Supporting Information for:

Decoding Key Transient Inter-Catalyst Interactions in a Reductive Metallaphotoredox-Catalyzed Allylation Reaction

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1,4-dihydro-4-phenyl-2,6-dimethyl-3,5-pyridinedicarboxylic acid diethyl ester (PhHEH) was synthesized according to a literature procedure.\(^1\) 1,4-dihydro-1,2,6-dimethyl-3,5-pyridinedicarboxylic acid diethyl ester (NMe-HEH) was prepared according to a literature procedure.\(^2\) 1,4-dihydro-4-phenyl-2,6-dimethyl-3,5-pyridinedinitrile (PhHNH) was prepared according to a literature procedure.\(^3\) 4CzIPN was synthesized according to a literature procedure.\(^4\) Benzaldehyde was freshly distilled prior to use and stored under inert atmosphere for a maximum of one month. All other materials were obtained from commercial sources and used as such.

Other electron donors

The electron donors in Scheme S1 were employed as replacement for HEH in the cobalt/organophotoredox catalyzed allylation of benzaldehyde. 4CzIPN (1.6 mg, 2 µmol), CoCl\(_2\)·6 H\(_2\)O (2.4 mg, 10 µmol), DPEPhos (5.4 mg, 10 µmol), K\(_3\)PO\(_4\) (31.8 mg, 0.15 mmol) and Electron Donor (0.15 mmol) were weighed in a flat-bottom Schlenk flask. In succession, THF (1 mL), 1 (16 µL, 0.1 µmol), and 2 (15 µL, 0.15 µmol) were added. The mixture was subjected to 3 freeze-pump-thaw cycles to remove dioxygen and stirred at 20 \(^\circ\)C under a nitrogen atmosphere and blue light irradiation (0.7 A, \(\lambda_{em} = 445\) nm, 1.2 \(\mu\)einstein s\(^{-1}\)) for 17 hours. The reaction mixture was evaporated and passed through a SiO\(_2\) plug using ethyl acetate as eluent. After evaporation, the products were analyzed using \(^1\)H NMR with mesitylene as internal standard. The outcome of the reactions is shown in Table S1.

Table S1. Conversion and yield using the various electron donors.

| Electron Donor: | NMe-HEH | PhHNH | PhHEH | Nifedipine |
|----------------|---------|-------|-------|------------|
| Conversion:    | 0       | 0     | 60    | 0          |
| Yield 3:       | 0       | 0     | 60    | 0          |

Discussion. The reason for the lower conversion of PhHEH was studied in more detail. First, Stern-Volmer analysis (see below) was performed, indicating that quenching of *4CzIPN is less effective for PhHEH than for HEH, but should still be the major path of the reaction corresponding to 57% of the excitations being quenched by PhHEH at the start of the reaction ([PhHEH] = 0.15 M, [Co\(^{II}\)] = 0.01), whereas 90% of the excitations being quenched by HEH, according to the following equation, where the sum of Q indicates all the possible quenchers in the solution (i.e., HEH and Co\(^{II}\)).

\[ \phi = \frac{k_{Q,HEH,S}[HEH]}{\sum_{Q} k_{Q,S}[Q] + k_d + k_{isc}} + \frac{k_{isc}}{k_{Q,S}[Q] + k_d + k_{isc}} + \frac{k_{Q,HEH,T}[HEH]}{\sum_{Q} k_{Q,T}[Q] + k_{risch}} \]

Based on this information, a slight decrease in efficiency is expected. However, in \textit{in situ} UV-vis analysis shows that reduction of [Co\(^{III}\)] to produce [Co\(^{II}\)] is highly inefficient with PhHEH: only around 50% of the cobalt was reduced over the period of 1 hour, whereas when using HEH this takes only 2 minutes (cf Figures S17 and S18). To explain this observation we calculated the \(pK_a\) and redox potentials of HEH and compared them to those obtained of PhHEH using the same method (see below).\(^1\) The \(pK_a\) is indeed more negative for PhHEH, which would facilitate deprotonation, and the redox potentials for the first and second oxidation are shifted 0.35 V and 0.38 V more reducing, respectively. This might cause mismatches between the potentials of PhHE\(^{+}\) and Co\(^{II}\), such that the reaction is in the Marcus inverted region, which would slow down the electron transfer rate and therefore the overall process. It thus seems important that the redox potentials are correctly matched to the process, in addition to the efficient deprotonation of the intermediate HEH\(^{**}\).
**Time-Correlated Single Photon Counting (TCSPC)**

Lifetime measurements were carried out on an Edinburgh Instruments LifeSpec-II based on the time-correlated single photon counting (TCSPC) technique, equipped with a PMT detector, double subtractive monochromator and a picosecond pulsed diode laser source with a wavelength of 405 nm. The photocatalyst 4CzIPN was dissolved in THF so that the absorbance of the solution in a 1 cm cuvette was $A = 0.1$ at the excitation wavelength. Samples with varying concentration of quencher were prepared and deaerated by argon purging prior to measuring TCSPC. The TCSPC data previously published$^5$, or newly obtained in case of PhHEH was used and fitted globally through a kinetic model.$^6$ The decay of the singlet and the triplet states of 4CzIPN can be described by the following equations. In here, we neglect non-radiative decay from the triplet state and combine fluorescence with non-radiative decay in a single constant: $k_d$.

$$\frac{d[S]}{dt} = -(k_d + k_{isc} + k_{Q,S}[Q])[S] + k_{risc}[T]$$

$$\frac{d[T]}{dt} = k_{isc}[S] - (k_{risc} + k_{Q,T}[Q])[T]$$

$[S]_0 = 1, [T]_0 = 0$

The equations were solved by describing system of equations in matrix form, calculating the eigenvalues, and then applying the initial conditions.$^6$ The rate constants were then globally fitted to the datasets with either [HEH], [Co(DPEPhos)Cl$_2$], or [PhHEH] as quenchers. The resulting values for the rate constants are shown in Table S2.

| Table S2. Fitted rate constants of the TCSPC data. |
|----------------|----------------|
| constant       | value          |
| $k_d$          | $1.34 \times 10^7$ s$^{-1}$ |
| $k_{isc}$      | $2.27 \times 10^7$ s$^{-1}$ |
| $k_{risc}$     | $6.14 \times 10^5$ s$^{-1}$ |
| $k_{Q,Co,S}$   | $1.31 \times 10^{10}$ M$^{-1}$ s$^{-1}$ |
| $k_{Q,Co,T}$   | $8.96 \times 10^8$ M$^{-1}$ s$^{-1}$ |
| $k_{Q,HE,H}$   | $8.24 \times 10^9$ M$^{-1}$ s$^{-1}$ |
| $k_{Q,HE,T}$   | $3.00 \times 10^9$ M$^{-1}$ s$^{-1}$ |
| $k_{Q,PhHEH,S}$| $1.38 \times 10^9$ M$^{-1}$ s$^{-1}$ |
| $k_{Q,PhHEH,T}$| $2.34 \times 10^8$ M$^{-1}$ s$^{-1}$ |

Figure S1. TCSPC data (normalized) and global fit for quenching with HEH.
Figure S2. TCSPC data (normalized) and global fit using [Co(DPEPhos)Cl₂] as quencher.

Figure S3. TCSPC data (normalized) and global fit using PhHEH as quencher.
Transient Absorption Spectroscopy (TAS)

Samples in THF (3 mL) were prepared in a nitrogen-filled glovebox and added to a quartz cuvette with four clear walls and a screwcap lid. Nanosecond transient absorptions were measured using an in-house assembled setup. The excitation wavelength of 450 nm was generated using a tunable Nd:YAG-laser system (Opolette). Probe light was generated using a 300 W xenon flash lamp (homebuilt). The probe beam was passed through the sample cell and orthogonally overlapped with the excitation beam. The probe light was passed through a monochromator (Kymera 193i, Andor) and, for kinetic traces, was detected using a Hamamatsu H8305-03 photomultiplier tube, the current amplified using a FEMTO DHP-100 current amplifier and measured using a YOKOGAWA DLM2052 oscilloscope. For obtaining the spectrum of the intermediate \( ^1[PC^-:HEH^+] \), the CCD detector (Kymera 193i, Andor) was used at a delay of 5 \( \mu s \) and gate-width of 0.5 \( \mu s \). Additionally, spurious laser light was detected in the absence of probe light, and the signal was corrected by subtracting the signal without probe light from the signal with probe light. Absorbance values were then calculated by dividing the signal by an averaged signal prior to the laser pulse (i.e., \( I/I_0 \)) and taking the -log\(_{10}\). Strong long-lived thermally activated delayed fluorescence hindered measuring signals in the range of 500-800 nm, and therefore two signals at 420 nm and 810 nm were collected. Although significant bleaching could be detected in experiments where both HEH and col were present due to irreversible reduction, triplo measurements showed that the data was reproducible.

![Figure S4](image.png)

**Figure S4.** TAS signals at 420 nm (left) and 810 nm (right) for just 4CzIPN (50 \( \mu M \)), or in the additional presence of HEH (0.2 mM) and both HEH and 2,4,6-collidine (75 mM).
Figure S5. TAS signals at 420 nm (left) and 810 (right) of 4CzIPN (50 µM) in the presence of HEH (0.2 mM), 2,4,6-collidine (75 mM) and (0.17 mM) [Co(DPEPhos)Cl₂] where indicated. Lifetimes are an average of 3 experiments.

Figure S6. Fit of the TAS signal of 4CzIPN (50 µM) observed at 420 nm in the presence of HEH (0.2 mM). A kinetic model fit yielded us with rate constants $k_{OHE,T}$ = $3.7 \cdot 10^9$ M⁻¹ s⁻¹ (corresponding well to the same constant determined by TCSPC of $3.0 \cdot 10^9$ M⁻¹ s⁻¹) and $k_{cr}$ = $1.22 \cdot 10^5$ s⁻¹. The $k_{cr}$ pathway can be considered to go through a reverse intersystem crossing prior to charge recombination (see Overall Kinetic Model section).
Figure S7. Difference UV-vis spectrum of the charge separated state complex $^3[\text{PC}^:\text{HEH}^{**}]$, measured at 5 µs delay after the laser pulse (width: 0.5 µs). Conditions: 4CzIPN (50 µM), HEH (200 µM) in THF (3 mL).

Figure S8. Molecular orbital diagram explanation for why reaction of $[\text{Co}^\text{II}]$ with the charge-separated state $[\text{PC}^:\text{HEH}^{**}]$ leads to fast charge recombination. A recombination pathway becomes available by double electron transfer yielding a low-spin cobalt complex $^2[\text{Co}^\text{II}]$ that subsequently relaxes to the ground state high-spin complex $^4[\text{Co}^\text{II}]$ after the recombination process is completed.
Figure S9. Transient at 525 nm showing the transient absorbance of the \(^{3}\text{[PC}^{\cdot\cdot}\text{-HEH}^{\cdot\cdot}]\) and its decay under the influence of several different metal complexes. The complexes react with the charge separated cage complex through the mechanism described in Figure S8. These interactions cause charge recombination and are therefore of negative influence on the reaction quantum efficiency. Conditions: 4CzIPN (50 µM), HEH (200 µM), metal complex (170 µM) in THF (3 mL). DCyPE = 1,2-bis(dicyclohexylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dtbbpy = 4,4'-bis-tert-butyl)-2,2'-bipyridine, dmgH = dimethylglyoximato, py = pyridine, bpy = 2,2'-bipyridine. Note that the [Co(dmgH)\(_2\)(py)Cl] complex was poorly soluble and therefore we cannot conclude it does not react with \(^{3}\text{[PC}^{\cdot\cdot}\text{-HEH}^{\cdot\cdot}]\).

Figure S10. Transients at 810 nm displaying the decay of the triplet excited state of 4CzIPN (50 µM) in the presence of HEH (200 µM) and metal complexes (170 µM). The decay is not significantly altered (except for [Co(dppp)Cl\(_2\)]), showing that the complexes only interact with \(^{3}\text{[PC}^{\cdot\cdot}\text{-HEH}^{\cdot\cdot}]\), and not with prior states.
Cyclic voltammetry (CV)

Cyclic voltammograms were recorded on a Princeton Applied Research PARSTAT 2273, using a glassy carbon working electrode (Ø 1 mm), a platinum wire counter electrode and Ag|AgCl sat. KCl reference electrode. Potentials were referenced to ferrocene by addition of a small amount of ferrocene after the experiment. Samples (2 mL) of [Co(DPEPhos)Cl₂] (5 mM) were prepared in a 3:1 mixture of MeCN:THF with tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) as supporting electrolyte. This solvent mixture was chosen because the waves were not reproducible in pure THF, and the complex was not sufficiently soluble in pure MeCN. CVs were recorded using a scan-rate of 100 mV s⁻¹, unless otherwise noted.

Figure S11. CV of 4CzIPN (5 mM) compared to that of [Co(DPEPhos)Cl₂] showing that PC•⁻ has enough reductive potential to reduce the cobalt complex.

Figure S12. Cyclic voltammograms of [Co(DPEPhos)Cl₂] at different scanrates.
Figure S13. Determination of the rate of the oxidative addition of 1 on reduced [Co(DPEPhos)Cl₄]²⁻. To do so, the peak current of the reoxidation peak was compared to the peak current of the reduction peak. The ratio $a = (i_{\text{red}}/i_{\text{ox}0})/(i_{\text{ox}}/i_{\text{red}0})$, where $i_{\text{red}}$ and $i_{\text{ox}}$ are the peak currents of the reduction and reoxidation wave, respectively, and subscript 0 indicates the peak currents in the absence of substrate 1, was determined. A plot of the natural logarithm of $a$ vs the time spent between the two peaks gives a straight line whose slope is the rate constant of oxidative addition times the concentration of 1 (0.05 M). Dividing the slope by the concentration of 1 thus yields the rate constant of oxidative addition $k = 1 \text{ M}^{-1} \text{s}^{-1}$. 

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**Spectroelectrochemistry**

Spectroelectrochemical study was carried out in an optically transparent thin-layer electrochemical (OTTLE) cell (OMNI-CELL SPECAC, by Prof. Frantisek Hartl’s group, University of Reading). The cell contains two Pt grid electrodes (working and counter) and a silver wire pseudo reference electrode. This cell is filled with 0.3 ml of a solution of [Co(DPEPhos)Cl₂](20 mM) in THF with TBAPF₆ as electrolyte (0.1 M) avoiding gas bubbles formation within the thin layer. In a second experiment, additionally 1 was present in 0.1 M. The optical path length is about 0.2 mm.

The OTTLE cell was placed in a Varian Cary 50 UV-vis spectrophotometer and the electrodes were connected to an IJ-Cambria CHI-660 potentiostat. Cyclic voltammetry was performed at 1 mV · s⁻¹ and UV-vis spectra were recorded periodically at 30 second intervals to monitor the evolution of the spectra. The voltages were ramped until a clear peak current was observed in the CV, after which the direction was changed. Note that for the different experiments, this occurred at different voltages. Partly, this is because of the different processes occurring in the experiment, but partly it is because the pseudoreference electrode can drift over time leading to a shift in potential. The actual voltages can be seen by the cyclic voltammetry in the main text. However, as the changes in the UV-vis were clearly occurring with the peak current, this shift in potential does not alter the conclusions of the experiment.

![Figure S14](image-url)  
**Figure S14.** Spectroelectrochemistry of [Co(DPEPhos)Cl₂]. a) cyclic voltammogram measured in the OTTLE cell at 1 mV s⁻¹. The blue dots indicate points where UV-vis spectra were recorded. b) Evolution of the UV-vis spectrum during the cyclic voltammetry. The spectra with thick, colored lines correspond to the indicated points in the cyclic voltammogram (a). The voltammetry was started at 0 V (yellow arrow / spectrum) towards the negative, at –1.05 V (green) the direction was changed, at 0.3 V (red) the direction was changed again. Conditions: [Co(DPEPhos)Cl₂] (20 mM), TBAPF₆ (0.1 M) in THF.

![Figure S15](image-url)  
**Figure S15.** Spectroelectrochemistry of [Co(DPEPhos)Cl₂] in the presence of 1. a) cyclic voltammogram measured in the OTTLE cell at 1 mV s⁻¹. The blue dots indicate points where UV-vis spectra were recorded. b) Evolution of the UV-vis spectrum during the cyclic voltammetry. The spectra with thick, colored lines correspond to the indicated points in the cyclic voltammogram (a). The voltammetry was started at 0 V (yellow arrow / spectrum) towards the negative, at –1.5 V (green) the direction was changed, at 1.0 V (red) the direction was changed again. Conditions: [Co(DPEPhos)Cl₂] (20 mM), TBAPF₆ (0.1 M), 1 (0.1 M) in THF.
Figure S16. Comparison of the UV-vis spectra obtained after reduction from spectroelectrochemistry at the most negative voltage in the presence and absence of 1.
In situ UV-vis spectroscopy

UV-vis spectra were measured on an Agilent Cary 60 spectrophotometer. Samples (3 mL) in a cuvette with four clear sides were irradiated from the side perpendicular to the measurement light with a single high-power blue LED ($\lambda_{em} = 445$ nm, 0.1 A), while periodically measuring spectra with 30 second intervals. The samples were stirred using a small stir bar and a 2mag cuvetteMIXdrive 1 magnetic stirrer. Spectra were corrected for precipitation of Co(0) (resulting in a wavelength-independent increase in absorbance) by subtracting the absorbance at 830 nm, where the complexes do not absorb.

The spectra were then fitted with multivariate curve resolution (pymcr) with three spectral species. The initial guesses were taken as the first spectrum, the last spectrum and the relevant spectrum obtained from spectroelectrochemistry (Figure S16).

Figure S17. a) Evolution of the UV-vis spectra during blue light irradiation of a mixture of 4CzIPN (2 µmol), CoCl$_2$ (10 µmol), DPEPhos (10 µmol), HEH (0.15 mmol), and 2,4,6-collidine (0.15 mmol) in THF (3 mL), i.e., a catalytic mixture without substrates 1 and 2. In the absence of 1 and 2, cobalt(II) is quickly reduced to cobalt(I), and then further to Co(0) leading to precipitation after some time elapsed. Note that the spectrum of the intermediate species shown here is almost indistinguishable from that in the experiment displayed in the main text. The same was observed using spectroelectrochemistry.
Figure S18. a) Evolution of the UV-vis spectra during blue light irradiation of a mixture of 4CzIPN (2 µmol), CoCl$_2$ (10 µmol), DPEPhos (10 µmol), PhHEH (0.15 mmol), and 2,4,6-collidine (0.15 mmol) in THF (3 mL), i.e., a catalytic mixture without substrates 1 and 2. b) Two spectral species fit from the data in a using multivariate curve resolution. The grey dashed line corresponds to the Co$^{1+}$-species observed by spectroelectrochemistry. c) the normalized concentrations of the species in b.

Figure S19. UV-vis / NIR spectrum of [Co(DPEPhos)Cl$_2$] in THF (Recorded on a Lambda 1050 PerkinElmer spectrophotometer equipped with a PMT, InGaAs and PbS detectors system, double beam optics, double monochromator and D2 and W light sources). The presence of absorption peaks in the NIR indicates the presence of low-lying electronic excited states. The incontinuity present at 1700 nm is due to absorbance of THF.
Density Functional Theory

Density functional theory was performed in Gaussian09 (Revision D.01) with an UltraFine grid. Calculations were done using B3LYP\textsuperscript{10-12} as the functional with dispersion correction GD3\textsuperscript{13} and implicit SMD\textsuperscript{14} solvation (THF). For geometry optimizations, 6-31G(d)\textsuperscript{15-19} was used as basis set on C, H, O, N, and P atoms, 6-31+G(d)\textsuperscript{18-20} on the Cl atoms and LANL2DZ\textsuperscript{21} on the Co atom. Potential energies were refined by calculation of single point energies on the previously optimized structures using the cc-pVTZ\textsuperscript{22} basis set on the C and H atoms, aug-cc-pVTZ\textsuperscript{22-24} on the O, N, P and Cl atoms, and LANL2TZ\textsuperscript{21,25} on the Co atom. The final Gibbs free energies are calculated as $G_f = V_{sp} + G_{opt} - V_{opt}$ where G and V are the Gibbs free energy and potential energy, and the subscripts $f$, $sp$ and $opt$ refer to the final, single point and optimization, respectively. Gibbs free energy corrections were computed at 298 K and 1 atm. A high-spin cobalt(II) center ($S = 3/2$) was assumed throughout and cross-checked by several geometry optimizations in low-spin ($S = 1/2$) that all consistently yielded a higher energy. All structures are monocationic. Vibrational frequency calculations were carried out on all optimized structures in order to ensure minima / transition states. In all the calculations the symmetry was disabled with the keyword nosymm.

Figure S20 shows the optimal pathways as calculated. The path can be split into an isomerization reaction (TS1, A\textsubscript{Z/E}, B\textsubscript{Z/E}, MC, where the subscript Z or E indicate the isomer of the allylic double bond), the C-C bond formation reaction (C\textsubscript{Z/E}, TS2\textsubscript{Z/E}, D\textsubscript{syn/anti}), where subscripts syn and anti correspond to the stereoisomers of the product’s OH groups arising from the Z or E orientation of what was the double bond, and protodemetalation (E\textsubscript{syn/anti}, TS3\textsubscript{syn/anti}, F\textsubscript{syn/anti}). During the process, we noticed that the position of the dangling primary OH group is an important parameter. We therefore checked the 3 isomers for intermediate E\textsubscript{syn} and F\textsubscript{anti} (F\textsubscript{syn} and F\textsubscript{syn}’ do not exist as minima, so we chose E in that case for fair comparison between isomers), and chose the path that corresponds to the lowest energy for this product (Figure S21 and Figure S23).

To exclude the possibility of the rotation of this group during the process, we calculated a transition state for such a rotation in the syn product D\textsubscript{syn} $\rightarrow$ D\textsubscript{syn}’’ and show that it is higher in energy (20.9 kcal mol\textsuperscript{-1}), therefore excluding rotation of this group during product formation. Because of this, the pathway is frozen by the lowest energy in the protodemetalation step all the way back to intermediate C. For both paths, a lower energy TS2 exists (13.5 kcal mol\textsuperscript{-1} and 17.3 kcal mol\textsuperscript{-1}, for Z and E, respectively). However, the protodemetalation step for these isomers are unfeasible (21.4 kcal mol\textsuperscript{-1}, and 23.9 kcal mol\textsuperscript{-1}), and therefore these paths were excluded. Pathways where the pendent alcohol remains deprotonated in structures MC, B, and C were considered, but have unfeasible high energies (Figure S22).

![Diagram](image)

**Figure S20.** Full path towards product formation from [Co\textsuperscript{11}allyH] calculated by density functional theory. Energies in kcal mol\textsuperscript{-1} referenced to intermediate MC. All structures are monocationic and high-spin ($S = 3/2$). During the step from intermediate E to F, the proton transfers from collidine (col) to the O\textsuperscript{−} on the coordinated product. Energies comprise a sum of the molecules shown in addition to the molecules absent in a calculation compared to others, such as 2, colHCl, col, or Cl\textsuperscript{−}.

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Figure S21. Gibbs Free Energies (kcal mol\(^{-1}\)) pathways of isomers with rotated CH\(_2\)OH-groups, and structures of the stereo-determining Zimmerman-Traxler transition states for the black and red paths (those corresponding to the lowest energy protodemetalation step. The C-C bond that is formed during the reaction is indicated by the pink dashed line.

Figure S22. Pendent alcohol deprotonated structures, showing that the alkoxide requires protonation in order to follow the reaction pathway, as deprotonated pathways are unfeasible in energy (all values in kcal/mol). The structure corresponding to \(C_{dp}\) is not a minimum structure, and is therefore not shown.
Figure S23. Structures, Newman projections (along the pink bond) and Gibbs free energies of the isomeric structures with the dangling OH group (red) rotated. For the syn isomer, the structures with the H-atom bonded to the oxygen of the product were not minima (i.e., $F'_\text{syn}$ and $F''_\text{syn}$ are not minima), and therefore the structures where the H is on collidine were compared (the proton transfer is expected to have a barrier similar to the anti pathway, i.e., 1-2 kcal mol$^{-1}$).

Which step is stereodetermining? From Figure S20 it seems that for the anti-path, the protodemetalation step will determine the reaction rate, whereas for the syn-path it is the Zimmerman-Traxler transition state $TS_2$. However, from control experiments using different bases (which should affect the protodemetalation step), only minimal changes were seen. The largest difference observed was between 91:9 with $K_3PO_4$ to 95:5 with collidine. It is likely that the error on the calculation for the protodemetalation steps is quite large compared to the C-C bond formation or isomerization, because a cationic species and a (naked) Cl$^-$ are included in the calculation. These local charges can likely be stabilized by solvent molecules which were not included in the calculation, leading to large errors. We also attempted to only include collidine-H$^+$ and not Cl$^-$, but comparison between the energies of monocationic and biscationic species also did not yield correct results. Therefore, we conclude that the energies of $E$, $TS_3$ and $F$ must in reality be lower than, or comparable to, that of $TS_2$, as was experimentally observed, and therefore the stereochemistry is determined by the relative stability of the two $TS_2$, see Figure S21.

The full computational dataset can be found at the following link:

https://doi.org/10.19061/iochem-bd-1-226
**Microkinetic modelling of the DFT results**

To show that the above discussion is valid, we performed microkinetic modelling of the DFT results. For this purpose, kinetic rate constants were determined by invoking transition state theory with the Eyring equation $k = \kappa \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT}$, where $k_B$ and $h$ are the Boltzmann and Planck constants, respectively, $\kappa$ is the transmission coefficient, which we assume to be 1, $R$ is the gas constant, $T$ is temperature and $\Delta G^\ddagger$ is the difference in Gibbs free energy between the reactant and the transition state. In conversions where no transition state was determined, e.g., when coordinating 2 on the open coordination site on Co, we assume a low kinetic barrier of 2 kcal mol$^{-1}$ above the endergonic side, which effectively puts the two states in pre-equilibrium with respect to sequential transition states of higher energy. A system of differential equations was designed based on the path in Figure S20, connecting the intermediates with the calculated rate constants.

The rate constants for bimolecular reactions were corrected for the difference in reference concentrations (ideal gas vs molarity) by multiplying the rate constant for the reaction joining two molecules times the correction factor 0.040874.$^{26}$ As described above, the protodemetalation step was ignored, and thus intermediate D was directly connected to the products. The full system of equations and constants is shown below.

\[
\begin{align*}
\frac{d[A_X]}{dt} &= k_{A_X \rightarrow A_E} [A_E] + k_{A_X \rightarrow B_Z} [B_Z] - k_{A_X \rightarrow A_E} [A_E] - k_{A_X \rightarrow B_Z} [A_X] \\
\frac{d[A_E]}{dt} &= k_{A_X \rightarrow A_E} [A_E] + k_{A_X \rightarrow B_Z} [B_Z] - k_{A_X \rightarrow A_E} [A_E] - k_{A_X \rightarrow B_Z} [A_X] \\
\frac{d[B_Z]}{dt} &= k_{A_X \rightarrow B_Z} [A_X] + k_{B_Z \rightarrow MC} [MC] + k_{B_Z \rightarrow C_Z} [C_Z] - k_{A_X \rightarrow B_Z} [B_Z] - k_{B_Z \rightarrow MC} [B_Z] - k_{B_Z \rightarrow C_Z} [B_Z] \\
\frac{d[B_E]}{dt} &= k_{A_X \rightarrow B_E} [A_E] + k_{B_E \rightarrow C_E} [C_E] - k_{A_X \rightarrow B_E} [B_E] - k_{B_E \rightarrow C_E} [B_E] \\
\frac{d[MC]}{dt} &= k_{B_Z \rightarrow MC} [B_Z] - k_{B_Z \rightarrow MC} [MC] \\
\frac{d[C_Z]}{dt} &= k_{B_Z \rightarrow C_Z} [B_Z] - k_{B_E \rightarrow C_E} [C_E] - k_{B_Z \rightarrow C_Z} [B_Z] - k_{B_E \rightarrow C_E} [B_E] \\
\frac{d[C_E]}{dt} &= k_{B_E \rightarrow C_E} [B_E] - k_{B_E \rightarrow C_E} [C_E] - k_{C_Z \rightarrow D_{sym}} [D_{sym}] - k_{C_Z \rightarrow D_{anti}} [D_{anti}] - k_{C_E \rightarrow D_{anti}} [D_{anti}] \\
\frac{d[P_{sym}]}{dt} &= k_{C_Z \rightarrow D_{sym}} [D_{sym}] - k_{C_Z \rightarrow D_{anti}} [D_{anti}] - k_{C_E \rightarrow D_{anti}} [D_{anti}] \\
\frac{d[P_{anti}]}{dt} &= k_{C_E \rightarrow D_{anti}} [D_{anti}] - k_{C_E \rightarrow D_{sym}} [D_{sym}] \\
\frac{d[D_{sym}]}{dt} &= k_{D_{sym} \rightarrow P_{sym}} [P_{sym}] - k_{D_{sym} \rightarrow P_{anti}} [P_{anti}] - k_{D_{sym} \rightarrow D_{anti}} [D_{anti}] - k_{D_{sym} \rightarrow D_{sym}} [D_{sym}] \\
\frac{d[D_{anti}]}{dt} &= k_{D_{anti} \rightarrow P_{anti}} [P_{anti}] - k_{D_{anti} \rightarrow P_{sym}} [P_{sym}] - k_{D_{anti} \rightarrow D_{anti}} [D_{anti}] - k_{D_{anti} \rightarrow D_{sym}} [D_{sym}]
\end{align*}
\]

The system of ordinary differential equations was integrated and evaluated using an in-house python script utilizing the library scipy.integrate.BDF.$^{27-29}$ The ratio of products syn:anti was examined after the system was allowed to react for 100 seconds (when it has reached a thermodynamic minimum state). The results obtained show $dr$ of 96:4 when a 1:1 B$_z$:B$_e$ state was prepared as the starting state. The system therefore describes well the experimental results ($dr$ of 95:5).
For $pK_a$ and redox potential calculations, the procedure reported for PhHEH\(^1\) was followed to compare the values for HEH. For $pK_a$, geometry optimizations were performed using the hybrid-meta-generalised gradient (GGA) $\omega$B97X-D\(^{10}\) functional with the 6-31+G(d,p) basis set. DMSO solvation was evaluated using the SMD implicit solvent model.\(^{14}\) Final electronic energies were refined using the same functional with the 6-311++G(d,p) basis set. For redox potential calculations, the PBE functional\(^{31,32}\) with D3BJ dispersion correction\(^{33}\) was used with the 6-31+G(d,p) basis set. Solvation (THF) was applied using the SMD model, and electronic energies were refined using the 6-311++G(d,p) basis set and same functional, dispersion correction and solvent model.

Compared to the reported values for PhHEH\(^1\), HE is harder to oxidize, less acidic when oxidized and less reducing when the radical cation is deprotonated, (cf. first $E_{1/2} = 1.1$ V and 0.75 V vs SCE, $pK_a = -6.3$ and $-7.9$, second $E_{1/2} = -0.7$ V and $-1.18$ V vs SCE, for HEH and PhHEH, respectively). Both HEH\(^{**}\) and PhHEH\(^{**}\) are not acidic enough to be deprotonated by the solvent THF: the $pK_a$ of THF•- was calculated to be $-15.5$.

![Figure S24. Redox potential and $pK_a$ calculation for HEH to HEPyH•.](image-url)
Kinetic analyses
The disappearance of starting material 1 was monitored during the reaction by a Mettler Toledo FTIR ReactIR 15 spectrometer equipped with an MTC detector and a diamond AgX Fiber Probe. The baseline was adjusted through a multipoint linear correction, and the absorbance of the band of interest (C=O stretch of 1 at 1815 cm\(^{-1}\)) was plotted versus time.

**Standard experiment:** 4CzIPN (1.6 mg, 2 µmol), CoCl\(_2\) · 6 H\(_2\)O (2.4 mg, 10 µmol), DPEPhos (5.4 mg, 10 µmol), K\(_3\)PO\(_4\) (31.8 mg, 0.15 mmol) and Hantzsch Ester (38 mg, 0.15 mmol) were weighed in a flat-bottom 3-neck tube made to fit the photoreactor. In succession, THF (1 mL), 1 (16 µL, 0.1 µmol), 2 (15 µL, 0.15 µmol) were added. The ReactIR probe was inserted into the reaction mixture and the mixture was deaerated by purging with solvent pre-saturated argon at 20 °C for 10 minutes. The mixture was stirred at 20 °C under blue light irradiation (0.7 A, 1.2 µeinstein s\(^{-1}\)) and IR spectra were recorded every 30 seconds. The extinction coefficient of the characteristic band of 1 (1815 cm\(^{-1}\)) was calculated by its known concentration at \(t = 0\). The reaction was stopped once the absorbance at 1815 cm\(^{-1}\) reached 0, or the absorbance seized to evolve.

**Figure S25.** a) Evolution of the IR spectrum over time. Conditions: 1 (0.1 mmol), 2 (0.15 mmol), HEH (0.15 mmol), K\(_3\)PO\(_4\) (0.15 mmol), CoCl\(_2\) · 6 H\(_2\)O (10 µmol), DPEPhos (10 µmol), 4CzIPN (2 µmol), THF (1 mL), blue light irradiation (0.1 A, 0.2 µeinstein s\(^{-1}\)). One spectrum was measured every 30 seconds. b) Zoom on the C=O stretch frequency of 1 after baseline correction. c) Plot of the concentration of 1 as a function of time, taken by the absorbance at 1815 cm\(^{-1}\).
Figure S26. a) Plot of the concentration of 1 (coloured circles) as a function of photons absorbed by the photoredox catalyst 4CzIPN at three different photon fluxes and quantum yield (solid lines, calculated from a first-order derivative of the datapoints using a Savitzky-Golay filter). The photon fluxes were determined by standard ferrioxalate actinometry. The initial rate of the reaction (v) as a function of photon flux, showing linear behavior which yields an initial quantum yield of 1.3%.

Figure S27. Conversion of the reaction as a function of time as determined by the disappearance of 1 under different conditions. Deviations from the standard conditions are listed in the legend. The rate of the reaction does not depend on the concentration of the reagents.
**Figure S28.** Disappearance of 1 as a function of time under blue LED irradiation, or in the dark. As can be seen, the reaction does not occur in the dark, but continues seamlessly when the irradiation is started again.

**Figure S29.** Disappearance of 1 as a function of time at 3 different concentrations of [Co(DPEPhos)Cl₂] (5 µmol, 10 µmol and 20 µmol). The same dependence is observed as with collidine: the reaction is faster with 5 mol% than with 20 mol%. Using this system, 5 mol% cobalt catalyst did not lead to full conversion presumably due to decomposition of the catalyst.
Overall Kinetic Model
In order to demonstrate that the conclusions of the work are plausible, a detailed kinetic model was developed (Scheme S2) and the unknown rate constants were globally fitted on the kinetic analysis using an in-house developed python script utilizing the library scipy.integrate.BDF,\textsuperscript{21-29} and the ‘minimize’ function in the lmfit library.\textsuperscript{30} data as explained below. Several simplifications were done that we justify below.

1) Because two bases are present during the reaction, the acid-base equilibria become complicated and would involve many different steps with unknown rate constants. We therefore consider the rates of protonation from protonated bases to be equal. Therefore, it does not matter which base the proton is attached to, and the equilibria can be neglected. The only exception is within the deprotonation of the charge separated state \([\text{PC}^+:\text{HE}^+]\), where different rates for different bases were considered.

2) The concentration of K\textsubscript{3}PO\textsubscript{4} was considered constant (even at different volumes), and therefore model it as a ‘spontaneous’ deprotonation that does not depend on the concentration of any base. This is because the base is heterogeneous and is in equilibrium between the dissolved and solid state.

3) In the cobalt cycle, the minor diastereomer was ignored and a single reaction path was designed only considering C-C bond formation and protodemetalation from the [Co\textsuperscript{II}-allylH] state.

4) All protonation and SET reactions are assumed sufficiently thermodynamically downhill such that reverse reactions do no occur.

5) We assume that the rate constants for SET by HE\textsuperscript{+} or PC\textsuperscript{+} are equal (indeed, as they are always produced at the same time, an average of the two could be considered when invoking the steady-state approximation).

In addition, many of the rate constants were measured experimentally, or were modelled by DFT. Table S3 shows the known rate constants (see Scheme S2 to know which reaction they refer to), and from which experiment they were determined. The subscript ‘Cg’ refers to the cage complexes either \([\text{PC}^+:\text{HE}^+]\) or \([\text{PC}^+:\text{HE}^+]\).

| Table S3. Known rate constants of the kinetic model in Scheme S2. |
|-----------------|-----------------|-----------------|
| constant         | value           | determined by   |
| \(k_\phi\)       | \(1.20 \cdot 10^{-3} \) M s\(^{-1}\)\(a\) | Actinometry     |
| \(k_d\)          | \(1.34 \cdot 10^{3} \) s\(^{-1}\)        | TCSPC           |
| \(k_{isc}\)      | \(2.27 \cdot 10^{2} \) s\(^{-1}\)        | TCSPC           |
| \(k_{risc}\)     | \(6.14 \cdot 10^{5} \) s\(^{-1}\)        | TCSPC           |
| \(k_{Q,HEH,S}\)  | \(8.24 \cdot 10^{6} \) M\(^{-1}\) s\(^{-1}\) | TCSPC           |
| \(k_{Q,HEH,T}\)  | \(3.00 \cdot 10^{5} \) M\(^{-1}\) s\(^{-1}\) | TCSPC           |
| \(k_{Q,Co,S}\)   | \(1.31 \cdot 10^{10} \) M\(^{-1}\) s\(^{-1}\) | TCSPC           |
| \(k_{Q,Co,T}\)   | \(8.96 \cdot 10^{8} \) M\(^{-1}\) s\(^{-1}\) | TCSPC           |
| \(k_{Cg_risc}\)  | \(1.22 \cdot 10^{2} / (1 - \Phi_{Eg,isc}) \)\(b\) | TAS             |
| \(k_{oa}\)       | \(1.0 \) M\(^{-1}\) s\(^{-1}\)          | CV              |
| \(k_{Ec}\)       | \(13.6 \) M\(^{-1}\) s\(^{-1}\)         | DFT             |
| \(k_{EC}\)       | \(5.08 \cdot 10^{6} \) s\(^{-1}\)        | DFT             |
| \(k_{Pdm}\)      | \(4.64 \cdot 10^{10} \) s\(^{-1}\)       | DFT             |

\(a\) Actinometry provided us with a photon flux of \(1.2 \cdot 10^{-6}\) einstein s\(^{-1}\), which was divided by the volume of the reaction. The rate constant is further multiplied in the kinetic model by the probability of absorption \(1 - 10^{-\Delta A_{tot}}\) where \(A_{tot}\) is the absorbance of the solution at 450 nm and by the ratio of the absorbance by PC and the total (i.e., \(A_{PC}/A_{tot}\)). In this reaction, however, we assume absorbance by only PC at 450 nm (therefore \(A_{PC}/A_{tot} = 1\).

\(b\) The value determined by TAS is the decay of the \([\text{PC}^+:\text{HE}^+]\) intermediate (see Figure S6). In the model we assume this goes through risc, followed by cage recombination. \(\Phi_{Eg,isc}\) is the part of \([\text{PC}^+:\text{HE}^+]\) that undergoes isc compared to cage recombination, i.e., \(k_{Eg,isc} / (k_{Eg,isc} + k_{Eg,rc})\).
Scheme S2. Reactions and corresponding rate constants considered in the kinetic model. HEPyH* is also considered as base-H*. SET steps can be performed by either PC** or HE* with assumed equal rate constants. In these steps, an electron is transferred from PC** or HE* to one of the cobalt intermediates. Cg = [PC**;HEH**].
In addition to the known rate constants, we assumed that the rates of SET \((k_{\text{set/2}})\) and protonation \((k_p)\) were fast, i.e., that they do not limit the overall process. Therefore, their rates can be set to a high value (e.g., \(10^6 \text{ M}^{-1} \text{s}^{-1}\)) without changing the process significantly. That leaves us with 4 unknown rate constants: \(k_{\text{Cg.deact}}\) and \(k_{dp}\) (different for each base, \(K_3\text{PO}_4\), col or HEPy), and the yield of intersystem crossing in the singlet cage \(\Phi_{\text{Cg.isc}}\). These constants were globally fitted to a well-behaved (there were issues with not reaching full conversion under some conditions) subset of the kinetic data (8 different conditions), which only differs in the concentrations of the reagents. Some minor mismatches are expected because each experiment was setup with freshly weighed materials, therefore having slight deviations between them. Considering this, the model describes the system well, as the fits follow the data points very well even though the rate constants are shared between all the data. Table S4 shows the fitted parameters, and Figure S30 the corresponding fits to the experimental data.

### Table S4. Fitted rate constants of the kinetic model in Scheme S2.

| constant         | value               |
|------------------|---------------------|
| \(k_{\text{Cg.deact}}\) | \(2.29 \cdot 10^7 \text{ s}^{-1}\) |
| \(k_{dp, K_3\text{PO}_4}\) | \(2.56 \cdot 10^3 \text{ M}^{-1} \text{s}^{-1}\) |
| \(k_{dp, \text{col}}\) | \(1.06 \cdot 10^5 \text{ M}^{-1} \text{s}^{-1}\) |
| \(k_{dp, \text{HEPy}}\) | \(5.74 \cdot 10^4 \text{ M}^{-1} \text{s}^{-1}\) |
| \(\Phi_{\text{Cg.isc}}\) | 0.99\(^a\) |

\(^a\) it should be noted that this value determines the overall maximum quantum yield, but the current experimental data can be fitted correctly by using a number between 0.1 and 0.99.

The initial quantum yield of the system can be well described as a competition between productive deprotonation, or charge recombination pathways from the \(1^1[\text{PC}^-:\text{HEH}^+]:\) state, assuming the initial formation yield of this intermediate is high:

\[
\Phi_{pr} = \frac{k_{dp}[\text{base}]}{k_{dp}[\text{base}] + k_{\text{Cg.deact}}[\text{Co}^{II}] + k_{\text{Cg.isc}}(1 - \Phi_{\text{Cg.isc}})}
\]

Or, equivalently, \(y=1/(a+bx)\), as shown in the main text Figure 2e, where the constants \(a\) and \(b\) are defined as follows.

\[
a = 1 + \frac{k_{\text{Cg.isc}}(1 - \Phi_{\text{Cg.isc}})}{k_{dp}[\text{base}]}, \quad b = \frac{k_{\text{Cg.deact}}[\text{Co}^{II}]}{k_{dp}[\text{base}]}
\]

---

**Figure S30.** Plots of the disappearance of 1 as a function of time measured by IR (red circles) and the corresponding global fit lines (black) by the model described above. The top row uses \(K_3\text{PO}_4\) as base, the bottom row uses 2,4,6-collidine as base. Deviations to standard conditions (see Kinetic Analyses section) are indicated in each plot.
We also compared the *in situ* UV-vis data to the model, where we can track the cobalt species over time. Using the fitted rate-constants from the kinetic data, we plotted the cobalt species over time. Again, a striking similarity is found between the experiment and the model, as can be seen in Figure S31 (and Figure 4 in the main text), further confirming that our model describes the reaction very well.

**Figure S31.** Comparison between the cobalt intermediate species from the model (a and b) and the experiment as determined from UV-vis (c). Conditions: standard conditions using collidine as a base, 3 mL THF. For the model, the photon flux (not determined in the UV-vis experiment) was adjusted to get full conversion within 50 min (0.9 µinstein s⁻¹). A striking similarity until the reaction completes is found between b and c, where we consider the spectra of Co(II) and Co(III)-allylH as indistinguishable (spectroelectrochemistry shows they are very similar). In the experiment, once there is no more substrate the complexes are further reduced to Co(0) and precipitation occurs, which is not covered by the kinetic model.
References

(1) Leitch, J. A.; Rossolini, T.; Rogova, T.; Dixon, D. J. α-Tertiary Dialkyl Ether Synthesis via Reductive Photocatalytic α-Functionalization of Alkyl Enol Ethers. ACS Catal. 2020, 10, 11430–11437.

(2) Tatunashvili, E.; Chan, B.; Nashar, P. E.; McErlean, C. S. P. σ-Bond Initiated Generation of Aryl Radicals from Aryl Diazonium Salts. Org. Biomol. Chem. 2020, 18, 1812–1819.

(3) Mahendra, M.; Doreswamy, B. H.; Adalaka, P.; Raval, K.; Varu, B.; Shah, A.; Sridhar, M. A.; Prasad, J. S. Synthesis and Crystal Structure of 3,5-Dicyano-2,6-Dimethyl-4-Phenyl-1,4-Dihydropyridine. Anal. Sci. 2003, 19, x55.

(4) Luo, J.; Zhang, J. Donor-Acceptor Fluorophores for Visible-Light-Promoted Organic Synthesis: Photoredox/Ni Dual Catalytic C(sp3)-C(sp2) Cross-Coupling. ACS Catal. 2016, 6, 873–877.

(5) Cristofol, A.; Limburg, B.; Kleij, A. W. Expedient Dual Co/Organophotoredox Catalyzed Stereoselective Synthesis of All-Carbon Quaternary Centers. Angew. Chem. Int. Ed. 2021, 60, 15266–15270.

(6) Haase, N.; Danos, A.; Pfumm, C.; Morherr, A.; Stachelek, P.; Mekic, A.; Brü, W.; Monkman, A. P. Kinetic Modeling of Transient Photoluminescence from Thermally Activated Delayed Fluorescence. 2018.

(7) Hickey, D. P.; Sandford, C.; Rhodes, Z.; Gensch, T.; Fries, L. R.; Sigman, M. S.; Minteer, S. D. Investigating the Role of Ligand Electronics on Stabilizing Electrocatalytically Relevant Low-Valent Co(I) Intermediates. J. Am. Chem. Soc. 2019, 141, 1382–1392.

(8) Camp, C. H. PyMCR: A Python Library for Multivariatecurve Resolution Analysis with Alternating Regression (MCR-AR). J. Res. Natl. Inst. Stand. Technol. 2019, 124, 1–11.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; K.; V.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foreman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01.

(10) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. 1993, 98, 5648–5652.

(11) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti Correlation-Energy Formula into a Functional of the Electron Density. Phys. Rev. B 1988, 37, 785–789.

(12) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J. Phys. Chem. 1994, 98, 11623–11627.

(13) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. J. Comput. Chem. 2006, 27, 1787–1799.

(14) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. J. Phys. Chem. B 2009, 113, 6378–6396.

(15) Harlharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. Theor. Chim. Acta 1973, 28, 213–222.

(16) Hehre, W. J.; Ditchfield, K.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. J. Chem. Phys. 1972, 56, 2257–2261.

(17) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. J. Chem. Phys. 1971, 54, 720–723.

(18) Frnc, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XXIII. A Polarization-Type Basis Set for Second-Row Elements. J. Chem. Phys. 1982, 77, 3654–3665.

(19) Gordon, M. S.; Binkley, S. J.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. Self-Consistent Molecular-Orbital Methods. 22. Small Split-Valence Basis Sets for Second-Row Elements. J. Am. Chem. Soc. 1982, 104, 2797–2803.

(20) Spitznagel, G. W.; Clark, T.; von Ragué Schleyer, P.; Hehre, W. J. An Evaluation of the Performance of Diffuse Function-augmented Basis Sets for Second Row Elements, Na–Cl. J. Comput. Chem. 1987, 8, 1109–1116.

(21) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. J. Chem. Phys. 1985, 82, 299–310.

(22) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon
and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(23) Woon, D. E.; Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. III. The Atoms Aluminum through Argon. *J. Chem. Phys.* **1993**, *98*, 1358–1371.

(24) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron Affinities of the First-Row Atoms Revisited. Systematic Basis Sets and Wave Functions. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(25) Roy, L. E.; Hay, P. J.; Martin, R. L. Revised Basis Sets for the LANL Effective Core Potentials. *J. Chem. Theory Comput.* **2008**, *4*, 1029–1031.

(26) Besora, M.; Maseras, F. Microkinetic Modeling in Homogeneous Catalysis. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, e1372.

(27) Hairer, E.; Wanner, G. *Solving Ordinary Differential Equations I: Nonstiff Problems*; Springer, 1993.

(28) Shampine, L. F.; Reichelt, M. W. The MATLAB Ode Suite. *SIAM J. Sci. Comput.* **1997**, *18*, 1–22.

(29) Byrne, G. D.; Hindmarsh, A. C. A Polyalgorithm for the Numerical Solution of Ordinary Differential Equations. *ACM Trans. Math. Softw.* **1975**, *1*, 71–96.

(30) Chai, J. Da; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom-Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

(31) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(32) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple (Vol 77, Pg 3865, 1996). *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.

(33) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.

(34) Hatchard, C. G.; Parker, C. A. A New Sensitive Chemical Actinometer - II. Potassium Ferrioxalate as a Standard Chemical Actinometer. *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* **1956**, *235*, 518–536.

(35) Newville, M.; Stensitzki, T.; Allen, D. B.; Ingargiola, A. LMFIT: Non-Linear Least-Square Minimization and Curve-Fitting for Python. September 21, 2014.