

Realizing Metal-Free Carbene-Catalyzed Carbonylation Reactions with CO

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Cite This: <https://dx.doi.org/10.1021/jacs.0c09938>



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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 could 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 *o*-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. Afterward, 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 past 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 frustrated Lewis pairs.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 B–H, Si–H, P–H, N–H,⁶ and even C–H⁷ and C–F bonds⁸ as well as challenging molecules like H₂ and NH₃.^{4,9} Additionally, it has recently been shown that reductive elimination at carbon can 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 C–H and C–F bonds. This analysis prompted us to turn our attention to catalytic carbonylation reactions with carbon monoxide, a task that to date has been restricted to transition metals.¹¹ Although CO is one of the most inert molecules (with a bond dissociation energy of 1072 kJ/mol vs 432 kJ/mol for H₂), it is known to react with ambiphilic carbenes to give the corresponding ketenes.¹² The latter are very reactive, and thus, the working hypothesis relied on the possibility that a ketene 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 select singlet carbenes can promote the stoichiometric and even catalytic carbonylation of an *o*-quinone to give 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.

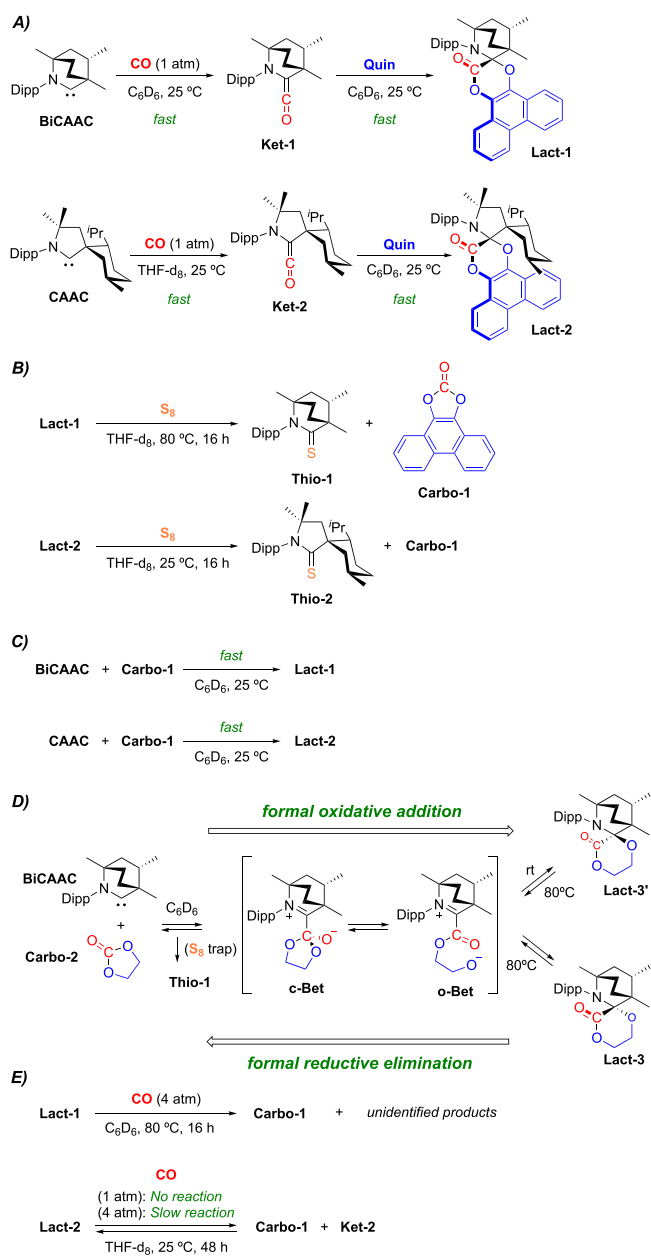
concluded that only carbenes featuring a sufficiently small singlet–triplet (S/T) gap could yield stable ketenes.¹³ This result prompted us to consider the bicyclic (alkyl)(amino)carbene BiCAAC¹⁴ and the cyclic (alkyl)(amino)carbene CAAC,^{15,16} which feature S/T gaps of 45.7 and 49.2 kcal/mol, respectively. 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 *o*-quinone to give the corresponding lactones, akin to the reactivity of alkyl- and aryl-substituted ketenes (RR'C=C=O).¹⁷ Indeed, the reactions 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 h 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 h 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

Received: September 16, 2020

Scheme 1. Stoichiometric Reactions Mimicking the Elementary Steps of the Postulated Catalytic Cycle



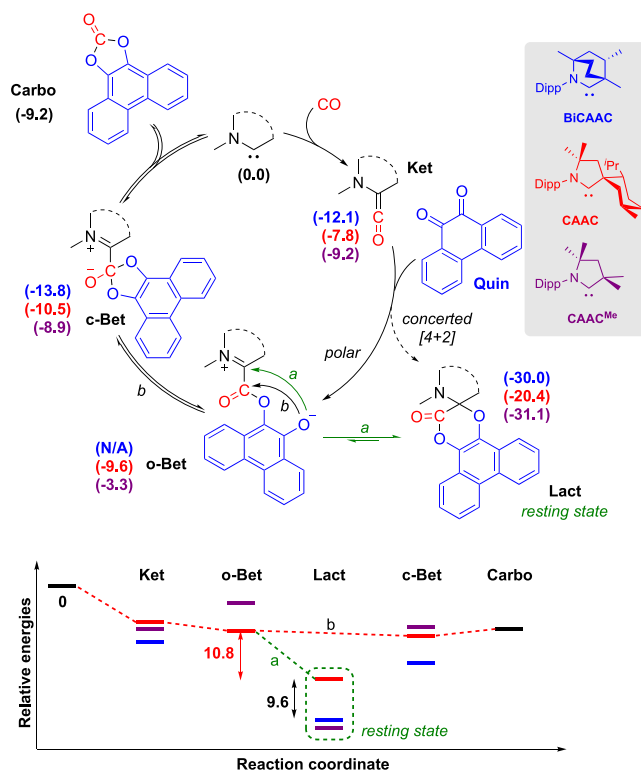
carbonates, we also investigated the reaction of BiCAAC and CAAC with Carbo-1 and observed the clean formation of the corresponding spirolactones Lact-1 and Lact-2, again as single diastereomers (Scheme 1C). These results demonstrate the reversibility of the reductive elimination step.

To understand the diastereoselectivity of the process, we reacted BiCAAC with ethylene carbonate (Carbo-2) in C_6D_6 at room temperature. The 1H NMR analysis showed the formation of a 74:26 mixture of the diastereomers Lact-3' and Lact-3 (Scheme 1D). When the mixture was heated at 80 °C, the ratio was reversed toward 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 (c-Bet) betaines.¹⁹ We believe that the diastereoselectivity observed with the o-

quinone is due to the better leaving group ability of the phenoxy anion, which facilitates the formation of the opened betaines and thus hampers 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 CO. However, heating a C_6D_6 solution of Lact-1 under 4 atm CO at 80 °C for 16 h led to Carbo-1 and a black residue from BiCAAC decomposition that was not characterized. With Lact-2 under 4 atm CO at room temperature, the solution turned slightly blue, indicating the formation of Ket-2, which was confirmed by the observation of the characteristic ^{13}C NMR signal of CCO at 278.8 ppm.^{12a} Notably, 1 atm CO was insufficient to observe any reaction, which demonstrates that this process is dependent on the CO pressure.

Encouraged by these results, we investigated the hypothetical catalytic process computationally (B3LYP-D3/TZVP), as shown in Scheme 2, employing BiCAAC, sterically

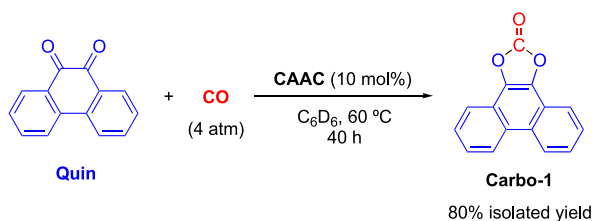
Scheme 2. Proposed Mechanism and Energy Diagram^a

^aDFT calculations were performed at the B3LYP-D3/TZVP level. Gibbs energies are shown in kcal/mol.

encumbered CAAC, and small CAAC^{Me} for comparison. The formation of ketenes is predicted to be exergonic in every case. Similarly, the reactions between the ketenes and 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. It should be noted that the relative energies between o-Bet, c-Bet and free carbonate plus CAAC are negligible and that the overall transformation is exergonic. Importantly, calculations indicate that the reductive elimination step should be possible with all of the carbenes, although it is significantly easier with the bulky CAAC than with BiCAAC and CAAC^{Me}.

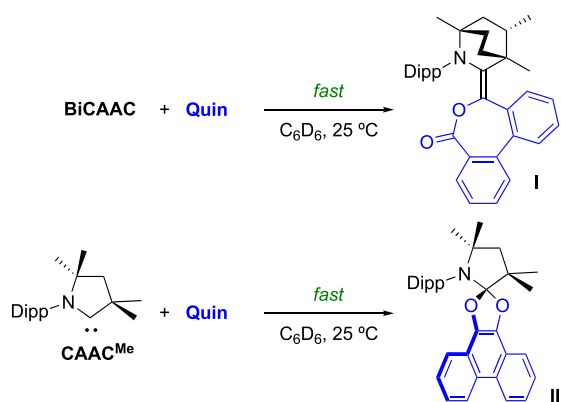
Together, the experimental and computational results discussed above suggested that a catalytic reaction should be achievable. We were delighted to find that indeed, with only 10 mol % CAAC in benzene after 40 h at 60 °C under 4 atm CO, the carbonylation of **Quin** was achieved and gave **Carbo-1**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

Scheme 3. Organocatalytic Carbonylation of Quin



On the other hand, all attempts to use BiCAAC and CAAC^{Me} as catalysts failed, even when more forcing experimental conditions were used. 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 *o*-quinone even at 80 °C and thereby leads to a viable catalyst.

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



Until now, carbene organocatalysis has been 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 them to mimic 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. Transition-metal-catalyzed carbonylation reactions are widely applied in industry on a large scale, employing CO gas as the 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 at <https://pubs.acs.org/doi/10.1021/jacs.0c09938>.

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

Crystallographic data in CIF format for **Lact-1**, **Lact-2**, **Carbo-1**, **I**, and **II** (ZIP)

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Notes

The authors declare no competing financial interest.

Metrical data for the solid-state structures of **Lact-1**, **Lact-2**, **Carbo-1**, **I**, and **II** have been deposited with the Cambridge Crystallographic Data Centre under reference numbers CCDC-1999858, CCDC-1999855, CCDC-1999854, CCDC-1999857, and CCDC-1999856, respectively.

■ ACKNOWLEDGMENTS

We are grateful to the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Catalysis Science Program, under Award DE-SC0009376 for financial support of this work and to 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. M.M.H. is thankful for a Feodor-Lynen scholarship from the Alexander von Humboldt foundation.

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