Electronic Supplementary Information

Unlocking Metal-Ligand Cooperative Catalytic Photochemical Benzene Carbonylation: A Mechanistic Approach

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1 General information

All manipulations unless stated otherwise were performed using Schlenk or glovebox techniques under dry argon or nitrogen atmosphere, respectively. THF, C₆H₆ and n-pentane were dried over Na/benzophenone, freshly distilled prior to use and stored under nitrogen atmosphere over molecular sieves (4Å). Anhydrous deuterated solvents were purchased from Eurisotop, degassed under a flux of Ar and stored over 4 Å molecular sieves. All commercial chemicals were purchased from suppliers and used as received if not otherwise stated. KHMDS (potassium bis(trimethylsilyl)amide) was purified before use, by extracting it with dry diethyl ether, followed by filtration over Celite or using a 0.2 μ m syringe filter and then evaporation to dryness under high vacuum in a glovebox. All ligands and complexes were synthesized according to literature procedures, without modification unless otherwise stated. Photochemical benzene carbonylation experiments were performed using guartz cuvettes (optical pathway of 10mm) as reaction vessel, sealed with a rubber septum and a generous amount of Parafilm. The temperature of the cuvette during spectrophotochemical experiments was controlled thanks to a Peltier effect holder (Quantum Northwest TC125); as light source, an ABB solar simulator (Oriel LCS-100, 1 Sun) or a Kessil PR160L lamp (λ_{max} = 390 nm, 52W) were used. The latter light source was used in combination with an EvoluChem PhotoRedOx Box photoreactor. GC-MS analyses were performed on a Shimadzu QP-2020 equipped with a capillary column (Shimadzu, SH-Rtx-Wax, fused silica column with crossband polar polyethylene glycol phase, 60 m × 0.32 mm × 0.5 μm film thickness). Temperature program: start temperature 120 °C, heating rate 15 °C/min, end temperature 240 °C for 7 min, run total 15 min. ¹H and ³¹P{¹H} NMR spectra were recorded at room temperature on an AVANCE III 400 BRUKER at Laboratoire Interfaces Traitements Organisation et DYnamique des Systèmes (ITODYS), Université Paris Cité or on a Magritek Spinsolve 80^{ULTRA}. CO-Self Exchange experiments were performed on the former machine, at -40°C. All UV-Visible spectra and spectrophotochemistry experiment were recorded using a Agilent Technology Cary 60 UV-Vis spectrometer; the light source used for sample irradiation during spectrophotochemistry is a LED Kessil PR160L (λ_{max} = 390 nm, 52W).

Chemical shifts δ are given in ppm and coupling constants *J* in Hz. Chemical shifts for ¹H NMR spectra are referenced relative to residual protium in the deuterated solvent (¹H δ = 7.16 ppm, C₆D₆, δ = 2.05 ppm, (CD₃)₂CO, δ = 1.38 ppm, cyclohexane-d₁₂,). ³¹P{¹H} shifts are referenced to H₃PO₄. The following abbreviations are used for describing NMR spectra: s (singlet), d (doublet), t (triplet), dd (doublets of doublets), ddd (doublet of doublets), vd (virtual doublet), vt (virual triplet), br (broad).

2 Synthesis and characterization of all the complexes

2.1 PNP^{tBu}

The synthesis of the PNP^{tBu} ligand was operated according to a literature procedure¹



Figure S1. Top: ³¹P{¹H} NMR (C_6D_6 , ppm): 37.6 (s). Bottom: ¹H NMR (C_6D_6 , ppm): 7.25 (d, 2H, m- C_5H_3N , ³J_{H-H} = 8.1 Hz), 7.17 (t, 1H, higher integral due to overlap with C_6D_6 residual protium signal, ³J_{H-H} = 8.1 Hz), 3.09 (d, 4H, CH_2P , ²J_{H-H} = 2.8 Hz),

2.2 [Rh(CO)(PNP^{tBu})]PF₆

The synthesis of the complex was adapted from a literature procedure.²



In an N₂ based glovebox, 21.5 mg (116.8 μ mol) of KPF₆ was suspended in approx. 1 mL of methanol and quantitatively transferred to a vial containing 19.1 mg (49.1 μ mol) of [Rh(CO)₂(μ -Cl)]₂. The resulting orange suspension was allowed to stir for few minutes. In the meanwhile, 43.2 mg (109.4 μ mol) of PNP^{tBu} was dissolved in approx. 0.5 mL of methanol and then dropwise added to the suspension, resulting in the formation of a yellow solid and the development of some CO bubbles. Two aliquots of approx. 0.3 mL of methanol were used to wash the vial containing the ligand. The suspension was then allowed to stir for 1h before reduced pressure was applied to the vial. The solid was then extracted with approx. 1 mL of dichloromethane and filtered through PTFE filter (0.2 μ m) and reduced pressure was applied to the solution to evaporate the solvent. The yellow solid was then washed with several aliquots of n-pentane before reduced pressure was applied again to dry the product.



Figure S2. Top ³¹P{¹H} NMR (acetone-d₆, ppm): 79.23 (d, 2P ¹J_{P-Rh} = 120 Hz), -143.93 (hep, 1P, ¹J_{P-F} = 707 Hz). Bottom: 1H – NMR (acetone-d₆, ppm): 8.04 (t, ³J_{H-H} = 7.6, 1H, pyridine-H4), 7.74 (d, ³J_{H-H} = 8.1, 2H, pyridine-H3,5), 4.17 (t, ²J_{P-H} = 4.1 Hz, 4H, CH₂P), 1.46 (m, ³J_{P-H} = 7.1 Hz, 36H, P(C(CH₃)₃)₂).

2.3 [Rh(CO)(*PNP^{tBu})] (1)

The synthesis of the complex was operated according to a literature procedure.³



Figure S3. Top: ${}^{31}P{}^{1H} - NMR (C_6D_6, ppm)$: 76.3 (dd, ${}^{1}J_{P-Rh} = 125$ Hz, ${}^{2}J_{P-P} = 244$ Hz), 73.4 (dd, ${}^{1}J_{P-Rh} = 125$ Hz, ${}^{2}J_{P-P} = 244$ Hz). Bottom: ${}^{1H} - NMR (C_6D_6, ppm)$: 6.42 (d, ${}^{3}J_{H-H} = 7.2$, 1H, pyridine-H4), 6.36 (d, ${}^{3}J_{H-H} = 8.8$, 1H, pyridine-H3), 5.37 (d, ${}^{3}J_{H-H} = 6.2$, 1H, pyridine-H5), 3.68 (d, ${}^{2}J_{P-H} = 4.25$ Hz, 1H, CHP), 2.74 (d, ${}^{2}J_{P-H} = 8.6$ Hz, 2H, CH₂P), 1.46(d, ${}^{3}J_{P-H} = 12.5$ Hz, 18H, P(C(CH₃)₃)₂), 1.09 (d, ${}^{3}J_{P-H} = 12.8$ Hz, 18H, P(C(CH₃)₃)₂).

2.4 [Rh(Cl)(PNP^{tBu})]

The synthesis of this complex was operated according to literature procedure.³



Figure S4. Top: ${}^{31}P{}^{1}H{}-NMR (C_6D_6, ppm)$: 57.38 (d, ${}^{1}J_{Rh-P} = 145 Hz$). Bottom: ${}^{1}H - NMR (C_6D_6, ppm)$: 6.89 (t, ${}^{3}J_{H+H} = 7.7 Hz$, 1H, pyridine-H4), 6.28 (d, ${}^{3}J_{H+H} = 7.7 Hz$, 2H, pyridine-H3,5), 2.56 (t, $J_{P+H} = 3.4 Hz$, 4H, CH₂P) 1.47 (t, ${}^{3}J_{P-H} = 6.7 Hz$, 36H, PC(CH₃)₃).

2.5 [Rh(OTf)(PNP^{tBu})] (4)

The synthesis of this complex was operated according to literature procedure.⁴



Figure S5. Top: ${}^{31}P{}^{1}H{}$ – NMR, copresence of n and n-N₂ (C₆D₆, ppm). 71.7 (d, 2P, ${}^{1}J_{P,Rh}$ = 125 Hz, n-N₂), 61.8 (d, 2P, ${}^{1}J_{P,Rh}$ = 145 Hz, n). Bottom: ${}^{1}H{}$ – NMR, copresence of n and n-N₂ (C₆D₆, ppm). 7.9 (d, 2H, J = 7.8 Hz, py, n-N₂), 7.4 (t, 1H, J = 7.8 Hz, py, n-N₂), 6.7 (t, 1H, J = 7.8, py, n), 6.3 (d, 2H, J = 7.8 Hz, py, n), 3.7 (vt, 4H, J = 4.2 Hz, PCH₂, n-N₂), 2.5 (vt, 4H, J = 3.3 Hz, PCH₂, n), 1.4 (vt, 36H, 'Bu, n), 1.1 (vt, 36H, 'Bu, n-N₂).

2.6 [Rh(N₂)(*PNP^{tBu})]

The synthesis of this complex was operated according to literature procedure.⁴



Figure S6. ${}^{31}P{}^{1}H{} - NMR$ (cyclohexane- d_{12} , ppm): 67.4 (dd, ${}^{1}J_{P-Rh} = 132$ Hz, ${}^{2}J_{P-P} = 269$ Hz), 63.5 (dd, ${}^{1}J_{P-Rh} = 132$ Hz, ${}^{2}J_{P-P} = 269$ Hz). Bottom: ${}^{1}H - NMR$ (cyclohexane- d_{12} , ppm). 6.12 (vt, 1H ${}^{3}J_{H+H} = 7.7$ Hz, py), 5.95 (d, 1H, ${}^{3}J_{H+H} = 8.8$ Hz, py), 5.22 (d, 1H, ${}^{3}J_{H+H} = 6.4$ Hz, py), 3.33 (d, 1H, ${}^{2}J_{H-P} = 4.0$ Hz, PCH), 2.88 (d, 2H, ${}^{2}J_{H-P} = 8.5$ Hz, PCH₂), 1.44 (m, 36 H, ${}^{1}Bu$).

2.7 [Rh(Ph)(PNP^{tBu})] (2)

2.7.1 Procedure A

Complex 2 can be obtained following a literature procedure.⁴



Figure S7. Top: ${}^{31}P{}^{1}H{}-NMR(C_6D_6, ppm)$: 58.75 (d, ${}^{1}J_{Rh,P}$ = 172 Hz). Bottom: ${}^{1}H-NMR(C_6D_6, ppm)$: 8.16 (d, ${}^{3}J_{H,H}$ = 7.7 Hz, 2H, Ph-H2,6), 7.25 (t, ${}^{3}J_{H,H}$ = 7.5 Hz, 2H, Ph-H3,5), 6.98 (t, ${}^{3}J_{H,H}$ = 7.8 Hz, Ph-H4, 2H, Py-H4), 6.46 (d, ${}^{3}J_{H,H}$ = 7.8 Hz, 2H, Py-H3,5), 2.87 (m, 4H CH₂P), 1.3 (t, 3JPH = 6.7 Hz, 36H, PC(CH₃)₃). Impurities are due to the residual presence of THF (3.57 and 1.40 ppm), pentane (1.23 and 0.87 ppm), unreacted and protonated KHMDS (0.13ppm) silicon grease (0.3 ppm).

2.7.2 Procedure B

Alternatively, complex **2** can be obtained in a slightly modified procedure starting from the neutral rhodium triflate species **4**. In an Ar-filled glovebox, a red-brown solution was prepared by dissolving 11.5 mg (17.8 μ mol) of [RhOTf(PNP^{tBu})] in ca. 1 mL of C₆H₆. Similarly, another solution was prepared dissolving 3.9 mg (19.6 μ mol) of purified KHMDS in ca. 1 mL of C₆H₆. Under moderate stirring, the latter solution was slowly added to the former, resulting in the immediate formation of brown solution. The solution was then stirred for 12 h at room temperature to maximize the yield. The work-up was conducted by evaporation of the solvent,

followed by an extraction with pentane and consequent filtration of the suspension using a 0.2 μ m Teflon syringe filter. The product was isolated by evaporation of pentane.



Figure S8. Top: ³¹P{¹H}-NMR (C_6D_6 , ppm):: 58.75 (d, ¹J_{Rh-P} = 172 Hz). Bottom: ¹H-NMR (C_6D_6 , ppm): 8.16 (d, ³J_{H-H} = 7.7 Hz, 2H, Ph-H2,6), 7.25 (t, ³J_{H-H} = 7.5 Hz, 2H, Ph-H3,5), 6.98 (t, ³J_{H-H} = 7.8 Hz, Ph-H4, 2H, Py-H4), 6.46 (d, ³J_{H-H} = 7.8 Hz, 2H, Py-H3,5), 2.87 (m, 4H CH₂P), 1.3 (t, ³J_{P-H} = 6.7 Hz, 36H, PC(CH₃)₃).

2.8 [Rh(C(O)Ph)(PNP^{tBu})] (3)



In a N_2 based glovebox, approx. 2.5 mg (4.34 µmol) of [Rh(Ph)(PNP)] were dissolved in 0.5 mL of C_6D_6 and transferred to a J.Young NMR tube. The content of the tube was then frozen using liquid N_2 , put under vacuum, melted, frozen, put under CO atmosphere, melted, and shaken to dissolve the gas in the liquid (x3). Among all these steps, a slight but noticeable change of color was observed. ³¹P{¹H}, ¹H NMR confirm the quantitative conversion, albeit with some visible impurities.



Figure S9. Top: ³¹P{¹H}-NMR (C₆D₆, ppm): 59.57 (d, ¹J_{Rh-P} = 187 Hz). Bottom: ¹H-NMR (C₆D₆, ppm): 8.87 (m, 2H, Ph-H2,6), 7.41 (t, ³J_{HH} = 7.6 Hz, 2H, Ph-H3,5), 7.23 (m, 1H, Ph-H4), 6.92 (t, ³J_{HH} = 7.9 Hz, 1H, Py-H4), 6.45 (d ³J_{HH} = 7.8 Hz, 2H, Py-H3,5), 2.92 (m, 4H, CH₂P), 1,26 (m, 36H).

The tube was then left in the dark for approximately 72 h after the synthesis, after which a noticeable change in the color is registered. ${}^{31}P{}^{1}H$ NMR reveals that the complex degraded overtime and the aldehydic peak of benzaldehyde is visible in the ${}^{1}H$ NMR at 9.54 ppm.



Figure S10. Top: ³¹P{¹H}-NMR of **3** after 72h left in the dark. Bottom: ¹H- NMR of **3** after 72h left in the dark. The aldehydic peak of benzaldehyde is visible at 9.54 ppm.

3 Photochemistry

All the photochemistry experiment were performed using Hellma QS quartz cuvettes, 10.00 mm optical pathway, equipped with a glass neck (total volume 6.15 mL).



Figure S11. Top: 3D-printed sample holder with reaction glass cuvette. Bottom: Photochemical reactor used for the photochemical benzene carbonylation. (A) 390 nm LED Kessil lamp. (B) Ventilator. (C) stirring plate. (D) sample holder with glass cuvette.

3.1 Spectrophotochemistry (SPC)

The cuvettes were filled with 3 mL of a 30 μ M solution of **1** in benzene. The temperature of the cuvette holder mounted in the spectrophotometer was controlled using specific equipment. A Kessil PR160L (λ_{max} = 390 nm, 52W). A total of 36 spectra, one every 5 minutes, were recorded for each experiment: the first one was recorded in absence of irradiation and after 2 minutes of resting time, to allow the temperature of the cuvette to be stabilized. Data were recorded at 4 different temperatures (10, 20, 40, 50°C).



Figure S12. Spectrophotochemistry experiment recorded at various temperatures: a. 10°C; b. 20°C; c. 40°C; d. 50°C.

3.2 Photochemical benzene carbonylation reaction (PBCR)

In a N_2 based glovebox, a quartz cuvette is filled with 3 mL of a 1 mM solution of **1** in benzene. The cuvette is stopped with a rubber septum, brought outside the glovebox, and sealed using a generous amount of parafilm. CO gas (1 atm.) is bubbled for 15 minutes, after which the cuvette is placed in front of the ABB solar simulator (10 cm distance from the optics) or in the photoreactor equipped with the Kessil LED and irradiated for 72 h. Below is a GC-MS trace of a run with the 390 nm Kessil LED lamp.



Figure S13. GC-MS trace after 72 h irradiation at 390 nm (Kessil LED) of a 1 mM solution of 1 in benzene under 1 atm of CO..

3.3 Benzaldehyde detection

Benzaldehyde was detected by means of GC-MS and quantified using a calibration curve obtained by external calibration. For this, 6 different solutions of benzaldehyde in benzene, with different concentrations (0.25, 0.5, 1, 2.5, 5, 10 mM) were employed and each standard was injected 3 times. This allowed the construction of confidence intervals, from which the error value associated to the measurements was extracted. TON was estimated by dividing the amount of benzaldehyde produced after irradiation by the amount of catalyst added in the system.



Figure S14. GC-MS calibration curve for benzaldehyde.

3.4 General cleaning

The quartz cuvettes were thoroughly cleaned after each run first rinsing three times with technical acetone and then three more times with distilled water. After the second rinsing, the cuvettes were left to dry in an oven at 120°C overnight before being quickly brought back to the glovebox. Once every two runs, the cuvettes were cleaned using freshly prepared acidic piranha solution, letting it work for 3 h. After this, the cuvettes were thoroughly washed to eliminate the residues of piranha solution, and then rinsed three times with acetone and water.

4 Benzene carbonylation using Rh(I) and Ir(I)-complexes

Table S1. Effect of light source on photochemical benzene carbonylation								
Entry	Light source	Power	Wavelength (nm)	Productivity (TON/W) ^[b]	Time	P _{co} (atm)	Selectivity	Complex
15	Hg/Xe-arc	200 W	λ < 366	0.01	40 h (25 °C)	0.2	100 %	trans-[Rh(CO)Cl(PPh₃)]
2 ⁵	Hg/Xe-arc	200 W	λ < 366	0.007	22 h (25°C)	0.8	100 %	lr(H)(CO)(dppe)
2 ⁶	Hg-arc lamp	500 W	λ > 290	0.148	33 h (25 °C)	1	54%	<i>trans</i> -[Rh(CO)Cl(PMe₃)
37	Hg-arc lamp	500 W	λ > 290	0.104	24 h (50 °C)	1	51%	trans-[Rh(CO)Cl(PMe₃)
4 ^[a]	LED	52 W	$\lambda_{max} = 390$	0.269	72 h (25 °C)	1	100%	1

[a] Reaction conditions: 1 mM of 1 in 3 mL of benzene, 1 atm of CO, 72 h in a quartz cuvette with 3 mL headspace irradiated with a Kessil-LED lamp (λ_{max} = 390 nm). Error corresponds to repeated (> 2) runs. [b] The TON were normalized by the power of the used light source for comparison (see main manuscript for absolute TON).

4.1 Mechanisms of Vaska-type rhodium complexes for photochemical benzene carbonylation

The difference in reactivity between the PPh₃ and the PMe₃-based Vaska-type complexes from Table S1 can be explained by different mechanisms at play. Below is a mechanistic proposal for the PPh₃-complex (see ref 5). Light is necessary for ligand dissociation to generate the active catalytic intermediate, a three-coordinate rhodium species. C-H activation and all subsequent steps take place on the ground state potential energy surface. Light thus generates a highly active catalysts, however, does not act as thermodynamic driving force within the catalytic cycle. Hence, the complex is kinetically active and promotes both benzene carbonylation, as well as the reverse benzaldehyde decarbonylation reaction, limited in each case to the thermodynamically controlled concentrations.



The PMe₃ version on the other hand, reacts with benzene in its excited state (see below and ref 7). Subsequent steps are thought to be then strongly downhill in energy. Light thus serves to drive the reaction beyond equilibrium concentration with important amount of benzaldehyde built-up using this complex. The difference between the PMe₃ and the PPh₃ ligands might be rationalized both in terms of sterics and electronics: The more sigma-donating PMe₃-ligand increases repulsion between the filled dz²-orbital and the benzene substrate. Photoexcitation depopulates the dz² orbital and thus increasing favorable interactions with the substrate. At the same time, the small steric bulk of PMe₃ allows for direct interaction of the four-coordinated excited states with the substrate.



5 CO self-exchange experiments

In a N₂ based glovebox, two J.Young NMR tubes were loaded with 0.4 mL of a 1.9 mM solution of **1** in 7:1 heptane:cyclohexaned₁₂, to prevent the occurrence of C-H activation reaction. A ³¹P{¹H}-NMR spectrum was recorded before adding ¹³CO. Three freezepump-thaw cycles were performed to put the samples under ¹³CO atmosphere. The samples were defrosted right before performing a t₀ ³¹P{¹H}-NMR measure. Right after the addition of the gas to the system, full ¹³CO incorporation is observed without any irradiation required: this is empathized by the phosphorus signal splitting, result of the coupling between ³¹P and the NMR active ¹³CO (²J_{P-C} = 12.7 Hz). After three hours of irradiation, a decrease of the signal/noise ratio is observed, likely due to the degradation of the complex under constant irradiation.



Figure S15. From bottom to top: ³¹P{¹H}-NMR spectrum of **1** under N₂ atmosphere; spectrum of **1** recorded at t_0 , right after addition of ¹³CO; spectrum of **1** under CO atmosphere after 3 h of irradiation.

To grasp some kinetic information on this process, a low temperature experiment at -40°C was performed. In a similar fashion to the one above described, a roughly 136 mM solution of **1** in 7:1 heptane:cyclohexane- d_{12} was prepared in a J.Young NMR tube and a ³¹P{¹H}-NMR was recorded. The sample was then put under ¹³CO atmosphere by performing three freeze-pump-thaw cycles, right after which a ³¹P{¹H}-NMR was recorded. More spectra were recorded after 0.5, 1, 2, 3 and 4 h, revealing the slow, but steady disappearance of the peaks related to **1**(¹²CO) and the consequent appearance of **1**(¹³CO). The analysis of the relative intensities of the peaks allows the estimation of a 75% conversion after 4 h at -40°C.



Figure S16. ³¹P(¹H))-NMR of the ¹³CO self-exchange experiment run at -40°C. From bottom to top: t₀ (right after ¹³CO addition), 1h, 2h, 3h, 4h, 5h.

6 Reactivity of various rhodium (I) dearomatized PNP complexes with benzene

Rh(I) complexes bearing a dearomatized PNP pincer ligand have been previously known to be able to react with benzene via C-H activation³. Studying the rate of the C-H activation for these complexes may provide valuable information on this step of the mechanism. For this test, four different complexes (two anionic and two neutrals) were considered, all bearing the dearomatized *PNP^{tBu} ligand and a different fourth ligand, triflate, chloride, N₂ and CO.

Triflate is the weakest of the group, being the best leaving group: it is known⁴ that the neutral [Rh(OTf)(PNP^{tBu})], when exposed to N₂, undergoes a reversible ligand substitution reaction, where the triflate goes in the outer sphere and N₂ bounds to the metal center, generating the cationic [Rh(N₂)(PNP^{tBu})]OTf. Therefore, the C-H activation reaction must be conducted under Ar atmosphere, to avoid the formation of the dearomatized [Rh(N₂)(*PNP^{tBu})]. Under these conditions, using benzene as a solvent, the product of the C-H activation [Rh(Ph)(PNP^{tBu})] is obtained within **1h** of reaction.

The neutral [RhCl(PNP^{tBu})] does not undergo equilibrium with N₂, and it is stable under nitrogen atmosphere. However, in a similar fashion with the triflate counterpart, when the anionic [RhCl(*PNP^{tBu})]⁻ is dissolved in pure benzene under N₂ atmosphere and

allowed to stir for 12 h, it generates a mixture of 91% of [Rh(N₂)(*PNP^{tBu})] and 9% of [Rh(Ph)(PNP^{tBu})]. Under Ar atmosphere over **9 h** of stirring, full conversion of the anionic to [Rh(Ph)(PNP^{tBu})]³ is observed.

The neutral dearomatized $[Rh(N_2)(*PNP^{tBu})]$ is stable in solid state for few days. However, when it is kept in a benzene solution at room temperature, slow conversion to $[Rh(Ph)(PNP^{tBu})]$ is observed within **4 days**.

When dissolved in benzene at room temperature, the neutral [Rh(CO)(*PNP^{tBu})] proved to be stable for **7 days** approximately, before starting to degrade to species unidentifiable by means of ³¹P{¹H} NMR. No C-H activation product was however detected.

This result allows the withdrawal of some conclusions. The ¹³CO self-exchange experiment previously described unequivocally shows that light is not required to displace the CO ligand and therefore the system undergoes a mobile equilibrium where the ligand exchanges freely with the other CO molecules present in the system. Therefore, based on these previous observations and on the ones just presented, one may conclude that the absence in reactivity of [Rh(CO)(*PNP^{tBu})] in benzene is not due to the intrinsic difficulty in abstracting from the ligand, but instead on the remarkable stability of the complex. In another words, the catalyst is found to be in a thermodynamic well and light seems to play a role in overcoming the energetic barrier of the system towards C-H activation.

Table S2. Thermal activity for C-H bond activation of different dearomatized rhodium pincer compleces						
Entry	complex	time	conversion	selectivity		
1	1	14 days	n.r.	n.a.		
2	$ \begin{array}{c} $	96 h	100 %	67 %		
2		9 h	100 %	90 %		
3		1 h	100 %	80 %		

7 Mechanistic modeling and Eyring plot

The benzene C-H activation intimate mechanism may be described according to three different pathways: a *dissociative* path, where the Rh-CO bond is cleaved before the interaction with benzene and the reaction goes via a tricoordinate, 14e species; an *associative* pathway, where the complex in the excited state reacts with benzene before CO detaches from the metal center, via a 18e, pentacoordinate intermediate; an *interexchange* mechanism, in which there's approximately the simultaneous formation of the Rh-Ph bond and the cleavage of the Rh-CO bond, passing from a transition state where both bonds are still being formed/cleaved respectively.

The following approximations were applied to all the pathways in order to simplify the reasoning:

- For the *dissociative* and *associative* mechanisms, the first step is considered reversible, albeit it's clearly not possible to regenerate a complex in the excited state from a complex in the ground state. Here we tacitly imply that the path with *k*₋₁ as constant rate generates the 1 in the ground state and that the newly formed complex is excited *via* an instantaneous vertical process.
- The reaction between complex **1** and benzene is likely to take place in two different steps, which are the ligand substitution and the proton migration to the ligand sidearm (that leads to its re-aromatization). Here, for simplicity, it is considered to be a concerted step, albeit this is likely not the case.



Figure S17. Schemes for the dissociative, associative and interexchange mechanisms for the C-H activation reaction

Moreover, the rate laws were determined according to the step described above.

Dissociative mechanism: $[RhCO^*]_t = [RhCO^*]_0 * e^{-k_1 t}$

Associative mechanism: $[RhCO^*]_t = [RhCO^*]_0 * e^{-K_1^{app}k_2t}$

Interexchange mechanism: $[RhCO^*]_t = [RhCO^*]_0 * e^{-k_1^{app}t}$

To derive these rate laws, the following approximations were made:

- For the *dissociative* mechanism it was hypothesized that, due to the extremely instable nature of the 14e tricoordinate intermediate, the first step is relatively slow, allowing to apply the steady state approximation on the intermediate. The reaction is driven to the products due to higher concentration of benzene (11.7 M) compared to CO (7 mM). Moreover, in the second step the backward reaction is considered significantly slower than the forward due to the high reactivity of the intermediate.
- For the *associative* mechanism it was hypothesized a fast 1st step, due to the ubiquitous presence of benzene in the second coordination sphere of the complex. This allowed the application of the pre-equilibrium approximation.
- Where it was needed the *pseudo* first order approximation was made, which allowed the inclusion of benzene concentration in the constants. This was done considering the huge concentration difference between benzene and 1 (30 μM).

The three rate laws derived are 1^{st} order kinetics: in order to discriminate between the three mechanisms, an Eyring plot must be performed. To do this, the results from section 3.1 were employed: $\ln(A_{317})$ vs t were plotted for all the experiment and fitted via linear regression: this allowed the extraction of the slope, proportional to the kinetic constant. This allowed the construction of the $\ln(k^{obs}/T)$ vs 1/T plot, from which the activation parameters were determined.



Figure S18. First-order approximation for the spectrophotochemical kinetic follow-up of the C-H activation step (top), as well as corresponding Eyring plot (bottom).

The values for the activation enthalpy and entropy are small, yet negative: this seems to indicate an associative-type mechanism, but it is not unequivocally identifiable according to these data. However, it should be noted that in the spectrophotochemistry experiment, no intermediate formation is observed and may be an indication of an *interchange dissociative* kind of mechanism.

8 Spectral Deconvolution

A modification of a home-made python script was used for the deconvolution of the UV-Vis spectra. The original script can be found at: <u>https://github.com/nvonwolff/Deconvolution-script</u>

In short, the observed spectrum was approximated by a linear combination of reference spectra, that were recorder independently. Deconvolution at different times allowed to get an approximate estimation of the concentration of the acyl complex **3** as well as the dearomatized complex **1**. Given the isosbestic points observed in the UV-Vis spectrum, complex decomposition was not taken into account (Figure 3 of the main manuscript).



Figure S19: Pseudo-first order approximation for the release of benzaldehyde from the acyl complex 3.





Figure S20: Spectral deconvolution of the reaction of the acyl complex 3 with CO over time.

9 DFT Calculations

All computed structures can be found at the free online ioCHEM-BD repository under the following link: https://doi.org/10.19061/iochem-bd-6-355

9.1 General

Optimizations and frequency calculations were done using the Gaussian 16 software suite in the B.01 revision (Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016). Single point energy calculations were performed using the ORCA software (4.1.1 release).⁸ Molecular visualization was carried out using Chemcraft (https://www.chemcraftprog.com).

All geometries were optimized using the M06-L functional,⁹ the def2-SVP basis set¹⁰ and W06 density fitting to increase computational efficiency,¹¹ as well as Grimme's empirical GD3 dispersion correction.¹² Frequency calculations at this level of theory confirmed stationary points and transition states and were used to compute thermodynamic properties at 298.15K, if not stated otherwise. Single point energies of the optimized structures were computed using the range-separated hybrid meta-GGA exchange-correlation functional ω B97M -V¹³ including non-local correlation (VV10),^{14,15} together with the triple- ζ def2-TZVPP basis set¹⁰ and density fitting with the RIJCOSX formalism using the auxiliary basis sets def2/J¹¹ and def2-TZVPP/C¹⁶ to speed up computational time. The choice of the ω B97M-V functional was rationalized given its excellent results in a recent benchmark study on transition metal reactions.¹⁷ Gibbs Free Energies, unless otherwise stated, were computed by adding the Free Energy correction terms from the frequency calculations to the single point energies at the ω B97M-V/def2-TZVPP level of theory in solution (SMD, Benzene) according to:

$$G_{SMD}^{\omega BP97M-V} = E_{el/SMD}^{\omega BP97M-V} + corr_{freq/T}^{M06-L},$$

where

is the thermal correction to the Gibbs Free Energy from the frequency calculation at temperature T.¹⁸ All structures were optimized in solution (benzene) using the integral equation formalism variant (IEFPCM) of the PCM model in the SMD variation of Truhlar and co-workers,¹⁹ unless otherwise stated. The so-obtained Gibbs free energies where then corrected for standard state changes between gas and liguid phase (1 atm to 1 M) according to:^{20,21}

$$\Delta G_M^0 = \Delta G_{atm}^0 + R_1 T ln(R_2 T^{\Delta n})$$

With R₁ the gas constant in J.K⁻¹mol⁻¹ and R₂ in L.atm.K⁻¹mol⁻¹ (0.08206) and $\Delta G_{1 atm}^0$ being the difference in Gibbs free energy obtained as described above. The entropies were adjusted according to:

$$S_{total,M}^{0} = S_{total,atm}^{0} - R_{1}ln([conc]A)$$

With $S_{total,M}^{0}$ being the total entropy obtained from the frequency calculation, [conc] being the concentration of the respective species under the desired conditions expressed in atm (e.g. 1M = 24.5 atm) and A the conversion factor between J and cal (0.239006). Below is a list of some relevant reaction Gibbs free energies, as well as calculated entropies.

9.2 Gibbs free energies and entropies

Table S3. Concentration	corrected calculated	d Gibbs free energies of react	ion
	concerca carcarace		

Products	ΔG_{1atm}^{0}	ΔG_{1M}^0	ΔG^0_{1M} [a]	ΔG_{1M}^{0} ^[b]
1 + CO + C ₆ H ₆	0.0	0.0	0.0	0.0
1CO + C ₆ H ₆	10.9	9.0	9.0	10.9
$1^* + CO + C_6H_6$	45.6	45.6	45.6	45.6
TS₁₋₂ + CO	57.3	55.4	55.4	55.4
2 + CO + CO	34.9	34.9	33.0	32.0
3 + CO	25.9	24.0	24.0	24.0
TS ₁₋₅ + CO	59.2	59.2	57.3	56.3
5 + CO + CO	46.9	46.9	45.0	43.9
1 + benzaldehvde	3.6	17	3.6	4.6

All values in kcal/mol.^[a]The concentration of CO was kept at 1 atm. ^[b]The concentration of CO was set to 7 mM, approximately the solubility of CO in benzene (<10 mM).

Table S4. Uncorrected and corrected reaction entropies

Products	ΔS_{1atm}^0 (cal.mol ⁻¹ K ⁻¹)	ΔS^0_{1M} (cal.mol ⁻¹ K ⁻¹)	
$1 + CO + C_6H_6$	0.0	0.0	
1CO + C ₆ H ₆	-42.0	-35.6	
1* + CO + C ₆ H ₆	6.0	6.0	
TS ₁₋₂ + CO	-35.3	-35.3	
2 + CO + CO	-8.4	-8.4	
3 + CO	-41.5	-35.2	
TS ₁₋₅ + CO	-2.2	-2.2	
5 + CO + CO	-6.1	-6.1	
1 + benzaldehyde	-6.3	-6.3	

Although we also probed the influence of CO concentration of the corrected Gibbs free energies, we reported in the manuscript the values for a 1M standard state, which indeed represents very well also the overall Gibbs free energy of reaction (1.7 kcal/mol).

9.3 TD-DFT/Excited State

TD-DFT calculations were run with two goals in mind: (1) to understand the nature of the transitions in the experimentally observed UV-Vis spectrum of complex **1** and (2) to get the energy for the excited state involved upon irradiation at 390 nm. We therefore chose to follow two distinct ways for the TD-DFT calculations.

UV/Vis Absorption spectrum

The UV/Vis absorption spectrum of **1** was modeled using the following procedure. The ω B97XD functional was used in combination with the def2-SVP basis set and SMD solvation (**Heptane**). A 50-50 Triplet-Singlet set-up was chosen for the TD-DFT and was solved for 70 states. The UV-Vis spectrum was visualized with Chemcraft and Lorentzian broadening was applied for a more realistic representation. The so-obtained UV-Vis data was normalized in the region of 260-500 nm and shifted by 26 nm to match the maximum absorption peak of the experimental spectrum. The band at around 390 nm correspond to the HOMO-1 (dz²) to LUMO transition.

Excited state calculations

In order to incorporate the excited state upon irradiation at 390 nm into the potential energy surface and the proposed mechanism, the same level of theory as for all other species has to be applied to derive reasonable values for the Gibbs free energy. Therefore, a different approach to the one described for UV-Vis simulations is followed. A simple TD-DFT run on the ground state of complex 1 at the same level of theory (SMD=benzene, solved for 5 states) was performed and the excited state corresponding to the HOMO-1 to LUMO transition was identified. If, several transitions contribute to the excited state, an NTO job on the excited state was performed in order to recover a single transition. Subsequently, the desired excited state was optimized. At each step of the optimization, it was probed if surface crossing occurs. In that case, the procedure is started again with a single point TD job at the specific geometry, followed, if necessary, by a NTO job and a novel optimization of the selected transition state (HOMO-1 to LUMO). This provided the electronic energy as well as the thermal correction to the Gibbs free energy

at the M06L level of theory. Unfortunately, attempts to obtain the single point energy at the ω B97M -V-Level of theory *via* ORCA failed, as it was not possible to converge the desired excited state. We therefore approximated the Gibbs free energy of the desired excited state by the energy of the triplet ground state, who's electronic structure should be a good rough approximation of the desired excited state.

10 Supplementary references

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