Supporting Information belonging to the paper:

‘Carbene Radicals’ in Co^{II}(por)-Catalyzed Olefin Cyclopropanation

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Figure S1. ESI-MS spectrum of the reaction mixture of Co(TPP) and 4eq EDA in toluene.

Figure S2. ESI-MS spectrum of the reaction mixture of Co(3,5-Di^tBu-ChenPyrin) and 4eq EDA in toluene.

Figure S3. ESI-MS spectrum of the reaction mixture of Co(3,5-Di^tBu-ChenPyrin) and 4eq EDA in CD₂Cl₂.

Figure S4. DFT optimized structures of species formed during subsequent reactions of Co(por) with methyl diazoacetate and methyl acrylate leading to *trans*-cyclopropane.

Figure S5. Structure of the ‘bridging carbene’ species **C'** (right) and the transition state leading to it.

Figure S6. Structures of species **B-C'** stabilized by hydrogen bonding to the amide moiety.

Table S1. Energy changes for the ‘carbene’ formation reactions between Co(por) and EDA.

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
A: Co(por) + EDA	0	0.00	0.00	0.00	0.00
B: MDA adduct to Co(por)	-0.38	-0.21	8.94	0.31	-28.94
TS1: N ₂ loss	13.72	12.42	21.98	12.69	-31.17
C: ‘terminal carbene’	-6.32	-8.60	-6.12	-7.69	-5.29
TS between C and C’	6.85	4.12	6.78	4.74	-6.84
C’: Co(por) ‘bridging carbene’	-9.16	-10.45	-7.59	-9.83	-7.50
B’: nitrogen bound MDA adduct	-4.52	-3.95	5.08	-3.56	-29.02
B’’: carbonyl bound MDA adduct	-4.15	-3.93	4.81	-3.37	-27.46
A: Co(por) + EDA amide stabilized	0	0.00	0.00	0.00	0.00
B: MDA adduct to Co(por) amide stabilized	-3.92	-3.26	7.22	-2.89	-33.95
TS1: N ₂ loss amide stabilized	9.17	7.98	18.9	8.23	-35.80
C: carbene radical amide stabilized	-11.20	-13.02	-9.22	-12.29	-10.30
TS between C and C’ amide stabilized	-14.14	-15.52	-12.02	-14.86	-9.52
C’: Co(por) bridging carbene amide stabilized	1.88	-0.64	3.15	-0.12	-10.97

Table S2. Energy changes for the between Co(por)(CHCOOMe) and methyl acrylate along the *trans*-cyclopropanation pathway

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
C’: ‘bridging carbene’	0	0.00	0.00	0.00	0.00
TS2: C-C radical coupling	9.04	8.31	17.49	8.85	-29.00
D: coupled to alkene	-16.55	-14.82	-4.27	-14.85	-35.48
TS3: cyclopropane- <i>trans</i> formation	-13.52	-12.83	-2.84	-12.68	-33.02
E: cyclopropane + Co ^{II} (por)	-39.27	-36.75	-35.94	-37.31	-4.61

Table S3. Energy changes for the reaction between Co(por)(CHCOOMe) and methyl acrylate along the *cis*-cyclopropanation pathway.

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
C’: ‘bridging carbene’	0	0.00	0.00	0.00	0.00
TS2: C-C radical coupling	9.85	9.66	19.89	9.90	-33.55
D: coupled to alkene	-14.81	-13.21	-2.58	-13.24	-35.76
TS3: cyclopropane- <i>cis</i> formation	-10.08	-9.57	0.31	-9.42	-32.64
E: cyclopropane + Co ^{II} (por)	-33.65	-31.48	-31.20	-31.95	-2.53

Table S4. Energy changes for the reaction between Co(por)(CHCOOMe) and styrene along the *trans*-cyclopropanation pathway.

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
C’: ‘bridging carbene’	0	0.00	0.00	0.00	0.00
TS2: C-C radical coupling	9.77	8.71	18.24	9.32	-29.92
D: coupled to alkene	-20.55	-19.63	-9.13	-19.32	-34.20
TS3: cyclopropane- <i>trans</i> formation	-17.51	-17.03	-6.49	-16.83	-34.70
E: cyclopropane + Co ^{II} (por)	-36.25	-34.66	-34.39	-34.92	-1.77

Table S5. Energy changes for the reaction between Co(por)(CHCOOMe) and styrene along the *cis*-cyclopropanation pathway.

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
C' : 'bridging carbene'	0	0.00	0.00	0.00	0.00
TS2 : C-C radical coupling	9.64	8.59	18.52	9.16	-31.42
D : coupled to alkene	-20.22	-19.16	-8.48	-18.94	-35.08
TS3 : cyclopropane- <i>cis</i> formation	-16.99	-16.58	-6.12	-16.37	-34.39
E : cyclopropane + Co ^{II} (por)	-33.23	-31.65	-31.34	-31.90	-1.87

Table S6. Energy changes for the reaction between Co(por)(CHCOOMe) and propene along the *trans*-cyclopropanation pathway.

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
C' : 'bridging carbene'	0	0.00	0.00	0.00	0.00
TS2 : C-C radical coupling	12.48	1.92	21.34	12.47	-29.76
D : coupled to alkene	-12.01	-21.56	-1.98	-10.92	-30.01
TS3 : cyclopropane- <i>trans</i> formation	-11.85	-21.42	-1.34	-11.15	-32.94
E : cyclopropane + Co ^{II} (por)	-38.33	-46.06	-35.49	-36.34	-2.86

Table S7. Energy changes for the reaction between Co(por)(CHCOOMe) and propene along the *cis*-cyclopropanation pathway.

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
C' : 'bridging carbene'	0	0.00	0.00	0.00	0.00
TS2 : C-C radical coupling	12.84	13.60	21.46	12.81	-29.04
D : coupled to alkene	-12.22	-11.32	-1.25	-11.13	-33.13
TS3 : cyclopropane- <i>cis</i> formation	-11.82	-10.94	-1.29	-11.28	-33.53
E : cyclopropane + Co ^{II} (por)	-36.94	-33.99	-33.67	-34.83	-3.92

Table S8. Energy changes for the reaction between Co(por)(CHCOOMe) and MDA to form bis-carbene species.

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
C' : 'bridging carbene'	0	0.00	0.00	0.00	0.00
B'	3.72	3.66	12.64	4.54	-27.19
TS1'	16.12	14.79	25.31	15.23	-33.65
F	-0.95	-4.02	-1.83	-2.59	-2.55
TS between F and F'	8.17	6.09	10.17	6.54	-12.17
F'	-7.49	-8.50	-4.30	-7.74	-11.54
F'' bis-'bridging carbene'	24.59	20.71	22.96	22.24	-2.42

Figure S7. Spin density (left) and SOMO (right) plots of the *trans* adducts **D**. Top: methyl acrylate; middle: styrene; bottom: propene.

Figure S8. Molecular structures of transition states **TS4** (left, carboxymethyl group of the radical carbene *trans* to the N₂ leaving group of MDA) and **TS4'** (right, carboxymethyl group of the radical carbene *cis* to the N₂ leaving group of MDA). Note that in both cases the hydrogen atom of MDA is on the same side with the hydrogen atom of the radical carbene leading to formation of the *cis* product (dimethyl maleate) after coupling of the carbon atoms.

Table S9. Energy changes for the ‘carbene dimerization’ reactions between Co^{II}(por)(CHCOOMe) and MDA producing dimethyl maleate.

	ΔE	ΔE_{ZPE}	$\Delta G^{\circ}_{298\text{K}}$	ΔH	ΔS_{sol}
C' : ‘bridging carbene’	0	0.00	0.00	0.00	0.00
TS4 :	13.86	13.11	22.96	13.66	-31.21
TS4' :	14.26	13.49	23.08	14.07	-30.24
Co^{II}(por) + dimethyl maleate (<i>cis</i> product)	-64.46	-65.23	-74.92	-64.65	34.45
Co^{II}(por) + dimethyl fumarate (<i>trans</i> product)	-71.58	-71.90	-80.68	-71.48	30.87

Olefin substrate inhibition or catalyst poisoning?

Cenini and coworkers reported that excess styrene slows down the rate of Co^{II}(TPP)-catalyzed cyclopropanation,¹ but to our best knowledge, Co^{II}(por) complexes do not form stable adducts with olefins at room temperature. Therefore we investigated computationally the thermodynamics of η^2 -interaction of the double bonds of methyl acrylate, styrene and propene with the model Co^{II}(por) system.

The investigated reactions (eq 1) have a positive free energies at RT in all cases (Table S10), in line with the reported low affinity of cobalt porphyrins for ethene.² These data suggest that catalysts inhibition by simple olefin coordination saturation is not a likely explanation for the observed drop in activity at high styrene concentrations,¹ because

with such low calculated affinities a negligible amount of the $\text{Co}^{\text{II}}(\text{por})$ species will be saturated under the catalytic conditions at the highest applied styrene concentrations. The observed slow reactions at high [styrene] should thus have a different reason.

Table S10. Computed free energies of formation and equilibrium constants for the formation of $\text{Co}(\text{por})(\text{olefin})$ (eq. 1). (DFT, BP86, def-TZVP).

Olefin	ΔG^{298} (kcal mol ⁻¹)	K^{298}
Methyl acrylate	+ 10.8	$1.2 \cdot 10^{-8}$
Styrene	+ 8.3	$7.8 \cdot 10^{-7}$
Propene	+ 8.0	$1.3 \cdot 10^{-6}$

Table S11. Energies of the olefin adducts $\text{Co}(\text{por})(\text{olefin})$ relative to $\text{Co}(\text{por}) + \text{olefin}$.

	ΔE	ΔE_{ZPE}	$\Delta G_{298\text{K}}^{\circ}$	ΔH	ΔS_{sol}
Co(por)(methyl acrylate)	1.04	1.42	10.79	1.81	-30.11
Co(por)(styrene)	-0.75	-0.92	8.32	-0.31	-28.94
Co(por)(propene)	-1.27	1.14	8.03	-0.62	-29.04

Free energies for olefin cyclopropanation at the b3-lyp, def-TZVP level

The (free) energies for ‘carbene’ formation from $\text{Co}(\text{por})$ and EDA, as well as the subsequent reaction of the ‘radical carbene’ with the olefins propene, methyl acrylate and styrene at the b3-lyp, def-TZVP level of theory were estimated from single point calculations using the BP86 optimized geometries (Figures S9-S11). The b3-lyp energies of the EDA adduct **B** and the transition state **TS1** are unrealistically high, and contrast with relative fast catalytic cyclopropanation reactions with experimental $\text{Co}(\text{por})$ systems. This is likely a direct result of the poor description of the Co–C bond by the b3-lyp functional, which is better described by the BP86 functional as explained in the main text. The calculated **TS2** barriers, which are dominated by the formation of new C–C bonds (cobalt-ligand bond changes are less important in this step) are not as strongly influenced by changing the functional as **TS1**. Nonetheless, the **TS2** barriers from single-point b3-lyp, def-TZVP calculations are roughly 5-6 kcal mol⁻¹ higher than the ones calculated at the BP86, def-TZVP level. The **TS2** barriers seem to be somewhat underestimated at the BP86 level (see main text), while the **TS2** barriers estimated from the single point b3-lyp calculations at the BP86 geometries could well be somewhat overestimated. For styrene a **TS2** barrier in between the BP86 value (18.2 kcal mol⁻¹) and the b3-lyp value (23.2 kcal mol⁻¹) leads to roughly equal **TS2** and **TS1** barriers (**TS1**: 22.0 kcal mol⁻¹ at the BP86, def-TZVP level), in excellent agreement with the experimentally observed first order kinetics in both [EDA] and [styrene] in the $\text{Co}(\text{TPP})$ -mediated cyclopropanation of styrene by EDA reported by Cenini and coworkers (ref 6, main text).¹

Figure S9. Free energy changes for the reaction of EDA with $\text{Co}^{\text{II}}(\text{por})$ (single point SCF, b3-lyp, def-TZVP).

Figure S10. Computed (single point SCF b3-lyp, def-TZVP) pathway for *trans*-cyclopropanation of propene ($\Delta G^\circ_{\text{PR}}$, green), styrene ($\Delta G^\circ_{\text{ST}}$, blue) and methyl acrylate ($\Delta G^\circ_{\text{MA}}$, red) mediated by $\text{Co}(\text{por})(\text{CHCOOMe})$. Free energies in kcal mol^{-1} relative to the resting state 'bridging carbene' species C'.

Species	Calculated [cm^{-1}] ^[a]	Calculated [cm^{-1}] ^[b]	Experimental [cm^{-1}]
EDA	1754 ^[c]	1684 ^[c]	1692 (DCM) ³ 1685 (benzene) ¹
C (terminal carbene)	1664	1597	1597 (DCM) ³
C' (bridging carbene)	1751	1681	1722 (benzene) ¹

References in the SI

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