

Ryerson University Library

& Archives

Article

Photochemically Switching Diamidocarbene Spin States Leads to Reversible Büchner Ring Expansions

Tharushi A Perera, Eric W Reinheimer, and Todd W. Hudnall

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.7b09264 • Publication Date (Web): 25 Sep 2017

Downloaded from http://pubs.acs.org on September 25, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036 Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Photochemically Switching Diamidocarbene Spin States Leads to Reversible Büchner Ring Expansions

Tharushi A. Perera,¹ Eric W. Reinheimer,² and Todd W. Hudnall^{1*}

¹Department of Chemistry and Biochemistry, Texas State University, 601 University Dr, San Marcos, TX 78666, USA. ²Rigaku Americas Corporation, 9009 New Trails Dr, The Woodlands, TX 77381, USA.

ABSTRACT: The discovery of thermal and photochemical control by Woodward and Hoffmann revolutionized how we understand chemical reactivity. Similarly, we now describe the first example of a carbene that exhibits differing thermal and photochemical reactivity. When a singlet ground state N,N'-diamidocarbene **1** was photolyzed at 380 nm, excitation to a triplet state was observed. The triplet state electronic structure was characteristic of the expected biradical $\sigma^{1}p_{\pi}^{1}$ spin configuration according to a combination of spectroscopic and computational methods. Surprisingly, the triplet state of **1** was found to engage a series of arenes in thermally reversible Büchner ring expansion reactions, marking the first examples where both cyclopropanation and ring expansion of arenes were rendered reversible. Not only are these photochemical reactions different from the known thermal chemistry of **1**, the reversibility enabled us to perform the first examples of photochemically induced arene exchange/expansion reactions at a single carbon center.

Introduction

The ability to access divergent reactivity of organic molecules by using thermal or photochemical control was exquisitely described by Woodward and Hoffmann in a series of papers dating back to 1965.1 From this work, the socalled "Woodward-Hoffmann rules" established a distinction between the stereospecificity observed under thermal and photochemical control based on the topology of orbital interactions.¹ In parallel to these findings, advances in quantum mechanics and molecular orbital theory helped to delineate the dichotomy between the structure and reactivity of triplet and singlet ground state carbenes.² While the origin of triplet carbenes dates back to the early 1800's when Dumas attempted to dehydrate methanol,3 the existence of singlet carbenes was first elucidated in the late 1950s by Breslow⁴ and Wanzlick.⁵ Now there are numerous examples describing the rational preparation of triplet and singlet carbenes.² Due to the biradical nature of the triplet ground state, where two nonbonding electrons with parallel spins populate orthogonal σ and p_{π} orbitals ($\sigma^{1}p_{\pi^{1}}$ or ${}^{3}B_{1}$ spin configuration, Figure 1A),^{2C, 6} these carbenes are typically considered to be transient species, with the longest lived species having a half-life of approximately one week in solution.^{2e, 7} However, these reactive intermediates hold great promise to access distinct and complex structural motifs which are highly desirable in the field of organic chemistry, drug discovery and organic ferro-magnetics.8

In contrast to the transient nature of triplet carbenes, singlet carbenes are comprised of two non-bonding, spinpaired valence electrons that occupy a single orbital (typically σ^2 or ${}^{1}A_{1}$ spin configuration, Figure 1B),^{2c, 6} making them more amenable to isolation. After the successful isolation and characterization of the first stable singlet carbenes by the groups of Bertrand in 1988⁹ and Arduengo in 1991,¹⁰ these molecules rose to prominence as the ligands of choice in areas ranging from homogenous¹¹ and organocatalysis¹² to the stabilization of highly reactive main group species.¹³



Figure 1. Electronic spin states of triplet (A) and singlet (B) carbenes.

Despite numerous modifications to the structure of singlet and triplet carbenes, there has been minimal success in preparing isolable triplet analogues, or singlet carbenes that display triplet reactivity. The most notable examples of singlet carbenes that exhibit moderate triplet reactivity are the cyclic(alkyl)amino carbenes (CAACs)¹⁴ and the diamidocarbenes (DACs)¹⁵ reported by Bertrand and Bielawski, respectively. Both CAACs and DACs were shown to thermally undergo [2+1] cycloaddition reactions in the presence of unsaturated organic molecules,¹⁶ activate ammonia,¹⁷ inserts into activated C-H bonds,^{14a, 18} and complex carbon monoxide.¹⁹ Additionally, CAACs have been shown to split H2,^{17a} a feat typically reserved for transition metal complexes.

Our group's recent interest in the redox-chemistry of main group complexes supported by the DAC, N,N'-dimesityl-4,6-diketo-5,5-dimethylpyrimidin-2-ylidene, 1,²⁰ triggered us to explore the photochemistry of this unique carbene. Similar to Woodward and Hoffmann's revelation

of thermal and photochemical control, we now disclose that DAC **1** exhibits a photochemical reactivity profile that is unique from the thermal reactions reported by Bielawski.¹⁸ In this article, we present the first example of a singlet carbene capable of achieving triplet reactivity. Upon irradiation with UV light, DAC **1** is excited to a triplet electronic state which we have then utilized to perform the first reversible Büchner ring expansion reactions.^{21,22,23}



Figure 2. (A) Photochemically (left) and thermally (right) controlled reactions with DAC 1 and various arenes, (B) UV – visible absorption spectrum of 1 in benzene (red line) and TD-DFT (CAM-B3LYP, pcm) vertical transition for 1 (black vertical line, height corresponds to the oscillator strength) in benzene, and (C) single crystal X-ray structure of 2a (hydrogen atoms are omitted for clarity), Pertinent Metric Parameters (atomic distances in Å): C4–C25: 1.516(3), C5–C26: 1.346(3), C26–C27: 1.435(3), C26–C28: 1.350(3), C28–C29: 1.437(3), C29–C30: 1.342(3), C30–C4: 1.509(3), Mes = 2,4,6-trimethylphenyl).

Results and discussion

Synthesis and Characterization

To investigate the photochemical reactivity of DAC 1, we photolyzed the carbene (0.27 mmol) in benzene (2 mL) at 380 nm (Figure 2A) using a home-built photoreactor (see ESI). The excitation wavelength was determined by measuring the UV-visible spectrum of 1 in benzene (Figure 2B). We also calculated the vertical electronic transitions for 1 in benzene ((TDDFT, CAM-B3LYP, pcm) using the gasphase optimized structure (B3LYP, vide infra). Importantly, the calculated singlet transition energies and oscillator strengths showed a good fit to the experimental spectrum of 1 (Figure 2B). Upon excitation of 1 in benzene at 380 nm, we found complete conversion to a new product by 'H NMR. From this reaction mixture, compound 2a was successfully isolated as an off-white solid in 94% yield by precipitation from hexanes (Figure 2A). The ¹H NMR spectrum of the isolated product, 2a (C₆D₆), revealed diagnostic proton signals in the alkene region between $\delta = 5 - 6$ ppm (ESI), consistent with the formation of the DAC-cycloheptatriene spirocyclic structure shown in Figure 2.²⁴ As additional confirmation, single crystals of **2a** were obtained and subjected to a X-ray diffraction analysis (Figure 2C), which revealed the presence of alternating C-C and C=C bonds (see Figure 2 caption) within the seven-membered ring.

Upon examination of the literature, we found that the insertion/ring expansion of carbenes into arenes is the well-known Büchner ring-expansion reaction; however, this chemistry had only been observed for triplet ground state carbenes.²⁵ In Büchner ring expansion reactions, the initial cyclopropanation product,^{16a} the bicyclic norcaradiene tautomer exists in equilibrium with the monocyclic cycloheptatriene tautomer formed by thermally allowed disrotatory electrocyclic ring opening.²⁶ Given that Büchner ring-expansion reactions had never been observed using

singlet ground state carbenes, we were prompted to further explore this unique photochemistry of **1**. When a variety of aromatic solvents and aryl halides were photolyzed (380 nm) with **1**, complexes $2\mathbf{b} - 2\mathbf{f}$ were isolated in good yield (Figure 2A). The 'H NMR (C₆D₆) spectra of $2\mathbf{b} - 2\mathbf{e}$ were also consistent with the formation of cyclohepta-



Figure 3. ¹H NMR spectra of 2b - 2e (alkene region) in C₆D₆.

Importantly, we examined the photochemical reactivity of other singlet carbenes (Figure 4) including: a cyclic (alkyl)amino carbene (CAAC),^{14a} mono amido(amino) carbene (MAAC),²⁷ and the N-heterocyclic carbene iPr²⁸ by irradiating them at their corresponding absorption λ_{max} (see ESI, Figure S22) in benzene and found that the triplet excited state was only accessible for 1. Whereas the CAAC decomposed during photolysis in benzene, MAAC and IPr displayed no photochemical reactivity (see ESI for data). Collectively, these results demonstrated that DAC 1 is unique, and orthogonal reactivity profiles can be accessed under thermal or photochemical control.



Figure 4. Structures of carbenes, CAAC, MAAC, and iPr explored in this study, (Et = ethyl, Dipp = 2,6-diiso-propylphenyl).

Kinetic Studies

We conducted a Hammett analysis of these photochemical reactions by photolyzing **1** in the presence of additional arenes with a variety of electron-donating and withdrawing substituents. In addition to the arenes described above, **1** was photolyzed in iodobenzene, nitrobenzene, and N,N-dimethylaniline. Photolysis of **1** in iodobenzene and nitrobenzene yielded ca. 5% of the ring expansion products, and we attribute this low yield to rapid photodissociation of these arenes in the presence of ultraviolet radiation.²⁹ In contrast, the photolysis of **1** in N,N-dimethylaniline afforded a C-H insertion product **2f** (Figure 2A). The salient spectroscopic features in the 'H NMR (C₆D₆) spectrum of



triene tautomers as evidenced by characteristic proton sig-

nals in the alkene region ($\delta = 5 - 6$, Figure 3), and all reac-

tions were regiospecific, yielding a single isomer (> 95%) in

all cases with the exception of the reaction with fluoroben-

2f include a triplet at δ = 5.64 (CH) and a doublet at δ = 3.38 (CH₂), similar results have obtained previously for the addition of toluene to 1 by Bielawski.¹⁸

5

The photokinetics of these reactions were investigated using UV-vis spectroscopy by monitoring the decrease in the absorbance of $1 (\lambda max = 380 \text{ nm})$ under pseudo-first order conditions upon photolysis in the presence of the respective arene (see ESI for full photokinetic data). Plots of the absorbance of 1 versus time for R = H, CH_3 , F, Cl and Br were first order, and log plots gave straight lines (see ESI), with the rate constants and half-lives ranging from 3.0 x 10-3 - 1.3 x 10-2 s-1 and 53.3 - 138.6 s, respectively. The formation of 2a was shown to occur approximately three times faster than 2c, 2d, or 2e, and we demonstrated that 1 inserts into benzene faster by photolyzing a 1:1 (v:v) benzene:bromobenzene solution of the carbene which gave a product distribution 2a:2e of 66:33 (see ESI). Despite obtaining excellent kinetic data for the photolysis of 1 in these arenes, the Hammett analysis did not give any discernible correlation. This was not surprising given that the purported triplet excited state of DAC 1 should be a biradical which would react rapidly regardless of the arene substituent. Moreover, we note that irradiation of the ring-expanded products 2a-2d may facilitate the thermal reversion described below (vide infra), and thus further complicate the Hammett analysis.

Characterization of the Triplet Excited State

We next focused our efforts on characterizing the triplet excited state of 1. Gratifyingly, irradiation of 1 (380 nm) in a 2-methyltetrahydrofuran (2MTHF) glass at 77 K resulted in a blue emission, which we attributed to relaxation from the triplet excited state to the singlet ground state. The emission spectrum (Figure 5A) was dominated by a broad

(fwhm = 3783 cm⁻¹), unstructured emission band at 440 nm which exhibited an exponential decay with a mean lifetime of 46 µs (Figure 5B). The same emission band could also be observed when using a 350, 360 or 390 nm excitation. The long microsecond lifetime observed was indicative of emission from a triplet state and corroborated our assignment of the excited state of **1**. To further characterize the triplet excited state, we studied the singlet and triplet spin states of **1** in silico (B₃LYP, Figure 5C and 5D, respectively).



Figure 5. (**A**) Photoemission spectrum of **1** in 2MTHF glass at 77 K with 380 nm excitation, (**B**) exponential decay lifetime curve for 1 in 2MTHF glass at 77 K with 380 nm excitation, (**C**) gas phase optimized singlet structure of **1**, (**1**^S), (**D**) gas phase optimized triplet structure of **1** (**1**^T), (**E**-H): selected orbitals of **1**^S and **1**^T (isovalue = 0.04, B3LYP for **1**^S, ROB3LYP for **1**^T, (**E**) HOMO of **1**^S, (**F**) HOMO and HOMO-1 of **1**^T, (**G**) LUMO of **1**^S, (**H**) LUMO of **1**^T. Hydrogen atoms have been omitted for clarity. Atom colors: blue = N, gray = C, red = O. Numbers in parentheses are energies in Hartrees.

The optimized triplet structure, $\mathbf{1}^{T}$, (Figure 5D) showed significant differences with regards to bond angles in comparison with the singlet structure, $\mathbf{1}^{S}$ (Figure 5C). Specifically, an increase in the N15–C1–N16 bond angle from 115° in $\mathbf{1}^{S}$ to 122° in $\mathbf{1}^{T}$ was observed, consistent with increased triplet carbene character as reported by Bielawski.³⁰ Close inspection of the resulting frontier orbitals of $\mathbf{1}^{S}$ and $\mathbf{1}^{T}$ (Figure 5E-5H, respectively) reveal that while the singlet HOMO is dominated by a lone pair of electrons occupying a sp²-like orbital (Figure 5E), the two highest occupied orbitals of $\mathbf{1}^{T}$ are consistent with the expected biradical $\sigma^{1}p_{\pi^{1}}$ (³B₁) spin configuration as evidenced by the restricted, open-shell orbitals. Specifically, the HOMO-1 was characteristic of the singly occupied σ orbital whereas the HOMO was the singly occupied p_{π} orbital (Figure 5F). Similarly, the LUMO of $\mathbf{1}^{s}$ is predominantly the vacant p_{π} orbital at the carbene carbon (Figure 5G) whereas the LUMO of $\mathbf{1}^{T}$ is localized primarily in the mesityl substituents (Figure 5H). Interestingly, the localization of the LUMO in $\mathbf{1}^{s}$ is different than what Bertrand recently reported for the 5-membered DAC; however, in addition to the smaller ring size, that DAC featured N-methyl substituents, which may lead to the observed disparity.³¹ The Mulliken spin density at the carbene carbon (1.67) in the DFT calculation of $\mathbf{1}^{T}$ also supported biradical character. Indeed, no other atoms were found to have spin densities greater than 0.08, indicating that the spin unpaired electrons are localized at the carbene carbon in $\mathbf{1}^{T}$. Collectively, these computational data

2

3

4

5

6

7

8

9

10

11 12

13 14

15

16

17

18

19

20

21

22

23

24 25

26

27

28 29

30 31

32

33

34

35

36

were consistent with the predicted biradical character of the triplet excited state of 1, and with the observed absorption band of 1 being dominated by a HOMO-to-LUMO transition.

The TD-DFT calculations provided the vertical electronic transitions of **1**^s in benzene which compared well with the experimental UV-visible absorption spectrum of **1** (Figure 2B, vide supra), and which supported the assessment that excitation of **1** is dominated by a HOMO–LUMO transition. For **1**^s, the destination orbital for all five lowest vertical singlet transitions is the LUMO as expected, and the departure orbitals are predominantly the HOMO through HOMO-6 (see ESI). In contrast to the singlet transitions, the orbital contributions for the lowest five triplet transitions were more complex, without dominant (> 80%) contributions. However, the lowest energy triplet transition, which consisted of HOMO-LUMO (58%) and HOMO-4-LUMO (26%) contributions, matched well with the lowest energy singlet transition (comprised of similar HOMO-LUMO (68%) and HOMO-4-LUMO (28%) contributions), suggesting that facile singlet-triplet intersystem crossing can take place at this level.



Figure 6. (A) Proposed Jablonski diagram for the formation of 2a – 2e, (B) proposed mechanism for the formation of 2a – 2e.

The calculated TD-DFT singlet-triplet (S-T) gap from these orbitals (48.1 kcal/mol) also compared well to the calculated S-T gap in the gas phase (43.5 kcal/mol). Perhaps most importantly, these calculated S-T gap energies matched well with the experimental emission energy of 1 in the 2MTHF glass (65.0 kcal/mol) which should correspond to relaxation from the triplet excited to the singlet ground state. While the experimental emission energy was greater than the calculated S-T energy gaps, the rigid matrix used to measure the emission of 1 (frozen 2MTHF) would inhibit geometric changes involved in the triplet relaxation giving a strained triplet geometry. Additionally, frozen solvents are oriented to the ground state and not the excited state, which often result in blue-shifted emissions.32 Based on our calculations, and experimental observations, it appears that the photochemistry of 1 follows Kasha's rule,³³ whereby photon emission takes place from the lower-lying excited triplet state of the carbene and not the higher energy singlet excited state. We also note that it may also be possible for direct excitation into the triplet excited state at lower energies, however this phenomenon was not observed experimentally.

Proposed Mechanism

The calculations that were conducted on **1**^T appeared to accurately model the reactive excited state of the diamidocarbene. The restricted open-shell orbitals and concomitant high spin density localized on the carbene center

are characteristic of a triplet biradical that is capable of inserting into arenes through a Büchner ring expansion mechanism. Moreover, the unique low-lying LUMO of 1 results a relatively small HOMO-LUMO energy gap when compared to other isolable carbenes.³⁴ Based on these data, we postulate that excitation of 1 leads to population of the singlet excited state (S^x) followed by rapid intersystem crossing to the associated triplet state (T^x) which then engages the arene in the observed Büchner ring expansion reactions according to the simplified Jablonski diagram shown in Figure 6A. Similarly, the proposed mechanism for the formation of 2a - 2e from 1 and the corresponding arene via photolysis at 380 nm is shown in Figure 6B. It is important to note that carbenes CAAC, MAAC and iPr did not show similar photochemical reactivity like 1 (DAC). We attribute this disparity to a combination of effects: (i) the higher HOMO-LUMO energy gaps in CAAC, MAAC and iPr when compared to DAC, and (ii) the lower lying LUMO of the DAC, which collectively, would impede excitation to a singlet excited state, and subsequent intersystem crossing to the necessary triplet state for the other carbenes.

Reversibility and Arene Exchange Studies

While storing compounds 2 during characterization, we observed that these complexes readily reverted to their reactant components 1 and the corresponding arene. This was surprising as norcaradienes and cycloheptatrienes prepared via Büchner ring-expansion reactions are typically thermally robust.^{25b, 35} To the best of our knowledge, these observations represented unprecedented examples of reversible Büchner ring-expansions. We first became aware of this unusual behavior from **2e** where the ¹H NMR spectrum of this compound in C₆D₆ revealed the slow reversion to **1** and bromobenzene at room temperature (Figure 7A

(left)). Analysis of the same NMR sample of **2e** after 48 h by 'H NMR spectroscopy showed complete reversion (see ESI). Similarly, **2b**, **2c** and **2d** displayed complete reversion at room temperature to form **1** and their respective arenes. The only complex that exhibited any prolonged stability was **2a** which was found to be stable in solution for



Figure 7. (**A**): reversibility of Büchner ring expansion reactions; and (**B**): stacked ¹H NMR spectra of **2e** in C_6D_6 (bottom), photolysis of **2e** in C_6D_6 after 4 h (second from bottom), photolysis of **2e** in C_6D_6 after 8 h (second from top), and of **2a** in C_6D_6 (top).

weeks at room temperature. However, heating a solution of 2a to 60 °C for 2 h yielded 1 and benzene in >95% yield (see ESI). With the exception of 2a, we also found that 2b - 2e reverted to their corresponding starting materials even in the solid state at room temperature as observed by ¹H NMR analysis of the isolated compounds within 2-3 days after synthesis. In agreement with this view, we note that the single crystal X-ray analysis of chlorobenzene adduct, 2d, could not be properly refined without modeling significant electron density corresponding to a free disordered chlorobenzene molecule that was released from DAC 1 even at 100K (see ESI for full discussion). Complex 2e displayed the fastest retro Büchner ring-expansion, while 2a was found to be the slowest (order of reversibility in solution and/or solid state at room temperature: 2e > 2d > 2c >2b > 2a).

Based on the observed rates of the retro Büchner ring expansions, we next investigated the potential to interconvert between different compounds of 2 (Figure 7A (right)). Remarkably, we found that the photolysis of 2e (R = Br) in excess C₆D₆ for 8h in a sealed quartz NMR tube led to the

complete exchange of the arene to afford compound 2a' (where all hydrogen atoms are deuterated for this experiment shown in Figure 7B) with liberation of bromobenzene. The stacked ¹H NMR spectra shown Figure 7B depict the clean conversion from 2e to 2a at time = 0 hours (bottom) to 8 hours (second from top), with the 'H NMR spectrum of pure 2a (top) for reference. Although the olefinic signals of 2a' (0) are not observable due to the incorporation of deuterium from the C_6D_6 solvent, the clear disappearance of 2e(x) with the formation of bromobenzene (*) and the aliphatic and aromatic signals of 2a can be seen. Similarly, photolysis of 2d (R = Cl) in excess benzene yielded 50:50 mixture of 2d:2a after 5 hours (see ESI). We also note that the reversion of 2d into 50% 1 and 50% chlorobenzene takes approximately 13 hours at room temperature (see ESI), indicating that irradiation of compounds 2 may facilitate the retro Büchner ring expansions. Interestingly, when the benzene complex 2a was photolyzed in an excess of either bromobenzene or chlorobenzene, the corresponding exchange reactions to give 2e or 2d, respectively were not observed to occur (see ESI).

These results suggested that **2e** and **2d** can be used to perform the first examples of photochemically-induced arene ring expansion exchange reactions, but **2a** was too thermally stable to undergo similar photochemical exchange. DFT calculations were performed to interrogate the thermodynamic parameters for the formation of **2a–2f** and the reversibility of **2a–2e**. The structures of **2a – 2f** were optimized (see ESI) at the B3LYP level of theory with the 6-31+G(d) basis set for the C, H, N and O atoms, while Def2-SVPD basis sets were used for F, Cl and Br atoms.³⁶



Figure 8. Calculated free energy diagram for the formation of **2a** and **2e** from **1**, benzene and bromobenzene via ring expansion by photolysis at 380 nm. Energies of **2a**, **2e**, **2a**', **2e**', **2a**^{TS1}, **2e**^{TS1}, **2a**^{TS2} and **2e**^{TS2} were obtained from optimization calculations.

Calculated gas-phase formation enthalpies and free energies for 2a – 2f are provided in the ESI. In agreement with the reversible nature of the Büchner ring expansion reactions, the Δ H and Δ G values calculated for **2a** – **2e** were all endothermic (Δ H range: 15.7-16.7 kcal/mol) and endergonic (ΔG range: 29.7–32.0 kcal/mol), whereas the formation of 2f(R = NMe2, which does not form through the Büchner ring expansion) is exothermic ($\Delta H = -22.5$ kcal/mol) and exergonic ($\Delta G = -8 \text{ kcal/mol}$). To further understand the ability to photochemically convert **2e** (R = Br) into 2a (R = H), we constructed a calculated free energy diagram for the formation of 2a and 2e from photolysis of 1 with benzene (Figure 8, left) and bromobenzene (Figure 8, right). For each reaction the free energies of the norcaradiene intermediates (2a' or 2e'), the transition states between the starting materials and the intermediate (2a^{TS1} or $2e^{TS_1}$), and the transition states between the intermediate and the cycloheptatriene products $(2a^{TS_2} \text{ or } 2e^{TS_2})$ were plotted. Transition states 2a^{TS1} and 2e^{TS1} were optimized with triplet spin states as the well-known mechanism for the cyclopropanation of alkenes with triplet carbenes proposes triplet biradical transition states.³⁷ In contrast, 2a^{TS2}

and **2e**^{TS2} were optimized as singlet spin states because the ring-opening of the norcaradiene is a thermally-allowed, concerted process. For both reactions, the rate determining step was the formation of the norcaradiene intermediates, 2a' and 2e', which were both endergonic by 41.0 and 41.4 kcal/mol, respectively with activation barriers defined by $2a^{TS_1}$ and $2e^{TS_1}$. For 2a, the transition state, $2a^{TS_1}$, was found to be higher in energy (59.6 kcal/mol) than the corresponding transition state for $2e (2e^{TS_1} = 58.5 \text{ kcal/mol})$, and the overall activation barrier from 2a back to DAC 1 and benzene (28.5 kcal/mol) was higher than that calculated for 2e reverting to 1 and bromobenzene (26.6 kcal/mol). While the $\Delta\Delta G$ between the retro Büchner ring expansions is small (only 1.9 kcal/mol), the calculated data were consistent with our experimental findings that 2a is more thermally stable than 2e. Similar results were also obtained for the complexes 2b, 2c, and 2d (see ESI). To address this issue further, we believe that the small calculated $\Delta\Delta G$ values can be attributed to the difficulty in accurately modeling excited electronic states. In these Büchner ring expansion reactions, the transition states result from the combination of an excited state DAC with a given arene,

and therefore are excited state species themselves. Although the energies of these transition states corroborate that **2a** is more thermally stable than the other ring-expanded products, it is possible that the highest energy transition state structure may be poorly computed by our methods, despite the use of several different functionals and basis sets.

Conclusion

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58

59 60

In summary, we have revised the long-standing precept that stable, isolable carbenes exist as a singlet ground state whereas transient carbenes are typically regarded as triplet ground state carbenes, is no longer valid. We now report that both spin states (and attendant reactivity), are accessible for the diamidocarbene 1. While 1 is isolated as a highly stable singlet electronic ground state carbene, photolysis at 380 nm allows for rapid conversion through intersystem crossing to an excited triplet state. The triplet excited state of 1 has been fully characterized through a combination of low temperature spectroscopic measurements and computational analyses. These studies indicated that the excited state of 1 can be characterized as the expected spin unpaired biradical structure, typical of triplet carbenes. The triplet excited state of 1 was also found to engage a series of aromatic compounds in the known Büchner ring expansion reaction to cleanly afford a single cycloheptatriene isomer in all cases (2a-2e). Remarkably, the photochemical reaction of 1 with benzene or toluene provided drastically different products than the known thermal products (which form from C-H activation processes) reported by Bielawski.¹⁸ In this regard, we equate the two distinct reactivity profiles of 1 as photochemical and thermal control similar to what Woodward and Hoffmann described for pericyclic electrocyclization reactions.

Beyond the novelty of accessing the triplet excited state of DAC 1, the subsequent Büchner ring expansion reactions were found to exhibit unprecedented reversibility, even in the solid state for some derivatives. This unique feature provided the first examples where both cyclopropanation and ring expansion reactions were rendered reversible, enabling the ability to interconvert 2d or 2e into 2a through atom-economic, high fidelity photochemical reactions. The surprising discoveries presented herein are likely to initiate new fundamental studies and expand the applications of stable carbenes. Similar to other reversible ringforming reactions, such as the Diels-Alder reaction, reversible Büchner ring expansion processes may also find applications ranging from structurally dynamic materials to novel methodologies in organic synthesis as the cycloheptatriene motif is commonly found in biologically active molecules.38 The photochemistry of 1 with various other organic substrates is currently under intense study in our laboratory.

ASSOCIATED CONTENT

Supporting Information. Experimental details including synthetic, spectroscopic, crystallographic, and computation data are provided. "This material is available free of charge via the Internet at http://pubs.acs.org."

AUTHOR INFORMATION

Corresponding Author

* <u>hudnall@txstate.edu</u>

ORCID Tharushi A. Perera: 0000-0001-7454-237X Eric W. Reinheimer: 0000-0002-9491-1571 Todd W. Hudnall: 0000-0002-9260-2986

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

T.W.H. is grateful to the National Science Foundation for grants (CAREER award: CHE-1552359 and CHE-1362140) supporting this research. The authors would like to thank Emeritus Professor Paul R. Sharp and Dr. Alice R. Karikachery at the Department of Chemistry, University of Missouri, Columbia for assistance with the low temperature emission and lifetime measurement studies, along with the Department of Chemistry, University of Missouri, Columbia for fluorimeter access. We would also like thank Dr. Lee Daniels for access to a single crystal X-ray diffractometer at Rigaku Americas Corporation, Dr. Mark Lee for HRMS analysis, and Dr. Christopher Dorsey for insightful conversations regarding the DFT studies.

REFERENCES

(1) (a) Hoffmann, R.; Woodward, R. B., *J. Am. Chem. Soc.* **1965**, 87, 2046-2048; (b) Zimmerman, H. E., *J. Am. Chem. Soc.* **1966**, 88, 1564-1565; (c) Geerlings, P.; Ayers, P. W.; Toro-Labbé, A.; Chattaraj, P. K.; De Proft, F., *Acc. Chem. Res.* **2012**, *45*, 683-695.

(2) (a) Chinoporos, E., *Chem. Rev.* **1963**, *63*, 235-255; (b) Stang, P. J., *Chem. Rev.* **1978**, *78*, 383-405; (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G., *Chem. Rev.* **1999**, *100*, 39-92; (d) Arduengo, A. J.; Bertrand, G., *Chem. Rev.* **2009**, *109*, 3209-3210; (e) Hirai, K.; Itoh, T.; Tomioka, H., *Chem. Rev.* **2009**, *109*, 3275-3332.

(3) Dumas, J. B.; Peligot, E., Ann. Chim. Phys. 1835, 58, 5-74.

(4) (a) Breslow, R., J. Am. Chem. Soc. **1957**, 79, 1762-1763; (b) Breslow, R., J. Am. Chem. Soc. **1958**, 80, 3719-3726.

(5) (a) Wanzlick, H. W.; Schikora, E., *Angew. Chem.* **1960**, *72*, 494; (b) Wanzlick, H.-W.; Schikora, E., *Chem. Ber.* **1961**, *94*, 2389-2393.

(6) Schuster, G. B., Adv. Phys. Org. Chem. 1986, 22, 311-361.

(7) (a) Tomioka, H.; Iwamoto, E.; Itakura, H.; Hirai, K., *Nature* **2001**, *412*, 626-628; (b) Iwamoto, E.; Hirai, K.; Tomioka, H., J. Am. Chem. Soc. **2003**, *125*, 14664-14665; (c) Kirmse, W., *Angew. Chem. Int. Ed.* **2003**, *42*, 2117-2119.

(8) Iwamura, H., Adv. Phys. Org. Chem. 1990, 26, 179-253.

(9) Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand, G., *J. Am. Chem. Soc.* **1988**, *110*, 6463-6466.

(10) Arduengo, A. J., III; Harlow, R. L.; Kline, M., J. Am. Chem. Soc. 1991, 113, 361-363.

(11) Peris, E.; Crabtree, R. H., Coord. Chem. Rev. 2004, 248, 2239-2246.

(12) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L., *Chem. Rev.* **2007**, *107*, 5813-5840.

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59 60 (13) Hudnall, T. W.; Ugarte, R. A.; Perera, T. A., Main Group Complexes with N-Heterocyclic Carbenes: Bonding, Stabilization and Applications in Catalysis. In *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools: Edition 2*; Diez-Gonzalez, S., Ed.; The Royal Society of Chemistry: London, 2017; pp 178-237.

(14) (a) Soleilhavoup, M.; Bertrand, G., *Acc. Chem. Res.* **2015**, *48*, 256-266; (b) Melaimi, M.; Jazzar, R.; Soleilhavoup, M.; Bertrand, G., *Angew. Chem. Int. Ed.* **2017**, 56, 10046-10068.

(15) Moerdyk, J. P.; Schilter, D.; Bielawski, C. W., Acc. Chem. Res. 2016, 49, 1458-1468.

(16) (a) Moerdyk, J. P.; Bielawski, C. W., *Nat. Chem.* **2012**, *4*, 275-280; (b) Martin, D.; Canac, Y.; Lavallo, V.; Bertrand, G., *J. Am. Chem. Soc.* **2014**, *136*, 5023-5030.

(17) (a) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G., *Science* **2007**, *316*, 439-441; (b) Hudnall, T. W.; Moerdyk, J. P.; Bielawski, C. W., *Chem. Commun.* **2010**, *46*, 4288-4290.

(18) Moerdyk, J. P.; Bielawski, C. W., Chem. Eur. J. 2013, 19, 14773-14776.

(19) (a) Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G., *Angew. Chem. Int. Ed.* **2006**, *45*, 3488-3491; (b) Hudnall, T. W.; Bielawski, C. W., *J. Am. Chem. Soc.* **2009**, *131*, 16039-16041.

(20) (a) Dorsey, C. L.; Squires, B. M.; Hudnall, T. W., *Angew. Chem. Int. Ed.* 2013, 52, 4462-4465; (b) Dorsey, C. L.; Mushinski, R. M.; Hudnall, T. W., *Chem. Eur. J.* 2014, 20, 8914-8917; (c) Rodrigues, R. R.; Dorsey, C. L.; Arceneaux, C. A.; Hudnall, T. W., *Chem. Commun.* 2014, 50, 162-164; (d) Deardorff, C. L.; Eric Sikma, R.; Rhodes, C. P.; Hudnall, T. W., *Chem. Commun.* 2016, 52, 9024-9027.

(21) For a report of an irreversible, non-regiospecific, photochemical Büchner ring expansions with a triplet silylene see: Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C., *J. Am. Chem. Soc.* **2002**, *124*, 3830-3831.

(22) During the submission of this manuscript, the following paper which reports the photochemical spin switching of aryl(trifluoromethyl) carbene was reported, see: Tsegaw, Y. A.; Kadam, P. E.; Tötsch, N.; Sanchez-Garcia, E.; Sander, W., J. Am. Chem. Soc., 2017, 139, 12310–12316.

23) For examples of thermal insertion-ring expansions of NHCs into main group hydrides see: (a) Iversen, K. J.; Wilson, D. J. D.; Dutton, J. L., *Organometallics* **2013**, *32*, 6209-6217; (b) Schmidt, D.; Berthel, J. H. J.; Pietsch, S.; Radius, U., *Angew. Chem. Int. Ed.* **2012**, *51*, 8881-8885; (c) Wang, T.; Stephan, D. W., *Chem. Eur. J.* **2014**, *20*, 3036-3039; (d) Lam, J.; Gunther, B. A. R.; Farrell, J. M.; Eisenberger, P.; Bestvater, B. P.; Newman, P. D.; Melen, R. L.; Crudden, C. M.; Stephan, D. W., *Dalton Trans.* **2016**, *45*, 15303-15316; (e) Al-Rafia, S. M. I.; McDonald, R.; Ferguson, M. J.; Rivard, E., *Chem. Eur. J.* **2012**, *18*, 13810-13820; (f) Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G.; MacDougall, D. J.; Mahon, M. F., *Angew. Chem. Int. Ed.* **2012**, *51*, 2098-2100.

(24) (a) Bauer, W.; Daub, J.; Maas, G.; Michna, M.; Rapp, K. M.;
Stezowski, J. J., *Eur. J. Inorg. Chem.* **1982**, *115*, 99-118; (b) Tamm,
M.; Kunst, A.; Bannenberg, T.; Herdtweck, E.; Sirsch, P.; Elsevier,
C. J.; Ernsting, J. M., *Angew. Chem. Int. Ed.* **2004**, *43*, 5530-5534; (c)
McNamara, O. A.; Maguire, A. R., *Tetrahedron* **2011**, *67*, 9-40.

(25) (a) Curtius, T., *Eur. J. Inorg. Chem.* **1883**, *16*, 2230-2231; (b) Buchner, E.; Curtius, T., *Chem. Ber.* **1885**, *18*, 2377-2379; (c) Wu, Y.-J. Buchner reaction. In *Name Reactions for Carbocyclic Ring Formations*; Li, J. J., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ 2010; pp 424-450.

(26) Liebman, J. F.; Greenberg, A., *Chem. Rev.* **1989**, *89*, 1225-1246.

(27) Blake, G. A.; Moerdyk, J. P.; Bielawski, C. W., Organometallics 2012, 31, 3373-3378.

(28) Bantreil, X.; Nolan, S. P., Nat. Protoc. 2011, 6, 69-77.

(29) (a) Durie, R.; Iredale, T.; Kingsbury, A., *Nature* **1949**, *164*, 786-786; (b) Galloway, D. B.; Bartz, J. A.; Huey, L. G.; Crim, F. F., J. Chem. Phys. **1993**, *98*, 2107-2114.

(30) Hudnall, T. W.; Tennyson, A. G.; Bielawski, C. W., Organometallics 2010, 29, 4569-4578.

(31) Rao, B.; Tang, H.; Zeng, X.; Liu, L.; Melaimi, M.; Bertrand, G., *Angew. Chem. Int. Ed.* **2015**, *54*, 14915-14919.

(32) Tamayo, A. B.; Garon, S.; Sajoto, T.; Djurovich, P. I.; Tsyba, I. M.; Bau, R.; Thompson, M. E., *Inorg. Chem.* **2005**, *44*, 8723-8732.

(33) Kasha, M., *Discuss. Faraday Soc.* 1950, 9, 14-19.
(34) (a) Hudnall, T. W.; Moorhead, E. J.; Gusev, D. G.;
Bielawski, C. W., *J. Org. Chem.* 2010, 75, 2763-2766; (b) Bissinger,
P.; Braunschweig, H.; Damme, A.; Krummenacher, I.; Phukan, A.
K.; Radacki, K.; Sugawara, S., *Angew. Chem. Int. Ed.* 2014, 53, 7360-7363.

(35) (a) Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Hubert, A. J.; Warin, R.; Teyssie, P., *J. Org. Chem.* **1981**, *46*, 873-876; (b) Galan, B. R.; Gembicky, M.; Dominiak, P. M.; Keister, J. B.; Diver, S. T., *J. Am. Chem. Soc.* **2005**, *127*, 15702-15703.

(36) (a) Lee, C.; Yang, W.; Parr, R. G., *Phys. Rev. B, PRB* **1988**, 37, 785-789; (b) Becke, A. D., *J. Chem. Phys.* **1993**, 98, 5648-5652; (c) Hellweg, A.; Rappoport, D., *Phys. Chem. Chem. Phys.* **2015**, *17*, 1010-1017.

(37) Skell, P. S.; Woodworth, R. C., J. Am. Chem. Soc. 1956, 78, 4496-4497.

(38) Liu, N.; Song, W.; Schienebeck, C. M.; Zhang, M.; Tang, W., *Tetrahedron* **2014**, *70*, 9281-9305.





TOC Graphic

83x47mm (300 x 300 DPI)



126x37mm (300 x 300 DPI)



208x140mm (300 x 300 DPI)



270x103mm (300 x 300 DPI)



121x26mm (300 x 300 DPI)



283x243mm (300 x 300 DPI)



202x130mm (300 x 300 DPI)



ACS Paragon Plus Environment



192x137mm (300 x 300 DPI)