

Investigation of the Photochemical Behaviour of Tricarbonyl-(cyclopentadienyl)manganese Derivatives with Carbamate Groups

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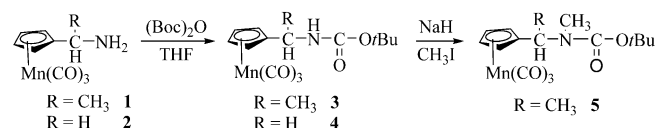
Photochemical properties of cymantrene carbamates were for the first time investigated. It was found that UV irradiation of Boc-substituted 1-aminoalkylcymantrenes yields dicarbonyl chelate complexes as a result of the coordination of the oxygen atom of the carbamate ligand to the manganese atom. These complexes show high thermodynamic and kinetic sta-

bility in solution at room temperature and in closed systems can be used for the creation of photochromic systems based on cymantrene carbamates.

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Introduction

Photochemical substitution of CO ligands in transition-metal carbonyl complexes is a well-known, simple and efficient method for modification of these compounds. In particular, in a series of tricarbonyl(cyclopentadienyl)-manganese (cymantrene) complexes, this method is traditionally used for the preparation of derivatives containing phosphanes, phosphites, olefins, acetylenes, amines, sulfides, nitriles and other σ - and π -donor molecules as ligands at the manganese atom.^[1a–1f,2–9] Some compounds having phosphane, pyridine, nitrile, sulfide and thioamide substituents in the Cp ring can form stable intramolecular chelates.^[1j,3–7] Recently, it was shown that cymantrene-based chelate complexes open new possibilities for the creation of photochromic systems.^[7] With the aim of searching for cymantrene derivatives, which can be used for the creation of reversible photochromic systems, we studied the photochemical behaviour of *tert*-butylcarbamates of α -aminoalkylcymantrenes (Scheme 1).



Scheme 1.

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Results and Discussion

UV irradiation of a colourless solution of Boc-substituted 1-aminoethylcymantrene (**3**) in benzene resulted in the appearance of a crimson colour, which persisted at 10–25 °C for several hours. The analysis of the photolysis products of **3** by TLC indicated the full disappearance of the initial compound ($R_f = 0.53$; hexane/ethyl acetate, 3:1). A similar picture was observed in the case of the photolysis of carbamates **4** and **5**.

Monitoring of the photolysis of compounds **3–5** in benzene by IR spectroscopy showed that, parallel with the disappearance of two $\nu(\text{CO})$ bands of the initial tricarbonyl complexes, two new $\nu(\text{CO})$ bands of equal intensities appeared that are associated with dicarbonyl manganese derivatives (Table 1). Simultaneously the $\nu(\text{CO})$ band of the carbamate group in the range of 1700 cm⁻¹ shifted to a low frequency range by ca. 50 cm⁻¹; in the case of carbamates **3** and **4** the centre of the $\nu(\text{NH})$ band was about 5–10 cm⁻¹ downshifted (Table 1).

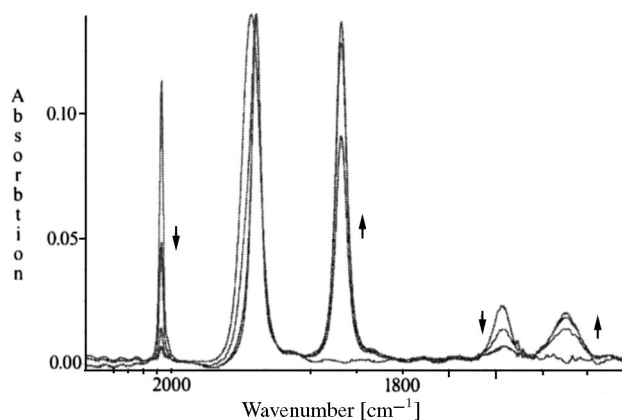
Similar spectral changes were observed in the case of photolysis of carbamates in hexane and THF (Table 1). The similarity of spectral parameters for complex **6** in benzene, hexane and THF indicates that, even with irradiation of the carbamates in THF, the carbamate group occupies a free coordination site of the manganese atom. In all solvents, isosbestic points were observed (Figure 1) indicating that, within the IR timescale, only two types of complexes exist in solution, namely, with three and two carbonyl ligands at the manganese atom. Thus, the IR spectra show that stabilization of dicarbonyl complexes **6–8** occurs as a result of intramolecular bonding between the manganese atom and the CO group in the carbamate substituent. The capacity of carbamates to act as a ligand at intermolecular interac-

Table 1. $\nu(\text{CO})$ frequencies for carbamates **3–5** and dicarbonyl complexes **6–8**.

Compound	$\nu(\text{CO})$	$\nu(\text{CO})$ of carbamate group	$\nu(\text{NH})$ of carbamate group
3	2040, 1930 ^[a]	1717 ^[a]	≈ 3424 (br.) ^[a]
	2018, 1932 ^[b]	1714 ^[b]	≈ 3310 (br.) ^[b]
	2025, 1948 ^[c]	1727 ^[c]	≈ 3451 (br.) ^[c]
6	1930, 1857 ^[a]	1666 ^[a]	≈ 3405 (br.) ^[a]
	1929, 1854 ^[b]	1658 ^[b]	≈ 3275 (br.) ^[b]
	1943, 1874 ^[c]	1675 ^[c]	≈ 3441 (br.) ^[c]
4	2022, 1933 ^[a]	1719 ^[a]	≈ 3438 (br.) ^[a]
7	1933, 1856 ^[a]	1668 ^[a]	≈ 3421 (br.) ^[a]
5	2020, 1935 ^[a]	1694 ^[a]	
8	2027, 1947 ^[c]	1708 ^[c]	
	1955, 1854 ^[a]	1640 ^[a]	
	1940, 1871 ^[c]	1649 ^[c]	

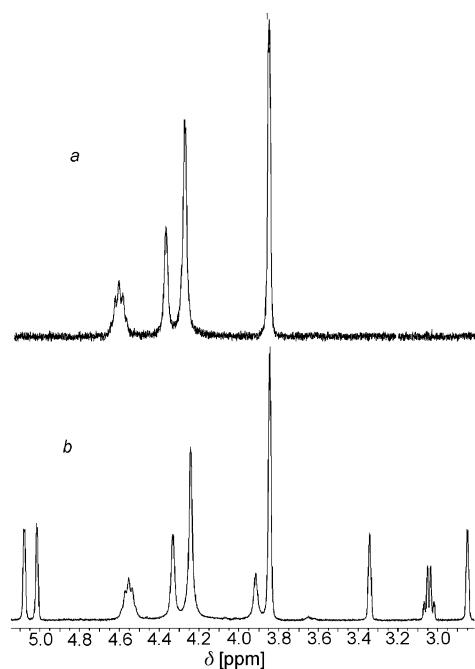
[a] The spectra were measured in benzene. [b] The spectra were measured in THF. [c] The spectra were measured in hexane.

tion is low. We found that photolysis of cymantrene in benzene in the presence of Boc-substituted phenylethylamine (**10**) resulted in the appearance of a light crimson colour due to the formation of the dicarbonyl complex, and this colour change was only observed with a cymantrene/**10** ratio of no less than 1:10.

Figure 1. IR spectra in the $\nu(\text{CO})$ range for **3** (2.6 mM in THF) over the course of irradiation. Overall irradiation time was 6 min.

The ^1H NMR spectra registered in the course of photolysis of carbamates **3–5** in benzene also indicated that only two types of complexes existed throughout the reaction. Coordination of the CO group of the carbamate fragment to the manganese atom results in a substantial difference in the spectra of tricarbonyl and dicarbonyl compounds. In particular, during the photolysis of carbamates **3** and **4**, the position and multiplicity of the signal for the protons at the 1-carbon of the substituent change. In the case of compound **3**, a doublet of quartets at $\delta = 4.58$ ppm ($J = 6.8$ Hz between $\text{CH}-\text{CH}_3$ and $J = 5.9$ Hz between $\text{CH}-\text{NH}$) turns

into a quartet at $\delta = 3.06$ ppm ($J = 6.7$ Hz), the doublet for the CH_2 protons of complex **4** at $\delta = 3.52$ ppm ($J = 5.8$ Hz) transforms into a singlet at $\delta = 3.11$ ppm (Figure 2 and Experimental Section). In the ^1H NMR spectrum of carbamate **5**, there are two sets of signals for two conformers resulting from the rotation about the C–N bond of the substituent. After photolysis only one signal set is observed for complex **8**, which is indicative of the lack of conformational isomerism in the coordinated carbamate group. Upon transformation of carbamates **3–5** into corresponding dicarbonyl compounds **6–8**, the signals for the β -protons of the Cp ring undergo an upfield shift, whereas the signals for the α -protons of the Cp ring are shifted downfield, so that anisotropy increases by an average value of 2 ppm. (The signal assignment for the α - and β -protons of the Cp ring is given in the Experimental Section.) In the case of chiral compounds, the chemical shifts for the diastereotopic α -H and α' -H, as well as for the β - and β' -protons of the Cp ring become significantly nonequivalent. For complexes **6** and **8**, the differences between the signals for β -H and β' -H are 0.49 and 0.94 ppm, whereas those for α -H and α' -H are 0.06 and 0.01 ppm, respectively. Significant differences between nonequivalent Cp signals were observed earlier for cymantrene and benzenetricarbonyl chromium derivatives and were considered characteristic properties of this type of chelate complex.^[3–7,10] The formation of the rigid chelate cycle hinders the internal rotation about the Mn–Cp-ring centroid bond. This creates two anisotropic areas in the cyclopentadienyl ring, one of which is under the influence of the CO groups and the other is affected by the coordinated carbamate groups.

Figure 2. ^1H NMR spectra of **3** (15 mM in $[\text{D}_6]\text{benzene}$) at 23 °C: (a) before irradiation, (b) after 5 min irradiation.

The formation of dicarbonyl compounds **6–8** exhibits itself in the UV spectra, where two new absorption bands appear near 420 (shoulder) and 520 nm (Figure 3). The position and intensity of these bands weakly depend on the nature of the solvent (hexane, benzene, ethanol and THF; see the Experimental Section). The parameters of the UV spectra are similar to those for cymantrene derivatives containing THF or alkylamines coordinated to the manganese atom; these cymantrene derivative have an absorption band at about 500 nm assigned to LF bands associated with “d–d” transitions rather than to metal–ligand charge transfer.^[8,9] This fact provides reason to suppose that in our case, these transitions have the same nature. This supposition is confirmed by DFT calculations. It follows from analysis of HOMO and LUMO coefficients that low-energy transitions of UV spectra have dominant d–d character. Nevertheless, collaboration of the carbamate group AO in forming of the first and second LUMO did not accept a partial CT character of transition.

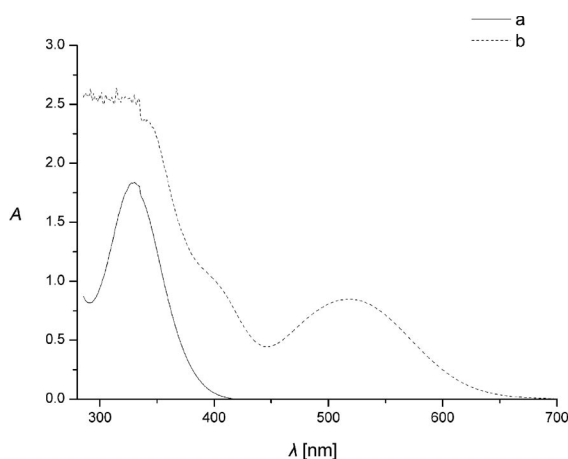


Figure 3. UV/Vis spectra of **3** (3.5 mM in benzene) at room temperature: (a) before irradiation, (b) after 5 min irradiation (100% conversion by IR spectra).

The circular dichroism (CD) spectra measured during irradiation of the (*R*) enantiomer of compound **3** in benzene, ethanol or THF show that, instead of one negative Cotton effect near 360 nm, three Cotton effects with alternating signs arise, the positions of which coincide with the absorption bands in the UV spectra. An increase in the rotary force of the Cotton effects for the dicarbonyl complex indicates that local symmetry around the Mn atom changes as a result of chelation of the side chiral substituent. A mirror-like picture of spectral changes in the CD spectra is observed upon irradiation of the (*S*) enantiomer of **3**. When the conversion of (*S*)-**3** achieves 50%, the Cotton effect bands are observed only for two compounds: the dicarbonyl and tricarbonyl complexes (Figure 4).

The data considered above have led to the conclusion that photolysis of cymantrenyl carbamates resulted in thermodynamically stable chelate dicarbonyl complexes, in which the Mn atom is coordinated to the O atom of the carbamate substituent. Unfortunately, our attempts to obtain crystals of chelate complexes for X-ray analysis failed.

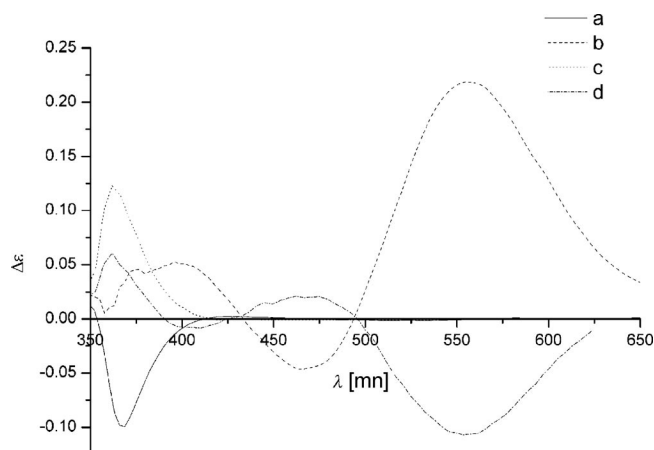


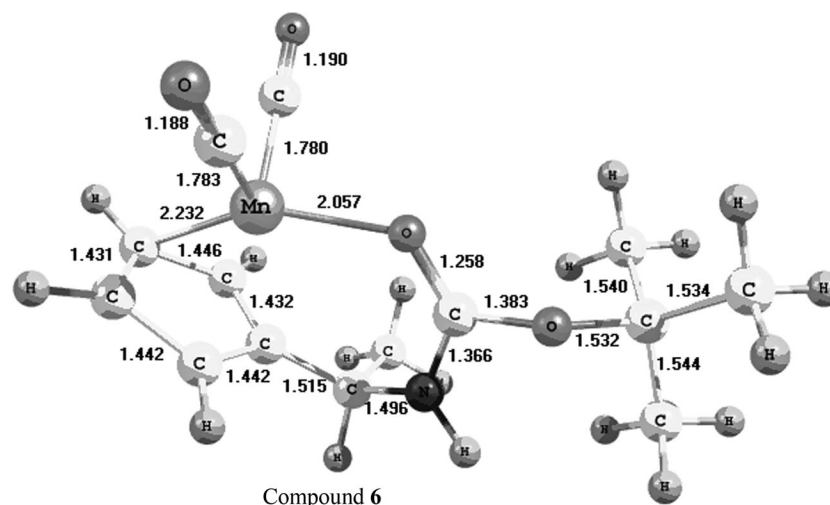
Figure 4. (a,b) CD spectra of (*R*)-**3** (2.45 mM in benzene) and (c,d) (*S*)-**3** (6.7 mM in benzene) at room temperature: (a and c) before irradiation, (b) after 5 min irradiation and (d) after 3 min irradiation.

However, the DFT calculations for these complexes confirm the proposed structure, and the global minimum differs in energy from the tricarbonyl complexes by 30 kcal mol^{−1} (Figure 5 and Table 2). The calculated values for the position and intensity of the ν(CO) bands of the carbamate group agreed with the experimental data (Table 2).

Irradiation of carbamates **3–5** by a UV lamp in the closed system, in which the CO formed was not removed from the reaction, yielded complexes **6–8**, which transformed into parent tricarbonyl complexes in a dark process at room temperature. After three- and fourfold repetition of the process: irradiation–dark reaction, both the total view of the IR spectrum and the stretching mode intensities for CO groups in the starting compound and the product did not change with the experimental accuracy (Scheme 2).

Direct reaction of the resulting dicarbonyl chelate proceeded with approximately the same rate whether the reaction mixture was irradiated with the full spectrum of the UV lamp or with a wavelength of 300–400 nm, which corresponds to the position of the longwave absorption band in the UV spectrum of the parent carbamate. In both cases, the half-conversion time was about 3 min, counting from the moment of switching on the lamp, or 30 s, counting from the moment of stabilization of the work of the lamp (10 min). The quantum yield for 366 nm irradiation is 0.98 ± 0.04 in all cases, which is in accord with the literature data.^[9,11] The reverse reaction proceeded much slower: the half-conversion time was 60–90 min, but a sharp acceleration of the reverse reaction occurred (half-conversion time was about 10 min) when the reaction mixture was irradiated with a wavelength of 480–530 nm corresponding to the maximum of the first longwave band in the UV spectra of chelates (Scheme 2).

Thus, we found that photolysis of cymantrenyl carbamates in closed systems can be used for the creation of novel photochromic systems. Availability of cymantrenyl

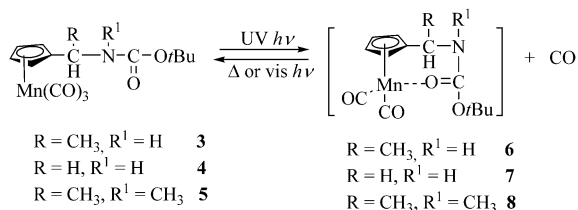


Compound 6

Figure 5. The calculated structure of chelate complex 6.

Table 2. Calculated energies and $\nu(\text{CO})$ for carbamates 3–5 and dicarbonyl complexes 6–8.

Compound	E [a.u.], ΔE [kcal mol ⁻¹]	E' [a.u.], $\Delta E'$ [kcal mol ⁻¹]	G [a.u.], ΔG [kcal mol ⁻¹]	Calculated $\nu(\text{CO})$
3	-1117.15, –	-1116.84, –	-1116.89, –	1991(770), 1930 (922), 1920 (909), 1678 (579)
6	-1003.80, +182.88	-1003.50, +171.08	-1003.55, +127.11	1933 (897), 1876 (1041), 1651 (449)
4	-1077.84, –	-1077.55, –	-1077.61, –	1989 (768), 1926 (914), 1921 (920), 1690 (593)
7	-964.49, +180.67	-964.21, +170.00	-964.26, +129.41	1936 (901), 1878 (1058), 1650 (560)
5	-1156.45, –	-1156.05, –	-1156.10, –	1993 (772), 1934 (925), 1919 (902), 1660 (570)
8	-1043.11, +159.08	-1042.72, +145.35	-1042.77, +113.38	1934 (895), 1874 (1030), 1654 (401)



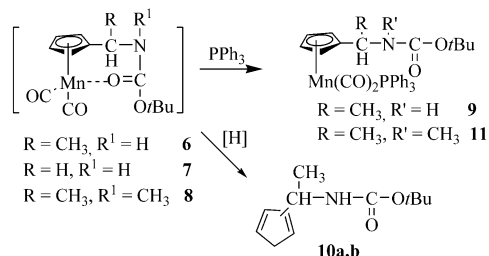
Scheme 2.

carbamates in the optically active form allows their use for selective excitation of circular polarized light.

The slow rate of the reverse reaction without initiation by visible light points to rather high thermodynamic and kinetic stability of chelates in ligand-substitution reactions. Thus, irradiation of compound 3 in the closed system in the presence of triphenylphosphane (1.5 equiv.) yields only chelate dicarbonyl complex 6. Moreover, the only product of the dark reaction of this chelate is the parent carbamate. Nevertheless, the substitution of CO for PPh₃ occurred in a yield of 41 % after 45 min, when the photolysis of an equimolecular mixture of carbamate 3 and triphenylphosphane was run in the photoreactor under an intensive argon flow. The yield of triphenylphosphane complex 9 increased to 83% when the irradiation of carbamate 3 was followed by the addition of PPh₃, then the dark reaction was performed

at 30–40 °C for 4–5 h. In this case, unreacted dicarbonyl complex 6 results in the formation of a product with $R_f = 0.85$ (hexane/ethyl acetate, 3:1). The generation of this product takes place in a yield of 60 % at the irradiation of compound 3 without PPh₃. It was isolated by column chromatography as a yellow oil. The IR spectrum of this oil has no bands in the range of 1800–2100 cm⁻¹ (MCO stretch), but there was a strong absorption at 1700 cm⁻¹ associated with the CO groups of the carbamates. In the ¹H NMR spectrum, there were six resonances from olefin protons in the range of 6–7 ppm, as well as the signals from the protons of the CH₃, *t*Bu, CH and NH groups (see Experimental Section). These data, as well as the presence of the molecular ion at $m/z = 209$ in the mass spectrum gave reason to believe that the fraction with $R_f = 0.85$ (hexane/ethyl acetate, 3:1) mainly contained two isomeric olefins 10a,b in a ratio of 1:1.3. Unfortunately, we failed to prepare pure samples for analysis, because these olefins partially decomposed in the course of chromatographic purification. Apparently, olefins 10a,b are formed due to decomplexation of the cyclopentadienyl ligand from the intermediate dicarbonyl manganese complex during isolation of photolysis products. Earlier, we observed the formation of cyclopentadienes in the photolysis of diphenylcymantrenylphosphane.^[2] Recently the photolysis of cymantrene derivatives in proton donor solvents has been reported as an efficient

method for the synthesis of substituted cyclopentadienes.^[12a,12b] Actually, the photolysis of carbamate **3** in a mixture of diethyl ether/methanol (1:2) gives the same mixture **10a,b** with a product yield of 86%. A similar picture was observed in the case of the photolysis of carbamates **4** and **5**. In the case of compound **5**, triphenylphosphane complex **11** was isolated and characterized (Scheme 3).



Scheme 3.

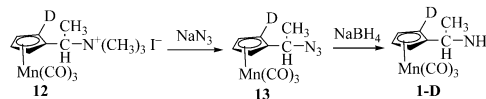
Conclusions

Photochemical properties of cymantrene carbamates were for the first time investigated by IR, NMR, UV and CD spectroscopic methods. It was found that UV irradiation of Boc-substituted 1-aminoalkylcymantrenes yields dicarbonyl chelate complexes as a result of the coordination of the oxygen atom of the carbamate ligand to the manganese atom. The possibility for the formation of chelate complexes was confirmed by DFT calculations. Dicarbonyl chelates show high thermodynamic stability in solution at room temperature and in closed systems can be used for the creation of photochromic systems based on cymantrene carbamates due to reverse dissociation and recombination of CO ligand.

Experimental Section

General Data: ¹H and ³¹P NMR spectra were registered with a Bruker Avance 400 (400.13 and 161.98 MHz, respectively) spectrometer. Chemical shifts were referenced to TMS by using residual solvent protons as an internal standard. ESI mass spectra were obtained with a Finnigan LCQ Advantage instrument. IR spectra were measured with a Magna 750-IR (Nicolet) IR Fourier spectrometer in a cell with KBr windows. UV spectra were recorded with a Specord M-40 UV/Vis spectrophotometer. CD spectra were measured with an automatic recording spectrometer SKD-2 (Institutes of Molecular Biology and Spectroscopy, RAS). Specific rotation angles were measured by using a Perkin–Elmer 341 polarimeter at a wavelength of 589 nm. Photochemical reactions were carried out by using a UV immersion lamp Normag TQ 150 (running of stationary conditions were realized in 3 min.) and filters passing bands of 300–400 nm and 480–530 nm. Tetrahydrofuran (THF), hexane and benzene were purified by conventional methods and distilled from sodium benzophenone ketyl under an atmosphere of argon. 1-Aminoethylcymantrene (**1**) and its (*R*) and (*S*) enantiomers and cymantrenecarbaldehyde were prepared according to the methods reported earlier.^[13,14] The signals for the α- and β-protons of the Cp ring were assigned by using phase-sensitive 2D NOESY, as well as comparing with the NMR spectra of deuterated ana-

logues. These deuterated compounds were prepared from α-deuteriocymantrenecarbaldehyde^[14] and 1-(*N,N,N*-trimethylammonium)-ethyl(α-deuteriocymantrene) iodide (**12**)^[13,15] according to Scheme 4.



Scheme 4.

1-Azidoethyl(α-deuteriocymantrene) (13): Sodium azide (8.1 g, 120 mmol) was dissolved in 75% aqueous diglyme (100 mL) with heating. The solution was filtered, then compound **12** (5 g, 12 mmol) was added. The reaction mixture was heated at 100 °C under an argon atmosphere in darkness for 55 h. Water (200 mL) was added and the organics were extracted with diethyl ether (3 × 200 mL). The organic layer was washed with water to pH 7 and dried with MgSO₄; then, the solvent was evaporated. The residue was distilled in vacuo. B.p. 101–102 °C/0.08 Torr. Yield: 2 g (61%). ¹H NMR (400.13 MHz, CDCl₃): δ = 1.45 (d, *J* = 6.6 Hz, 3 H, CH₃), 4.24 (qd, *J* = 6.6 Hz, 1 H, CHCH₃), 4.65 (m, 1 H, Cp-H), 4.81 (m, 2 H, Cp-H) ppm. C₁₀H₈MnN₃O₃ (273.13): calcd. C 43.90, H 2.95, Mn 20.12; found C 44.09, H 3.02, Mn 19.93.

1-Aminoethylcymantrene (1-D): NaBH₄ (0.68 g, 18 mmol) was added in portion to a solution of **13** (2 g, 7.3 mmol) in 2-propanol (30 mL), and the reaction mixture was heated at reflux for 16 h. Then, 20% H₃PO₄ (100 mL) was added dropwise, and the organics were extracted with diethyl ether. The aqueous layer was brought to pH 10 with 2 N NaOH, and the organics were extracted with diethyl ether. The combined ether layers were washed with water to pH 8 and dried with MgSO₄, and the solvent was evaporated. The residue was distilled in vacuo. B.p. 87–88 °C/8 × 10^{−2} Torr (ref.^[15] b.p. 80–81 °C/6 × 10^{−2} Torr). Yield: 1 g (55%). ¹H NMR (400.13 MHz, CDCl₃): δ = 1.28 (d, *J* = 6.4 Hz, 3 H, CH₃), 3.74 (qd, *J* = 6.4 Hz, 1 H, CHCH₃), 4.58 (m, 1 H, βH-Cp), 4.64 (m, 1 H, βH-Cp), 4.71, 4.81 (m, 0.5 H, αH-Cp) ppm.

Cymantrenecarbaldehyde Oxime (14): Cymantrenecarbaldehyde (14 g, 60 mmol), NH₂OH·HCl (6.4 g, 91 mmol) and sodium acetate (9.3 g, 113 mmol) were dissolved in ethanol (100 mL), and the reaction mixture was heated at reflux for 1 h. Then the reaction mixture was cooled and concentrated to 1/4 volume. Water (100 mL) was added to the residue, and the organics were extracted with diethyl ether (3 × 100 mL). The organic layer was washed with 2 N H₂SO₄ (75 mL) and water to pH 7 and dried with MgSO₄. The solvent was evaporated, and the residue was crystallized from benzene. Yellow crystalline oxime was isolated. M.p. 144–145 °C. Yield: 11.2 g (76%). ¹H NMR (400.13 MHz, [D₆]acetone) showed a mixture of two isomers in a ratio of 2:1. Major isomer: δ = 5.05 (m, 2 H, Cp-H), 5.69 (m, 2 H, Cp-H), 7.16 (s, 1 H, CH), 11.01 (s, 1 H, NOH) ppm; minor isomer: δ = 5.05 (m, 2 H, Cp-H), 5.39 (m, 2 H, Cp-H), 7.82 (s, 1 H, CH), 10.51 (s, 1 H, NOH) ppm. MS (ESI): *m/z* = 247 [M⁺], 163 [M⁺/3CO]. C₉H₆MnNO₄ (247.15): calcd. C 43.76, H 2.45, N 5.66, Mn 22.25; found C 44.01, H 2.38, N 5.70, Mn 21.95.

Aminomethylcymantrene (2): Zn (13.5 g, 206 mmol) was gradually added to a solution of oxime **15** (8.5 g, 34.4 mmol) in acetic acid (35 mL) and water (2.5 mL). The process was exothermic. Then, the reaction mixture was heated at reflux for 30 min, cooled to 80 °C and filtered off. The precipitate on the filter was washed with acetic acid. The combined filtrates were neutralized to pH 9 with 25% ammonia water, and the organics were extracted with diethyl ether. The organic layer was washed with 2 N NaOH (50 mL) and

dried with MgSO_4 , and the solvent was evaporated. The residue was distilled in vacuo. B.p. 110–111 °C/ 8×10^{-2} Torr (ref.^[16] b.p. 80–81 °C/ 6×10^{-2} Torr). Product **2** was isolated as a yellow oil. Yield: 6 g (75%). ^1H NMR (400.13 MHz, $[\text{D}_8]\text{toluene}$): δ = 0.75 (br. s, 2 H, NH_2), 3.05 (m, 2 H, CH_2), 4.05 (m, 2 H, Cp-H), 4.21 (m, 2 H, Cp-H) ppm. MS (ESI): m/z = 233 $[\text{M}^+]$, 149 $[\text{M}^+/\text{3CO}]$.

Boc-Substituted 1-Aminoethylcymantrene (3): A solution of 1-aminoethylcymantrene (**1**; 2.47 g, 10 mmol) and $(\text{Boc})_2\text{O}$ (2.5 g, 11.5 mmol) in THF (30 mL) was stirred for 1 h. Then, the solvent was evaporated, and the residue was crystallized from hexane. Yellow crystals of **3** were isolated. M.p. 76–77 °C. Yield: 3.33 g (96%). ^1H NMR (400.13 MHz, $[\text{D}_6]\text{benzene}$): δ = 0.91 (d, J = 6.8 Hz, 3 H, CHCH_3), 1.54 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 3.67 (m, 2 H, Cp-H β), 4.26 (m, 2 H, αH -Cp), 4.35 (br. s, 1 H, NH), 4.58 (m, 1 H, CHCH_3) ppm. IR (benzene): $\tilde{\nu}$ = 2040 $[\text{v}(\text{CO})]$, 1930 (MCO), 1717 $[\text{v}(\text{C}=\text{O})]$ cm^{-1} . IR (hexane): $\tilde{\nu}$ = 2025, 1948 $[\text{v}(\text{CO})]$; 1727 $[\text{v}(\text{C}=\text{O})]$ cm^{-1} . IR (THF): $\tilde{\nu}$ = 2018, 1932 $[\text{v}(\text{CO})]$, 1714 $[\text{v}(\text{C}=\text{O})]$ cm^{-1} . UV (benzene): λ (ϵ , L mol^{-1}) = 330 (531) nm. UV (THF): λ (ϵ , L mol^{-1}) = 331 (946) nm. $\text{C}_{15}\text{H}_{18}\text{MnNO}_5$ (347.33): calcd. C 51.88, H 5.22, N 4.03, Mn 15.82; found C 51.99, H 5.22, N 4.09, Mn 15.9.

Boc-Substituted Aminomethylcymantrene (4): The compound was synthesized by the same procedure as **3** starting from **2** (6 g, 26 mmol) and Boc_2O (6.5 g, 30 mmol). The yield of **4** was 8.3 g (96%). Yellow solid. M.p. 86–87 °C. ^1H NMR (400.13 MHz, $[\text{D}_6]\text{benzene}$): δ = 1.51 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 3.52 (m, J = 5.8 Hz, 2 H, CH_2), 3.88 (m, 2 H, βH -Cp), 4.22 (m, 2 H, αH -Cp), 4.31 (br. s, 1 H, NH) ppm. IR (benzene): $\tilde{\nu}$ = 2022, 1933 $[\text{v}(\text{CO})]$; 1719 $[\text{v}(\text{C}=\text{O})]$ cm^{-1} . UV (benzene): λ (ϵ , L mol^{-1}) = 332 (1372) nm. $\text{C}_{14}\text{H}_{16}\text{MnNO}_5$ (333.3): calcd. C 50.46, H 4.84, N 4.20, Mn 16.49; found C 50.63, H 4.88, N 4.15, Mn 16.65.

Boc-Substituted (N-Methyl-1-aminoethyl)cymantrene (5): A solution of **3** (3.47 g, 10 mmol) in DMFA (20 mL) was cooled to 0 °C under an atmosphere of argon with stirring. Then, a 60% suspension of sodium hydride (1.2 g, 30 mol) was gradually added, and the mixture was kept at 0 °C for 1 h. Methyl iodide (5.04 mL, 80 mmol) was added. The mixture was heated to room temperature and stirred for 2 h and then poured into water (50 mL); the organics were extracted with diethyl ether ($3 \times 75\text{ mL}$). The organic layer was dried with MgSO_4 , the solvent was evaporated and a yellow oil was isolated. The product was purified by silica gel column chromatography (benzene). Yield: 2.6 g (71%). ^1H NMR (400.13 MHz, $[\text{D}_6]\text{benzene}$): revealed a mixture of two conformers in a ratio of 3:2. Major conformer: δ = 1.01 (d, J = 7.1 Hz, 3 H, CHCH_3), 1.55 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.46 (s, 3 H, NCH_3), 3.84 (m, 1 H, Cp-H β), 4.01 (m, 1 H, Cp-H β'), 4.24 (m, 1 H, Cp-H α), 4.46 (m, 1 H, Cp-H α'), 5.38 (m, 1 H, CHCH_3) ppm; minor conformer: δ = 1.01 (d, J = 7.1 Hz, 3 H, CHCH_3), 1.55 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.53 (s, 3 H, NCH_3), 3.84 (m, 1 H, Cp-H β), 4.01 (m, 1 H, Cp-H β'), 4.17 (m, 1 H, Cp-H α), 4.52 (m, 1 H, Cp-H α'), 5.07 (m, 1 H, CHCH_3) ppm. IR (benzene): $\tilde{\nu}$ = 2020, 1935 $[\text{v}(\text{CO})]$; 1694 $[\text{v}(\text{C}=\text{O})]$ cm^{-1} . IR (hexane): $\tilde{\nu}$ = 2027, 1947 $[\text{v}(\text{CO})]$; 1708 $[\text{v}(\text{C}=\text{O})]$ cm^{-1} . UV (benzene): λ (ϵ , L mol^{-1}) = 330 (725) nm. UV (hexane): λ (ϵ , L mol^{-1}) = 330 (301) nm. $\text{C}_{16}\text{H}_{20}\text{MnNO}_5$ (361.36): calcd. C 53.18, H 5.54, N 3.88, Mn 15.24; found C 53.77, H 5.98, N 3.85, Mn 14.83.

Boc-Substituted (1-Aminoethylcyclopentadienyl)dicarbonyl(triphenylphosphane)manganese (9)

Method A: A solution of compound **3** (870 mg, 2.5 mmol) and PPh_3 (650 mg, 2.5 mmol) in benzene (300 mL) was placed in a photoreactor and cooled to 7 °C under an atmosphere of argon with stirring. The solution was then irradiated using the UV immersion lamp. Just after the beginning of irradiation the solution colour became crimson. The irradiation was run at 7–9 °C for 45 min. An

hour later the solution became yellow, and its TLC showed two zones. The solution was filtered, the solvent was evaporated. 1.3 g of the crude product was obtained. The mixture of two products was separated by column chromatography on SiO_2 (benzene). Two fractions were isolated: complex **9** in a yield of 500 mg (41%) R_f = 0.64 (hexane/ethyl acetate, 3:1) and olefin **10** in a yield of 250 mg (48%) R_f = 0.85 (hexane/ethyl acetate, 3:1). Complex **6** exists as yellow crystals. M.p. 176–178 °C. ^1H NMR (400.13 MHz, $[\text{D}_6]\text{benzene}$): δ = 1.51 (d, J = 6.6 Hz, 3 H, CHCH_3), 1.75 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 4.05 (m, 2 H, Cp-H β), 4.65 (m, 2 H, Cp-H α), 4.92 (br. s, 1 H, NH), 5.11 (m, 1 H, CHCH_3), 7.29 (m, 10 H, PPh_3), 7.83 (m, 5 H, PPh_3) ppm. ^{31}P NMR (161.98 MHz, $[\text{D}_6]\text{benzene}$): δ = 92.6 (s, PPh_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1940, 1875 $[\text{v}(\text{CO})]$ cm^{-1} . $\text{C}_{32}\text{H}_{33}\text{MnNO}_4\text{P}$ (581.65): calcd. C 66.09, H 5.71, N 2.41, P 5.33; found C 66.12, H 5.64, N 2.35, P 5.19.

Method B: A solution of compound **3** (870 mg, 2.5 mol) in benzene (300 mL) was cooled to 7 °C under an atmosphere of argon with stirring. The solution was then irradiated using the UV immersed lamp. Just after the beginning of irradiation the solution gained a crimson colour. The irradiation was run at 7–9 °C for 30 min. Then, PPh_3 (980 mg, 0.00375 mol) was added, and the reaction mixture was stirred at 35–40 °C for 4 h and kept overnight. Two products were formed. The solution was filtered, the solvent was evaporated. 1.4 g of an oily residue was obtained. This oil was separated by column chromatography on SiO_2 (benzene). Two fractions were isolated: complex **9** in a yield of 1 g (83%) and olefin **8** in a yield of 80 mg (15%). The spectral characteristics of this complex were identical to those of **6** obtained by method A.

Boc-Substituted 1-Aminoethylcyclopentadienes (10a,b): A solution of compound **3** (501 mg, 1.4 mmol) in benzene (300 mL) or diethyl ether/methanol (1:2) was cooled to 7 °C under an atmosphere of argon with stirring. The solution was then irradiated using the UV immersed lamp. Immediately after the beginning of irradiation the solution became crimson. The reaction mixture was irradiated at 7–9 °C for 45 min and kept in darkness overnight. The solution was filtered, the solvent was evaporated and the crude product (350 mg) was purified by column chromatography on SiO_2 (benzene). Compounds **10a,b** were isolated as yellow oils. Yield in benzene: 177 mg (59%). Yield in diethyl ether/MeOH: 251 mg (86%). ^1H NMR (400.13 MHz, $[\text{D}_6]\text{benzene}$) revealed a mixture of two isomers in a ratio of 1:1.3. Major isomer: δ = 1.33 (d, J = 6.6 Hz, 3 H, CHCH_3), 1.65 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.85 (m, 2 H, CH_2 -Cp), 4.48 (m, 1 H, CHCH_3), 6.04 (m, 1 H, CH-Cp), 6.33 (m, 1 H, CH-Cp), 6.60 (m, 1 H, CH-Cp) ppm; minor isomer: δ = 1.26 (d, J = 6.6 Hz, 3 H, CHCH_3), 1.65 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.85 (m, 2 H, CH_2 -Cp), 4.40 (m, 1 H, CHCH_3), 4.89 (br. s, 1 H, NH), 6.22 (m, 1 H, CH-Cp), 6.42 (m, 1 H, CH-Cp), 6.49 (m, 1 H, CH-Cp) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1700 $[\text{v}(\text{C}=\text{O})]$ cm^{-1} . MS (ESI): m/z = 209 $[\text{M}^+]$.

Boc-Substituted Dicarbonyl(N-methyl-1-aminoethylcyclopentadienyl)(triphenylphosphane)manganese (11): As in the case of the synthesis of **6** by method B, compound **5** (0.90 g, 0.0025 mol) and PPh_3 (0.98 g, 0.00375 mol) gave an oily residue, from which complex **11** was isolated as a yellow powder by column chromatography on SiO_2 (benzene) in a yield of 0.8 g (54%). M.p. 148–149 °C. ^1H NMR of **7** (400.13 MHz, $[\text{D}_6]\text{benzene}$) showed a mixture of two conformers in a ratio of 1:1.2. Major isomer: δ = 1.20 (d, J = 6.1 Hz, 3 H, CHCH_3), 1.50 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.76 (s, 3 H, NCH_3), 4.05 (m, 1 H, Cp-H β), 4.53 (m, 1 H, Cp-H β'), 4.64 (m, 1 H, Cp-H α), 4.82 (m, 1 H, Cp-H α'), 5.61 (m, 1 H, CHCH_3), 7.29 (m, 10 H, PPh_3), 7.80 (m, 5 H, PPh_3) ppm; minor isomer: δ = 1.20 (d, J = 6.1 Hz, 3 H, CHCH_3), 1.50 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.86 (s, 3 H, NCH_3), 4.05 (m, 1 H, Cp-H β), 4.53 (m, 1 H, Cp-H β'), 4.64 (m, 1 H, Cp-

Ha), 4.82 (m, 1 H, Cp-Ha'), 5.86 (m, 1 H, CHCH₃), 7.29 (m, 10 H, PPh₃), 7.80 (m, 5 H, PPh₃) ppm. ³¹P NMR (161.98 MHz, [D₆]benzene): δ = 93.2 (s, PPh₃) ppm. C₃₃H₃₅MnNO₄P (595.68): calcd. C 66.54, H 5.93, N 2.35, P 5.20; found C 66.65, H 5.99, N 2.22, P 5.25.

The General Irradiation Procedure for the Spectral Study of Intramolecular Dicarboxyl Carbamate Complexes: Solutions of tricarboxyl compounds **3–5** in a required solvent (benzene, hexane, ethanol or THF; c = 2–4 mM) were placed under an argon atmosphere into an IR or UV cell, and the samples were irradiated with UV light for 1–2 min with turning of lamp followed by the registration of the spectra, then were repeated. To prepare samples for NMR spectra, these solutions (c = 10–15 mM) were filtered into an NMR tube, bubbled with argon and irradiated with the UV lamp for 4 min. Distance between lamp and sample was 5 cm in all cases. Width of irradiation window was 2 cm in IR cell, 1 cm in UV cell and 5 mm in NMR tube.

Ferrioxalate actinometry was used for 366-nm irradiation.^[17] Photoproduct was identified by UV/Vis and IR spectra by comparison with spectra for authentic samples. Quantitative analyses were made by monitoring electronic spectral changes. Quantum yields were determined from initial spectral changes where optical density changes were linear with irradiation time. The quantum yield is 0.98 ± 0.04 in all cases. This value is for conversion of <15%.

Intramolecular Complex 6: ¹H NMR (400.13 MHz, [D₆]benzene): δ = 0.75 (d, J = 6.7 Hz, 3 H, CHCH₃), 1.13 [s, 9 H, C(CH₃)], 2.87 (m, 1 H, Cp-H β), 3.06 (q, J = 6.7 Hz, 1 H, CHCH₃), 3.36 (m, 1 H, Cp-H β'), 3.94 (br. s, 1 H, NH), 5.04 (m, 1 H, α H-Cp), 5.10 (m, 1 H, α' H-Cp) ppm. IR (benzene): $\tilde{\nu}$ = 1930, 1857 [v(CO)]; 1666 [v(C=O)] cm⁻¹. IR (hexane): $\tilde{\nu}$ = 1943, 1874 [v(CO)]; 1674 [v(C=O)] cm⁻¹. IR (THF): $\tilde{\nu}$ = 1929, 1854 [v(CO)]; 1658 [v(C=O)] cm⁻¹. UV (benzene): λ (ϵ , L mol⁻¹) = 330 (1651), 426 (178), 516 (245) nm. UV (THF): λ (ϵ , L mol⁻¹) = 331 (2760), 426 (212), 511 (246) nm.

Intramolecular Complex 7: ¹H NMR (400.13 MHz, [D₆]benzene): δ = 1.09 [s, 9 H, C(CH₃)], 2.72 (m, 2 H, Cp-H β), 3.11 (s, 2 H, CH₂), 3.70 (br. s, 1 H, NH), 5.07 (m, 2 H, Cp-Ha) ppm. IR (benzene): $\tilde{\nu}$ = 1933, 1856 [v(CO)]; 1668 [v(C=O)] cm⁻¹. UV (benzene): λ (ϵ , L mol⁻¹) = 332 (4253), 426 (271), 516 (200) nm.

Intramolecular Complex 8: ¹H NMR (400.13 MHz, [D₆]benzene): δ = 0.91 (d, J = 7.0 Hz, 3 H, CHCH₃), 1.12 [s, 9 H, C(CH₃)], 2.21 (s, 3 H, NCH₃), 2.71 (m, 1 H, Cp-H β), 3.25 (m, 1 H, CHCH₃), 3.65 (m, 1 H, Cp-H β), 5.17 (m, 2 H, Cp-Ha) ppm. IR (benzene): $\tilde{\nu}$ = 1955, 1854 [v(CO)]; 1640 [v(C=O)] cm⁻¹. IR (hexane): $\tilde{\nu}$ = 1940, 1841 [v(CO)]; 1649 [v(C=O)] cm⁻¹. UV (benzene): λ (ϵ , L mol⁻¹) = 330 (1649), 426 (179), 515 (179) nm. UV (hexane): λ (ϵ , L mol⁻¹) = 330 (546), 426 (177), 523 (136) nm.

The General Irradiation Procedure in Closed Systems: Solutions of 2–4 mM tricarboxyl compounds **3–5** in benzene were saturated with argon and placed into an IR cell, then the samples were irradiated with UV light of full spectra or 300–400 nm band followed by the registration of the spectra. Irradiated solutions were kept in the darkness or were irradiated with visible light of 480–530 nm at room temperature followed by the registration of spectra. Distance between lamp and sample was 5 cm in all cases. Width of irradiation window was 2 cm in IR cell. Both the total view of the IR spectrum and the stretching mode intensities for CO groups in the starting compound and the product after three- and fourfold repetition of the process: irradiation–dark reaction did not change.

Calculation: Theoretical calculations were carried out using the Gaussian98^[18] implementations of B3LYP [Becke three-parameter exchange functional (B3) and Lee–Yang–Parr correlation func-

tional (LYP)] density functional theory with the default pruned fine grids for energies with geometry optimization. The basis set for manganese was LanL2DZ.

Supporting Information (see footnote on the first page of this article): Table of molecular orbital coefficients and figure of the structure of dicarboxyl chelate complex **6** with number of atoms.

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