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Organometallic Photochromic Systems

Synthesis and Spectroscopic Studies of the Photochromism of Bifunctional Derivatives of Cymantrene in Solution and without Solvent

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Abstract: Four monosubstituted cymantrene derivatives (**5**–**8**) containing two functional groups (allyl and amide) in a dendritic substituent were synthesized. The irradiation of these compounds with an Hg lamp in solution and under solvent-free conditions gives two types of dicarbonyl chelates with Mn–olefin or Mn–amide coordination bonds. Olefin chelates (**19** and **21**) were isolated for the first time, and they undergo reverse photochemical intramolecular isomerization to the amide chelates in solution and as pure liquids. For the first time, it was shown that the photochromism of cymantrene functional derivatives can be observed without the use of a solvent.

Introduction

Ligand exchange at the metal atom is a fundamental property of transition-metal half-sandwich complexes and is applied widely as the basis for the synthesis of various compounds.[1–7] In particular, the photoinduced ligand exchange of some functional derivatives of cymantrene [(cyclopentadienyl)tricarbonylmanganese], (benzene)tricarbonylchromium, and related π-complexes is often accompanied by a substantial color change of the solution and the formation of photochromic systems.[8–17] Traditionally, photoinduced ligand exchange for cymantrene derivatives is performed by irradiation of solutions in alkanes, benzene, tetrahydrofuran (THF), or acetonitrile. However, there are examples of the photolysis of these compounds under conditions more suitable for application in devices for the recording of optical information. Thus, Tsuchida found that molecular nitrogen coordinates reversibly to the Mn atom upon the irradiation of the copolymer of (vinyl)methylcymantrene with octyl methacrylate.[18] The ultrafast chelation of the ligand to a manganese center through the sulfur atom was also observed upon the photolysis of a suspension of $Mn\{\eta^5\text{-}C_5H_4C(O)C(SCH_3)_3\}(CO)_3$ in polyacrylonitrile.[19] The solid-phase exchange of CO for triphenylphosphine occurs upon the photolysis of a silica gel supported mixture of cymantrene and PPh_3.[20] Recently, we found that cymantenylamides with branched substituents have low melting points and are able to form transparent thin layers between KBr windows; the irradiation of these thin layers results in photoinduced intermolecular ligand exchange.[21]

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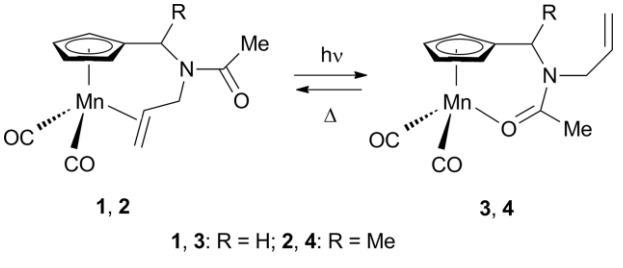
Results and Discussion

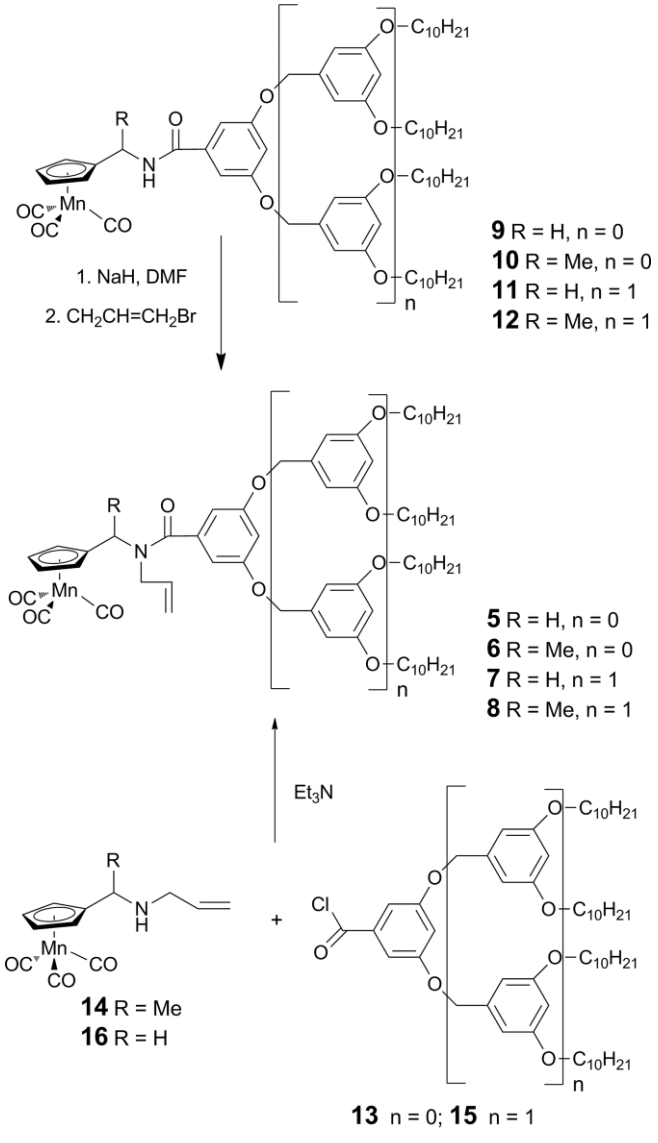
We reported previously that the irradiation of yellow ($\lambda \approx$ 333 nm) solutions of (allyl)dicarbonylmanganese chelates **1** and **2** with n-donating amide substituent results in the formation of the crimson isomeric dicarbonyl amide compounds **3** and **4**, respectively ($\lambda \approx$ 515 nm, Scheme 1),[10] which thermally fully isomerize back to the starting chelates **1** and **2** in 30–40 min. These are examples of intramolecular photochromic transformations between olefin chelates **1** and **2** and their amide isomers **3** and **4**, respectively. Compounds **1** and **2** are crystalline, and their photochromic properties were observed only in solution. We expected that bifunctional cymantrene derivatives with branched substituents could be low-melting solids or liquids and that their photochemical reactions could occur not only in solution but also without solvent. The aim of this work is the synthesis and study of photochemical properties of four allylamide–cymantrene derivatives (**5**–**8**) with branched substituents at the amide carbonyl group.



Scheme 1.

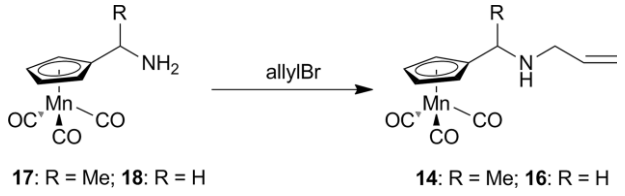
The synthesis of **5** by direct allylation of amide **9** proceeds in an acceptable yield of 39 % (Scheme 2). However, for **10**–**12**, this reaction proceeds slowly and gives *N*-allyl(cyman-

trenylalkyl)amides **6**–**8** in yields of 25, <5, and <1 %, respectively. For the preparation of **6**–**8**, the reactions of 3,5-didecyloxybenzoyl chloride (**13**) with *N*-allyl-1-cymantrenylethylamine (**14**), benzoyl chloride (**15**) with *N*-allyl-1-cymantrenylmethylamine (**16**), and **15** with **14** appeared to be more efficient. Allylamines **14** and **16** were synthesized under solvent-free conditions by mechanical grinding of mixtures of 1-cymantrenylalkylamines **17** or **18** and allyl bromide according to a previously reported method (Scheme 3).[22] The overall yields of these two-step syntheses were 50, 15, and 27 % for **6**–**8**, respectively. As expected, tricarbonyl complexes **5**–**8** are liquids, which allowed both solution and solvent-free photochemical studies.



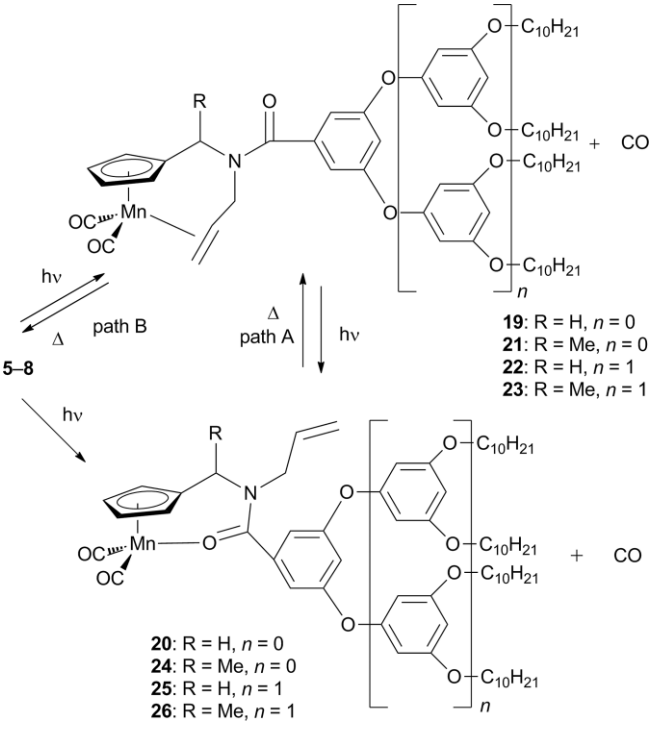
Scheme 2.

The photolyses of tricarbonyl complexes **5**–**8** result in color changes from light yellow (λ_{max} ≈ 330 nm) to crimson (λ_{max} ≈ 520 nm). The reactions were monitored in parallel by IR and UV/Vis spectroscopy. The irradiation of a solution of **5** in benzene or THF results simultaneously in the formation of both chelate **19** with ν(CO) at $\tilde{\nu}$ = 1975 and 1917 cm^{-1} and its isomer **20**



Scheme 3.

with ν(CO) at $\tilde{\nu}$ = 1930 and 1857 cm^{-1} in benzene (Scheme 4). The band assignment in this region is based on our previous results.[10,23] For allylamides **6**–**8**, the simultaneous formation of olefin (**21**–**23**) and amide (**24**–**26**) chelates in ratios of 2:1 is observed in benzene. The chelate ratios were estimated from the IR spectra with the assumption that the extinctions are similar for both chelates. The ν(CO) regions of the IR spectra for the photolysis of **7** in benzene are presented in Figure 1. Two types of chelate are also observed in the ^{1}H NMR spectra of irradiated solutions of allylamides **5**–**8** in [D$_6$]benzene.



Scheme 4.

If the irradiation was stopped, the amide chelates formed in solution thermally fully isomerized back to the corresponding olefin chelates with conversion half-times of 10 min for **20** and **25** and 2 h for **24** and **26** (Scheme 4, path A; Figure 1). Remarkably, the amide–olefin isomerization prevails substantially over the reaction with CO to give the parent complexes **5**–**8**; the formation of **5**–**8** is observed in the dark only after 12–24 h (Scheme 4, path B).

Amide–olefin isomerization results in the disappearance of the crimson coloration, and the band of the olefin chelate (λ_{max}

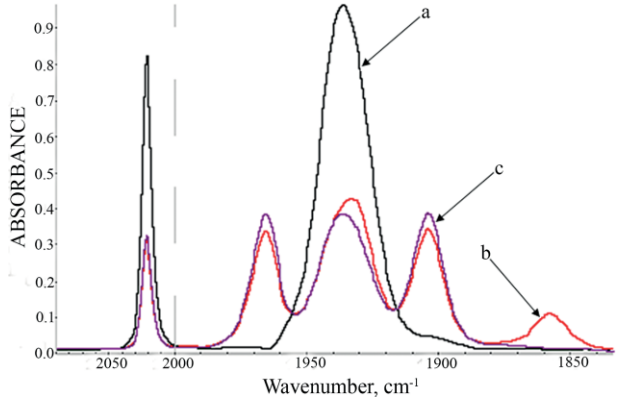


Figure 1. IR monitoring in the ν(CO) region of the photolysis of **7** and the dark isomerization of **25** to **22** in benzene: spectra of **7** (a) before irradiation and (b) after irradiation for 4 min (60 % conversion); (c) dark isomerization of **25** to **22**.

≈ 330 nm) appears in the UV/Vis spectrum (Figure 2). It can be seen in Figure 2 that chelate **21** and tricarbonyl complex **6** have similar UV/Vis spectra. The same is true for olefin chelates **19**, **22**, and **23**. Therefore, the color changes of the solutions upon the irradiation of **5**–**8** are associated with the formation of the corresponding amide chelates.

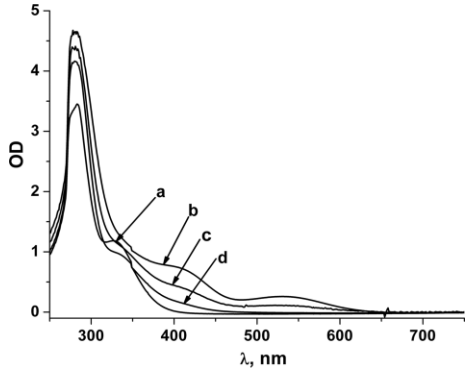


Figure 2. UV/Vis spectra (10.3 mM in benzene, *l* = 1 mm) of (a) complex **6**, (b) amide chelate **24**, (c) 40 % isomerization of **24** to olefin chelate **21**, and (d) chelate **21**.

The olefin chelates **19** and **21** were isolated as oils; the ^{1}H NMR spectra of these compounds confirm their structures and are in good agreement with the spectra of related olefin chelates.[10,24]

The irradiation of light yellow [λ_{max} ≈ 332 nm; ν(CO): $\tilde{\nu}$ = 1966, 1904 cm^{-1}] solutions of the olefin chelates **19** and **21** in benzene or THF results in their photoisomerization to the corresponding amide chelates, which are red-crimson [first long-wave transition λ_{max} ≈ 510 nm; ν(CO): $\tilde{\nu}$ = 1933, 1858 cm^{-1}; Figure 2]. In the dark reaction, the colors of solutions of **20** and **24** disappear rapidly, and the bands of the parent chelates **19** and **21** appear again in the IR and UV/Vis spectra. The IR and UV/Vis spectra of both chelates are not changed after three irradiation–dark reaction cycles. Thus, we observed a reversible intramolecular photochromic transformation between olefin and amide chelates with a thermal-isomerization half-time of 10 min (Scheme 4, path A).

Because tricarbonyl dendrimeric cymantrenyl derivatives **5**–**8** as well as chelates **19** and **21** are liquids, we studied photoreactions of these compounds, solvent-free as capillary layers between KBr windows. For example, IR monitoring of the photolysis of allylamide–cymantrene **5** placed between KBr windows indicated simultaneous formation of both olefin chelate **19** and amide chelate **20** (Figure 3). In the dark reaction, chelate **20** isomerizes to **19**, but the formation of the tricarbonyl complex **5** is not observed. The same is true for compounds **6**–**8**. Thus, the solvent does not affect the results of both the photolysis of compounds **5**–**8** and the dark isomerization reaction of amide chelates. Figure 4 demonstrates an example of the photochromic transformation upon photolysis of compound **6** as capillary layer using a template. It is seen that the slower diffusion in the pure compound as compared to that in solution allows the obtaining of a print of the template after irradiation.

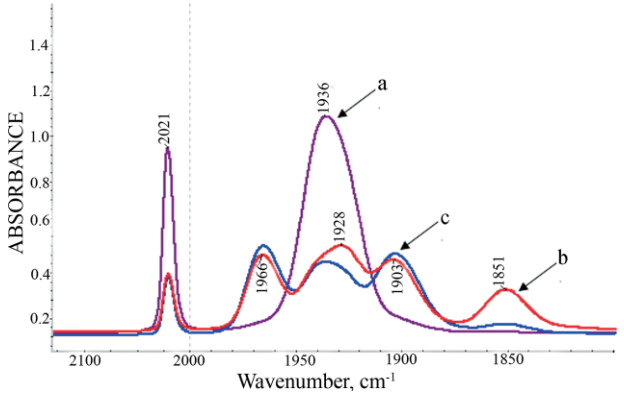


Figure 3. IR monitoring in the ν(CO) region of the photolysis of **7** and the dark isomerization of **25** to **22** as capillary layer: (a) spectrum of **7**; (b) 4 min after irradiation of **7** (60 % conversion); (c) after dark isomerization of **25** to **22**.

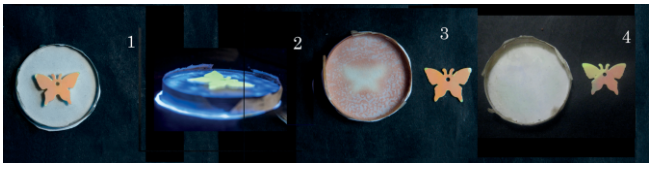


Figure 4. Photograph of the irradiation of **6** as capillary layer using a template: (1) before irradiation; (2) irradiation with Wood's lamp; (3) at the end of irradiation; (4) 2 h after the end of irradiation (dark isomerization of **24** to **21**).

Photolysis of the isolated liquid dicarbonyl olefin chelates **19** and **21** as capillary layers results in a similar spectral picture except for the bands of the corresponding tricarbonyl complexes. The IR spectra show photoinduced olefin/amide isomerization and dark amide/olefin isomerization (Figure 5). IR monitoring shows that the capillary layer irradiation/dark reaction cycle can be repeated no less than three times.

Thus, in this work we, for the first time, observed processes of intramolecular ligand exchange in a series of bifunctional cymantrene derivatives without solvent participation. These results are promising for obtaining photochromic devices for recording and storage of optical information.

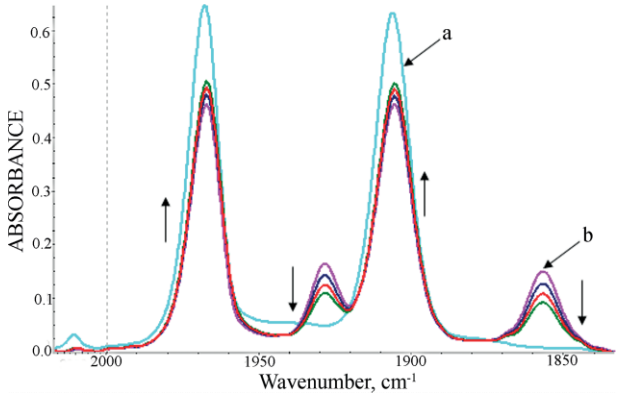


Figure 5. IR monitoring in the ν(CO) region of the photolysis of **21** and the dark isomerization of **24** as capillary layer: (a) spectrum of **21**; (b) 4 min after the irradiation **21** (30 % convertion) and dark isomerization of **24** for 30 min.

Conclusions

To study intra- and intermolecular ligand exchange without the use of a solvent, a series of liquid bifunctional branched cymantrene derivatives **5**–**8** containing π-donating olefins and n-donating amide groups as side substituents were synthesized. The irradiation of solutions of **5**–**8** results in the formation of both amide and olefin chelates. For the first time it was shown that the solvent-free photoreactions of these liquid compounds in capillary layers give the amide and olefin products, as was observed for solutions. In solution and without solvent, the amide chelates undergo thermal intramolecular isomerization to the corresponding olefin chelates. The individual (isolated) dicarbonyl olefin chelates **19** and **21** also photoisomerize to the corresponding amide chelates **20** and **24** in solution and without solvent, and these amide chelates thermally transform back to olefin chelates **19** and **21**. The photoisomerization and thermal isomerization between the olefin and amide chelates are accompanied by distinctive color changes and can be repeated at least three times without substantial changes to the spectral parameters of these photochromic systems. These results are promising for the achievement of cymantrene-based photochromic systems for recording optical information without solvent.

Experimental Section

Materials and Methods: ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 400 and Bruker Avance 600 spectrometers. Chemical shifts δ are relative to tetramethylsilane (TMS) in ppm, and residual solvent protons were used as an internal standard ([D_6]benzene: δ = 7.26 ppm; [D_6]acetone: δ = 2.05 ppm; $CDCl_3$: δ = 7.26 ppm). Signals in the ^{1}H NMR spectra were assigned on the basis of 2D COSY and NOESY experiments. Signals in the ^{13}C NMR spectra were assigned on the basis of 2D HeterCOR and JMODECHO experiments. IR spectra were recorded with a Tensor 37 (Bruker) FTIR spectrometer with a resolution of 2 cm^{-1} with samples in CaF_2 cells. UV/Vis spectra were recorded with a Specord M-40 spectrophotometer. Raman spectra were recorded with a laser Raman spectrometer with a LabRAM 300 microscope at a resolution of 2 cm^{-1}, and the samples were excited with the 632.8 nm line of an He–Ne laser. The laser power was 2.5 mW. EI mass spectra were recorded with Kratos MS 890 and Finnigan POLARIS Q spectrometers at 70 eV and an anion chamber temperature of 250 °C. Photochemical reactions were performed with a Hereaus TQ 150 Hg immersion lamp equipped with a water-cooled S49 glass jacket. THF and benzene were purified by conventional methods and distilled from sodium benzophenone ketyl under argon. Silica gel 60 (Merck) was used for column chromatography. The starting materials 1-cymantrenylethylamine (**17**),[25] cymantrenylmethylamine (**18**),[26] 3,5-didecyloxybenzoyl chloride (**13**), 3,5-bis(3,5-didecyloxybenzyloxy)benzoyl chloride (**15**), *N*-(cymantrenylmethyl)-3,5-didecyloxybenzamide (**9**), and *N*-[(1-cymantrenyl)ethyl]-3,5-didecyloxybenzamide (**10**) were prepared according to the procedures described recently.[21] Other chemicals were obtained commercially and used without further purification.

***N*-Allyl-*N*-(cymantrenylmethyl)-3,5-didecyloxybenzamide (5):** A 60 % suspension of NaH (0.2 g, 4.5 mmol) was added to a solution of **9** (1.0 g, 1.5 mmol) in *N*,*N*-dimethylformamide (DMF; 20 mL) under argon at 0 °C; the mixture was stirred at 0 °C for 30 min. Then, allyl bromide (1.1 mL, 12 mmol) was added dropwise, and the reaction mixture was brought to room temperature and stirred for 1 h. The mixture was poured onto ice water (50 mL), and the products were extracted with CH_2Cl_2 (3 × 75 mL) and dried with $MgSO_4$. The solvent was removed under vacuum, and **5** (yellow oil) was isolated by column chromatography (hexane/ethyl acetate, 4:1). Yield 39 % (0.4 g, 0.6 mmol). ^{1}H NMR (600 MHz, C_6D_6, 328 K): δ = 1.02 (t, *J* = 7.1 Hz, 6 H, CH_3), 1.27 (m, 24 H, CH_2), 1.43 (m, 4 H, CH_2), 1.77 (m, 4 H, CH_2), 3.83 (t, *J* = 6.4 Hz, 4 H, OCH_2), 3.90 (m, 2 H, CH_2=), 4.07 (m, 2 H, H-Cp), 4.17 (m, 2 H, H-Cp), 4.65 (s, 2 H, NCH_2), 5.06 (d, *J* = 11.8 Hz, 2 H, CH_2), 5.60 (m, 1 H, CH), 6.59 (t, 1 H, Ar-H), 6.88 (d, *J* = 1.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (C_6D_6): δ = 14.39 (2 C, $C_{10}H_{21}$), 23.13 (2 C, $C_{10}H_{21}$), 26.43 (2 C, $C_{10}H_{21}$), 29.59 (2 C, $C_{10}H_{21}$), 29.79 (4 C, $C_{10}H_{21}$), 30.01 (2 C, $C_{10}H_{21}$), 30.03 (2 C, $C_{10}H_{21}$), 32.34 (2 C, $C_{10}H_{21}$), 42.28 (br., 1 C, CH_2Cp), 51.45 (br., 1 C, CH_2CH=), 68.26 (2 C, OCH_2), 81.86 (2 C, Cp), 85.13 (br., 2 C, Cp), 100.19 (1 C, C_1Cp), 103.40 (1 C, 4-C_6H_3), 105.75 (2 C, 2,6-C_6H_3), 117.56 (1 C, CH_2=), 133.78 (1 C, CH=), 138.52 (1 C, 1-C_6H_3), 161.00 (2 C, 3,5-C_6H_3), 171.29 (br., 1 C, NC=O), 225.28 (3 C, MnC=O) ppm. IR (benzene): $\tilde{\nu}_{vCO}$ = 2021 (s), 1936 (s), 1674 (w) cm^{-1}. Raman: $\tilde{\nu}$ = 1639 (w) (CH=CH_2) cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 330 nm (942 dm^3 mol^{-1} cm^{-1}). ESI-MS: *m*/*z* = 605 [M – 3 CO]$^+$. $C_{39}H_{56}MnNO_6$ (689.81): calcd. C 67.90, H 8.32, Mn 7.96, N 2.03; found C 67.88, H 8.04, Mn 7.6, N 2.01.

***N*-Allyl-*N*-[(1-cymantrenyl)ethyl]-3,5-didecyloxybenzamide (6):** The synthesis of **6** from **10** (2.0 g, 3 mmol) was performed similarly to that of **5**. Yellow oil, yield 28 % (0.6 g, 0.9 mmol). ^{1}H NMR (C_6D_6, 328 K): δ = 1.05 (t, *J* = 7.0 Hz, 6 H, CH_3), 1.38 (m, 24 H, CH_2), 1.47 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.50 (m, 4 H, CH_2), 1.82 (m, 4 H, CH_2), 3.80 (dd, *J* = 16.1, 5.8 Hz, 1 H, CH_2CH=), 3.87 (t, *J* = 6.4 Hz, 4 H, OCH_2), 3.99 (dd, *J* = 16.0 Hz, 1 H, CH_2CH=), 4.05 (m, 1 H, H-Cp), 4.21 (m, 1 H, H-Cp), 4.50 (m, 1 H, H-Cp), 4.72 (m, 1 H, H-Cp), 5.08 (m, 2 H, CH_2), 5.26 (m, 1 H, CH), 5.81 (m, 1 H, CH=), 6.79 (t, 1 H, Ar-H), 6.88 (d, *J* = 1.9 Hz, 2 H, 2 H, Ar-H) ppm. ^{13}C NMR (C_6D_6): δ = 14.39 (2 C, $C_{10}H_{21}$), 17.56 (1 C, CH_3CH), 23.13 (2 C, $C_{10}H_{21}$), 26.42 (2 C, $C_{10}H_{21}$), 29.60 (2 C, $C_{10}H_{21}$), 29.78 (4 C, $C_{10}H_{21}$), 30.01 (4 C, $C_{10}H_{21}$), 32.33 (2 C, $C_{10}H_{21}$), 44.24 (br., 1 C, CHCp), 49.04 (br., 1 C, NCH_2), 68.25 (2 C, OCH_2), 78.90 (2 C, Cp), 84.00 (br., 2 C, Cp), 102.83 (1 C, 4-C_6H_3), 104.75 (1 C, C_1Cp), 105.64 (2 C, 2,6-C_6H_3), 116.81 (1 C, CH_2=), 135.61 (1 C, CH=), 139.32 (1 C, 1-C_6H_3), 161.11 (2 C, 3,5-C_6H_3), 171.00 (br., 1 C, NC=O), 225.03 (3 C, MnC=O) ppm. IR (benzene): $\tilde{\nu}_{vCO}$ = 2019 (s), 1938 (s), 1671 (w) cm^{-1}. IR (thin layer): $\tilde{\nu}_{vCO}$ = 2019 (s), 1934 (s), 1668 (w) cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 328 nm (1146 dm^3 mol^{-1} cm^{-1}). ESI-MS: *m*/*z* = 619 [M – 3 CO]$^+$. $C_{40}H_{58}MnNO_6$ (703.84): calcd. C 68.26, H 8.32, Mn 7.81, N 1.99; found C 67.99, H 8.41, Mn 7.7, N 2.08.

Compound 6 from (Allyl)(1-cymantrenylethyl)amine (14). Stage A: Allyl bromide (0.8 mL, 8 mmol) was added dropwise to amine **17** (2.0 g, 8 mmol), and the mixture was shaken thoroughly. After the reaction mixture had solidified, it was rubbed thoroughly with a glass rod and kept at room temperature for 12 h. Then, 1 N NaOH was added, and the product was extracted with AcOEt. The organic layer was separated, washed with 1 N NaOH and brine, and dried with $MgSO_4$. The solvent was removed under vacuum, and **14** (yellow oil) was isolated by column chromatography (hexane/AcOEt, 2:1). Yield 52 % (1.2 g, 4.2 mmol). ^{1}H NMR ([D$_6$]acetone): δ = 1.37 (d, J = 6.6 Hz, 3 H, CH_3), 3.34 (m, 2 H, NCH_2), 5.56 (q, J = 6.6 Hz, 1 H, CH), 4.89 (m, 2 H, H-Cp), 5.08 (d, J = 10.4 Hz, 1 H, CH_2=), 5.10 (m, 1 H, H-Cp), 5.13 (m, 1 H, H-Cp), 5.26 (dm, J = 17.2 Hz, 1 H, CH_2=), 5.90 (ddt, J = 16.1, 10.3, 5.8 Hz, 1 H, CH=) ppm. ^{13}C NMR (C_6D_6): δ = 22.07 (1 C, CH_3CH), 49.90 (1 C, CHCp), 49.93 (1 C, CH_2CH=), 80.66 (1 C, Cp), 81.15 (1 C, Cp), 82.37 (1 C, Cp), 83.34 (1 C, Cp), 110.62 (1 C, C_1Cp), 115.52 (1 C, CH_2=), 137.44 (1 C, CH=), 225.70 (3 C, MnC=O) ppm. IR (thin layer): $\tilde{\nu}$ = 2017 (s, MnCO), 1919 (s, MnCO), 1644 (w, CH=CH_2) cm^{-1}. Raman: $\tilde{\nu}$ = 1643 (w, CH=CH_2) cm^{-1}. $C_{13}H_{14}MnNO_3$ (287.20): calcd. C 54.37, H 4.91, Mn 19.13, N 4.88; found C 54.31, H 4.81, Mn 18.9, N 4.77. **Stage B:** A solution of **14** (0.31 g, 1.1 mmol) in CH_2Cl_2 (10 mL) was cooled to –5 °C under argon in a round flask, and Et_3N (0.3 mL, 2.1 mmol) and benzoyl chloride (0.5 g, 1.1 mmol) were added successively. The reaction mixture was brought to room temperature and stirred for 2 h, a saturated solution of NH_4Cl (20 mL) was added dropwise, and the reaction mixture was stirred for 20 min. The organic layer was separated, washed with 20 % H_3PO_4 (20 mL) and aqueous $NaHCO_3$ (20 mL), and dried with $MgSO_4$, and the solvent was removed under vacuum; **6** (yellow oil) was isolated by column chromatography (hexane/AcOEt, 4:1). Yield 95 % (0.7 g, 1.1 mmol). The spectral characteristics of **6** are similar to those given above.

***N*-Allyl-*N*-(cymantrenylmethyl)-3,5-bis(3,5-didecyloxybenzyloxy)benzamide (7) from (Allyl)(cymantrenylmethyl)amine (16). Stage A:** *N*-Allylcymantrenylmethylamine (**16**) was prepared similarly to **14** from **18** (3.0 g) and allyl bromide (1.1 mL). Yield 0.8 g (23 %). ^{1}H NMR ([D$_6$]acetone): δ = 3.27 (m, 2 H, CH_2), 3.40 (s, 2 H, CH_2), 4.86 (m, 2 H, H-Cp), 5.00 (m, 2 H, H-Cp), 5.03–5.22 (m, 2 H, CH_2), 5.87 (m, 1 H, CH) ppm. ^{13}C NMR (C_6D_6): δ = 46.00 (1 C, CH_2Cp), 52.08 (1 C, CH_2CH=), 81.77 (2 C, Cp), 82.65 (2 C, Cp), 105.40 (1 C, C_1Cp), 115.82 (1 C, CH_2=), 137.14 (1 C, CH=), 225.58 (3 C, MnC=O) ppm. IR (thin layer): $\tilde{\nu}$ = 2017 (s, MnCO), 1922 (s, MnCO), 1645 (w, CH=CH_2) cm^{-1}. $C_{12}H_{12}MnNO_3$ (273.17): calcd. C 52.75, H 4.44, N 5.13; found C 54.65, H 5.00, N 4.70. **Stage B:** Compound **7** was prepared similarly to **6** by stage B with **16** (0.2 g, 0.8 mmol) and **15** (0.8 g, 0.8 mmol). Yield 0.6 g (62 %). ^{1}H NMR ([D$_6$]acetone, 328 K): δ = 0.88 (t, J = 6.5 Hz, 12 H, CH_2CH_3), 1.30 (m, 48 H, CH_2), 1.46 (m, 8 H, CH_2), 1.77 (m, 8 H, CH_2), 3.92 (m, 2 H, CH_2=), 3.97 (t, J = 6.5 Hz, 8 H, OCH_2), 4.22 (m, 2 H, Cp), 4.89 (s, 2 H, NCH_2), 5.05 (s, 4 H, CH_2), 5.16 (m, 2 H, Cp), 5.23–5.26 (m, 2 H, CH_2CH=), 5.76 (m, 1 H, CH), 6.42 (t, 2 H, Ar-H), 6.54 (d, J = 1.4 Hz, 4 H, Ar-H), 6.60 (d, J = 2.0 Hz, 2 H, Ar-H), 6.72 (t, J = 2.1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (C_6D_6): δ = 14.39 (4 C, $C_{10}H_{21}$), 23.13 (4 C, $C_{10}H_{21}$), 26.51 (4 C, $C_{10}H_{21}$), 29.74 (4 C, $C_{10}H_{21}$), 29.80 (4 C, $C_{10}H_{21}$), 29.86 (4 C, $C_{10}H_{21}$), 30.03 (4 C, $C_{10}H_{21}$), 30.06 (4 C, $C_{10}H_{21}$), 32.34 (4 C, $C_{10}H_{21}$), 42.29 (br., 1 C, CH_2Cp), 51.76 (br., 1 C, NCH_2), 68.11 (4 C, OCH_2), 70.41 (2 C, OCH_2), 81.96 (2 C, Cp), 84.91 (br., 2 C, Cp), 99.65 (1 C, Cp), 101.51 (2 C, Ph), 104.73 (2 C, Ph), 105.11 (2 C, 2,6-C_6H_3), 106.11 (4 C, Ph), 107.83 (2 C, Ph), 118.06 (1 C, CH_2=), 133.34 (1 C, CH=), 137.52 (1 C, Ph), 139.62 (2 C, Ph), 159.57 (2 C, Ph), 160.61 (2 C, Ph), 161.22 (4 C, Ph), 170.24 (br., 1 C, NC=O), 225.23 (3 C, MnC=O) ppm. IR (benzene): $\tilde{\nu}_{vCO}$ = 2021, 1936, 1647 (NC=O) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 2021, 1936 cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 330 nm (1073 dm^3 mol^{-1} cm^{-1}).

***N*-Allyl-*N*-(1-cymantrenylethyl)-3,5-bis(3,5-didecyloxybenzyloxy)benzamide (8) from (Allyl)(1-cymantrenylethyl)amine (14):** Compound **8** was prepared similarly to **6** from **14** (0.4 g, 1.6 mmol) and **15** (1.6 g, 1.6 mmol). Yield 1.0 g (51 %). ^{1}H NMR ([D$_6$]acetone, 328 K): δ = 0.92 (t, 12 H, CH_2CH_3), 1.35 (m, 51 H, CH_2 and CH_3), 1.52 (m, 8 H, CH_2), 1.81 (m, 8 H, CH_2), 4.03 (t, J = 6.5 Hz, 8 H, OCH_2), 4.85 (m, 1 H, Cp), 5.03 (m, 1 H, $CHCH_3$), 5.06–5.21 (m, 2 H, CH_2CH=), 5.13 (m, 1 H, Cp), 5.32 (m, 1 H, Cp), 5.78 (br. m, 1 H, CH), 6.48 (br. t, 2 H, Ar-H), 6.67 (m, 6 H, Ar-H), 6.76 (br. t, 1 H, Ar-H) ppm. IR (benzene): $\tilde{\nu}_{vCO}$ = 2021, 1931, 1671 cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 330 nm (1340 dm^3 mol^{-1} cm^{-1}). $C_{74}H_{110}MnNO_{10}$ (1228.62): calcd. C 72.34, H 9.03, Mn 4.5, N 1.14; found C 71.84, H 9.18, Mn 4.3, N 0.96.

General Procedure for the Spectral Studies of the Photochemical Reactions of Tricarbonyl Complexes 5–8 and Dicarbonyl Chelates 19 and 21: A solution of the complex under study in a suitable solvent (benzene or THF; 2–4 mM) was placed in an IR or UV cell under argon and irradiated with an Hg lamp (steady radiation of the lamp was achieved 2 min before irradiation); liquid compounds for IR study were placed between KBr windows and irradiated under the same conditions. The IR spectra were registered every 3 min. To prepare samples for NMR spectroscopy, a solution of the compound (10^{-2}–10^{-3} M) was filtered into an NMR tube, bubbled with argon, and irradiated with the Hg lamp at 5–8 °C for 4 min to achieve 25–30 % conversion. The distance between the lamp and the sample was 5 cm in all cases. The width of the irradiation window was 2 cm for the IR cell, 1 cm for the UV cell, and 5 mm for the NMR tube. All dark reactions of the chelates were monitored similarly for at least 72 h. The "irradiation–dark reaction" procedure for ca. 2 mM solutions of all amides in benzene, THF, or hexane was performed in the IR cell and repeated 3–5 times. Samples irradiated in NMR tubes or UV cells had free volume for the accumulation of liberated CO (open system). For irradiation in the IR cells, there was no free volume, and the liberated CO was retained in solution (closed system).

General Procedure for the Preparation of the Dicarbonyl Chelates 19 and 21: A solution of the tricarbonyl compound in benzene (250 mL) was placed into a photochemical reactor and irradiated under a UV immersion lamp under argon at 7–10 °C for 40 min. The reaction was monitored by IR spectroscopy of the reaction solution. The solvent was removed by rotary evaporation at low temperature, and the residue was separated by silica gel column chromatography with hexane as the eluent. Remarkably, the irradiation of chiral complex **6** resulted in two diastereomeric olefin chelates **21** and **21a** in a ratio of 4:1.

{[(η^2-Allyl)(3,5-didecyloxybenzoyl)amino]methyl}-η^5-cyclopentadienyl)dicarbonylmanganese (19): According to the general irradiation procedure, compound **5** (0.31 g, 0.45 mmol) gave **19** as a yellow oil (0.21 g, 71 %). ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 6 H, $2CH_3$), 1.27 (m, 20 H, CH_2), 1.43 (m, 4 H, CH_2), 1.44 (m, 1 H, CH_2=), 1.61 (m, 4 H, CH_2), 1.76 (m, 4 H, CH_2), 1.84 (m, 1 H, CH=), 2.42 (d, J = 12.4 Hz,1 H, CH_2=), 2.81 (m, 1 H, NCH_2), 3.39 (d, J = 14.2 Hz, 1 H, $CpCH_2$), 3.51 (m, 1 H, NCH_2), 3.93 (br. t, 4 H, OCH_2), 4.18 (m, 1 H, H-Cp), 4.28 (m, 1 H, H-Cp), 4.85 (d, J = 13.4 Hz, 1 H, $CpCH_2$), 5.13 (m, 1 H, H-Cp), 5.28 (m, 1 H, H-Cp), 6.49 (m, 2 H, Ph), 6.58 (m, 1 H, Ph) ppm. ^{13}C NMR (C_6D_6): δ = 14.38 (2 C, $C_{10}H_{21}$), 23.12 (2 C, $C_{10}H_{21}$), 26.46 (2 C, $C_{10}H_{21}$), 29.63 (2 C, $C_{10}H_{21}$), 29.79 (4 C, $C_{10}H_{21}$), 30.0 (2 C, $C_{10}H_{21}$), 30.03 (2 C, $C_{10}H_{21}$), 31.35 (1 C, CH_2N), 32.32 (2 C, $C_{10}H_{21}$), 40.85 (br., 1 C, CH_2=), 49.0 (br., 1 C, CH_2Cp), 59.19 (br., 1 C, CH=), 68.33 (2 C, OCH_2), 70.71 (br., 1 C, Cp), 86.58 (1 C, Cp), 87.35 (1 C, Cp), 88.23 (br.,1 C, Cp), 94.57 (1 C, 1-Cp), 103.3 (1 C, 4-C_6H_3), 106.1 (1 C, C_1Cp), 106.46 (2 C, 2,6-C_6H_3), 139.09 (1 C, 1-C_6H_3), 160.98 (2 C, 3,5-C_6H_3), 170.82 (1 C, NC=O), 233.38 (1 C, MnC=O), 234.01 (1 C, MnC=O) ppm.

IR (THF): $\tilde{\nu}_{vCO}$ = 1965 (s), 1903 (s), 1645 (w) cm^{-1}. IR (hexane): $\tilde{\nu}_{vCO}$ = 1975 (s), 1917 (s), 1652 (w) cm^{-1}. IR (benzene): $\tilde{\nu}_{vCO}$ = 1966 (s), 1905 (s), 1650 (w) cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 332 nm (842 $dm^3\ mol^{-1}\ cm^{-1}$). ESI-MS: m/z = 605 $[M - 2\ CO]^+$. $C_{38}H_{56}MnNO_5$•MeCOOEt: calcd. C 67.46, H 8.63, N 1.87; found C 67.37, H 8.81, N 1.97.

{[(Allyl)(κ*O*-3,5-didecyloxybenzoyl)amino]methyl}-η⁵-cyclopentadienyl}dicarbonylmanganese (20): IR (benzene): $\tilde{\nu}_{vCO}$ = 1927 (s), 1857 (s), 1631 (w) cm^{-1}. IR (THF): $\tilde{\nu}_{vCO}$ = 1854 (s), 1926 (s) cm^{-1}.

({1-[(η²-Allyl)(3,5-didecyloxybenzoyl)amino]ethyl}-η⁵-cyclopentadienyl)dicarbonylmanganese (21): According to the general irradiation procedure, compound **6** (114 mg, 0.17 mmol) gave **21** as a yellow oil (85 mg, 67 %). ^1H NMR ($CDCl_3$): δ = 0.89–0.92 (m, 9 H, CH_3, 2 CH_3), 1.29 (m, 24 H, CH_2), 1.45 (m, 4 H, CH_2), 1.53–1.65 (m, 2 H, CH_2=), 1.78 (m, 4 H, CH_2), 1.91 (m, 1 H, NCH_2), 2.38 (m, 1 H, CH=), 3.04 (br. d, J = 15.0 Hz,1 H, NCH_2), 3.65 (m, 1 H, H-Cp), 3.95 (m, 1 H, H-Cp), 3.97 (t, 4 H, OCH_2), 4.35 (m, 1 H, H-Cp), 5.09 (m, 1 H, H-Cp), 5.45 (m, 1 H, CH), 6.53 (m, 1 H, Ph), 6.65 (m, 2 H, Ph) ppm. ^{13}C NMR (C_6D_6): δ = 14.38 (2 C, $C_{10}H_{21}$), 18.07 (1 C, CH_3CH), 23.12 (2 C, $C_{10}H_{21}$), 26.42 (2 C, $C_{10}H_{21}$), 29.61 (2 C, $C_{10}H_{21}$), 29.77 (4 C, $C_{10}H_{21}$), 30.00 (2 C, $C_{10}H_{21}$), 30.01 (2 C, $C_{10}H_{21}$), 30.17 (1 C, CH_2N), 32.32 (2 C, $C_{10}H_{21}$), 38.21 (br., 1 C, CH_2=), 45.0 (br., 1 C, CHCp), 56.74 (br., 1 C, CH=), 68.39 (2 C, OCH_2), 70.82 (1 C, Cp), 84.19 (1 C, Cp), 87.82 (1 C, Cp), 88.21 (1 C, Cp), 103.38 (1 C, 4-C_6H_3), 104.48 (1 C, C_1Cp), 105.46 (2 C, 2,6-C_6H_3), 140.09 (1 C, 1-C_6H_3), 161.24 (2 C, 3,5-C_6H_3), 169.82 (1 C, NC=O), 233.30 (1 C, MnC=O), 234.63 (1 C, MnC=O) ppm. IR (THF): $\tilde{\nu}_{vCO}$ = 1967 (s), 1904 (s), 1642 (w) cm^{-1}. IR (benzene): $\tilde{\nu}_{vCO}$ = 1958 (s), 1896 (s) cm^{-1}. IR (capillary layer): $\tilde{\nu}_{vCO}$ = 1963 (s), 1901 (s), 1647 (w) cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 323 nm (sh, 990 $dm^3\ mol^{-1}\ cm^{-1}$). ESI-MS: m/z = 619 $[M - 2\ CO]^+$. $C_{39}H_{58}MnNO_5$•C_6H_{14}: calcd. C 70.94, H 9.52, N 1.84; found C 70.77, H 9.25, N 2.08.

({1-[(η²-Allyl)(3,5-didecyloxybenzoyl)amino]ethyl}-η⁵-cyclopentadienyl)dicarbonylmanganese (21a): According to the general irradiation procedure, compound **6** (114 mg, 0.17 mmol) gave **21a** as a yellow oil (21 mg, 16 %). ^1H NMR ($CDCl_3$): δ = 0.97–1.07 (m, 9 H, CH_3, 2 CH_3), 1.37 (m, 24 H, CH_2), 1.47 (m, 5 H, CH_2, CH_2=), 1.76 (m, 4 H, CH_2), 1.84 (br. m, 1 H, CH_2=), 2.46 (m, J = 12.2 Hz,1 H, NCH_2), 2.57 (m, 1 H, CH=), 3.07 (br., 1 H, NCH_2), 3.64–3.96 (br., 6 H, OCH_2, 2 H-Cp), 4.23 (br., 1 H, CH), 4.41 (m, 1 H, H-Cp), 4.73 (m, 1 H, H-Cp), 5.60 (br., 1 H, CH), 6.84 (m, 1 H, Ph), 7.04 (m, 2 H, Ph) ppm. ^{13}C NMR (C_6D_6): δ = 14.38 (2 C, $C_{10}H_{21}$), 16.31 (1 C, CH_3CH), 23.12 (2 C, $C_{10}H_{21}$), 26.47 (2 C, $C_{10}H_{21}$), 29.63 (2 C, $C_{10}H_{21}$), 29.79 (4 C, $C_{10}H_{21}$), 30.01 (2 C, $C_{10}H_{21}$), 30.04 (2 C, $C_{10}H_{21}$), 32.32 (2 C, $C_{10}H_{21}$), 37.49 (1 C, CH_2N), 42.45 (br., 1 C, CH_2=), 56.20 (br., 1 C, CHCp), 68.30 (2 C, OCH_2), 71.94 (br., 1 C, CH=), 84.59 (1 C, Cp), 86.09 (1 C, Cp), 87.92 (1 C, Cp), 98.32 (1 C, Cp), 103.37 (1 C, 4-C_6H_3), 105.57 (1 C, C_1Cp), 106.0 (2 C, 2,6-C_6H_3), 139.17 (1 C, 1-C_6H_3), 160.95 (2 C, 3,5-C_6H_3), 170.93 (1 C, NC=O), 233.20 (1 C, MnC=O), 235.30 (1 C, MnC=O) ppm. IR (THF): $\tilde{\nu}_{vCO}$ = 1967 (s), 1904 (s), 1642 (w). IR (benzene): $\tilde{\nu}_{vCO}$ = 1958 (s), 1896 (s) cm^{-1}. IR (capillary layer): $\tilde{\nu}_{vCO}$ = 1963 (s), 1901 (s), 1647 (w) cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 323 nm (sh, 990 $dm^3\ mol^{-1}\ cm^{-1}$). ESI-MS: m/z = 619 $[M - 2\ CO]^+$.

({1-[(Allyl)(κO-3,5-didecyloxybenzoyl)amino]ethyl}-η⁵-cyclopentadienyl)dicarbonylmanganese (24): IR (benzene): $\tilde{\nu}_{vCO}$ = 1927 (s), 1857 (s), 1631 (w) cm^{-1}. IR (capillary layer): $\tilde{\nu}_{vCO}$ = 1930, 1858 cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 387 (1280), 532 nm (505 $dm^3\ mol^{-1}\ cm^{-1}$).

[({(η²-Allyl)[3,5-bis(3,5-didecyloxybenzyloxy)benzoyl]amino}-methyl)-η⁵-cyclopentadienyl]dicarbonylmanganese (22): IR (benzene): $\tilde{\nu}_{vCO}$ = 1965, 1904 cm^{-1}. IR (capillary layer): $\tilde{\nu}_{vCO}$ = 1966, 1904 cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 330 nm (1333 $dm^3\ mol^{-1}\ cm^{-1}$).

[({(Allyl)[κ*O*-3,5-bis(3,5-didecyloxybenzyloxy)benzoyl]amino}-methyl)-η⁵-cyclopentadienyl]dicarbonylmanganese (25): IR (benzene): $\tilde{\nu}_{vCO}$ = 1933 (s), 1858 (s), 1631 (w) cm^{-1}. IR (capillary layer): $\tilde{\nu}_{vCO}$ = 1929, 1851 cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 417 (333), 520 nm (123 $dm^3\ mol^{-1}\ cm^{-1}$).

[(1-{(η²-Allyl)[3,5-bis(3,5-didecyloxybenzyloxy)benzoyl]amino}-ethyl)-η⁵-cyclopentadienyl]dicarbonylmanganese (23): IR (benzene): $\tilde{\nu}_{vCO}$ = 1966, 1903 cm^{-1}. IR (capillary layer): $\tilde{\nu}_{vCO}$ = 1965, 1904 cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 294 (3400), 520 nm (123 $dm^3\ mol^{-1}\ cm^{-1}$).

[(1-{(Allyl)[κ*O*-3,5-bis(3,5-didecyloxybenzyloxy)benzoyl]amino}-ethyl)-η⁵-cyclopentadienyl]dicarbonylmanganese (26): IR (benzene): $\tilde{\nu}_{vCO}$ = 1936 (s), 1857 (s) cm^{-1}. IR (capillary layer): $\tilde{\nu}_{vCO}$ =1929, 1854 cm^{-1}. UV/Vis (benzene): λ_{max} (ε) = 410 (633), 527 nm (123 $dm^3\ mol^{-1}\ cm^{-1}$).

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