Dicarbonyl chelates from 1-cymantrenylalkylamides: formation, properties, and kinetics of the dark reaction with carbon monoxide

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Photolysis of carboxamides with aminomethyl-, 1-aminoethyl-, and aminobenzylcymantrenes led to six-membered dicarbonyl chelates with the Mn—O bond, which are stable in solutions. In the presence of carbon monoxide, the chelates undergo a dark reverse reaction with the formation of the starting tricarbonyl complexes. It was found that the rate determining step of the thermal reaction of the chelates with CO was the chelate ring opening according to the S_N1 mechanism of ligand substitution.

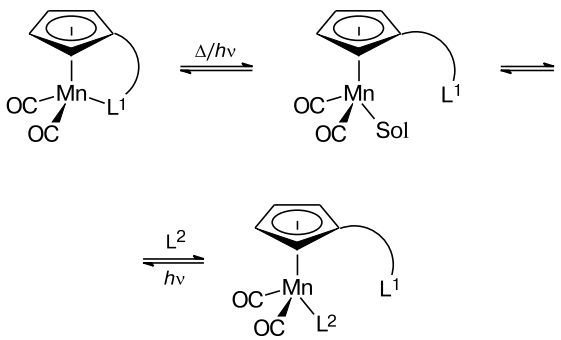
Key words: cymantrene, amides, photolysis, dicarbonyl chelates, carbon monoxide, photochromism.

Nowadays, a potential possibility of using photochromic materials in the development of photo devices, playing the role of molecular switches, memory elements, and chemical sensors, stimulates research on the synthesis and studies of photochemical properties of organic, inorganic, and organometallic photochromic compounds.[1—6] Recently,[7—10] a possibility of application for this purpose of cymantrene functional derivatives capable of forming reversible photochromic systems due to the intra- and intermolecular ligand exchange processes was demonstrated.

The key step of this type photochromic systems is the thermo- and/or photoinduced chelate ring opening in the dicarbonyl chelates formed upon photolysis of cymantrene functional derivatives (Scheme 1). The feasibility of the ring opening depends on the lability degree of the coordination bond of the Mn atom with n- or π-donor groups of the substituent. Earlier, it was shown that such groups include pyridines,[9,10] nitriles,[11] alkenes,[9,11] as well as ketones[8,9] and carbamates.[7,9] To study the influence of the nature of the carbonyl group in the cymantrene side chain on the ability to form dicarbonyl chelates, in the present work we considered a photochemical behavior of a number of alkyl- and arylcarboxamides with aminomethyl-, 1-aminoethyl-, and 1-aminobenzylcymantrenes **1**—**6** and kinetics of a reverse thermal reaction of chelates with carbon monoxide.

The irradiation with a mercury lamp of the light yellow solutions of amides **1**—**6** (Scheme 2) in benzene or THF under argon led to the change of the color to crimson and the registration of two absorption bands in the 400—550 nm region of the electronic spectrum (Fig. 1, Table 1). A sim-

Scheme 1



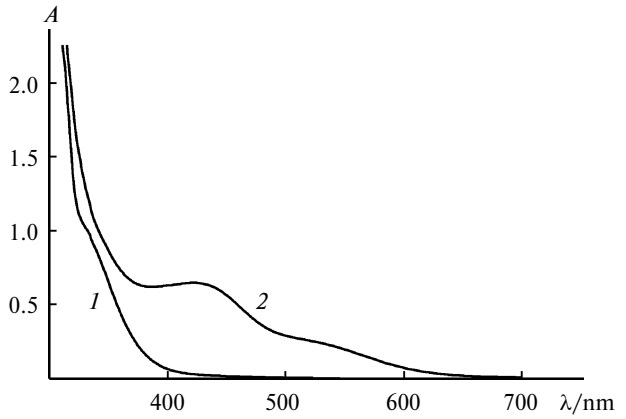


Fig. 1. Electron absorption spectra of solutions of compounds **2** (1.2 mmol L^{-1}) (*1*) and **8** (5 mmol L^{-1}) (*2*) in benzene.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 0914—0922, April, 2015.

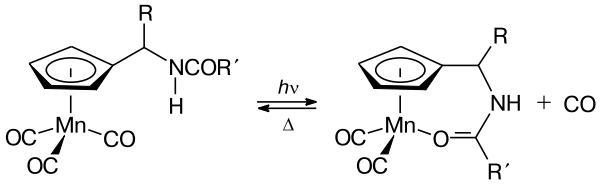
Table 1. Calculated energy values and ν(CO) for compounds **1**, **3**, **7**, **9**, **18**, and **19** and experimental data of IR and UV spectroscopy for compounds **1**—**12**

Compound	*E*	*E*′	ν(CO)/cm^{-1}			ν(NH) /cm^{-1}	λ_{max}/nm (ε/L mol^{-1} cm^{-1})
	a.u.		Ligand		Amide, experiment		
			Experiment	Calculations			
1	−1931.8315045	−1931.636833	2020, 1936	2113, 2054, 2045	1690	3419	330 sh (986)
7	−1818.4725039	−1818.286140	1930, 1857	2053, 2003	1650	3403	396 пл, 506 (327)
7TS	−1818.4257301	−1818.240782	—	—	—	—	—
18	−1818.4294186	−1818.243795	—	2066, 2004	—	—	—
2	—	—	2020, 1937	—	1675	3444	328 sh (1185)
8	—	—	1930, 1859	—	1631	3429	438 (887), 533 (339)
3	−1971.1423472	−1970.919407	2021, 1936*	2112, 2056, 2038	1685	3419	331 (1309)
9	−1857.787444	−1857.572879	1932, 1859	2056, 2006	1654	3402	392 (146), 506 (67)
9TS	−1857.7391427	−1857.525313	—	—	—	—	—
19	−1857.7430197	−1857.529172	—	2068, 2015	—	—	—
4	—	—	2019, 1938	—	1672	3440	332 (1697)
10	—	—	1930, 1859	—	1632	3424	435 (437), 532 (147)
5	—	—	2017, 1938	—	1673	3457	339 (2089)
11	—	—	1929, 1857	—	1628	3445	427 (454), 493 (280)
6	—	—	2022, 1940	—	1691	3433	330 (1086)
12	—	—	1930, 1858	—	1650	3388	505 (349)

* The frequencies of two antisymmetric vibrations are identical.

ilar picture was observed earlier[7] in the photolysis of related cymantrene carbamate derivatives, which resulted in the formation of stable six-membered chelate complexes with the Mn—O=CN bond.

Scheme 2



1—6 **7—12**

Compound	R	R′	Compound	R	R′
1, **7**	H	Me	**4**, **10**	Me	Ph
2, **8**	H	Ph	**5**, **11**	Me	Bu^t
3, **9**	Me	Me	**6**, **12**	Ph	Me

The IR monitoring of the photolysis of the amides showed the disappearance of the MCO stretching vibration bands of the starting complexes and the appearance of two bands of equal intensities at ~1930 and ~1858 cm^{-1}, corresponding to the symmetric and asymmetric stretching vibrations of the CO ligands (Fig. 2, see Table 1). The positions of these bands are virtually the same as the frequencies of the CO ligands in the IR spectra of similar carbamate chelates.[7] At the same time, as in the case of carbamates, the low-frequency shift of the amide group ν(CO) and ν(NH) by 30—50 and 12—55 cm^{-1}, respectively, is observed, that indicates the involvement of the amide group in the stabilization of chelates **7**—**12** (see Scheme 2). Besides, upon photolysis of amides **2**, **4**, and **6** the band of the noncoordinated amide group completely disappears at the end of the reaction. Therefore, the phenyl ring is not essentially coordinated to the manganese atom in the intermediate 16-electron manganese carbonyl complex.

The ^{1}H NMR spectra of chelates **7**—**12** considerably differ from the spectra of amides **1**—**6** and are well consistent with the structure of dicarbonyl six-membered chelates with the Mn—O=CN bond (Table 2). Similar changes in the ^{1}H NMR spectra were observed earlier[7] for the formation of carbamate chelates from tricarbonyl com-

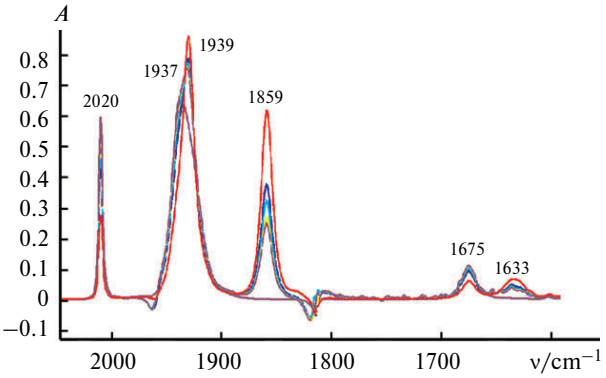


Fig. 2. IR monitoring of amide **2** photolysis in benzene.
Note. Figures 2 and 5 are available in full color in the on-line version of the journal (http://www.springerlink.com).

Table 2. Kinetic parameters of the dark reaction of chelates **7**—**12** and **17** with CO in benzene at 24 °C

Exposed compound*	Chelate	$k_{app} \cdot 10^4$ /s^{-1} **	$\tau_{1/2}$ /min
$CymCH_2NHCOMe$ (**1**)	**7**	2.35(0.03)	52
1 + **16**	**7** + **17**	2.38(0.08)	53
$CymCH_2NHCOPh$ (**2**)	**8**	1.82(0.02)	64
CymCH(Me)NHCOMe (**3**)	**9**	0.89(0.01)	129
CymCH(Me)NHCOPh (**4**)	**10**	1.18(0.03)	103
$CymCH(Me)NHCOBu^t$ (**5**)	**11**	1.03(0.01)	115
CymCH(Ph)NHCOMe (**6**)	**12**	1.17(0.03)	99
16	**17**		>650

* Cym is cymantrene.
** A standard deviation is given in parentheses.

plexes. In particular, the transformation of compounds **1**—**6** to the corresponding dicarbonyl chelates **7**—**12** was accompanied by the downfield shift of the signals for the α-protons of the Cp-ring, whereas the signals for the β-protons displace upfield. Besides, on going from chiral amides **3**—**6** to chelates **9**—**12** the difference between the chemical shifts of the diastereotopic α-H and α´-H atoms, as well as of β- and β´-protons of the Cp-ring, changes (Fig. 3).

The structure of the dicarbonyl amide chelates was confirmed by the DFT calculations of dicarbonyl complexes **7** and **9**, for which the global energy minima turned out to be higher than the energy of tricarbonyl amides **1**

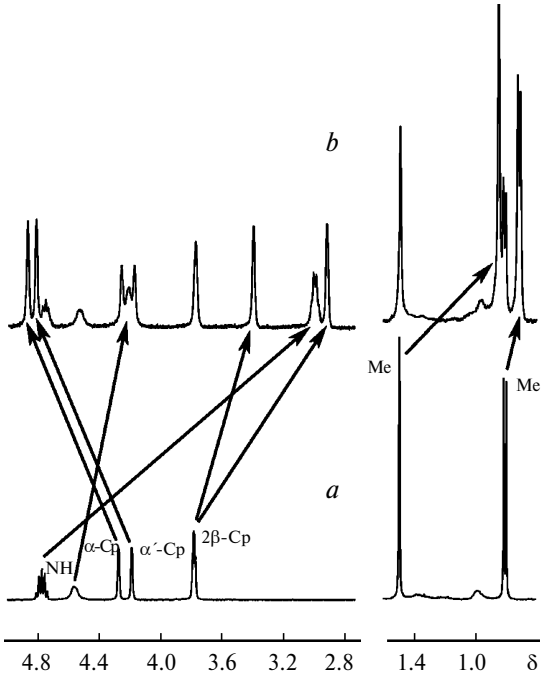


Fig. 3. ^{1}H NMR spectra of compound **3** in benzene-d_6 before (*a*) and after (*b*) irradiation (65% conversion of **3** to **9**).

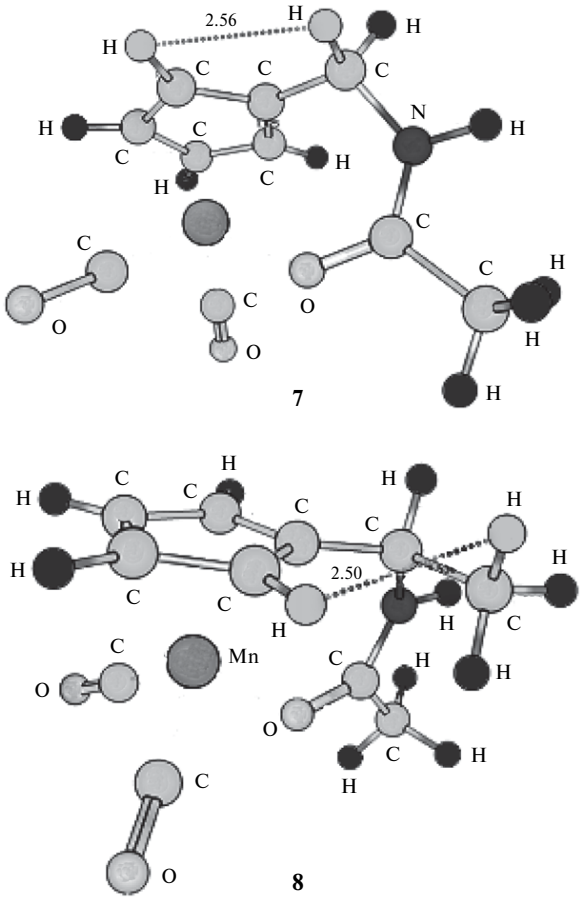


Fig. 4. The optimized structures of chelates **7** and **9**. Indicated are the interatomic distances (Å).

and **3** by 29 and 26 kcal mol^{-1}, respectively (see Table 1). The calculated geometrical parameters of the chelates have values of principal bond lengths and bond angles standard for cymantrene derivatives[9,10] (Fig. 4). Besides, the calculated frequencies ν(CO) in the IR spectrum qualitatively agree with the experimental values (see Table 1).

Half-times for amide-chelate transformation in 10 m*M* solutions under similar conditions are close and equal to ~3 min. The evaluation of the quantum yield (ϕ) of the photoreaction of **1** in THF gives the value 0.8±0.1 relative to the value $\phi = 0.8$ obtained earlier[9,12] for the photolysis of [(1-η^2–allyloxy-2-pyrid-2-ylethyl)-η^5-cyclopentadienyl](dicarbonyl)manganese.

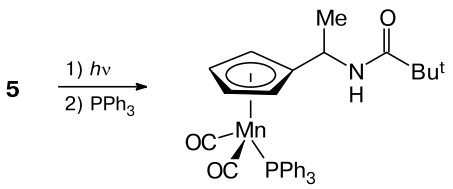
Dicarbonyl chelates **7**—**12** are quite stable compounds when stored in solutions under argon. Parameters of their IR and ^{1}H NMR spectra remain unchanged during 4 h at ~20 °C and more than 12 h at 5 °C. However, attempts to isolate the chelates failed. The evaporation of benzene or THF from the solutions leads to their rapid decomposition and the formation of 1- and 2-substituted cyclopentadienes and polymeric products. In particular, in the case of compounds **7** and **12** we obtained the mixtures (~1 : 1) of, respectively, 1- and

2-(acetamidomethyl)cyclopentadienes (**13a** and **13b**) and 1- and 2-(1-acetamido-1-phenylmethyl)cyclopentadienes (**14a** and **14b**).

In the presence of carbon monoxide, chelates **7**—**12** undergo a reverse thermal reaction with the formation of the starting tricarbonyl complexes; the half-times of transformation at 24 °C are 60—130 min. The irradiation of the dicarbonyl chelates with visible light in the 480—530 nm range under the same conditions leads to a sharp acceleration of the reverse reaction and the decrease of the half-time to ~10 min. Three-five repetitions of the cycle: irradiation of the amides and the subsequent dark reaction of the chelates with CO did not lead to any changes in the IR spectra of neither the starting amides, nor the chelate complexes. Therefore, a reversible photochromic pair between the cymantrenylamides and the corresponding dicarbonyl chelates exists in the reaction medium in the presence of carbon monoxide.

Photolysis of amides **1**—**6** in the presence of 2—4 equiv. of triphenylphosphine gives only amide chelates **7**—**12**, though a parallel formation of the corresponding dicarbonylphosphine complexes could have been expected. This means that the intramolecular chelation is a more efficient process than the intermolecular substitution of the CO ligand. It should be noted that the dark thermal reaction of chelate **11** with carbon monoxide in the presence of 2 equiv. of PPh_3 does not lead to the dicarbonylphosphine complex either. Thus, carbon monoxide is more efficient ligand than PPh_3. However, the irradiation of compound **5** in the presence of 1.5 equiv. of PPh_3 with the immediate removal of forming CO from the reaction mixture makes it possible to obtain triphenylphosphine complex **15** in 56% yield (Scheme 3).

Scheme 3



15

The ligand exchange at the Mn atom in cymantrene derivatives and related complexes can occur either by the associative or the dissociative mechanism.[10,13] To establish the pathway of the reaction of amide chelates **7**—**12** with carbon monoxide, we studied the kinetics of this reaction in the dark in benzene at 24 °C. Examples of the IR monitoring of the reaction course and kinetic graphs are given in Figs 5—7. In all the cases, the rate of the disappearance of the chelate for the equimolar amounts of reagents is described by the first order equation with the value $R \geq 0.999$ (see Table 2).

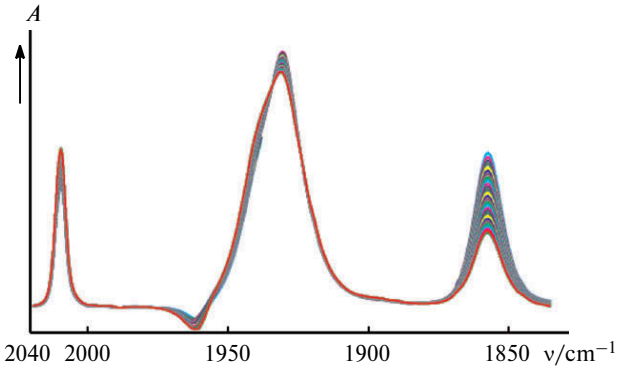


Fig. 5. IR monitoring of transformation of compound **10** to **4** in benzene at 24 °C (60% conversion).

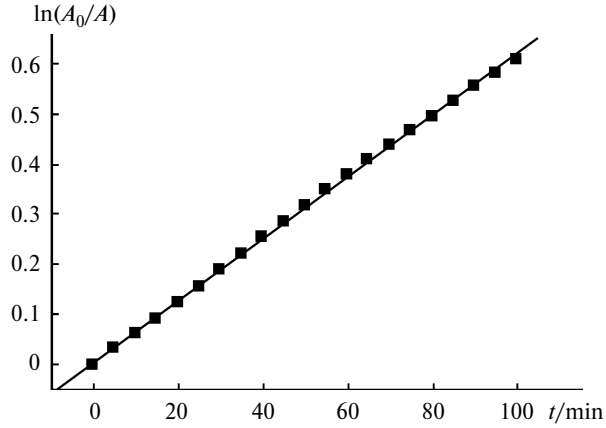


Fig. 6. The $\ln(A_0/A)$ dependence of the band at $\lambda = 1857$ cm^{-1} on the conversion time of compound **11** to **5** for a 12 m*M* solution in benzene at 24 °C ($R = 0.9996$).

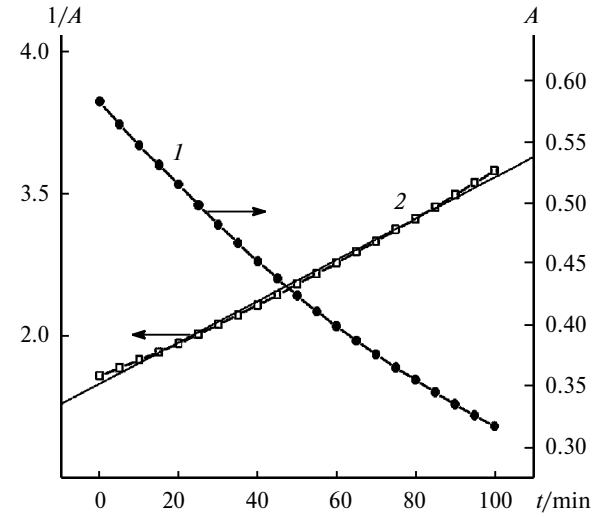
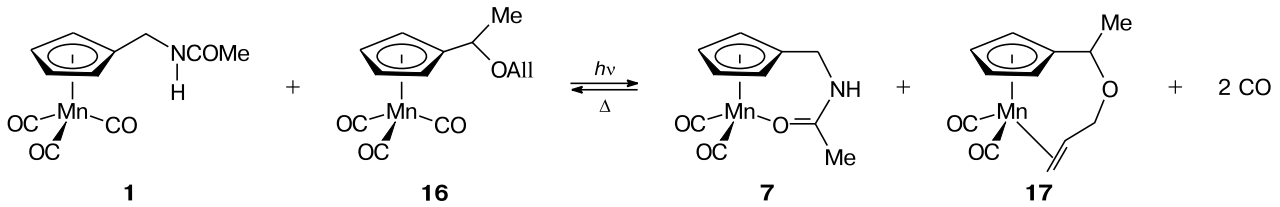


Fig. 7. The kinetics of compound **11** consumption (*1*) and the $1/A$ dependence of the band at $\lambda = 1857$ cm^{-1} on the **11** → **5** conversion time (*2*) for a 12 m*M* solution in benzene at 24 °C ($R = 0.992$).

Scheme 4



To confirm the first order, we studied the reaction rate for the double concentration of CO. The double excess of CO was achieved by the irradiation of a 1 : 1 mixture of amide **1** and 1-allyloxyethylcymantrene (**16**) in benzene (Scheme 4). We found that the irradiation of compound **16** leads to the formation of chelate **17**, which in the presence of CO is reverted to the starting complex with the half-time >650 min, which is larger almost by an order of magnitude than $\tau_{1/2}$ for the transformation **7** → **1**. In this connection, after irradiation the concentration of carbon monoxide in the reaction mixture remains about twice as large as the concentration of chelate **7** until a 50% conversion of the dark reaction was reached. The rate constant of the disappearance of **7** and its half-time obtained in this case are virtually the same as those for the reaction in the absence of complex **17** (Fig. 8, see Table 2).

The kinetic data obtained showed that the rate-determining step of the thermal reaction of chelates **7**—**12** with CO is the chelate ring opening at the Mn—O bond with the formation of the solvated manganese carbonyl complex (Scheme 5). Therefore, the ligand substitution in the amide chelate follows the S_N1 mechanism. This conclusion agrees with the mechanism suggested earlier[10,14,15] for the thermal reactions of related chelates with CO, pyridine, phosphines, and phosphites.

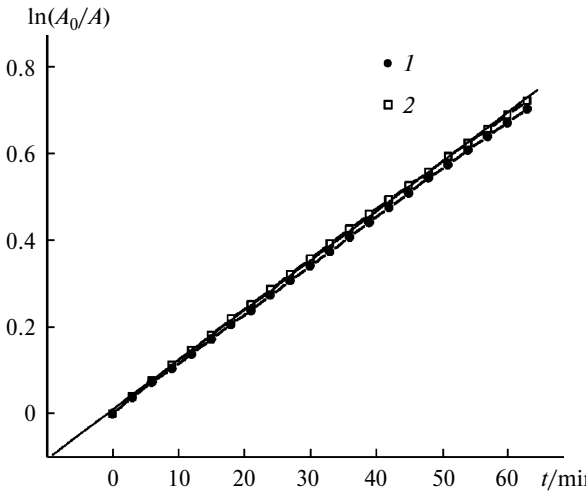
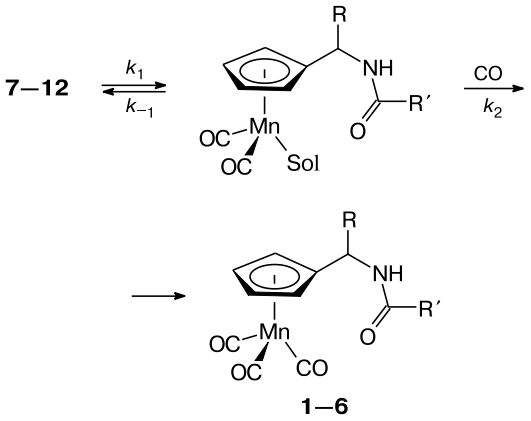


Fig. 8. The $\ln(A_0/A)$ dependence of the band at λ = 1858 cm^{-1} on the time after irradiation of a 11.2 m*M* solution of **1** in benzene in the absence (*1*, R = 0.9998) and in the presence of 1 equiv. of **15** (*2*, R = 0.9995) at 24 °C.

Scheme 5



k_2[CO] >> k_{-1}

As it is seen from Table 2, for compounds **9** and **10** the k_{app} values are half as large and the $\tau_{1/2}$ values are twice as large compared to the corresponding values for chelates **7** and **8**. From this it follows that the introduction of the Me group into the CH_2 fragment of the chelates under consideration noticeably affects the rate of the dark reaction. This fact agrees with the results of the DFT calculations of the activation energy of the chelate ring opening for compounds **7** and **9**: 28.5 and 29.9 kcal mol^{-1}, respectively. Chelates **11** and **12** substituted at position C(1) of the side chain also react at a lower rate than chelates **7** and **8**. The similar frequencies of stretching vibrations of the CO ligands for chelates **7**—**12** (see Table 1) show that the structure of the side chain does not affect the electron-donating properties of the O=CN ligand.[16,17] Therefore, the decrease in the k_{app} value on going from chelates **7** and **8** to complexes **9**—**12**, apparently, is related not to the ligand electron nature, but to the steric hindrance arising upon the ring opening. In the case of compounds **9** and **10**, such a hindrance can arise due to the interaction between the α H atoms of the Cp-ring and the Me group at C(1) position of the side chain. In fact, the calculations of the geometrical parameters for chelates **7** and **9**, as well as the corresponding transition states **7TS** and **9TS** and the inter-

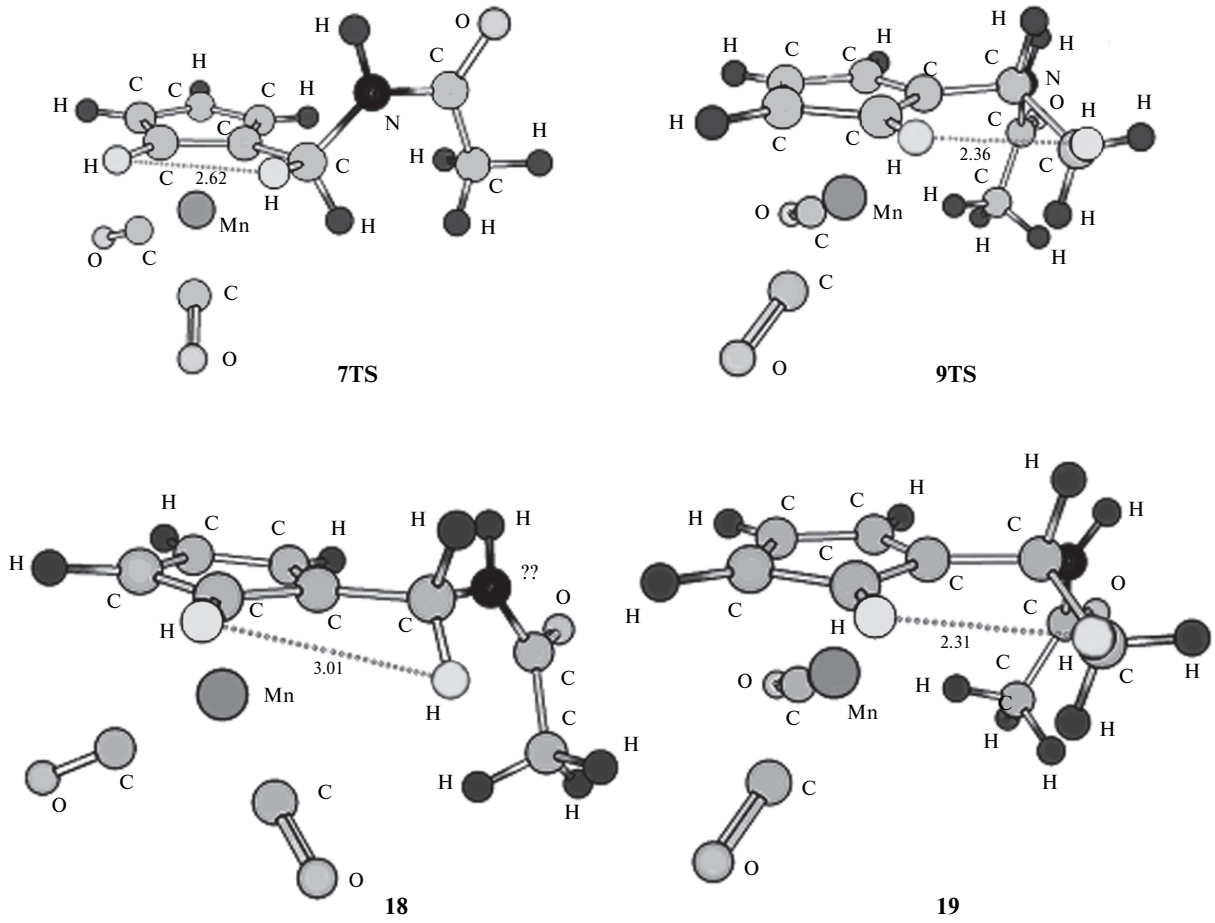


Fig. 9. The optimized structures of transition states **7TS** and **9TS** and the intermediates **18** and **19**. Indicated are the interatomic distances (Å).

mediates **18** and **19**, show that the distance between the closest H atoms in the unsubstituted structures **7**, **7TS**, and **18** is larger than in their homologs **9**, **9TS**, and **19** (see Figs 4 and 9). It should be emphasized that the minimal distance is observed in the intermediate **19**, and it is 0.7 Å shorter than in compound **18**.

In conclusion, it was found that photolysis of amides **1**—**6**, like that of cymantrenyl carbamates[7] and ketones,[8] led to the formation of thermodynamically stable dicarbonyl chelates due to the coordination of the carbonyl group to the Mn atom. The evaluation of the quantum yield of photolysis of amide **1** in THF gives the value 0.7—0.9. The process of the formation of chelates is accompanied by a bathochromic shift of the first long-wavelength absorption band from 330 to 530 nm. The structure of the chelates was confirmed by IR, UV, and ^{1}H NMR spectroscopy, as well as by DFT calculations using the B3LYP/6-31G* method. It was found that amide chelates in the presence of carbon monoxide undergo the dark thermal reaction with recovery of the starting tricarbonyl complexes, thus forming the photochromic pairs. The kinetic studies of the dark thermal transformation of chelates **7**—**12** to the corresponding starting tricarbonyl complexes showed that the rate-determining step of the thermal reaction of chelates with CO is the chelate ring opening following the S_N1 mechanism of ligand substitution.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 and 100.61 MHz, respectively), using the solvent as a reference, δ relative to Me_4Si, for benzene $\delta_H = 7.26$). Signals in the ^{1}H NMR spectra were assigned using the 2D HH—COSY and HH—ROESY experiments. IR spectra were recorded on a Magna 750-IR (Nicolet) IR Fourier-transform spectrometer with a 2 cm^{-1} resolution in cuvettes. Kinetic studies were carried out on a Tensor 37 (Bruker) FTIR-spectrometer at 24 °C. Mass spectra (EI) were obtained on Kratos MS 890 and Finnigan POLARIS Q spectrometers (70 eV). UV spectra were recorded on a Specord M-40 spectrophotometer. Photochemical reactions carried out using an Hereaus TQ 150 immersion Hg lamp. Reaction progress and purity of products were monitored by analytical TLC on Silufol UV-245 plates (Kavalier). Merck silica gel 60 was used for column chromatography. THF and benzene were purified by standard methods and distilled over sodium benzophenone ketyl or metallic sodium under argon. *N*-Acetyl-1-cymantrenylmethylamine (**1**),[18]

N-benzoyl-1-cymantrenylmethylamine (**2**),[18] *N*-acetyl-1-cymantrenylethylamine (**3**),[19] *N*-benzoyl-1-cymantrenylethylamine (**4**),[19] and *N*-pivaloyl-1-cymantrenylethylamine (**5**)[19] were synthesized as described earlier. Cymantrenyl phenyl ketone and acetylcymantrene were obtained by known methods.[20,21]

***N*-Acetyl-1-cymantrenyl-1-phenylmethylamine (6).** A mixture of cymantrenyl phenyl ketone (15 g, 48.7 mmol), $NH_2OH \cdot HCl$ (5.1 g, 73 mmol), and sodium acetate (8.0 g, 97.4 mmol) in EtOH (100 mL) was refluxed for 6 h using a reflux condenser. Then, the reaction mixture was cooled to ~20 °C and concentrated *in vacuo* to 1/4 of the volume. After addition of water (100 mL) to the residue, the product was extracted with AcOEt (100 mL), the organic layers were washed with (3×100 mL) and a saturated aqueous NaCl, dried with $MgSO_4$, the solvent was evaporated. The residue was crystallized from hexane with AcOEt. The yield of cymantrenyl phenyl ketone oxime (**20**) was 12.0 g (76%), m.p. 132—133 °C, a mixture of two isomers in the ratio of 1 : 0.9. ^{1}H NMR (acetone-d_6), δ, major isomer: 5.45 (m, 2 H, H_β, Cp); 5.59 (m, 2 H, H_α, Cp); 7.83—7.97 (m, 5 H, Ph); 10.89 (s, 1 H, NOH); minor isomer: 5.51 (m, 2 H, H_β, Cp); 5.96 (m, 2 H, H_α, Cp); 7.83—7.97 (m, 5 H, Ph); 11.62 (s, 1 H, NOH). Found (%): C, 55.81; H, 3.09; Mn, 17.1; N, 4.39. $C_{15}H_{10}MnNO_4$. Calculated (%): C, 55.75; H, 3.12; Mn, 17.0; N, 4.33.

Zinc dust (11.0 g, 167 mmol) was added in portions to a solution of compound **20** (10.8 g, 33.4 mmol) in a mixture of acetic acid (125 mL) and water (12 mL). Then, the reaction mixture was refluxed for 3 h, cooled to 80 °C, and filtered. A precipitate was washed with acetic acid. The combined solutions were neutralized to pH 9 with a 25% aqueous ammonia and extracted with diethyl ether (300 mL). The organic layers were washed with 2 *N* NaOH (50 mL), dried with $MgSO_4$, and the solvent was evaporated. The residue was separated by column chromatography (AcOEt—hexane (5 : 3)) to isolate four products.

Acetoxy-1-cymantrenyl-1-phenylmethane. The yield was 810 mg (7%), m.p. 78—79 °C (hexane). ^{1}H NMR (acetone-d_6), δ: 2.13 (s, 3 H, Me); 4.88 (m, 1 H, H_β, Cp); 4.90 (m, 1 H, H_β, Cp); 5.13 (m, 1 H, H_α, Cp); 5.17 (m, 1 H, H_α, Cp); 6.54 (s, 1 H, CH); 7.36—7.43 (m, 3 H, Ph); 7.50 (m, 2 H, Ph). MS, *m/z* (I_{rel} (%)): 268 $[M - 3\,CO]^+$ (100), 153 (57), 114 (40). Found (%): C, 58.01; H, 3.85; Mn, 15.6. $C_{17}H_{13}MnNO_5$. Calculated (%): C, 57.97; H, 3.72; Mn, 15.6.

Hydroxy-1-cymantrenyl-1-phenylmethane. The yield was 600 mg (6%), m.p. 82—83 °C (hexane). ^{1}H NMR (acetone-d_6), δ: 4.80 (m, 1 H, H_β, Cp); 4.83 (m, 1 H, H_β, Cp); 4.96 (m, 1 H, H_α, Cp); 5.02 (d, 1 H, CH, J = 4.3 Hz); 5.08 (m, 1 H, H_α, Cp); 5.51 (d, 1 H, OH, J = 4.6 Hz); 7.28—7.39 (m, 3 H, Ph); 7.50 (m, 2 H, Ph). MS, *m/z* (I_{rel} (%)): 226 $[M - 3\,CO]^+$ (82), 208 (35), 153 (100).

1-Cymantrenylphenylmethylamine. The yield was 5.4 g (52%). ^{1}H NMR (acetone-d_6), δ: 4.79 (m, 1 H, H_β, Cp); 4.81 (m, 1 H, H_β, Cp); 5.06 (m, 1 H, H_α, Cp); 5.25 (m, 1 H, H_α, Cp); 5.37 (s, 1 H, CH); 7.23 (t, 1 H, Ph, J = 7.3 Hz); 7.32 (t, 2 H, Ph, J = 7.8 Hz); 7.46 (d, 2 H, Ph, J = 7.4 Hz). MS, *m/z* (I_{rel} (%)): 226 $[M - 3\,CO]^+$ (83), 208 (28), 153 (100). Found (%): C, 58.41; H, 4.11; Mn, 17.2; N, 4.42. $C_{15}H_{12}MnNO_3$. Calculated (%): C, 58.27; H, 3.91; Mn, 17.77; N, 4.53.

N-Acetyl-1-cymantrenyl-1-phenylmethylamine (**6**). The yield was 1.3 g (11%), m.p. 129—130 °C (hexane). ^{1}H NMR (acetone-d_6), δ: 1.95 (s, 3 H, Me); 4.80 (m, 1 H, H_β, Cp); 4.90 (m, 1 H, H_β, Cp); 5.04 (m, 1 H, H_α, Cp); 5.26 (m, 1 H, H_α, Cp); 5.95 (d, 1 H, CH, J = 9.2 Hz); 7.23 (t, 1 H, Ph, J = 7.3 Hz); 7.32 (t, 2 H, Ph, J = 7.2 Hz); 7.46 (d, 2 H, Ph, J = 7.6 Hz). ^{1}H NMR (benzene-d_6), δ: 1.57 (s, 3 H, Me); 3.72 (m, 1 H, H_β, Cp); 3.79 (m, 1 H, H_β, Cp); 4.05 (m, 1 H, H_α, Cp); 4.21 (m, 1 H, H_α, Cp); 5.32 (br.d, 1 H, NH, J = 7.5 Hz); 5.99 (d, 1 H, CH, J = 8.7 Hz); 7.03—7.15 (m, 5 H, Ph). IR (benzene), ν/cm^{-1}: 3388, 2022, 1939, 1691 (NC=O). EAS (benzene, λ/nm (ε/L mol^{-1} cm^{-1})): 330 (1086). MS, *m/z* (I_{rel} (%)): 267 $[M - 3\,CO]^+$ (100), 226 (22), 208 (17), 153 (42), 113 (79). Found (%): C, 58.18; H, 4.10; Mn, 15.4; N, 3.94. $C_{17}H_{14}MnNO_4$. Calculated (%): C, 58.13; H, 4.02; Mn, 15.64; N, 3.99.

1-Allyloxycymantrenylethane (16). Sodium borohydride (2.8 g, 74 mmol) was added in portions to a solution of acetylcymantrene (18 g, 73 mmol) in EtOH (100 mL), and the mixture was stirred for 1 h at 10 °C. Then, the reaction mixture was poured into the icy water and extracted with CH_2Cl_2 (3×100 mL), the organic layers were washed with water and dried with Na_2SO_4. The solvent was evaporated, 1-cymantrenylethanol (**21**) was isolated by column chromatography (AcOEt—hexane (1 : 1)). The yield was 17.0 g (94%), m.p. 51—52 °C (*cf.* Ref. 22: m.p. 55—56 °C). ^{1}H NMR ($CDCl_3$), δ: 1.50 (d, 3 H, Me, J = 6.4 Hz); 4.64 (q, 1 H, CH, J = 6.3 Hz); 4.70 (m, 1 H, H_β, Cp); 4.75 (m, 1 H, H_β, Cp); 4.87 (m, 1 H, H_α, Cp); 4.93 (m, 1 H, H_α, Cp).

A solution of compound **21** (3.0 g, 12 mmol) in THF (50 mL) was added dropwise to a suspension of 60% NaH (0.8 g, 20 mmol) in hexane (7 mL) at 0 °C under argon, and the mixture was stirred for 15 min. Then, a solution of allyl bromide (1.6 mL, 20 mmol) in THF (10 mL) was added to the suspension through the septum. The reaction temperature was raised to ~20 °C, and the mixture was stirred for 3 h and neutralized with 10% aqueous solution of NH_4Cl (50 mL). The layers were separated and the aqueous layer was extracted with AcOEt (3×100 mL). The organic layers were combined, washed with saturated aqueous NaCl (100 mL), and dried with Na_2SO_4. The solvent was evaporated, the product was isolated by column chromatography (AcOEt—hexane (1 : 3)). The yield was 2.7 g (77%). ^{1}H NMR (acetone-d_6), δ: 1.38 (d, 3 H, Me, J = 6.4 Hz); 4.09 (m, 2 H, CH_2); 4.26 (q, 1 H, CH, J = 6.4 Hz); 4.84 (m, 1 H, H_β, Cp); 4.86 (m, 1 H, H_β, Cp); 5.07 (m, 1 H, H_α, Cp); 5.09 (m, 1 H, H_α, Cp); 5.12 (m, 1 H, $=CH_2$); 5.31 (m, 1 H, $=CH_2$); 5.92 (m, 1 H, =CH). ^{1}H NMR (benzene-d_6), δ: 1.08 (d, 3 H, Me, J = 6.4 Hz); 3.71—3.74 (m, 2 H, CH_2O); 3.74 (q, 1 H, CH, J = 6.4 Hz); 3.84 (m, 1 H, H_β, Cp); 3.86 (m, 1 H, H_β, Cp); 4.21 (m, 1 H, H_α, Cp); 4.31 (m, 1 H, H_α, Cp); 5.03 (dm, 1 H, $=CH_2$, J = 10.5 Hz); 5.21 (dm, 1 H, $=CH_2$, J = 17.2 Hz); 5.80 (m, 1 H, =CH). IR (hexane), ν/cm^{-1}: 2026, 1944. Found (%): C, 54.54; H, 4.71; Mn, 18.6. $C_{13}H_{13}MnO_4$. Calculated (%): C, 54.18; H, 4.55; Mn, 19.0.

Spectral studies of photochemical reactions of tricarbonyl complexes and a reverse dark reaction (general procedure). A solution of a tricarbonyl compound (2—4 mmol L^{-1}) in a required solvent (benzene or THF) was placed in an IR or a UV cell under argon and irradiated with both nonfiltered light and at λ = 365 nm using a mercury lamp (before irradiation, the lamp was brought out to the regime for 2 min). The spectra were recorded every 2—4 min. The total irradiation time for all the samples was 10—25 min. To obtain the samples for monitoring by NMR, the solutions of compounds (10—15 mmol L^{-1}) were filtered into the NMR tubes, the solutions were bubbled with argon and irradiated with a mercury lamp for 4 min at 8—10 °C until a 25—40% conversion was reached. The distance between the lamp and the sample in all the cases was 5 cm, ^{1}H NMR spectra were recorded

in 5-mm tubes. IR monitoring of all the dark reactions of chelates was carried out similarly for 72 h. The procedure irradiation—dark reaction for 2 m*M* solutions of all the amides in benzene were carried out in CaF_2 cells and repeated no less than 3 times.

(κ*O*-Acetylaminomethyl-η^5-cyclopentadienyl)(dicarbonyl)-manganese (7). ^{1}H NMR (benzene-d_6), δ: 0.80 (s, 3 H, Me); 2.68 (d, 2 H, CH_2, J = 2.4 Hz); 3.15 (m, 2 H, H_β, Cp); 4.95 (br.t, 1 H, NH); 4.84 (m, 2 H, H_α, Cp). IR (benzene), ν/cm^{-1}: 3403, 1930, 1857, 1650 (NC=O). UV (benzene, λ/nm (ε/L mol^{-1} cm^{-1})): 484 (517).

1-(Acetamidomethyl)cyclopentadiene (13a). ^{1}H NMR (benzene-d_6), δ: 1.40 (s, 3 H, Me); 2.62 (m, 2 H, CH_2); 3.98 (dm, 2 H, NCH_2, J = 5.1 Hz); 4.72 (br.s, 1 H, NH); 5.86 (m, 1 H, H, Cp); 6.26 (m, 1 H, H, Cp); 6.42 (m, 1 H, H, Cp).

2-(Acetamidomethyl)cyclopentadiene (13b). ^{1}H NMR (benzene-d_6), δ: 1.47 (s, 3 H, Me); 2.67 (m, 2 H, CH_2); 4.03 (dm, 2 H, NCH_2, J = 5.9 Hz); 4.72 (br.s, 1 H, NH); 6.07 (m, 1 H, H, Cp); 6.18 (m, 1 H, H, Cp), 6.34 (m, 1 H, H, Cp).

(κ*O*-Benzoylaminomethyl-η^5-cyclopentadienyl)(dicarbonyl)-manganese (8). ^{1}H NMR (benzene-d_6), δ: 2.98 (br.d, 2 H, CH_2); 3.22 (m, 2 H, H_β, Cp); 4.97 (m, 2 H, H_α, Cp); 5.76 (br.t, 1 H, NH); 6.83 (br.m, 5 H, Ph). IR (benzene), ν/cm^{-1}: 3424, 1930, 1859, 1631 (NC=O). UV (benzene, λ/nm (ε/L mol^{-1} cm^{-1})): 438 (887); 533 (339).

[1-(κ*O*-Acetylamino)ethyl-η^5-cyclopentadienyl](dicarbonyl)-manganese (9). ^{1}H NMR (benzene-d_6), δ: 0.71 (d, 3 H, Me, J = 6.6 Hz); 0.84 (s, 3 H, Me); 2.93 (m, 1 H, H_β, Cp); 3.10 (q, 1 H, CH, J = 6.6 Hz); 3.40 (m, 1 H, H_β, Cp); 4.22 (br.s, 1 H, NH); 4.83 (m, 1 H, H_α, Cp); 4.88 (m, 1 H, H_α, Cp). IR (benzene), ν/cm^{-1}: 3402, 1932, 1859, 1654 (NC=O). UV (benzene, λ/nm (ε/L mol^{-1} cm^{-1})): 392 (146); 506 (67).

[1-(κ*O*-Benzoylamino)ethyl-η^5-cyclopentadienyl](dicarbonyl)manganese (10). ^{1}H NMR (benzene-d_6), δ: 0.86 (d, 3 H, Me, J = 6.4 Hz); 3.04 (m, 1 H, H_β, Cp); 3.21 (q, 1 H, CH, J = 6.4 Hz); 3.40 (m, 1 H, H_β, Cp); 4.94 (m, 1 H, H_α, Cp); 4.99 (m, 1 H, H_α, Cp); 5.51 (br.s, 1 H, NH); 6.82 (m, 2 H, Ph); 6.96 (m, 3 H, Ph). IR (benzene), ν/cm^{-1}: 3424, 1930, 1859, 1632 (NC=O). UV (benzene, λ/nm (ε/L mol^{-1} cm^{-1})): 435 (437); 532 (147).

[1-(κ*O*-Pivaloylamino)ethyl-η^5-cyclopentadienyl](dicarbonyl)manganese (11). ^{1}H NMR (benzene-d_6), δ: 0.63 (s, 9 H, 3 Me); 0.91 (d, 3 H, Me, J = 6.4 Hz); 3.06 (m, 1 H, H_β, Cp); 3.20 (q, 1 H, CH, J = 6.4 Hz); 3.27 (m, 1 H, H_β, Cp); 4.54 (br.s, 1 H, NH); 4.98 (m, 1 H, H_α, Cp); 5.01 (m, 1 H, H_α, Cp). IR (benzene), ν/cm^{-1}: 3445, 1929, 1857, 1628 (NC=O). UV (benzene, λ/nm (ε/L mol^{-1} cm^{-1})): 427 (454); 493 (280).

[1-(κ*O*-Acetylamino)-1-phenylmethyl-η^5-cyclopentadienyl)]-(dicarbonyl)manganese (12). ^{1}H NMR (benzene-d_6), δ: 0.88 (s, 3 H, Me); 3.02 (m, 1 H, H_β, Cp); 3.23 (m, 1 H, H_β, Cp); 4.17 (s, 1 H, CH); 4.61 (br.s, 1 H, NH); 4.71 (m, 1 H, H_α, Cp); 4.93 (m, 1 H, H_α, Cp); 6.90—7.20 (m, 5 H, Ph). IR (benzene), ν/cm^{-1}: 3433, 1931, 1859, 1650 (NC=O). UV (benzene, λ/nm (ε/L mol^{-1} cm^{-1})): 505 (349).

1-(Acetamido-1-phenylmethyl)cyclopentadiene (14a). ^{1}H NMR (benzene-d_6), δ: 1.47 (s, 3 H, Me); 2.61 (d, 2 H, CH_2, J = 6.6 Hz); 5.14 (br.s, 1 H, NH); 5.85 (s, 1 H, HCPh); 6.16—6.35 (m, 3 H, H_{Cp}); 7.16—7.31 (m, 5 H, Ph).

2-(Acetamido-1-phenylmethyl)cyclopentadiene (14b). ^{1}H NMR (benzene-d_6), δ: 1.47 (s, 3 H, Me); 2.69 (s, 2 H, CH_2); 5.21 (br.s, 1 H, NH); 6.07 (m, 1 H, HCPh); 6.16—6.35 (m, 3 H, H_{Cp}); 7.16—7.31 (m, 5 H, Ph).

(*N*-Pivaloyl-1-aminoethylcyclopentadienyl)(dicarbonyl)(triphenylphosphine)manganese (15). A solution of compound **5** (0.35 g, 1.05 mmol) in benzene (300 mL) was placed into a photochemical reactor and irradiated with the light of an immersion Hg lamp at 7 °C for 30 min under argon, with the forming CO being gradually removed. Then, PPh_3 (0.45 g, 1.8 mmol) was added to the reaction mixture and it was stirred for 4 h at 35—40 °C or 12 h at ~20 °C. The solvent was evaporated, the product was isolated by column chromatography (benzene). The yield was 0.35 g (56%), m.p. 150—151 °C (hexane). ^{1}H NMR (benzene-d_6), δ: 1.37 (s, 9 H, 3 Me); 1.42 (d, 3 H, Me, J = 6.6 Hz); 3.90 (m, 2 H, H_β, Cp); 4.39 (m, 1 H, H_α, Cp); 4.52 (m, 1 H, H_α, Cp); 5.37 (dq, 1 H, CH, J_1 = 6.6 Hz, J_2 = 8.7 Hz); 6.10 (d, 1 H, NH, J = 8.7 Hz); 7.12 (m, 10 H, PPh_3); 7.66 (m, 5 H, PPh_3). ^{31}P NMR (benzene-d_6), δ: 92.1 (s). Found (%): C, 68.07; H, 5.84; N, 2.41; P, 5.48. $C_{32}H_{33}MnNO_3P$. Calculated (%): C, 67.96; H, 5.84; N, 2.48; P, 5.49.

[1-(η^2-Allyloxy)ethyl-η^5-cyclopentadienyl](dicarbonyl)manganese (17). ^{1}H NMR (benzene-d_6), δ, major isomer: 1.03 (d, 3 H, Me, J = 6.5 Hz); 1.73 (dm, 1 H, CH_2=, J = 8.8 Hz); 2.31 (dm, 1 H, CH_2=, J = 12.3 Hz); 2.77 (ddm, 1 H, CH=, J_1 = 12.3 Hz, J_2 = 8.8 Hz); 2.95 (q, 1 H, C<u>H</u>Cp, J = 6.5 Hz); 2.98 (dm, 1 H, OCH_2, J = 14.7 Hz); 3.61 (m, 1 H, H_{Cp}); 3.63 (m, 1 H, H_{Cp}); 4.29 (m, 1 H, H_{Cp}); 4.33 (dm, 1 H, OCH_2, J = 14.7 Hz); 4.71 (m, 1 H, H_{Cp}). IR (benzene), ν/cm^{-1}: 1964, 1902.

Evaluation of relative quantum yield of photolysis of compound 1. A 1.74 m*M* solution of compound **1** in THF (2.0 mL) (ε_{328} = 1011, ε_{365} = 356) was added to a 1.78 m*M* solution of [(1-η^2-allyloxy-2-pyrid-2-ylethyl)-η^5-cyclopentadienyl](dicarbonyl)manganese[9] in THF (1.5 mL) (ε_{328} = 1090, ε_{365} = 471), and the mixture was saturated with argon. The aliquots of this mixture with a total absorption of 0.74 (0.37 optical density for each component) at 365 nm were placed into a IR cell (KBr, l = 0.21 mm, S = 4.5 cm^2), the cell was placed 5 cm apart from a mercury lamp and irradiated with λ = 365 nm light using filters. A decrease in the concentration of both complexes was determined based on the optical density of the IR bands at 2020 cm^{-1} (ε = 8484) for amide **1** and at 1901 cm^{-1} (ε = 8026) for [(1-η^2-allyloxy-2-pyrid-2-ylethyl)-η^5-cyclopentadienyl]-(dicarbonyl)manganese, which do not overlap with the ν(CO) of the products. It was found that for the 7—9% conversion of compound **1** to the corresponding chelate **6**, a 5—6% h photoisomerization of [(1-η^2–allyloxy-2-pyrid-2-ylethyl)-η^5-cyclopentadienyl]-(dicarbonyl)manganese to the pyridine chelate is observed, for which the quantum yield is 0.8.[9] The evaluation of the relative quantum yield of photolysis of **1** based on these data gives the value 0.8±0.1.

DFT calculations. Quantum chemical calculations were performed by the Becke—Lee—Yang—Parr (B3LYP) hybrid method[23,24] with the 6-31G* bases.[25] To confirm the extreme points on the potential energy surface, the frequencies of the normal vibrations of molecules were calculated, using the GAUSSIAN-98 computer program.[26]

This work was financially supported by the Russian Academy of Sciences (Program P-8 "Development of Methodology of Organic Synthesis and Design of Compounds with Valuable Applied Properties") and the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Program OKh-1).

References

1. L. Ordronneau, H. Nitadori, I. Ledoux, A. Singh, J. A. G. Williams, Munetaka Akita, V. Guerchais, H. Le Bozec, *Inorg. Chem.*, 2012, **51**, 5627.
2. B. A. McClure, J. J. Rack, *Inorg. Chem.*, 2011, **50**, 7586.
3. Y.-M. Hervault, C. M. Ndiaye, L. Norel, C. Lagrost, S. Rigaut, *Org. Lett.*, 2012, **14**, 4454.
4. T. T. To, E. J. Heilweil, C. B. Duke III, K. R. Ruddick, C. E. Webster, T. J. Burkey, *J. Phys. Chem. A*, 2009, **113**, 2666.
5. P. Zhang, D. J. Berg, R. H. Mitchell, A. Oliver, B. Patrick, *Organometallics*, 2012, **31**, 8121.
6. 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.
7. 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, **24**, 3636.
8. E. J. Heilweil, J. O. Johnson, K. L. Mosley, P. P. Lubet, C. E. Webster, T. J. Burkey, *Organometallics*, 2011, **30**, 5611.
9. 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.
10. 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.
11. M. I. Rybinskaya, L. M. Korneva, *J. Organomet. Chem.*, 1982, **231**, 25.
12. A. A. Sorencen, G. K. Yang, *J. Am. Chem. Soc.*, 1991, **113**, 7061.
13. L. Li, G. Zhang, Z. Pang, *J. Organomet. Chem.*, 2010, **695**, 588.
14. R. J. Angelici, W. Loewen, *Inorg. Chem.*, 1967, **6**, 682.
15. Z. Pang, R. F. Johnston, *Polyhedron*, 1999, **18**, 3469.
16. D. M. Teller, S. J. Skoog, R. G. Bergman, T. B. Gunnoe, W. D. Harman, *Organometallics*, 2000, **19**, 2428.
17. B. H. G. Swennenhuis, R. Poland, N. J. DeYonker, Ch. E. Webster, D. J. Darensbourg, A. A. Bengah, *Organometallics*, 2011, **30**, 3054.
18. E. S. Kelbysheva, L. N. Telegina, I. A. Godovikov, T. V. Strelkova, M. G. Ezernitskaya, B. V. Lokshin, N. M. Loim, *Russ. Chem. Bull.* (*Int. Ed.*), 2013, **62**, 2083 [*Izv. Akad. Nauk, Ser. Khim.*, 2013, 2083].
19. E. S. Kelbysheva, L. N. Telegina, I. A. Godovikov, T. V. Strelkova, A. F. Smol´yakov, F. M. Dolgushin, N. M. Loim, *Russ. Chem. Bull.* (*Int. Ed.*), 2012, **61**, 2326 [*Izv. Akad. Nauk, Ser. Khim.*, 2012, 2304].
20. S. Pitter, G. Huttner, O. Walter, L. Zsolnai, *J. Organomet. Chem.*, 1993, **454**, 183.
21. E. O. Fischer, K. Pleszke, *Chem. Ber.*, 1958, **91**, 2719.
22. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, I. B. Zlotina, *Dokl. Akad. Nauk SSSR*, 1964, **154**, 391 [*Dokl. Chem.* (*Engl. Transl.*), 1964].
23. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
24. C. Lee, W. Yang, R. G. Parr, *Phys. Rev.*, 1988, **150**, 785.
25. T. H. Dunning, Jr., P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. P. Schaefer III, Plenum Press, New York, 1976, pp. 1—28.
26. M. J. Frisch, G. W. Trucks, H. B. Schlege, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, Jr., J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Strain, M. C. Kudin, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, Revision A.5, Gaussian, Inc., Pittsburgh (PA), 1998.

Received October 1, 2014;
in revised form November 24, 2014