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A Straightforward Access to Cyclic (Alkyl)(amino)carbene Copper (I) Complexes

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Abstract: The synthesis and characterization of cyclic (alkyl)(amino)carbene, bicyclic (alkyl)(amino)carbene and cyclic (amino)(barrelene)carbene copper (I) complexes is reported. These complexes are obtained via a scalable, versatile, green, and cost/user-friendly strategy.

Introduction

Cyclic (alkyl)(amino)carbenes (CAACs) are strong σ -donors and π -acceptors singlet carbenes which have been used as potent ligands for copper chemistry.^{1,2} Thanks to the strong bond they form with metal centers, CAACs can stabilize both low and high oxidation states making (CAAC)Cu(I) complexes particularly attractive for catalysis and material science alike. In catalysis, Engle and co-workers recently demonstrated that these ligands trigger remarkable Markovnikov regioselectivity for the carboboration and silylation of terminal alkynes.^{3,4} In material science, the Bochmann and Thompson groups independently reported record photoluminescent properties, akin to that of heavy metals, with a CAAC copper carbazole complex.⁵ In our lab we also took advantage of CAAC's to stabilize a reactive Cu⁰₂Cu¹ metal cluster, which allowed for demonstrating absolute templating of M(111) cluster surrogates by galvanic exchange.⁶ Importantly, CAAC copper complexes are effective carbene transfer reagents through transmetalation, allowing for the preparation of a broad variety of metal complexes (e.g; Au, Ag, Pd and Ir).^{6,7}

Despite these results, the development of CAACs as ligands is still slow in this field compared to popular diamino N-heterocyclic carbene (NHC) variants. Traditionally (CAAC)Cu(I) complexes are prepared under inert atmosphere in a two-step sequence beginning by the deprotonation of the corresponding conjugate acid with a strong base (*i.e.* KHMDS) followed by the addition of a copper salt (e.g. CuCl) (Figure 1).⁸ This is in sharp contrast with NHC's, whose copper complexes are readily accessible by simply treating the NHC iminium precursor with a weak base in the presence of a suitable copper(I) source.⁹ Looking for a similar alternative, Cazin and co-workers disclosed an elegant preparation of (CAAC)CuCl involving reaction of a CAAC iminium chloride salt (CAAC^H.Cl) with Cu₂O.¹⁰ Aside from

providing only one example, this methodology requires dry and inert conditions. It also involves the additional step of converting CAAC^H.BF₄ or CAAC^H.HCl₂ salts (obtained from synthesis¹¹ or commercially¹²) to the corresponding CAAC^H.Cl salts through anion metathesis using an ion exchange resin (Scheme 1).

Herein, continuing our ambition to make CAAC chemistry widely accessible,¹³ we describe a practical and green¹⁴ methodology for the preparation of (CAAC)Cu(I) chloride complexes. We showcase that these complexes are readily available in good yields by simply refluxing CAAC^H.BF₄ with copper chloride and sodium acetate in toluene (Scheme 1). This methodology extends to other members of the CAAC family such as bicyclic (alkyl)(amino)carbenes (BiCAACs)¹⁵ and cyclic (amino)(barrelene)carbenes (CABC).^{8c} The later was previously inaccessible by the free carbene route demonstrating the advantage of the weak base approach.¹⁶ Lastly, to showcase this methodology, we performed a multigram synthesis of a catalytically relevant CAAC ligand in air using ACS grade solvents and reagents.¹⁷

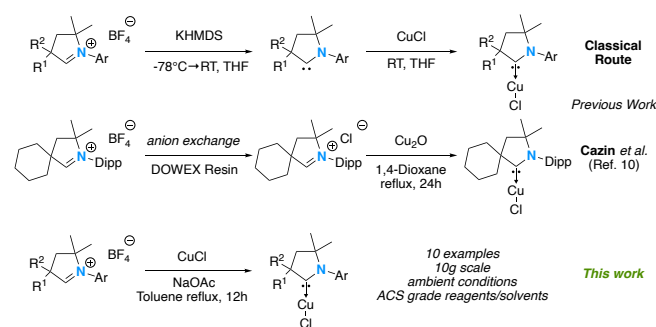


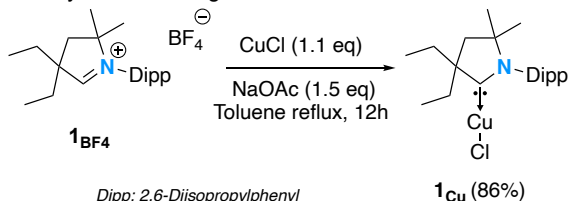
Figure 1. Overview of general synthetic pathways to cyclic (alkyl)(amino)carbenes copper (I) complexes

Results and Discussion

We began our study with the metalation of CAAC^H conjugate acid **1**BF₄, which is routinely used in our laboratory. When **1**BF₄ was reacted with sodium acetate and copper chloride in refluxing toluene for 12 h, a clean reaction was observed (Scheme 1). **1**c_u

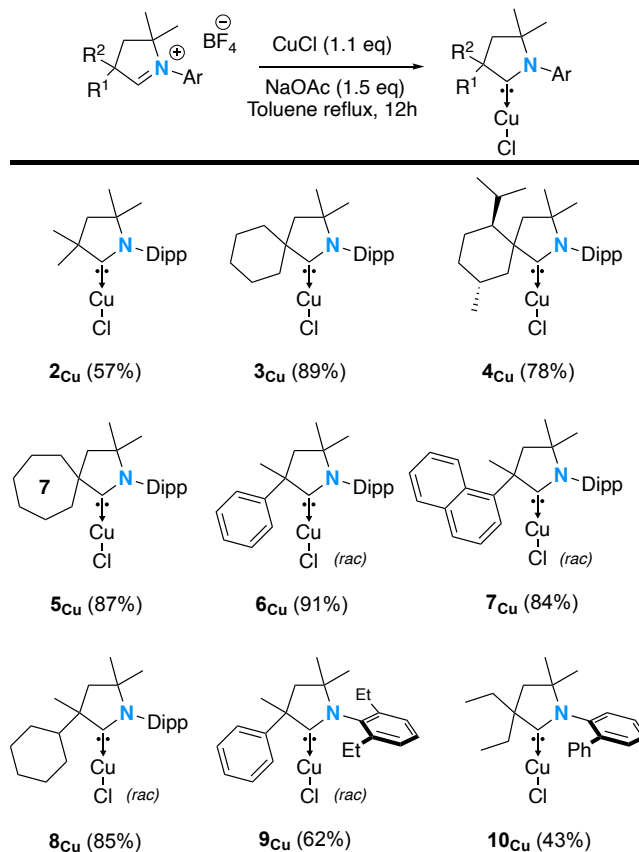
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was isolated in analytically pure microcrystalline powder form in 86% yield by simple filtration in air over a pad of silica gel and further precipitation from a concentrated solution of dichloromethane with pentane. This protocol which avoids the use of a strong base represents a significant improvement over the previous synthetic strategies.



Scheme 1. Preparation of 1_{Cu} . Isolated yields in parentheses.

Using these conditions, we next evaluated the scope of this methodology with a range of diversely substituted CAAC^H iminium salts 2_{BF_4} - 10_{BF_4} . As shown in Scheme 2, this reaction is broadly applicable, yielding the corresponding copper chloride complexes in good to excellent yields (>78%) with the least sterically hindered salts resulting in lower yields of the corresponding copper complexes 2_{Cu} , 9_{Cu} , 10_{Cu} (43%-57%). The later were found to slowly decompose when left standing in aerated solutions. This observation is in marked contrast with the more sterically hindered 3_{Cu} - 8_{Cu} which are bench stable over a month and likely explains the higher yield obtained with these complexes. Their structures were confirmed spectroscopically with characteristic $^{13}C\{^1H\}$ NMR signal for the corresponding copper-carbene carbon $Cu-C^{CAAC}$ observed around $\delta = 250$ ppm ($CDCl_3$). We also obtained the solid-state structures of compounds 5_{Cu} , 7_{Cu} and 8_{Cu} which were not described so far (Figure 2).



Scheme 2. Preparation of differently substituted CAAC copper(I) chloride complexes (2_{Cu} - 10_{Cu}). Isolated yields in parentheses.

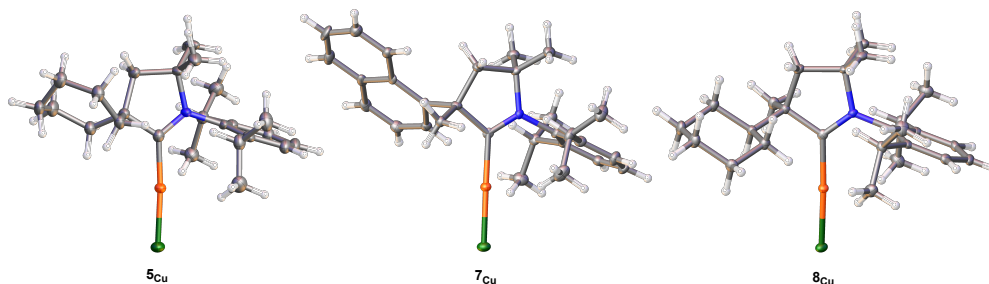
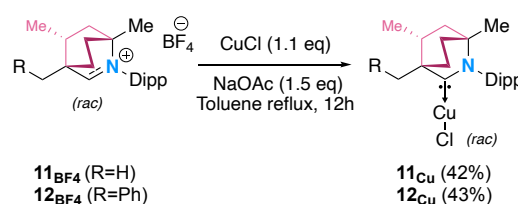


Figure 2. Molecular structure of 5_{Cu} , 7_{Cu} and 8_{Cu} in the solid state (ellipsoids set at the 33% probability level). Selected bond length and angles of 5_{Cu} : Cu1-C1 1.872(3) [Å], Cu1-C1-Cl 175.6(1) [°], 7_{Cu} : Cu1-C1 1.885(3) [Å], Cu1-C1-Cl 177.1(1) [°], 8_{Cu} : Cu1-C1 1.879(2) [Å], Cu1-C1-Cl 176.14(7) [°]

To further delineate the scope of this reaction, we next considered the smallest BiCAACs in our ligand arsenal.¹⁵ Under the same experimental conditions, iminium salts 11_{BF_4} and 12_{BF_4} resulted in formation of desired copper complexes 11_{Cu} and 12_{Cu} which were isolated under ambient conditions in 42% and 43% yield, respectively (Scheme 3). We found both complexes to slowly decompose when left standing in aerated solution over a week. Note that although these yields are quite modest 11_{Cu} cannot be prepared by reaction of $CuCl$ with the parent free carbene due to the competing formation of the corresponding cationic biscarbene copper complex $[(BiCAAC)_2Cu]^+$.¹⁸ The structure of both BiCAAC complexes was unambiguously established by NMR spectroscopy with characteristic $^{13}C\{^1H\}$ NMR signal for the corresponding copper-carbene carbon $Cu-C^{BiCAAC}$ observed

around $\delta = 257$ ppm ($CDCl_3$), and further characterized by X-ray diffraction for complex 11_{Cu} (Figure 3).



Scheme 3. Preparation of BiCAAC copper(I) chloride complexes 11_{Cu} and 12_{Cu} . Isolated yields in parentheses.

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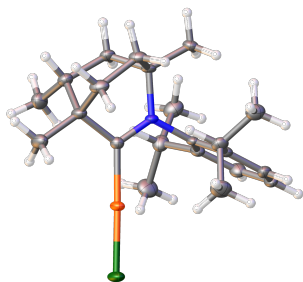
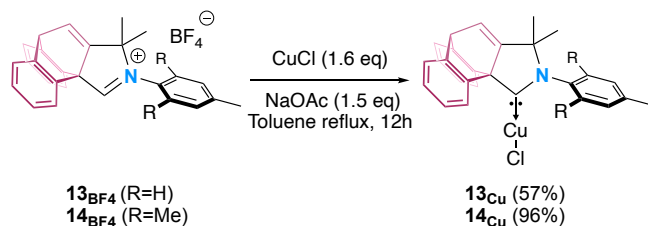


Figure 3. Molecular structure of **11_{Cu}** in the solid state (ellipsoids set at the 33% probability level). Selected bond length and angles of **11_{Cu}**: Cu1-C1 1.879(2) [Å], Cu1-C1-Cl 178.69(7) [°]

Given these encouraging results, we also considered cyclic (amino)(barrelene)carbenes (CABC), our most recent addition to the CAAC ligand library. We have shown that copper complexes of *N*-alkyl substituted CABC are accessible by deprotonation with KHMDS and metalation at low temperature (47% yield).^{8c} This is in marked contrast with the *N*-aryl variants which have so far remained elusive. Gratifyingly, using our new methodology *N*-tolyl **13_{Cu}** and *N*-mesityl **14_{Cu}** CABC copper complexes were both isolated in 57% and 96% yield respectively (Scheme 4). Both complexes were isolated under atmospheric conditions by simple filtration over celite and were found to be air and moisture stable in the solid state, likely due to their rigid barrelene structural motif. The structure of both CABC complexes was unambiguously established by NMR spectroscopy [¹³C{¹H} NMR signal for the corresponding copper-carbene carbon Cu-C^{CABC} observed around δ = 240 ppm (CD₂Cl₂)], and further characterized by X-ray diffraction. (Figure 4 and 5). Surprisingly (CABC)CuCl **14_{Cu}** crystallizes as a μ₂-chloro bridge dimer diverging from archetypical linear (carbene)CuCl structure. Similar bonding mode which has been reported for (CAAC)AgCl¹⁹ and (CAAC)ZnCl₂²⁰ could likely originate from the reduced steric hindrance of the CABC skeleton.²¹



Scheme 4. Preparation of CABC copper(I) chloride complexes **13_{Cu}** and **14_{Cu}**. Isolated yields in parentheses.

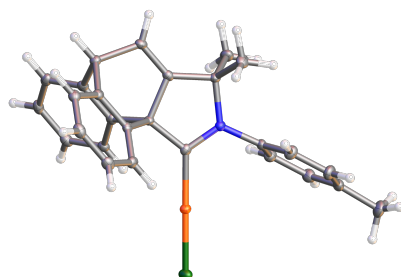


Figure 4. Molecular structure of **13_{Cu}** in the solid state (ellipsoids set at the 33% probability level). Selected bond length and angles of **13_{Cu}**: Cu1-C1 1.875(2) [Å], Cu1-C1-Cl 176.87(6) [°]

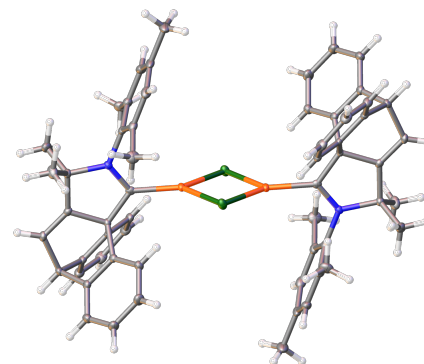
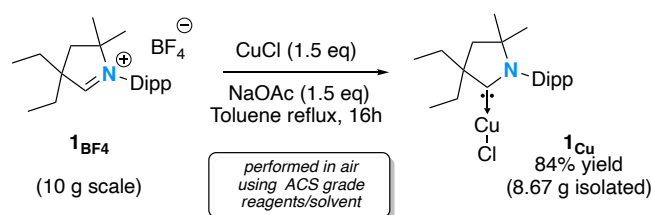


Figure 5. Molecular structure of **14_{Cu}** in the solid state (ellipsoids set at the 33% probability level). Selected bond length and angles of **14_{Cu}**: Cu1-C1 1.875(2) [Å], Cu1-C1-Cl 127.54(6) and 136.91(6) and 127.54(6) [°]

Finally, to demonstrate the usefulness of this strategy,²² we performed a 10 g scale metalation of **1_{BF4}** in air using ACS grade toluene and reagents without further purification. In this case we were pleased to isolate up to 8.67g of **1_{Cu}** (84% yield) (Scheme 5). Although a small drop in the isolated yield (2%) was to be expected, the advantage of performing the reaction in air using a simple round bottom flask equipped with a reflux condenser makes this methodology broadly accessible.



Scheme 5. Large Scale "in air" synthesis of **1_{Cu}**

Conclusion

In conclusion we have reported a new synthetic strategy for accessing CAAC, BiCAAC and CABC copper(I) complexes in good to excellent yields. This methodology can be performed in air without taking any specific precautions regarding the purity of the reagents. Combined with our recently reported protocol for preparing CAAC^H iminiums,¹³ these copper complexes can be obtained in only 3-steps from the aldehyde and the aniline (e.g. **1_{BF4}** is prepared in 62% yield over 2 steps which after metalation affords **1_{Cu}** in 52% overall yield). We believe that these findings which could extend to other transition metals, will streamline applications for CAAC copper complexes.

Experimental Section

General considerations: NMR spectra were recorded on a Bruker 300 or a Jeol 400 spectrometer at 25°C. ¹H NMR chemical shifts are reported relative to TMS (δ in ppm) and were referenced via residual proton resonances of the corresponding deuterated solvent (CHCl₃: 7.26 ppm; C₆D₅H: 7.16 ppm, CD₂Cl₂: 5.32 ppm) whereas ¹³C{¹H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances (CDCl₃: 77.16 ppm; C₆D₆: 128.0 ppm CD₂Cl₂: 53.84 ppm). Coupling constants are given in Hertz. Mass spectra were performed at the UC San

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Diego Mass Spectrometry Laboratory on an Agilent 6230 Accurate-Mass TOF-MS spectrometer. Single crystal X-ray diffraction data were collected on Bruker Apex diffractometers using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Conjugate acids of CAAC,¹³ BiCAAC^{9b} and CABC^{9c} were prepared according to previously reported protocols.

General synthetic procedure for the preparation of carbene-Cu-Cl complexes: In a sealed Schlenk flask under argon atmosphere appropriate conjugate acids of CAAC, BiCAAC or CABC (1 eq.) were placed together with copper(I) chloride (1.1 eq for CAAC and BiCAAC and 1.6 eq for CABC) and sodium acetate (1.5 eq). Solids were then suspended in dry toluene and reaction mixture were heated at 130 °C (oil bath temperature) for 12h. (Yields did not improve when performing the reaction for up to 24 hours). The reaction mixture was then cooled to room temperature and the suspension filtered over a short pad of silica gel covered with Celite® (CABC were directly filtered through Celite®) that was further washed with dichloromethane. The combined filtrates were concentrated to approx. 2 mL and the resulting complexes were precipitated by addition of an n-hexane/pentane mixture. Further filtration and washing with n-hexane/pentane (1:1 ratio) afforded the desired Cu complexes as analytically pure white powders.

Exemplary data for a carbene copper complexes: [CAAC] **5**_{Cu} starting from **5**_{BF4} (200 mg, 0.47 mmol), copper(I) chloride (51 mg, 0.52 mmol), and sodium acetate (80 mg, 0.94 mmol) in toluene (8 ml) complex were isolated as a white powder (178 mg, 87%). Single crystals for X-ray diffraction were grown from slow diffusion of hexane into a saturated dichloromethane solution. ¹H NMR (400 MHz, 25 °C, CDCl₃): $\delta = 7.38$ (t, $J = 7.7$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 2H), 2.77 (sept, $J = 6.7$ Hz, 2H), 2.20 – 2.09 (m, 2H), 2.02 (s, 2H), 2.01 – 1.90 (m, 2H), 1.80 – 1.51 (m, 8H), 1.30 (d, $J = 5.4$ Hz, 12H), 1.28 (s, 6H). ¹³C{¹H} NMR (100 MHz, 25 °C, CDCl₃): $\delta = 247.5$ (C_{carb}-Cu), 145.1, 134.3, 129.8, 124.8, 80.3, 61.4, 47.8, 39.2, 29.4, 29.2, 29.1, 27.3, 24.6, 22.5. HRMS: calc. for [M-Cl]⁺ C₂₄H₃₇CuN m/z : 402.2222; found: 402.2213; [BiCAAC] **11**_{Cu} starting from racemic **11**_{BF4} (300 mg, 0.75mmol), copper(I) chloride (83 mg, 0.84 mmol) and sodium acetate (125 mg, 1.5 mmol) in toluene (12 mL) racemic complex were isolated as a white powder (130 mg, 42%). Single crystals for X-ray diffraction were grown from slow diffusion of hexane into a saturated dichloromethane solution. ¹H NMR (400 MHz, 25 °C, CDCl₃): $\delta = 7.36$ (t, $J = 7.7$ Hz, 1H), 7.25 – 7.17 (m, 2H), 2.92 (sept, $J = 6.9$ Hz, 1H), 2.59 (sept, $J = 6.9$ Hz, 1H), 2.15 – 1.94 (m, 2H), 1.81 – 1.61 (m, 3H), 1.67 (s, 3H), 1.56 – 1.51 (m, 1H), 1.48 – 1.37 (m, 1H), 1.32 – 1.19 (m, 12H, overlapping *i*Pr-CH₃ and Me), 1.05 – 0.96 (m, 9H, overlapping *i*Pr-CH₃ and Me). ¹³C{¹H} NMR (100 MHz, 25 °C, CDCl₃): $\delta = 257.6$ (C_{carb}-Cu), 144.4, 143.9, 141.2, 129.7, 125.1, 124.8, 63.1, 49.0, 44.3, 36.7, 33.1, 30.4, 29.0, 28.4, 25.9, 25.6, 25.6, 23.8, 23.6, 22.9, 20.4. HRMS: calc. for [M-Cl]⁺ C₂₂H₃₃CuN m/z : 374.1909; found: 374.1903; [CABC] **14**_{Cu} starting from **14**_{BF4} (0.15 g, 0.31 mmol), copper(I) chloride (0.05 g, 0.50 mmol), and sodium acetate (0.05 g, 0.66 mmol) in toluene (8 mL) complex were isolated as a yellow solid (147 mg, 96%). Single crystals for X-ray diffraction were grown from

slow diffusion of diethyl ether into a saturated dichloromethane solution. ¹H NMR (400 MHz, 25 °C, CD₂Cl₂): $\delta = 7.87$ –7.85 (m, 2H), 7.41–7.39 (m, 2H), 7.13 (s, 2H), 7.10 – 6.99 (m, 4H), 6.81 (d, $J = 5.8$ Hz, 1H), 5.33 (d, $J = 3.9$ Hz, 1H), 2.40 (s, 3H), 2.31 (s, 6H), 1.31 (s, 6H). ¹³C{¹H} NMR (100 MHz, 25 °C, CD₂Cl₂): $\delta = 244.5$ (C_{carb}-Cu), 156.5, 146.4, 145.6, 139.7, 137.3, 134.6, 130.6, 128.7, 125.5, 125.2, 124.0, 122.0, 81.3, 77.9, 73.8, 52.0, 28.3, 21.1, 19.9. HRMS: calc. for [C₂₉H₂₇ClCuNNa]⁺ m/z : 510.1025; found: 510.1020.

Procedure for large scale preparation of 1_{Cu} under ambient conditions: In air, a 500 mL round bottom flask equipped with a magnetic stirring bar and a reflux condenser was charged with **1**_{BF4} (10.0 g, 24.9 mmol), copper(I) chloride (3.7 g, 38 mmol), sodium acetate (4.10 g, 50.0 mmol, ACS reagent grade, anhydrous) and 300 ml of toluene (ACS reagent grade). The reaction mixture was stirred overnight at 130 °C (oil bath temperature) and then filtered on a Buchner funnel (ca. 10 cm diameter) topped with a silica gel (ca. 3 cm) and celite® (ca. 1cm) eluting with DCM (ca. 100 ml). Volatiles were then evaporated under vacuo to provide a white residue. Recrystallization from a pentane/DCM mixture afforded the titled compound as an analytically pure white microcrystalline powder (**1**_{Cu}: 8.67 g, 84% yield). **1**_{Cu}: ¹H NMR (400 MHz, CDCl₃): $\delta = 7.39$ (t, $J = 7.7$ Hz, 1H), 7.25 (d, $J = 7.7$ Hz, 2H), 2.83 (sept, $J = 6.5$ Hz, 2H), 1.98 (s, 2H), 1.84 (ddt, $J = 41.6, 14.0, 7.2$ Hz, 4H), 1.35 (s, 6H), 1.30 (dd, $J = 6.8, 2.2$ Hz, 12H), 1.08 (t, $J = 7.5$ Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): $\delta = 250.5$ (C_{carb}-Cu), 145.2, 134.7, 129.9, 124.9, 81.1, 62.7, 42.5, 31.2, 29.4, 29.3, 27.4, 22.5, 9.7. Spectral data agree with those previously reported.⁴

Deposition Numbers CCDC 2239161 (**5**_{Cu}), 2239160 (**6**_{Cu}), 2239154 (**7**_{Cu}), 2239153 (**11**_{Cu}), 2239155 (**13**_{Cu}), and 2239156 (**14**_{Cu}) 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 (All other characterization data, original spectra, are provided in the Supporting Information).

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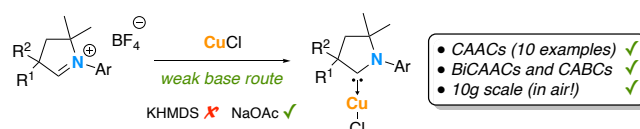
Keywords: carbenes • copper • iminium

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TOC



Cyclic (Alkyl)(amino)carbene Copper (I) complexes are typically obtained by deprotonating the carbene's conjugate acid with a strong base under inert atmosphere. Herein we show that these complexes can also be obtained in air using a weak base.