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Synthesis of chiral β-aminoalcohol-substituted carbene complexes of manganese and influence of the chiral carbene ligand on the diastereoselectivity of the CO/PR_3 exchange

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

The acetoxy(phenyl)carbene complex $[Cp(CO)_2Mn{=}C(OAc)Ph]$ (**2**) reacts with chiral β-aminoalcohols HOR* [HOR* = *N*,*N*-dimethyl alaninol (**3**), *N*,*N*-dimethyl valinol (**4**), *N*,*N*-dimethyl leucinol (**5**), *N*,*N*-dimethylphenyl alaninol (**6**), and *N*-formylprolinol (**7**)] by displacement of the acetoxy substituent and formation of the β-aminoalkoxy(phenyl)carbene complexes $[Cp(CO)_2Mn{=}C(OR^*)Ph]$ (**8**–**12**). Irradiation of **9**–**12** in the presence of PR_3 (R = Ph, OMe) affords the carbene(carbonyl)cyclopentadienyl(PR_3)manganese complexes $[Cp(CO)(PR_3)Mn{=}C(OR^*)Ph]$. The substitution proceeds diastereoselectively, the diastereomeric excess ranging from 28% to > 90%. The highest diastereoselectivity (> 90%) is observed in the reaction of **9** ($R^* = CH_2C(NMe_2)HCMe_2H$) with PR_3. In solution, complex **9** is not stable configurationally and epimerizes within a few days. The reaction of **2** with $HOC_2H_4SCH_2Ph$ affords $[Cp(CO)_2Mn{=}C(OC_2H_4SCH_2Ph)Ph]$ (**22**) which, on photolysis, is transformed, by loss of a CO ligand, into a chelating carbene complex (**24**). In the presence of PR_3 compound **24** cannot be converted thermally into $[Cp(CO)(PR_3)Mn{=}C(OC_2H_4SCH_2Ph)Ph]$.

Keywords: Carbene complexes; Substitution; Diastereoselectivity; Chiral complexes

1. Introduction

Chiral transition metal complexes play a prominent role in enantioselective synthesis and catalysis. In these complexes the chiral information is either localized within the ligand sphere or at the metal (chiral-at-metal complexes) [1]. Although a wide variety of aminoacids and carbohydrates are available from the chiral pool, the number of reports on their use as chiral auxiliaries for the synthesis of chiral-at-metal complexes is rather restricted.

In recent years, interest has focused on the transformation of carbohydrates via organometallic compounds especially via transition metal carbene complexes [2]. The first synthesis of carbohydratocarbene complexes was reported by Beck et al. in 1990 [3]. The synthesis involved addition of carbohydrates to isocyanide complexes of Au and Pt. Later on, additional routes were developed such as Michael-addition to α,β-unsaturated carbene complexes [4], addition of carbonylmetallates to carbohydrate acid chlorides [5], or addition of monodeprotonated protected carbohydrates to the carbyne carbon atom in cationic carbyne complexes [6].

Recently we reported on the synthesis of a series of chiral carbohydratocarbene complexes of the type $[Cp(CO)_2M{=}C(OR^*)R']$ (M = Mn, Re; OR* = gluco- and galactopyranosyloxy and glycerolyl; R′ = Ph, Tol) and on the influence of the carbohydrato substituent on the diastereoselectivity of the CO/phosphane exchange in the manganese complexes [6–8]. Photolysis of the chiral carbohydratocarbene complexes in the presence of phosphanes or phosphites (PR_3) afforded the chiral-at-metal carbene complexes $[Cp(CO)(PR_3)M{=}C(OR^*)R']$. The diastereoselectivity of

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the substitution varied considerably and depended on the type of carbohydrato substituent and on the entering PR_3. The observed diastereomeric excess (de) values ranged from 0% to higher than 96%. In general, the diastereoselectivity increased with increasing nucleophilicity of PR_3 and increasing flexibility of the alkoxy substituent. When 1,2-*O*-isopropylideneglycerol was used as the carbene substituent, within error limits complete stereocontrol of the replacement of CO by PR_3 was achieved independent of the entering phosphorus compound. (*R*)-1,2-*O*-Isopropylideneglycerol gave rise to the formation of complexes with the *S* configuration at manganese (S_{Mn}) and, conversely, (*S*)-1,2-*O*-isopropylideneglycerol afforded the R_{Mn} complexes [8].

As a working hypothesis we assumed that the 'coordinatively unsaturated' species resulting from photoinduced loss of a CO ligand from the carbene(dicarbonyl) complexes is stabilized by intramolecular chelating interaction of the β-alkoxy group with the free coordination site at the metal (see Fig.1, A and B) thus also determining the stereoselectivity of the reaction. However, it was not possible to detect any chelating intermediate.

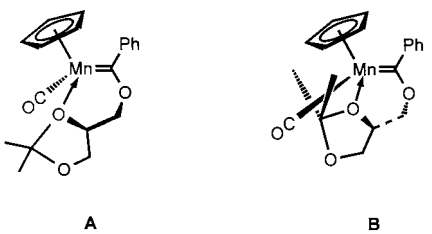


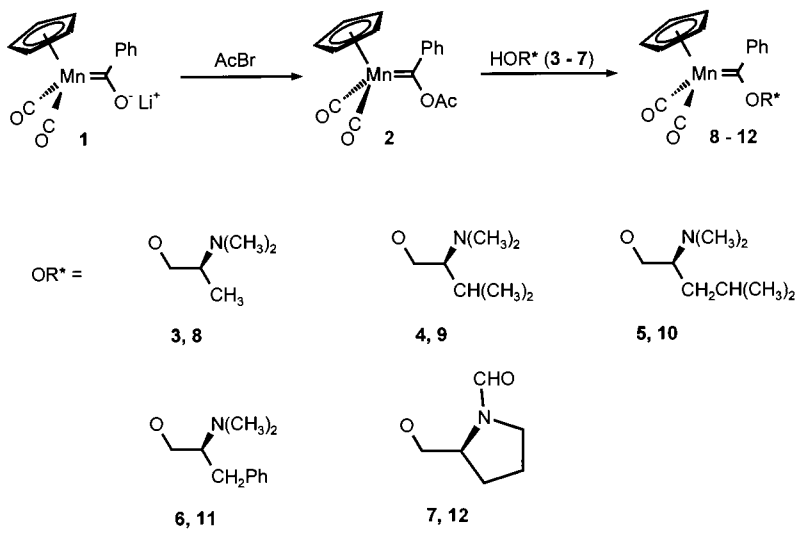
Fig. 1. Possible stabilization of the 'coordinatively unsaturated' carbene complex by intramolecular chelating interaction.

We therefore extended our investigations to β-aminoalcohols and now report on the synthesis of chiral dicarbonyl aminoalkylidenealkoxycarbene complexes and on the diastereoselectivity of the CO/PR_3 exchange in these complexes.

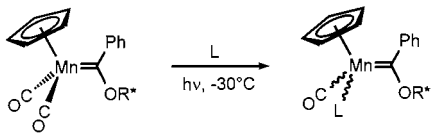
2. Results and discussion

Reaction of the lithium benzoylmanganate **1** with one equivalent of acetyl bromide in dichloromethane at − 50°C gave the thermolabile acetoxy carbene complex **2** as described previously [7]. When 1.5 equivalent of *N*,*N*-dimethyl alaninol (**3**) was added, the color of the solution changed immediately from red to brown and the *v*(CO) absorptions shifted towards smaller wave numbers. Chromatographic work-up afforded the carbene complex **8** (Scheme 1) as a red oil in 57% yield.

The analogous reactions of **2** with *N*,*N*-dimethyl valinol (**4**), *N*,*N*-dimethyl leucinol (**5**), *N*,*N*-dimethyl phenylalaninol (**6**), and *N*-formyl prolinol (**7**) gave the complexes **9**–**12** (Scheme 1) in (after chromatography) 58–79% yield. All complexes are stable at room temperature and in air. They are readily soluble in polar solvents such as dichloromethane, THF, diethyl ether and toluene, but almost insoluble in pentane. As expected, for all complexes **8**–**12** two *v*(CO) absorptions of nearly equal intensity are observed in dichloromethane. The positions of these absorptions are almost independent of the aminoalcohol-substituent OR* but are at ca. 20 cm^{-1} smaller wave numbers than those of the corresponding glycerol-substituted complexes [8]. In contrast, in pentane complex **9** exhibits five *v*(CO) absorptions indicating the presence of an equilibrium mixture of at least three isomers, pre-



Scheme 1.



OR*	4	5	6	7
L = $PTol_3$	13	15	17	19
L = $P(OMe)_3$	14	16	18	20

Scheme 2.

sumably rotational isomers. A resonance in the ^{13}C-NMR spectrum at rather low field ($\delta = 333.4–334.3$) confirms the structure shown in Scheme 1. The resonance of the carbene carbon atom in the related galactopyranosyl-, glucopyranosyl-, and isopropylideneglycerol-substituted carbene complexes prepared earlier is observed in the same range [8]. In contrast to the latter complexes and to **11**, for **8**–**10** and **12** only one CO resonance is observed indicating rapid rotation around the Mn–C(carbene) bond or the presence of a pseudo-mirror plane.

Photolysis of **9**–**12** in toluene in the presence of 1.5 equivalent of tritolylphosphane or trimethylphosphite at −30°C afforded the carbene(carbonyl)-(cyclopentadienyl)(PR_3)manganese complexes **13**–**20** (Scheme 2).

The product complexes also turned out to be photolabile and decomposed quickly on prolonged irradiation to form $Cp(CO)_3Mn$ and unidentified products thus limiting irradiation to ca. 3–6 min. Total transformation of the dicarbonyl complexes **10**–**12** led to low yields. The most photosensitive complexes were the leucinol-substituted complexes **15** and **16**. Despite very short irradiation times it was not possible to isolate these complexes free from large amounts of impurities. The formation of these complexes was therefore established by their IR spectra only. All other complexes (**13**, **14**, **17**–**20**) were isolated in yields ranging from 42 (**13**) to 85% (**20**).

The complexes **14** and **17** are rather labile and decompose at ambient temperature within a few days, in solution (acetone) even within a few hours. All other complexes are stable at room temperature and in air. In dichloromethane, all complexes **13**–**20** exhibit only one ν(CO) absorption each. Its position is nearly independent of the aminoalcohol substituent. As expected, the absorption of the $P(OMe)_3$-substituted complexes is at 18–20 cm^{-1} higher wave number compared to that of the $PTol_3$-substituted compound. The spectra in pentane indicate the presence of rotational isomers.

The complicated structure of the ^1H-NMR spectra with its many overlapping resonances renders the exact determination of the diastereomeric excess by NMR spectroscopy rather difficult. The de values were determined by integration of the cyclopentadienyl resonances. For the $P(OMe)_3$-substituted complexes the de values were additionally confirmed by those obtained by integration of the OMe signals of the trimethylphosphite substituent. The diastereomeric excess determined for the complexes **17**–**20** varies between 28 and 46%. In contrast, for freshly prepared **13** and **14** only one diastereomer could be detected (de > 90%). However, within several days the de value decreased to ca. 30% due to epimerization. The diastereomeric excess thus determined is in qualitative agreement with the ^{31}P-NMR spectra which are similar to those of the related isopropylideneglycerol-substituted carbene complexes [8].

Based on the influence on the diastereoselectivity the different aminoalcohols can be divided into two groups: those with a monosubstituted carbon substituent R = CH_2R' at the C_β atom of $-O-C_\alpha H_2-C_\beta HR-NMe_2$ group (**5**–**7**) and **4** which carries a disubstituted carbon atom CMe_2H at C_β. A very high diastereoselectivity (> 90%) independent of the entering PR_3 is only observed with complexes **13** and **14** derived from **4**. The de of **17**–**20** (with a CH_2R' substituent at C_β) is only moderate and in the range 28–46%. Surprisingly, *N*-formyl prolinol exerts only a modest influence on the diastereoselectivity [46% (**19**) and 34% (**20**)] although it is the aminoalcohol sterically most closely related to 1,2-O-isopropylideneglycerol investigated earlier (de > 96% independent of PR_3). Obviously, the substituent at C_β exerts the most influence on the stereoselectivity of the substitution reaction.

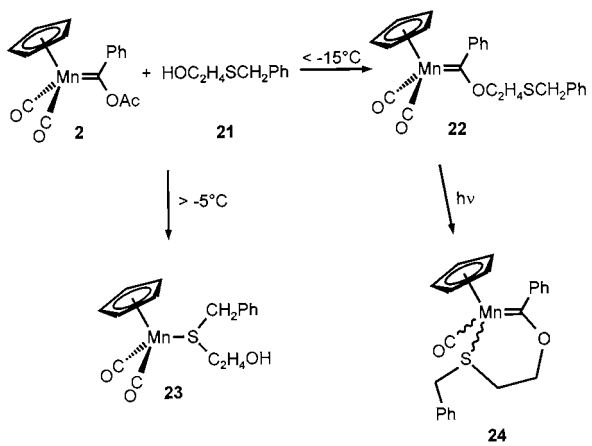
Since it was not possible to detect a chelating intermediate in any of these substitution reactions by IR spectroscopy, we extended our investigations to mercaptoalcohol-substituted carbene complexes. It is well known that the coordinating ability of thioethers to low-valent complexes is superior to that of amines. We therefore reasoned that by use of a mercaptoalcohol-substituent we will have a better chance of generating and identifying the chelating complex and subsequently transforming it into a carbene(carbonyl)cyclopentadienyl(PR_3)manganese complex.

When a solution of **2** in dichloromethane was charged with 1.5 equivalent of the β-mercaptoalcohol derivative **21** and then allowed to warm to a maximum of −15°C, the formation of a new dicarbonyl complex was detected by IR spectroscopy. Chromatographic work-up on silica afforded the mercapto(phenyl)-carbene complex **22** in ca. 76% yield (Scheme 3). However, when the solution was allowed to warm to a temperature higher than −5°C and then kept at that temperature, the major product isolated after chromatography was the thioether complex **23** (Scheme 3).

Complex **23** was presumably formed via displacement of the carbene ligand in **22** (or **2**) by free **21** which was present in excess. The constitution of **23** was established by spectroscopic means (IR, NMR, and mass spectroscopy) and by an independent synthesis from $[Cp(CO)_3Mn]$ and **21**.

From the observation of six ν(CO) absorptions in the IR spectrum of the carbene complex **22** in pentane it follows that at least three rotamers of **22** are present in solution. In contrast, the NMR spectra exhibit only one set of resonances indicating that isomerization is rapid with respect to the NMR time-scale.

Irradiation of a solution of **22** in dichloromethane at -30°C for a few minutes led to the formation of a new complex which in the IR spectrum showed only one absorption at 1854 cm^{-1} and whose mass spectrum is in accordance with the constitution (**24**) shown in Scheme 3. Although **24** proved to be stable in solution at temperatures below 0°C for a short period of time, it could not be isolated in a pure form. On chromatography compound **24** quickly decomposed. When triphenylphosphane or trimethylphosphite was added to solutions of **24** in dichloromethane no reaction was observed, neither at -50°C (for 50 h) nor at elevated temperatures. In boiling dichloromethane only decomposition of **24** and the formation of $[Cp(CO)_3Mn]$ in addition to other unidentified products were observed. Presumably due to the high stability of the Mn–S bond, thermal opening of the C,S-chelate ring requires temperatures at which either the chelate complex or the substitution product quickly decompose. Whether Mn–S dechelation of **24** and addition of PR_3 to the resulting free coordination site can be induced photochemically is at present under investigation.



Scheme 3.

3. Experimental

3.1. General

All operations were carried out under either nitrogen or argon by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium–benzophenone ketyl or CaH_2 and were freshly distilled prior to use. The silica gel used for chromatography (J.T. Baker, silica gel for flash chromatography) was saturated with argon. The yields refer to analytically pure compounds and were not optimized. The complexes **1** [9] and **2** [7], the aminoalcohols *N*,*N*-dimethyl alaninol (**3**), *N*,*N*-dimethyl leucinol (**4**), *N*,*N*-dimethyl valinol (**5**), *N*,*N*-dimethyl phenylalaninol (**6**), [10,11] and *N*-formylprolinol (**7**) [12] as well as $PTol_3$ [13] were prepared according to literature procedures. $P(OMe)_3$ and acetyl bromide were purchased from Fluka. IR: FT-IR spectrophotometer, Bio-Rad. ^{1}H-NMR, ^{31}P-NMR and ^{13}C-NMR: Bruker WM 250, Bruker AC 250, Bruker DRX 600, Jeol JNX 400. Unless specifically mentioned, ^{1}H-NMR spectra were recorded at 250 MHz and ^{13}C- and ^{31}P-NMR spectra at 400 MHz. All spectra were recorded at room temperature (r.t.) in CD_3COCD_3. Chemical shifts are reported relative to the residual solvent peaks (^{1}H $\delta = 2.05$ and ^{13}C $\delta = 29.8$) or to external H_3PO_4 (^{31}P). MS: Finnigan MAT 312 (EI) or Finnigan MAT 312/AMD5000 (FAB).

3.2. General procedure for the synthesis of the complexes *8*–*12*

At -50°C 4.5 mmol of the corresponding aminoalcohol derivative (**3**–**7**) was added to a solution of **2**, prepared from 3.0 mmol of acetyl bromide and 3.0 mmol of **1** in 50 ml of CH_2Cl_2. The resulting solution was stirred for 0.5 h at -50°C, warmed to 0°C and stirred for another 2.5 h at 0°C. The solvent was removed at r.t. in vacuo. The dark brown residue was dissolved in CH_2Cl_2–pentane (2/1) and chromatographed at -30°C on silica gel first with CH_2Cl_2–pentane and then with CH_2Cl_2–pentane–triethylamine.

3.2.1. Dicarbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-propane-1-yloxy(phenyl)carbene]-manganese (*8*)

Chromatography with CH_2Cl_2–pentane (6/1) afforded a yellow band (30 mg) and then elution with CH_2Cl_2–pentane–NEt_3 (2/1/0.3) gave a red–brown band. Removal of the solvent from the red–brown fraction afforded complex **8** as a red oil. Yield: 500 mg

(57% relative to **1**). IR (pentane) ν(CO) (cm^{-1}): 1972 m, 1962 vs, 1914 m, 1900 vs. ^{1}H-NMR: $\delta = 1.08$ (d, $^3J = 6.7$ Hz, 3 H, CH_3), 2.24 (s, 6 H, $N(CH_3)_2$), 2.77–3.05 (m, 1 H, CH), 4.30–4.50 (m, 2 H, CH_2), 4.69 (s, 5 H, Cp), 6.96–6.99 (m, 2 H, Ph), 7.22–7.39 (m, 3 H, Ph). ^{13}C-NMR: $\delta = 12.6$ (CH_3), 41.6 (NCH_3), 42.6 (CH_2), 59.3 (CHN), 74.0 (OCH_2), 88.0 (Cp), 123.5, 127.9, 1128.9, 135.6, 155.8 (Ph), 233.1 (CO), 334.3 (Mn=C). MS (EI, 70 eV) m/z (%): 367 (11) [M^+], 311 (11) [$M^+ - 2CO$], 197 (28) [CpMnPh$^+$], 120 (18) [CpMn$^+$], 86 (100) [$NMe_2CH(CH_3)CH_2^+$], 55 (75) [Mn$^+$]. Anal. Found: C, 63.78; H, 6.75; N, 3.16. Calc. for $C_{19}H_{22}MnNO_3$ (395.4): C, 63.79; H, 6.63; N, 3.54%.

3.2.2. Dicarbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-3-methyl-butane-1-yloxy(phenyl)-carbene]manganese (9)

Chromatography with CH_2Cl_2–pentane (2/1) gave a dark red band (30 mg). Subsequently, elution with CH_2Cl_2–pentane–NEt_3 (1/2/0.3) afforded a red–brown band which was collected. Removal of the solvent from the second fraction in vacuo yielded complex **9** (630 mg, 67% relative to **1**) as a red oil. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1955 vs, 1884 vs. ^{1}H-NMR: $\delta = 0.92$, 0.98 (d each, $^3J = 6.6$ Hz, together 6 H, $CH(CH_3)_2$), 2.29 (s, 6 H, $N(CH_3)_2$), 2.39–2.45 (m, 1 H, CH), 4.39–4.60 (m, 2 H, CH_2), 4.68 (s, 5 H, Cp), 6.20–6.97 (m, 2 H, Ph), 7.22–7.39 (m, 3 H, Ph). ^{13}C-NMR: $\delta = 20.2$, 21.1 (CH_3), 28.6 (NCH_3), 42.1 ($CH(CH_3)_2$), 69.8 (CHN), 74.0 (OCH_2), 88.1 (Cp), 123.1, 127.7, 128.2, 156.1 (Ph), 233.1 (CO), 334.0 (Mn=C). MS (EI, 70 eV) m/z (%): 395 (0.4) [M^+], 339 (0.2) [$M^+ - 2CO$], 197 (7) [CpMnPh$^+$], 114 (100) [$(CH_2CH(NMe_2)CH(CH_3)_2)^+$], 58 (100) [$CH_2CH(CH_3)_2^+$], 55 (98) [Mn$^+$]. Anal. Found: C, 63.78; H, 6.75; N, 3.16. Calc. for $C_{21}H_{26}MnNO_3$ (395.4): C, 63.79; H, 6.63; N, 3.54%.

3.2.3. Dicarbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-4-methyl-pentane-1-yloxy(phenyl)-carbene]manganese (10)

Chromatography with CH_2Cl_2–pentane (2/1) gave a dark red band. Subsequent elution with CH_2Cl_2–pentane–NEt_3 (1/2/0.3) afforded a dark brown band which was collected. Removal of the solvent from this fraction in vacuo yielded complex **10** (1.06 g, 79% relative to **1**) as a red oil. IR (pentane) ν(CO) (cm^{-1}): 1972 s, 1963 vs, 1914 s, 1908 s, 1900 vs. ^{1}H-NMR: $\delta = 0.81$–0.95 (m, 6 H, $-CH(CH_3)_2$), 1.18–1.37, 1.42–1.51 (m each, together 2 H, CH_2), 1.54–1.94 (m, 1 H, CH), 2.28 (s, 6 H, $N(CH_3)_2$), 2.86–3.01 (m, 1 H, CH), 4.01–4.49 (m, 2H, CH_2).4.68 (s, 5H, Cp), 6.95–6.98 (m, 1H, Ph), 7.64 (m, 4 H, Ph). ^{13}C-NMR: $\delta = 22.6$, 23.4 (CH_3), 25.4 (NCH_3), 38.4 (CH_2), 41.2 ($CH(CH_3)_2$), 61.2 (NCH), 76.6 (OCH_2), 88.0 (Cp), 123.3, 127.6, 127.8, 128.2, 155.8 (Ph), 233.1 (CO), 334.2 (Mn=C). MS (EI, 70 eV) m/z (%): 409 (0.6) [M^+], 353 (0.3) [$M^+ - 2CO$], 128 (100) [$(CH_2CH(NMe_2)CH_2CH(CH_3)_2)^+$], 120 (6) [MnCp$^+$], 58 (32) [$CH_2CH(CH_3)_2^+$], 55 (27) [Mn$^+$]. Anal. Found: C, 66.24; H, 7.50; N, 3.70. Calc. for $C_{22}H_{28}MnNO_3 \cdot 0.3C_5H_{12}$ (433.4): C, 65.77; H, 7.44; N, 3.33%.

3.2.4. Dicarbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-3-phenyl-propane-1-yloxy(phenyl)-carbene]manganese (11)

Chromatography with CH_2Cl_2–pentane (2/1) gave first a yellow and then a red band. Subsequent elution with CH_2Cl_2–pentane–diethyl ether–NEt_3 (1/2/0.6/0.4) afforded a yellow band which was collected. Removal of the solvent from this fraction in vacuo yielded complex **11** (1.58 g, 73% relative to **1**) as a brown oil. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1955 vs, 1887 vs. ^{1}H-NMR: $\delta = 2.38$ (br, 6 H, $N(CH_3)_2$), 2.18–2.21 (m, 1 H, CH), 2.75–2.97 (m, 4 H, CH_2O, CH_2Ph), 4.66 (s, 5 H, Cp), 6.90–7.35 (m, 10 H, Ph). ^{13}C-NMR: $\delta = 34.3$ (CH_2Ph), 41.7 ($N(CH_3)_2$), 65.8 (CH), 75.7 (CH_2O), 87.9, 88.0 (Cp), 123.2, 126.6, 128.1, 129.2, 140.7, 155.5 (Ph, Bn), 232.8, 233.0 (CO), 334.1 (Mn=C). MS (EI, 70 eV) m/z (%): 415 (0.2) [$M^+ - CO$], 371 (13) [$M^+ - CH_2CHNMe_2$], 120 (58) [MnCp$^+$], 105 (100) [$(CH_3CH_2Ph)^+$], 91 (25) [$C_7H_7^+$], 77 (63) [$C_6H_5^+$], 55 (63) [Mn$^+$]. It was not possible to to obtain complex **11** in an analytically pure form free of NEt_3.

3.2.5. Dicarbonyl(cyclopentadienyl)[(2S)-N-formyl-pyrrolidine-2-methylenyloxy(phenyl)carbene]-manganese (12)

Chromatography with CH_2Cl_2–pentane (2/1) gave first a dark red band. Subsequent elution with CH_2Cl_2–pentane–NEt_3 (1/2/0.3) afforded a red–brown band which was collected. Removal of the solvent from this fraction in vacuo yielded complex **12** (840 mg, 58% relative to **1**) as a red oil. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1955 vs, 1884 vs. ^{1}H-NMR: $\delta = 1.75$–2.03 (m, 4 H, 3-CH_2, 4-CH_2), 3.20–3.75 (m, 3 H, 5-CH_2, 2-CH), 4.37 (br, 2 H, CH_2O), 4.69, 4.71 (s each, together 5 H, Cp), 6.87–6.97 (m, 2 H, Ph), 7.26–7.42 (m, 3 H, Ph), 8.24, 8.30 (br, together 1 H, CHO). ^{13}C-NMR: $\delta = 28.9$, 29.0 (3-CH_2, 4-CH_2), 43.3 (5-CH_2), 46.9 (2-CH), 75.5, 77.9 (OCH_2), 87.5, 88.1 (Cp), 122.6, 127.2, 127.6, 128.1, 128.5, 128.6, 154.4, 154.8 (Ph), 232.0 (CO), 333.4, 333.5 (Mn=C), CHO not detected. MS (EI, 70 eV) m/z (%): 393 (10) [M^+], 337 (24) [$M^+ - 2CO$], 120 (74) [MnCp$^+$], 55 (100) [Mn$^+$]. Anal. Found: C, 60.41; H, 6.07; N, 3.13. Calc. for $C_{20}H_{20}MnNO_4$ (393.3): C, 61.07; H, 5.13; N, 3.56%.

3.3. General procedure for the synthesis of the complexes 13–20

A solution of 0.6 mmol of **9**–**12** and 0.9 mmol of the corresponding PR_3 in 30 ml of toluene was irradiated at

−30°C (for the irradiation time see below). To remove CO a slow stream of argon was passed through the solution. The solvent was removed at r.t. in vacuo. The residue was dissolved in CH_2Cl_2–pentane (2/1) and chromatographed at −20°C on silica gel with CH_2Cl_2–pentane–diethyl ether–triethylamine (2/1/0.3/0.3).

3.3.1. Carbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-3-methyl-butane-1-yloxy(phenyl)carbene]-(tritolylphosphane)manganese ***(13)***

$PR_3 = P(C_6H_4CH_3\text{-}p)_3$, irradiation time 5 min. Chromatography with CH_2Cl_2–pentane–NEt_3 (1/2/0.3) afforded complex **13** (120 mg, 42% relative to **9**) as a >95:5 mixture of diastereomers (de > 90%) in the form of an orange oil. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1833 s. ^{1}H-NMR: $\delta = 0.77$–1.03 (m, together 6 H, $CH(CH_3)_2$), 2.21–2.39 (m, 17 H, $N(CH_3)_2$, $C_6H_4CH_3$, CHN, $CH(CH_3)_2$), 3.43–3.88 (m, 2 H, CH_2), 4.40 (d, $^3J_{PH}$ = 1.7 Hz, 5 H, Cp), 6.58–6.67 (m, 2 H, Ph), 6.94–7.67 (m, 15 H, arom.). ^{13}C-NMR: $\delta = 21.2$, 21.4 (CH_3), 25.8 (NCH_3), 41.3, 41.5, 41.7 ($CH(CH_3)_2$), 63.5, 63.8, 64.2, 65.0 (CHN), 72.3, 72.6 (OCH_2), 87.1, 87.3, 87.4 (Cp), 123.3, 125.5, 125.7, 126.5, 126.7, 126.8, 127.1, 127.4, 128.2, 128.7, 128.9, 129.0, 129.3, 129.6, 129.9, 130.6, 132.7, 133.8, 136.1, 136.3, 139.7, 142.8 (arom.), 237.9 (CO), 326.6 (Mn=C). ^{31}P-NMR: $\delta = 84.1$, 84.3, 89.9. MS (EI, 70 eV) m/z (%): 643 (0.1) [$M^+ - CO$], 304 (53) [$PTol_3^+$], 114 (39) [$CH_2CH(NMe_2)CHMe_2^+$], 100 (100) [$NMe_2CHCHMe_2^+$], 58 (36) [$CH_2CH(CH_3)_2^+$].

3.3.2. Carbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-3-methyl-butane-1-yloxy(phenyl)carbene]-(trimethylphosphite)manganese ***(14)***

$PR_3 = P(OMe)_3$, irradiation time 6 min. Chromatography with CH_2Cl_2–pentane–NEt_3 (1/2/0.3) afforded complex **14** (200 mg, 67% relative to **9**) as a >95:5 mixture of diastereomers (de > 90%) in the form of an orange oil. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1851 s. ^{1}H-NMR: $\delta = 0.92$–0.99 (m, 6 H, $CH(CH_3)_2$), 1.80–1.95 (m, 1 H, CH), 2.30 (s, 6 H, $N(CH_3)_2$), 2.39–2.45 (m, 1 H, $CH(CH_3)_2$), 3.62, 3.63 (d each, $^3J_{PH} = 11$ Hz, together 9 H, $P(OCH_3)_3$), 4.46–4.67 (m, 2 H, CH_2), 4.42, 4.41 (d each, $^3J_{PH} = 1.7$ Hz, together 5H, Cp), 6.95–7.36 (m, 5 H, Ph). ^{31}P-NMR: $\delta = 204.6$. MS (EI, 70 eV) m/z (%): 491 (0.4) [M^+], 339 (1.2) [$M^+ - CO - L$], 244 (17) [$CpMn[P(OMe)_3]^+$], 100 (100) [$Me_2CHNMe_2^+$], 114 (57) [$Me_2CH(CH_2)NMe_2^+$], 58 (42) [$CH_2CH(CH_3)_2^+$].

3.3.3. Carbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-4-methyl-pentane-1-yloxy(phenyl)-carbene](tritolylphosphane)manganese ***(15)***

$PR_3 = P(C_6H_4CH_3\text{-}p)_3$, irradiation of **10** for 3.5 min. During irradiation, complex **15** rapidly decomposed again and therefore could not be isolated free of large amounts of impurities. Its intermediary formation was only established by its IR spectrum in CH_2Cl_2 ν(CO): 1832 cm^{-1}.

3.3.4. Carbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-4-methyl-pentane-1-yloxy(phenyl)-carbene](trimethylphosphite)manganese ***(16)***

$PR_3 = P(OMe)_3$, irradiation of **10** for 3.0 min. During irradiation, complex **16** rapidly decomposed again and therefore could not be isolated free of large amounts of impurities. Its intermediary formation was only established by its IR spectrum in CH_2Cl_2 ν(CO): 1852 cm^{-1}.

3.3.5. Carbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-3-phenyl-propane-1-yloxy(phenyl)-carbene](tritolylphosphane)manganese ***(17)***

$PR_3 = P(C_6H_4CH_3\text{-}p)_3$, irradiation time 4.5 min. Chromatography with CH_2Cl_2–pentane–NEt_3 (1/2/0.3) afforded complex **17** (270 mg, 62% relative to **11**) as a 36:64 mixture of diastereomers (de 28%) in the form of an orange oil. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1834 vs. ^{1}H-NMR: $\delta = 2.12$–2.57 (m, 16 H, $N(CH_3)_2$, $C_6H_4CH_3$, CH), 2.75–3.08 (m, 4 H, CH_2O, CH_2Ph), 4.38, 4.43 (s each, together 5 H, Cp), 6.80–7.95 (m, 22 H, Ph, $C_6H_4CH_3$). MS (FAB, NBA) m/z (%): 719 (0.8) [M^+], 691 (1) [$M^+ - 2CO$]. Anal. Found: C, 75.58; H, 7.09; N, 2.28. Calc. for $C_{45}H_{46}MnNO_2P$ (718.8): C, 75.20; H, 6.45; N, 1.95%.

3.3.6. Carbonyl(cyclopentadienyl)[(2S)-2-N,N-dimethylamino-3-phenyl-propane-1-yloxy(phenyl)-carbene](trimethylphosphite)manganese ***(18)***

$PR_3 = P(OMe)_3$, irradiation time 5 min. Orange oil. Ratio of diastereomers 31:69 (de = 38%). Yield: 170 mg (52% based on **11**). IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1852 vs. ^{1}H-NMR: 2.11–2.21 (m, 1 H, CH), 2.30, 2.34 (s each, 6 H, $N(CH_3)_2$), 2.68–3.20 (m, 4 H, CH_2O, CH_2Ph), 3.57 and 3.59 (d each, $^3J_{PH} = 11.5$ and 11.0 Hz, together 9 H, $P(OCH_3)_3$), 4.41–4.44 (m, 5 H, Cp), 6.93–7.53 (m, 10 H, Ph). ^{13}C-NMR: $\delta = 40.5$, 40.6 (CH_2Ph), 51.3, 51.4 ($P(OCH_3)_3$), $N(CH_3)_2$), 57.9 (CHN), 64.3 (CH), 69.0 (CH_2O), 85.6, 85.7 (Cp), 125.7, 125.9, 126.1, 126.6, 127.9, 128.2, 128.3, 128.4, 128.5, 128.9, 129.2, 129.3, 129.4, 140.3, 140.6, 155.4, 156.5 (Ph, Bn), 235.9, 236.3 (CO), 324.6, 324.9 (Mn=C). ^{31}P-NMR: $\delta = 204.7$, 211.3, 214.5. MS (EI, 70 eV) m/z (%): 539 (4) [M^+], 244 (17) [$CpMn[P(OMe)_3]^+$], 162 (100) [$(CH_2C(NMe_2)CH_2Ph)^+$], 148 (84) [$(Me_2NCHCH_2Ph)^+$], 146 (95) [$(C_{10}H_{12}N)^+$].

3.3.7. Carbonyl(cyclopentadienyl)[(2S)-N-formyl-pyrrolidine-2-methylenyloxy(phenyl)carbene]-(tritolylphosphane)manganese ***(19)***

$PR_3 = P(C_6H_4CH_3\text{-}p)_3$, irradiation time 6 min. Chromatography with CH_2Cl_2–pentane–NEt_3 (1/2/0.3) afforded complex **19** (320 mg, 82% relative to **12**) as a

27:73 mixture of diastereomers (de = 46%) in the form of an orange oil. IR (CH_2Cl_2): ν(CO) (cm^{-1}) 1833 s. ^{1}H-NMR: δ = 1.85–2.23 (m, 4 H, 3-CH_2, 4-CH_2), 2.38 (s, 9 H, $C_6H_4CH_3$), 3.20–3.75 (m, 3 H, 5-CH_2, 2-CH), 4.31 (m, 2 H, CH_2O), 4.42, 4.44 (s each, together 5 H, Cp), 7.16–7.65 (m, 5 H, Ph), 8.27, 8.39 (br, together 1 H, CHO). ^{13}C-NMR: δ = 21.2, 21.4 ($C_6H_4CH_3$), 23.3, 28.4 (3-CH_2, 4-CH_2), 43.9 (5-CH_2), 47.3 (2-CH), 72.8, 75.5 (OCH_2), 87.6 (Cp), 125.6, 126.9, 127.3, 128.7, 129.3, 130.0, 132.8, 133.8, 134.2, 135.8, 136.0, 139.4, 139.9, 142.8, 155.4, 164.8 (Ph), 238.3 (CO), 324.0 (Mn=C). ^{31}P-NMR: δ = 82.9, 83.5. MS (FAB, NBA) m/z (%): 699 (3) [M^+], 641 (3) [$M^+ - 2CO$]. Anal. Found: C, 71.48; H, 6.50; N, 1.88. Calc. for $C_{40}H_{41}MnNO_3P$ (669.7): C, 71.74; H, 6.17; N, 2.09%.

3.3.8. Carbonyl(cyclopentadienyl)[(2S)-N-formyl-pyrrolidine-2-methylenyloxy(phenyl)carbene]-(trimethylphosphite)manganese (**20**)

PR_3 = $P(OMe)_3$, irradiation time 6 min. Chromatography afforded complex **20** (200 mg, 85% relative to **12**) as a 33:67 mixture of diastereomers (de = 34%) in the form of an orange oil. IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1851 s. ^{1}H-NMR: δ = 1.79–2.19 (m, 4 H, 3-CH_2, 4-CH_2), 3.30–3.34 (m, 2 H, 5-CH_2), 3.52 and 3.61 (d each, $^3J_{PH}$ = 11.6 and 11.1 Hz, 9 H, $P(OCH_3)_3$), 3.49–3.55 (m, 1 H, 2-CH), 4.01–4.37 (m, 2 H, CH_2O), 4.42, 4.44 (d each, $^3J_{PH}$ = 1.46 and 1.65 Hz, 5 H, Cp), 7.07–7.48 (m, 5 H, Ph). ^{13}C-NMR: δ = 22.6, 22.7, 23.7, 23.8 (CH_3), 27.8, 27.9, 28.0 (NCH_3), 43.3, 46.5 ($CH(CH_3)_2$), 51.4 ($P(OCH_3)_3$), 56.6, 56.7 (CHN), 76.4, 78.9 (OCH_2), 85.7, 85.8 (Cp), 124.2, 126.2, 126.7, 128.0, 128.4, 128.7, 156.0, 156.2, 156.5 (Ph), 238.3 (m, CO), 324.0 (m, Mn=C). ^{31}P-NMR: δ = 203.6, 210.8, 214.6. MS (EI, 70 eV) m/z (%): 491 (0.4) [M^+], 339 (1.2) [$M^+ - CO - L$], 244 (17) [MnCp[$P(OMe)_3$]$^+$], 100 (100) [$Me_2CHNMe_2^+$], 114 (57) [$Me_2CH(CH_2)NMe_2^+$], 58 (42) [$CH_2CH(CH_3)_2^+$].

3.4. Dicarbonyl(cyclopentadienyl)[1-benzylmercaptoethane-2-yloxy(phenyl)carbene]manganese (**22**)

760 mg (4.5 mmol) of 1-benzylmercaptoethane-2-ol (**21**) was added at −50°C to a solution of **2** freshly prepared from 860 mg (3.0 mmol) of **1**, 0.43 ml (3.0 mmol) of TMEDA and 0.21 ml (3.0 mmol) of acetylbromide in 50 ml of CH_2Cl_2. Within 2 h, the solution was allowed to warm up to −15°C and stirred for another 2 h at −15°C. The solvent was removed at r.t, in vacuo. The residue was dissolved in 12 ml of CH_2Cl_2–pentane (1/2) and chromatographed on silica at −30°C with CH_2Cl_2–pentane (1/2). An orange fraction was eluted which, after removal of the solvent in vacuo, afforded a dark brown oil. Yield: 1.29 g (76% relative to **1**). IR (pentane) ν(CO) (cm^{-1}): 1983 sh, 1973 sh, 1965 vs, 1923 sh, 1915 sh, 1903 vs. ^{1}H-NMR: δ = 2.90 (t, ^3J = 6.42 Hz, 2 H, OCH_2CH_2SBn), 3.78 (s, 2 H, CH_2Ph), 4.54 (t, ^3J = 6.42 Hz, 2 H, OCH_2CH_2SBn), 4.71 (s, 5 H, Cp), 6.74–7.04 (m, 1 H, arom.), 7.23–7.31 (m, 2 H, arom.), 7.32–7.38 (m, 7 H, arom.). ^{13}C-NMR: δ = 36.0 (SCH_2Bn), 75.5, 81.8 (OCH_2CH_2SBn), 87.4 (Cp), 122.8, 127.3, 127.5, 128.4, 128.9, 138.6, 154.9 (Ph, Bn), 232.0 (CO), 333.4 (Mn=C). MS (EI, 70 eV) m/z (%): 432 (3) [M^+], 376 (4) [$M^+ - 2CO$], 151 (70) [$(CH_2CH_2SBn)^+$], 120 (10) [$MnCp^+$], 91 (100) [$C_7H_7^+$], 55 (40) [Mn^+]. Anal. Found: C, 63.82; H, 5.03. Calc. for $C_{23}H_{21}MnO_3S$ (432.4): C, 63.89; H, 4.89%.

3.5. Dicarbonyl(cyclopentadienyl)[1-benzylmercaptoethane-2-ol-S]manganese (**23**)

The reaction of 250 mg (1.5 mmol) of 1-benzylmercaptoethane-2-ol with **2** and the subsequent chromatography were carried out as described in Section 3.4, except that the solution was allowed to warm to r.t. and was stirred at r.t. for 3 h. On chromatography first an orange–red fraction (containing **22**) and then with CH_2Cl_2–pentane–Et_2O (2/1/0.3) a dark red–brown band were eluted. Removal of the solvent from the second fraction gave **23** in the form of an orange oil. Yield: 280 mg (54% based on **1**). IR (pentane) ν(CO) (cm^{-1}): 1938 vs, 1874 vs. ^{1}H-NMR: 2.74 (br, 2 H, CH_2S), 3.87 (br, 2 H, CH_2O), 4.05 (br, 1 H, OH), 4.56 (br, 5 H, Cp), 7.47 (br, 5 H, Ph). ^{13}C-NMR: δ = 44.5 (CH_2SBn), 48.7 (SCH_2Ph), 59.5 (CH_2OH), 81.8 (Cp), 126.8, 126.7, 128.3, 128.5, 129.0, 129.7, 136.5 (Ph, Bn), 234.1 (CO). MS (EI, 70 eV) m/z (%): 344 (5) [M^+], 288 (28) [$M^+ - 2CO$], 168 (52) [$(HOCH_2CH_2SBn)^+$], 120 (25) [$MnCp^+$], 91 (100) [$C_7H_7^+$], 55 (21) [Mn^+]. Anal. Found: C, 55.82; H, 5.15. Calc. for $C_{16}H_{17}MnO_3S$ (344.3): C, 55.82; H, 4.98%.

3.6. Generation of monocarbonyl(cyclopentadienyl)-[1-benzylmercaptoethane-1-yloxy-S-(phenyl)carbene]-manganese (**24**)

A solution of 260 mg (0.6 mmol) of **22** in 30 ml of CH_2Cl_2–pentane (1/1) was irradiated for 4.5 min at −30°C, while a slight Ar stream was passed through the solution. The solvent was then removed in vacuo at a temperature below −30°C. All attempts to purify the product by column chromatography failed since, even at very low temperature, the complex **24** decomposed on contact with silica. IR (CH_2Cl_2, −30°C) ν(CO): 1854 s cm^{-1}. MS (EI, 70 eV) m/z (%): 404 (0.4) [M^+], 390 (0.7) [$M^+ - CH_2$], 376 (2) [$M^+ - CO$], 120 (10) [$MnCp^+$], 91 (100) [$C_7H_7^+$], 55 (29) [Mn^+].

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