Realizing Metal-Free Carbene-Catalyzed Carbonylation Reactions with CO

Jesse L. Peltier,^a Eder Tomás-Mendivil,^{a,b} Daniel R. Tolentino,^a Max M. Hansmann,^a Rodolphe Jazzar,^a Guy Bertrand^{a*}

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

^b Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country (UPV-EHU), Donostia-San Sebastián, 20018 Gipuzkoa, Spain

Supporting Information Placeholder

ABSTRACT: Many organic and main group compounds, usually acids or bases, can accelerate chemical reactions when used in substoichiometric quantities, a process known as organocatalysis. In marked contrast, very few of these compounds are able to activate carbon monoxide and, until now, none of them catalyze its chemical transformation, a classical task for transition metals. Herein, we report that a stable singlet ambiphilic carbene activates CO and catalytically promotes the carbonylation of an *ortho*-quinone into a cyclic carbonate. These findings pave the way for the discovery of metal-free catalyzed carbonylation reactions.

At the end of the 19th century, Sabatier discovered that thin slivers of reduced nickel could promote the addition of H₂ to ethylene. Afterwards, it was widely accepted that a transition metal was required to activate small molecules in all chemical and biological systems¹, and to promote their reaction with substrates. However, in the last decade, a handful of main group compounds have been shown to achieve the same task,² as exemplified by the hydrogenation of multiple bonds using a Frustrated Lewis Pair.³ In 2007, we wrote that in possessing a lone pair of electrons and an accessible vacant orbital, singlet carbenes resemble transition metal centers, and thus could potentially mimic their chemical behavior.^{4,5} Indeed, some stable electrophilic carbenes can split enthalpically strong bonds like BH, SiH, PH, NH,⁶ and even CH⁷ and CF bonds,⁸ as well as challenging molecules like H₂ and NH₃.^{4,9} Additionally, it has recently been shown that a reductive elimination at carbon could also occur.¹⁰ However, the third essential step of a classical transition metal catalytic cycle, namely the transformation of the reactants, is hampered by the lack of reactivity of CH and CF bonds. This analysis prompted us to turn our attention to catalytic carbonylation reactions with carbon monoxide, a task so far restricted to transition metals.¹¹ Although CO is one of the most inert molecules (bond-dissociation energy of 1072 vs 432 kJ/mol for H₂), it is known to react with ambiphilic carbenes to give the corre-

sponding ketenes.¹² The latter are very reactive, and thus the working hypothesis relied on the possibility that ketenes would react with a substrate, and that the resulting adduct would undergo a reductive elimination, releasing the product and regenerating the carbene. As a proof of principle, herein we report that selected singlet carbenes can promote the stoichiometric and even catalytic carbonylation of an *ortho*-quinone into a cyclic carbonate.

We started our investigation by performing stoichiometric reactions representing the different elementary steps of the putative catalytic cycle. First, the carbene must react with CO to form a ketene. From a computational study, Frenking *et al.* concluded that only carbenes featuring a sufficiently small singlet-triplet (S/T) gap could yield stable ketenes.¹³ This result prompted us to consider the bicyclic (alkyl)(amino)carbene **BiCAAC**¹⁴ and the cyclic (alkyl)(amino)carbene **CAAC**,^{15,16} which feature a S/T gap of 45.7 and 49.2 kcal/mol, respectively. Indeed, these two carbenes instantaneously react with carbon monoxide in benzene or THF at room temperature to afford the corresponding ketenes **Ket-1** and the previously reported **Ket-2**,^{12a} which were isolated in 85 and 90% yield, respectively (Scheme 1A).

The second step involves the reaction between amino-ketenes and an *ortho*-quinone to give the corresponding lactones, akin to the reactivity of alkyl and aryl substituted ketenes (RR'C=O).¹⁷ Indeed, the reaction of **Ket-1** and **Ket-2** with 9,10-phenanthrenequinone (**Quin**) at room temperature quickly and quantitatively led to the corresponding [4+2] cycloadducts **Lact-1** and **Lact-2** as single diastereomers (Scheme 1A), despite the introduction of a new chiral center (*vide infra*).

To check the feasibility of the reductive elimination, we first treated **Lact-1** and **Lact-2** with elemental sulfur, a classical trapping agent for singlet carbenes.^{10a} In the case of **Lact-1**, heating at 80 °C for 16 hours in THF was necessary to obtain **Thio-1** along with the release of the cyclic carbonate **Carbo-1** (Scheme 1B). With **Lact-2** derived from **CAAC**, we were pleased to observe the clean formation of the thiolactam **Thio-2** along with a quantitative amount

of carbonate **Carbo-1** after 16 hours at room temperature. Since **Lact-1** and **Lact-2** can be regarded as products resulting from the insertion of carbenes into the C-O single bond of the corresponding cyclic carbonates, we also investigated the reaction of **BiCAAC** and **CAAC** with **Carbo-1** and observed the clean formation of the corresponding spirolactones **Lact-1** and **Lact-2**, again as a single diastereomer (Scheme 1C). These results demonstrate the reversibility of the reductive elimination step.

Scheme 1. Stoichiometric reactions mimicking the elementary steps of the postulated catalytic cycle.

To understand the diastereoselectivity of the process, we reacted **BiCAAC** with ethylene carbonate (**Carbo-2**) in C₆D₆ at room temperature. The ¹H NMR analysis showed the formation of a 74/26 mixture of **Lact-3'**/**Lact-3** diastereomers (Scheme 1D). By heating the mixture at 80 °C the ratio was reversed towards the

thermodynamic product (**Lact-3**). This mixture also reacted at 80 °C with elemental sulfur leading to **Thio-1** and **Carbo-2**. Importantly, these observations strongly suggest that unlike in organometallic catalysis,¹⁸ the reductive elimination involves a polar stepwise process *via* opened (**o-Bet**) and closed betaines (**c-Bet**).¹⁹ We believe that the diastereoselectivity observed with the *ortho*-quinone is due to the better leaving group ability of the phenoxy anion, which facilitates the formation of the opened betaines, and thus hampered the observation of the kinetic diastereomers.

To close the catalytic cycle, we reacted the spirolactones with carbon monoxide (Scheme 1E). With **Lact-1**, no reaction was observed at room temperature, even under 4 atm of carbon monoxide. However, heating a C₆D₆ solution of **Lact-1** under 4 atm of CO at 80 °C for 16 hours led to **Carbo-1** and a black residue from **BiCAAC** decomposition, which was not characterized. With **Lact-2**, under 4 atm of CO, at room temperature, the solution turned slightly blue, indicating the formation of **Ket-2**, which was confirmed by the observation of the characteristic ¹³C NMR CCO signal at 278.8 ppm.^{12a} Notably, 1 atm of CO was insufficient to observe any reaction, which demonstrates that this process is CO pressure-dependent.

Scheme 2. Proposed mechanism and energy diagram. DFT calculations at B3LYP-D3/def2-TZVP level (Gibbs energies in kcal/mol). For clarity, *ortho*-benzoquinone is shown, although all calculations have been done for 9,10-phenanthrenequinone (Quin**).**

Encouraged by these results, we investigated the hypothetical catalytic process computationally (B3LYP-D3/def2-TZVP), as shown in Scheme 2, employing **BiCAAC**, sterically encumbered **CAAC** and small **CAAC^{Me}** for comparison. The formation of ketenes is predicted to be exergonic in every case. Similarly, the reaction between the ketenes and 9,10-phenanthrenequinone (**Quin**)

leading to spirolactones (**Lact**) are exergonic; the latter are the most stable intermediates, and thus can be regarded as the resting state of the catalytic cycle. Note that the relative energies between **o-Bet**, **c-Bet** and free carbonate plus **CAAC** are negligible and the overall transformation is exergonic. Importantly, calculations indicate that the reductive elimination step should be possible with all carbenes, although significantly easier with the bulky **CAAC** than with **BiCAAC** and **CAAC^{Me}**.

Together, the experimental and computational results discussed above suggested that a catalytic reaction should be achievable. We were delighted to find that indeed, with only 10 mol% **CAAC** in benzene after 40 hours at 60 °C under 4 atm of CO, the carbonylation of 9,10-phenanthrenequinone (**Quin**) was achieved and gave **Carbo-1** in 80% isolated yield (Scheme 3).

Scheme 3. Organocatalytic carbonylation of Quin-1.

On the other hand, all attempts to use **BiCAAC** and **CAAC^{Me}** as catalysts failed, even upon using more forcing experimental conditions. We discovered that **BiCAAC** and the small **CAAC^{Me}** readily react with **Quin** leading irreversibly to adducts **I**,²⁰ and **II**,²¹ respectively, thus quenching the catalytic cycle (Scheme 4). As a control experiment, we confirmed that the bulky **CAAC** did not react with the α -quinone even at 80 °C and thereby leads to a viable catalyst.

Scheme 4. Deactivation of BiCAAC and CAAC^{Me}

Until now, carbene organocatalysis was limited to weakly basic carbenes featuring large HOMO/LUMO gaps, allowing them to behave as good leaving groups (e.g., thiazol-2-ylidenes,²² 1,2,4-triazol-5-ylidenes,²³ and 1,2,3-triazol-4-ylidenes²⁴). However, this work demonstrates that strongly ambiphilic carbenes such as CAACs are highly desirable in small molecule catalysis. Their electronic properties allow for mimicking all of the elementary steps involved in transition metal catalytic cycles, but their mechanism can be different, as shown by the reductive elimination process described herein, thus opening up new possibilities in catalytic transformations. TM-catalyzed carbonylation reactions are widely applied in industry in large scale employing CO gas as C1-source.¹¹

We are aware that the carbonylation of quinones is not of synthetic utility, but since not only carbenes, but also other low-valent main-group compounds, such as silylenes, phosphinidenes and borylenes are able to bind CO,²⁵ these findings pave the way for the discovery of other metal-free catalyzed carbonylation reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/xxx. Metrical data for the solid-state structures of **Lact-1**, **Lact-2**, **Carbo-1**, **I**, and **II** are available free of charge from the Cambridge Crystallographic Data Centre under reference numbers CCDC-1999858, CCDC-1999855, CCDC-1999854, CCDC-1999857, and CCDC-1999856 respectively.

AUTHOR INFORMATION

Corresponding Author

*guybertrand@ucsd.edu

ORCID

Jesse L. Peltier: 0000-0002-3493-2127

Eder Tomás-Mendivil: 0000-0002-4247-6731

Daniel R. Tolentino: 0000-0003-0151-6001

Max M. Hansmann: 0000-0003-3107-1445

Rodolphe Jazzar: 0000-0002-4156-7826

Guy Bertrand: 0000-0003-2623-2363

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

We are grateful to the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Catalysis Science Program, under Award # DE-SC0009376 for financial support of this work, the Tribal Membership Initiative fellowship administered by the UC San Diego Graduate Division for financial support of J.L.P. E.T.-M. is thankful to the Basque Government for a Doctoral Research Staff Improvement Program scholarship and to Dr. Zoraida Freixa for her support.

REFERENCES

- (1) Pilak, O.; Mamat, B.; Vogt, S.; Hagemeyer, C. H.; Thauer, R. K.; Shima, S.; Vonnrhein, C.; Warkentin, E.; Ermler, U. The Crystal Structure of the Apoenzyme of the Iron-Sulphur Cluster-Free Hydrogenase. *J. Mol. Biol.* **2006**, *358*, 798-809.
- (2) (a) Power, P. P. Main-group elements as transition metals. *Nature* **2010**, *463*, 171-177. (b) Yao, S.-L.; Xiong, Y.; Driess, M. Zwitterionic and donor-stabilized N-Heterocyclic silylenes (NHSis) for metal-free activation of small molecules. *Organometallics* **2011**, *30*, 1748-1767. (c) Melen, R. L. Frontiers in molecular p-block chemistry: From structure to reactivity. *Science* **2019**, *363*, 479-484. (d) Lgar, M. A.; Pranckevicius, C.; Braunschweig, H. Metallomimetic chemistry of boron. *Chem. Rev.* **2019**, *119*, 8231-8261. (e) Moerdijk, J. P.; Schilter, D.; Bielawski, C. W. *N,N*-Diamidocarbenes: Isolable divalent carbons with bona fide carbene reactivity. *Acc. Chem. Res.* **2016**, *49*, 1458-1468. (f) Chu, T.; Nikonov, G. I.

Oxidative addition and reductive elimination at main-group element centers. *Chem. Rev.* **2018**, *118*, 3608–3680.

- (3) (a) Stephan, D. W. The broadening reach of frustrated Lewis pair chemistry. *Science* **2016**, *354*, aaf7229. (b) Lam, J.; Szkop, K. M.; Mosafari, E.; Stephan, D. W. FLP catalysis: Main group hydrogenations of organic unsaturated substrates. *Chem. Soc. Rev.* **2019**, *48*, 3592–3612.
- (4) 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.
- (5) Martin, D.; Soleilhavoup, M.; Bertrand, G. Stable singlet carbenes as mimics for transition metal centers. *Chem. Sci.* **2011**, *2*, 389–399.
- (6) (a) Frey, G. D.; Masuda, J. D.; Donnadieu, B.; Bertrand, G. Activation of Si–H, B–H, and P–H bonds at a single nonmetal center. *Angew. Chem. Int. Ed.* **2010**, *49*, 9444–9447. (b) Würtemberger-Pietsch, S.; Schneider, H.; Marder, T. B.; Radius, U. Adduct formation, B–H activation and ring expansion at room temperature from reactions of HBCat with NHCs. *Chem. Eur. J.* **2016**, *22*, 13032–13036. (c) Mohapatra, C.; Samuel, P. P.; Li, B.; Niepotter, B.; Schurmann, C. J.; Herbst-Irmer, R.; Stalke, D.; Maity, B.; Koley, D.; Roesky, H. W. Insertion of cyclic alkyl(amino) carbene into the Si–H bonds of hydrochlorosilanes. *Inorg. Chem.* **2016**, *55*, 1953–1955. (d) Zhukhovitskiy, A. V.; Mavros, M. G.; Queeney, K. T.; Wu, T.; Van Voorhis, T.; Johnson, J. A. Reactions of persistent carbenes with hydrogen-terminated silicon surfaces. *J. Am. Chem. Soc.* **2016**, *138*, 8639–8652. (e) Lastovickova, D. N.; Bielawski, C. W. Diamidocarbene induced B–H Activation: A new class of initiator-free olefin hydroboration reagents. *Organometallics* **2016**, *35*, 706–712.
- (7) Turner, Z. R. Chemically non-innocent cyclic (alkyl)(amino)carbenes: Ligand rearrangement, C–H and C–F bond activation. *Chem. Eur. J.* **2016**, *22*, 11461–11468.
- (8) Petrasia, E.; Eunsung, L. Activation of C–F, Si–F, and S–F Bonds by N-Heterocyclic Carbenes and Their Isoelectronic Analogues. *Synlett*, **2020**, *31*, 1349–1360.
- (9) Moerdijk, J. P.; Blake, G. A.; Chase, D. T.; Bielawski, C. W. Elucidation of carbene ambiphilicity leading to the discovery of reversible ammonia activation. *J. Am. Chem. Soc.* **2013**, *135*, 18798–18801.
- (10) (a) Tolentino, D. R.; Neale, S. E.; Isaac, C. J.; Macgregor, S. A.; Whitteley, M. K.; Jazsar, R.; Bertrand, G. Reductive elimination at carbon under steric control. *J. Am. Chem. Soc.* **2019**, *141*, 9823–9826. (b) Teator, A. J.; Tian, Y.; Chen, M.; Lee, J. K.; Bielawski, C. W. An Isolable, Photoswitchable N-Heterocyclic Carbene: On-Demand Reversible Ammonia Activation. *Angew. Chem. Int. Ed.* **2015**, *54*, 11559–11563. (c) Eichhorn, A. F.; Fuchs, S.; Flock, M.; Marder, T. B.; Radius, U. Reversible oxidative addition at carbon. *Angew. Chem. Int. Ed.* **2017**, *56*, 10209–10213.
- (11) (a) Beller, M.; Wu, X.-F. *Transition metal catalyzed carbonylation reactions*. Springer: Amsterdam, **2013**. (b) Peng, J. B.; Geng, H. Q.; Wu, X.-F. The chemistry of CO: Carbonylation. *Chem* **2019**, *5*, 526–552.
- (12) (a) Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. CO fixation to stable acyclic and cyclic alkyl amino carbenes: Stable amino ketenes with a small HOMO-LUMO gap. *Angew. Chem. Int. Ed.* **2006**, *45*, 3488–3491. (b) Siemeling, U.; Färber, C.; Bruhn, C.; Leibold, M.; Selent, D.; Baumann, W.; von Hopffgarten, M.; Goedecke, C.; Frenking, G. N-heterocyclic carbenes which readily add ammonia, carbon monoxide and other small molecules. *Chem. Sci.* **2010**, *1*, 697–704. (c) Martin, D.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. An air-stable oxallyl radical cation. *Angew. Chem., Int. Ed.* **2013**, *52*, 7014–7017. (d) Schulz, T.; Färber, C.; Leibold, M.; Bruhn, C.; Baumann, W.; Selent, D.; Porsch, T.; Holthausen, M. C.; Siemeling, U. Carbonylation of the simplest persistent diaminocarbene. *Chem. Commun.* **2013**, *49*, 6834–6836. (e) Mahoney, J. K.; Martin, D.; Thomas, F.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. Air-persistent monomeric (amino)(carboxy) radicals derived from cyclic (alkyl)(amino) carbenes. *J. Am. Chem. Soc.* **2015**, *137*, 7519–7525. (f)

- Paul, U. S. D.; Sieck, C.; Haehnel, M.; Hammond, K.; Marder, T. B.; Radius, U. Cyclic (alkyl)(amino)carbene complexes of rhodium and nickel and their steric and electronic parameters. *Chem. Eur. J.* **2016**, *22*, 11005–11014. (g) Paul, U. S. D.; Radius, U. Synthesis and reactivity of cyclic (alkyl)(amino)carbene stabilized nickel carbonyl complexes. *Organometallics* **2017**, *36*, 1398–1407. (h) Schulz, T.; Färber, C.; Leibold, M.; Bruhn, C.; Prochnow, P.; Bandow, J. E.; Schneider, T.; Porsch, T.; Holthausen, M. C.; Siemeling, U. Diastereoselective synthesis of a bicyclic β -lactam with penicillin G-like spectrum of activity by carbonylation of an acyclic diaminocarbene. *Chem. Commun.* **2014**, *50*, 2341–2343. (i) Hudnall, T. W.; Bielawski, C. W. An *N,N*-diamidocarbene: studies in C–H insertion, reversible carbonylation, and transition-metal coordination chemistry. *J. Am. Chem. Soc.* **2009**, *131*, 16039–16041. (j) Hudnall, T. W.; Moerdijk, J. P.; Bielawski, C. W. Ammonia N–H activation by a *N,N*-diamidocarbene. *Chem. Commun.* **2010**, *46*, 4288–4290.
- (13) Goedecke, C.; Leibold, M.; Siemeling, U.; Frenking, G. When does carbonylation of carbenes yield ketenes? A theoretical study with implications for synthesis. *J. Am. Chem. Soc.* **2011**, *133*, 3557–3569.
- (14) Tomás-Mendivil, E.; Hansmann, M. M.; Weinstein, C. M.; Jazsar, R.; Melaimi, M.; Bertrand, G. Bicyclic (alkyl)(amino)carbenes (BICAACs): Stable carbenes more ambiphilic than CAACs. *J. Am. Chem. Soc.* **2017**, *139*, 7753–7756.
- (15) Lavallo, V.; Canac, Y.; Präsaang, 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 makes the difference! *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709.
- (16) For recent reviews: (a) Soleilhavoup, M.; Bertrand, G. Cyclic (alkyl)(amino)carbenes (CAACs): Stable carbenes on the rise. *Acc. Chem. Res.* **2015**, *48*, 256–266. (b) Melaimi, M.; Jazsar, R.; Soleilhavoup, M.; Bertrand, G. Cyclic (alkyl)(amino)carbenes (CAACs): Recent developments. *Angew. Chem. Int. Ed.* **2017**, *56*, 10046–10068. (c) Paul, U. S. D.; Radius, U. What wanzlick did not dare to dream: cyclic (alkyl)(amino)carbenes (caacs) as new key players in transition-metal chemistry. *Eur. J. Inorg. Chem.* **2017**, 3362–3375. (d) Jazsar, R.; Soleilhavoup, M.; Bertrand, G. Cyclic (alkyl)- and (aryl)-(amino)carbene coinage metal complexes and their applications. *Chem. Rev.* **2020**, *120*, 4141–4168. (e) Roy, S.; Mondal, K. C.; Roesky, H. W. Cyclic alkyl(amino) carbene stabilized complexes with low coordinate metals of enduring nature. *Acc. Chem. Res.* **2016**, *49*, 357–369.
- (17) Allen, A. D.; Tidwell, T. T. Ketenes and other cumulenes as reactive intermediates. *Chem. Rev.* **2013**, *113*, 7287–7342.
- (18) Troisi, L.; Granito, C.; Perrone, S.; Rosato, F. Synthesis of benzo-fused five- and six-membered heterocycles by palladium-catalyzed cyclocarbonylation. *Tetrahedron Lett.* **2011**, *52*, 4330–4332.
- (19) Falivene, L.; Cavallo, L. Guidelines to select the N-heterocyclic carbene for the organopolymerization of monomers with a polar group. *Macromolecules* **2017**, *50*, 1394–1401.
- ((20) A bismuth-ylide is known to react in similar manner, see: Matano, Y.; Rahman, M. M.; Yoshimune, M.; Suzuki, H. Synthesis and reactions of bismuthonium salts and ylides bearing an α -ester group. *J. Org. Chem.* **1999**, *64*, 6924–6927.
- (21) Other group 14 ambiphilic species react in similar manner with ortho-quinones, see among other: (a) Rupar, P. A.; Staroverov, V. N.; Baines, K. M. Reactivity studies of N-heterocyclic carbene complexes of germanium(II). *Organometallics* **2010**, *29*, 4871–4881. (b) Azhakar, R.; Ghadwal, R. S.; Roesky, H. W.; Hey, J.; Stalke, D. Reactions of stable N-heterocyclic silylenes with ketones and 3,5-di-tert-butyl-o-benzoquinone. *Organometallics* **2011**, *30*, 3853–385. (c) Jiang, H.; Chen, F.; Zhu, C.; Zhu, R.; Zeng, H.; Liu, C.; Wu W. Two C–O bond formations on a carbonic carbon: palladium-catalyzed coupling of N-tosylhydrazones and benzo-1,2-quinones to construct benzodioxoles. *Org. Lett.* **2018**, *20*, 3166–3169. On the contrary,

unsaturated NHCs undergo ring-contraction reactions with *ortho*-quinones, see: (d) Ping, L.; Bak, J.; Kim, Y.; Bouffard, J. Addition, substitution, and ring-contraction reactions of quinones with N-heterocyclic carbenes. *J. Org. Chem.* **2018**, *83*, 9240-9249.

(22) Breslow, R. On the Mechanism of Thiamine Action. IV. Evidence from Studies on Model System. *J. Am. Chem. Soc.* **1958**, *80*, 3719-3726.

(23) (a) Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A.; Rovis, T. Organocatalytic reactions enabled by N-heterocyclic carbenes. *Chem. Rev.* **2015**, *115*, 9307-9387. (b) Bugaut X.; Glorius, F. Organocatalytic umpolung: N-heterocyclic carbenes and beyond. *Chem. Soc. Rev.* **2012**, *41*, 3511-3522. (c) Wang, N.; Xu, J.; Lee, J. K. The importance of N-heterocyclic carbene basicity in organocatalysis. *Org. Biomol. Chem.* **2018**, *16*, 8230-8244.

(24) (a) Berry M. T.; Castrejon, D.; Hein J. E. Oxidative esterification of aldehydes using mesoionic 1,2,3-triazolyl carbene organocatalysts. *Org. Lett.* **2014**, *16*, 3676-3679. (b) Liu, W.; Zhao, L. L.; Melaimi, M.; Cao, L.; Xu, X.; Bouffard, J.; Bertrand, G.; Yan, X. Mesoionic Carbene (MIC)-Catalyzed H/D Exchange at Formyl Groups. *Chem.* **2019**, *5*, 2484-2494. (c) Guisado-Barrios, G.; Soleilhavoup, M.; Bertrand, G. 1H-1,2,3-Triazol-5-ylidenes: Readily Available Mesoionic Carbenes. *Acc. Chem. Res.* **2018**, *51*, 3236-3244.

(25) (a) Puschmann, F. F.; Stein, D.; Heift, D.; Hendriksen, C.; Gal, Z. A.; Grützmacher, H.-F.; Grützmacher, H. Phosphination of carbon monoxide: A simple synthesis of sodium phosphaeethynolate (NaOCP). *Angew. Chem. Int. Ed.* **2011**, *50*, 8420-8423. (b) Finze, M.; Bernhardt, E.; Terheiden, A.; Berkei, M.; Willner, H.; Christen, D.; Oberhammer, H.; Aubke, F. Tris(trifluoromethyl)borane carbonyl, (CF₃)₃BCO Synthesis, physical, chemical and spectroscopic properties, gas phase, and solid state structure. *J. Am. Chem. Soc.* **2002**, *124*, 15385-15398. (c) Braunschweig, H.; Dewhurst, R. D.; Hupp, F.; Nutz, M.; Radacki, K.; Tate, C. W.; Vargas, A.; Ye, Q. Multiple complexation of CO and related ligands to a main-group element. *Nature* **2015**, *522*, 327-330. (d) Dahcheh, F.; Martin, D.; Stephan, D. W.; Bertrand, G. Synthesis and reactivity of a CAAC-aminoborylene adduct: A hetero-allene or an organoboron isoelectronic with singlet carbenes. *Angew. Chem. Int. Ed.* **2014**, *53*, 13159-13163. (e) Braunschweig, H.; Krummenacher, I.; Légaré, M.-A.; Matler, A.; Radacki, K.; Ye, Q. Main-group metallomimetics: Transition metal-like photolytic CO substitution at boron. *J. Am. Chem. Soc.* **2017**, *139*, 1802-1805. (f) Hansmann, M. M.; Bertrand, G. The transition metal-like behavior of main group elements: ligand exchange at a phosphinidene. *J. Am. Chem. Soc.* **2016**, *138*, 15885-15888. (g) Hansmann, M. M.; Jazzar, R.; Bertrand, G. Singlet (phosphino)phosphinidenes are electrophilic. *J. Am. Chem. Soc.* **2016**, *138*, 8356-8359. (h) Ganesamoorthy, C.; Schoening, J.; Wölper, C.; Song, L.; Schreiner, P. R.; Schulz, S. A silicon-carbonyl complex stable at room temperature. *Nat. Chem.* **2020**, *12*, 608-614.