

# UC San Diego

## UC San Diego Previously Published Works

### Title

An Air-Stable “Masked” Bis(imino)carbene: A Carbon-Based Dual Ambiphile

### Permalink

<https://escholarship.org/uc/item/6fk2v3tw>

### Journal

Journal of the American Chemical Society, 145(4)

### ISSN

0002-7863

### Authors

Loh, Ying Kai  
Melaimi, Mohand  
Munz, Dominik  
[et al.](#)

### Publication Date

2023-02-01

### DOI

10.1021/jacs.2c12847

Peer reviewed

# An Air-Stable “Masked” Bis(imino)carbene: A Carbon-Based Dual Ambiphile

Ying Kai Loh, Mohand Melaimi, Dominik Munz, and Guy Bertrand\*



Cite This: *J. Am. Chem. Soc.* 2023, 145, 2064–2069



Read Online

ACCESS |



Metrics & More



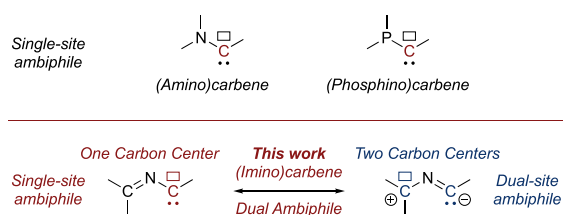
Article Recommendations



Supporting Information

**ABSTRACT:** Carbenes, once considered laboratory curiosities, now serve as powerful tools in the chemical and material sciences. To date, all stable singlet carbenes are single-site ambiphiles. Here we describe the synthesis of a carbene which is a carbon-based *dual* ambiphile (both single-site and dual-site). The key is to employ imino substituents derived from a cyclic (alkyl)(amino)carbene (CAAC), which imparts a 1,3-dipolar character to the carbene. Its *dual* ambiphilic nature is consistent with the ability to activate simple organic molecules in both 1,1- and 1,3-fashion. Furthermore, its 1,3-ambiphilicity facilitates an unprecedented reversible intramolecular dearomative [3 + 2] cycloaddition with a proximal arene substituent, giving the carbene the ability to “mask” itself as an air-stable cycloadduct. We perceive that the concept of *dual* ambiphilicity opens a new dimension for future carbene chemistry, expanding the repertoire of applications beyond that known for classical single-site ambiphilic carbenes.

Carbenes are an intriguing class of neutral organic molecules featuring a divalent carbon atom.<sup>1</sup> With only six valence electrons, they defy the octet rule. While the parent carbene ( $\text{H}_2\text{C}:$ ) has a triplet ground state and is only stable in interstellar medium, amino and phosphino carbenes have a singlet ground state which permits their isolation under standard laboratory conditions.<sup>2,3</sup> With regards to their reactivity and applications, stable singlet carbenes are classical single-site ambiphiles, with both donor and acceptor orbitals on the carbene center (Figure 1, top).<sup>4</sup> This feature was



**Figure 1.** Amino and phosphino carbenes are archetypical single-site ambiphiles (top). Present work on an (imino)carbene which is a carbon-based *dual* ambiphile (bottom).

highlighted in 2007, when our group demonstrated that a cyclic (alkyl)(amino)carbene (CAAC) can split  $\text{H}_2$  across a single carbon center,<sup>5</sup> drawing analogy to the oxidative addition chemistry of transition metals.<sup>6</sup>

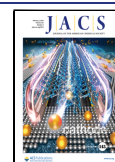
Another nitrogen-based substituent, which has never been employed in carbene chemistry, is the imino group. Its unsaturated nature allows for an allylic-type delocalization to a 1,3-dipolar resonance form (Figure 1, bottom). Strongly polarized zwitterions with separated donor and acceptor sites can act as dual-site ambiphiles.<sup>7</sup> Hence, we reasoned that (imino)carbenes could exhibit ambiphilicity based on both one carbon center and two carbon centers, a feature which is to date unknown in organic chemistry.<sup>8</sup>

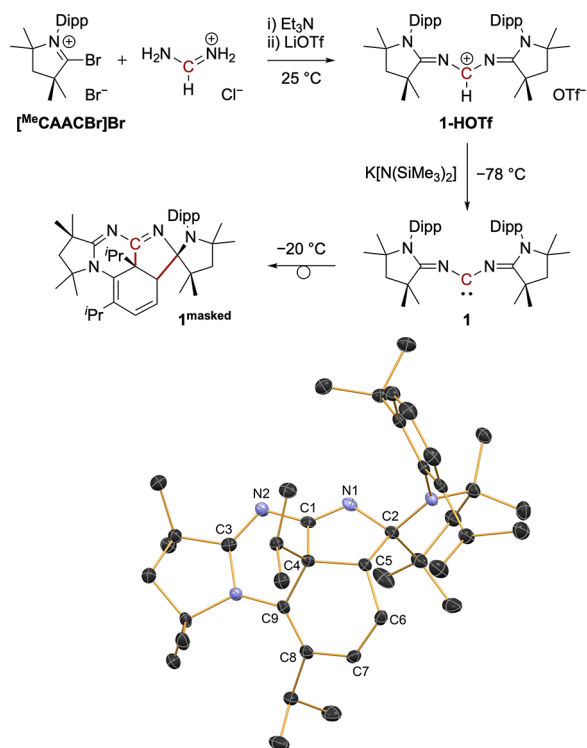
N-Heterocyclic imines (NHIs)<sup>9</sup> derived from conventional N-heterocyclic carbenes (NHCs)<sup>10,11</sup> are powerful  $2\sigma$ ,  $4\pi$  electron donor ligands with a large steric profile. NHIs have recently received significant attention due to their ability to stabilize a wide range of highly electron-deficient main group systems.<sup>12–26</sup> However, the moderate electrophilic properties of these NHIs limit them to being purely Lewis basic ligands. On the other hand, CAACs have higher nucleophilicity than NHCs, but are immensely more electrophilic,<sup>27–29</sup> leading us to believe that an NHI based on a CAAC might be a suitable donor to tame an (imino)carbene, but at the same time possess sufficient electrophilicity to act as a secondary Lewis acidic site.<sup>30</sup> Herein, we disclose a bis(imino)carbene (with CAAC-based NHIs) which possesses a *dual* ambiphilic nature—both single-site and dual-site reactivity (Figure 1, bottom). Its unique 1,3-ambiphilic character facilitates a reversible intramolecular dearomative [3 + 2] cycloaddition with a proximal arene substituent, giving the carbene the ability to “mask” itself as an air-stable cycloadduct.

The conjugate acid (**1-HOTf**) of the desired carbene **1** was readily obtained by reaction of  $[\text{Me}^c\text{CAACBr}]\text{Br}$  with formamidinium hydrochloride in the presence of excess triethylamine, followed by anion exchange (Scheme 1). Treating **1-HOTf** with  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  in THF at  $-78^\circ\text{C}$  immediately afforded a bright yellow solution, which decolorized upon warming to room temperature. Variable temperature NMR monitoring revealed the initial formation of the target bis(imino)carbene **1**, which is stable up to  $-20^\circ\text{C}$ . The  $^1\text{H}$

Received: December 2, 2022

Published: January 17, 2023



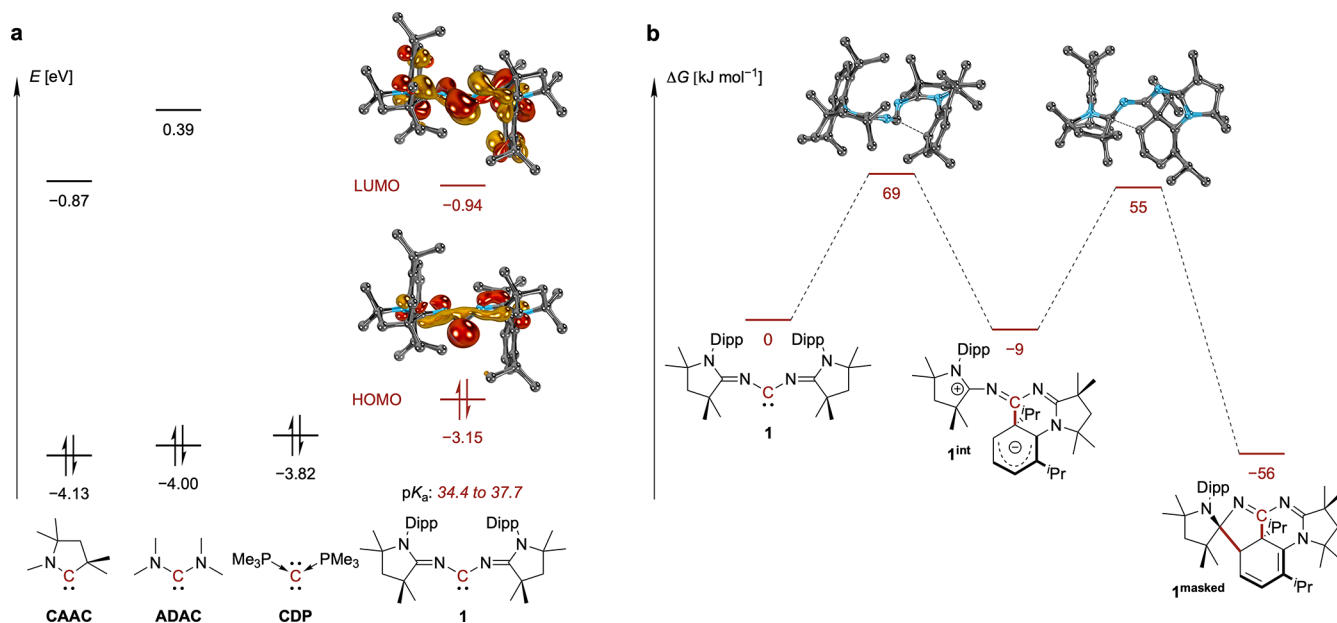
**Scheme 1. Synthesis of Bis(imino)carbene 1, its Isomerization to 1<sup>masked</sup>, and Solid-State Structure of 1<sup>masked</sup>**


NMR spectrum displays only one set of signals associated with the two NHI units. The characteristic carbene signal appears at 234.9 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR, in excellent agreement with DFT calculations (233.8 ppm). This shift falls between those of CAACs (ca. 310 ppm)<sup>31</sup> and NHCs (ca. 210 ppm),<sup>32</sup> and is slightly upfield-shifted compared to acyclic ( $^i\text{Pr}_2\text{N}$ )<sub>2</sub>C: (255.5 ppm).<sup>33</sup> Above  $-20\text{ }^\circ\text{C}$ , **1** rearranges quantitatively to an unsymmetrical species with two inequivalent NHI units. Single crystals of this isomer were obtained by slow evaporation of a

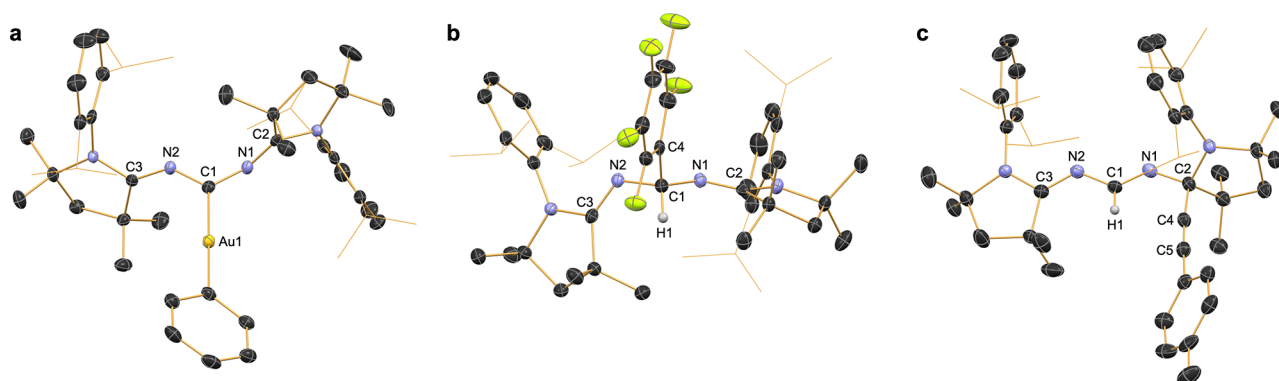
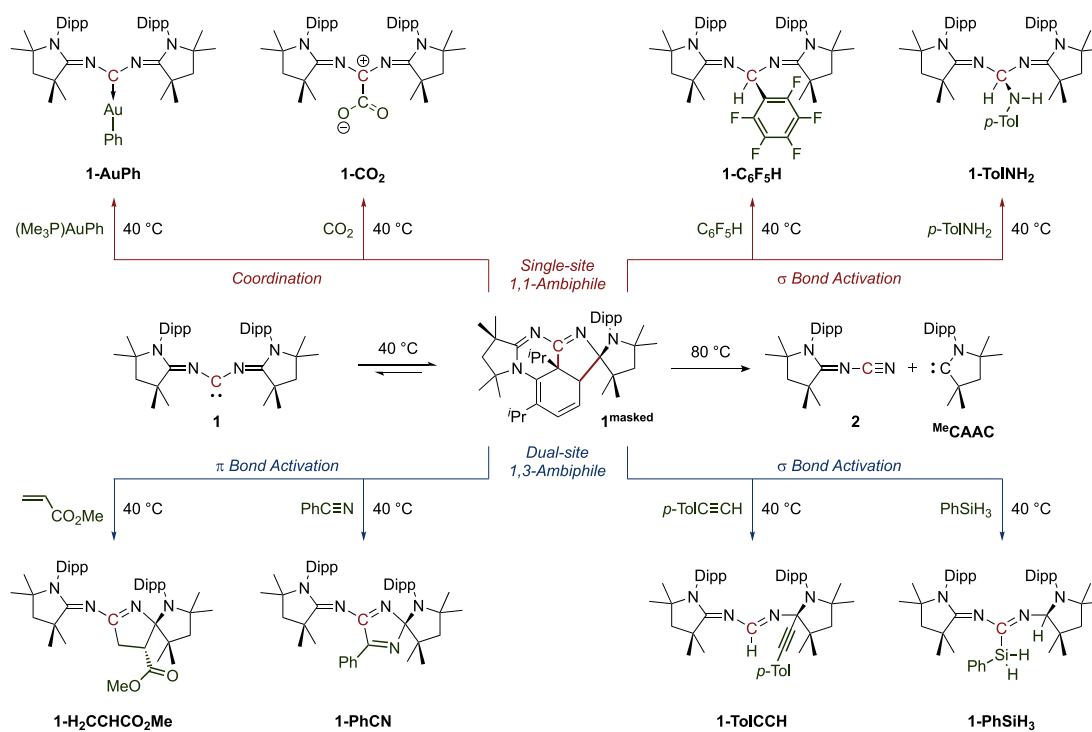
benzene solution at room temperature. X-ray diffraction analysis revealed the polycyclic compound **1<sup>masked</sup>**, resulting from a [3 + 2] cycloaddition involving the dearomatization of a Dipp (2,6-diisopropylphenyl) substituent (Scheme 1). Non-activated arenes generally do not participate in cycloaddition chemistry without photochemical activation or transition metal mediation,<sup>34</sup> with the exception of transient triplet carbenes<sup>35,36</sup> or extremely ambiphilic main group centers (B, Al, Si, P).<sup>23–25,37–45</sup> Hence, bis(imino)carbene **1** represents the first *singlet* carbene able to thermally activate an inert arene ring.

This unprecedented behavior led us to perform DFT analysis to gain further insights. Interestingly, while the HOMO of **1** is centered on the central carbene carbon, the LUMO is a  $\pi$ -type orbital with contributions from the carbene carbon and the peripheral CAAC carbon atoms, supporting the notion of having both carbene-centered and CAAC-centered acceptor sites (Figure 2a). The effect of having strong donor NHI substituents on bis(imino)carbene **1** is reflected by the very high HOMO energy level relative to those of other nucleophilic carbenes such as CAAC and acyclic di(amino)carbenes ADAC. In fact, its donor strength even exceeds that of carbenes, e.g., carbodiphosphorane CDP, which formally feature a zerovalent carbon atom bearing two electron lone pairs.<sup>46</sup> As such, we set out to determine experimentally the basicity of bis(imino)carbene **1**. Our group recently reported a systematic approach to scale carbene Brønsted basicity by proton exchange between the carbene conjugate acid and a neutral organic superbases.<sup>47</sup> While **1-HOTf** could be cleanly deprotonated by the Schwesinger phosphazene ((Me<sub>2</sub>N)<sub>3</sub>PN)<sub>3</sub>PN<sup>t</sup>Bu, an equilibrium was established with the cyclic bent allene (PhN(XyO)C)<sub>2</sub>C, while the carbene (Ph<sub>3</sub>P)<sub>2</sub>C was unable to deprotonate **1-HOTf**. These investigations suggest that **1** has a pK<sub>a</sub> value between 34.4 and 37.7 in acetonitrile, ranking it among the most basic carbenes and organic superbases.

We next turned our attention to elucidating the mechanism of the [3 + 2] cycloaddition. Computations suggest a two-step



**Figure 2.** (a) Calculated HOMO and LUMO energy levels of **1** with comparisons to representative carbene and carbene systems ( $r^2\text{SCAN-3c}$ ). (b) Calculated mechanism of the dearomative [3 + 2] cycloaddition of **1** to **1<sup>masked</sup>** (DLPNO-CCSD(T)(CPCM=THF)/def2-TZVPV// $r^2\text{SCAN-3c}$ ).

Scheme 2. Reactivity of “Masked” Carbene  $1^{\text{masked}}$  as a Carbon-Based *Dual* Amphiphile

**Figure 3.** Solid-state structures of **1-AuPh** (a), **1-C<sub>6</sub>F<sub>5</sub>H** (b), and **1-TolCCH** (c). Thermal ellipsoids set at 50% probability. For clarity, H atoms are omitted and <sup>i</sup>Pr groups are simplified as wireframes.

closed-shell process (Figure 2b). First, **1** undergoes a dearomative nucleophilic attack on the *ortho* position of the Dipp to form the zwitterionic Meisenheimer-type intermediate **1<sup>int</sup>**.<sup>48</sup> Subsequent charge recombination between the *meta* position of the Dipp and the CAAC carbon closes the ring to afford **1<sup>masked</sup>**. The small activation barrier (69 kJ mol<sup>-1</sup>) associated with the initial dearomatization event is a manifestation of the pronounced nucleophilic character of **1**.

Reversible bond activation plays a central role in transition metal catalysis. Recently, a few reports have emerged showing that highly ambiphilic main group systems can not only activate inert arenes but also do so in a reversible fashion.<sup>23–25,42–45</sup> DFT analysis suggested that the energy difference between **1** and **1<sup>masked</sup>** was only 56 kJ mol<sup>-1</sup>, and that the barrier for rearomatization of **1<sup>masked</sup>** to **1** was 125 kJ mol<sup>-1</sup>, hinting at the possibility of regenerating **1** by cycloreversion (Figure 2b). Hence, we set out to confirm the equilibrium between **1<sup>masked</sup>** and **1**. Treating **1<sup>masked</sup>** at 40 °C with (Me<sub>3</sub>P)AuPh, a transition metal complex well-known to

react with nucleophilic carbenes,<sup>10</sup> led to the quantitative conversion of **1<sup>masked</sup>** to a new species with equivalent NHI units (Scheme 2). In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, a diagnostic signal at 220.3 ppm was observed, which is slightly upfield-shifted with respect to “free” carbene **1** (234.9 ppm). X-ray diffraction analysis confirmed the formation of bis(imino)-carbene-gold complex **1-AuPh** (Figure 3a). Hence, **1<sup>masked</sup>** acts as a surrogate of “free” carbene **1** and consequently can be regarded as a “masked” carbene.

The utility of **1<sup>masked</sup>** as a “masked” bis(imino)carbene is not limited to the formation of transition metal complexes, but can also be harnessed for the  $\sigma$  bond activation of simple organic molecules. Gentle heating of **1<sup>masked</sup>** at 40 °C in the presence of C<sub>6</sub>F<sub>5</sub>H and *p*-TolNH<sub>2</sub> led to single-site C–H and N–H bond insertions, affording 1,1-addition products **1-C<sub>6</sub>F<sub>5</sub>H** (Figure 3b) and **1-TolNH<sub>2</sub>** respectively, highlighting the carbene character of **1** (Scheme 2). Interestingly, with *p*-TolCCH and PhSiH<sub>3</sub>, nonclassical C–H and Si–H dual-site 1,3-addition products **1-TolCCH** (Figure 3c) and **1-PhSiH<sub>3</sub>** were obtained

respectively (Scheme 2). This reactivity suggests that the secondary acceptor site on the CAAC carbon is more sterically hindered, allowing exclusively small anionic fragments such as *p*-TolCC<sup>-</sup> and H<sup>-</sup> to slip in. Overall, we show that **1**<sup>masked</sup> is amenable toward C–H bond activation in both single- and dual-site fashion, with selectivity governed by the substrate size (C<sub>6</sub>F<sub>5</sub>H versus *p*-TolCCH). Moreover, for the dual-site activation of *p*-TolCCH and PhSiH<sub>3</sub>, the position of the H atom (carbene- versus CAAC-center) is determined by its protic or hydridic nature, in line with frustrated Lewis pair systems.<sup>49</sup>

We then turned our attention to  $\pi$  bond activation. While carbenes are known to undergo [2 + 1] cycloaddition with alkenes, **1**<sup>masked</sup> undergoes a nonclassical [3 + 2] cycloaddition with methyl acrylate at 40 °C to afford **1**-H<sub>2</sub>CCHCO<sub>2</sub>Me as a single diastereomer, which was confirmed by X-ray diffraction analysis (Scheme 2). Arguably, this stems from the preference of **1** to form a five-membered ring instead of a strained three-membered ring. Notably, such a reactivity pattern resembles nitrile ylides, which are highly reactive species that participate in 1,3-dipolar cycloaddition reactions.<sup>50</sup> The 1,3- $\pi$  bond activation can also be extended to the triple bond of benzonitrile to afford **1**-PhCN, which was characterized by X-ray diffraction spectroscopy (Scheme 2). While nitriles are generally considered to be electron-rich species which undergo electrophilic activations, the facile nature of the cycloaddition with benzonitrile reflects the exceptionally strong nucleophilic character of bis(imino)carbene **1**.

To date, only one type of air-stable carbene has been reported, which is based on the NHC scaffold.<sup>51</sup> Its stability has been attributed to the strong electronic perturbation by the two halogen atoms at the 4, 5-position of the imidazole ring, with the overall effect of sharply reducing the carbene's basicity and electrophilicity, hence attenuating its reactivity. To evaluate the air stability of **1**<sup>masked</sup>, we exposed a powder sample to air and moisture at room temperature. Impressively, no sign of decomposition was observed by <sup>1</sup>H NMR even after a month, reflecting its air-stable nature, despite **1** being superbasic. **1**<sup>masked</sup> also appears to be remarkably air-persistent in C<sub>6</sub>D<sub>6</sub>, with a half-life of 13 h. Importantly, subjecting **1**<sup>masked</sup> to CO<sub>2</sub> (1 bar) at 40 °C in the presence of air and moisture quantitatively afforded **1**-CO<sub>2</sub> as confirmed by X-ray crystallography, thereby establishing its status as an air-stable carbene surrogate (Scheme 2).<sup>52</sup> Next, we set out to probe its thermal stability. Heating **1**<sup>masked</sup> at 80 °C for 1 h led to its conversion to NHI-substituted nitrile **2** and MeCAAC (Scheme 2). This presumably involves the cycloreversion of **1**<sup>masked</sup> to **1**, followed by cheletropic fragmentation to **2** and MeCAAC. Notably, this process is reminiscent of the release of N<sub>2</sub> from diazoalkanes in the generation of transient carbenes.

In conclusion, we disclose the synthesis of the acyclic bis(imino)carbene **1**, which is a carbon-based dual ambiphile. Its unique 1,3-ambiphilic nature facilitates an unprecedented intramolecular dearomative [3 + 2] cycloaddition with the proximal Dipp group to furnish **1**<sup>masked</sup>, which is air-stable in the solid state despite its superbasic nature. Importantly, this process is fully reversible, and cycloreversion to regenerate “free” carbene **1** proceeds under mild conditions. This allows **1**<sup>masked</sup> to be directly employed as an air-stable “masked” carbene, providing access to coordination compounds, and elicit both single- and dual-site activation of simple organic substrates, showcasing its dual ambiphilic nature. We perceive that our present strategy opens an avenue to discover new

carbene reactivity and applications beyond that known for classical single-site ambiphilic carbenes.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c12847>.

General methods and materials, experimental procedures and characterization data, X-ray structure determination, computational details, NMR spectra, and crystallographic data (PDF)

### Accession Codes

CCDC 2215574–2215580 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## ■ AUTHOR INFORMATION

### Corresponding Author

Guy Bertrand – UCSD–CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, United States; [orcid.org/0000-0003-2623-2363](https://orcid.org/0000-0003-2623-2363); Email: [guybertrand@ucsd.edu](mailto:guybertrand@ucsd.edu)

### Authors

Ying Kai Loh – UCSD–CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, United States; [orcid.org/0000-0003-4019-5458](https://orcid.org/0000-0003-4019-5458)

Mohand Melaimi – UCSD–CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, United States

Dominik Munz – Coordination Chemistry, Saarland University, 66123 Saarbrücken, Germany; [orcid.org/0000-0003-3412-651X](https://orcid.org/0000-0003-3412-651X)

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.2c12847>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the NSF (CHE-1954380). Thanks are due to A\*STAR for a postdoctoral fellowship for Y.K.L. The authors gratefully acknowledge the scientific support and HPC resources provided by the Erlangen National High Performance Computing Center (NHR@FAU) of the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU). The hardware is funded by the German Research Foundation (DFG). We would also like to thank Dr. M. Gembicky (for X-ray crystallographic analyses) and Dr. A. Mrse (for VT-NMR studies).

## ■ REFERENCES

(1) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. Stable carbenes. *Chem. Rev.* **2000**, *100*, 39–91.

- (2) Arduengo, A. J., III; Harlow, R. L.; Kline, M. A stable crystalline carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
- (3) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. Analogous  $\alpha,\alpha$ -bis-carbenoid triply bonded species: synthesis of a stable  $\lambda^3$ -phosphinocarbene– $\lambda^3$ -phosphaacetylene. *J. Am. Chem. Soc.* **1988**, *110*, 6463–6466.
- (4) Bellotti, P.; Koy, M.; Hopkinson, M. N.; Glorius, F. Recent advances in the chemistry and applications of N-heterocyclic carbenes. *Nat. Rev. Chem.* **2021**, *5*, 711–725.
- (5) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. Facile splitting of hydrogen and ammonia by nucleophilic activation at a single carbon center. *Science* **2007**, *316*, 439–441.
- (6) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Stable singlet carbenes as mimics for transition metal centers. *Chem. Sci.* **2011**, *2*, 389–399.
- (7) Munz, D.; Meyer, K. Charge frustration in ligand design and functional group transfer. *Nat. Chem. Rev.* **2021**, *5*, 422–439.
- (8) Drance, M. J.; Tanushii, A.; Radosevich, A. T. Two-site O–H addition to an iridium complex featuring a nonspectator tricoordinate phosphorus ligand. *J. Am. Chem. Soc.* **2022**, *144*, 20243–20248.
- (9) Ochiai, T.; Franz, D.; Inoue, S. Applications of N-heterocyclic imines in main group chemistry. *Chem. Soc. Rev.* **2016**, *45*, 6327–6344.
- (10) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* **2014**, *510*, 485–496.
- (11) Nesterov, V.; Reiter, D.; Bag, P.; Frisch, P.; Holzner, R.; Porzelt, A.; Inoue, S. NHCs in main group chemistry. *Chem. Rev.* **2018**, *118*, 9678–9842.
- (12) Dielmann, F.; Back, O.; Henry-Ellinger, M.; Jerabek, P.; Frenking, G.; Bertrand, G. A crystalline singlet phosphinonitrene: a nitrogen atom–transfer agent. *Science* **2012**, *337*, 1526–1528.
- (13) Franz, D.; Szilvási, T.; Irran, E.; Inoue, S. A monotypic aluminum telluride with an Al=Te double bond stabilized by N-heterocyclic carbenes. *Nat. Commun.* **2015**, *6*, 10037.
- (14) Wünsche, M. A.; Witteler, T.; Dielmann, F. Lewis base free oxophosphonium ions: tunable, trigonal-planar Lewis acids. *Angew. Chem., Int. Ed.* **2018**, *57*, 7234–7239.
- (15) Loh, Y. K.; Fuentes, M. Á.; Vasko, P.; Aldridge, S. Successive protonation of an N-heterocyclic imine derived carbonyl: super-electrophilic dication versus masked acylium ion. *Angew. Chem., Int. Ed.* **2018**, *57*, 16559–16563.
- (16) Mehlmann, P.; Witteler, T.; Wilm, L. F. B.; Dielmann, F. Isolation, characterization and reactivity of three-coordinate phosphorus dicationic isoelectronic to alanes and silylium cations. *Nat. Chem.* **2019**, *11*, 1139–1143.
- (17) Inoue, S.; Leszczyńska, K. An acyclic imino-substituted silylene: synthesis, isolation and its facile conversion into a zwitterionic silaimine. *Angew. Chem., Int. Ed.* **2012**, *51*, 8589–8593.
- (18) Lui, M. W.; Merten, C.; Ferguson, M. J.; McDonald, R.; Xu, Y.; Rivard, E. Contrasting reactivities of silicon and germanium complexes supported by an N-heterocyclic guanidine ligand. *Inorg. Chem.* **2015**, *54*, 2040–2049.
- (19) Ochiai, T.; Franz, D.; Irran, E.; Inoue, S. Formation of an imino-stabilized cyclic tin(II) cation from an amino(imino)-stannylene. *Chem.—Eur. J.* **2015**, *21*, 6704–6707.
- (20) Ochiai, T.; Franz, D.; Wu, X.-N.; Inoue, S. Isolation of a germanium(II) cation and a germylene iron carbonyl complex utilizing an imidazolin-2-iminato ligand. *Dalton Trans.* **2015**, *44*, 10952–10956.
- (21) Ochiai, T.; Franz, D.; Wu, X.-N.; Irran, E.; Inoue, S. A tin analogue of carbenoid: isolation and reactivity of a lithium bis(imidazolin-2-imino)stannylene. *Angew. Chem., Int. Ed.* **2016**, *55*, 6983–6987.
- (22) Ochiai, T.; Szilvási, T.; Franz, D.; Irran, E.; Inoue, S. Isolation and structure of germylene-germyliumylidenes stabilized by N-heterocyclic imines. *Angew. Chem., Int. Ed.* **2016**, *55*, 11619–11624.
- (23) Wendel, T. D.; Porzelt, A.; Herz, F. A. D.; Sarkar, D.; Jandl, C.; Inoue, S.; Rieger, B. From Si(II) to Si(IV) and back: reversible intramolecular carbon–carbon bond activation by an acyclic iminosilylene. *J. Am. Chem. Soc.* **2017**, *139*, 8134–8137.
- (24) Wendel, D.; Reiter, D.; Porzelt, A.; Altmann, J.; Inoue, S.; Rieger, B. Silicon and oxygen's bond of affection: an acyclic three-coordinate silanone and its transformation to an iminosiloxysilylene. *J. Am. Chem. Soc.* **2017**, *139*, 17193–17198.
- (25) Eisner, T.; Kostenko, A.; Hanusch, F.; Inoue, S. Room temperature observable interconversion between Si(IV) and Si(II) via reversible intramolecular insertion into an aromatic C–C bond. *Chem.—Eur. J.* **2022**, *28*, No. e202202330.
- (26) Zhao, X.-X.; Fujimori, S.; Kelly, J. A.; Inoue, S. Isolation and reactivity of stannyleneoids stabilized by amido/imino ligands. *Chem.—Eur. J.* **2023**, *29*, No. e202202712.
- (27) Melaimi, M.; Jazzar, R.; Soleilhavoup, M.; Bertrand, G. Cyclic (alkyl)(amino)carbenes (CAACs): recent developments. *Angew. Chem., Int. Ed.* **2017**, *56*, 10046–10068.
- (28) Kushvaha, S. K.; Mishra, A.; Roesky, H. W.; Mondal, K. C. Recent advances in the domain of cyclic (alkyl)(amino) carbenes. *Chem.—Asian J.* **2022**, *17*, No. e202101301.
- (29) Kim, H.; Lee, E. Ambiphilic singlet carbenes: electron donors and acceptors. *Bull. Korean Chem. Soc.* **2022**, *43*, 1328–1341.
- (30) Goettel, J. T.; Gao, H.; Dotzauer, S.; Braunschweig, H. <sup>Me</sup>CAAC=N<sup>−</sup>: A cyclic (alkyl)(amino)carbene imino ligand. *Chem.—Eur. J.* **2020**, *26*, 1136–1143.
- (31) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. Stable cyclic (alkyl)(amino)carbenes as rigid or flexible, bulky, electron-rich ligands for transition-metal catalysts: a quaternary carbon atom makes the difference. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705–5709.
- (32) Dröge, T.; Glorius, F. The measure of all rings—N-heterocyclic carbenes. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940–6952.
- (33) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. Bis(diisopropylamino)carbene. *Angew. Chem., Int. Ed.* **1996**, *35*, 1121–1123.
- (34) Remy, R.; Bochet, C. G. Arene–alkene cycloaddition. *Chem. Rev.* **2016**, *116*, 9816–9849.
- (35) Buchner, E.; Curtius, T. Ueber die einwirkung von diazoessigäther auf aromatische kohlenwasserstoffe. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2377–2379.
- (36) Perera, T. A.; Reinheimer, E. W.; Hudnall, T. W. Photochemically switching diamidocarbene spin states leads to reversible Büchner ring expansions. *J. Am. Chem. Soc.* **2017**, *139*, 14807–14814.
- (37) Suzuki, H.; Tokitoh, N.; Okazaki, R. A novel reactivity of a silylene: the first examples of [1 + 2] cycloaddition with aromatic compounds. *J. Am. Chem. Soc.* **1994**, *116*, 11572–11573.
- (38) Liu, L. L.; Zhou, J.; Cao, L. L.; Andrews, R.; Falconer, R. L.; Russell, C. A.; Stephan, D. W. A transient vinylphosphinidene via a phosphirene–phosphinidene rearrangement. *J. Am. Chem. Soc.* **2018**, *140*, 147–150.
- (39) Liu, L. L.; Zhou, J.; Andrews, R.; Stephan, D. W. A room-temperature-stable phosphanorcaradiene. *J. Am. Chem. Soc.* **2018**, *140*, 7466–7470.
- (40) Liu, L. L.; Cao, L. L.; Zhou, J.; Stephan, D. W. Facile cleavage of the P=P double bond in vinyl-substituted diphosphenes. *Angew. Chem., Int. Ed.* **2019**, *58*, 273–277.
- (41) Guo, R.; Jiang, J.; Hu, C.; Liu, L. L.; Cui, P.; Zhao, M.; Ke, Z.; Tung, C.-H.; Kong, L. BNN-1,3-dipoles: isolation and intramolecular cycloaddition with unactivated arenes. *Chem. Sci.* **2020**, *11*, 7053–7059.
- (42) Liu, L. L.; Zhou, J.; Cao, L. L.; Kim, Y.; Stephan, D. W. Reversible intramolecular cycloaddition of phosphalkene to an arene ring. *J. Am. Chem. Soc.* **2019**, *141*, 8083–8087.
- (43) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. Reversible, room-temperature C–C bond activation of benzene by an isolable metal complex. *J. Am. Chem. Soc.* **2019**, *141*, 11000–11003.
- (44) Su, Y.; Do, D. C. H.; Li, Y.; Kinjo, R. Metal-free selective borylation of arenes by a diazaborinine via C–H/C–F bond activation and dearomatization. *J. Am. Chem. Soc.* **2019**, *141*, 13729–13733.

(45) Zhang, X.; Liu, L. L. Modulating the frontier orbitals of an aluminylene for facile dearomatization of inert arenes. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202116658.

(46) Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. Carbodiphosphoranes: the chemistry of divalent carbon(0). *Angew. Chem., Int. Ed.* **2006**, *45*, 8038–8042.

(47) Vermersch, F.; Yazdani, S.; Junor, G. P.; Grotjahn, D. B.; Jazsar, R.; Bertrand, G. Stable singlet carbenes as organic superbases. *Angew. Chem., Int. Ed.* **2021**, *60*, 27253–27257.

(48) Rohrbach, S.; Smith, A. J.; Pang, J. H.; Poole, D. L.; Tuttle, T.; Chiba, S.; Murphy, J. A. Concerted nucleophilic aromatic substitution reactions. *Angew. Chem., Int. Ed.* **2019**, *58*, 16368–16388.

(49) Stephan, D. W. The broadening reach of frustrated Lewis pair chemistry. *Science* **2016**, *354*, aaf7229.

(50) Janulis, E. P. D., Jr.; Wilson, S. R.; Arduengo, A. J., III The synthesis and structure of a stabilized nitrilium ylide. *Tetrahedron Lett.* **1984**, *25*, 405–408.

(51) Arduengo, A. J., III; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. An air stable carbene and mixed carbene “dimers”. *J. Am. Chem. Soc.* **1997**, *119*, 12742–12749.

(52) Sugahara, T.; Guo, J.-D.; Hashizume, D.; Sasamori, T.; Tokitoh, N. Reversible isomerizations between 1,4-digerma-benzenes and 1,4-digerma-dewar-benzenes: air-stable activators for small molecules. *J. Am. Chem. Soc.* **2019**, *141*, 2263–2267.

## Recommended by ACS

### Direct Transformation of SiH<sub>4</sub> to a Molecular L(H)<sub>2</sub>Co=Si=Co(H)<sub>2</sub>L Silicide Complex

Rex C. Handford, T. Don Tilley, *et al.*

JANUARY 25, 2023  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

### Photoinduced Halogen-Atom Transfer by *N*-Heterocyclic Carbene-Ligated Boryl Radicals for C(sp<sup>3</sup>)-C(sp<sup>3</sup>) Bond Formation

Ting Wan, Timothy Noël, *et al.*

DECEMBER 30, 2022  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

### Al-Sc Bonded Complexes: Synthesis, Structure, and Reaction with Benzene in the Presence of Alkyl Halide

Genfeng Feng, Makoto Yamashita, *et al.*

DECEMBER 05, 2022  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

### Air and Moisture Stable *para*- and *ortho*-Quinodimethane Derivatives Derived from *bis-N*-Heterocyclic Olefins

Subhadip Jana, Anukul Jana, *et al.*

JANUARY 20, 2023  
ORGANIC LETTERS

READ 

Get More Suggestions >