



REVERSIBLE COORDINATION OF THE CARBONYL LIGANDS IN CYMANTRENE AS A WAY TO CREATE PHOTOACTIVE SYSTEMS

L. N. Telegina* and E. S. Kelbysheva

*Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia*

Cite this: *INEOS OPEN*,
2021, 4 (6), 224–231
DOI: 10.32931/io2129r

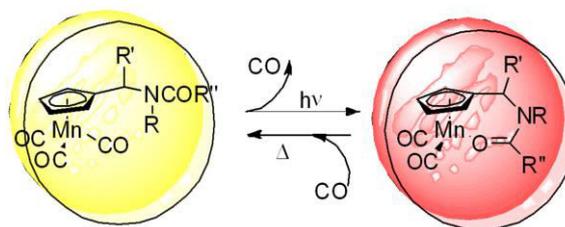
Received 25 January 2022,
Accepted 28 February 2022

<http://ineosopen.org>

Abstract

The article describes the main properties and applications of tri- and dicarbonyl derivatives of cymantrene bearing a C=O donor fragment capable of coordinating with manganese atoms. Recent reports of different research groups, including our, show that these compounds can be of interest for the creation of photosensitive smart materials owing to the possibility of formation of photochromic systems between hemilabile di- and tricarbonyl complexes. The properties of these complexes of cymantrene with ketone, amide, and carbamate groups of both monomeric and cascade structures are considered.

Key words: cymantrene, photochemistry, dicarbonyl complex, photochromic properties, hemilabile complex.



Introduction

One of the important directions for creating smart materials is the search for compounds that change their physicochemical properties under the influence of external factors, such as light, medium pH, pressure, or temperature. Of practical interest are the photosensitive and photochromic materials in which irradiation causes a transition between two discrete hemilabile states [1–3]. Since photochromism implies a reversible change in color when switching of states changes an electronic structure of the entire system, it becomes possible to control the physicochemical properties of these materials. Photoswitches can find application in the creation of drug carriers, electronic devices, molecular machines, UV and chemosensors, catalysts, as well as the reagents for fluorescence microscopy and IR spectroscopy [4–14].

One of the main requirements to photochromic systems, besides a high quantum yield, is the absence of side reactions and good resolution of spectral parameters from chromophore groups. To meet these requirements, it is necessary to use reversible monomolecular reactions, for example, photoinduced isomerization [15–17] and cyclization [18–20]. In the case of organometallic compounds, the photoinduced ligand exchange can also be used to create photochromic and photosensitive systems [21–23]. For cymantrenyl derivatives, the ligand exchange reactions are well studied and widely used for obtaining new mono- and binuclear compounds [24–27]. Upon irradiation of manganese tricarbonyl derivatives, the CO ligand is removed to form a 16-electron intermediate which interacts with a new *n*- or π -donor ligand, resulting in hemilabile dicarbonyl complexes. The ligand exchange in the cymantrene derivatives proceeds *via* the S_N1 mechanism [28]. Under the conditions of a thermal dark reaction or irradiation, the Mn–

ligand bond in these dicarbonyl complexes breaks also with the formation of manganese in the 16-electron state. The process may progress in two directions. The first way is the formation of a bond with the same ligand to obtain the initial dicarbonyl complex or the addition of a new ligand in the presence of another *n*- or π -donor in the system [29]. The second direction is the cleavage of the manganese–cyclopentadienyl ring bond with the formation of organic cyclopentadienyl derivatives [30]. The first way is preferable to create photosensitive materials.

A photochromic reversible transformation from the cymantrenyl derivatives was observed for the first time by To *et al.* in 2008 [28] using UV-vis and IR spectroscopy and was further developed in other studies [31, 32]. For example, after irradiation of a purple solution of **1** in heptane, the color of the solution changed due to the rupture of the Mn–N bond followed by the formation of new chelate complex **2**, where Mn was bonded with the O atom of the carbonyl group. The intensity of the bands at 425 and 572 nm decreased in the UV-vis spectra and that of the band at 750 nm increased; the intensity of the band at 750 nm decreased with an increase in the intensity of the bands at 425 and 572 nm for 10 min after photolysis under dark conditions (Fig. 1). The absorbance at 572 nm decreased by 3%, indicating the formation of a side product. During visible irradiation, a peak at 680 nm was observed in the difference spectra that corresponded to a photoproduct with structure **2**. Thus, these compounds formed reversible photochromic systems in solutions owing to the intermolecular exchange of ligands at the manganese atom with a fast photochromic response.

The stability and tunability are important advantages of cymantrene. All its tri- and dicarbonyl derivatives feature a number of characteristic parameters in the IR and NMR spectra, which makes the identification of these compounds easy and reliable. In particular, Schatzschneider and colleagues actively

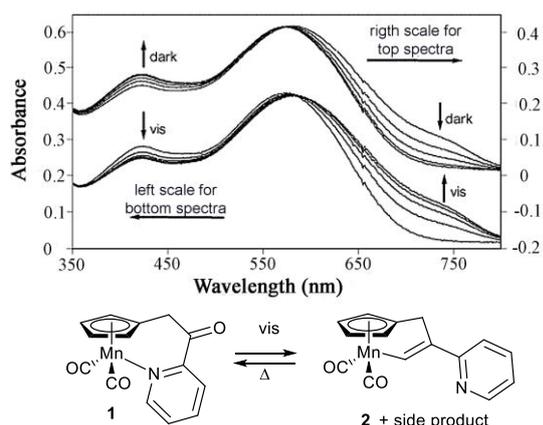


Figure 1. UV-vis spectra of **1** during visible irradiation (bottom spectra) and subsequent dark reaction (top spectra) [33]. (Adapted with permission from H. W. P. N'Dongo *et al.*, *J. Inorg. Biochem.*, **2008**, *102*, 2114–2119. DOI: 10.1016/j.jinorgbio.2008.07.019. Copyright (2008) American Chemical Society)

used in their works the fact that CO ligands have characteristic bands in the IR spectra [33–35]. Thus, they were the first to obtain a bioconjugate in which cymantrene acted as an IR label (Fig. 2) [33]. The following studies on the biomolecules with the cymantrenyl fragments unlocked the great potential of these compounds as a new promising tool for the characterization and localization of metal-containing biomarkers using IR spectroscopy [33–35]. The authors showed that the ability to release CO ligands from manganese can be used in biological processes. A half-life of the photolytic decarbonylation was several hours under conditions compatible with biosystems, so the significant general photodamage to cells was to be expected [34].

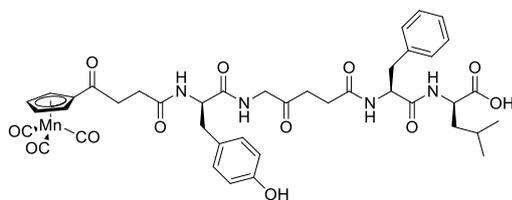


Figure 2. Cymantrene-[Leu5]enkephalin peptide bioconjugate.

Recently, the promising molecular switches have been obtained based on the hydrazone derivatives of cymantrene which combined a rhodamine fluorescent label with a photoactive cymantrenyl moiety [36]. It was found that these compounds can be used as chemosensors for metal ions such as Hg^{2+} (Fig. 3). Moreover, the dissociation of CO followed by the formation of a chelate complex with a bond between the metal center and the carbonyl group oxygen atom led to fluorescence enhancement (Fig. 3), which allowed the authors to effectively recognize the metal ions inside the cells.

All these properties make the cymantrene derivatives promising objects for the creation of new photosensitive smart materials.

We selected the cymantrenylalkyl derivatives containing the carbonyl ligand for a detailed study of their photo- and thermally induced ligand exchange with subsequent modification to create photosensitive and photochromic materials.

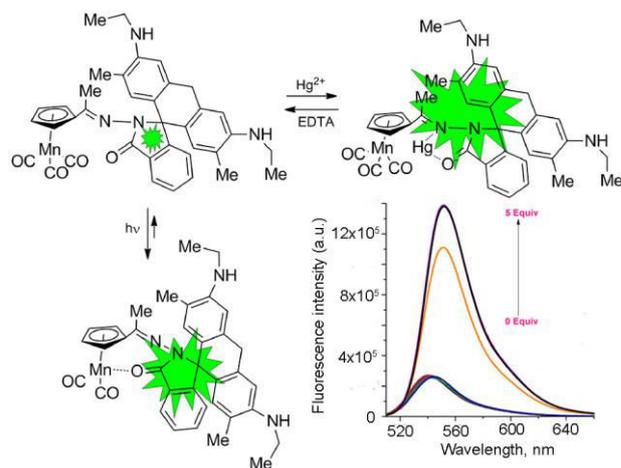


Figure 3. Light-responsive behavior of the cymantrenyl rhodamine hydrazone [36]. (Reprinted with permission from S. Dewangan *et al.*, *Appl. Organomet. Chem.*, **2018**, *32*, e4612. DOI: 10.1002/aoc.4612. Copyright (2018) John Wiley & Sons Ltd)

Photochemical behavior of the monomeric cymantrene derivatives

The first stage in obtaining highly efficient photochromic systems was to study the possibility of formation of chelate complexes between the manganese atoms and the oxygen atoms of the carbonyl groups in the amide and carbamate derivatives. For this purpose, compounds **1–9** were obtained and studied for the photochemical behavior [30, 36–38].

The irradiation of the derivatives with the carbonyl groups led to the elimination of the CO ligand from the manganese atom. Even in benzene, a crimson color of the solution was initially observed in the absence or presence of other external ligands, although the colors of the complexes with these ligands are usually different. This fact evidenced the formation of the dicarbonyl complexes featuring a bond between the Mn and carbonyl group O atoms.

Using IR and NMR spectroscopy, it was shown that the irradiation of tricarbonyl cymantrene derivatives **3–11** with both a full spectrum light mercury lamp or light with $\lambda_{\text{max}} = 366 \text{ nm}$ resulted in the loss of one of the CO ligands and manganese atoms in the 16-electron state, which formed a new bond with the oxygen atom of the C=O groups to give a six-membered chelate ring. In the IR spectra, the disappearance of the bands of $\nu(\text{MCO})$ vibrations of the tricarbonyl complexes and the appearance of the bands of symmetric and antisymmetric stretching vibrations of the CO ligands of the dicarbonyl derivatives were observed (Fig. 4, Table S1 in the Electronic supplementary information (ESI)). There was also a low-frequency shift of the $\nu(\text{CO})$ bands of the amide group by 30–50 cm^{-1} and $\nu(\text{NH})$ vibrations by 12–55 cm^{-1} , which indicated the involvement of the amide group in the stabilization of chelates **12–20** (Scheme 1, Fig. 4). The ^1H NMR spectra demonstrated drastic changes on going from the tricarbonyl complexes to the dicarbonyl derivatives. Thus, the signals of the α -protons of the Cp-ring were found to be downfield shifted, while those of the β -protons—upfield shifted (Table S1 in the ESI). It should be noted that, in the case of all chiral derivatives, the differences between the chemical shifts of the diastereotopic α - and α' -pro-

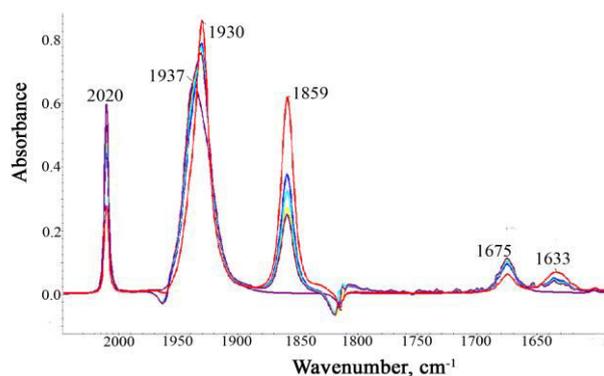
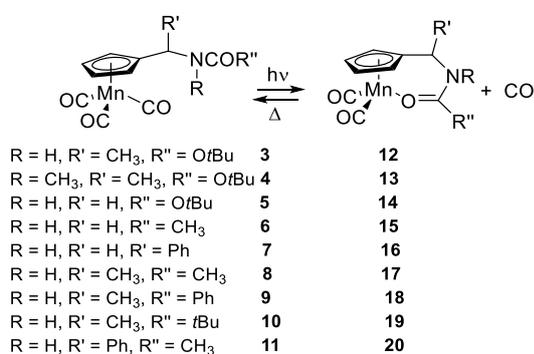


Figure 4. IR monitoring of the photolysis of amide **4** in benzene [30]. (Reprinted with permission from L. N. Telegina *et al.*, *Eur. J. Inorg. Chem.*, **2009**, 3636–3643. DOI: 10.1002/ejic.200900458. Copyright (2009) John Wiley & Sons Ltd)



Scheme 1. Photolysis of compounds **3–11** and thermal reactions of the corresponding dicarbonyl complexes.

tons of the Cp-ring appeared to be changed in the spectra of the chelates compared to those of the starting compounds. These changes in the spectra confirmed the formation of chelate complexes **12–20** with the Mn–O bonds. The values of quantum yield were high, reaching, for example, 0.98 for carbamate **3**.

Unfortunately, all the attempts to isolate the chelates were unsuccessful. When the solvent was removed, the decomposition of the chelate complexes was observed. The DFT calculations confirmed the proposed structures for dicarbonyl complexes **12–16** and showed that the global energy minima of these compounds are about 30 kcal/mol higher than that for tricarbonyl complexes **3–7**.

It should be noted that the irradiation of both carbamates **3–5** and amides **6–11** led to a change in the color of their solutions from pale yellow to crimson. The UV-vis spectra showed two new bands in the region of 400–550 nm (Fig. 5, Table S1 in the ESI). Based on the DFT calculations, a transition at about 500 nm was attributed to the d–d transition.

The chelate complexes underwent ligand exchange in the presence of external ligands such as CO and PPh₃ both under dark conditions and upon irradiation. The study of the kinetics of a dark reaction with an external substrate showed that the half-lives for the reactions of **10–18** with carbon monoxide were 60–130 min and those for the reactions with triphenylphosphine by the first-order equation and proceeded according to the S_N1 mechanism. It should be noted that the introduction of a methyl group at the first position of the Cp ring side chain led to a decrease in the rate of ligand exchange in all cases, which was

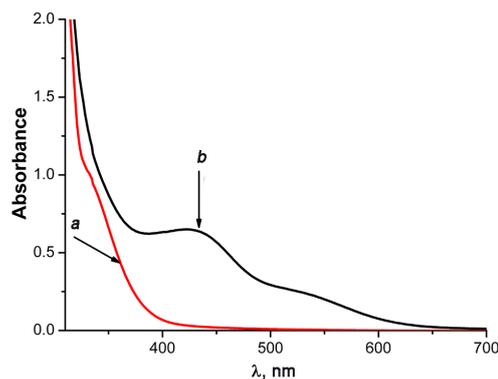


Figure 5. UV-vis spectra of the solutions of **6** ($c = 1.2$ mM) (*a*) and **15** ($c = 5$ mM) (*b*) in benzene [38]. (Reprinted with permission from E. S. Kelbysheva *et al.*, *Russ. Chem. Bull.*, **2015**, 64, 914–922. DOI: 10.1007/s11172-015-0955-x. Copyright (2015) Springer Nature)

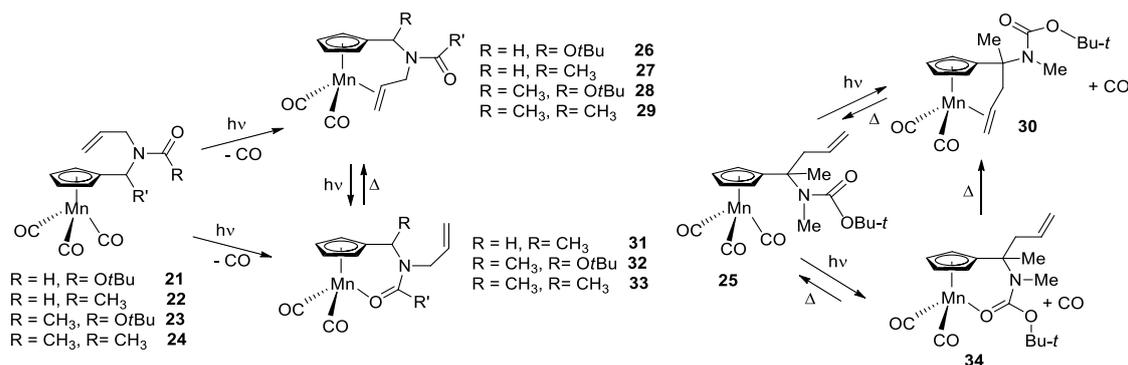
apparently related to the steric factors, increased by more than 1.5 times (Table S2 in the ESI). All ligand exchange reactions under dark conditions were described by the first-order equation and proceeded according to the S_N1 mechanism. It should be noted that the introduction of a methyl group at the first position of the Cp ring side chain led to a decrease in the rate of ligand exchange in all cases, which was apparently related to the steric factors.

Thus, the carbonyl group in carbamates and amides based on cymantrene form hemilabile chelates which can undergo ligand exchange processes with external ligands with changes in their optical and spectral parameters.

To obtain the photosensitive materials with switchable optical properties, the second stage of our research was the preparation of monomeric compounds containing two donor groups, one of which was a carbamate or amide group. An olefin moiety was chosen as the second donor group. Thus, a number of cymantrene derivatives (**21–25**) were obtained [39].

Monitoring of the course of irradiation of complexes **21–25** with both a full spectrum lamp and monochromatic light with $\lambda_{\max} = 366$ nm by IR and ¹H NMR spectroscopy showed the formation of dicarbonyl complexes. The photolysis of compound **21** led to only olefin chelate **26**. In the other cases, two types of chelates were detected. These were compounds **27–30** in which manganese formed a bond with the olefin moiety and complexes **31–34** in which the manganese atom was bound to the oxygen atom of the carbonyl group (Scheme 2, Table S1 in the ESI). The ratio of the olefin chelate to the chelate with the Mn–O bond changed from 1:5 to 4:1 and depended on the size of a cycle in the forming possible chelates with the Mn–olefin bond and the presence of a bulky substituent at the first position of the Cp ring side chain (Table S3 in the ESI). The ratio of the resulting chelates was also strongly influenced by the introduction of an amide substituent instead of a carbamate one.

The study of the reverse thermal reactions showed that all carbamate and amide complexes **31–33** were isomerized to the olefin chelates with half-conversion times of 3–67 min (Table S2 in the ESI). The replacement of the carbamate substituent for an amide unit led to a decrease in the rate of dark isomerization (Table S2 in the ESI). The disappearance of the band at about 500 nm for chelates **31–33** and an increase in the intensity of the band at 330 nm for **27–30** were observed in the UV-vis spectra. A crimson color of the solution changed to yellow, which is



Scheme 2. Photolysis of compounds **21–25** and thermal reactions of the corresponding dicarbonyl complexes.

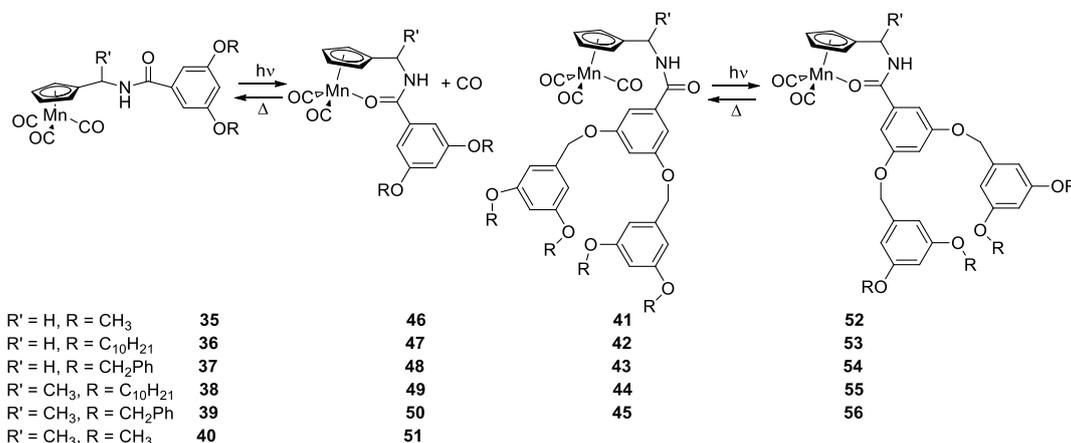
characteristic of all the olefin complexes. In all cases, the products of the thermodynamic control were olefin chelates **27–30**.

The olefin chelates were stable and isolated; compounds **26** and **27** were also characterized by X-ray diffraction. The study of the photoinduced internal ligand exchange in the olefin chelates showed that the irradiation of complexes **27–29** leads to the formation of chelates **31–33** which rapidly isomerize under dark conditions to the olefin chelates. The irradiation–reverse isomerization cycle was repeated 3–5 times. The spectral parameters remained unchanged. The study of the kinetics of a reverse reaction showed that it can be described by the first-order equation and proceeds according to the S_N1 mechanism. The photolysis of olefin complex **30** did not lead to the formation of carbamate chelate **34**, in contrast to the above-described olefin complexes; **34** was only a kinetic product of the irradiation of **25**.

Thus, complexes **27–29** and **31–33** formed photochromic pairs with rapid isomerization of the chelates with the Mn–O bond to the olefin complexes. Based on the results obtained, we decided to continue the investigations on the creation of new photosensitive materials using only the amide derivatives of cymantrene.

Photochemical behavior of the cascade cymantrene derivatives

In order to study the effect of cascade fragments [40] on the optical, spectral, and photochemical properties of new photosensitive materials with photoactive cymantrenyl moieties



Scheme 3. Structures of the cascade tri- and dicarbonyl complexes.

for their further application, at the next stage we obtained two series of compounds with cascade structures: **35–40** and **41–45** (Scheme 3) [41].

The investigations by IR and ¹H NMR spectroscopy showed that, as in the case of monomeric amides **6–11**, six-membered chelates **46–56** with the Mn–O bond were formed during the photolysis of the cascade derivatives (Scheme 3). The parameters of the spectra of the new dicarbonyl chelates were close to those for complexes **6–11**. Upon irradiation of tricarbonyl complexes **35–45**, a color of the solution changed from pale yellow to crimson and new long-wavelength maxima appeared in the range of 430–530 nm in the UV-vis spectra. Resulting cascade chelates **46–56** were stable in solution for 4–6 h; however, all attempts to isolate these dicarbonyl compounds appeared to be unsuccessful. Thus, the bulky substituent did not affect the ability of the amide fragment to undergo photoinduced ligand exchange reactions with the formation of dicarbonyl six-membered chelates **46–56**.

In a CO atmosphere, chelates **46–56** reacted with carbon monoxide to give the starting tricarbonyl complexes. The kinetic studies demonstrated that the reaction proceeds according to the S_N1 mechanism, like the above-described reactions of thermally induced ligand exchange. Based on the obtained kinetic parameters (Table S2 in the ESI), it was impossible to draw an unambiguous conclusion about the influence of the substituent nature on the rate of a thermal reverse reaction. Apparently, the kinetic parameters were affected not only by the bulkiness of the substituent at the nitrogen atom but also by the possible solvation effects and the electronic structure of the molecule as a whole. In contrast to chelates **15–20** [37–38], the presence of a

methyl group at the first position of the Cp ring side chain had a multidirectional effect on the half-life for different substituents at the nitrogen atom (Table S2 in the ESI). However, the values of reaction rate constants in the case of all cascade chelates were slightly lower than in the case of monomeric analogs **15–20** [37–38]. Consequently, the introduction of a bulky substituent at the carbonyl group did not affect the possibility of occurrence of thermally induced ligand exchange and cascade chelates **46–56** were hemilabile complexes.

Most of the cascade compounds obtained by our research group were solid compounds. The exceptions were amides **38** and **44**, which can form quite a thin transparent layer between KBr plates. The study of the irradiation–reverse thermal reaction cycle based on **38** and **44** in the absence of solvent by IR spectroscopy showed that the photolysis without the removal of CO leads to the formation of chelates **49** and **55**, which completely convert to the starting tricarbonyl compounds under dark conditions (Fig. 6). Thus, amides can form hemilabile systems with a photochromic response both in solution and without a solvent, which makes the cascade complexes based on alkylcymantrenylamides promising models for further development of photosensitive materials.

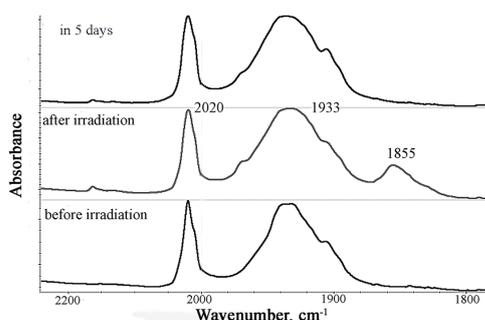
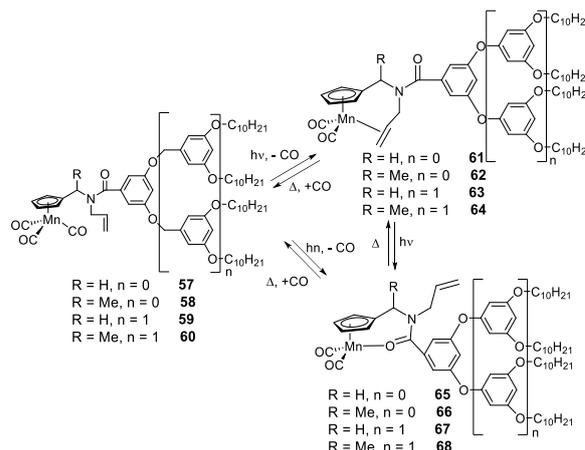


Figure 6. IR spectra of a thin layer of **38** between KBr plates and the product of its irradiation [41]. (Reprinted with permission from E. S. Kelbysheva *et al.*, *Russ. Chem. Bull.*, **2015**, *64*, 2646–2654. DOI: 10.1007/s11172-015-1203-0. Copyright (2015) Springer Nature)

The next step was aimed at obtaining the cascade compounds in which the cymantrenyl moiety would contain two donor groups, namely, amide and allyl and studying their photochemical behavior. For these purposes, tricarbonyl compounds **57–60** were synthesized [42].

Monitoring of the photolysis of tricarbonyl compounds **57–60** using IR and NMR spectroscopy in benzene and THF with a full spectrum lamp or monochromatic light (366 nm) showed that, in all cases, the formation of olefin (**61–64**) and amide (**65–68**) chelates is observed (Scheme 4). The type and parameters of the spectra of the new chelates were close to those of monomeric olefin (**27–30**) and amide (**31–34**) chelates [39]. The ratio of the olefin complexes to the amide derivatives was 2:1. The irradiation of tricarbonyl compounds **57–60** ($\lambda_{\text{max}} = 330$ nm) led to the appearance of an absorption maximum at 520 nm in the UV-vis spectra, which is characteristic of the amide complexes. As in the case of the bifunctional monomeric compounds and monofunctional cascade derivatives of cymantrene, a color of the solution changed from pale yellow to crimson.

The study of the dark processes showed that chelates **65–68** completely convert to compounds **61–64** both in the presence



Scheme 4. Photolysis of compounds **57–60** and thermal reactions of the corresponding dicarbonyl complexes.

and absence of CO, which is accompanied by the disappearance of the band at 520 nm and a transition of the solution color from crimson to yellow. The reverse thermal substitution of the chelating ligand for CO was observed only after 12–24 h for chelates **61–64** with the formation of the initial tricarbonyl complexes and proceeded according to the S_N1 mechanism. The kinetic parameters for the reactions of thermal isomerization and intermolecular thermally induced ligand exchange practically did not depend on the bulkiness of a substituent at the nitrogen atom; however, the introduction of a methyl group at the first position of the Cp ring side substituent significantly affected the reaction rate (Table S2 in the ESI).

Olefin complexes **60** and **61** were isolated, and the investigation of their photochemical behavior showed that the irradiation of dicarbonyl olefins leads to the formation of amide chelates **65** and **66** which were thermally isomerized to compounds **61** and **62**. A color of the solution upon irradiation of **61** and **62** ($\lambda_{\text{max}} = 330$ nm) became crimson due to the formation of complexes **65** and **66** ($\lambda_{\text{max}} = 520$ nm); under dark conditions, a color of the solution returned to the original one. The irradiation–thermal reaction cycle was repeated at least three times with no changes in the spectral parameters.

Compounds **57–60** and **65–66** were oils and their photochemical properties were studied in a capillary layer between KBr plates. It was shown that, upon irradiation in the absence of a solvent, the photochemical behavior of both tricarbonyl compounds and dicarbonyl complexes completely coincides with the course of photolysis in solution. The optical, spectral, thermodynamic, and kinetic parameters of the systems turned out to be similar. The use of a template upon photolysis enabled the production of an impression of this template after irradiation (Fig. 7). Consequently, the environment for photo- and thermally induced ligand exchange did not significantly affect the reaction mechanism and parameters, which makes these systems promising objects for the creation of photosensitive materials.

Photochemical behavior of the cymantrene derivatives bearing luminescent groups

The data considered above show that the thermodynamic and kinetic parameters of photochromic systems depend on the

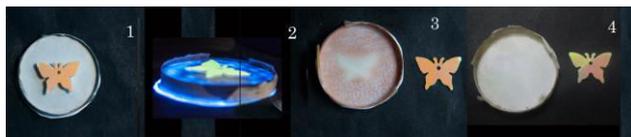


Figure 7. Photographs obtained during the irradiation of **58** in a capillary layer between quartz glasses using a butterfly-shaped template: before irradiation (1); upon exposure to Wood's lamp (2) (the radiation range from 300 nm to 400 nm); after the completion of the irradiation (3); in 2 h after the completion of the irradiation (4) (dark isomerization of **66** to **62**) [42]. (Reprinted with permission from E. S. Kelbysheva *et al.*, *Eur. J. Inorg. Chem.*, **2016**, 3767–3773. DOI: 10.1002/ejic.201600343. Copyright (2016) John Wiley & Sons Ltd)

availability of internal and external ligands. In this regard, derivatives **69–72** were obtained to study the possibility of tuning the parameters of photochromic systems using a structural factor (Fig. 8) [43]. In compounds **69–72**, the carbonyl group was a part of the quinazolinone cycle. In addition to the rigidly bound carbonyl group, quinazolinones exhibit pronounced fluorescence, which enabled the creation of systems with both photochromic properties and a fluorescence response.

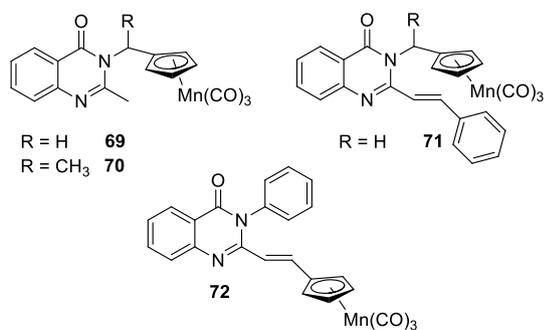
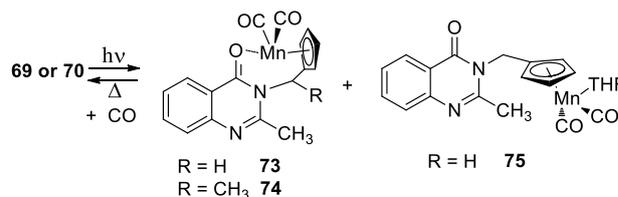


Figure 8. Quinazolinone derivatives of cymantrene.

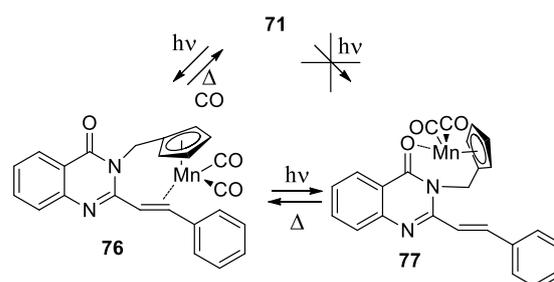
The IR and NMR spectroscopic studies showed that the photolysis of compounds **69** and **70** in the absence of external ligands in benzene leads to the formation of chelate complexes **73** and **74** with the Mn–O bond (Scheme 5). If the CO ligand was not removed from the reaction sphere, a reverse thermal reaction of the addition of carbon monoxide was observed (Table S2 in the ESI). The irradiation of **69** in a THF solution resulted in complex **75** in which the Mn atom was bound to the THF molecule, while upon photoinduced elimination of the CO ligand from **70**, only complex **74** was formed (Scheme 5). The data obtained were confirmed by the DFT calculations. The UV-vis spectra in benzene showed the appearance of two new bands at 450 and 570 nm. A change in the solution color from pale yellow to crimson was observed upon irradiation, as in the all previously described cases of the formation of chelates featuring a bond between the Mn and carbonyl group O atoms. The new band and crimson color disappeared under dark conditions. Thus, tri- and dicarbonyl complexes formed intermolecular photochromic systems, and the introduction of a bulky methyl group led to an increase in the stability of dicarbonyl complexes, which opened up the way for controlling the parameters of photochromic systems.

According to the IR, NMR, and UV-vis spectroscopic analysis, the photolysis of bifunctional derivative **71** afforded only olefin chelate **76** which slowly transformed into a tricarbonyl complex



Scheme 5. Photolysis of compounds **69–70** and thermal reactions of the corresponding dicarbonyl complexes.

bonyl complex under thermal conditions in the presence of CO (Scheme 6). Compound **76** was isolated and its structure was also proven by X-ray diffraction. It should be noted that the study of the fluorescence properties revealed close parameters of the spectra of tricarbonyl complex **71** and an organic analog. On passing to dicarbonyl chelate **76**, a considerable increase in the fluorescence intensity was observed. The investigation of the photolysis of chelate **76** showed that the olefin chelate isomerized upon irradiation with a monochromatic light ($\lambda_{\max} = 366$ nm) to chelate **77**, in which manganese is bound to the carbonyl group, with a change in the solution color from yellow to crimson. Under dark conditions, the solution color returned to its original yellow, and **77** turned into **76** with a half-life of 3 min (Scheme 6). Thus, **76** and **77** formed a photochromic pair, and the rate of dark isomerization was high.

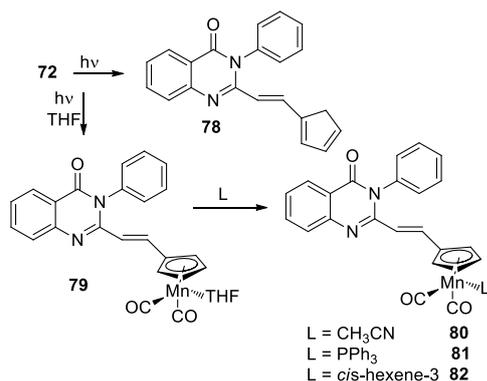


Scheme 6. Photolysis of compounds **71** and **76** and thermal reactions of the corresponding dicarbonyl complexes.

A study of the photolysis of **72** using the conventional techniques showed that the formation of dienes **78** was observed in the absence of external ligands (Scheme 7). The introduction of additional *n*- or π -donor molecules, such as THF, acetonitrile, and *cis*-hexene-3, into the reaction sphere led to the formation of dicarbonyl complexes with external ligands. The study of competitive ligand exchange for dicarbonyl complex with THF **79** showed that the THF molecule can be replaced for stronger ligands such as triphenylphosphine, *cis*-hexene-3 or phenylacetylene under dark conditions (Scheme 7). Therefore, **72** can be used to create chemosensors for detecting molecules with *n*- and π -donor groups.

Conclusions

The main application areas of the tri- and dicarbonyl derivatives of cymantrene bearing a carbonyl donor fragment capable of coordinating with the manganese atom were highlighted. This class of compounds can be used for the creation of photosensitive smart materials by producing the photochromic systems between the hemilabile di- and tricarbonyl complexes. It was also shown that the compounds



Scheme 7. Photolysis of compound **72**.

with a carbonyl group can serve as IR labels and chemosensors in biological systems.

The photochemical behavior of the tri- and dicarbonyl complexes of cymantrene with ketone, amide, and carbamate groups of both monomeric and cascade structures indicated that the carbonyl groups are efficient ligands for the preparation of hemilabile complexes in which the Mn atom is bound to the oxygen one. The carbonyl ligand can be easily replaced for an internal ligand such as an olefin group or an external ligand, e. g., CO or PPh₃.

The introduction of the cymantrenyl fragments containing amide groups into cascade molecules does not practically change the properties of hemilabile chelates, which opens up a promising way for creating materials with a photochromic response in the absence of a solvent.

The study of the photochromic properties of the derivatives bearing a carbonyl group in the quinazolinone ring also revealed the possibility of creating photochromic systems with changing fluorescence properties. The thermodynamic and kinetic stability of the chelates with the Mn–O bond based on the quinazolinone derivatives is lower than that for the amides and carbamates.

The introduction of two donor groups into the same side chain of a cymantrene derivative can be used for the development of photosensitive and photochromic materials with readily modifiable thermodynamic properties.

Currently, the preliminary studies have been carried out that demonstrated a fundamental possibility of using the cymantrene derivatives to create photosensitive materials and biological markers. The next stages in the development of this field are the search for methods for obtaining the macromolecular or composite materials with different numbers of cymantrenyl moieties and investigation of their photochemical and mechanical behavior. This will enable the creation of new sensors, molecular devices, and biological labels.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

Corresponding author

* E-mail: popova-ln@mail.ru. Tel: +7(499)135-3535 (L. N. Telegina)

Electronic supplementary information

Electronic supplementary information (ESI) available online: tables that summarize the properties of the compounds under consideration. For ESI, see DOI: 10.32931/102129r.

References

1. K. Li, Y. Xiang, X. Wang, J. Li, R. Hu, A. Tong, B. Z. Tang, *J. Am. Chem. Soc.*, **2014**, *136*, 1643–1649. DOI: 10.1021/ja411689w
2. A. M. Rice, C. R. Martin, V. A. Galitskiy, A. A. Berseneva, G. A. Leith, N. B. Shustova, *Chem. Rev.*, **2020**, *120*, 8790–8813. DOI: 10.1021/acs.chemrev.9b00350
3. Y. Hai, H. Ye, Z. Li, H. Zou, H. Lu, L. You, *J. Am. Chem. Soc.*, **2021**, *143*, 20368–20376. DOI: 10.1021/jacs.1c09958
4. J. Li, R. Wang, Y. Sun, P. Xiao, S. Yang, X. Wang, Q. Fan, W. Wu, X. Jiang, *ACS Appl. Mater. Interfaces*, **2021**, *13*, 54830–54839. DOI: 10.1021/acsami.1c17813
5. L. Zhao, M. Gong, J. Yang, J. Gu, *Langmuir*, **2021**, *37*, 13952–13960. DOI: 10.1021/acs.langmuir.1c02579
6. M. Qin, Y. Huang, F. Li, Y. Song, *J. Mater. Chem. C*, **2015**, *3*, 9265–9275. DOI: 10.1039/C5TC01939G
7. D. Dattler, G. Fuks, J. Heiser, E. Moulin, A. Perrot, X. Yao, N. Giuseppone, *Chem. Rev.*, **2020**, *120*, 310–433. DOI: 10.1021/acs.chemrev.9b00288
8. W. Fang, E. Sairanen, S. Vuori, M. Rissanen, I. Norrbo, M. Lastusaari, H. Sixta, *ACS Sustainable Chem. Eng.*, **2021**, *9*, 16338–16346. DOI: 10.1021/acssuschemeng.1c05938
9. M. Kondo, K. Nakamura, C. G. Krishnan, S. Takizawa, T. Abe, H. Sasai, *ACS Catal.*, **2021**, *11*, 1863–1867. DOI: 10.1021/acscatal.1c00057
10. K. Obara, Y. Kageyama, S. Takeda, *Small*, **2022**, *18*, 2105302. DOI: 10.1002/smll.202105302
11. Y. Liang, Y. Yang, C. Zou, K. Xu, X. Luo, T. Luo, J. Li, Q. Yang, P. Shi, C. Yuan, *J. Alloys Compd.*, **2019**, *783*, 848–854. DOI: 10.1016/j.jallcom.2018.12.384
12. E. C. Gentry, R. R. Knowles, *Acc. Chem. Res.*, **2016**, *49*, 1546–1556. DOI: 10.1021/acs.accounts.6b00272
13. C. Falenczyk, M. Schiedel, B. Karaman, T. Rumpf, N. Kuzmanovic, M. Grötli, W. Sippl, M. Jung, B. König, *Chem. Sci.*, **2014**, *5*, 4794–4799. DOI: 10.1039/C4SC01346H
14. E. Orgiu, P. Samorì, *Adv. Mater.*, **2014**, *26*, 1827–1845. DOI: 10.1002/adma.201304695
15. A. Sarmah, A. Wasfi, P. Hobza, N. Tit, *Chem. Mater.*, **2021**, *33*, 8786–8799. DOI: 10.1021/acs.chemmater.1c02883
16. K. Kajiwara, S. Pradhan, T. Haraguchi, C. Sinha, R. Parida, S. Giri, G. Roymahaptra, T. Akitsu, *Symmetry*, **2020**, *12*, 797. DOI: 10.3390/sym12050797
17. R. C. Amaral, N. Y. Murakami Iha, *Dalton Trans.*, **2018**, *47*, 13081–13087. DOI: 10.1039/C8DT02721H
18. Z. Huo, V. Badets, H. Ibrahim, M. Goldmann, H. Xu, T. Yi, C. Boudon, L. Ruhlmann, *Eur. J. Org. Chem.*, **2021**, 6636–6645. DOI: 10.1002/ejoc.202100918
19. J. Liu, A. K.-W. Chan, M. Ng, E. Y.-H. Hong, N. M.-W. Wu, L. Wu, V. W.-W. Yam, *Organometallics*, **2019**, *38*, 3542–3552. DOI: 10.1021/acs.organomet.9b00359
20. H.-B. Cheng, G.-F. Hu, Z.-H. Zhang, L. Gao, X. Gao, H.-C. Wu, *Inorg. Chem.*, **2016**, *55*, 7962–7968. DOI: 10.1021/acs.inorgchem.6b01009
21. R. T. Magar, D. J. Breen, B. R. Schrage, C. J. Ziegler, J. J. Rack, *Inorg. Chem.*, **2021**, *60*, 16120–16127. DOI: 10.1021/acs.inorgchem.1c01558
22. C. Chen, J. C. Peters, G. C. Fu, *Nature*, **2021**, *596*, 250–256. DOI: 10.1038/s41586-021-03730-w
23. D. Unjaroen, J. B. Kasper, W. R. Browne, *Dalton Trans.*, **2014**, *43*, 16974–16976. DOI: 10.1039/C4DT02430C

24. K. Wu, M. A. Conger, R. Waterman, M. Liptak, W. E. Geiger, *Polyhedron*, **2019**, *157*, 442–448. DOI: 10.1016/j.poly.2018.10.039
25. I. Kulai, A. Karpus, L. Soroka, D. A. Valyaev, V. Bourdon, E. Manoury, R. Poli, M. Destarac, S. Mazières, *Polym. Chem.*, **2019**, *10*, 267–277. DOI: 10.1039/C8PY01279B
26. D. Heinrich, W. Schmolke, D. Lentz, *J. Fluorine Chem.*, **2016**, *192*, 105–112. DOI: 10.1016/j.jfluchem.2016.10.015
27. S. Mishra, V. Tirkey, A. Ghosh, H. R. Dash, S. Das, M. Shukla, S. Saha, S. M. Mobin, S. Chatterjee, *J. Mol. Struct.*, **2015**, *1085*, 162–172. DOI: 10.1016/j.molstruc.2014.12.070
28. T. T. To, C. B. Duke III, C. S. Junker, C. M. O'Brien, C. R. Ross II, C. E. Barnes, C. E. Webster, T. J. Burkey, *Organometallics*, **2008**, *27*, 289–296. DOI: 10.1021/om701101h
29. A. A. Bengali, W. Y. Fan, K. T. Abdulrazak, *Organometallics*, **2009**, *28*, 3123–3128. DOI: 10.1021/om801185t
30. L. N. Telegina, M. G. Ezernitskaya, I. A. Godovikov, K. K. Babievskii, B. V. Lokshin, T. V. Strelkova, Y. A. Borisov, N. M. Loim, *Eur. J. Inorg. Chem.*, **2009**, 3636–3643. DOI: 10.1002/ejic.200900458
31. E. J. Heilweil, J. O. Johnson, K. L. Mosley, P. P. Lubet, C. E. Webster, T. J. Burkey, *Organometallics*, **2011**, *30*, 5611–5619. DOI: 10.1021/om2003656
32. C. B. Duke III, R. G. Letterman, J. O. Johnson, J. W. Barr, S. Hu, C. R. Ross II, C. E. Webster, T. J. Burkey, *Organometallics*, **2014**, *33*, 485–497. DOI: 10.1021/om400928k
33. H. W. P. N'Dongo, I. Neundorf, K. Merz, U. Schatzschneider, *J. Inorg. Biochem.*, **2008**, *102*, 2114–2119. DOI: 10.1016/j.jinorgbio.2008.07.019
34. U. Schatzschneider, *Eur. J. Inorg. Chem.*, **2010**, 1451–1467. DOI: 10.1002/ejic.201000003
35. W. Hu, K. Splith, I. Neundorf, K. Merz, U. Schatzschneider, *J. Biol. Inorg. Chem.*, **2012**, *17*, 175–185. DOI: 10.1007/s00775-011-0840-5
36. S. Dewangan, T. Barik, S. Mishra, S. Mawatwal, S. Kumari, S. Giri, S. Das, R. Dhiman, C. Wölper, S. Chatterjee, *Appl. Organomet. Chem.*, **2018**, *32*, e4612. DOI: 10.1002/aoc.4612
37. E. S. Kelbysheva, L. N. Telegina, I. A. Godovikov, T. V. Strelkova, M. G. Ezernitskaya, B. V. Lokshin, N. M. Loim, *Russ. Chem. Bull.*, **2013**, *62*, 2083–2085. DOI: 10.1007/s11172-013-0302-z
38. E. S. Kelbysheva, L. N. Telegina, I. A. Godovikov, T. V. Strelkova, Yu. A. Borisov, M. G. Ezernitskaya, B. V. Lokshin, N. M. Loim, *Russ. Chem. Bull.*, **2015**, *64*, 914–922. DOI: 10.1007/s11172-015-0955-x
39. E. S. Kelbysheva, M. G. Ezernitskaya, T. V. Strelkova, Y. A. Borisov, A. F. Smol'yakov, Z. A. Starikova, F. M. Dolgushin, A. N. Rodionov, B. V. Lokshin, N. M. Loim, *Organometallics*, **2011**, *30*, 4342–4353. DOI: 10.1021/om200407c
40. G. R. Newkome, G. R. Baker, S. Arai, M. J. Saunders, P. S. Russo, K. J. Theriot, C. N. Moorefield, L. E. Rogers, J. E. Miller, T. R. Lieux, M. E. Murray, B. Phillips, L. Pascal, *J. Am. Chem. Soc.*, **1990**, *112*, 8458–8465. DOI: 10.1021/ja00179a034
41. E. S. Kelbysheva, L. N. Telegina, O. V. Abramova, T. V. Strelkova, N. S. Ikonnikov, A. N. Rodionov, M. G. Ezernitskaya, B. V. Lokshin, N. M. Loim, *Russ. Chem. Bull.*, **2015**, *64*, 2646–2654. DOI: 10.1007/s11172-015-1203-0
42. E. S. Kelbysheva, L. N. Telegina, A. N. Rodionov, T. V. Strelkova, M. G. Ezernitskaya, B. V. Lokshin, N. M. Loim, *Eur. J. Inorg. Chem.*, **2016**, 3767–3773. DOI: 10.1002/ejic.201600343
43. E. S. Kelbysheva, L. N. Telegina, T. V. Strelkova, M. G. Ezernitskaya, E. V. Nosova, Y. A. Borisov, B. V. Lokshin, N. M. Loim, *Eur. J. Inorg. Chem.*, **2018**, 1945–1952. DOI: 10.1002/ejic.201800244

This article is licensed under a Creative Commons Attribution-NonCommercial 4.0 International Licence.

