Photochemical Carbene Transfer Reactions of Aryl/Aryl Diazoalkanes – Experiment and Theory

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Abstract: The photochemical carbene transfer reaction is a timely strategy in organic synthesis and generally proceeds via singlet carbene intermediates. In this combined experimental and computational studies, we show that the photolysis reaction of diaryl diazoalkanes gives access to both singlet and triplet diarylcarbene intermediates. The electronic properties of substituents of the aryl substituents show a strong influence on the electronic properties of the carbene intermediate and result in significantly reduced singlet triplet energy gaps. Depending on the spin state and electronic properties of the carbene intermediate, the reaction with alkynes provides access towards chemo- and regioselective cyclopropagation, cascade, or C-H functionalization reactions.

Introduction

The spin state of carbene intermediates is an important area of research in chemistry and of prime importance to understand the chemical properties and reactivity of carbenes.[1] In this context, experimental and theoretical studies on the influence of electronic effects on the carbene spin state remains a central area of research in physical organic chemistry.[2-4] In particular, matrix-isolation, ultrafast spectroscopy, or latest developments in computational chemistry represent important state-of-the-art techniques to characterize short-lived carbene intermediates.[2-4] These studies demonstrated that the electronic properties of substituents significantly impact on the spin state of carbenes and their singlet-triplet splitting. For example, donor/acceptor carbenes exhibit a singlet ground state in chlorinated solvent as demonstrated both experimentally and computationally.[3] This singlet carbene can be accessed via the photolysis of donor/acceptor diazoalkanes and utilized in carbene transfer reactions, as recently demonstrated (2, Scheme 1b).[6] Contrarily, the spin state of aryl/aryl carbenes is much more dependent on the nature of the electronic properties of the substituents of the aromatic ring. While for diphenyl carbene the triplet ground state is favored over the singlet state by 4.6 kcal/mol,[8] the energy of the singlet and triplet state of electron-rich bis(4-methoxyphenyl)carbene is almost degenerate with the singlet state being 0.3 kcal/mol energetically favored as described by Sander and co-authors.[4] In the same report, Sander could experimentally observe that the triplet carbene is formed as the primary product of UV-light photolysis of bis(4-methoxyphenyl)diazomethane in an Ar matrix at 3 K. This triplet carbene features interesting photochemical properties and can be selectively switched from triplet to singlet state by irradiation with 450 nm blue light and reverted by with 365 nm light, which results from the small singlet triplet energy gap (Scheme 1a). Thermal annealing by heating at 25 K results in formation of the singlet carbene.[4]

In this context, we hypothesized that different spin states of carbene intermediates can be accessed and used in organic synthesis under photochemical conditions. Specifically, the electronic properties of the carbene intermediate should influence its spin state and thus allow for spin-dependent reactions of photochemically generated carbene intermediates. As a consequence, this approach should then enable orthogonal reaction pathways of carbene intermediates that can be controlled by the electronic properties under otherwise identical conditions (Scheme 1b).

As part of our ongoing research interest in photochemical applications of diazoalkanes,[9-10] we observed a marked dependency of the visual appearance and absorption properties of aryl/aryl diazoalkanes on their electronic properties (Scheme 1c). While electron-poor substituted aryl/aryl diazoalkanes absorb visible light in the purple light region, the absorption maxima of electron-neutral donor/donor diazoalkanes is red-shifted towards the dark green light region.[11] Introduction of electron-donating groups results in a further bathochromic shift towards the light green region of the visible part of the electromagnetic spectrum. This observation prompted us to further study aryl/aryl diazoalkanes to access different spin states of donor/donor carbene intermediates that can be utilized in orthogonal, photochemical organic synthesis (5-S vs. 5-T, Scheme 1c).[12]

In a similar context, yet using transition metal catalysts,[13] the Davies group recently reported on the effect of one electron-donating and -withdrawing groups on the reactivity of aryl/aryl diazoalkanes in Rh(II)-catalyzed stereoselective cyclopropanation reactions (8).[14] Shortly thereafter, the Zhou and Franz groups reported on similar observations in Rh(II)-catalyzed Si-H insertion reactions (9).[15,16] In these cases the reactivity of the carbene intermediate is controlled by the Rh(II) catalyst and thus represents the singlet carbene reactivity (4-Rh, Scheme 1d).
**Results and Discussion**

**Experimental Studies:** We initiated our studies on the reaction of aryl/aryl diazoalkanes with phenyl acetylene (6a) and evaluated the reaction of electron-poor aryl/aryl diazoalkanes (3a) first.\(^{[17]}\) We assumed that the introduction of one electron-withdrawing group could be utilized to control the reactivity of the carbene intermediate and that this carbene more resembles a classic donor/acceptor carbene. Indeed, under blue light conditions the cyclopropene product 7a was obtained in excellent yield after only 20 minutes reaction time (Scheme 2a), which is in line with the reactivity of donor/acceptor carbones. We next turned our attention towards electron-neutral aryl/aryl diazoalkane 3b in the reaction with phenyl acetylene (Scheme 2b). No cyclopropenation reaction occurred under identical conditions, instead a highly selective cascade reaction occurred and indene product 8a was obtained in excellent yield as the sole product. Finally, we probed the reactivity electron-rich aryl/aryl diazoalkanes (3c, Scheme 2c). Neither the cyclopropene nor the indene product was observed, instead a selective C-H functionalization of the terminal alkynyl C(sp)-H bond (9a) occurred with excellent yield, which represents an intriguing reactivity of free carbones, which can otherwise only be accessed from strongly nucleophilic N-heterocyclic carbones.\(^{[18]}\)

All above reactions were investigated under UV light conditions and in all cases the reaction pathway was unaffected, although a significantly reduced yield of the respective products was observed in all cases, which suggests that the light source only has a minor influence on the reaction pathways. When irradiated with green light, a considerable influence of the absorption properties of the diazoalkanes on the reaction yield was observed. Electron-poor aryl/aryl diazoalkanes, which absorb only poorly in the green light range, reacted only in low yield to the corresponding cyclopropane. In contrast, electron-neutral and electron-rich aryl/aryl diazoalkanes absorb in the green light range (Scheme 1c) and significantly better yields were obtained, with the best yields for most red-shifted and

**Scheme 1**. Carbene Transfer Reactions.

**Scheme 2**. Carbene transfer reactions of electronically distinct aryl/aryl diazoalkanes with phenyl acetylene.
In contrast to the reaction of donor/acceptor diazoalkanes, the photolysis ofaryl/aryl diazoalkanes needs to be performed under an inert atmosphere and exclusion of air and moisture to obtain high reaction yields. However, it should be noted that electron-poor diazoalkane 3 reacts in reasonable yield (78%) to the cyclopropene product in air, while electron-rich substrate 3c requires strict exclusion of air. Further studies on the compatibility of solvent showed a strong solvent dependency and only chlorinated solvents are compatible with the present reaction conditions. In all other solvent either decomposition of the diazoalkane or significantly reduced yields were observed (see Table S1 in ESI). Importantly, when studying the reaction of aryl/aryl diazoalkanes with phenyl acetylene in the presence of Rh(II)- or Cu(I)-based catalysts only the decomposition of diazoalkane was observed (Scheme 2d).

We subsequently studied the application of the photolysis reaction of aryl/aryl diazoalkanes in electronic-controlled carbene transfer reactions with alkynes. Different terminal aromatic alkynes smoothly reacted with electron-poor aryl/aryl diazoalkane 3a in a very efficient cyclopropenation reaction, with diminutive amounts of indene as by-product (7a-i, r.r. up to >20:1). Contrarily aliphatic alkynes, reacted in selective C-H functionalization of the propargylic C-H bond in almost high yield (10a-c).

We then turned our attention to the reaction of electron-neutral aryl/aryl diazoalkane 3b with terminal aryl and alkyl alkynes. An almost quantitative yield of the corresponding indene products (8a-j) was obtained in the case of aryl acetylenes bearing halogen or electron-withdrawing groups in all positions of the aromatic ring. Slightly reduced yields were obtained, when electron-donating groups, such as alkyl- or methoxy-groups were introduced. In all cases the indene products were obtained as the only reaction product and a high selectivity for the position of the double bond was observed (r.r. >20:1). Similarly, aliphatic, terminal alkynes gave indene products (8k-o).

Scheme 3. Investigations on the multi-state reactivity of donor/donor diazoalkanes with alkynes. Reaction conditions: In an oven dried reaction tube the diazoalkane (0.2 mmol, 1 eq.) was added and the reaction tube was purged with argon for three times then 0.5 mL of degassed and dry DCM was added. Alkyne (2 mmol, 10 eq.) was dissolved in 0.5 mL of degassed and dry DCM and added to the reaction tube by syringe and then irradiated with blue LED (470 nm, 3W) for 30 mins at room temperature under argon atmosphere. The crude reaction mixture was purified by silica gel column chromatography.
Finally, we studied electron-rich aryl/aryl diazoalkane 3c that underwent C(sp)-H insertion reaction into a variety of different terminal aryl alkynes in very good to almost quantitative yield (9a-i). Under the present reaction conditions, TMS-acetylene smoothly reacted to give the C-H functionalization product in excellent yield (9i). Aliphatic alkynes however, did not undergo C(sp)-H insertion, instead a highly efficient C(sp)<sup>3</sup>-H insertion in the propargylic position was observed in high yields (10d-f). It should be noted that this C(sp)<sup>3</sup>-H functionalization can be readily applied to install a quaternary carbon of the underlying reaction mechanism and the involvement of singlet or triplet carbene intermediates, we performed computational investigations by studying geometrical and electronic properties of neutral and electron-rich aryl/aryl carbenes and no reaction was observed with electron-poor diazoalkane 3a. Next, we studied the reaction of aryl/aryl diazoalkanes with organo sulfides in rearrangement reactions. An excellent yield of the rearrangement products 18a and 19a was obtained for electron-poor aryl/aryl diazoalkane 3a in the reaction with allyl phenyl sulfide 13 and phenyl benzyl sulfide 14. A significantly reduced yield of 18b and 19b was observed for the electron-neutral aryl/aryl diazoalkane 3b. Electron-rich diazoalkane 3c gave the products 18c and 19c in good isolated yield. The reaction outcome with different sulfides thus shows that the product yields are strongly dependent on the electronic properties of the diazoalkane precursor (Scheme 4). A similar trend was observed in the presence of oxygen (cf. Scheme 2). This data now provides further experimental evidence of the participation of singlet and triplet carbene intermediates depending on the electronic properties of the diazoalkane precursor.

**Theoretical Studies:** To gain an understanding of the underlying reaction mechanism and the involvement of singlet or triplet carbene intermediates, we performed computational studies on the reaction of carbenes 5a-c with phenyl acetylene and 3-methyl but-1-yne.

We set out our investigations by studying geometrical and electronic properties of carbenes 5a-c at different levels of theory. Specifically, we performed calculations using the B3LYP-D3 functional to obtain a first data set of singlet-triplet energy splitting, which could provide a reasonable approximation for subsequent investigations of the reaction mechanism. For benchmarking of B3LYP-D3 calculations, we next performed coupled cluster calculations with the DLPNO-CCSD(T) method that was recently demonstrated as a viable method to obtain a more accurate singlet triplet energy splitting, which can then serve as an estimate of calculation uncertainties when using the more simple B3LYP-D3 functional. With the B3LYP functional, we observed a significant difference in the singlet-triplet energy splitting of carbenes 5a-c, which strongly depends on the substitution pattern of the aromatic ring. For diphenyl carbene (5b), this energy gap was calculated

![Scheme 4. Reactions with different carbene trapping reagents; for compounds a R<sup>1</sup> = OMe, R<sup>2</sup> = NO<sub>2</sub>; b R<sup>1</sup> = R<sup>2</sup> = H; c R<sup>1</sup> = R<sup>2</sup> = OMe.](image-url)

| # | Functional/ method | ∆E<sub>ST</sub> / ∆G<sub>ST</sub> (kcal/mol) |
|---|-------------------|----------------------------------|
| 5a | B3LYP-D3 | 0.8 (-0.3) |
| | DLPNO-CCSD(T) | 3.3 (1.7) |
| | CCSD(T) | 0.3 (-1.4) |
| 5c | B3LYP-D3 | 4.6 (4.0) |
| | DLPNO-CCSD(T) | 3.2<sup>a</sup> |
| | Experimental | 4.6<sup>a</sup> |
| 5b | B3LYP-D3 | 0.0 (-0.3) |
| | DLPNO-CCSD(T) | 3.3 (1.7) |
| | CCSD(T) | 0.3 (-1.4) |

<sup>a</sup> Calculations were performed at the following levels of theory: B3LYP-D3/def2-tzvp(DCM)/B3LYP-D3/def2-svp(DCM); DLPNO-CCSD(T)/cc-PVDZ/B3LYP-D3/def2-tzvp; CCSD(T)/cc-PVDZ/B3LYP-D3/def2-tzvp. Positive values indicate an energetically favored singlet state, negative values indicate an energetically favored triplet state. ∆G<sub>ST</sub> is the Gibbs energy gap calculated in DCM.
to be 4.5 kcal/mol, which is close to the CCSD(T) calculations that showed an energy gap of 3.2 kcal/mol. The data obtained on B3LYP-D3 level is reasonably close to the experimentally observed energy gap of 4.6 kcal/mol. For the more electron-rich bis(4-methoxyphenyl)carbene a smaller energy gap of only 0.4 kcal/mol (0.1 kcal/mol for DLPNO-CCSD(T)) was calculated, which is an overestimation of the calculation of Sander using CCSD(T). In the case of the (4-nitrophenyl)(4-methoxyphenyl)carbene an energy gap of -0.3 kcal/mol was calculated with the B3LYP functional, while a slightly larger $\Delta G_{S/T}$ was obtained when using the DLPNO-CCSD(T) method ($\Delta G_{S/T} = 1.7$ kcal/mol).

Although singlet triplet splittng energies from calculations using the B3LYP-D3 functional do not perfectly reflect experimentally observed or high level CCSD(T) calculations, an important aspect can be deduced: In the case of diphenyl carbene 5b, $\Delta G_{S/T}$ is the largest and can thus provide a rationale for the observed triplet carbene reactivity. For carbones 5a and 5c the singlet triplet splitting is significantly smaller, which can rationalize for the coexistence of both spin states in solution and a facile intersystem crossing and thus for the markedly different reactivity of 5a and 5c. In this context, Sander reported on the reversible switching of spin states of 5c by different light sources or temperature annealing in Ar matrices at temperatures between 3 and 25 K. Under the present conditions (298 K), we could show that different wavelengths had no effect on the reaction pathway (cf. Scheme 2 and discussion above) and that spin switching by different wavelengths is not viable at room temperature. However, it is important to note that thermal relaxation at temperatures as low as 25 K resulted in an equilibrium shift towards the singlet carbene of 5c. We therefore consider that thermally induced intersystem crossing via a low intersystem crossing barrier ($\Delta G^\ddagger = 1.4$ kcal/mol for 5c) rationalizes for the observed reactivity of 5a and 5c.

As part of these calculations, we also studied the geometric properties and electron-distribution by NBO analysis of all possible carbene intermediates. The geometries of the triplet state of all carbene intermediates 5a-c are remarkably close and only small deviations in bond or torsion angles were observed. However, in singlet state the influence of the electron-withdrawing nitro group in (4-nitrophenyl)(4-methoxyphenyl)carbene 5a-S leads to a rotation of the electron-poor 4-nitrophenyl group to a near orthogonal position, while the other aryl ring rotates to a near-coplanar orientation with the carbene empty p-orbital. It is remarkable that this free singlet carbene now shows similar structure features as the singlet donor/acceptor carbones (Table 2) or aryl/aryl carbones in the corresponding Rh-carbene complexes as recently described by Davies and co-workers. NBO analysis of these carbene intermediates shows that singlet carbene 5c is significantly higher nucleophilic than 5a and 5b. Furthermore, 5a has a more positive charge on the singlet carbene carbon, which indicates that it is more electrophilic and thus facilitates cyclopropenation, similar to a phenyl-(carbomethoxy)carbene singlet carbene 20-S (Table 2) or the 2-naphthyl- (carbomethoxy)carbene, which was studied by McMahon.

| #   | Bond angle: $\phi$ | Torsional angle: $\alpha$ | Torsional angle: $\beta$ | NPA charge |
|-----|-------------------|--------------------------|--------------------------|------------|
| 5b  | 119.1°            | 148.5°                   | -34.8°                   | 0.035      |
|     | Singlet state     |                          |                          |            |
|     | 141.6°            | 156.5°                   | -25.0°                   | 0.224      |
|     | Triplet state     |                          |                          |            |
| 5c  | 119.2°            | 152.0°                   | -30.8°                   | -0.038     |
|     | Singlet state     |                          |                          |            |
|     | 141.0°            | 156.0°                   | -25.6°                   | 0.188      |
|     | Triplet state     |                          |                          |            |
| 5a  | 124.7°            | 177.1°                   | -82.4°                   | 0.106      |
|     | Singlet state     |                          |                          |            |
|     | 141.9°            | 166.4°                   | -33.5°                   | 0.251      |
|     | Triplet state     |                          |                          |            |
| 20  | 120.5°            | 177.3°                   | -89.6°                   | 0.023      |
|     | Singlet state     |                          |                          |            |
|     | 135.5°            | 0.002°                   | 0.005°                   | 0.157      |
|     | Triplet state     |                          |                          |            |

[a] Calculations were performed at B3LYP-D3/def2-tzvp(DCM)/B3LYP-D3/def2-svp(DCM). Natural population analysis (NPA) was performed with NBO methods. The partial charges of the carbene carbon were listed.
Calculations on the reaction of diphenyl carbene

We next studied both spin states of the diphenyl carbene intermediate in the reaction with terminal alkynes on the B3LYP-d3 level of theory. In the reaction of singlet diphenyl carbene 5b-S with phenyl acetylene, two transition states were identified that lead to the direct formation of the cyclopropane (via TS1), ΔG = 10.5 kcal/mol and the insertion into the C(sp)-H (via TS2, ΔG = 12.7 kcal/mol). In the case of triplet diphenyl carbene 5b-T two further transition states could be located. The relatively high lying TS2 (27.5 kcal/mol) can account for C(sp)-H functionalization, yet is not feasible due to its high barrier. The addition of triplet carbene 5b-T to the distal acetylene carbon atom proceeds via the lowest-lying transition state TS1 (ΔG = 11.4 kcal/mol) to give INT1T. As the triplet carbene intermediate is energetically favored over the singlet carbene intermediate, the addition pathway via INT1T leading to the indene product is energetically preferred. INT1T further undergoes a radical cyclization via TS3, followed by intersystem crossing to give INT2t. Final [1,2]-hydrogen shift and rearomatization gives the desired indene product as the preferred reaction product in the reaction of diphenyl carbene with aliphatic alkynes (Scheme 5, right part), which is consistent with the experimental data. In the reaction with 3-methyl but-1-yn we considered all of the above transition states and identified two additional transition states that can account for C(sp)-H functionalization. In this case, calculations with the B3LYP-D3 functional gave data that is partially in line with the experimental results. These calculations gave consistent results regarding transition states on the singlet spin surface, which are high in activation free energy and do not account for product formation. Contrarily, calculations on the triplet spin surface gave slightly contradictory results, which suggest C(sp)-H functionalization (ΔG = 12.7 kcal/mol) being slightly favored by 0.9 kcal/mol over indene formation (ΔG = 13.6 kcal/mol), which can be attributed to spin contamination in the triplet state (Table 3).

To better rationalize for the reaction pathways of diphenyl carbene on the triplet spin surface, we performed calculations using the DLPNO-CCSD(T) method. These provide more accurate calculations in the case of unpaired electrons and indeed provide a good rationale on the reaction of triplet diphenyl carbene 5b-T with 3-methyl but-1-yn and show that transition state TS1T that leads to indene formation is 1.0 kcal/mol lower in energy compared to the C(sp)-H functionalization (Table 3).

Table 3. Activation free energy in the reaction of triplet diphenyl carbene with 3-methyl but-1-yn.

| #H | TS1T | TS3T |
|----|------|------|
| 5a (B3LYP-D3) | 13.6 | 12.7 |
| 5a (DLPNO-CCSD(T)) | 14.3 | 15.3 |

[a] Calculations were performed at the following levels of theory: B3LYP-D3/def2-tzvp(DCM)/B3LYP-D3/def2-svp(PCM); DLPNO-CCSD(T)/B3LYP-D3/def2-svp(PCM). The relative Gibbs energies are shown in kcal/mol as ΔG against the respective carbene intermediate.

Scheme 5. Theoretical calculations on the reaction mechanism of diphenylcarbene with phenyl acetylene at the B3LYP-D3/def2-tzvp(PCM)/ B3LYP-D3/def2-svp(PCM) level of theory.
Calculations of Bis(4-methoxyphenyl)carbene and (4-nitrophenyl)(4-methoxyphenyl)carbene

A significant perturbation of transition state free energies was observed when studying the reaction of bis(para-methoxyphenyl)carbene 5c. This variation in the electronic structure of the carbene intermediate and the almost degenerate singlet and triplet state result have a major effect on the activation free energy of the first bond-forming event for most reaction pathways and as a result, different reaction pathways are preferred, depending on the alkyne reaction partner. The presence of two electron-donating methoxy groups leads to a significant increase of electron density at the carbene atom (see the NBO analysis in Table 2) and thus facilitates a formal C-H functionalization mechanism via the low-lying transition state TS2 to give a carbocation and acetylide ion pair INT1 that is stabilized by weak hydrogen-bonding and π-π stacking between

Scheme 6. Theoretical calculations on the reaction mechanism of bis(4-methoxyphenyl)carbene with phenyl acetylene and 3-methylbut-1-ynyl at the B3LYP-D3/def2-tzvp(PCM)/B3LYP-D3/def2-svp(PCM) level of theory.

Table 4. Activation free energies of the first transition state in the reaction of Bis(4-methoxyphenyl)carbene and (4-nitrophenyl)(4-methoxyphenyl)carbene with phenyl acetylene or 3-methylbut-1-ynyl.

| Carbene[a] | Singlet spin state intermediates | Triplet spin state intermediates |
|------------|---------------------------------|---------------------------------|
|            | TS1s Cyclopropene | TS2s C(s)-H | TS3s C(s)-H | TS1r indene | TS2r C(s)-H | TS3r C(s)-H |
| 5a (4NO2/4MeO) Ph | 10.6 | 17.2 | 14.0 | 12.9 | 33.5 | 12.3 |
| 5a (4NO2/4MeO) iPr | 15.5 | 20.4 | 14.0 | 12.9 | 33.5 | 12.3 |
| 5c (4,4'MeO) Ph | 12.0 | 9.8 | - | 11.3 | 27.5 | - |
| 5c (4,4'MeO) iPr | 15.7 | 13.0 | 13.8 | 14.1 | 33.1 | 12.7 |

[a] Calculations were performed at the following levels of theory: B3LYP-D3/def2-tzvp(PCM)/B3LYP-D3/def2-svp(PCM) The relative Gibbs energies are shown in kcal/mol as ΔG‡ against the respective carbene intermediate.
alkynyl anion and diaryl cation. Subsequent, barrierless nucleophilic addition results in the formation of the new C-C bond (Scheme 6, left). Transition states leading to cyclopropene or C(sp^3)-H functionalization are disfavored on the singlet spin surface. Similarly, transition states leading to formation of the indene or C-H functionalization are disfavored on the triplet spin surface (Table 2).

The reaction profile with 3-methyl but-1-yne is similarly perturbed. In this case, bis(para-methoxyphenyl)carbene reacts as a triplet carbene via TS3r and hydrogen atom abstraction to give two radicals (INT4r) that undergo a radical recombination and intersystem crossing to the C(sp^3)-H functionalization product (Scheme 6, right). Importantly, other reaction pathways are strongly disfavored and proceed via relatively high-lying transition states (See Table 4 and ESI).

A distinct perturbation of transition state free energies was observed in the case of (4-nitrophenyl)(4-methoxyphenyl)carbene 5a-S and 5a-T.[11] In this case, calculations on the singlet triplet splitting with the B3LYP functional suggest a more stabilized singlet state (cf. Table 2). Indeed, for the reaction with phenyl acetylene, the calculated energies of transition states suggest that cyclopropene formation is almost identical to indene formation. However, as the singlet carbene is the energetically preferred intermediate, the cyclopropene is thus formed as the main reaction product. Contrarily, in the reaction with 3-methyl but-1-yne, the lowest activation free energy was calculated for C(sp^3)-H functionalization via a similar pathway as for the reaction of bis(4-methoxyphenyl)carbene and is thus favored pathway on the triplet spin surface (Table 4).

Conclusion

In summary, we herein report on the reaction of aryl/aryl diazoalkanes with terminal alkynes. Visible light photolysis furnishes a diaryl carbene intermediate that selectively reacts either in cyclopropenation, C-H functionalization or cascade reactions with terminal alkyne reaction partners, depending on the electronic properties of the aryl substituents. Control experiments with electron-poor olefins and sulfides provide further evidence of different spin states of the carbene intermediate. We further conducted detailed theoretical studies and could show that electron-donating or -withdrawing groups significantly alter the electronic and geometric properties of diaryl carbenes, which results in a significant perturbation of transition states in the reaction with alkynes and can rationalize the reaction outcome. This report now opens up applications of aryl/aryl diazoalkanes in electronically controlled photochemical carbene transfer reactions via singlet and triplet spin states.

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Keywords: photochemistry • carbene • singlet • triplet • DFT calculations

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