenyl-shifted product **1′**. As shown in Figure 5, the carbene lone pair does not change significantly until after the transition state, where it transforms into the $C_{carbene}$–C_{Ph} σ-bond. The initial C–C_{Ph} σ-bond, however, transforms very early into a 2e3c-bond type orbital by interaction with the carbene p-orbital and results in the final C=C π-orbital.

Conclusions

The recently reported *N*-mesityl substituted fcCAAC **A** is highly reactive due to its particularly pronounced ambiphilicity. **A** can be isolated in crystalline form, but is not thermally stable in solution due to an intramolecular insertion of the divalent carbon atom into a methyl C–H bond. Its homologue **1**, which contains the sterically less demanding *p*-C_6H_4-*t*Bu *N*-substituent, is an even stronger ambiphile according to NMR spectroscopic data. It cannot undergo the C(sp^3)–H insertion reaction found for **A**. Nevertheless, **1** is too short-lived for isolation due to a

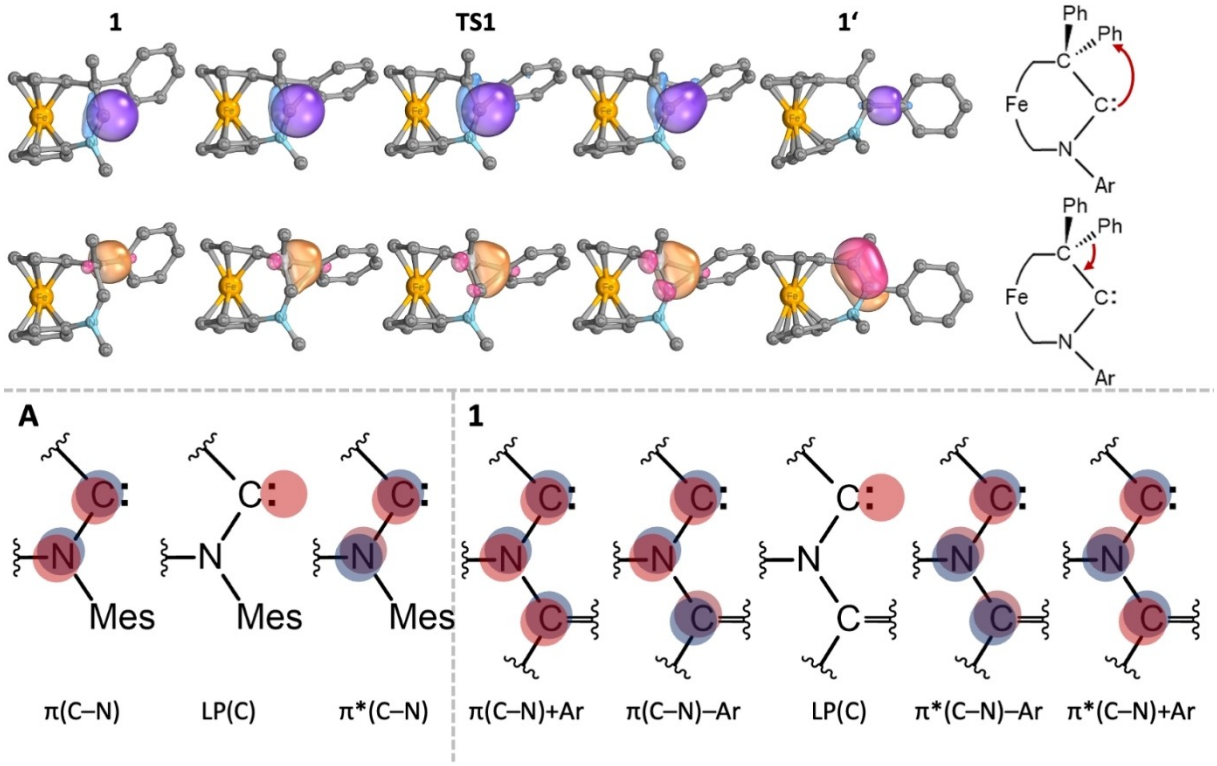


Figure 5. Top: IBOs representing the change of the carbene lone pair and C–C σ-bond along the IRC path of the phenyl migration in **1** with schematic Lewis structures (hydrogen atoms and unreactive aryl substituents omitted); bottom: schematic representation of the frontier molecular orbitals of **A** and **1** (top view).

rapid 1,2-migration of a phenyl group, affording the cyclic enamine **1′** in a process unprecedented for CAACs and reminiscent of the Fritsch-Buttenberg-Wiechell (FBT) rearrangement of alkylidene carbenes or carbenoids. The migratory aptitude of phenyl groups in the FBT rearrangement is known to be particularly high. Homologues which contain alkyl instead of phenyl groups at C_α are expected to be much more resistant towards such rearrangements. At the same time, alkyl groups at C_α have to be conformationally restricted to prevent C(sp^3)–H insertion reactions with the $C_{carbene}$ atom. The phenyl groups present in **A** and **1** originate from benzophenone, which is reacted with 1-bromo-1′-lithioferrocene at the beginning of the multi-step sequence leading to the cyclic imine fc(CPh_2CH=N).[8] Preliminary experiments indicate that the conformationally restricted dialkylketones adamantanone and fenchone are suitable for our purposes. Note that fenchone is commercially available in enantiomerically pure form. We envisage that this will open the door to the synthesis of enantiopure chiral fcCAACs. Our findings will be reported in due course.

Experimental Section

General Considerations

All reactions involving air-sensitive compounds were performed in an inert atmosphere (argon or dinitrogen) by using standard Schlenk techniques or a conventional glovebox. Starting materials were procured from standard commercial sources and used as received. The cyclic imine fc(CPh_2CH=N) and the iodonium reagent (p-tBu-C_6H_4)$_2$I(OTf) were prepared by adapted versions of the published procedures.[8,34] The synthesis and crystal structure of (F_5C_6)$_2$I(OTf) are described in the Supporting Information as a sideline of our investigation (vide supra). NMR spectra were recorded at ambient temperature with Varian NMRS-500 and MR-400 spectrometers operating at 500 and 400 MHz, respectively, for ^{1}H. The ^{77}Se NMR spectrum was recorded with a Varian NRMS-500 spectrometer with neat dimethylselenide as external standard ($\delta = 4$ ppm).[35] Elemental analyses were carried out with a HEKAtech Euro EA-CHNS elemental analyser at the Institute of Chemistry.

Synthesis of [1–H](OTf)

Toluene (10 mL) was added to fc(CPh_2CH=N) (125 mg, 0.33 mmol), (p-tBu-C_6H_4)$_2$I(OTf) (200 mg, 0.37 mmol) and CuCl (0.4 mg, 4 μmol). The mixture was stirred for 2 h, during which time a colour change from yellow to dark brown was observed. The solid was separated by decanting the supernatant off after centrifugation (2000 rpm, 10 min) and was subsequently washed with toluene (3×5 mL). Recrystallization from a mixture of THF (6 mL) and diethyl ether (4 mL) afforded the product as dark purple crystals. Yield 117 mg (54%). $C_{35}H_{32}NSF_3FeO_3$ (659.54): calcd. C 63.74, H 4.89, N 2.12, S 4.86%; found C 63.97, H 4.87, N 2.17, S 4.59%. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 9.52$ (s, 1 H, N=CH), 7.61–7.46 (m, 10 H, Ph), 7.38 (m, 4 H, C_6H_4), 5.05, 4.53, 4.49, 4.39 (4 m, 4×2 H, cyclopentadienyl), 1.33 ppm (s, 9 H, CMe_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): $\delta = 187.1$ (N=CH), 156.9, 142.3, 138.8 (3×aryl C_{ipso}), 130.3, 129.9, 129.6, 128.1, 123.0 (5×aryl CH), 100.9, 86.5 (2×cyclopentadienyl C_{ipso}), 74.4, 74.1, 72.2, 69.3 (4×cyclopentadienyl CH), 61.8 (Ph_2C), 35.6 (CMe_3), 31.3 ppm (CMe_3); CF_3 not detected. ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -78.9$ ppm.

Synthesis of 1′: C_6D_6 (1 mL) was added to [**1**–H](OTf) (40 mg, 0.06 mmol) and (Me_3Si)$_2$NK (12 mg, 0.06 mmol) in a 5 mm NMR tube. The tube was briefly shaken, leading to a colour change from purple to orange. Crystals suitable for XRD were obtained by slow evaporation of the solvent after removing insoluble material by filtration. Yield ≥90% (NMR). $C_{34}H_{31}NFe$ (509.46): calcd. C 80.16, H 6.13, N 2.75%; found C 79.73, H 5.83, N 2.72%. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.32$ (m, 2 H, Ar), 7.17 (m, 2 H, Ar), 7.06 (m, 4 H, Ar), 6.97 (m, 2 H, Ar), 6.86 (m, 1 H, Ar), 6.79 (m, 2 H, Ar), 6.69 (m, 1 H, Ar), 4.58, 4.54, 4.07, 3.95 (4 m, 4×2 H, cyclopentadienyl), 1.07 ppm (s, 9 H, CMe_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): $\delta = 147.6$ (Ar C_{ipso}), 145.5 (C=CN), 145.1, 144.6, 139.6 (3×Ar C_{ipso}), 131.7, 130.5, 128.0, 127.9, 127.4, 125.7, 125.6, 123.9 (8×Ar CH), 116.6 (*C*=CN), 109.8, 87.2 (2×cyclopentadienyl C_{ipso}), 70.8, 68.8, 68.1, 65.5 (4×cyclopentadienyl CH), 34.1 (CMe_3), 31.4 ppm (CMe_3).

Synthesis of 1=Se: Benzene (1.5 mL) was added to [**1**–H](OTf) (30 mg, 0.05 mmol), (Me_3Si)$_2$NK (10 mg, 0.05 mmol) and grey selenium (7 mg, 0.09 mmol). The mixture was stirred for 5 min. Insoluble material was removed by filtration through a short pad of Celite. Volatile components were removed from the orange filtrate under vacuum. The residue was purified by column chromatography (silica gel; 1. Et_2O, 2. Et_2O–EtOAc 1:1), which afforded the product as red crystals. Yield 11 mg (43%). $C_{34}H_{31}NFeSe$ (558.42): calcd. C 69.40, H 5.31, N 2.38%; found C 69.13, H 5.84, N 1.89%. ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 7.59$ (m, 4 H, Ar), 7.46, 7.39 (2 m, 2×2 H, Ar), 7.35–7.22 (m, 6 H, Ar), 4.46, 4.39, 4.34, 4.10 (4 m, 4×2 H, cyclopentadienyl), 1.30 ppm (s, 9 H, CMe_3). ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6): $\delta = 223.4$ (C=Se), 151.7, 150.8, 148.1 (3×aryl C_{ipso}), 132.5, 127.6, 127.5 (3×aryl CH), 127.40 (2 very closely spaced signals, aryl CH), 103.0, 90.9 (2×cyclopentadienyl C_{ipso}), 73.0, 72.9 (2×cyclopentadienyl CH), 71.5 (Ph_2C), 70.4, 67.6 (2×cyclopentadienyl CH), 35.3 (CMe_3), 31.7 ppm (CMe_3). ^{77}Se (95 MHz, acetone-d_6): $\delta =$ 1082 ppm.

Synthesis of 1=C=O: A 100 mL pressure Schlenk tube containing [**1**–H](OTf) (50 mg, 0.08 mmol) and (Me_3Si)$_2$NK (15 mg, 0.08 mmol) was cooled with liquid nitrogen. Toluene (5 mL) was added dropwise via syringe in a manner that it froze on the glass wall before getting in contact with the solid reactants. The atmosphere was removed under vacuum. The sealed vessel was placed in a cooling bath kept at −80 °C and was immediately filled with CO (1 atm). The stirred mixture was allowed to warm up to ambient temperature over the course of 3 h. Stirring was continued for 1 h. Volatile components were removed under vacuum. The orange residue was extracted with toluene (2×3 mL). Insoluble material was removed from the combined extracts by filtration. The filtrate was reduced to dryness under vacuum, affording a bright yellow powdery solid, which was washed with *n*-hexane (0.5 mL) and dried under vacuum. Yield 31 mg (77%). $C_{35}H_{31}NFeO$ (537.47): calcd. C 78.21, H 5.81, N 2.61%; found C 76.95, H 6.36, N 2.74%. ^{1}H NMR (400 MHz, C_6D_6, 70 °C): $\delta = 7.62$, 7.23, 6.98 (3 m, 3×4 H, aryl CH), 6.92 (m, 2 H, aryl CH), 4.19, 4.11, 4.02, 3.88 (4 br., 4×2 H, cyclopentadienyl CH), 1.22 ppm (s, 9 H, CMe_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): $\delta = 211.9$ (C=C=O), 145.6, 142.0, 129.9, 126.7, 115.2 (5×aryl), 101.5, 95.4 (2×cyclopentadienyl C_{ipso}), 81.9 (*C*=C=O), 51.6 (Ph_2C), 34.0 (CMe_3), 31.7 ppm (CMe_3). IR(ATR): $\nu_{CCO} = 2075$ cm^{-1}.

Synthesis of [Cu(1)$_2$][CuBr$_2$]

THF (4 mL) was added to [**1**–H](OTf) (75 mg, 0.11 mmol), (Me_3Si)$_2$NK (24 mg, 0.12 mmol) and [CuBr(SMe_2)] (27 mg, 0.13 mmol). The mixture was stirred for 30 min. Volatile components were removed under vacuum. Toluene (5 mL) was added. Insoluble material was removed by filtration through a short pad of Celite. The brown filtrate was reduced to dryness under vacuum. The remaining light brown solid was washed with Et_2O (3×2 mL), affording a yellow,

powdery solid, which was finally dried under vacuum. Yield 35 mg (47%). Crystals suitable for XRD were obtained by recrystallization from toluene. $C_{75}H_{70}N_2Br_2Cu_2Fe_2$ (1397.96): calcd. C 64.44, H 5.05, N 2.00%; found C 63.84, H 5.21, N 2.00%. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 7.57$, 7.47, 7.43 (4 m, 4×4 H, Ar), 7.38 (m, 2 H, Ar), 4.50, 4.28, 4.24, 4.10 (4 m, 4×2 H, cyclopentadienyl), 1.32 ppm (s, 9 H, CMe_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): $\delta = 259.5$ (CCu), 153.2, 148.5, 143.7 (3×aryl C_{ipso}), 131.0, 129.0, 128.3, 127.2, 124.2 (5×aryl CH), 107.5, 91.0 (2×cyclopentadienyl C_{ipso}), 73.0, 72.5, 70.1, 67.1 (4×cyclopentadienyl CH), 65.2 (Ph_2C), 35.2 (CMe_3), 31.5 ppm (CMe_3).

X-ray Crystallography

For each data collections a single crystal was mounted on a micromount and all geometric and intensity data were taken from this sample by ω-scans. Data collections were carried out using either a Stoe StadiVari diffractometer equipped with a 4-circle goniometer and a DECTRIS Pilatus 200 K detector or a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. The data sets were corrected for absorption (by multi scans), Lorentz and polarisation effects. The structures were solved by direct methods (SHELXT) and refined using alternating cycles of least-squares refinements against F^2 (SHELXL-2014/7).[36] H atoms were included in the models in calculated positions with the 1.2 fold isotropic displacement parameter of their bonding partner. Experimental details for each diffraction experiment are given in Table S1 in the Supporting Information. Deposition Numbers 2376278 (for [**1**–H](OTf)), 2376279 (for **1′**), 2376280 (for **1**=Se), 2376281 (for [Cu(**1**)$_2$][$CuBr_2$]·toluene), 2376282 (for $(F_5C_6)_2I$(OTf)), 2379083 (for fc(CPh_2CH=NBF_3)) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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[1] Seminal paper: A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[2] Selected recent reviews: a) P. Bellotti, M. Koy, M. N. Hopkinson, F. Glorius, *Nat. Rev. Chem.* **2021**, *5*, 711–725; b) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485–496.
[3] a) J. Zinke, C. Bruhn, U. Siemeling, *Z. Anorg. Allg. Chem.* **2023**, *649*, e202200334; b) B. A. Correia Bicho, R. Guthardt, C. Bruhn, D. Großhennig, T. Orth, F. Pfeiffer, U. Siemeling, *Eur. J. Inorg. Chem.* **2022**, e202101014; c) A. R. Petrov, A. Derheim, J. Oetzel, M. Leibold, C. Bruhn, S. Scheerer, S. Oßwald, R. F. Winter, U. Siemeling, *Inorg. Chem.* **2015**, *54*, 6657–6670; d) S. Rittinghaus, C. Färber, C. Bruhn, U. Siemeling, *Dalton Trans.* **2014**, *43*, 3508–3520; e) U. Siemeling, C. Färber, M. Leibold, C. Bruhn, P. Mücke, R. F. Winter, B. Sarkar, M. von Hopffgarten, G. Frenking, *Eur. J. Inorg. Chem.* **2009**, 4607–4612; f) U. Siemeling, C. Färber, C. Bruhn, *Chem. Commun.* **2009**, 98–100.
[4] a) C. Goedecke, M. Leibold, U. Siemeling, G. Frenking, *J. Am. Chem. Soc.* **2011**, *133*, 3557–3569; b) U. Siemeling, C. Färber, C. Bruhn, M. Leibold, D. Selent, W. Baumann, M. von Hopffgarten, C. Goedecke, G. Frenking, *Chem. Sci.* **2010**, *1*, 697–704.
[5] For a recent comprehensive study addressing the correlation of NHC ring size or N-$C_{carbene}$-N bond angle and NHC ambiphilicity, see: F. Vermersch, V. T. Wang, M. Abdellaoui, R. Jazzar, G. Bertrand, *Chem. Sci.* **2024**, *15*, 3707–3710.
[6] Seminal paper: V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709.
[7] Selected recent reviews: a) K. Breitwieser, D. Munz, *Adv. Organomet. Chem.* **2022**, *78*, 79–132; b) S. Kumar Kushvaha, A. Mishra, H. W. Roesky, K. Chandra Mondal, *Chem. Asian J.* **2022**, *17*, e202101301; c) M. Melaimi, R. Jazzar, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2017**, *56*, 10046–10068; d) U. S. D. Paul, U. Radius, *Eur. J. Inorg. Chem.* **2017**, 3362–3375.
[8] J. Volk, M. Heinz, M. Leibold, C. Bruhn, T. Bens, B. Sarkar, M. C. Holthausen, U. Siemeling, *Chem. Commun.* **2022**, *58*, 10396–10399.
[9] Selected recent reviews: a) X. Peng, A. Rahim, W. Peng, F. Jiang, Z. Gu, S. Wen, *Chem. Rev.* **2023**, *123*, 1364–1416; b) C. Pan, L. Wang, J. Han, *Chem. Rec.* **2023**, *23*, e202300138; c) D. Wan, Q. Li, M. Li, Z. Du, Y. Fu, *Curr. Org. Chem.* **2021**, *25*, 1298–1320; d) D. R. Stuart, *Chem. Eur. J.* **2017**, *23*, 15852–15863; e) K. Aradi, B. L. Tóth, G. L. Tolnai, Z. Novák, *Synlett.* **2016**, *27*, 1456–1485; f) B. Olofsson, *Top. Curr. Chem.* **2015**, *373*, 135–166; g) M. S. Yusubov, A. V. Maskaev, V. V. Zhdankin, *Arkivoc* **2011**, *i*, 370–409.
[10] W. Tyrra, H. Butler, D. Naumann, *J. Fluorine Chem.* **1993**, *60*, 79–83.
[11] M. K. Gosh, J. Rzymkowski, M. Kalek, *Chem. Eur. J.* **2019**, *25*, 9619–9623.
[12] C. Pan, L. Wang, J. Han, *Org. Lett.* **2020**, *22*, 4776–4780.
[13] M. Bielawski, D. Aili, B. Olofsson, *J. Org. Chem.* **2008**, *73*, 4602–4607.
[14] a) K. Verlinden, H. Buhl, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.* **2015**, 2416–2425; b) D. M. Buck, D. Kunz, *Organometallics* **2015**, *34*, 5335–5340; see also: c) R. Weiss, S. Reichel, M. Handke, F. Hampel, *Angew. Chem. Int. Ed.* **1998**, *37*, 344–347.
[15] Seminal paper: N. Muller, D. E. Pritchard, *J. Chem. Phys.* **1959**, *31*, 768–771.
[16] Review: H. V. Huynh, *Chem. Rev.* **2018**, *118*, 9457–9492.
[17] L. Wallbaum, D. Weismann, D. Löber, C. Bruhn, P. Prochnow, J. E. Bandow, U. Siemeling, *Chem. Eur. J.* **2019**, *25*, 1488–1497.
[18] D. Martin, Y. Canac, V. Lavallo, G. Bertrand, *J. Am. Chem. Soc.* **2014**, *136*, 5023–5030.
[19] G. Meng, L. Kakalis, S. P. Nolan, M. Szostak, *Tetrahedron Lett.* **2019**, *60*, 378–381.
[20] For reviews, see: a) E. Jahnke, R. R. Tykwinski, *Chem. Commun.* **2010**, *46*, 3235–3249; b) R. Knorr, *Chem. Rev.* **2004**, *104*, 3795–3849.
[21] For recent papers addressing the migratory aptitude of substituents in FBT and closely related rearrangements, see: a) H. J. A. Dale, C. Nottingham, C. Poree, G. C. Lloyd-Jones, *J. Am. Chem. Soc.* **2021**, *143*, 2097–2107; b) X. Yang, K. Languet, D. M. Thamattoor, *J. Org. Chem.* **2016**, *81*, 8194–8198.
[22] The few known specific decomposition reactions of CAACs or the closely related, and even more reactive, cyclic (amino)(aryl)carbenes (CAArCs) to corresponding isomeric compounds are limited to C–H insertions and ring contractions/expansions; see: a) J. Lorkowski, P. Yorkgitis, M. R. Serrato, M. Gembicky, C. Pietraszuk, G. Bertrand, R. Jazzar, *Angew. Chem. Int. Ed.* **2024**, *63*, e202401020; b) X. Zhang, S. Yang, X. Zeng, *J. Org. Chem.* **2024**, *89*, 7795–7803; c) J. Lorkowski, D. Bouetard, P. Yorkgitis, M. Gembicky, T. Roisnel, N. Vanthuyne, D. Munz, L. Favereau, G. Bertrand, M. Mauduit, R. Jazzar, *Angew. Chem. Int. Ed.* **2023**, *62*, e202305404; d) W. Chu, T. Zhou, E. Bisz, B. Dziuk, R. Lalancette,

R. Szostak, M. Szostak, *Chem. Commun.* **2022**, *58*, 13467–13470; e) J. Lorkowski, M. Krahfuß, M. Kubicki, U. Radius, C. Pietraszuk, *Chem. Eur. J.* **2019**, *25*, 11365–11374; f) Z. Turner, *Chem. Eur. J.* **2016**, *22*, 11461–11468; see also: g) A. DeHope, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2007**, *46*, 6922–6925.

[23] a) V. Farkas, D. Csókás, Á. Erdélyi, G. Turczel, A. Bényei, T. Nagy, S. Kéki, I. Pápai, R. Tuba, *Adv. Sci.* **2024**, *11*, 2400118; b) A. Madron du Vigné, N. Cramer, *Organometallics* **2022**, *41*, 2731–2741.

[24] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans.***1987**, *2*, S1–S19.

[25] For reviews, see: a) V. G. Granik, *Russ. Chem. Rev.* **1984**, *53*, 383–400; b) P. W. Hickmott, *Tetrahedron* **1982**, *38*, 1975–2050; see also: c) S. Arumugam, M. Bhattacharya, S. M. N. V. T. Gorantla, K. C. Mondal, *Chem. Asian J.* **2023**, *18*, e202201041; d) Y. Wang, Q. Liao, C. Xi, *Org. Lett.* **2020**, *12*, 2951–2953; e) D. A. Bock, C. W. Lehmann, B. List, *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 20636–20641; f) K. L. Brown, L. Damm, J. Dunitz, A. Eschenmoser, R. Hobi, C. Kratky, *Helv. Chim. Acta* **1978**, *61*, 3108–3135.

[26] a) S. V. C. Vummaleti, D. J. Nelson, A. Poater, A. Gomez-Suarez, D. B. Cordes, A. M. Z. Slawin, S. P. Nolan, L. Cavallo, *Chem. Sci.* **2015**, *6*, 1895–1904; b) A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, *Organometallics* **2013**, *32*, 5269–5272.

[27] E. Tomás-Mendivil, M. M. Hansmann, C. M. Weinstein, R. Jazzar, M. Melaimi, G. Bertrand, *J. Am. Chem. Soc.* **2017**, *139*, 7753–7756.

[28] R. Hamze, R. Jazzar, M. Soleilhavoup, P. I. Djurovich, G. Bertrand, M. E. Thompson, *Chem. Commun.* **2017**, *53*, 9008–9011.

[29] Review: A. A. Danopoulos, T. Simler, P. Braunstein, *Chem. Rev.* **2019**, *119*, 3730–3961.

[30] See, for example: M. Gernert, U. Müller, M. Haehnel, J. Pflaum, A. Steffen, *Chem. Eur. J.* **2017**, *23*, 2206–2216.

[31] L. L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, R. Suter, A. M. Tondreau, H. Grützmacher, *Chem. Sci.* **2016**, *7*, 2335–2341.

[32] a) A. S. Romanov, M. Bochmann, *J. Organomet. Chem.* **2017**, *847*, 114–120; b) A. S. Romanov, M. Bochmann, *Organometallics* **2015**, *34*, 2439–2454; c) G. D. Frey, R. D. Dewhurst, S. Kouzar, B. Donnadieu, G. Bertrand, *J. Organomet. Chem.* **2008**, *693*, 1674–1682.

[33] For the only notable exception see: M. T. Proetto, K. Alexander, M. Melaimi, G. Bertrand, N. C. Gianneschi, *Chem. Eur. J.* **2021**, *27*, 3772–3778.

[34] M. Zhu, N. Jalalian, B. Olofsson, *Synlett.* **2008**, 592–596.

[35] H. Duddeck, *Prog. Nucl. Magn. Reson. Spectrosc.* **1995**, *27*, 1–323.

[36] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

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