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Bis[cyclic (alkyl)(amino)carbene] isomers: Stable *trans*-bis(CAAC) versus facile olefin formation for *cis*-bis(CAAC)†

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Isomeric bis(aldiminium) salts with a 1,4-cyclohexylene framework were synthesized. The first isolable bis(CAAC) was prepared from the *trans*-stereoisomer and its ditopic ligand competency was proven by conversion to iridium(i) and rhodium(i) complexes. Upon deprotonation, the *cis*-isomer yielded an electron rich olefin via a classic, proton-catalyzed pathway. The C=C bond formation from the desired *cis*-bis(CAAC) was shown to be thermodynamically very favorable and to involve a small activation barrier. Compounds that can be described as insertion products of the *cis*-bis(CAAC) into the E–H bonds of NH₃, CH₃CN and H₂O were also identified.

First reported in 2005,¹ cyclic (alkyl)(amino)carbenes (CAACs) have been rapidly incorporated into the main-group and organometallic ligand toolkit. Their exceptional σ -donating and π -accepting abilities led to the isolation of a flurry of compounds of fundamental and applied interest.² Prominent examples include homoleptic late transition metal compounds in low oxidation states,³ main-group and organoradical spin carriers,⁴ elements in unusual oxidation states,⁵ and high-performing transition metal catalysts.⁶ The growing library of accessible CAACs is facilitating steric and electronic profile tuning of their complexes for tailored applications.^{7–9} Along with the much used five-membered Me₂CAAC,¹ CyCAACs,¹ and AdCAAC,¹⁰ other examples include CAACs incorporating imine or phosphine pendant arms,¹¹ six-membered CAAC-6,¹² and bicyclic BiCAACs¹³ (Chart 1). The steady expansion of the CAAC library was facilitated by the straightforward access to the respective aldiminium-salt precursors starting from ubiquitous building blocks, via an elegant protonation-cyclization-hydroiminiumation sequence reported by Bertrand.¹⁴

Despite the growing library of CAAC ligands and the tremendous success of bis(NHC)¹⁵ (NHC = *N*-heterocyclic carbene) and bisphosphine analogs,¹⁶ no bis(CAAC) has been reported to date. We reasoned that this notable absence could be remedied in few synthetic steps, by formally derivatizing CyCAAC,¹ which was shown to be a competent ligand. The cyclohexyl scaffold could be used to build two desirable bis(CAAC)s: A bidentate *cis*-stereoisomer and a ditopic *trans*-stereoisomer (Chart 1). Our investigations targeting these derivatives will be reported herein.

Aldiminium precursors **3a** and **4a** were obtained in gram quantities via standard CAAC-building protocols,¹⁴ adapted to accommodate the second CAAC moiety (Scheme 1). A commercially available isomeric mixture of cyclohexane-1,4-dimethanols was converted to cyclohexyl-1,4-dicarboxaldehydes and, following condensation with DippNH₂ (Dipp = 2,6-diisopropylphenyl), pure *trans*-diimine **1a** could be isolated in 29% overall yield. Double deprotonation of this precursor with *n*-butyllithium followed by reaction of the resulting aza-allyl anion with 3-bromo-2-methylpropene generated *cis*- and *trans*-**2a**, which were isolated as a mixture.

Layering benzene solutions of this mixture with acetonitrile resulted in selective crystallization of *trans*-**2a** as large colorless blocks in 10% yield. This compound was then subjected to the hydroiminiumation procedure, leading to dialdiminium tetrafluoroborate salt **3a**. *cis*-Dialdiminium tetrafluoroborate **4a** was more conveniently obtained by carrying on the hydroiminiumation

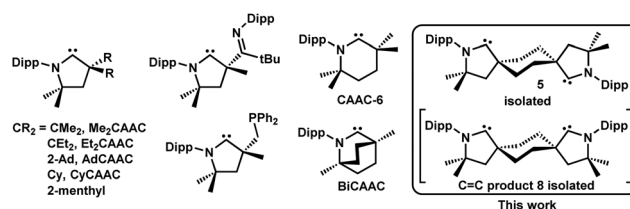


Chart 1 Selected examples of CAACs.

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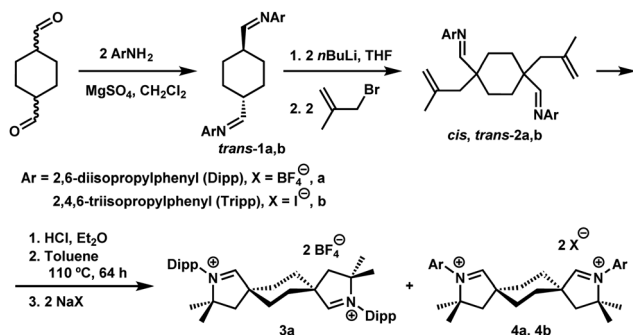
† Electronic supplementary information (ESI) available. CCDC 2131007–2131017.

For ESI and crystallographic data in CIF or other electronic format see DOI:

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‡ These authors contributed equally to this work.





Scheme 1 Succession of reactions leading to the synthesis of bis(CAAC) precursors **3a** and **4a,b**.

reaction with a mixture of *cis*- and *trans*-**2a**. Extraction of the product mixture with CHCl₃ and recrystallization by layering CH₂Cl₂ solutions with hexanes yielded **4a** in 67% yield. The configuration of the aldiminium fragments was readily assessed by ¹H NMR, based on coupling patterns for the cyclohexylene linker protons (in CD₂Cl₂, **3a** exhibits two doublet resonances at 1.93 and 2.65 ppm and **4a** features a pair of multiplets at 2.20 and 2.52 ppm), and confirmed by single-crystal X-ray diffraction (Fig. 1).

Addition of two equivalents of potassium hexamethyldisilazide (KHMDS) to *trans*-aldiminium salt **3a** in THF produced the expected dicarbene **5** (Scheme 2 and Fig. 2), displaying a characteristic ¹³C NMR resonance corresponding to the carbene carbons at 315.2 ppm in C₆D₆. Under an inert atmosphere, **5** could be handled at room-temperature and no decomposition was observed by ¹H NMR after storing the solid at -40 °C for a month. The ditopic nature of **5** was probed *via* reaction with IrCl(CO)(PPh₃)₂ or [Rh(cod)Cl]₂ in benzene, which yielded complexes **6** (Fig. 3) and **7** (Fig. S67, ESI[†]), respectively, as yellow, crystalline precipitates. The four ligands in **6** adopt a

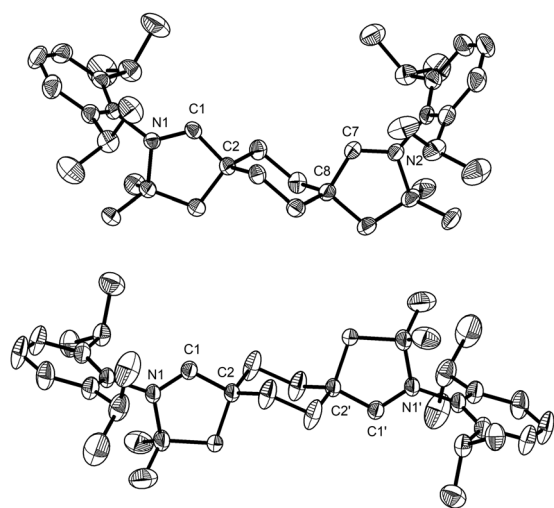
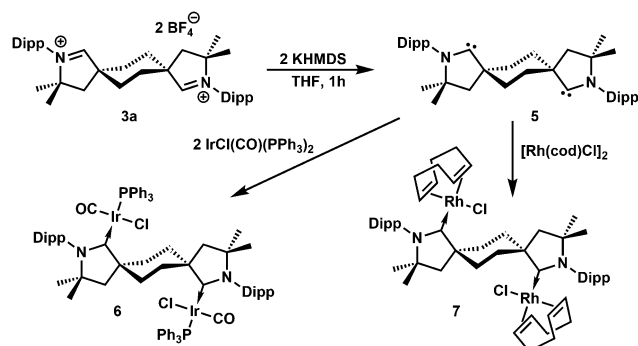


Fig. 1 Solid-state structures of the dications in **3a** (top) and **4a** (bottom) with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: **3a**: C1–N1 1.272(4), C1–C2 1.491(4); N1–C1–C2 114.7(2); **4a**: C1–N1 1.275(2), C1–C2 1.482(3); N1–C1–C2 114.76(17).



Scheme 2 Synthesis of free dicarbene **5** and its metal complexes **6** and **7**.

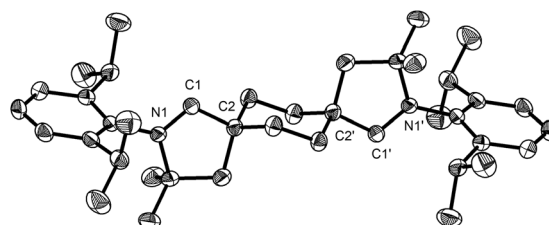


Fig. 2 Solid-state structure of **5** with 50% probability thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.3065(16), C1–C2 1.5232(17); N1–C1–C2 105.92(10).

square planar coordination geometry at iridium, with PPh₃ *trans* to the carbene, as previously observed in analogous IrCl(CO)(NHC)(PPh₃) complexes.¹⁷ The spectral signature of **6** (δ_{carbene} 255 ppm, δ_{CO} 174 ppm, δ_{P} 22 ppm, ν_{CO} 1950 cm⁻¹) is also similar to that of IrCl(CO)(NHC)(PPh₃) (δ_{carbene} 178 ppm, δ_{CO} 171 ppm, δ_{P} 25 ppm, ν_{CO} 1945 cm⁻¹).¹⁷

Addition of two equivalents of Et₃N, iPr₂NET, LiHMDS, LDA, MeLi or Me₃SiCH₂Li to a suspension **4a** in THF of led to intractable mixtures. When lithium-2,2,6,6-tetramethylpiperidide (LiTMP) was employed, an elimination reaction took place, regenerating *cis*-**2a**. A similar behavior was reported by Bertrand for CAAC-6.¹² Immediately upon addition of two equivalents of KHMDS to **4a** at -78 °C, (Fig. S55 and S56, ESI[†]), a singlet resonance was detected at

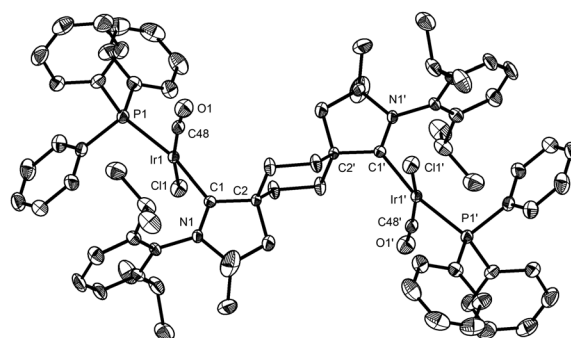
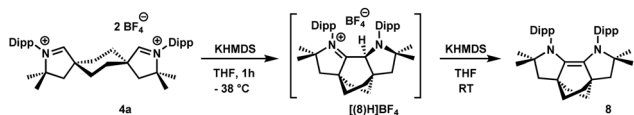


Fig. 3 Solid-state structure of **6** with 50% probability thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1–C1 2.035(3), Ir1–P1 2.3111(8), O1–C48 1.100(3), C1–Ir1–P1 168.68(7), C48–Ir1–C1 168.69(9), N1–C1–C2 109.3(2).



Scheme 3 Synthesis of **8** via [(8)H]BF₄.

318.0 ppm by ¹³C NMR, suggesting the formation of a CAAC. It rapidly disappeared upon warming to −38 °C with concurrent emergence of a new set of resonances suggestive of a less symmetric compound. In the ¹H NMR spectrum, a singlet at 5.08 ppm, within the range observed for protonated NHC-CAAC dimers (4.90–5.32 ppm in CD₃CN;¹⁸ 4.58, 4.72 ppm in CDCl₃),¹⁹ was assigned to the protonated olefin intermediate [(8)H]BF₄ (Scheme 3). Ultimately, warming up the mixture to room temperature led to the formation of a higher-symmetry compound, confirmed *via* X-ray crystallography to be olefin **8** (Fig. S68, ESI[†]); whole-molecule disorder precluded a detailed discussion of bonding parameters. Similar electron-rich olefins were recently reported by Sarkar.²⁰ Solutions of **8** in toluene were stable up to 110 °C and the solid could be handled in air. The substantial steric crowding in **8** forces the nitrogen atoms to become pyramidalized (sum of nitrogen bond angles 351.4(4)°). Furthermore, two methyl groups within the Dipp fragments are forced into close proximity to the opposing aryl ring, giving rise to a strongly shielded ¹H NMR resonance at −0.02 ppm.

DFT studies showed that, upon single deprotonation of **4a** to a free mono-CAAC, the cyclohexane backbone readily changes conformation from chair to twist boat ($\Delta G_{\text{c-tb}}^{\ddagger} = 24 \text{ kJ mol}^{-1}$, Fig. S72, ESI[†]). A second conformational change from twist boat to boat, accompanied by the formation of a C–C bond to give [8(H)]⁺, is similarly facile ($\Delta G_{\text{tb-b}}^{\ddagger} = 12 \text{ kJ mol}^{-1}$). The two-step transformation is overall exergonic ($\Delta G = -72 \text{ kJ mol}^{-1}$) and expected to take place rapidly even at −38 °C due to the associated small energy barriers. The calculated ¹H NMR chemical shifts of [8(H)]⁺ are in good agreement with the experimental values, with a characteristic singlet at 5.91 ppm *vs.* 5.08 ppm observed experimentally for the protonated olefin. A hypothetical *cis*-bis(CAAC) resulting from double deprotonation of **4a** gave a potential energy surface similar to single deprotonation, with greater energy barriers for conformational changes of the cyclohexane ring ($\Delta G_{\text{c-tb}}^{\ddagger} = 52$ and $\Delta G_{\text{tb-b}}^{\ddagger} = 40 \text{ kJ mol}^{-1}$, Fig. S73, ESI[†]). This likely stems from the increased repulsion associated with two carbon atoms with lone pairs. The formation of **8** from the *cis*-bis(CAAC) is overall highly exergonic ($\Delta G = -262 \text{ kJ mol}^{-1}$) as a C=C double bond is formed between the two carbenic carbon atoms.

The calculations support the intermediacy of [8(H)]BF₄ en route from **4a** to **8**. Furthermore, even though double deprotonation of **4a** could take place prior to conformational changes, the energy barriers associated with the cyclohexane ring flip are minor. This suggests that the *cis*-bis(CAAC) species obtained *via* double deprotonation of **4a** is not isolable under any conditions. While these results might initially seem surprising, they become less so upon comparison with data calculated for the

dimerization of Me₂CAAC, which show $\Delta G_{\text{dimer}} = -75$ and -99 kJ mol^{-1} for *cis* and *trans* product geometries, respectively. Thus, dimerization of two CAACs is always thermodynamically favored but generally kinetically blocked by very high activation barriers ($\Delta G_{\text{cis}}^{\ddagger} = 189$ and $\Delta G_{\text{trans}}^{\ddagger} = 188 \text{ kJ mol}^{-1}$) that arise in large part from the entropic penalty of dimerization ($-T\Delta S = 81 \text{ kJ mol}^{-1}$). No such penalty exists when the two CAAC moieties are part of the same molecule, which supports the facile formation of **8**.

Cyclic voltammetry of **8** in THF revealed two reversible redox waves ($E_{1/2} = -0.32$ and 0.49 vs. Fc/Fc^+ , Fig. S59, ESI[†]), corresponding to the oxidation of **8** to its radical cation and further to the dication, respectively. Both oxidations are anodically-shifted in comparison to the values reported by Sarkar,²⁰ potentially due to the inductive effect of the *N*-aryl substituent in **8** leading to a less electron rich system. The C₂-symmetric radical cation was isolated as purple tetrafluoroborate salt **9** following the oxidation of **8** with [Ph₃C][BF₄]. It was characterized by EPR (Fig. S60, ESI[†]) and its structure was confirmed by X-ray crystallography (Fig. 4).

Attempting to destabilize the electron rich olefin **8** in favor of a free *cis*-bis(CAAC), the Dipp substituents in **4a** were replaced with Tripp (2,4,6-triisopropylphenyl) (Scheme 1). However, deprotonation of **4b** also led to C=C bond formation and this chemistry will not be detailed here. We then turned our attention to complex formation directly from **4a**, by employing metal reagents featuring Brønsted-basic ligands (Scheme 4). The reaction of NHC salt precursors with Cu₂O or Ag₂O to yield the corresponding metal complexes has been extensively explored.²¹ Extrapolation of this method to CAACs is less common,²² arguably due to the weaker acidity of aldiminium-CAAC salts. Heating an acetonitrile solution of **4a** with Cu₂O over several days in an NMR tube resulted in crystallization of colorless blocks that were identified as ether **12** by single-crystal X-ray diffraction (Fig. S71, ESI[†]). The structure is reminiscent of the (Me₂CAACH)₂O ether obtained as a side-product while preparing (Me₂CAAC)₂Ge.²³ Refluxing **4a** and Fe(HMDS)₂ in acetonitrile led to crystallization of **11** (Fig. S65, ESI[†]). The presence of (Me₃Si)₂NH in the NMR of the product mixture suggests that deprotonation may indeed take place. However, scaling up the reaction led to the isolation of **10** instead (Fig. S70, ESI[†]). The origin of the nitrogen atom is presumably (Me₃Si)₂NH, a byproduct from the reaction of Fe(HMDS)₂

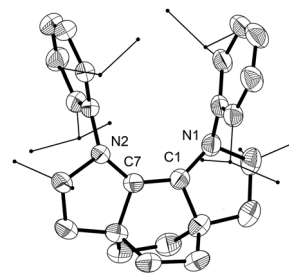
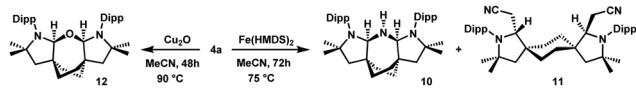


Fig. 4 Solid-state structure of the cation in **9** with 50% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C1–C7 1.409(3), C1–N1 1.357(3), C7–N2 1.360(3).





Scheme 4 Reactivity of **4a** towards transition metal complexes with Brønsted-basic ligands.

and **4a**. Attempted complex formation using $\text{Ca}(\text{HMDS})_2$, $\text{Mg}(\text{SiTMS}_3)_2$, $\text{Pd}(\text{OAc})_2$, or $[\text{PtMe}_2(\mu\text{-SMe}_2)]_2$ gave intractable mixtures.

In conclusion, two isomeric CAAC-aldiminium salts **3a** and **4a**, derived from the same parent aldehydes, were synthesized on multi-gram scale. *trans*-Stereoisomer **3a** was doubly deprotonated to yield the first isolable bis(CAAC) **5**, which proved to easily form dinuclear metal complexes, as exemplified by iridium complex **6** and rhodium complex **7**. Upon double deprotonation with KHMDs , *cis*-stereoisomer **4a** formed the electron-rich olefin **8**. Experimental and computational studies suggest the process follows the classic Lewis-acid catalyzed NHC dimerization pathway. DFT calculations showed that the intramolecular C=C bond formation in a free *cis*-bis(CAAC) derived from **4a** is highly exergonic (-262 kJ mol^{-1} vs. -75 kJ mol^{-1} for *cis*-dimerization of Me_2CAAC) and involves, for entropic reasons, a small activation barrier that can be lowered even more by proton catalysis. Reaction of **4a** with metal complexes featuring Brønsted-basic ligands led to the identification of **10**, **11**, and **12**, which can be described as insertion products of a bis(CAAC) into the N-H, C-H and O-H bonds of NH_3 , CH_3CN and H_2O , respectively. Whether their formation involves a free CAAC intermediate that has been observed at low-temperature by NMR, as described for mono(CAAC)s,²⁴ or the transient formation of metal complexes, remains to be investigated. 17 years after the first report of a CAAC ligand, our study adds the first bis(CAAC) ligand to the organometallic toolkit.

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Conflicts of interest

There are no conflicts to declare.

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