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

 Braulio M. Puerta Lombardi,‡<sup>a</sup> Ethan R. Pezoulas,‡<sup>a</sup> Roope A. Suvinen,<sup>id</sup><sup>b</sup> Alexander Harrison,<sup>a</sup> Zachary S. Dubrawski,<sup>id</sup><sup>a</sup> Benjamin S. Gelfand,<sup>id</sup><sup>a</sup> Heikki M. Tuononen,<sup>id</sup><sup>\*b</sup> and Roland Roesler,<sup>id</sup><sup>\*a</sup>

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 NH<sub>3</sub>, CH<sub>3</sub>CN and H<sub>2</sub>O were also identified.

First reported in 2005,<sup>1</sup> cyclic (alkyl)(amino)carbenes (CAACs) have been rapidly incorporated into the main-group and organometallic ligand toolkit. Their exceptional  $\sigma$ -donating and  $\pi$ -accepting abilities led to the isolation of a flurry of compounds of fundamental and applied interest.<sup>2</sup> Prominent examples include homoleptic late transition metal compounds in low oxidation states,<sup>3</sup> main-group and organoradical spin carriers,<sup>4</sup> elements in unusual oxidation states,<sup>5</sup> and high-performing transition metal catalysts.<sup>6</sup> The growing library of accessible CAACs is facilitating steric and electronic profile tuning of their complexes for tailored applications.<sup>7–9</sup> Along with the much used five-membered Me<sub>2</sub>CAAC,<sup>1</sup> CyCAACs,<sup>1</sup> and AdCAAC,<sup>10</sup> other examples include CAACs incorporating imine or phosphine pendant arms,<sup>11</sup> six-membered CAAC-6,<sup>12</sup> and bicyclic BiCAACs<sup>13</sup> (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.<sup>14</sup>

Despite the growing library of CAAC ligands and the tremendous success of bis(NHC)<sup>15</sup> (NHC = *N*-heterocyclic carbene) and bisphosphine analogs,<sup>16</sup> 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,<sup>1</sup> 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,<sup>14</sup> 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 DippNH<sub>2</sub> (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

<sup>a</sup> Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4, Canada. E-mail: roesler@ucalgary.ca

<sup>b</sup> Department of Chemistry, Nanoscience Centre, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland. E-mail: heikki.m.tuononen@jyu.fi

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‡ These authors contributed equally to this work.

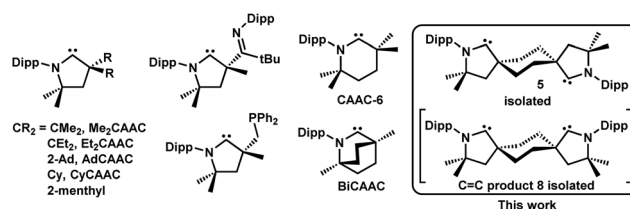
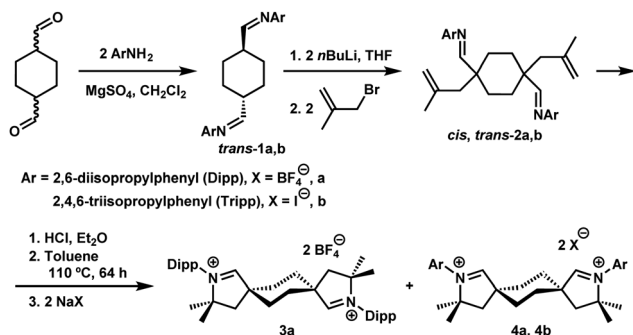


Chart 1 Selected examples of CAACs.

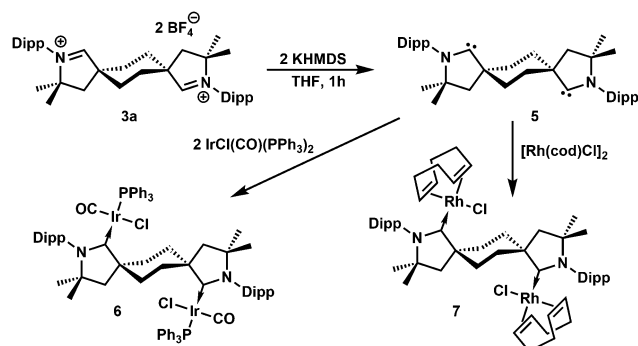




Scheme 1 Succession of reactions leading to the synthesis of bis(CAAC) precursors **3a** and **4a,b**.

reaction with a mixture of *cis*- and *trans*-**2a**. Extraction of the product mixture with CHCl<sub>3</sub> and recrystallization by layering CH<sub>2</sub>Cl<sub>2</sub> solutions with hexanes yielded **4a** in 67% yield. The configuration of the aldiminium fragments was readily assessed by <sup>1</sup>H NMR, based on coupling patterns for the cyclohexylene linker protons (in CD<sub>2</sub>Cl<sub>2</sub>, **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 <sup>13</sup>C NMR resonance corresponding to the carbene carbons at 315.2 ppm in C<sub>6</sub>D<sub>6</sub>. Under an inert atmosphere, **5** could be handled at room-temperature and no decomposition was observed by <sup>1</sup>H NMR after storing the solid at -40 °C for a month. The ditopic nature of **5** was probed *via* reaction with IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> or [Rh(cod)Cl]<sub>2</sub> in benzene, which yielded complexes **6** (Fig. 3) and **7** (Fig. S67, ESI<sup>†</sup>), respectively, as yellow, crystalline precipitates. The four ligands in **6** adopt a



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

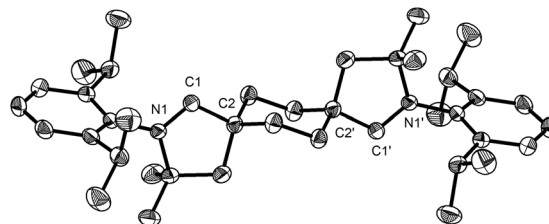


Fig. 2 Solid-state structure of **5** with 50% probability thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.3065(16), C1–C2 1.5232(17); N1–C1–C2 105.92(10).

square planar coordination geometry at iridium, with PPh<sub>3</sub> *trans* to the carbene, as previously observed in analogous IrCl(CO)(NHC)(PPh<sub>3</sub>) complexes.<sup>17</sup> The spectral signature of **6** ( $\delta_{\text{carbene}}$  255 ppm,  $\delta_{\text{CO}}$  174 ppm,  $\delta_{\text{P}}$  22 ppm,  $\nu_{\text{CO}}$  1950 cm<sup>-1</sup>) is also similar to that of IrCl(CO)(NHC)(PPh<sub>3</sub>) ( $\delta_{\text{carbene}}$  178 ppm,  $\delta_{\text{CO}}$  171 ppm,  $\delta_{\text{P}}$  25 ppm,  $\nu_{\text{CO}}$  1945 cm<sup>-1</sup>).<sup>17</sup>

Addition of two equivalents of Et<sub>3</sub>N, iPr<sub>2</sub>NET, LiHMDS, LDA, MeLi or Me<sub>3</sub>SiCH<sub>2</sub>Li 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.<sup>12</sup> Immediately upon addition of two equivalents of KHMDS to **4a** at -78 °C, (Fig. S55 and S56, ESI<sup>†</sup>), a singlet resonance was detected at

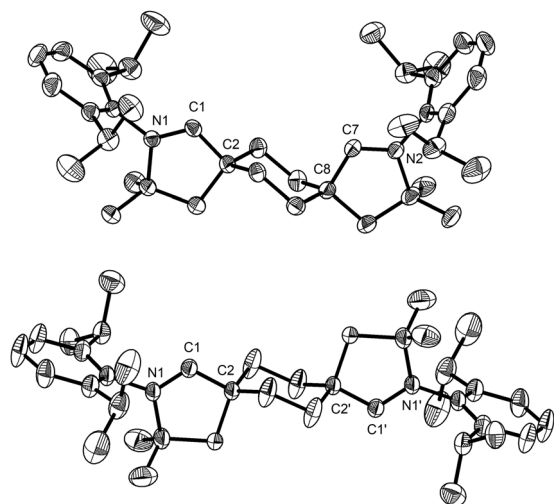


Fig. 1 Solid-state structures of the dications in **3a** (top) and **4a** (bottom) with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: **3a**: C1–N1 1.272(4), C1–C2 1.491(4); N1–C1–C2 114.7(2); **4a**: C1–N1 1.275(2), C1–C2 1.482(3); N1–C1–C2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

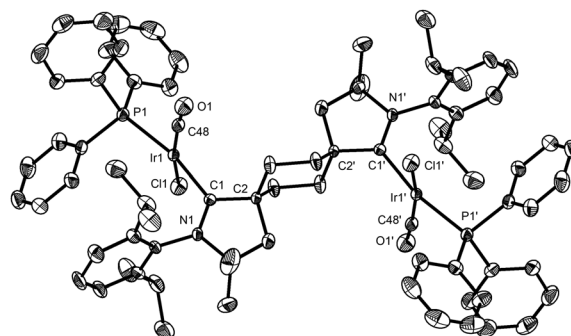
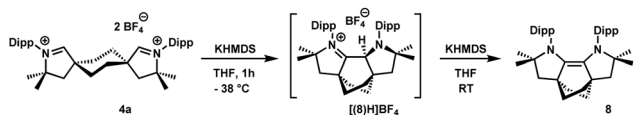


Fig. 3 Solid-state structure of **6** with 50% probability thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1–C1 2.035(3), Ir1–P1 2.3111(8), O1–C48 1.100(3), C1–Ir1–P1 168.68(7), C48–Ir1–C1 168.69(9), N1–C1–C2 109.3(2).



Scheme 3 Synthesis of **8** via  $[(8)H]BF_4$ .

318.0 ppm by  $^{13}C$  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  $CD_3CN$ ;<sup>18</sup> 4.58, 4.72 ppm in  $CDCl_3$ ),<sup>19</sup> was assigned to the protonated olefin intermediate  $[(8)H]BF_4$  (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<sup>†</sup>); whole-molecule disorder precluded a detailed discussion of bonding parameters. Similar electron-rich olefins were recently reported by Sarkar.<sup>20</sup> 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  $351.4(4)^\circ$ ). 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 ( $\Delta G_{c-tb}^\ddagger = 24$  kJ mol<sup>-1</sup>, Fig. S72, ESI<sup>†</sup>). 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 ( $\Delta G_{tb-b}^\ddagger = 12$  kJ mol<sup>-1</sup>). The two-step transformation is overall exergonic ( $\Delta G = -72$  kJ mol<sup>-1</sup>) 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 ( $\Delta G_{c-tb}^\ddagger = 52$  and  $\Delta G_{tb-b}^\ddagger = 40$  kJ mol<sup>-1</sup>, Fig. S73, ESI<sup>†</sup>). 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 ( $\Delta G = -262$  kJ mol<sup>-1</sup>) as a C=C double bond is formed between the two carbenic carbon atoms.

The calculations support the intermediacy of  $[8(H)]BF_4$  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  $Me_2CAAC$ , which show  $\Delta G_{dimer} = -75$  and  $-99$  kJ mol<sup>-1</sup> 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 ( $\Delta G_{cis}^\ddagger = 189$  and  $\Delta G_{trans}^\ddagger = 188$  kJ mol<sup>-1</sup>) that arise in large part from the entropic penalty of dimerization ( $-T\Delta S = 81$  kJ mol<sup>-1</sup>). 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<sup>†</sup>), 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,<sup>20</sup> potentially due to the inductive effect of the *N*-aryl substituent in **8** leading to a less electron rich system. The  $C_2$ -symmetric radical cation was isolated as purple tetrafluoroborate salt **9** following the oxidation of **8** with  $[Ph_3C][BF_4]$ . It was characterized by EPR (Fig. S60, ESI<sup>†</sup>) 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  $Cu_2O$  or  $Ag_2O$  to yield the corresponding metal complexes has been extensively explored.<sup>21</sup> Extrapolation of this method to CAACs is less common,<sup>22</sup> arguably due to the weaker acidity of aldiminium-CAAC salts. Heating an acetonitrile solution of **4a** with  $Cu_2O$  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<sup>†</sup>). The structure is reminiscent of the  $(Me_2CAACH)_2O$  ether obtained as a side-product while preparing  $(Me_2CAAC)_2Ge$ .<sup>23</sup> Refluxing **4a** and  $Fe(HMDS)_2$  in acetonitrile led to crystallization of **11** (Fig. S65, ESI<sup>†</sup>). The presence of  $(Me_3Si)_2NH$  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<sup>†</sup>). The origin of the nitrogen atom is presumably  $(Me_3Si)_2NH$ , a byproduct from the reaction of  $Fe(HMDS)_2$

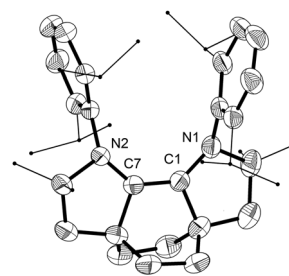
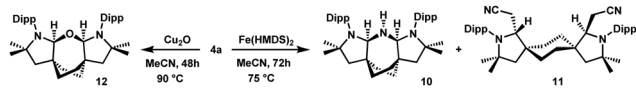


Fig. 4 Solid-state structure of the cation in **9** with 50% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): C1–C7 1.409(3), C1–N1 1.357(3), C7–N2 1.360(3).





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  $\text{KHMDs}$ , *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 ( $-262 \text{ kJ mol}^{-1}$  vs.  $-75 \text{ kJ mol}^{-1}$  for *cis*-dimerization of  $\text{Me}_2\text{CAAC}$ ) 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  $\text{NH}_3$ ,  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$ , respectively. Whether their formation involves a free CAAC intermediate that has been observed at low-temperature by NMR, as described for mono(CAAC)s,<sup>24</sup> 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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