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[Co(TPP)]-Catalyzed Carbene Transfer from Acceptor–Acceptor Iodonium Ylides via *N*-enolate Carbene Radicals

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Square-planar cobalt(II)-systems have emerged as powerful carbene transfer catalysts for the synthesis of numerous (hetero)cyclic compounds via cobalt(III)-carbene radical intermediates. Spectroscopic detection and characterization of reactive carbene radical intermediates is limited to a few scattered experiments, centering around *mono*-substituted carbenes. Here, we reveal the unique formation of disubstituted cobalt(III)-carbene radicals derived from a cobalt(II)-porphyrin complex and acceptor–acceptor λ^3 -iodanelylidenes (iodonium ylides) as carbene precursors and their catalytic application. Particularly noteworthy is the fact that iodonium ylides generate novel *bis*-carbenoid species via reversible ligand modification of the paramagnetic [Co(TPP)]-catalyst. Two interconnected catalytic cycles are involved in the overall mechanism, with a *mono*-carbene radical and an unprecedented *N*-enolate-carbene radical intermediate at the heart of each respective cycle. Notably, *N*-enolate formation is not a deactivation pathway, and both the *N*-enolate and carbene radical moieties can be transferred to styrene. The findings are supported by extensive experimental and computational studies.

Metal carbenes have emerged over several decades as highly versatile intermediates, enabling synthetic chemists to access a wide variety of structural motifs. Their synthetic utility ranges from cyclopropanes to numerous C-H and X-H insertion reactions as well as several ring-closing and expansion transformations.¹ Previous work has focused mostly on platinum-group metals^{2,3} and such systems are still among the most successful ones. Over the past decades, attention has shifted largely towards 1st-row transition metals with a higher abundance and lower toxicity compared to their 2nd- and 3rd-row counterparts. Akin to their noble-metal analogues, these systems typically react via classical Fischer-type carbenes.^{4,5} A unique outlier of special interest are cobalt-based systems, as they tend to react via single-electron radical-type pathways that provide new and useful catalytic protocols.⁶ Specifically cobalt-porphyrin complexes such as [Co(TPP)] (cobalt(II)-tetraphenylporphyrin) have shown to be useful for a wide variety of cyclization and insertion reactions mostly inaccessible with traditional Fischer-type carbene chemistry (Fig. 1a).^{7,8,9,10,11,12,13,14,15,16,17}

At the core of the metallo-radical reactions is a metal-to-substrate single-electron transfer process, from cobalt to the carbene moiety, which imbues the carbene with radical properties. The resulting carbene radical intermediate proceeds to react via single-electron, stepwise radical-type pathways as opposed to conventional two-electron reactivity (Fig 1a).¹⁸

Due to their reactive nature, spectroscopic detection and characterization of carbene radical intermediates has been limited to a few scattered experiments, mostly involving the detection of minor amounts at low temperatures together with other species (including ‘bridging carbenes’)^{18a,d,19} or indirect detection with spin trapping agents.^{7m,12a} This is partially because almost all studies employing *mono*-substituted carbene precursors, which provide limited steric protection and/or electronic stabilization. Disubstituted carbenes, and in particular acceptor–acceptor carbenes are anticipated to have a (radical) stabilizing effect, thus

facilitating detection and characterization of these key intermediates. Furthermore, development of efficient protocols for carbene transfer from disubstituted carbene precursors would also expand the scope of cobalt(II)-catalyzed group transfer reactions substantially. However, activation of disubstituted acceptor–acceptor diazo compounds has proven to be far more difficult (Fig. 1b). The Zhang group developed enantioselective porphyrins equipped with hydrogen-bond donor motifs that facilitate carbene radical formation,²⁰ and some of these can activate specific disubstituted diazo compounds. Nevertheless, this remains in general a challenging task, as the complexity of these catalysts demand lengthy syntheses and also the inherent toxicity and potentially explosive nature of diazo compounds calls for the development of alternative approaches. As such, hypervalent iodine(III) analogues (i.e. iodonium ylides) are useful alternative precursors for carbene formation.^{21,22} However, to the best of our knowledge, there are no reported examples of homogeneous cobalt systems capable of catalytic carbene transfer from iodonium ylides (Scheme 2A).²³ For Fe^{II}- and closed-shell Co^{III}-porphyrin-based systems, a likely reason for this behavior is the observed formation of catalytically inactive *N*-enolate species (Fig. 1c).²⁴ For these diamagnetic systems, the cyclic diester carbenes rapidly rearrange to *mono*- or *bis-N*-enolate modified porphyrins with the pendant carbonyl group serving as a 5th or 6th ligand (Fig. 1c). None of these reported *N*-enolate structures is catalytically active, and hence it is tempting to consider the reaction shown in Fig. 1c as a general catalyst deactivation pathway. Herein we demonstrate that this assumption is incorrect for open-shell cobalt systems. Building on this seminal work, we decided to investigate catalytic carbene transfer from acceptor–acceptor iodonium ylides mediated by homogeneous cobalt(II)-based systems, which uncovered an efficient protocol for styrene cyclopropanation via unique radical-type intermediates (Fig. 1d).

Fig. 1 | Applications and challenges of cobalt(III)-carbene radicals. **a**, Single-electron transfer from cobalt to the carbene moiety enabling radical reactivity and successful synthesis of a variety of (hetero)cycles. **b**, Challenges in the activation of acceptor-acceptor-disubstituted-carbene precursors. **c**, Coordination chemistry of acceptor-acceptor metal carbenes leading to *N*-enolate species (Mansuy and coworkers). **d**, Application of iodonium ylides in cobalt-catalyzed carbene transfer reactions, revealing novel *N*-enolate type carbene radical species. Both carbene radical and *N*-enolate moieties are reactive carbene-delivering functionalities in cyclopropanation of styrene (this work).

Results and Discussion: We first set out to test the catalytic activity of $[Co(TPP)]$ in the cyclopropanation of styrene using either dimethyldiazomalonate ($DMM \cdot N_2$) or dimethylmalonate iodonium ylide ($DMM \cdot IY$) as a model reaction (Table 1). The diazo substrate yielded little to no cyclopropane product (<10%, based on 1H -NMR) even when heated to 60 °C for 60 h (Entry 1 & 2). This reactivity is consistent with previously reported attempts to activate acceptor-acceptor diazo compounds.²⁵ In marked contrast, the analogous reaction using the corresponding iodonium ylide yielded 99% cyclopropane in <1 h at 20 °C (Entry 3). Further screening of solvents (Entry 3–10) revealed that apolar solvents work best, of which C_6D_6 , CD_2Cl_2 and toluene- d_8 gave the highest yields. Temporal reaction monitoring (Supplementary Fig. S6) shows slightly higher yields in C_6D_6 than in non-deuterated benzene. Optimization of the catalyst loading, $DMM \cdot IY$ equivalents and time (Entries 11–16) revealed that quantitative yields can be obtained with a 2.5 mol% catalyst loading in just 5 minutes. Several control experiments confirm a crucial role of the $[Co(TPP)]$ catalyst as well as the ylide carbene precursor. Reactions in the presence of air or TEMPO as a trapping agent gave rise to reduced or no yield, respectively, confirming that radical-type reactions are operative. (Supplementary Table S7).

Table 1 | Screening of carbene precursors ($Y = N_2$ or IPh) in the cyclopropanation of styrene with $[Co(TPP)]$ and optimization of reaction conditions using $DMM \cdot IY$.

Entry	Cat. loading (mol%)	solvent	Y	Time (min.)	Yield (%) ^a
1	5	C_6D_6	N_2	60	0 ± 0%
2	5	C_6D_6	N_2	3600	10 ± 3% ^b
3	5	C_6D_6	IPh	60	99 ± 4%
4	5	Tol- d_8	IPh	60	98 ± 5%
5	5	CD_2Cl_2	IPh	60	98 ± 1%
6	5	$CDCl_3$	IPh	60	66 ± 4%
7	5	THF- d_8	IPh	60	58 ± 0%
8	5	DMSO- d_6	IPh	60	84 ± 1%
9	5	CD_3OD	IPh	60	4% ^c
10	5	CD_3CN	IPh	60	31% ^c
11	5	C_6D_6	IPh	60	81 ± 4% ^d
12	5	C_6D_6	IPh	5	99 ± 3%
13	2.5	C_6D_6	IPh	5	99 ± 1%
14	2.0	C_6D_6	IPh	5	79 ± 1%
15	1.0	C_6D_6	IPh	5	48 ± 1%
16	0.1	C_6D_6	IPh	5	4 ± 1%

^a Yields based on 1H -NMR integration using 1,3,5-trimethoxybenzene as internal standard. Performed in duplicate; ^b 60 °C ^c Single run experiment; catalyst poorly soluble; ^d 1:1 styrene: $DMM \cdot IY$.

Mechanistic investigations. Based on previous work regarding hypervalent iodine reagents in cobalt-catalyzed nitrene transfer,²⁶ we suspected that *bis*-carbenoid intermediates might play a role in the catalysis.²⁷ This was first investigated by reacting DMM•IY and [Co(TPP)] in the absence of styrene. Using positive-mode cold electrospray ionization high resolution mass spectrometry (ESI⁺-HR-MS), two major peaks at m/z = 801 Da and m/z = 931 Da match those of *mono*- and *bis*-carbenoid complexes, respectively (Fig. 2g). The isotopic patterns are in line with *mono*-cations and subsequent reduction of the ionization voltage resulted in a complete collapse of both signals, suggesting the ionization of neutral species. Peaks at m/z = 671 Da and 1620 Da, respectively, match that of the free [Co(TPP)] catalyst and a water adduct of a dimeric form of the *mono*-carbenoid species (Supplementary Fig. S27). MS-MS analysis

(Supplementary Fig. S37) shows m/z = 671 Da and m/z = 801 Da to be fragments of m/z = 931 Da. However, the presence of some *mono*-carbenoid species cannot be excluded solely based on these MS experiments.

To shed more light on the stoichiometry of the reaction, UV/Vis spectroscopy was used to probe changes in the porphyrin's Soret and Q-bands. Titrating the [Co(TPP)] catalyst with 0 to 2.5 eq. of DMM•IY in CH₂Cl₂ revealed a transition of the Soret peak at 410 nm to 430 nm (significantly lower intensity), with clear isosbestic points at 383, 424, 518 and 542 nm (Fig. 2e.). Full conversion is observed with 2 eq. of the iodonium ylide, above which the spectrum does not change anymore. This reveals rapid formation of a single, new species without a detectable second, long-lived intermediate. The Q-band at 528 nm fully collapses into the

Fig. 2 | Spectroscopic detection and characterization of the *N*-enolate-carbene radical I^{E-T} . **a**, Experimental (black) and simulated (red) X-band EPR spectrum of species I^{E-T} obtained in a reaction between DMM•IY and [Co(TPP)] in benzene at RT (Freq. 9.6434 GHz, mod. amp. 1 G, power 20 mW). **b**, Spectrum of I^{E-T} measured in toluene glass at 40 K (Freq. 9.6435 GHz, mod. amp. 4 G, and power 0.633 mW). **c**, Spectrum of ^{13}C - I^{E-T} measured at RT of the reaction between ^{13}C -DMM•IY and [Co(TPP)] in benzene at RT (Freq. 9.6449 GHz, mod. amp. 4 G, power 0.633 mW). **d**, Spectrum of ^{13}C - I^{E-T} measured in toluene glass at 40 K (Freq. 9.6429 GHz, mod. amp. 4G, power 0.633 mW). Simulated parameters are mentioned in the text and are listed in Suppl. Table S9. **e**, Solid-state crystal structure of I^{E-T} at 100 K (ORTEP, thermal ellipsoids at 50% probability level). TPP phenyl groups, solvent molecules, disordered O₂-CH₃ positions and all protons except H24 omitted for clarity. Selected bond lengths (Å): Co1–N1 2.1195(17), Co1–N2 1.9700(18), Co1–N3 1.9464(17), Co1–N4 1.9752(16), Co1–O1 1.952(2), Co1–C24 2.045(2), N1–C21 1.489(3), C2–N1 1.464(3), C2–C1 1.381(3), C1–C20 1.396(3), C20–C19 1.387(3), C19–N1 1.457(3), C21–C22 1.400(4), C21–C23 1.441(3), C22–O1 1.260(3), C22–O2 1.416(4), C23–O3 1.217(3), C23–O4 1.356(3), C24–C25 1.486(3), C24–C26 1.486(3), C25–O5 1.206(3), C26–O7 1.213(3), C26–O8 1.351(3). **f**, UV/Vis spectra of a series of reactions between [Co(TPP)] and varying equivalents of DMM•IY in CH₂Cl₂ at t = 0 min. **g**, ESI⁺-HR-MS spectrum of a reaction between [Co(TPP)] and DMM•IY, showing the presence of *mono*- (m/z = 801 Da) and *bis*-carbenoid complexes (m/z = 931; 932[+H⁺]) and residual (or fragmentation to) [Co(TPP)] (m/z = 671).

baseline. Coupled with the bathochromic shift of the Soret peak, this points to a substantial perturbation of the (electronic) structure of the porphyrin macrocycle induced by oxidation of Co^{II} to Co^{III} with a concomitant chemical reaction between a carbene moiety and the porphyrin ring.^{24,26a} We ascribe this to selective formation of *N*-enolate-carbene radical species $\text{I}^{\text{E-T}}$ (Fig. 3), which is supported by TD-DFT calculations (Supplementary Information).

Turning to X-band EPR spectroscopy, an isotropic spectrum was obtained at room temperature in benzene characteristic of an $S = \frac{1}{2}$ system with small ^{59}Co hyperfine interactions (HFIs) ($A^{\text{Co}_{\text{iso}}} = 85.6$ MHz) and an isotropic g -value ($g_{\text{iso}} = 1.998$). This is indicative of a cobalt-bound, but organic-centered radical undergoing restricted tumbling in solution (Fig. 2a). Additional EPR measurements at 40 K (Fig. 2b) in toluene glass corroborate these findings, showing a complex HFI pattern and a rhombic g -tensor in line with a cobalt-bound, organic-centered radical ($g_{11} = 1.997$; $g_{22} = 2.006$; $g_{33} = 2.008$) with an $S = \frac{1}{2}$ and small ^{59}Co -HFIs ($A^{\text{Co}_{11}} = 21$, $A^{\text{Co}_{22}} = -173$; $A^{\text{Co}_{33}} = -103$ MHz). ^{13}C -labeling of the ylidic carbon gave a similar isotropic X-band EPR spectrum in benzene at room temperature as for the ^{12}C -analog (^{13}C - $\text{I}^{\text{E-T}}$: $g_{\text{iso}} = 1.998$, $A^{59\text{Co}_{\text{iso}}} = 85.6$ MHz; $A^{13\text{C}_{\text{iso}}} = 104.7$ MHz), but now with 9 effective hyperfine lines instead of 8. This is caused by additional coupling with a *single* $I = \frac{1}{2}$ ^{13}C -nucleus (Fig. 2c). At 40 K in toluene glass (Fig. 2d), a rhombic spectrum was obtained similar to ^{12}C - $\text{I}^{\text{E-T}}$,

indicative of a cobalt-bound, carbene-centered radical species ($g_{11} = 1.998$; $g_{22} = 2.004$; $g_{33} = 2.006$). ^{59}Co -HFIs match the previously obtained values ($A^{\text{Co}_{11}} = 21$; $A^{\text{Co}_{22}} = -173$; $A^{\text{Co}_{33}} = -103$ MHz), but with additional ^{13}C -HFIs stemming from a *single* ^{13}C nucleus ($A^{13\text{C}_{11}} = 260$; $A^{13\text{C}_{22}} = 30$; $A^{13\text{C}_{33}} = 30$ MHz). These values are in good agreement with the DFT (B3LYP/ZORA-def2-TZVPP) calculated EPR parameters of *N*-enolate-carbene complex $\text{I}^{\text{E-T}}$ (Supplementary Table S9). Complementary data were obtained with in-situ ATR-FT-IR studies (Supporting Information).

On the basis of the combined spectroscopic evidence, we conclude that the reaction between $\text{DMM}\cdot\text{IY}$ and $[\text{Co}(\text{TPP})]$ results in formation of the unprecedented *N*-enolate-carbene radical species $\text{I}^{\text{E-T}}$ (Fig. 3). Additional proof for the structure of $\text{I}^{\text{E-T}}$ comes from NMR and single-crystal X-ray diffraction (SC-XRD) characterization of the diamagnetic *N*-enolate-alkyl species $\text{I}^{\text{A-E}}$, which is readily obtained by HAT to the carbene radical moiety of $\text{I}^{\text{E-T}}$ (Fig. 2f). For more details about the formation and characterization of diamagnetic complex $\text{I}^{\text{A-E}}$, see section “HAT-induced catalyst deactivation” (*vide infra*).

Having characterized the novel *N*-enolate-carbene radical intermediate $\text{I}^{\text{E-T}}$, we proceeded to investigate its potential role in the catalytic reaction with styrene. $[\text{Co}(\text{TPP})]$ was exposed to 2 eq. $\text{DMM}\cdot\text{IY}$ to form $\text{I}^{\text{E-T}}$ quantitatively, after which an excess of styrene was added. To our surprise, this “single-turnover” experiment produced 2 equivalents of

Fig. 3 | Formation of *N*-enolate-carbene radical $\text{I}^{\text{E-T}}$ obtained by reaction between $[\text{Co}(\text{TPP})]$ and $\text{DMM}\cdot\text{IY}$, based on the spectroscopic evidence (EPR, UV/Vis, CSI⁺-HR-MS and *in-situ* ATR-FT-IR). The *mono*-terminal carbene radical intermediate I^{T} is not detectable during UV/Vis titrations leading to formation of $\text{I}^{\text{E-T}}$, but can be detected in single turnover experiments between $\text{I}^{\text{E-T}}$ and 1 eq. styrene. Complex $\text{I}^{\text{E-T}}$ deactivates to diamagnetic *N*-enolate-alkyl species $\text{I}^{\text{A-E}}$ via HAT (e.g. from toluene). Phenyl rings of the TPP ligand omitted for clarity.

Fig. 4 | Trapping and reactivity studies. **a**, X-band EPR spectrum of I^T obtained in toluene- d_8 glass at 40 K after reacting I^{E-T} with 1 eq. of styrene (microwave freq. 9.6443 GHz, mod. amp. 5 G, and power 6.325 mW). **b**, EPR spectrum of I^E measured after freeze quenching the catalytic reaction mixture obtained in the ‘reverse order’ of addition: {(1) DMM•IY, (2) [Co(TPP)], (3) styrene} (microwave freq. = 9.643446 GHz, mod. amp. = 4 G, power 0.6325 mW). **c**, EPR spectra measured after freeze quenching the catalytic reaction mixtures obtained with two orders of addition, ‘regular order’ {(1) DMM•IY, (2) styrene, (3) [Co(TPP)]} and ‘reverse order’ {(1) DMM•IY, (2) [Co(TPP)], (3) styrene}, compared to the spectra of [Co(TPP)], I^T and I^{E-T} . **d**, Hammett plot for the [Co(TPP)]-catalyzed cyclopropanation of styrene using DMM•IY.

cyclopropane **1**, thus indicating that both the carbene radical moiety *and* the enolate moiety of I^{E-T} can be transferred as a carbene group to styrene (Fig. 3).

Clearly, and in stark contrast with previous work pertaining closed-shell Co^{III} -porphyrins, formation of the *N*-enolate moiety is reversible for the paramagnetic [Co^{II}(TPP)], and is not a catalyst deactivation pathway. Armed with this knowledge, I^{E-T} was exposed to 1 eq. of styrene in a single-turnover reaction and studied by X-band EPR spectroscopy (Fig. 4a). Interestingly, this produced a spectrum indicative of a cobalt-bound organic-centered radical that is distinctly different from I^{E-T} . Simulation ($g_{11} = 2.018$; $g_{22} = 1.988$; $g_{33} = 2.047$; $A^{Co_{11}} = 15$, $A^{Co_{22}} = 30$; $A^{Co_{33}} = 135$ MHz) in comparison to the computed EPR parameters suggest the formation of *mono*-terminal carbene species I^T (Supplementary Fig. S12 and Table S9).

These findings suggest that the initial carbene transferred from I^{E-T} to styrene is the carbene radical moiety, after which the *N*-enolate moiety of the newly formed Co^{III} -*N*-enolate adduct I^E rearranges to I^T . In the presence of

additional styrene, the latter reacts to produce a second equivalent of cyclopropane (Fig. 3.).

When running the catalytic reaction by adding the reagents in the order {(1) DMM•IY, (2) styrene, (3) [Co(TPP)]}, followed by freeze quenching the reaction mixture after 20 seconds, a mixture was obtained containing mainly [Co(TPP)] and the *mono*-carbene radical species I^T (Fig. 4c.), while upon reversing the order of addition to {(1) DMM•IY, (2) [Co(TPP)], (3) styrene} we detected a new, previously unencountered species. The relatively large *g*-anisotropy of the latter species points to a cobalt-centered radical, and based on a comparison with DFT calculated EPR parameters we ascribe this spectrum to the *N*-enolate adduct I^E ($g_{11} = 2.051$; $g_{22} = 2.168$; $g_{33} = 2.027$. $A^{Co_{11}} = -109$, $A^{Co_{22}} = -124$; $A^{Co_{33}} = 390$ MHz) (Fig. 4b and c). These data suggest that in reactions where the catalyst reacts first with the ylide, carbene transfer proceeds mostly from the *N*-enolate-carbene radical intermediate I^{E-T} , while in reactions wherein styrene is present from the beginning the *mono*-carbene radical I^T is the dominant carbene transfer intermediate.

We decided to gather more mechanistic information via Hammett analysis of the carbene-transfer reactions (Supplementary Information). To account for radical contributions to the Hammett parameters, the $\sigma_{II}^\bullet$ radical spin-delocalization substituents^{28a} were included as well as the classical $\sigma^{+/-}$ Hammett constants (Fig. 4d).^{28b} Changing the order of addition of reagents does not have a noticeable influence on the obtained Hammett parameters (Supplementary Fig. S53–54 and Tables S13–14), suggesting that both carbene radicals (I^{E-T} and I^T) have similar electronic properties. Interestingly, the large $|\rho^-/\rho^\bullet|$ values suggest a significant buildup of *negative charge* in the transition state, implying that the carbene radicals are distinctly nucleophilic.^{7j,18a}

HAT-induced catalyst deactivation: Cobalt(III)–carbene radicals are known to deactivate rapidly through hydrogen-atom-transfer (HAT) from either the starting diazo reagent or the solvent.^{7b,19} Detailed spectroscopic (EPR, NMR, UV/Vis, ATR-FT-IR) and mass spectrometric studies (Supplementary Information) revealed that HAT from the solvent (toluene) or other hydrogen sources (e.g. trace impurities) indeed leads to deactivation of both *mono*-carbene radical intermediate I^T and *N*-enolate carbene radical intermediate I^{E-T} to produce alkyl species I^A and I^{E-A} , respectively (Fig. 3). HAT-deactivation is observed to be significantly faster for I^T than for I^{E-T} , in good agreement with supporting DFT studies (Supplementary Information). The *N*-enolate moiety clearly has a protective function, making the barrier for HAT-deactivation higher. The diamagnetic alkyl species I^{E-A} could be isolated and was characterized in detail by 1H -, ^{13}C -, 1H - 1H -COSY, 1H - ^{13}C -HSQC and HMBC NMR spectroscopy (Supplementary Information) and single-crystal X-ray diffraction studies (Fig. 2f.; Supplementary Information). NMR, IR studies, bond-length analysis and use of the

harmonic oscillator model for aromaticity²⁹ reveal that TPP *N*-enolate functionalization leads to desymmetrization of the macrocycle. However, the overall aromaticity is largely retained (HOMA value: 0.91; Supplementary Information). The modified pyrrole ring still binds to cobalt, but has a substantially elongated Co–N bond.

Computational DFT studies: To gain further insight into the mechanism of the metalloradical-catalyzed cyclopropanation reaction we turned to density functional theory calculations. The results are shown in Fig. 5. A detailed account is provided in the supporting information. Herein we summarize the main results, which are in excellent agreement with the experimental data:

(a) The overall reaction mechanism for [Co(TPP)]-catalyzed styrene cyclopropanation is quite intricate, and consists of two interconnected catalytic cycles with low reaction barriers; a “*mono*-carbene cycle” in which *mono*-carbene radical complex I^T is the key intermediate, and a “*bis*-carbene

cycle” in which *N*-enolate-carbene radical I^{E-T} is the key carbene transfer species.

(b) The first and second addition of DMM•IY both proceed via low barrier transition states to produce I^T and I^{E-T} . Interestingly, the order of stability for the *mono*-carbenoids is $I^T > I^B \approx I^E$ whereas for the *bis*-carbenoids, the relation is reversed ($I^{E-T} > I^{B-T} > I^{T-T}$).

(c) The “*bis*-carbene cycle” is reconnected to the “*mono*-carbene cycle” via intramolecular rearrangement of I^E to I^B , followed by formation of I^T . Although slow, the highest barrier of this process (TS10: $\Delta\Delta G^\ddagger = +23.1$ kcal·mol⁻¹) is still readily accessible at RT. This explains why I^E is detectable with EPR spectroscopy (Fig. 4b). These data explain that *N*-enolate formation is reversible and that treatment of I^{E-T} with excess styrene produces 2 eq. of cyclopropane.

(d) The barrier for styrene addition to I^T is substantially lower than the barrier for styrene addition to I^{E-T} (+10.8 vs. +18.3 kcal·mol⁻¹), and the “*mono*-carbene cycle” should be

Fig. 5 | Full catalytic cycle for the [Co(TPP)]-catalyzed reaction of DMM•IY and styrene. Free energies (ΔG°_{298K} in kcal·mol⁻¹) are reported relative to the *mono*- and *bis*-benzene adducts of [Co(TPP)] for 5- and 6-coordinate species, respectively. All calculations were performed at the BP86/def2-TZVP/disp3 (m4-grid) level of theory at the doublet spin surface ($S = 1/2$). Inset Figures show spin density plots of I^T (left) and I^{E-T} (right). Phenyl rings of the TPP ligand omitted for clarity.

faster than the “bis-carbene cycle”. Combined with the fact that the ylide is much less soluble than styrene, this explains that the *mono*-carbene cycle is the dominant catalytic pathway under reaction conditions where all components are present before adding the catalyst.

(e) However, formation of I^{E-T} from *mono*-carbene radical I^T is competitive with styrene addition to I^T at equimolar concentrations (+11.2 vs. +10.8 kcal·mol⁻¹), and hence both cycles are relevant. While accessible at RT, the computed barrier for formation of I^E from I^E is relatively high. Hence, under conditions where the ylide reacts with the catalyst before styrene is added, the catalytic reaction should be largely trapped in the “bis-carbene cycle”. Experimental detection of I^E with EPR spectroscopy for a reaction carried out by adding the reagents in the order {(1) DMM•IY, (2) [Co(TPP)], (3) styrene} (Fig. 4c) confirms this.³⁰

NEVPT2–CASSCF electronic structure calculations

To check for possible multireference/multiconfigurational contributions to the electronic structures of the key carbene transfer intermediates I^T and I^{E-T} ,³¹ and to provide an accurate description of their frontier molecular orbitals, we also performed NEVPT2-corrected CASSCF calculations (Supporting Information). These calculations confirm that these species have a doublet ($S = \frac{1}{2}$) ground state without significant multireference character, well-separated from higher spin states, and that their electronic structures are properly described by DFT (Supplementary Tables S26–S27 and Fig. S70–S71).

Conclusions

In this work we demonstrated that the acceptor–acceptor iodonium ylide DMM•IY is a highly suitable precursor to generate, detect and characterize disubstituted carbene radicals at [Co(TPP)], which are productive in carbene transfer catalysis, and enable efficient and fast catalytic cyclopropanation of styrenes. Reaction of [Co(TPP)] with 2 eq. of DMM•IY produces the unprecedented *N*-enolate-carbene radical intermediate I^{E-T} , containing a Co^{III}-carbene radical moiety and an enolate-modified porphyrin ring generated by carbene attack at one of the pyrrole rings of the TPP ligand. In contrast to what might be expected, formation of the *N*-enolate is a reversible process, and not a route to catalyst deactivation. The carbene radical and the *N*-enolate moieties are both carbene-delivering functionalities capable of carbene transfer to other substrates.

The mechanism of the cyclopropanation reaction proceeds via two interconnected catalytic cycles. The key carbene transfer intermediate in one cycle is *mono*-carbene I^T , and in the other cycle it is the novel and unusual *N*-enolate-carbene radical I^{E-T} . Catalyst deactivation involves HAT from the solvent or trace impurities to the carbene radical moieties of these intermediates. The *N*-enolate moiety clearly

has a protective function, making the barrier for HAT-deactivation higher. Facile and energetically favorable carbene formation coupled with comparably high deactivation barriers leads to the observed highly selective formation of donor–acceptor cyclopropanes in quantitative yield.

The interplay of opposing stabilities between terminal and *N*-bridging carbene (radical) moieties dictated by the Co^{II/III}-redox cycle plays an important role, and explains the unique active participation of the otherwise catalytically inactive *N*-enolate species. We envision that further application of these unique Co^{III}-carbene radicals has the potential to unlock new scaffolds via the superior facile activation of acceptor–acceptor iodonium ylides over diazo compounds.

Supporting Information

Experimental details; synthetic procedures; catalytic studies; XRD, EPR, NMR, UV/Vis, in-situ ATR-FT-IR and CSI⁺-MS spectroscopic data, (additional) DFT and NEVPT2-CASSCF calculations.

Keywords: carbene radical, iodonium ylides, cobalt catalysis, cobalt porphyrin, cyclopropanation, mechanistic studies

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Competing Interests

The authors declare no competing interest.

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