CYMANTRENE DERIVATIVES CONTAINING IMINO GROUPS:
SPECTRAL AND PHOTOCHEMICAL PROPERTIES

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Abstract

The investigation of a photochemical behavior of imino derivatives of cymantrene reveals a possibility of formation of four-membered hemilabile chelate complexes. In the presence of external ligands, such as CO, MeCN, or PPh₃, the ligand exchange between imino groups at the Mn atom in dicarbonyl chelates and the external ligand is observed. It is shown that MeCN or PPh₃ can be substituted for CO under dark conditions, resulting in intermolecular photochromic systems between tricarbonyl complexes and dicarbonyl derivatives with MeCN and PPh₃ ligand, respectively.

Key words: cymantrene, imines, ligand exchange, dicarbonyl complexes, photolysis.

Introduction

The synthesis of new organometallic compounds that would possess unique properties and reactivity is a major task for the further development of chemistry. One of the fundamental methods for obtaining metal complexes is the photochemical substitution of ligands in the coordination sphere of transition metal atoms, which results in modification of steric, geometric, and electronic characteristics of the molecules and, thus, changes the compound properties. It was shown that the loss of CO upon photolysis of cymantrenylalkylisothioureas (cymantrene) derivatives gives rise to a 16e manganese intermediate which is stabilized owing to the formation of a new coordination bond with the donor group [1–3]. This is often accompanied by color changes, which can be considered as a basis for creation of intra- and intermolecular photochromic systems [2, 3]. Earlier we have shown that the nitrogen atom can be coordinated by the manganese atom and the stability of the resulting complexes depends on the nature of the N-donor functional groups. Thus, the triazole complexes featuring Mn–N bonds appeared to be stable and were isolated in the individual forms [3c], whereas the chelate derivatives based on isothioureas, where the metal center is bound with the nitrogen atom, convert to the complexes with Mn–S bonds during dark reactions, resulting in an intramolecular photochromic pair (Scheme 1) [2f]. Consequently, cymantrene derivatives containing nitrogen donors in a side substituent are promising candidates for the creation of hemilabile complexes which stability would strongly depend on the nature of the functional groups.

Transition metal complexes based on Schiff bases exhibit a range of interesting properties that encourage their extensive use in different fields of chemistry. Imines can serve as precursors for biologically active compounds [4] and ligands for various metals [5]. For example, chiral transition metal complexes of Schiff bases efficiently catalyze asymmetric cyclopropanation and epoxidation of alkenes; they are used in allylation and aromatic C–H bond activation (orthometalation) through intramolecular π²-binding of arenes [6]. Multidentate imine ligands containing nitrogen and oxygen atoms are used for the synthesis of transition metal complexes that play an important role in biological systems [7]. A low-energy barrier of the metal-to-ligand charge transfer makes these molecules attractive for application in electron transfer processes and as reagents for fluorescence spectroscopy and luminescent probes [8].

Results and discussion

In order to obtain new photosensitive hemilabile complexes based on cymantrene, in this work we synthesized N(1-cymantrenylethylidene)aniline 1 and N-(phenyl-cymantrenylethylidene)aniline 2 and studied their spectral, photochemical, and electrochemical properties.
Complexes 1 and 2 were obtained upon refluxing the corresponding ketones with aniline in benzene using the Dean–Stark distilling trap (Scheme 2).

Scheme 2. Synthesis of imines 1 and 2.

The photochemical behavior and changes in the spectral properties of complexes 1 and 2 upon irradiation were studied using IR, NMR, and UV-vis spectroscopies; the resulting data were confirmed by DFT calculations.

The IR monitoring of the photolysis of compounds 1 and 2 with monochromatic light of a Hg lamp with $\lambda = 365$ nm under an inert atmosphere in benzene in a closed system (see Experimental) revealed the disappearance of vCO stretching bands of the starting tricarbonyl complexes and the appearance of two bands at 1942 and 1869 cm$^{-1}$ corresponding to the MCO moiety (Table 1). The positions of the new bands correspond to the CO ligand frequencies in the IR spectra of dicarbonyl complexes containing the manganese–nitrogen bonds [2f, 3c,d].

To confirm the structure of the dicarbonyl complex, DFT calculations of tricarbonyl complex 1 and a range of possible dicarbonyl derivatives in benzene were performed using a DFT-B3LYP/6-311+G* basis (Fig. 1) (for the detailed description of DFT calculations see Electronic Supplementary Information (ESI)). These calculations showed that the most stable complex in benzene is chelate dicarbonyl derivative 3. This is evidenced by the data from Table 2, namely, the enthalpy and Gibbs energy for model reaction (1), which are negative. The equili-

Table 1. Calculated IR frequencies of compounds 1, 3, and 5, the experimental IR and UV-vis spectral data for complexes 1–8, and the kinetic data for the reverse dark reaction

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Measured ν(CO), cm$^{-1}$</th>
<th>Calculated ν(CO), cm$^{-1}$</th>
<th>$\Delta_{max}$, nm (ε)</th>
<th>$10^5 k_{obs}$ (s$^{-1}$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2023, 1940$^b$</td>
<td>2079, 2006, 1999$^b$</td>
<td>328 (3398)$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2024, 1939$^b$</td>
<td>2062, 1972, 1970$^b$</td>
<td>323 (2904)$^b$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2024, 1942$^b$</td>
<td>–</td>
<td>339 (3683)$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2024, 1941$^b$</td>
<td>–</td>
<td>333 (4627)$^b$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1942, 1868$^b$</td>
<td>1998, 1933$^b$</td>
<td>349 (8275)$^b$</td>
<td>1.16 (0.05)</td>
</tr>
<tr>
<td></td>
<td>1983, 1918$^b$</td>
<td>–</td>
<td>377 (12569)$^b$</td>
<td>0.89 (0.03)</td>
</tr>
<tr>
<td>4</td>
<td>1942, 1869$^b$</td>
<td>–</td>
<td>346 (5302)$^b$</td>
<td>0.77 (0.03)</td>
</tr>
<tr>
<td></td>
<td>1939, 1860$^b$</td>
<td>–</td>
<td>364 (10867)$^b$</td>
<td>0.75 (0.02)</td>
</tr>
<tr>
<td>5</td>
<td>1941, 1862$^a$</td>
<td>–</td>
<td>400 (1643)$^b$</td>
<td>0.35 (0.01)</td>
</tr>
<tr>
<td>6</td>
<td>1941, 1877$^a$</td>
<td>–</td>
<td>450 (1279)$^b$</td>
<td>0.25 (0.02)</td>
</tr>
<tr>
<td>7</td>
<td>1942, 1875$^a$</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ $k_{obs}$ for the reaction of dicarbonyl complexes 3–8 with CO in the dark at 24 °C; $^b$ benzene; $^c$ acetonitrile.

Figure 1. Optimized structures of compounds 1, 3, 5, and dimer D.

Table 2. Calculated thermodynamic characteristics of the model reactions (298.15 K, 1 atm)

<table>
<thead>
<tr>
<th>Entry</th>
<th>$\Delta H^\circ$, kcal/mol</th>
<th>$\Delta G^\circ$, kcal/mol</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1*$$\rightarrow$3</td>
<td>–7.97</td>
<td>–7.58</td>
</tr>
<tr>
<td>2</td>
<td>$1* +$PhH $\leftrightarrow$ 1*Bz</td>
<td>–4.76</td>
<td>+5.63</td>
</tr>
<tr>
<td>3</td>
<td>$1* + 1*$$\rightarrow$D</td>
<td>–15.48</td>
<td>+1.28</td>
</tr>
<tr>
<td>4</td>
<td>$1*$$\rightarrow$3</td>
<td>–6.03</td>
<td>–6.10</td>
</tr>
<tr>
<td>5</td>
<td>$1* +$MeCN$\rightarrow$5</td>
<td>–28.89</td>
<td>–18.58</td>
</tr>
<tr>
<td>6</td>
<td>$1* + 1*$$\rightarrow$D</td>
<td>–12.87</td>
<td>+3.49</td>
</tr>
</tbody>
</table>
to the tricarbonyl complex was 1:1 and 2:1, respectively) for 1 min gave rise to ν(CO) at 1863 cm⁻¹, which upon further irradiation shifts to 1860 cm⁻¹. The band split into two components, and it was demonstrated that the peak intensity of the band at 1870 cm⁻¹ reduces during irradiation, while the intensity of the band at 1860 cm⁻¹ increases. The photolysis of 1 and 2 in the presence of MeCN is likely to proceed through the formation of dicarbonyl complexes with the Mn-N bond with the imino nitrogen atom, in which the imino group at the manganese atom is substituted for the acetonitrile ligand.

The DFT calculations showed that the enthalpy and Gibbs energy of formation of complex 3 from 1 in MeCN are negative, and the equilibrium constant (K_e) is equal to 3.6 × 10⁴, which indicates quite a high concentration of chelate 3 during irradiation of 1 (Table 2). Model reaction (5) features very high negative values of the enthalpy and Gibbs energy and also high values of the equilibrium constant (Table 2); therefore, acetonitrile complex 5 appears to be more stable than chelate 3.

Hence, the results of the IR spectroscopic analysis and DFT calculations show that the photolysis of 1 and 2 in benzene leads to the formation of four-membered dicarbonyl chelates 3 and 4 containing the Mn-N bond with the imino groups, whereas the main reaction products upon irradiation in the presence of n-donor acetonitrile ligand are acetonitrile dicarbonyl complexes 5 and 6 (Scheme 3).

The irradiation of the light-yellow benzene and acetonitrile solutions of imines 1 and 2 with a mercury lamp under an argon atmosphere afforded a change in the color to bright orange. The UV-vis spectrum revealed a first low-frequency band in the range of 350–370 nm (Fig. 2, Table 1). Hence, acetonitrile complexes 5 and 6 and chelate complexes 3 and 4 have close maxima.

The times of half decrease concentration of starting imines 1 and 2 upon photolysis of 4.10⁻³ M benzene solutions appear to be close, composing about 3 min. A change in the concentration of the initial tricarbonyl complexes was evaluated by IR spectroscopy. According to the IR and UV-vis spectral data, the quantum yield of the photoreaction of 1 in benzene is 0.89.

The dicarbonyl chelates resulting from complexes 1 and 2 in benzene under an argon atmosphere in the absence of CO are highly unstable compounds. The removal of CO from the reaction sphere leads to the rapid decomposition of the dicarbonyl complexes and formation of 1- and 2-substituted cyclopentadienes and polymer products. Therefore, we failed to register the NMR spectra of the chelate complexes in the absence of other ligands. Monitoring the irradiation of deuterobenzene solutions of 1 and 2 in the presence of 2 equivalents of MeCN, we detected chelate complexes 3 and 4. Thus, the positions of the α-proton signals of the Cp ring appeared to be upfield shifted by 0.55 ppm, whereas the positions of the β-proton signals underwent a downfield shift by 0.35 ppm compared to the signals of the initial complexes, which is in good agreement with the previous results obtained for the chelate complexes where the Mn atom is bound with the nitrogen donor [2f, 3c,d]. However, the main reaction products were acetonitrile complexes 5 and 6, for which the signals of the α-protons were observed at 5.06 ppm and the signals of the β-protons were registered at 4.13 ppm. Therefore, the signals of the Cp ring protons appeared to be upfield shifted compared to those of the tricarbonyl derivatives, which is typical for the complexes with solvents [3]. The irradiation of compounds 1 and 2 in the presence of acetonitrile is likely to afford first chelates 3 and 4, which then react with a molecule of acetonitrile to yield complexes 5 and 6. This is in good agreement with the data of the IR spectra and DFT calculations.

In the presence of CO, the reverse thermal reaction takes place during which chelates 3 and 4 gradually convert to starting tricarbonyl complexes 1 and 2. The IR monitoring of the dark reaction showed that the half-life times compose 100–130 min at 24 °C (Table 1). The triple recycling "irradiation–dark reaction" does not lead to essential changes in the IR spectra of either the initial tricarbonyl complexes or the chelate derivatives. The kinetic studies of the reactions of chelates 3 and 4 with CO demonstrated that the rate of the chelate conversion is described by the first-order equation with the values of R no less than 0.99. The resulting kinetic data indicate that the ligand substitution in chelates containing manganese–imino nitrogen bonds in the dark proceeds by the Sx1 mechanism [2d, 3e]. A rate-determining step of the thermal reaction is the opening of a chelate ring at the manganese atom, which results in a 16e dicarbonyl complex. Consequently, in the presence of carbon monoxide, the tricarbonyl complexes and the corresponding dicarbonyl chelates form intermolecular reversible photochromic systems.

In the presence of CO, dicarbonyl acetonitrile complexes 5 and 6 also convert to the corresponding tricarbonyl derivatives. The kinetic studies of the reverse thermal reaction showed that it is described, as well as in the case of the chelate complexes, by
The first-order equation ($R$ is no less than 0.99), i.e., it proceeds by the Sx1 mechanism with the half-life time of 150 min at 24 °C (Table 1). Hence, complexes 1 and 2 form photochromic systems with acetonitrile complexes 5 and 6.

The investigation of photolysis of complexes 1 and 2 in benzene in the presence of another external ligand (triphenylphosphine, 2 eq.) by IR, UV-vis, and NMR spectroscopies showed that first both chelate and triphenylphosphine complexes 7 and 8 are formed. Further irradiation affords mainly compounds 7 and 8. Upon photolysis for 2 min, the ratio of complexes 3 and 7 composes 1:3, while in 6 min it composes already 1:8. The photolysis is likely to proceed, as well as in the case of the acetonitrile external ligand, through the initial formation of chelate complexes in which the manganese atom reacts with the external ligand giving rise to complexes 7 and 8. In the case when CO remains in the reaction sphere, the IR monitoring of the dark reaction showed that the intensity of MCO bands of the triphenylphosphine complexes reduces and the intensity of the band at 2024 cm$^{-1}$ associated with the initial tricarbonyl compounds increases (Fig. 3, Table 1). Therefore, CO displaces the triphenylphosphine ligand with a change in a solution color from reddish-orange to pale yellow, forming an intermolecular photochromic system.

Upon removal of CO after irradiation for 2 min, chelate complexes 3 and 4 convert to the dicarboxyl triphenylphosphine derivatives (Fig. 4) featuring the half-life times of 163 and 205 min at 24 °C, respectively. The substitution of the imino group by PPh$_3$ in the dark is described by the first-order reaction, as was the case with carbon monoxide ($R$ is no less than 0.99). In acetonitrile, the formation of the triphenylphosphine complex was detected upon application of the large excess (10 eq. and above) of the external ligand. At the lower concentration of PPh$_3$, only the formation of acetonitrile complexes 5 and 6 was evidenced by the spectra.

Complexes 5-8 were isolated and characterized by spectroscopic methods. Unfortunately, we failed to isolate complexes 5 and 6 in analytically pure forms. The IR, NMR and UV-vis monitoring of the thermal reactions of complexes 5 and 6 in benzene with two equivalents of PPh$_3$ revealed the slow conversion of dicarboxyl acetonitrile complexes 5 and 6 to triphenylphosphine derivatives 7 and 8. Hence, dicarboxyl acetonitrile complexes 5 and 6 can serve as a basis for the creation of chemosensors.

The investigation of cyclic voltammograms of imines 1 and 2 showed that these compounds have two anodic peaks at 1154 and 1623 mV (1) (Fig. 5) and 944 and 1747 mV (2). The irradiation with a monochromatic light with $\lambda = 365$ nm gives rise to acetonitrile complexes 5 and 6. The cyclic voltammograms of compound 5 evidence the irreversible oxidation at 503, 912, 1494, and 1692 mV (Fig. 5). The first two peaks are likely to be associated with the following abstraction of two electrons from the manganese atom bound with the acetonitrile ligand. In the case of complex 6, there are observed three anodic peaks at 803, 1141, and 1342 mV. In all cases, the oxidation is a single-electron irreversible process.

**Experiment and calculations**

**General remarks**

The $^1$H and $^{31}$P NMR spectra were registered on a Bruker Avance 400 spectrometer at 400.13 and 161.98 MHz, respectively, using a residual solvent signal as an internal standard; the values of $\delta$ were calculated relative to Me$_2$Si (benzene 7.26 ppm, acetone 2.05 ppm). The IR spectra were recorded on a Nicolet Magna 750-FTIR spectrometer with the resolution of 2 cm$^{-1}$ in CaF$_2$ cells. The kinetic studies were performed on a Bruker Tensor 37 spectrometer at 24 °C. The EI mass spectra were obtained with Kratos MS 890 and Finnigan POLARISQ instruments at the ionizing electron energy of 70 eV.

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eV. The UV-vis spectra were registered on a Cary 300 spectrophotometer. The photochemical reactions were carried out using a Hereaus TQ 150 Hg immersion lamp equipped with an S49 glassy cooling jacket. The monochromatic light with a wavelength of 365 nm was derived by passing the light of the mercury lamp through a UFS-6 + BS-7 filter. The reaction course and purity of the products were monitored by analytical TLC on Silufol UV-245 (Kavalier) plates. The column chromatography was carried out on silica gel 60 (Merck). N(1-Cymantrenylethylidene)benzeneamine I was obtained according to the previously published procedure [9].

Syntheses

N-(1-Cymantrenylethylidene)aniline (1). 1H NMR (CDCl3): δ 1.43 (s, 3H, CH3), 3.90 (m, 2H, Cpg), 4.84 (m, 2H, Cpg), 6.76 (d, J = 7.4 Hz, 2H, Ph), 6.92 (t, J = 7.4 Hz, 1H, Ph), 7.14 (t, J = 7.9 Hz, 2H, Ph) ppm. IR (benzene, νcm⁻¹): 2133, 1940 (MCO). IR (acetonitrile), νcm⁻¹: 2024, 1939 (MCO). UV-vis (benzene, λ [nm] : ε [L/mol·cm]⁻¹): 328: 3398. UV-vis (acetonitrile, λ [nm] : ε [L/mol·cm]⁻¹): 323 : 2904. MS, m/z (Irel. %): 237 [M–3CO]⁺ (100).

N-(Phenylemantrenylmethylene)aniline (2). A solution of cymantrenylethylphenylketone (5.04 g, 16.4 mmol) and aniline (1.60 g, 16.4 mmol) in toluene (100 mL) was refluxed using the Dean–Stark distilling trap for 18 h in the presence of a catalytic amount of p-toluenesulfonic acid. The solvent was removed under vacuum; the resulting solid residue was crystallized from hexane to give 1.50 g of compound 2. Yield: 25%. Mp: 133–134 °C. 1H NMR (CDCl3): δ 5.16 (m, 2H, Cph), 5.41 (m, 2H, Cpg), 6.72 (d, J = 7.3 Hz, 2H, Ph), 6.93 (t, J = 7.4 Hz, 1H, Ph), 7.16 (t, J = 7.4 Hz, 2H, Ph), 7.29 (m, 2H, Ph), 7.36 (m, 3H, Ph) ppm. 1H NMR (CDCl3): δ 3.90 (m, 2H, Cpg), 4.89 (m, 2H, Cpg), 6.71 (t, J = 7.9 Hz, 1H), 6.80 (d, J = 7.1 Hz, 2H, Ph), 6.84 (m, 3H, Ph), 6.95 (m, 4H, Ph) ppm. IR (benzene), νcm⁻¹: 2024, 1942 (MCO). IR (acetonitrile), νcm⁻¹: 2024, 1941 (MCO). UV-vis (benzene, λ [nm] : ε [L/mol·cm]⁻¹): 339 : 3683. UV-vis (acetonitrile, λ [nm] : ε [L/mol·cm]⁻¹): 333 : 4627. MS, m/z (Irel. %): 299 [M–3CO]⁺ (100). Anal. Calcd for C19H17NO2Mn: C, 65.81; H, 3.68; N, 3.66; Mn, 14.33. Found: C, 66.07; H, 3.54; N, 4.37; Mn, 14.20%.

General procedure for the spectroscopic studies of the photochemical reactions of the tricarbonyl compounds and their reactions in the dark. Solutions of the tricarbonyl compounds in the required solvent (benzene or acetonitrile, concentrations ranging within 2–4·10⁻³ M) were placed under an argon atmosphere in the IR or UV-vis cells and irradiated with the mercury lamp (before irradiation, the lamp was set to the required mode for 2 min) featuring the wavelength of 365 nm at room temperature; the spectra were registered each 1–2 min. The irradiation of the samples was carried out until complete conversion of the tricarbonyl complexes or 50–70% isomerization of the dicarbonyl chelates. The total irradiation time for all the samples ranged within 6–10 min. To obtain the samples for NMR monitoring, the solutions of the compounds with the concentrations of 10–15·10⁻³ M were filtered into NMR tubes filled with argon and irradiated with the mercury lamp at 8–10 °C for 4 min to 25–30% conversion. The distance between the lamp and the sample was 5 cm in all cases. The NMR spectra were registered in 5 mm NMR tubes. The monitoring of all reactions in the dark was carried out analogously for 72 h. The irradiation–dark reaction cycle for 2·10⁻³ M benzene solutions of the tricarbonyl complexes were repeated at least 2 times in the IR cells.

(qN-(1-η⁵-cyclopentadienylethylidene)aniline)(dicarbonyl)manganese (3). 1H NMR (CDCl3): δ 1.69 (s, 3H, CH3), 4.29 (m, 1H, Cpg), 4.31 (m, 1H, Cpg), 4.62 (m, 1H, Cpg), 4.65 (m, 1H, Cpg), 6.39 (m, 2H, Ph), 6.47 (m, 1H, Ph), 6.77 (m, 2H, Ph) ppm. IR (benzene), νcm⁻¹: 1942, 1868 (MCO). UV-vis (benzene, λ [nm] : ε [L/mol·cm]⁻¹): 349 : 8275.

(qN-(phenyl-η⁵-cyclopentadienylmethylene)aniline)(dicarbonyl)manganese (4). 1H NMR (CDCl3): δ 4.11 (m, 1H, Cpg), 4.15 (m, 1H, Cpg), 4.64 (m, 1H, Cpg), 4.67 (m, 1H, Cpg), 6.43 (m, 1H, Cpg), 6.58 (m, 2H, Ph), 6.72–7.03 (m, 7H, Ph) ppm. IR (benzene), νcm⁻¹: 1942, 1869 (MCO). UV-vis (benzene, λ [nm] : ε [L/mol·cm]⁻¹): 377 : 12569.

General procedure for the synthesis of acetonitrile complexes 5 and 6. A solution of the corresponding tricarbonyl complex (0.25 mmol) in acetonitrile (30 mL) in a glassy photoreactor with external water cooling and internal glassy cooling jacket for an immersion Hg lamp was thermostated to 7 °C under stirring in an argon atmosphere and irradiated with the light of the immersion Hg lamp. The irradiation was carried out at 7–9 °C for 30 min and, then, the reaction mixture was left under an argon atmosphere for 1 h. The solution was filtered and evaporated under vacuum.

N-(1-η⁵-Cyclopentadienylethylidene)aniline(acetonitrile dicarbonyl)manganese (5). Yield: 0.039 g (51%). 1H NMR (CDCl3): δ 0.82 (s, 3H, CH3CN), 1.83 (s, 3H, CH3), 4.15 (m, 2H, Cpg), 5.07 (m, 2H, Cpg), 6.75 (d, J = 7.3 Hz, 2H, Ph), 6.94 (t, J = 7.3 Hz, 1H, Ph), 7.16 (m, 2H, Ph) ppm. IR (acetonitrile), νcm⁻¹: 1939, 1869 (MCO). UV-vis (acetonitrile, λ [nm] : ε [L/mol·cm]⁻¹): 346 : 5302.

N-(Phenyl-η⁵-cyclopentadienylmethylene)aniline(acetonitrile dicarbonyl)manganese (6). Yield: 0.050 g (54%). 1H NMR (CDCl3): δ 0.98 (s, 3H, CH3CN), 4.06 (m, 2H, Cpg), 4.98 (m, 2H, Cpg), 6.62(m, 1H, Ph), 6.78 (m, 3H, Cpg), 6.97 (m, 2H, Ph), 7.26 (m, 2H, Ph), 7.36 (m, 2H, Ph) ppm. IR (acetonitrile), νcm⁻¹: 1941, 1872 (MCO). UV-vis (acetonitrile, λ [nm] : ε [L/mol·cm]⁻¹): 364 : 10867.

General procedure for the synthesis of the triphenyolphosphine complexes. A solution of the corresponding tricarbonyl complex (0.5 mmol) and PPh3 (2.5 mmol) in benzene (60 mL) in a glassy photoreactor with the external cooling and an internal glassy jacket for an immersion Hg lamp was thermostated to 7 °C under stirring in an argon atmosphere and, then, treated with the light of the Hg immersion lamp. The irradiation was carried out for 30 min at 7–9 °C. Then, the reaction mixture was left under an argon atmosphere for 1 h. The resulting solution was filtered off and evaporated under vacuum. The triphenyolphosphine complexes were purified by column chromatography on silica gel (eluent: hexane/ethyle acetate 3:1).

N-(1-η⁵-Cyclopentadienylethylidene)aniline(dicarbonyl) (triphenyolphosphine)manganese (7). Yield: 0.119 g (43%). Mp: 167–169 °C. 1H NMR (CDCl3): δ 1.81 (s, 3H, CH3), 3.84 (m, 2H, Cpg), 5.08 (m, 2H, Cpg), 6.76 (d, J = 7.7 Hz, 6H, Ph), 6.94 (t, J = 7.7 Hz, 1H, Ph), 6.98 (m, 2H, Ph), 7.16 (m, 5H, Ph), 7.58 (t, J = 7.9 Hz, 6H, Ph) ppm. 13C NMR (CDCl3): δ 92.16 (s, PPh3). IR
(benzene), νcm⁻¹: 1941, 1877 (MCO). UV-vis (benzene, λ [nm]; ε [L/mol·cm]): 400 : 1643 (sh). Anal. Calcd for C₇H₈O₂N₂MnP: C, 71.35; H, 4.90; N, 2.52; Mn, 9.89. Found: C, 71.43; H, 4.94; N, 2.46; Mn, 9.7%.

N-(Phenyl-$p$-cyclopentadienylmethylene)aniline(dicarbonyl)(triphenylphosphine)manganese (8). Yield: 0.145 g (47%). Mp: 181–182 °C. (H NMR (CD₂Cl₂): δ 3.81 (m, 2H, Cp), 5.14 (m, 2H, C), 6.41 (d, J = 8.2 Hz, 6H, Ph), 6.45 (m, 3H, Ph), 6.75–7.05 (m, 9H, Ph), 7.75 (t, J = 8.1 Hz, 6H, Ph), 7.75 (t, J = 7.7 Hz, 2H, Ph) ppm. 31P (CD₂Cl₂): δ 91.04 (s, PPh₃). IR (benzene), νcm⁻¹: 1942, 1875 (MCO). UV-vis (benzene, λ [nm]; ε [L/mol·cm]): 450: 1279. Anal. Calcd for C₇H₈O₂N₂MnP: C, 73.91; H, 4.73; N, 2.27; Mn, 8.90. Found: C, 73.77; H, 4.69; N, 2.36; Mn, 9.1%.

**Definition of the quantum yield.** The quantum yield was determined by the ferroxalate actinometry upon irradiation with the light with the wavelength of 365 nm [10]. The product was identified based on the UV-vis and IR spectra by comparing them to the spectra of the samples obtained previously and characterized in benzene. The quantitative analysis was carried out by monitoring the changes in the UV-vis spectra at 400 nm for compounds 1 and 3 and changes in the intensities of the IR bands at 2020 cm⁻¹ for 1 and at 1869 cm⁻¹ for 3. The quantum yield was defined from the initial spectral changes where the absorbance linearly depends on the irradiation time. The absorbance of all the samples did not exceed 1. The conversion was less than 15%. The quantum yield was determined three times. The definition accuracy was equal to 10%. The measurement accuracy was calculated as a sum of the measurement and instrumental accuracy.

**Electrochemical studies.**

The electrochemical measurements were carried out in a standard three electrode system using an IPC-PRO potentiostat (Russia) connected to PC. The working electrode was a glass-carbon disc with a size of 0.03 cm²; the counter electrode was a platinum plate of the larger size. The measurements were carried out in acetonitrile bearing 0.1 M tetraethylammonium tetrafluoroborate relative to the saturated silver-chloride electrode; the rate of the potential sweep was 100 mV/s.

**Calculations.**

The quantum chemical calculations at the DFT B3LYP [11–13] level of theory were carried out using GAUSSIAN 09 [14]. The following parameters were calculated: geometric parameters of the compounds, electron density distribution, full conversion energies, conversion entropies, normal vibration modes. The geometric structures of the molecules and the normal modes were calculated using 6-31G* atomic bases. To take into account the solvation effect, the polarized continuum model (PCM) within SCRF was used [15].

**Conclusions.**

The investigation of the photochemical properties of imines 1 and 2 showed that, in the absence of external ligands, the removal of the CO group from the manganese atom affords unstable four-membered chelates 3 and 4. In the presence of carbon monoxide, dicarbonyl complexes 3 and 4 undergo the reverse dark reaction, resulting in the initial tricarbonyl complexes. Upon photolysis and the following dark reaction, the solution color changes from light-yellow to bright-orange and back; thus, an intermolecular photochromic system can be realized. In the presence of external ligands, such as acetonitrile and triphenylphosphine, the irradiation of 1 and 2 leads to the formation of mainly dicarbonyl complexes with the manganese–external ligand bond. It was shown that, in the presence of CO, in the case of acetonitrile and triphenylphosphine ligands, the ligand exchange takes place with the formation of initial complexes 1 and 2; thus, the acetonitrile and triphenylphosphine complexes form photochromic systems with the tricarbonyl compounds. The acetonitrile complexes were isolated. It was found that in the presence of external ligands such as carbon monoxide or triphenylphosphine, acetonitrile can be substituted for these ligands.

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**Electronic supplementary information.**

Electronic supplementary information (ESI) available online: structures and energies of the compounds calculated by DFT. For ESI, see DOI: 10.32931/to2028a

**References.**


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