

CO-Preserving Photoinduced Transfer of Cymantrenyl Moiety: a Tandem Experimental and Computational Investigation

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Abstract: Cyclopentadienyl manganese tricarbonyl (cymantrene) is known to undergo photochemical reactions by releasing one of its CO ligands. Here we present the first example of a photorearrangement of a cymantrenylmethyl fragment, where it retains all its three CO ligands. A tandem experimental and DFT (density functional theory)-based

computational investigation allows us to explain this unexpected behavior: the rearrangement, indeed, begins with the release of one CO ligand, but cage effect of the solvent captures this CO molecule, allowing it to rapidly reattach once the rearrangement takes place.

Introduction

Photochemical reactions are initiated by the absorption of energy in the form of light. Since the beginning of scientific chemistry, researchers have been interested in light as a source of energy inducing chemical reactions.^[1] Absorbing light, a molecule reaches an electronically excited state which may have drastically different distribution of electrons (wavefunction) leading to qualitatively different chemical behavior compared to the ground state. These phenomena may be quantitatively described by means of ground-state and excited-state potential-energy hypersurface topology.^[2–7] In some cases, use of photochemical steps significantly shortens synthetic routes, allowing transformation of simple substrates into complex, polycyclic, or highly functionalized compounds.^[8,9] New product families or libraries difficult to achieve with ground-state reactions are thus available, opening new per-

spectives in the search of biologically active compounds or catalytic agents.^[10]

Quinazolinones are an important class of compounds with notable photophysical properties, widely used in the design of new organic materials. They find use as fluorescent probes and dyes,^[11–15] molecular switches^[16] and even in organic light-emitting devices.^[17,18] Owing to their commercial availability and intricate electronic structure bringing about their photochemical properties, many approaches for their functionalization were developed. In particular, derivatives of quinazolinones with organometallic substituents were found to possess remarkable photo- and electrochemical properties and biological activity.^[19–21]

Another important class of photoactive compounds contain cymantrene moiety.^[22–26] They have attracted attention as catalysts and directing agents in various processes,^[27,28] IR labels and bioprobes in bioactive molecules,^[29,30] as well as chemosensors.^[31]

Cymantrenes' *modus operandi* upon excitation consists in releasing one carbonyl with the formation of a 16-electron Mn complex and then filling the emerged Mn valence with whatever is present nearby before proceeding to the thermodynamic sink.^[32–34]

Previously we have studied^[35] the alkylation reaction of methyl- and styrylquinazolin-4-ones with bromomethylcymantrene in the presence of sodium hydride, which led to N-substituted products containing quinazolinone and cymantrene fragments within one molecule exhibiting notable photochromic and fluorescent properties.^[36]

At the same time, identical alkylation of quinazolinone **1** (Scheme 1, see Experimental Section for details) led to the formation of a mixture of products of 4O- and 3 N-substituted quinazolines (**3** and **4**) in a ratio of approximately 1:1. **3** and **4** are easily distinguishable in ¹H and ¹³C NMR thanks to their CH₂ groups, see Figure 1. Later experiments (see below) have shown that **3** rearranges into **4** upon photoexcitation, preserving all

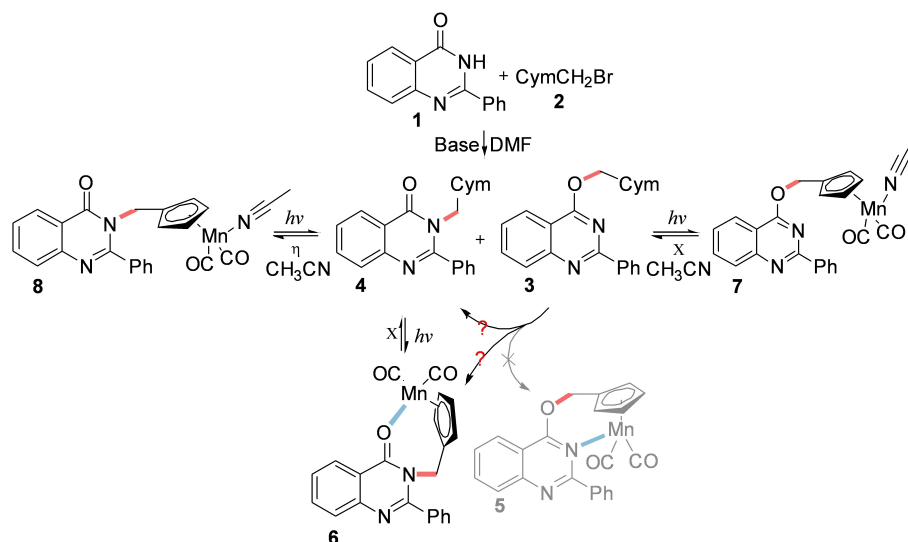
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Scheme 1. Photochemical reactions of studied quinazolinones.

three CO ligands. This behavior contradicts the universally accepted photochemistry of cymantrene and calls for a deeper investigation.

In this work we study the photoinduced rearrangement of **3** into **4** both experimentally and employing quantum chemical modeling. This tandem investigation allows us to establish the underpinnings of this unexpected behavior. In short, it comes out that **3** does release one of its CO ligands, but then quickly catches it back thanks to a cage effect. To the best of our knowledge, this is the first case where cage effect determines the outcome of a reaction in cymantrene photochemistry.

Results and Discussion

Investigating the photochemical properties of **4** and **3** in benzene we observed that the former shows the expected behavior upon excitation (Scheme 1: CO elimination, followed by formation of **6** with a Mn–O bond, proved by NMR, UV-Vis, and IR, see Experimental Section for details). On the other hand, compound **3** does not provide **5**, but instead results in a mixture of **4** and **6**. To the best of our knowledge, this photochemical transfer of the cymantrenyl moiety from oxygen to nitrogen (**3** to **4**) is the first literature example where cymantrene does not release one of its carbonyls upon photoexcitation. Meanwhile in acetonitrile both **3** and **4** react in accord with theoretical expectations (Scheme 1) providing products **7** and **8**, correspondingly (see below).

In more detail, IR monitoring (Figure 1a) of tricarbonyl complex **4** photolysis in the benzene solution for 4 min using monochromatic light of a Hg lamp with $\lambda = 365$ nm showed the disappearance of $\nu(\text{MCO})$ bands of the initial complex, corresponding to symmetric and degenerate stretching vibrations. At the same time, two new $\nu(\text{MCO})$ bands of equal intensity appeared in the region of 1932 and 1862 cm^{-1} with a simultaneous low-frequency shift of the $\nu(\text{O}=\text{CN})$ band by

56 cm^{-1} , which is typical for formation of chelates with the Mn–O bond from the O=C–N fragment of quinazolinone-4-one^[36] (**6** in Scheme 1). The ^1H NMR spectrum (Figure 1cA, B) of the resulting dicarbonyl complex differed significantly from the spectrum of the starting tricarbonyl compound **4** and was in good agreement with the structure of the proposed six-membered chelate with the Mn–O=C–N bond.^[36] In particular, upon conversion of compound **4** into the corresponding dicarbonyl chelate **6**, the signals from the α -protons of the Cp-ring underwent a downfield shift, while the signals from β -protons was shifted upfield, so that the difference in chemical shifts increased to 0.6 ppm on average. The signal from the protons of the CH_2 group of the cymantrenylmethyl substituent was shifted upfield by 1.24 ppm. Upon irradiation, the benzene solution changed its color from pale yellow to crimson, and the appearance of two new bands at 462 and 544 nm was observed in the UV-Vis spectra (Figure 1d). In a closed system without removal of CO, the reverse thermal reaction of ligand exchange was observed and the formation of the initial tricarbonyl complex **4** proceeded with a half-life of 9 min, while the color of the solution and the spectral characteristics returned to the original ones. The irradiation-thermal reaction cycle was repeated three times and showed a perfect reproducibility. Thus, **4** shows the expected behavior upon excitation.

On contrary, photolysis of O-substituted quinazolinone **3** in benzene using monochromatic light ($\lambda_{\text{max}} = 365$ nm) led to unexpected results. Upon irradiation for 4 min, vibrations corresponding to $\nu(\text{O}=\text{CN})$ and $\nu(\text{MCO})$ bands appeared in the IR spectra (Figure 1b) at 1683 and 1627 cm^{-1} , and 1932 and 1862 cm^{-1} , correspondingly. This indicated the formation of compounds having a free O=C–N group, and an O=C–N group bound to Mn. At the same time, ^1H NMR spectra (Figure 1cC, D) showed diminishing of signals from **3** and appearance of new signals, completely coinciding with the signals from compounds **4** and **6** in a ratio of 1:10. No formation of other compounds in the NMR spectra was observed. UV-Vis spectra also confirm the

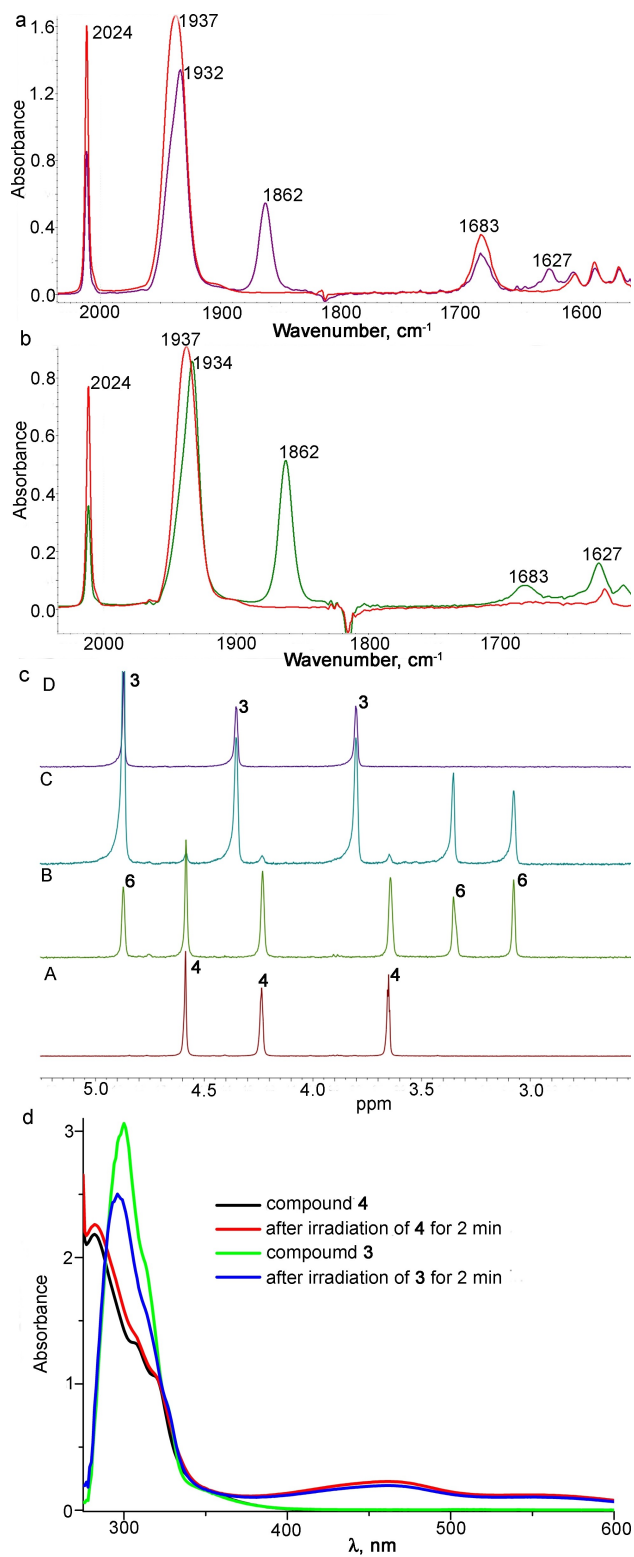


Figure 1. a) IR spectra of compound **4** in benzene (red line - before irradiation, purple line - after irradiation for 4 min); b) IR spectra of compound **3** (red line - before irradiation, green line - after irradiation for 4 min). c) ¹H NMR spectra in benzene-d₆: A) compound **4**; B) after irradiation of **4** for 4 min; C) after irradiation of **3** for 4 min; D) compound **3**. d) UV-Vis spectra of compound **4** and **3** in benzene before and after irradiation for 2 min.

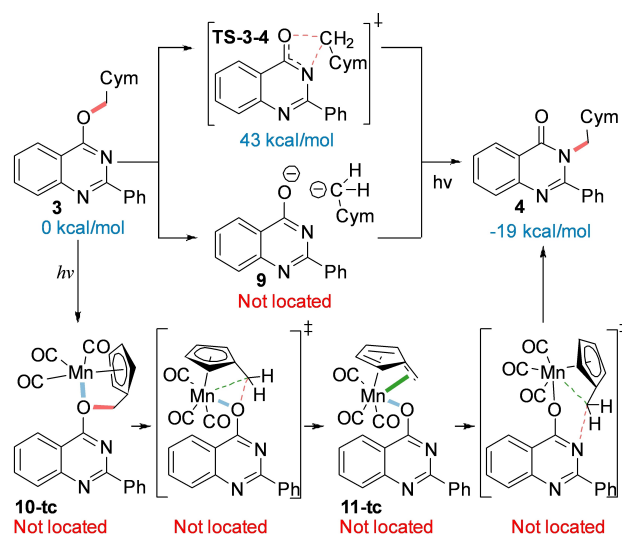
formation of complexes **4** and **6** as a result of photolysis. In a closed system, thermal ligand exchange is observed with the transition of chelate **6** to compound **4** with a half-life of 9 min, which coincides with the kinetic data obtained for the thermal reaction of the transition of **6** to **4**.

One can consider dicarbonyl **5** (grey in Scheme 1) a reasonable product of **4** photolysis in benzene, but experimental NMR, UV-Vis, and IR spectra (Figure 1) show no signs of its existence. Instead, a mixture of tricarbonyl **4** and dicarbonyl **6** is formed. Interestingly, in NMR and UV-Vis monitoring of this reaction, **4** appeared before **6** (Figure 1), suggesting that the rearrangement may proceed without CO leave.

Substituent transfer reactions from the O atom to the N atom in the quinazolinone ring were previously described only for allyl substituents and proceeded in the presence of a palladium catalyst.^[37] Examples of tautomeric intramolecular rearrangements in quinazolinones with heterocycle opening are also known.^[38] Thus, the question arises about the mechanism of the photoinduced migration of the cymantrenylmethyl group.

To rule out the possibility that this rearrangement is thermally driven (that is, it is not photochemical), we modeled migration of the cymantrenyl fragment from oxygen to nitrogen in the ground state at PBE0^[39]-D3BJ^[40,41]/def2-TZVP^[42] level of theory using Gaussian16 A.03.^[43] Solvation effects were included using PCM (polarizable continuum model)^[44] and quasiharmonic corrections for free energies were computed using GoodVibes.^[45]

This migration can occur via synchronous or dissociative-associative^[46] mechanism (top and 2nd rows in Scheme 2). We were unable to locate the zwitterionic complex **9**, however transition state (TS) for synchronous transfer (TS-3-4) was readily located with activation free energy of 43 kcal/mol. According to Eyring equation^[47] this activation energy corre-



Scheme 2. Initially proposed reaction mechanisms, none of which were confirmed by calculations. Compounds in the bottom row were computed at both ground and 1st excited (singlet) states. Relative energies of the located compounds are shown in blue.

sponds to the rate constant of 10^{-19} at room temperature, ruling out possibility of such reaction in benzene below its boiling point. This result was confirmed experimentally: heating **3** in benzene up to 60°C did not lead to any migration.

But what if manganese participates in the rearrangement, forming an additional bond with the cymantrene-bearing oxygen atom? To test this hypothesis, we synthesized compound^[48] **3_{Ph}**, which is identical to **3** but for replacement of cymantrenyl group with phenyl. **3_{Ph}** did not show the substituent migration from oxygen to nitrogen neither upon photoexcitation, nor at 60°C , even in presence of cymantrene, thus asserting the role of Mn in this rearrangement.

The simplest rearrangement mechanism involving Mn is depicted in Scheme 2, bottom. However, we were not able to locate the corresponding intermediates or TSs either in ground or excited state (using TD-DFT) at the same level of theory as above.

Notably, when we computed frequencies of pre-optimized^[49] transition state guesses, we observed only the imaginary frequency corresponding to the CO elimination. Thus, the computational investigation above does not explain the experimental observations but seems to reaffirm the long-known observation that cymantrenyl derivatives eliminate CO molecule upon excitation.

If so, then the experimental observation of preservation of the number of CO ligands in the product **4** implies that CO molecule, when eliminated, remains close to its counterpart,

and reattaches quickly after the rearrangement. This behavior is known as "cage effect".^[50–52] It can occur in dense solvents and prohibit volatile molecules from leaving the solvent cell (or cage) in which the reaction began. Cage effect was previously shown to control the product ratio in photodecomposition of asymmetric diazenes.^[53]

In earlier articles on photochemistry of cymantrenyl derivatives,^[54] cage effect was suggested to be responsible for the observed low quantum yields in these reactions: that is, upon photoexcitation the eliminated CO remains in the same solvent cell and readily returns back to Mn after its relaxation. In contrast to this purely kinetic effect, which does not affect the product of a photoinduced reaction, in the present case we, to the best of our knowledge, present the first instance where cage effect affects the product ratio of a photoinduced reaction involving cymantrene.

To prove that cage effect indeed controls the **3**→**4** rearrangement, we have conducted this reaction in an ultrasound bath. We assumed that ultrasonic irradiation would break solvent cages, freeing CO and forcing reaction to stop at the dicarbonyl complex **6**. Figure 2 vividly shows that ultrasound affects this reaction in the predicted way, proving the role of cage effect. Upon irradiation for 30 sec in the absence of an ultrasound bath, only signals related to chelate **6** appeared in a closed system and the ratio of **3** and **6** was 3.3:1 (Figure 2, Table 1). Subsequent irradiation for 30 sec led to an increase in the amount of chelate **6** and the appearance of signals from the

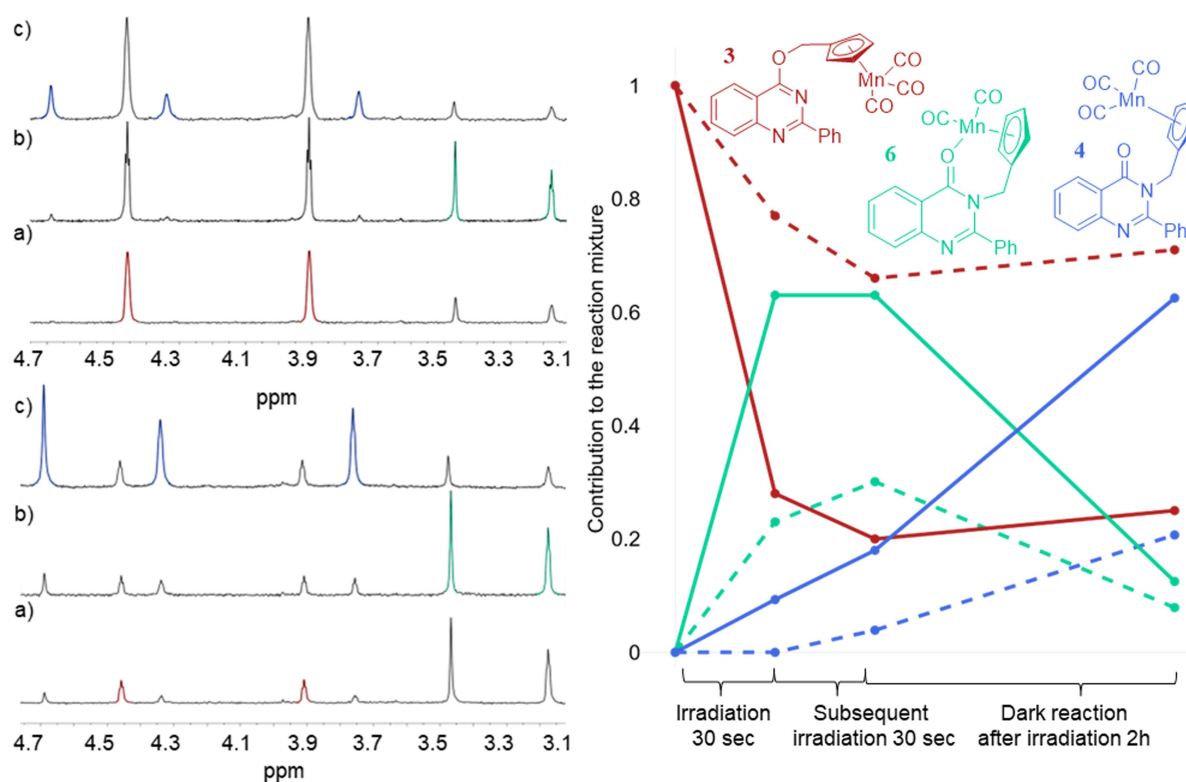


Figure 2. Investigation of ultrasonic irradiation influence on the reaction outcome. Colors represent compounds. Left: ¹H NMR spectra of the reaction mixture after 30 and 60 seconds of photolysis, and then after two hours of dark reaction; top is without ultrasound, and bottom—with it (see Figure S7 for a complete spectrum). Right: Relative concentrations of quinazoliones in the reaction mixture. Dashed line represent experiment without ultrasound, solid—with it.

Reaction conditions and time	3	6	4
Irradiation for 30 sec. without ultrasound	1	0.30	0
Subsequent irradiation for 30 sec. without ultrasound	1	0.46	0.06
Dark reaction after irradiation without ultrasound	1	0.11	0.29
Irradiation for 30 sec. with ultrasound	1	2.22	0.33
Subsequent irradiation for 30 seconds with ultrasound	1	3.22	0.90
Dark reaction after irradiation with ultrasound	1	0.5	2.5

tricarbonyl complex **4**. After 2 h under dark conditions, the ratio of **3** and **6** changed to 9.4:1, and the thermal transition of chelate **6** to **4** was observed. During photolysis with simultaneous ultrasonic irradiation, again, only formation of complexes **4** and **6** was observed. However, now complex **4** and chelate **6** became the main compounds in the reaction mixture upon irradiation for 30 sec (Figure 2, Table 1). After subsequent UV and ultrasonic irradiation, the amount of **3** decreased almost 2-

fold, and the signal intensity of compound **4** increased approximately 1.5-fold. Thus, intensive removal of the CO ligand from the solvent cell led to increased yield of dicarbonyl **6**.

Furthermore, ultrasound significantly accelerates the reaction (increases conversion of **3**), which is also consistent with breaking the cage effect: reduced reattachment of the eliminated CO prevents regeneration of **3** and increases the observed quantum yield of the reaction.

With the cage effect in play, it is highly probable that CO elimination caused by photoexcitation is indeed the first step of the reaction. After the loss of CO, the molecule likely relaxes into its ground state, so the subsequent steps can be modeled using time-independent DFT.

After CO elimination upon photoexcitation, Mn gains a free coordination site, which can be filled with either carbonyl oxygen or 3-nitrogen atom of the quinazolinone moiety leading to **10-dc** or **5**, correspondingly. Both **10-dc** and **5** can rearrange into **6**, which then catches the CO molecule held nearby in the solvent cell (Figure 3). Modeling of all the involved stationary

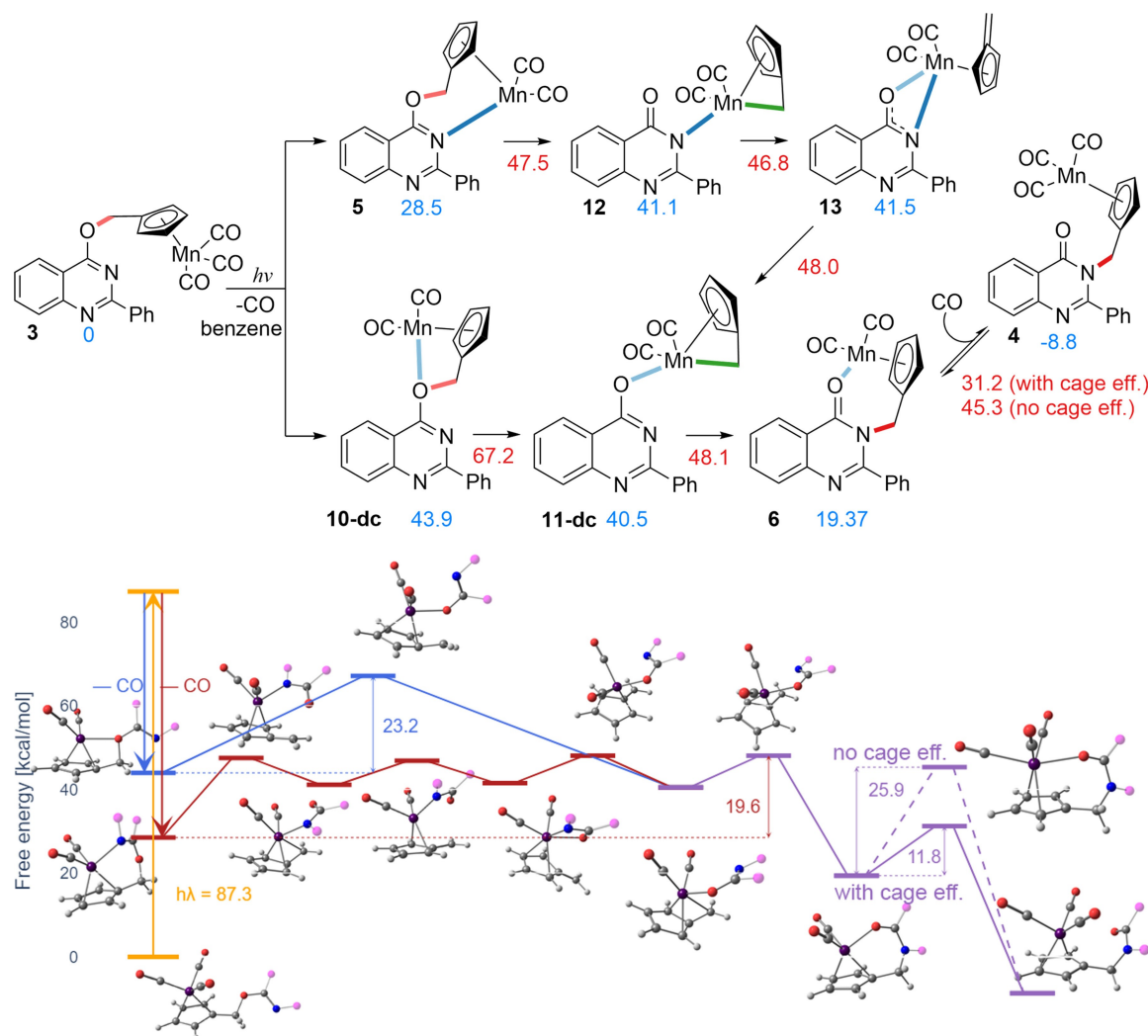


Figure 3. The two competing reaction mechanism. Top: Schematic representation with relative energies of intermediates shown in blue, and those of transition states - in red. Bottom: Free energy surface along the reaction coordinate. Values near arrows represent activation energies in kcal/mol.

points were successful and provided an activation free energy of 23.2 and 19.6 kcal/mol for the paths starting from **10-dc** and **5**, correspondingly. These activation free energies are completely feasible at room temperature, explaining formation of **4** upon photoexcitation of **3**.

Notably, cage effect significantly speeds up the CO reattachment: if CO leaves the solvent cell, then activation energy also includes the translational entropy penalty for the two molecules encounter, which amounts to ~ 10 kcal/mol^[55] at room temperature. Presence of the cage effect discards this entropic penalty because the molecules are held together and do not need to travel the solution to encounter each other, leading to decrease in the activation free energy of the CO reattachment stage by 14.1 kcal/mol.

Such low activation free energies explain our inability to detect **5** in spectra: its half-life period of rearrangement into **6** is only 26 seconds.

Of note, our results do not unambiguously distinguish which of the two routes (through **10-dc** and **5**) contributes more to the reaction flow. This uncertainty is based on the so far unexplored relaxation routes of the exited substrate **3**. **5** with bearing a Mn–N bond is 3.6 kcal/mol more stable than **10-dc** with bearing an O–Mn one; however, dynamic, and electronic effects controlling release of CO and subsequent relaxation may drastically affect this picture.

Conclusion

In conclusion, although the studied reaction preserves all three carbonyl ligands, it begins with release of one of them, like all the other photoinduced reactions of cymantrenyl derivatives. The initially formed 16-electron Mn complex has very high reactivity and produces complexes with a solvent molecule in case of MeCN or an intramolecular Mn–O or Mn–N bond in benzene. In the case of photolysis of **3** in benzene, the formed complex undergoes a rearrangement, during which Mn and CpCH₂ exchange their substituents without breaking the Mn–Cp ring bond; though the oxygen and nitrogen atoms in the quinazolinones are positioned very close to each other, this exchange proceeds in several steps with an overall activation free energy of ~ 20 kcal/mol. The activation free energy of the subsequent return of the eliminated CO is only 12 kcal/mol if CO is captured within a solvent cell (that is, it has no translational entropy), but amounts to 26 kcal/mol if it escapes from it.

Thus, even in this complex case the cymantrenyl moiety strictly follows its *modus operandi*. At the same time, the cage effect controls the outcome of the reaction, making it look like CO elimination never happened. Consequently, solvent's ability to sustain cages might influence chemical reactions taking place in it on par with proticity and dielectric permittivity. Barry et al. have recently demonstrated that this ability is linked to solvent's microviscosity, which may vary significantly even between otherwise very similar solvents.^[56]

Experimental Section

Quantum chemical calculations: Coordinates of localized structures are available as a set of supplementary XYZ files. Comment line for each molecule includes: Name corresponding to the Schemes in the main article, system charge and multiplicity, total electronic energy at PBE0-D3BJ/def2SVP/PCM(benzene) (PCM(acetonitrile) for **7** and **8**) level of theory (*E*), total Gibbs free energy at the same level of theory at 298 K computed with Grimme's and Head-Gordon's quasi-harmonic corrections as implemented in GoodVibes (*qhG(298 K)*), number of imaginary frequencies (*NumImFreq*) characterizing if the structure correspond to energy minimum or transition state. Additionally provided are electronic (*Erel*) and Gibbs free (*Grel*) energies relative to the **3** in kcal/mol.

Materials and methods: ¹H NMR spectra were measured on a Bruker Avance™ 400 spectrometer with working frequencies of 400.13. Proton chemical shifts were determined relative to the residual signal from deuterated solvent (7.16 ppm for benzene-d₆, 2.05 ppm for acetone-d₆ and 7.26 ppm for CDCl₃) and counted to TMS. IR spectra were recorded on a Tensor 37 (Bruker) IR Fourier spectrometer with a resolution of 2 cm⁻¹ in CaF₂ cells. The UV-Vis spectra were registered on a Carry 300 spectrophotometer. ESI mass spectra were obtained with a Finnigan LCQ Advantage instrument. The photochemical reactions were carried out using an Hg immersion lamp Hereaus TQ 150 equipped with a water-cooled S49 glass jacket. The reaction course and product purity were controlled by TLC using Silufol UV-245 (Kavalier) plates. Silica gel 60 Merck was used for column chromatography. Solvents were purified by standard methods and distilled under argon. The ultrasonic irradiation was conducted using tip ultrasonic bath (Elmasonic S120, Elma). Ultrasonic frequency and electric power of the ultrasonic bath was 37 kHz and 200 W respectively.

Alkylation of 2-phenylquinazoline-4-one with cymantrenylmethyl bromide (synthesis of **3 and **4**):** To a solution of 0.5 g (2.3 mmol) of 2-phenylquinazoline-4-one in 15 mL of DMF in argon atmosphere with stirring, 10 mmol of a 60% NaH suspension was added in portions, and the mixture was kept at this temperature for 15 min. Then, 1.0 g (3.6 mmol) of cymantrenylmethyl bromide in 10 mL of DMF was added dropwise to the reaction mixture, and it was warmed to 60 °C and stirred for 48 h. The mixture was poured into ice water (100 mL) and the products were extracted with CH₂Cl₂ (3 × 75 mL). The organic extracts were dried over Na₂SO₄, the solvent was evaporated, the residue was followed by column chromatography (hexane: AcOEt) 2:1.

2-Phenyl-4-cymantrenylmethoxy-3H-quinazoline (3**):** Yield of **3** 0.32 g (31%). ¹H NMR (acetone-d₆): 5.00 (m, 2H, H–Cp), 5.42 (m, 2H, H–Cp), 5.55 (s, 2H, CH₂), 7.54 (m, 3H, Ar), 7.66 (t, 1H, Ar, J = 7.7 Hz), 7.98 (m, 2H, Ar), 8.28 (d, 1H, Ar, J = 7.8 Hz), 8.66 (m, 2H, Ar). ¹H NMR (benzene-d₆): 3.80 (m, 2H, H–Cp), 4.35 (m, 2H, H–Cp), 4.87 (s, 2H, CH₂), 7.08 (t, 1H, Ar), 7.30 (t, 1H, Ar), 7.33 (t, 1H, Ar), 7.40 (t, 2H, Ar), 8.06 (d, 1H, Ar), 8.11 (d, 1H, Ar), 8.96 (d, 2H, Ar). ¹³C NMR (acetone-d₆): 61.85 (CH₂), 82.64 (2C–Cp), 85.18 (2C–Cp), 99.32 (C–Cp), 114.89 (Ci), 123.45, 126.91, 127.90, 128.31 (2 C), 130.69, 134.08, 137.86 (Ci), 152.03 (Ci), 159.44 (Ci), 166.10 (Ci), 225.29 (3CO). Found, (%): C, 62.88; H, 3.38; N, 6.52; Mn, 12.4. C₂₃H₁₅MnN₂O₄. Calcd. (%): C, 63.02; H, 3.45; N, 6.39; Mn, 12.5. IR, (νCO, cm⁻¹): (benzene) 2022 (s), 1938 (s). UV-vis, λ_{max} (benzene)/nm 312, (ε/dm³mol⁻¹cm⁻¹ 11060), 327 (4553). UV-vis, λ_{max} (acetonitrile)/nm 312 (ε/dm³mol⁻¹cm⁻¹ 9520), 327 (4517). ESI-MS *m/z* for C₂₀H₁₅MnN₂O [M–3CO] 354.0.

2-Phenyl-3-cymantrenylmethyl-3H-quinazolin-4-one (4**):** Yield of **4** 0.40 g (38%). ¹H NMR (acetone-d₆): 4.73 (m, 2H, H–Cp), 4.78 (m, 2H, H–Cp), 4.94 (s, 2H, CH₂), 7.58 (t, 1H, Ar, J = 7.7 Hz), 7.67 (m, 6H, Ar), 7.85 (t, 1H, Ar, J = 7.5 Hz), 8.27 (d, 1H, Ar, J = 7.7 Hz). ¹H NMR (benzene-d₆): 3.65 (m, 2H, H–Cp), 4.24 (m, 2H, H–Cp), 4.59 (s, 2H,

CH₂), 7.04 (m, 4H, Ar), 7.11 (m, 2H, Ar), 7.26 (t, 1H, Ar), 7.72 (d, 1H, Ar), 8.52 (d, 1H, Ar). ¹³C NMR (acetone-d₆): 42.00 (CH₂), 82.22 (2C–Cp), 85.48 (2C–Cp), 98.90 (C*i*-Cp), 121.01 (Ci), 126.53, 126.97, 127.55, 128.64 (2 C), 129.92, 134.46, 135.63 (Ci), 147.43 (Ci), 155.42 (Ci), 161.60 (Ci), 224.76 (3CO). Found, (%): C, 62.97; H, 3.43; N, 6.48; Mn, 12.3. C₂₃H₁₅MnN₂O₄. Calcd., (%): C, 63.02; H, 3.45; N, 6.39; Mn, 12.5. IR, (νCO, cm⁻¹): (benzene) 2022 (s), 1937 (s), 1683 (w). UV-vis, λ_{max} (acetonitrile)/nm 317 (ε/dm³mol⁻¹cm⁻¹ 3915). UV-vis, λ_{max} (acetone/nitrile)/nm 317 (ε/dm³mol⁻¹cm⁻¹ 4038). ESI-MS *m/z* for C₂₀H₁₅MnN₂O [M-3CO] 354.0.

A of 2-phenylquinazoline-4-one with benzylbromide (synthesis of 3_{ph} and 4_{ph}): To a solution of 0.4 g (1.9 mmol) of 2-phenylquinazoline-4-one in 15 mL of DMF in argon with stirring, 10 mmol of a K₂CO₃ was added, and the mixture was kept at this temperature for 15 min. Then, 0.3 mL (2.2 mmol) of benzyl bromide in 10 mL of DMF was added dropwise to the reaction mixture, and it was warmed to 45 °C and stirred for 6 h. The mixture was poured into ice water (100 mL) and the products were extracted with CH₂Cl₂ (3 × 75 mL). The organic extracts were dried over Na₂SO₄, the solvent was evaporated, the residue was followed by column chromatography (hexane: AcOEt) 2:1.

2-Phenyl-4-benzyloxy-3H-quinazoline (3_{ph}): Yield of 3_o 0.19 g (34%). ¹H NMR (CDCl₃): 5.79 (s, 2H, CH₂), 7.38 (m, 2H, Ar), 7.43 (m, 2H, Ar), 7.50 (m, 3H, Ar), 7.59 (m, 2H, Ar), 7.83 (t, 1H, Ar, J = 8.3 Hz), 8.00 (d, 1H, Ar, J = 8.3 Hz), 8.22 (d, 1H, Ar, J = 8.2 Hz), 8.60 (m, 2H, Ar). ¹H NMR (acetone-d₆): 5.85 (s, 2H, CH₂), 7.37 (t, 1H, Ar, J = 7.3 Hz), 7.44 (m, 2H, Ar), 7.55 (m, 3H, Ar), 7.60 (m, 1H, Ar), 7.67 (m, 2H, Ar), 7.94 (m, 2H, Ar), 8.23 (d, 2H, Ar, J = 7.8 Hz). ¹³C NMR (acetone-d₆): 68.33 (CH₂), 115.31 (Ci), 123.38, 126.83, 127.90, 128.12, 128.23 (2 C), 128.35 (4 C), 128.53 (2 C), 130.58, 133.91, 136.82 (Ci), 138.02 (Ci), 151.97(Ci), 159.46 (Ci), 166.49 (Ci).^[57]

2-Phenyl-3-benzyl-3H-quinazolin-4-one (4_{ph}): Yield of S_N 0.18 g (33%). ¹H NMR (CDCl₃): 5.28 (s, 2H, CH₂), 6.95 (m, 2H, Ar), 7.21 (m, 3H, Ar), 7.36 (m, 5H, Ar), 7.47 (m, 1H, Ar), 7.54 (m, 1H, Ar), 7.78 (m, 2H, Ph), 8.38 (d, 1H, Ar, J = 8.1 Hz). ¹³C NMR (CDCl₃): 48.73 (CH₂), 98.42 (Ci), 126.98 (2 C), 127.13, 127.19, 127.46, 127.61, 128.01 (2 C), 128.54 (2 C), 128.62 (2 C), 129.92, 134.60, 135.57 (Ci), 147.13 (Ci), 156.29 (Ci), 160.59 (Ci).^[48]

General procedure for spectral studies of photochemical reactions of tricarbonyl complexes 3–4: A solution of a complex under study in a required solvent (benzene, toluene, or acetonitrile; c 2–4 mM) was placed under an argon atmosphere into IR or UV cells and irradiated with an Hg lamp (steady radiation of the lamp was achieved 2 min before irradiation) for 10 sec–4 min. To prepare samples for NMR monitoring, solutions of compounds (c 10⁻²–10⁻³ M) were filtered into an NMR tube, bubbled with argon, and irradiated with the Hg lamp at 5–8 °C for 1 min (close system) or 4 min (open system) up to 50–80% conversion. The distance between the lamp and the sample was 5 cm in all cases. The width of the irradiation window was 2 cm in the case of IR cell, 1 cm in the case of UV cell, and 5 mm in the case of NMR tube. Monitoring of all dark reactions of chelates was carried out similarly at least for 72 h, the IR spectra were registered every 5 min. The “irradiation-dark reaction” procedure for ca. 2 mM solutions of all compounds in benzene was carried out in the IR cell and repeated 3–5 times.

Samples irradiated in NMR tubes had free volume for the accumulation of carbon monoxide liberated (open system). In the case of irradiation in IR or UV cell, there was no free volume and carbon monoxide liberated retained in solution (closed system).

[2-Phenyl-3-(η⁵-cyclopentadienylmethyl)-3H-κO-quinazolin-4-one](dicarbonyl)manganese (6): ¹H NMR (benzene-d₆): 3.08 (m, 2H, H–Cp), 3.35 (s, 2H, CH₂), 4.87 (m, 2H, H–Cp), 6.83 (t, J = 7.5 Hz, 1H, Ar), 7.06 (m, 4H, Ar), 7.43 (m, 2H, Ar), 7.62 (m, 2H, Ar). IR, (νCO,

cm⁻¹): (benzene) 1933 (s), 1863 (s), 1626 (w). UV-Vis, λ_{max} (benzene)/nm 462 (ε/dm³mol⁻¹cm⁻¹ 830), 544 (443).

[2-Phenyl-4-(η⁵-cyclopentadienylmethyl)-3H-quinazoline](acetonitrile)(dicarbonyl)manganese (7): ¹H NMR (benzene-d₆): 0.63 (s, 3H, CH₃CN), 4.15 (m, 2H, H–Cp), 4.68 (m, 2H, H–Cp), 5.24 (s, 2H, CH₂), 6.90 (m, 1H, Ph), 6.22 (m, 2H, Ph), 7.35 (m, 2H, Ph), 8.00 (m, 1H, Ar), 8.15 (m, 1H, Ar), 8.93 (m, 1H, Ar). IR, (νCO, cm⁻¹): (benzene) 1935 (s), 1864 (s). UV-Vis, λ_{max} (acetonitrile)/nm 336 (ε/dm³mol⁻¹cm⁻¹ 1031).

[2-Phenyl-3-(η⁵-cyclopentadienylmethyl)-3H-quinazolin-4-one](acetonitrile)(dicarbonyl)manganese (8): ¹H NMR (benzene-d₆): 0.75 (s, 3H, CH₃CN), 3.89 (m, 2H, H–Cp), 4.30 (m, 2H, H–Cp), 4.82 (s, 2H, CH₂), 7.08–7.15 (m, 5H, Ph), 7.23 (m, 2H, Ar), 7.71 (m, 2H, Ar). IR, (νCO, cm⁻¹): (benzene) 1933 (s), 1863 (s), 1626 (w). UV-Vis, λ_{max} (acetonitrile)/nm 385 (ε/dm³mol⁻¹cm⁻¹ 192).

Procedure of the irradiation: A solution of compound 3 (0.0275 g (0.625 mM)) in deuterobenzene was filtered and bubbled with argon in glass flask, hermetically sealed, and at a temperature of 6–8 °C, it was irradiated with Hg with a Hereaus TQ 150 immersion lamp equipped with an S49 glass cooling jacket (before irradiation, the lamp was put on mode for 2 min). The total exposure time was 2 min. The distance between the lamp and the sample was 5 cm. Yield of 3 0.019 g (69%). Yield of 2 0.005 g (18%).

Procedure of the cooperative photo- and ultrasonic irradiation: A solution of compound 3 (0.0275 g (0.625 mM)) in deuterobenzene was filtered and bubbled with argon in glass flask, hermetically sealed, and at a temperature of 6–8 °C, it was irradiated with Hg under the action of ultrasound with a Hereaus TQ 150 immersion lamp equipped with an S49 glass cooling jacket (before irradiation, the lamp was put on mode for 2 min); spectra were recorded every 30 sec. The total exposure time was 1 min. The distance between the lamp and the sample was 5 cm. Yield of 3 0.0065 g (23%). Yield of 2 0.017 g (62%).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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RESEARCH ARTICLE

The non-exchangable CO: When one observes that the reaction product contains the same quantity of CO ligands as the substrate, it is natural to suspect that they do not detach during the reaction. We present a reaction where this is not the case and highlight the role of cage effect in this conundrum.



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**CO-Preserving Photoinduced
Transfer of Cymantrenyl Moiety: a
Tandem Experimental and Computa-
tional Investigation**

