Diastereoselective Substitution of PR_3 for CO in Carbene(dicarbonyl)-cyclopentadienyl Complexes of Manganese − Synthesis of (S_{Mn})- and (R_{Mn})-[Cp(CO)(PR_3)Mn=C(OR*)R′] Complexes

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Chiral carbene complexes [Cp(CO)$_2$Mn=C(OR*)Ph] (**4a**−**e**) were prepared by reaction of [Cp(CO)$_2$Mn=C(OAc)Ph] (**2**) with HOR* [HOR* = 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (**3a**), 2,3,4,6-tetra-*O*-acetyl-D-galactopyranose (**3b**), 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**3c**), (*S*)- (**3d**) and (*R*)-1,2-*O*-isopropylideneglycerol (**3e**)]. The replacement of a CO ligand with $PTol_3$ in **4a**−**e** proceeded diastereoselectively to give [Cp(CO)($PTol_3$)Mn=C(OR*)Ph] (**5a**−**e**). The diastereoselectivity increased in the order **a**, **b**, **c**, **d**: de = 8% (**5a**), 33% (**5b**), 70% (**5c**), > 96% (**5d**). For (*R*)-**5d** the isomer with the (*S*) configuration at manganese (S_{Mn}) was formed predominantly. For (*S*)-**5d**, only (R_{Mn},*S*)-**5d** was detected (de > 96%). Photolysis of (*R*)-**4d** in the presence of phosphites or phosphanes afforded (S_{Mn})-[Cp(CO)(PR_3)Mn=C(OR*)Ph] [PR_3 = $P(OPh)_3$ (**8**), $P(OMe)_3$ (**9**), $P(OMe)_2Ph$ (**10**), $P(OMe)Ph_2$ (**11**), PPh_3 (**12**), $P(C_6H_4Cl\text{-}p)_3$ (**13**)] with a de > 96%. Photolysis of (*S*)-**4d** in the presence of $P(OMe)_3$ gave (R_{Mn},*S*)-**9**. Complex (*R*)-**14** [related to (*R*)-**4d**] was obtained from [Cp(CO)$_2$Mn=C(OAc)Tol-*p*] and **3d**. Replacement of CO by PR_3 in (*R*)-**14** gave (S_{Mn},*R*)-[Cp(CO)(PR_3)Mn=C(OR*)Tol-*p*] [R = Tol-*p* (**15**), OMe (**16**), C_6H_4Cl-*p* (**17**)] with a de > 96%. In solution, the $PTol_3$-substituted complex **5d** is configurationally stable whereas the $P(OMe)_3$ complex **9** epimerizes slowly at room temperature in CH_2Cl_2, Et_2O, and THF within about one week.

Introduction

Chiral transition-metal complexes play a prominent role in enantioselective synthesis and catalysis. In these complexes either the metal[1] or one or more ligands carry the chiral information. Although a wide variety of carbohydrates are available from the chiral pool, the number of reports on their use as chiral auxiliaries in transition-metal chemistry is rather restricted.[2] The preparation of new carbohydrates via organometallic compounds was recently described by Dötz et al.[3]

Recently, we reported the synthesis of chiral complexes of manganese and rhenium. These complexes, of the type [Cp(CO)$_2$M=C(OR*)R′] (M = Mn, Re, OR* = mannofuranosyl, glucofuranosyl, fructopyranosyl, R′ = Ph, Tol), were obtained by addition of the monoanion of the corresponding protected carbohydrate to the cationic carbyne complexes [Cp(CO)$_2$M≡CR′]$^+$.[4]

Another route to chiral carbene complexes involves nucleophilic substitution by chiral alcoholates, such as (−)-mentholate and borneolate, of the acetoxy substituent in acetoxycarbene complexes of manganese [Cp(CO)$_2$Mn=C(OAc)R′].[5][6]

Photolysis of the chiral carbohydratocarbene complexes in the presence of phosphanes or phosphites (L) afforded chiral-at-metal carbene complexes of the type [Cp(CO)(L)M=C(OR*)R′]. The diastereomeric excess (de) ranged from 0 to 80% and depended on the nature of the carbohydrate and the entering phosphorus ligand. The diastereoselectivity increased with increasing nucleophilicity of L. The highest diastereoselectivity was obtained with OR* = 2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranosyl and L = tritolylphosphane.

In this paper we report (a) on the synthesis of chiral dicarbonyl(carbohydratocarbene) complexes by alcoholysis of [acetoxy(aryl)carbene]dicarbonyl(cyclopentadienyl)manganese with protected carbohydrates and chiral alcohols, (b) on the synthesis of diastereomerically pure carbene(carbonyl)phosphane complexes, and (c) on the ready access to pure compounds of both configurations at the chiral metal center.

Results and Discussion

Successive reaction of the lithium benzoylmanganate **1** with TMEDA and acetyl bromide gave the thermolabile acetoxy carbene complex **2** as described previously.[5] The reaction of **2** with partially protected carbohydrates that are unprotected either in the 6-position [1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (**3a**)] or in the 1-position [2,3,4,6-tetra-*O*-acetyl-D-galactopyranose (**3b**) and 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**3c**)] afforded the chiral-at-ligand dicarbonyl(cyclopentadienyl)[alkoxy(phenyl)carbene] complexes **4a**−**c** in 40−66% yield (Scheme 1). The complexes (*R*)- and (*S*)-**4d** were obtained from the reaction of **2** with the enantiomerically pure alcohols (*S*)- and (*R*)-1,2-*O*-isopropylideneglycerol, (*S*)- and (*R*)-**3d**.[7]

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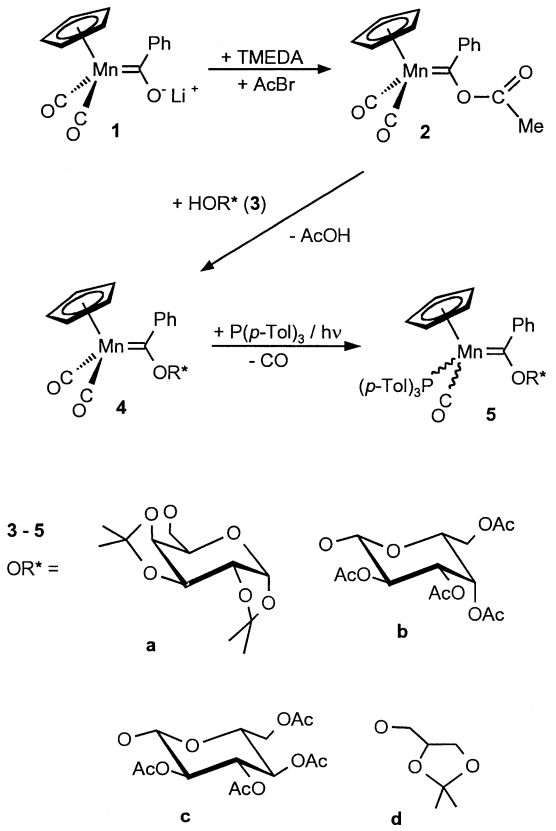
Scheme 1

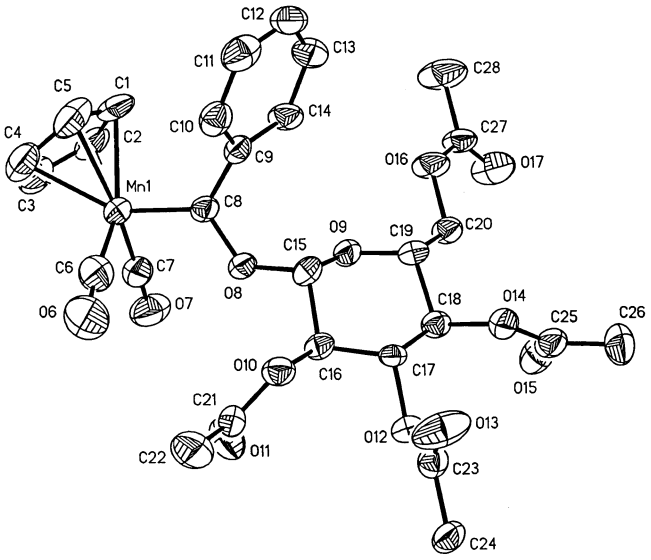


The NMR spectra of **4a**−**c** unambiguously show that the carbohydrato residue is bonded to the carbene carbon atom by the oxygen atom at C-6 (**4a**) or at C-1 (**4b**, **c**). The absence of a low-field resonance for the 1-H atom at the anomeric center in **4b** and **4c** indicates an β-configuration of the glucosyl and the galactosyl groups. This configuration was confirmed by the X-ray structural analysis of **4c** (Figure 1).

Complex **4c** exhibits a pseudo-octahedral geometry (Figure 1). The Mn−C(carbene) distance [1.857(7) Å] is comparable to that usually observed in CpL_2Mn(carbene) complexes.[4][8] The carbene ligand adopts the sterically least congested conformation. The carbene plane [C(8), Mn(1), C(9), O(8)] is slightly twisted with respect to the plane formed by the atoms C(7), Mn(1), and C(8) [torsion angle C(7)−Mn(1)−C(8)−O(8) −27.9(8)°] and strongly twisted with respect to the phenyl plane [torsion angle Mn(1)−C(8)−C(9)−C(10) 64.0(9)°].

In our earlier studies on the selectivity of the CO/PR_3 exchange in carbohydratocarbene complexes, the highest diastereoselectivity was observed for PR_3 = tri(*p*-tolyl)phosphane. Therefore, tri(*p*-tolyl)phosphane was also used in the initial studies with **4a**−**d**. Photolysis of the complexes **4a**−**d** in toluene at −30°C for several minutes in the presence of tritolylphosphane afforded the carbene complexes **5a**−**d** in moderate to high yield (Scheme 1). The compounds **5b** and **5c** are slightly photolabile. Partial decomposition had already occurred during irradiation, thus reducing the yield. Total transformation of the dicarbonyl complexes led to a low yield. Since the starting materials, complexes **4b** and **4c**, can be easily separated from the product complexes **5b** and **5c**, irradiation was terminated before **4b** and **4c** were completely consumed.

Figure 1. Structure of complex **4c** in the crystal (without H atoms)[a]



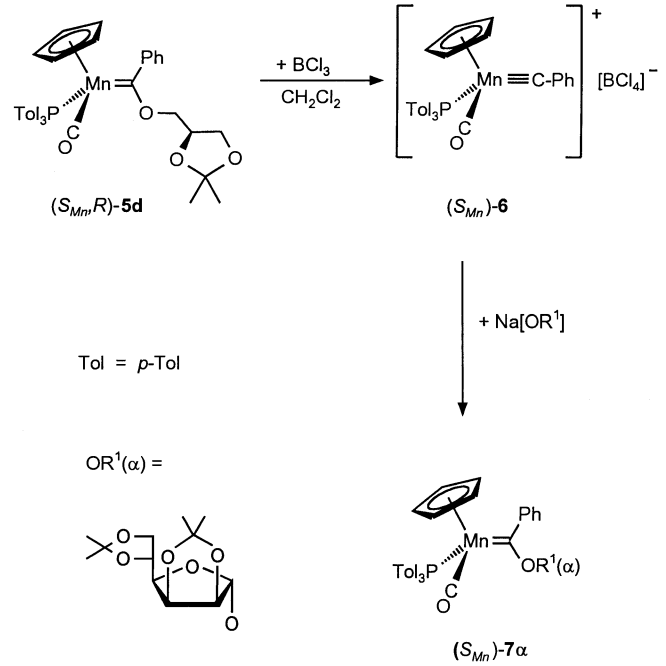
[a] Selected distances [Å] and angles [°] (standard deviations in parentheses): Mn(1)−C(6) 1.773(10), Mn(1)−C(7) 1.747(9), Mn(1)−C(8) 1.857(7), C(6)−O(6) 1.156(12), C(7)−O(7) 1.168(11), C(8)−O(8) 1.375(8); C(6)−Mn(1)−C(7) 89.4(4), C(6)−Mn(1)−C(8) 88.4(4), Mn(1)−C(8)−C(9) 124.8(5), Mn(1)−C(8)−O(8) 119.2(5), C(9)−C(8)−O(8) 116.0(6).

The ^{1}H-NMR signals of the cyclopentadienyl protons were easily detected and appeared as doublets due to coupling with the phosphorus atom. For **5a**−**c** two doublets were observed in each case: δ = 4.49, 4.53 ($^3J_{PH}$ = 1.82 Hz, 1.80 Hz; **5a**), 4.60, 4.63 ($^3J_{PH}$ = 1.79 Hz, 1.55 Hz; **5b**), and 4.64, 4.71 ($^3J_{PH}$ = 1.71 Hz, 1.45 Hz; **5c**). Therefore, the complexes **5a**−**c** were obtained as mixtures of diastereomers. The diastereomeric excess varied considerably. The diastereomeric excess, as determined by integration of the Cp resonances in the reaction mixtures, was 8% (**5a**), 33% (**5b**), and 70% (**5c**). In contrast to **5a**−**c**, each of the two glycerol derivatives (*R*)-**5d** and (*S*)-**5d** exhibit only one doublet for the cyclopentadienyl ring (δ = 4.45, $^3J_{PH}$ = 1.6 Hz). Similarly, only one ^{13}C-resonance signal for the Cp carbon atoms, and one ^{31}P signal for the tritolylphosphane ligand were detected for (*R*)-**5d** and (*S*)-**5d**. From these results a de of > 96% was deduced.

Complex (*R*)-**5d** was assigned the (S_{Mn}) configuration [(S_{Mn},*R*)-**5d**].[9] In order to corroborate the assignment, the complex was transformed into the known β-mannofuranosylcarbene complex (S_{Mn})-**7β**.[5] The structure of (S_{Mn})-**7β** has already been established by X-ray analysis.[5] Treatment of (S_{Mn},*R*)-**5d** with BCl_3 gave the chiral cationic carbyne complex (S_{Mn})-**6** by abstraction of [OR*]$^-$. Subsequent reaction with the sodium salt of an α,β mixture of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose Na[OR^1] afforded the α-mannofuranosylcarbene complex (S_{Mn})-**7α** (Scheme 2).

The identity of (S_{Mn})-**7α** was confirmed by comparison of its ^{1}H-NMR spectrum with that of an authentic sample.

Scheme 2



When the same reaction sequence was applied to (*S*)-**5d** the diastereomer (R_{Mn})-**7α** was obtained. Therefore, (*S*)-**5d** was assigned the (R_{Mn}) configuration.

The carbohydrate substituent clearly exerts considerable influence on the diastereoselectivity of the CO exchange reaction. From earlier experiments it followed that the photo-induced Mn−CO dissociation is the initiating and rate-limiting step of the substitution reaction. The range of diastereoselectivities observed can be rationalized by the different abilities of the OR* groups to intramolecularly stabilize the diastereomeric intermediates. It is very likely that an oxygen atom of the OR* substituent coordinates to the vacant coordination site of the intermediate resulting from loss of a CO ligand.

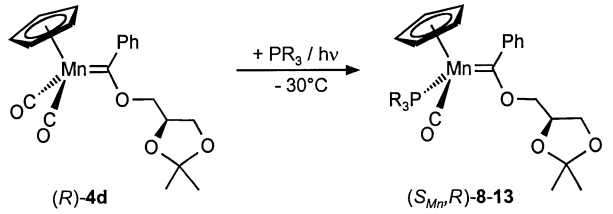
In the synthesis of complex **5a** the coordinating oxygen atom in the intermediate is presumably the pyranosyl oxygen atom, giving rise to the formation of a six-membered metallaheterocycle. However, due to the anomeric effect the pyranosyl oxygen atom is relatively electron-poor. Therefore, the coordination is weak and, consequently, the diastereomeric excess is only 8%.

The intermediate in the synthesis of **5b** and **5c** can be stabilized by interaction with either the carbonyl oxygen atom of the acetate group at C-2 (formation of an eight-membered metallacycle) or with the pyranosyl oxygen atom (formation of a five-membered metallacycle). The reactions of tri(*p*-tolyl)phosphane with tetramethyl- and tetrabenzyl-protected gluco- and galactopyranosylcarbene complexes instead of **4b** and **4c** gave diastereoselectivities similar to those of **4b** and **4c**.[10] Therefore, the formation of an eight-membered metallacycle by interaction of manganese with the carbonyl oxygen atom of the acetate group at C-2 in the intermediate is unlikely. The difference in the de values is probably caused by steric interaction of the acetoxy substituent at C-4 with the cyclopentadienyl ring.

The significantly higher diastereoselectivity in the reaction of (*R*)-**4d** and (*S*)-**4d** with $PTol_3$, as compared to that of **4a**−**c**, is probably due to the higher flexibility of the isopropylideneglycerol substituent in forming the most stable metallacyclic intermediate.

In contrast to furanosyl- and pyranosylcarbene complexes, the high diastereoselectivity of the PR_3/CO exchange is not confined to tritolylphosphane as the entering nucleophile. Within the limits of error, the replacement of CO by $P(OPh)_3$, $P(OMe)_3$, $P(OMe)_2Ph$, $P(OMe)Ph_2$, PPh_3, and $P(C_6H_4Cl\text{-}p)_3$ in (*R*)-**4d** also proceeded diastereospecifically (de > 96%) to afford (S_{Mn},*R*)-**8**−**13** (Scheme 3).

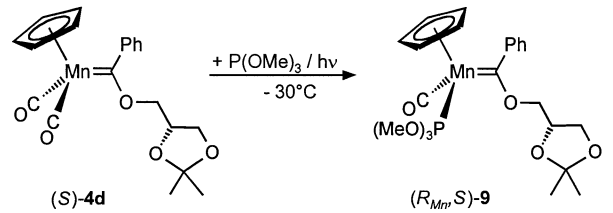
Scheme 3



PR_3	$P(OPh)_3$	$P(OMe)_3$	$P(OMe)_2Ph$	$P(OMe)Ph_2$	PPh_3	$P(C_6H_4Cl\text{-}p)_3$
	8	**9**	**10**	**11**	**12**	**13**

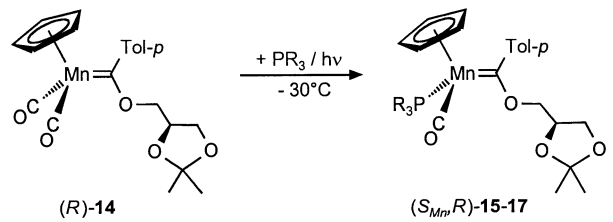
Analogously, the photolysis of (*S*)-**4d** in the presence of $P(OMe)_3$ gave (R_{Mn},*S*)-**9** (Scheme 4).

Scheme 4



The reaction of (*R*)-**14** with PR_3 afforded the complexes (S_{Mn},*R*)-**15**−**17** (Scheme 5) with a de > 96%. Complex (*R*)-**14** was prepared from [$Cp(CO)_2Mn$=C(OAc)Tol-*p*] and (*S*)-**3d**[7] in an analogous way to (*R*)-**4d**.

Scheme 5



R = Tol-*p* (**15**), OMe (**16**), C_6H_4Cl-*p* (**17**)

In contrast, photolysis of [Cp(CO)$_2$Mn=C(β-*O*-mannofuranosyl)Tol-*p*] in the presence of phosphites or phosphanes gave much lower de values [PR_3 = $P(OPh)_3$ (0%), $P(OMe)_3$ (12%), $P(C_6H_4Cl\text{-}p)_3$ (56%)].

All NMR spectra of the complexes **8**−**17** showed the expected resonances to confirm the formation of only one diastereomer in each case. However, the 600-MHz NMR spectra of these complexes indicated the presence of two isomers in solution. Most of the complexes exhibited two sets of ^{1}H- and ^{13}C-resonance signals for the diastereotopic methyl groups of the isopropylidene function [$\Delta\delta(^1H)$ = 0.01−0.03 ppm, $\Delta\delta(^{13}C)$ = 0.1 ppm; see Experimental Section]. For complex **8** two doublets for the carbonyl and the carbene carbon atom [$\Delta\delta(^{13}C)$ = 0.2 ppm] were observed, and for the complexes **8** and **10**−**12** two ^{31}P signals [$\Delta\delta(^{31}P)$ = 0.2 ppm] were detected.

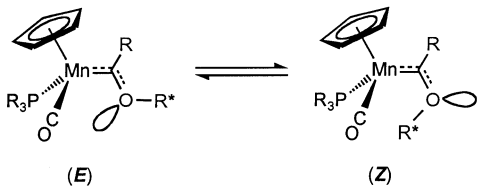
Both isomers are in equilibrium, as shown by variable-temperature NMR spectroscopy. Complex (S_{Mn},*R*)-**5d** exhibits two sets of resonance signals for the diastereotopic methyl groups. The ratio of the two sets at room temperature was 1:1. When the solution was cooled the ratio was 5:1 (at −23°C) and > 20:1 (at −43°C). Warming the solution to ambient temperature restored the original 1:1 ratio.

In order to determine whether or not the splitting of the signals indicated the presence of a mixture of diastereomers, a diastereomeric mixture of (S_{Mn},*R*)-**5d** and (S_{Mn},*S*)-**5d** was prepared from (S_{Mn})-**6** and a mixture of the sodium salts of 1,2-(*S*)- and 1,2-(*R*)-*O*-isoproylidene gycerol [(*S*)- and (*R*)-**3d**]. For (S_{Mn},*R*)-/(S_{Mn},*S*)-**5d** the shift difference between the ^{31}P signals was $\Delta\delta(^{31}P)$ = 1.9 ppm, and this value is approximately 10 times larger than that observed with **8** and **10**−**12**. Therefore, the splitting of the signals cannot be due to a mixture of diastereomers.

Hindered rotation around (a) the C(carbene)−aryl bond, (b) the Mn=C(carbene) bond, and (c) the C(carbene)−O bond may account for the splitting of signals. Complex (S_{Mn},*R*)-**15** exhibits a simple A_2B_2 pattern for the C(carbene)−C_6H_4Me hydrogen atoms. Therefore, option (a) can be ruled out. Barriers to rotation around the C(carbene)−C(aryl) bonds in neutral aryl-substituted, heteroatom-stabilized carbene complexes are usually very low.[11] However, substantial barriers were observed in cationic benzylidene complexes of iron and ruthenium, [Cp(CO)$_2$M=C(C_6H_4R)H]$^+$ and [Cp(CO)(PPh_3)M=C(C_6H_4R)H]$^+$ (M = Fe, Ru; R = H, F, Me, OMe: $\Delta G^{\neq}$ = 9.0−14.5 kcal/mol).[12]

The two remaining possibilities, (b) and (c), have been observed in various carbene complexes.[13][14] The bonding situation in [Cp(CO)$_2$Mn=C(OMe)Ph] and [Cp(CO)$_2$Mn=CMe_2] has also been analyzed theoretically.[15] The splitting of the Cp resonance signal in [Cp(CO)(PPh_3)Mn=C(OMe)-Ph] at low temperature (below −90°C) was attributed by Geoffroy et al. to a hindered rotation around the Mn=C(carbene) bond. An activation barrier of $\Delta G^{\neq}$ = 9.8 kcal/mol was calculated.[8a] However, for the complexes (S_{Mn},*R*)-/(R_{Mn},*S*)-**5d** and (S_{Mn},*R*)-**8**−**17** we consider hindered rotation around the C(carbene)−O bond [(*E*)/(*Z*) isomerization with respect to the C−O partial double bond, see Scheme 6] to be a preferable explanation for the NMR-spectroscopic observations since a splitting of signals was not observed with either the corresponding mannofuranosylcarbene or the gluco- and galactopyranosylcarbene complexes. The bulkiness of the OR* substituents in these complexes presumably disfavors the (*Z*) conformation. The strong temperature dependence of the equilibrium constant also agrees well with (*E*)/(*Z*) isomerism.

Scheme 6



Similarly, two sets of ^{13}C- and ^{31}P-NMR signals were reported for the alkoxy(amino)carbene complexes of platinum *cis*-[$Cl_2(PPh_3)$Pt=C(NHR′)OR″] (R′ = Me, Et; R″ = 1,2,3,4-tetra-*O*-deoxy-β-D-glucosyl) and these were explained in terms of hindered rotation around the carbene carbon−heteroatom bond.[2c]

Epimerization studies were carried out with the $PTol_3$- and the $P(OMe)_3$-substituted complexes (S_{Mn},*R*)-**5d** and (S_{Mn},*R*)-**9**. In pentane and CH_2Cl_2, (S_{Mn},*R*)-**5d** was configurationally stable for at least 96 hours at room temperature. However, in neat $P(OMe)_3$ substitution of the coordinated $PTol_3$ by $P(OMe)_3$ was observed. The substitution presumably proceeds by an associative mechanism. An associative mechanism has also been suggested for the substitution of PPh_3 by $PTol_3$ in the related complex [Cp(CO)(PPh_3)Mn=C(OMe)Et]. The reaction rate was observed to increase with increasing $PTol_3$ concentration.[8a]

The $P(OMe)_3$-substituted complex (S_{Mn},*R*)-**9** was stable in pentane or acetone, but slowly epimerized in dichloromethane, diethyl ether, and tetrahydrofuran. The (S_{Mn},*R*)-/(R_{Mn},*R*)-**9** ratio after 96 hours at room temperature was 4.4 (CH_2Cl_2), 2.76 (Et_2O), and 4.8 (THF). The epimerization rate was enhanced by exposure to daylight. After 96 hours at room temperature in the dark, the (S_{Mn},*R*)-/(R_{Mn},*R*)-**9** ratio was only 6.5 as opposed to 2.76 when exposed to light. The epimerization is very likely to proceed by dissociation and readdition of $P(OMe)_3$. Consequently, when $P(OCD_3)_3$ was added to a solution of (S_{Mn},*R*)-**9** in Et_2O the (S_{Mn},*R*)-/(R_{Mn},*R*)-**9** ratio after 96 hours was within the limits of error, and was the same as that in the absence of uncoordinated phosphite. In addition, $P(OCD_3)_3$ was incorporated into the complex.

In contrast to our results with carbene complexes, the phosphite-substituted benzoyl complex [Cp(NO){$P(OEt)_3$}-Mn−C(O)Ph] is configurationally stable[16] whereas the PPh_3-substituted acyl complexes [Cp(NO)(PPh_3)-Mn−C(O)C_6H_4R] racemize in toluene (half-life for R = H: 21 minutes at 25°C). A dissociative mechanism was deduced from kinetic studies.[17][18] A linear relationship between the Hammett σ constants of the *para* substituents and the rates of racemization was observed. However, the

steric effect seemed to be the most important factor in determining the configurational stability of the complexes.[1b] The higher configurational stability of (S_{Mn},*R*)-**5d** as compared to phosphite-substituted complex (S_{Mn},*R*)-**9** is probably due to the stronger Mn−P bond in the phosphane complex.

Our results demonstrate that diastereomerically pure carbene(phosphane) and -(phosphite) complexes of manganese are readily available through PR_3/CO exchange in chiral [Cp(CO)$_2$Mn=C(OR*)R′] complexes. Both configurations at manganese [(R_{Mn}) and (S_{Mn})] are accessible by choosing either an (*S*)- or an (*R*)-glycerol derivative as the chiral auxiliary. The carbene(phosphane) complexes are configurationally stable. Reaction of these complexes with Lewis acids gives a convenient method for the preparation of enantiomerically pure chiral-at-metal [Cp(CO)LMn(carbyne)]$^+$ complexes (see Scheme 2). The configuration at the manganese atom does not change on addition of nucleophiles to the carbyne carbon atom in these complexes [e. g. (S_{Mn})-**6**], meaning that a large number of enantiomerically pure carbene complexes is readily accessible. Finally, oxidative decomplexation of the carbene ligand and addition of other nucleophiles (L′) should now offer a simple route to other chiral complexes of manganese [Cp(CO)(PR_3)MnL′].

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Experimental Section

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**[19] and **2**,[5] the carbohydrates 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose and 2,3,4,6-tetra-*O*-acetyl-D-galactopyranose,[20][21] 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose[22] as well as $PTol_3$ and tris(*p*-chlorophenyl)phosphane[23] were prepared according to literature procedures. $PPh(OMe)_2$ and $PPh_2(OMe)$ were purchased from Strem Chemicals, Inc. $P(OPh)_3$ was obtained from Janssen, TMEDA from Merck. $P(OMe)_3$ 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 in [D$_6$]acetone at room temp. Chemical shifts are reported relative to the residual solvent peaks [^{1}H: δ(H) = 2.05 and ^{13}C: δ(*C*H$_3$) = 29.8] or to external H_3PO_4 (^{31}P). − MS: Finnigan MAT 312 (EI) or Finnigan MAT 312/AMD5000 (FAB).

General Procedure for the Synthesis of the Complexes **4a**−**c**, (*R*)-**4d**, (*S*)-**4d** *and* (*R*)-**14**: 4.5 mmol of the corresponding carbohydrate or glycerol derivative was added at −50°C to a solution of **2** or its tolylcarbene analogue, prepared from 3.0 mmol of acetyl bromide and 3.0 mmol of **1** or Li[Cp(CO)$_2$Mn−C(=O)Tol-*p*], respectively, 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 a further 4.5 h at 0°C. The solvent was removed in vacuo at room temp. The dark brown residue was dissolved in CH_2Cl_2/pentane {6:1 (**4a**), 2:1 (**4b**), 8:3 (**4c**), 2:1 [(*R*)- and (*S*)-**4d**, (*R*)-**14**]} and chromatographed at −20°C on silica gel with mixtures of CH_2Cl_2, pentane and ether (see below for ratios).

General Procedure for the Synthesis of the Complexes **5a**−**d**, **8**−**13**, *and* **15**−**17**: A solution of 0.6 mmol of **4a**−**d** or **14**, and 0.9 mmol of the corresponding PR_3 in 30 ml of toluene was irradiated (see below for duration) at −30°C while passing a slow stream of argon through the solution. The solvent was removed in vacuo at room temp. The residue was dissolved in CH_2Cl_2/pentane (see below for ratio) and chromatographed at −20°C on silia gel.

Dicarbonyl(cyclopentadienyl)[(1:2,3:4-di-O-isopropylidene-D-galactopyranos-6-yloxy)phenylcarbene]manganese (**4a**): Chromatography with CH_2Cl_2/pentane (6:1) afforded a yellow band (30 mg) and then elution with CH_2Cl_2/pentane/Et_2O (6:1:0.5) gave a dark red band. Removal of the solvent from the dark red fraction afforded complex **4a** as a sticky brown oil. Yield: 1.47 g (66%, based on **2**). − IR (CH_2Cl_2): ν(CO) = 1959 cm^{-1} vs, 1888 s. − ^{1}H NMR: δ = 1.30, 1.32, 1.34, 1.52 (4 × s, 3 H each, Me), 4.10−4.69 (m, 6 H, 2-H, 3-H, 4-H, 5-H, CH_2), 4.78 (s, 5 H, Cp), 5.46−5.53 (m, 1 H, 1-H), 7.02−7.06 (m, 2 H, Ph), 7.27−7.39 (m, 3 H, Ph). − ^{13}C NMR: δ = 24.7, 25.1, 26.3, 26.4 (Me), 67.8 (C-6), 71.3 (C-4), 71.6 (C-2), 71.8 (C-5), 75.5 (C-3), 87.9 (Cp), 97.1 (C-1), 109.2, 109.9 (*C*Me$_2$), 123.7, 128.2, 154.9 (Ph), 232.7, 232.9 (2 × CO), 334.3 (Mn=C). − MS (EI, 70 eV): *m*/*z* (%) = 524 (8) [M$^+$], 509 (5) [M$^+$ − Me], 468 (100) [M$^+$ − 2 CO], 120 (26) [CpMn$^+$]. − $C_{26}H_{29}MnO_8$·1/5 pentane (538.6): calcd. C 60.18, H 5.87; found C 60.21, H 5.77.

Dicarbonyl(cyclopentadienyl)[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)phenylcarbene]manganese (**4b**): Chromatography with CH_2Cl_2/pentane (7:3) gave a yellow band (60 mg). Subsequent elution with CH_2Cl_2/pentane/Et_2O (7:3:1) first gave a dark red and then an orange band. Removal of the solvent of the orange fraction afforded complex **4b** as an orange oil. Crystallization from 75 ml of CH_2Cl_2/pentane (2:1) gave an orange powder. Yield: 730 mg (40%, based on **2**), m.p. 68°C (dec.). − IR (CH_2Cl_2): ν(CO) = 1971 cm^{-1} vs, 1903 s. − ^{1}H NMR: δ = 1.92, 2.03, 2.08, 2.16 (4 × s, 3 H each, Me), 4.05−4.18 (m, 3 H, H-5, CH_2), 4.83 (s, 5 H, Cp), 5.19−5.24 (m, 1 H, 3-H), 5.37−5.38 (m, 1 H, H-4), 5.43−5.46 (m, 1 H, 1-H), 5.52−5.63 (m, 1 H, 2-H), 7.04−7.07 (m, 2 H, Ph), 7.30−7.39 (m, 3 H, Ph). − ^{13}C NMR: δ = 20.4, 20.5, 20.6 (Me), 62.3 (C-6), 68.0 (C-4), 69.4 (C-2), 71.3 (C-5), 72.3 (C-3), 88.5 (Cp), 99.1 (C-1), 124.2, 128.2, 129.6, 153.9 (Ph), 169.7, 170.0, 170.4, 170.6 (*C*OMe), 231.3, 232.5 (2 CO), 334.2 (Mn=C). − MS (EI, 70 eV): *m*/*z* (%) = 612 (0.5) [M$^+$], 556 (0.4) [M$^+$ − 2 CO], 331 (40) [OR*$^+$ − OH], 225 (9) [CpMnC(Ph)O$^+$], 55 (58) [Mn$^+$]. − $C_{28}H_{29}MnO_{12}$ (612.1): calcd. C 54.91, H 4.77; found C 55.02, H 4.99.

Dicarbonyl(cyclopentadienyl)[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)phenylcarbene]manganese (**4c**): Chromatography with CH_2Cl_2/pentane (8:3) gave a yellow band (200 mg), and then elution with CH_2Cl_2/pentane/Et_2O (8:3:1) gave first a brown and then an orange band. The orange band afforded **4c** as an orange powder. Recrystallization from 7 ml of CH_2Cl_2 gave **4c** as light orange plates. Yield: 910 mg (46%, based on **2**), m.p. 130°C (dec.). − IR (CH_2Cl_2): ν(CO) = 1972 cm^{-1} vs, 1905 s. − ^{1}H NMR: δ = 1.95, 1.97, 2.03, 2.07 (4 × s, 3 H each, Me), 3.71−3.78 (m, 1 H, 5-H), 4.05−4.24 (m, 2 H, CH_2), 4.83 (s, 5 H, Cp), 5.08−5.39 (m, 4 H, 1-H, 2-H, 3-H, 4-H), 7.32−7.35 (m, 2 H, Ph), 7.38−7.44 (m, 3 H, Ph). − ^{13}C NMR: δ = 20.4 (4 Me), 62.5 (C-6), 68.9 (C-4), 71.8 (C-2), 72.9 (C-5), 73.1 (C-3), 88.6 (Cp), 98.8 (C-1), 124.2, 128.1, 128.5, 153.5 (Ph), 169.6, 169.9, 170.2, 170.6 (4 *C*OMe), 231.4, 232.3 (2 CO), 333.8 (Mn=C). − MS (70 eV): *m*/*z* (%) = 612 (2) [M$^+$], 556 (0.4) [M$^+$ − 2 CO], 331 (66) [OR*$^+$ − OH], 271 (6) [OR*$^+$ − OH

− HOAc], 225 (15) [CpMnC(Ph)O$^+$]. − $C_{28}H_{29}MnO_{12}$·4/3 CH_2Cl_2 (725.3): calcd. C 48.54, H 4.40; found C 48.76, H 4.51.

Dicarbonyl(cyclopentadienyl)[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy)phenylcarbene]manganese [(*R*)-**4d**]: Chromatography with CH_2Cl_2/pentane (2:1) gave first a yellow band (20 mg) and then a red band (80 mg). Elution with CH_2Cl_2/pentane/Et_2O (2:1:0.5) gave a brown/red band which contained (*R*)-**4d**. Evaporation of the solvent afforded (*R*)-**4d** as a sticky brown oil. Yield: 690 mg (41%, based on **2**). − IR (pentane): ν(CO) = 1975 cm^{-1} sh, 1964 vs, 1918 sh, 1905 s. − ^{1}H NMR: δ = 1.30, 1.34 (2 × s, 3 H each, Me), 3.87−3.93 (m, 1 H, 2-H), 4.12−4.18 (m, 1 H, 3-H), 4.43−4.53 (m, 3 H, CH_2-1, 3-H), 4.74 (s, 5 H, Cp), 7.00−7.03 (m, 2 H, Ph), 7.27−7.39 (m, 3 H, Ph). − ^{13}C NMR: δ = 25.6, 27.0 (Me), 66.9 (C-3), 74.9 (C-2), 77.0 (C-1), 88.1 (Cp), 110.1 (CMe_2), 123.7, 128.1, 128.3, 155.5 (Ph), 232.9 (2 CO), 334.5 (Mn=C). − MS (EI, 70 eV): *m/z* (%) = 396 (24) [M$^+$], 381 (6) [M$^+$ − Me], 340 (77) [M$^+$ − 2 CO], 120 (52) [MnCp$^+$], 55 (100) [Mn$^+$]. − $C_{20}H_{21}MnO_5$·1/4 pentane (414.1): calcd. C 61.60, H 5.84; found C 61.79, H 5.50.

Dicarbonyl(cyclopentadienyl)[(2S)-2,3-(isopropylidenedioxy)-prop-1-yloxy)phenylcarbene]manganese [(*S*)-**4d**]: Chromatography with CH_2Cl_2/pentane (2:1) gave first a yellow band (20 mg) and then a red band (80 mg). Elution with CH_2Cl_2/pentane/Et_2O (2:1:0.5) gave a brown/red band which contained (*S*)-**4d**. Evaporation of the solvent afforded (*S*)-**4d** as a sticky brown oil. Yield: 750 mg (45%, based on **2**). − The spectroscopic data are identical to those of (*R*)-**4d**. − MS (EI, 70 eV): *m/z* (%) = 396 (9) [M$^+$], 381 (2) [M$^+$ − Me], 340 (35) [M$^+$ − 2 CO], 120 (61) [MnCp$^+$], 55 (100) [Mn$^+$]. − $C_{20}H_{21}MnO_5$ (396.1): calcd. C 60.61, H 5.34; found 61.14, H 5.41.

Carbonyl(cyclopentadienyl)[(α-1:2,3:4-di-O-isopropylidene-D-galactopyranos-6-yloxy)phenylcarbene](tritolylphosphane)-manganese (**5a**). Irradiation time: 11 min. Chromatography with CH_2Cl_2/pentane (6:1) gave a yellow band. Further elution with CH_2Cl_2/pentane/Et_2O (12:2:1) gave two red bands which gave **5a** as a mixture of diastereomers in a ratio of 54:46 (determined by ^{1}H-NMR spectroscopy). Removal of the solvent and crystallization from 8 ml of pentane afforded **5a** as an orange powder. Yield: 290 mg (45%, based on **4a**), m.p. 45°C (dec.). − IR (pentane): ν(CO) = 1849 cm^{-1} s. − ^{1}H NMR: δ = 1.26, 1.28, 1.31, 1.32, 1.34, 1.38, 1.42, 1.52 (8 × s, total 12 H, Me), 2.33, 2.34 (2 × s, total 9 H, $C_6H_4CH_3$), 3.85−4.09 (m, 1 H, H-5), 4.10−4.35 (m, 3 H, 4-H, CH_2), 4.36−4.42 (m, 1 H, 3-H), 4.49, 4.53 (2 d, $^3J_{PH}$ = 1.8 Hz each, total 5 H, Cp), 4.58−4.62 (m, 1 H, 2-H), 4.47−5.53 (m, 1 H, 1-H), 6.62−6.66 (m, 2 H, Ph), 7.00−7.56 (m, 15 H, arom.). − ^{13}C NMR: δ = 21.2 ($C_6H_4CH_3$), 24.5, 24.6, 24.7, 25.1, 25.2, 26.3, 26.6, 26.7 (Me), 68.0, 68.4 (C-6), 71.3, 71.4 (C-4), 71.4, 71.6 (C-2), 71.8, 72.0 (C-5), 72.2, 72.7 (C-3), 87.7, 88.0 (Cp), 97.3 (C-1), 125.9, 126.1, 126.8, 127.2, 127.6, 128.3, 129.1, 129.2, 129.3, 130.0, 130.1, 130.2, 133.7, 133.8, 133.9, 134.2, 135.8, 135.9, 136.2, 136.3, 139.6, 139.7, 153.4, 153.9 ($C_6H_4CH_3$, Ph), 237.7, 237.9 ($^2J_{PC}$ = 33.0 Hz each, CO), 326.0 (Mn=C). − MS (FAB, NBOH, NaI): *m/z* (%) = 823 (35) [MNa$^+$], 800 (4) [M$^+$], 772 (7) [M$^+$ − CO], 468 (100) [M$^+$ − CO − $PTol_3$]. − $C_{46}H_{50}MnO_7P$ (800.3): calcd. C 68.98, H 6.30; found C 68.14, H 6.54.

Carbonyl(cyclopentadienyl)[(2,3,4,6-tetra-O-acetyl-β-D-galacto-pyranosyloxy)phenylcarbene](tritolylphosphane)manganese (**5b**): Irradiation time: 9 min. Chromatography with CH_2Cl_2/pentane (7:3) first gave a yellow band (20 mg). Further elution with CH_2Cl_2/pentane/Et_2O (7:3:1) gave a red band which, after removal of the solvent, gave **5b** as an orange oil in a 66:34 ratio of diastereomers (determined by ^{1}H-NMR spectroscopy). Yield: 130 mg (19%, based on **4b**). − IR (CH_2Cl_2): ν(CO) = 1848 cm^{-1} s. − ^{1}H NMR: δ = 1.91, 1.94, 1.97, 1.98, 2.01, 2.04, 2.07, 2.08 (8 × s, total 12 H, COMe), 2.31 (s, 9 H, $C_6H_4CH_3$), 3.97−4.10 (m, 3 H, 5-H, CH_2), 4.60 (d, $^3J_{PH}$ = 1.8 Hz), 4.63 (d, $^3J_{PH}$ = 1.6 Hz, total 5 H, Cp), 4.80−4.98 (m, 1 H, 3-H), 5.15−5.19 (m, 1 H, 4-H), 5.24−5.73 (m, 2 H, 1-H, 2-H), 6.87−7.44 (m, 17 H, arom.). − ^{13}C NMR (600 MHz): δ = 20.4, 20.5, 20.6 (Me), 21.1, 21.2 ($C_6H_4CH_3$), 61.9 (CH_2), 68.2 (C-4), 69.1 (C-2), 71.6 (C-5), 71.7 (C-3), 87.5, 87.6 (Cp), 95.0 (C-1), 126.9, 127.0, 129.2, 129.3, 129.4, 129.5, 130.0, 133.5, 133.6, 133.7, 133.8, 133.9, 139.9, 152.6 (C_6H_4, Ph), 169.9, 170.0, 170.4, 170.6 (*C*OMe), *C*O and Mn=*C* not detected. − MS (FAB, NBOH, NaI): *m/z* (%) = 911 (2) [MNa$^+$], 888 (3) [M$^+$], 860 (10) [M$^+$ − CO], 556 (18) [M$^+$ − CO − $PTol_3^+$], 513 (34) [M$^+$ − CO − $PTol_3$ − Ac], 424 (39) [CpMnPTol_3^+]. − $C_{48}H_{50}MnO_{11}P$·1/4 CH_2Cl_2 (910.1): calcd. C 63.68, H 5.59; found C 63.47, H 5.50.

Carbonyl(cyclopentadienyl)[(2,3,4,6-tetra-O-acetyl-β-D-gluco-pyranosyloxy)phenylcarbene](tritolylphosphane)manganese (**5c**): Irradiation time: 13 min. Chromatography with CH_2Cl_2/pentane (8:3) gave a yellow band and subsequent elution with CH_2Cl_2/pentane/Et_2O (8:3:1) gave an orange band. Removal of the solvent of the orange fraction in vacuo at room temp. afforded complex **5c** as an orange oil in a 85:15 ratio of diastereomers (determined by ^{1}H-NMR spectroscopy). Yield: 120 mg (24%, based on **4c**). − IR (CH_2Cl_2): ν(CO) = 1848 cm^{-1} s. − ^{1}H NMR: δ = 2.00, 2.01, 2.08, 2.09 (4 × s, 3 H each, COMe), 2.36 (s, 9 H, $C_6H_4CH_3$), 4.15−4.28 (m, 2 H, CH_2), 4.44−4.50 (m, 1 H, 5-H), 4.64 (d, $^3J_{PH}$ = 1.7 Hz), 4.71 (d, $^3J_{PH}$ = 1.5 Hz, total 5 H, Cp), 4.86−5.41 (m, 4 H, 1-H, 2-H, 3-H, 4-H), 6.90−7.36 (m, 17 H, arom.). − ^{13}C NMR (600 MHz): δ = 20.4, 20.5, 20.6, 20.7, 20.8, 20.9 (COCH_3), 21.2 ($C_6H_4CH_3$), 63.0 (CH_2), 68.9 (C-4), 70.5 (C-2), 71.1 (C-5), 72.9 (C-3), 87.5, 87.8 (Cp), 94.1 (C-1), 124.2, 126.7, 127.0, 128.1, 128.8, 129.4, 129.5, 133.7, 133.8, 139.9 (C_6H_4, Ph), 152.7, 153.6 (Ph), 169.8, 169.9, 170.0, 170.1, 170.4, 170.5 (*C*OMe), 236.4 (d, $^2J_{PC}$ = 30.2 Hz, CO), 323.5 (d, $^2J_{PC}$ = 33.3 Hz, Mn=C). − ^{31}P NMR: δ = 79.8, 81.7. − MS (FAB, NBOH, NaI): *m/z* (%) = 911 (2) [MNa$^+$], 886 (5) [M$^+$ − 2 H], 860 (9) [M$^+$ − CO], 513 (51) [M$^+$ − CO − $PTol_3$ − Ac], 424 (65) [CpMnPTol_3^+]. − $C_{48}H_{50}MnO_{11}P$·1/5 pentane (903.7): calcd. C 65.13, H 5.89; found C 65.58, H 5.80.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]phenylcarbene}(tritolylphosphane)manganese [(S_{Mn},*R*)-**5d**]: Irradiation time: 9 min. Chromatography with pentane/CH_2Cl_2 (2:1) gave a yellow band and subsequent elution with CH_2Cl_2/pentane/Et_2O (4:2:1) gave a red band. The red fraction contained (S_{Mn},*R*)-**5d**. Removal of the solvent and crystallization from 10 ml of pentane gave (S_{Mn},*R*)-**5d** as an orange powder. Yield: 220 mg [51%, based on (*R*)-**4d**], m.p. 56°C (dec.). − $[\alpha]_D^{20}$ = +11 (*c* = 1, CH_2Cl_2). − IR (pentane): ν(CO) = 1875 cm^{-1} sh, 1859 s. − ^{1}H NMR: δ = 1.28, 1.29, 1.32, 1.34 (4 × s, total 6 H, Me), 2.35 (s, 9 H, $C_6H_4CH_3$), 3.62−3.65 (m, 1 H, 2-H), 3.71−4.77 (m, 2 H, CH_2), 4.04−4.07 (m, 1 H, 1-H), 4.28−4.37 (m, 1 H, 1-H), 4.45 (d, $^3J_{PH}$ = 1.6 Hz, 5 H, Cp), 6.65−6.70 (m, 2 H, Ph), 7.00−7.33 (m, 15 H, arom.). − ^{13}C NMR (600 MHz): δ = 21.2 ($C_6H_4CH_3$), 25.6, 27.1 (Me), 67.2 (C-3), 73.5 (C-2), 75.5 (C-1), 87.5 (Cp), 109.6 (CMe_2), 127.2, 129.3, 129.4 (Ph), 133.8, 133.9, 134.2, 134.4, 135.9, 136.3, 139.4, 139.8 (C_6H_4), 154.7 (Ph), 238.0 (d, $^2J_{PC}$ = 34.1 Hz, CO), 335.2 (d, $^2J_{PC}$ = 28.0 Hz, Mn=C). − ^{31}P NMR (600 MHz): δ = 84.1. − MS (EI, 70 eV): *m/z* (%) = 672 (0.02) [M$^+$], 644 (0.06) [M$^+$ − CO], 480 (0.13) [CpPTol_3(CO)$_2$Mn$^+$], 424 (2.2) [MnCpPTol_3^+], 340 (1.3) [M$^+$ − CO − $PTol_3$], 304 (100) [PTol_3^+]. − $C_{40}H_{42}MnO_4P$ (672.2): calcd. C 71.41, H 6.30; found C 70.00, H 6.54.

Carbonyl(cyclopentadienyl){[(2S)-2,3-(isopropylidenedioxy)-prop-1-yloxy]phenylcarbene}(tritolylphosphane)manganese [(R_{Mn},*S*)-**5d**]: Irradiation time: 9 min. Chromatography with pentane/CH_2Cl_2 (2:1) gave a yellow band and subsequent elution with CH_2Cl_2/pentane/Et_2O (4:2:1) gave a red band. The red fraction contained (R_{Mn},*S*)-**5d**. Removal of the solvent and crystallization from 10 ml of pentane gave (R_{Mn},*S*)-**5d** as an orange powder. Yield: 230 mg [53%, based on (*S*)-**4d**], m.p. 56°C (dec.). − $[\alpha]_D^{20}$ = −12 (*c* = 1, CH_2Cl_2). − The IR and NMR spectra were identical with those of (S_{Mn},*R*)-**5d**. − MS (EI, 70 eV): *m/z* (%) = 672 (0.04) [M^+], 644 (0.13) [M^+ − CO], 480 (0.5) [$CpPTol_3(CO)_2Mn^+$], 424 (8) [$MnCpPTol_3^+$], 340 (8) [M^+ − CO − $PTol_3$], 304 (100) [$PTol_3^+$]. − $C_{40}H_{42}MnO_4P$ (672.2): calcd. C 71.41, H 6.30; found C 70.54, H 6.51.

Carbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyloxy)phenylcarbene](tritolylphosphane)manganese [(S_{Mn})-**7α**]: 0.25 ml (0.4 mmol) of a solution of BCl_3 in hexane was added to 130 mg (0.2 mmol) of [S_{Mn},*R*]-**5d** in 6 ml of CH_2Cl_2 at −70°C. 50 ml of pentane precooled to −70°C was then added to the above solution. The carbyne complex (S_{Mn})-**6** precipitated as a brown powder. After decanting, the residue was washed with 7 ml of Et_2O and several times with 10 ml portions of pentane, both precooled to −70°C. Complex (S_{Mn})-**6** was dried in vacuo at −40°C to give an orange powder. The complex was identified by comparison of its IR spectrum [ν(CO) = 2012 cm^{-1} s, in CH_2Cl_2] with that reported in ref.[5] The residue was dissolved in 10 ml of CH_2Cl_2, precooled to −70°C, and a solution of 140 mg (0.5 mmol) of the sodium salt of 2,3:5,6-di-*O*-isopropylidenemannofuranose in 5 ml of CH_2Cl_2 was added at −70°C. The solution was warmed to room temp. and the solvent removed in vacuo. The workup and the purification were carried out analogously to those reported in ref.[5] Complex (S_{Mn})-**7α** was identified by a comparison of its IR [ν(CO) = 1862 cm^{-1} s, in pentane] and its ^{1}H-NMR spectrum with those reported in ref.[5]

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]phenylcarbene}(triphenyl phosphite)manganese [(S_{Mn},*R*)-**8**]: Irradiation time: 9 min. The purification of the reaction products was carried out analogously to that of (S_{Mn},*R*)-**5d**. Red oil. Yield: 250 mg [61%, based on (*R*)-**4d**]. − IR (pentane): ν(CO) = 1899 cm^{-1} sh, 1888 sh, 1868 s. − ^{1}H NMR (600 MHz): δ = 1.24, 1.28, 1.32 (3 × s, total 6 H, Me), 3.74−3.84, 3.93−4.08, 4.28−4.49 (3 × m, total 5 H, CH_2-1, 2-H, CH_2-3), 4.12 (d, $^3J_{PH}$ = 1.9 Hz, 5 H, Cp), 7.05−7.53 (m, 20 H, Ph, OPh). − ^{13}C NMR (600 MHz): δ = 25.6, 27.1 (Me), 67.2 (C-3), 67.3 (C-2), 75.2 (C-1), 86.6 (Cp), 109.8 (*C*Me_2), 122.6, 124.8, 124.9, 125.1, 127.5, 127.7, 128.2, 128.7, 128.9, 129.0, 129.4, 129.6, 130.2, 130.7, 153.0, 154.9, 155.2 (Ph, OPh), 235.6 (d, $^2J_{PC}$ = 44.0 Hz, CO) 235.8 (d, $^2J_{PC}$ = 47.9 Hz, CO), 327.2 (d, $^2J_{PC}$ = 41.5 Hz, Mn=C), 327.4 (d, $^2J_{PC}$ = 42.7 Hz, Mn=C). − ^{31}P NMR (600 MHz): δ = 194.9, 195.2. − MS (EI, 70 eV): *m/z* (%) = 678 (1.4) [M^+], 585 (0.4) [M^+ − OPh], 547 (0.4) [M^+ − OR*], 430 (5.7) [$CpMn(P(OPh)_3)^+$], 340 (56) [M^+ − CO − $P(OPh)_3$], 310 (36) [$P(OPh)_3^+$], 217 (100) [$P(OPh)_2^+$]. − $C_{37}H_{36}MnO_7P\cdot 1/3$ pentane (702.6): calcd. C 66.10, H 5.74; found C 66.41, H 5.69.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]phenylcarbene}(trimethyl phosphite)manganese [(S_{Mn},*R*)-**9**]: Irradiation time: 8 min. The purification of the reaction products was carried out analogously to that of (S_{Mn},*R*)-**5d**. Red oil. Yield: 180 mg [60%, based on (*R*)-**4d**]. − IR (pentane): ν(CO) = 1867 cm^{-1} s. − ^{1}H NMR (600 MHz): δ = 1.30, 1.33, 1.34 (3 × s, total 6 H, Me), 3.61, 3.62 (d, $^3J_{PH}$ = 11.0 Hz, total 9 H, OMe), 3.85−3.98, 4.11−4.43 (both m, total 5 H, CH_2-1, 2-H, CH_2-3), 4.45, 4.46 (d, $^3J_{PH}$ = 1.7 Hz, total 5 H, Cp), 7.11−7.32 (m, 5 H, Ph). − ^{13}C NMR (600 MHz): δ = 25.6, 25.7, 27.0, 27.1 (Me), 52.2 (OMe), 67.4, 67.5, 75.3, 75.4, 75.5, 75.6 (C-1, C-2, C-3), 86.6 (Cp), 109.8 (*C*Me_2), 125.1, 125.2, 127.0, 127.1, 127.4, 128.7, 128.9, 129.3, 130.1, 130.2, 156.9, 157.2 (Ph), 237.0 (m, CO), 324.8 (m, Mn=C). − ^{31}P NMR: δ = 204.6. − MS (EI, 70 eV): *m/z* (%) = 492 (11) [M^+], 477 (0.6) [M^+ − Me], 461 (3) [M^+ − OMe], 340 (100) [M^+ − $P(OMe)_3$ − CO], 93 (66) [$P(OMe)_2^+$]. − $C_{22}H_{30}MnO_7P$ (492.4): calcd. C 53.65, H 6.14. A correct elemental analysis could not be obtained.

Carbonyl(cyclopentadienyl){[(2S)-2,3-(isopropylidenedioxy)-prop-1-yloxy]phenylcarbene}(trimethyl phosphite)manganese [(R_{Mn},*S*)-**9**]: Irradiation time: 8 min. The purification of the reaction products was carried out analogously to that of (S_{Mn},*R*)-**5d**. Red oil. Yield 170 mg [58%, based on (*S*)-**4d**]. − All spectroscopic data were identical to those of (S_{Mn},*R*)-**9**. − MS (EI, 70 eV): *m/z* (%) = 492 (11) [M^+], 477 (0.6) [M^+ − Me], 461 (3) [M^+ − OMe], 340 (100) [M^+ − $P(OMe)_3$ − CO], 93 (66) [$P(OMe)_2^+$]. − $C_{22}H_{30}MnO_7P$ (492.4). A correct elemental analysis could not be obtained.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-yloxy]phenylcarbene}dimethoxy(phenyl)phosphane]-manganese [(S_{Mn},*R*)-**10**]: Irradiation time: 11 min. The workup and the purification of the reaction products were carried out analogously to those of (S_{Mn},*R*)-**5d**. Red oil. Yield: 210 mg [65%, based on (*R*)-**4d**]. − IR (pentane): ν(CO) = 1884 cm^{-1} sh, 1866 s. − ^{1}H NMR (600 MHz): δ = 1.25, 1.28, 1.29 (3 × s, total 6 H, Me), 3.55 (d, $^3J_{PH}$ = 11.3 Hz), 3.63 (d, $^3J_{PH}$ = 11.7 Hz, total 6 H, OCH_3), 3.75−4.14 (m, 5 H, CH_2-1, 2-H, CH_2-3), 4.42 (s, 5 H, Cp), 6.99−7.05, 7.13−7.17, 7.38−7.41, 7.48−7.49 (all m, total 10 H, arom.). − ^{13}C NMR (600 MHz): δ = 25.6, 25.7, 27.1 (Me), 52.5, 52.6, 53.1 (OMe), 67.2, 67.4, 74.9, 75.1, 75.2, 75.5 (C-1, C-2, C-3), 87.1 (Cp), 109.8 (*C*Me_2), 125.4, 125.5, 127.1, 127.2, 127.3, 128.7, 128.8, 130.0, 130.07, 130.11, 130.14, 130.4, 141.9, 142.0, 142.3, 157.1, 157.3 (Ph), 236.7 (d, $^2J_{PC}$ = 30.1 Hz, CO), 322.7 (m, Mn=C). − ^{31}P NMR (600 MHz): δ = 226.0, 226.1 − MS (EI, 70 eV): *m/z* (%) = 538 (11) [M^+], 510 (5) [M^+ − CO], 407 (1.4) [M^+ − OR*], 340 (100) [M^+ − CO − L]. − $C_{27}H_{32}MnO_6P\cdot 1/3$ pentane (562.3): calcd. C 61.21, H 6.45; found C 61.12, H 6.58.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]phenylcarbene}(methoxydiphenylphosphane)-manganese [(S_{Mn},*R*)-**11**]: Irradiation time: 8 min. The purification of the reaction products was carried out analogously to that of (S_{Mn},*R*)-**5d**. Red oil. Yield: 190 mg [54%, based on (*R*)-**4d**]. − IR (pentane): ν(CO) = 1861 cm^{-1} s. − ^{1}H NMR (600 MHz): δ = 1.23, 1.24, 1.25, 1.28 (4 × s, total 6 H, Me), 3.56 (d, $^3J_{PH}$ = 12.0 Hz), 3.58 (d, $^3J_{PH}$ = 12.1 Hz, total 3 H, OMe), 3.50−3.52, 3.62−3.63, 3.71−3.75, 3.87−3.90, 4.04, 4.11−4.13 (total 5 H, CH_2-1, 2-H, CH_2-3), 4.47 (d, $^3J_{PH}$ = 1.6 Hz, 5 H, Cp), 6.93−6.96, 7.12−7.17, 7.30−7.32, 7.30−7.32, 7.43, 7.60, 7.61 (all m, total 15 H, Ph) − ^{13}C NMR (600 MHz): δ = 25.5, 25.6, 27.0 (Me), 53.3 (OMe), 67.1, 67.4, 74.4, 74.9, 75.0, 75.2 (C-1, C-2, C-3), 87.2, 87.3 (Cp), 109.4, 109.5 (*C*Me_2), 125.3, 125.4, 127.1, 127.4, 127.5, 128.4, 128.5, 128.7, 128.8, 130.5, 131.0, 131.1, 131.7, 131.8, 142.3, 142.5, 156.0, 156.2 (Ph), CO and Mn=C not detected. − ^{31}P NMR: δ = 193.4, 193.7 − MS (EI, 70 eV): *m/z* (%) = 584 (6) [M^+], 556 (4) [M^+ − CO], 340 (100) [M^+ − CO − L], 336 (31) [$CpMnL^+$], 216 (33) [L^+], 55 (64) [Mn^+]. − $C_{32}H_{34}MnO_5P$ (584.5): calcd. C 65.75, H 5.86; found C 65.90, H 5.78.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]phenylcarbene}(triphenylphosphane)manganese [(S_{Mn},*R*)-**12**]: Irradiation time: 11 min. The workup and the purifi-

cation of the reaction products were carried out as desribed for the reaction of (*R*)-**4d** with tritolylphosphane. Recrystallization from pentane/CH_2Cl_2 (10:1) afforded dark red crystals. Yield: 290 mg [48%, based on (*R*)-**4d**], m.p. 110°C. − IR (pentane): ν(CO) = 1877 cm^{-1}sh, 1862 s. − ^{1}H NMR: δ = 1.29, 1.32, 1.35, 1.38 (4 × s, total 6 H, Me), 3.63−4.43 (m, 5 H, CH_2-1, 2-H, CH_2-3), 4.47 (d, $^3J_{PH}$ = 1.7 Hz, 5 H, Cp), 6.67−6.71 (m, 2 H, Ph), 7.00−7.07, 7.31−6.65 (m, total 18 H, arom.). − ^{13}C NMR: δ = 25.6, 25.7, 27.2 (Me), 67.2, 67.5, 73.6, 74.4, 75.5 (C-1, C-2, C-3), 87.6 (Cp), 109.6, 109.7 (*C*Me_2), 125.7, 125.8, 127.1, 127.3, 127.4, 127.6, 128.2, 128.5, 128.6, 128.7, 129.0, 129.2, 129.4, 129.5, 129.6, 130.0, 130.2, 133.9, 134.0, 134.3, 138.9, 139.2, 154.5, 154.6 (Ph), 237.7 (d, $^2J_{PC}$ = 30.5 Hz, CO), 326.0 (d, $^2J_{PC}$ = 30.5 Hz, Mn=C), 325.9 (d, $^2J_{PC}$ = 29.3 Hz, Mn=C). − ^{31}P NMR: δ = 87.16, 87.30. − MS (EI, 70 eV): *m/z* (%) = 630 (0.1) [M^+], 602 (0.07) [M^+ − CO], 340 (19) [M^+ − CO − L], 262 (100) [L^+]. $C_{37}H_{36}MnO_4P$ (630.6): calcd. C 70.47, 5.75; found C 70.66, H 5.90.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]phenylcarbene}[tris(p-chlorophenyl)phosphane]-manganese [(S_{Mn},*R*)-**13**]: Irradiation time: 10 min. Workup and purification of the reaction products were carried out analogously to those of (S_{Mn},*R*)-**5d**. Red oil. Yield 310 mg [70%, based on (*R*)-**4d**]. − IR (pentane): ν(CO) = 1860 cm^{-1} s. − ^{1}H NMR: δ = 1.31, 1.35, 1.38 (3 × s, total 6 H, Me), 3.54−3.57, 3.73−3.78, 3.82−3.93, 4.06−4.14, 4.38−4.46 (5 × m, 5 H, CH_2-1, 2-H, CH_2-3), 4.55 (d, $^3J_{PH}$ = 1.6 Hz, 5 H, Cp), 6.68−6.72, 7.04−7.13, 7.31−7.49 (3 × m, 17 H, arom.). − ^{13}C NMR: δ = 25.5, 25.6, 27.1, 27.2 (Me), 66.9, 67.2, 73.6 (C-1, C-2, C-3), 87.7 (Cp), 109.7, 109.8 (*C*Me_2), 125.8, 125.9 (Ph), 127.4 (C_6H_4), 128.3 (Ph), 129.0, 129.1 (C_6H_4), 129.2, 129.4, 129.8 (Ph), 135.3, 135.4, 136.2 (C_6H_4), 137.0, 137.4, 153.4 (Ph), 237.1 (d, $^2J_{PC}$ = 30.2 Hz, CO), 327.2 (d, $^2J_{PC}$ = 31.7 Hz, Mn=C). − ^{31}P NMR: δ = 87.9, 88.0. − MS (FAB, NBOH): *m/z* (%) = 732 (100) [M^+, ^{35}Cl], 484 (10) [CpMnL$^+$]. − $C_{37}H_{33}Cl_3MnO_4P$ (733.9): calcd. C 60.65, 4.54; found C 60.27, H 4.88.

[Acetoxy(tolyl)carbene]dicarbonyl(cyclopentadienyl)manganese: The preparation was carried out analogously to **2**.[5] The complex was identified by comparison of its IR data [ν(CO) = 1983 cm^{-1} s, 1917 s, in CH_2Cl_2] with those of the corresponding phenylcarbene complex **2**.[5]

Dicarbonyl(cyclopentadienyl)[{(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy}tolylcarbene]manganese [(*R*)-**14**]: The preparation and workup were carried out analogously to those of (*R*)-**4d**. Evaporation of the solvent afforded (*R*)-**14** as a brown oil. Yield: 1.05 g [53%, based on the acetoxy(tolyl)carbene complex]. − IR (pentane): ν(CO) = 1976 cm^{-1} sh, 1964 vs, 1917 sh, 1903 s. − ^{1}H NMR: δ = 1.30, 1.35 (2 × s, 3 H each, Me), 2.33 (s, 3 H, $C_6H_4CH_3$), 3.87−3.93 (m, 1 H, 2-H), 4.12−4.18 (m, 1 H, 3-H), 4.44−4.51 (m, 3 H, CH_2-1, 3-H), 4.72 (s, 5 H, Cp), 6.95−6.98 (m, 2 H, C_6H_4), 7.15−7.18 (m, 3 H, C_6H_4). − ^{13}C NMR: δ = 21.1 ($C_6H_4CH_3$) 25.6, 27.0 (Me), 66.9 (C-3), 74.9 (C-2), 77.0 (C-1), 87.8 (Cp), 110.0 (*C*Me_2), 124.0, 128.7, 130.0, 138.1, 152.9 (Ph), 232.8 (2 × CO), 335.2 (Mn=C). − MS (EI, 70 eV): *m/z* (%) = 410 (10) [M^+], 395 (2) [M^+ − Me], 354 (50) [M^+ − 2 CO], 280 (5) [M^+ − OR*], 120 (40) [MnCp$^+$], 55 (100) [Mn^+]. − $C_{21}H_{23}MnO_5$·1/3 pentane (434.4): calcd. C 62.67, H 6.62; found C 62.55, H 5.98.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]tolylcarbene}(tritolylphosphane)manganese [(S_{Mn},*R*)-**15**]: The irradiation and the workup were carried out analogously to those of (S_{Mn},*R*)-**5d**. Red powder. Yield: 230 mg [46%, based on (*R*)-**14**], m.p. 52°C (dec.). − IR (pentane): ν(CO) = 1874 cm^{-1} sh, 1857 s. − ^{1}H NMR: δ = 1.29, 1.31, 1.34, 1.37 (4 × s, total 6 H, CH_3), 2.24 (s, 9 H, $C_6H_4CH_3$), 2.34 (s, 9 H, $PC_6H_4CH_3$), 3.58−3.87, 3.98−4.12, 4.28−4.35 (all m, total 5 H, CH_2-1, 2-H, CH_2-3), 4.44 (d, $^3J_{PH}$ = 1.6 Hz, 5 H, Cp), 6.60 (d, *J* = 7.8 Hz, 2 H, C_6H_4), 6.80 (d, *J* = 7.9 Hz, 2 H, C_6H_4), 7.13−7.30 (m, 12 H, C_6H_4). − ^{13}C NMR: δ = 21.1 ($C_6H_4CH_3$), 25.4, 25.5 (Me), 66.9, 67.2, 75.4 (C-1, C-2, C-3), 87.5, 87.7 (Cp), 109.7, 109.8 (*C*Me_2), 124.1, 125.9, 126.0 (C_6H_4), 128.0 (PC_6H_4), 128.7 (C_6H_4), 128.9, 128.0 (PC_6H_4), 129.5, 129.8, 130.0, 130.2 (C_6H_4), 135.2, 135.3, 136.1 (PC_6H_4), 137.2, 137.4, 151.1 (C_6H_4), 154.7 (Ph), 237.5 ($^2J_{PC}$ = 31.6 Hz, CO), 328.1 ($^2J_{PC}$ = 30.2 Hz, Mn=C). − ^{31}P NMR: δ = 89.0. − MS (EI, 70 eV): *m/z* (%) = 686 (0.05) [M^+], 658 (0.1) [M^+ − CO], 304 (100) [$PTol_3^+$], 120 (22) [CpMn]. − $C_{41}H_{35}MnO_4P$ (672.2): calcd. C 72.67, H 5.21; found C 72.17, H 6.46.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]tolylcarbene}(trimethyl phosphite)manganese [(S_{Mn}, *R*)-**16**]: Irradiation time: 8 min. The purification of the reaction products was carried out analogously to that of (S_{Mn},*R*)-**5d**. Red oil. Yield: 170 mg [56%, based on (*R*)-**14**]. − IR (pentane): ν(CO) = 1882 cm^{-1} sh, 1870 sh, 1862 s. − ^{1}H NMR: δ = 1.30, 1.33, 1.34 (3 × s, total 6 H, Me), 2.29 (s, 9 H, $C_6H_4CH_3$), 3.60 (d, $^3J_{PH}$ = 11.0 Hz, 9 H, OMe), 3.80−3.89, 4.07−4.14, 4.24−4.41 (all m, total 5 H, CH_2-1, 2-H, CH_2-3), 4.45 (s, 5 H, Cp), 7.04−7.17 (m, 4 H, Tol). − ^{13}C NMR: δ = 21.1 ($C_6H_4CH_3$), 25.7, 25.8 (Me), 52.1 (OCH_3), 67.5, 67.6, 74.9, 75.2, 75.5 (C-1, C-2, C-3), 86.5 (Cp), 109.8, 109.8 (*C*Me_2), 125.3, 125.4, 128.0, 130.0, 136.6, 136.7, 154.6, 154.9 (C_6H_4), 236.8 (d, $^2J_{PC}$ = 46.4 Hz, CO), 325.5, 325.6 (d, both $^2J_{PC}$ = 41.5 Hz, Mn=C). ^{31}P NMR: δ = 204.8. − MS (EI, 70 eV): *m/z* (%) = 506 (12) [M^+], 475 (3) [M^+ − OMe], 375 (2) [M^+ − OR*], 254 (100) [M^+ − $P(OMe)_3$ − CO], 120 (34) [$CpMn^+$], 55 (56) [Mn^+]. − $C_{23}H_{32}MnO_7P$·1/3 pentane (530.2): calcd. C 55.85, H 6.84; found C 56.57, H 6.69.

Carbonyl(cyclopentadienyl){[(2R)-2,3-(isopropylidenedioxy)-prop-1-yloxy]tolylcarbene}[tris(p-chlorophenyl)phosphane]-manganese [(S_{Mn},*R*)-**17**]: Irradiation time: 12 min. The workup and the purification of the reaction products were carried out analogously to those of (S_{Mn},*R*)-**5d**. Red powder. Yield 280 mg [60%, based on (*R*)-**14**], m.p. 72−75°C. − IR (pentane): ν(CO) = 1868 cm^{-1} sh, 1961 s. − ^{1}H NMR: δ = 1.31, 1.34, 1.38 (3 × s, total 6 H, Me), 2.27 (s, 3 H, $C_6H_4CH_3$), 3.55−3.60, 3.74−3.92, 4.07−4.15, 4.44−4.47 (all m, total 5 H, CH_2-1, 2-H, CH_2-3), 4.55 (s, 5 H, Cp), 6.58−6.70, 6.79−6.90, 7.12−7.40 (m, total 16 H, arom.). − ^{13}C NMR: δ = 21.1 ($C_6H_4CH_3$), 25.5, 27.0 (Me), 67.1, 72.2, 75.7 (C-1, C-2, C-3), 87.4, 87.9 (Cp), 109.7, 109.8 (*C*Me_2), 125.9, 127.9, 128.9, 129.0, 130.0, 135.2, 135.3, 136.1, 136.9, 137.2, 137.3, 151.1 (C_6H_5, C_6H_4), 237.5 (d, $^2J_{PC}$ = 31.6 Hz, CO), 328.0 ($^2J_{PC}$ = 28.9 Hz, Mn=C). − ^{31}P NMR: δ = 88.2. − MS (FAB, NBOH): *m/z* (%) = 748 (85) [M^+, ^{35}Cl], 484 (100) [CpMnL$^+$]. − $C_{38}H_{35}Cl_3MnO_4P$ (772.1): calcd. C 61.72, 5.09; found C 62.12, H 4.89.

X-ray Structural Analysis of **4c**: $C_{28}H_{31}MnO_{12}·CH_2Cl_2·CH_4O$, molecular mass 731.4, crystal size 0.3 × 0.3 × 0.3 mm (obtained by slow diffusion of pentane into a solution of **4c** in CH_2Cl_2/methanol); monoclinic crystal system, space group C_2, *a* = 16.793(4), *b* = 12.929(3), *c* = 16.992(4) Å, β = 109.63(1)°; *V* = 3476.6(14) Å^3, *Z* = 4, $d_{calcd.}$ = 1.397 g cm^{-3}; μ (Mo-K_α) = 0.577 mm^{-1}, *F*(000) = 1520. Wyckoff scan, 2θ range 4−54°, scan speed variable 2.0−30.0° min^{-1} in ω. 4117 independent reflections with 3978 [$F > 3\sigma(F)$]. Data were collected at −31°C with the crystal mounted in a glass capillary on a Siemens P4 diffractometer (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å). The structure was solved (Patterson methods) and refined by using the SHELXTL

PLUS (VMS) program package. 397 parameters refined, $R = 0.068$, $Rw = 0.065$. Largest difference peak (hole) +0.60 eÅ^{-3} (−0.50 eÅ^{-3}). The positions of the hydrogen atoms were calculated by assuming ideal geometry ($d_{C-H} = 0.96$ Å) and their coordinates were refined together with the attached C atoms as a "riding model". The dichloromethane was disordered and was isotropically refined in two different positions assuming equal occupation. Methanol was also isotropically refined. The positions of all other atoms were refined anisotropically by full-matrix least-squares methods. Complete lists of atomic coordinates and thermal parameters were deposited.[24]

[1] For leading references on chiral-at-metal transition metal complexes see: [1a] H. Brunner, *Angew. Chem.* **1971**, *83*, 274; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 249. – [1b] H. Brunner, *Adv. Organomet. Chem.* **1980**, *18*, 151.

[2] [2a] K. H. Dötz, W. Straub, R. Ehlenz, K. Peseke, R. Meisel, *Angew. Chem.* **1995,** *107,* 2023−2024; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1856−1858. – [2b] R. Aumann, *Chem. Ber.* **1992**, *125*, 2773−2778. – [2c] T. Pill, K. Polborn, W. Beck, *Chem. Ber.* **1990**, *123*, 11−17. – [2d] J. M. Dalla Riva Toma, D. E. Bergstrom, *J. Org. Chem.* **1994**, *59*, 2418−2422. – [2e] J. Burger, P. Klüfers, *Chem. Ber.* **1995**, *128*, 75−79.

[3] [3a] K.-H. Dötz, O. Neuß, M. Nieger, *Synlett* **1996**, 995−996. – [3b] K. H. Dötz, W.-C. Haase, M. Klumpe, M. Nieger, *J. Chem. Soc., Chem. Commun.* **1997**, 1217−1218. – [3c] R. Ehlenz, O. Neuß, M. Teckenbrock, K. H. Dötz, *Tetrahedron* **1997**, *53*, 5143−5158.

[4] H. Fischer, J. Schleu, G. Roth, *Chem. Ber.* **1995**, *128*, 373−378.

[5] H. Fischer, J. Schleu, *Chem. Ber.* **1996**, *129*, 385−390.

[6] J. Schleu, Thesis, Universität Konstanz, **1996**.

[7] Although the stereogenic center is not involved in the substitution of the alcoholates in **3d** and **3e** for the acetoxy group in **2** its designation changes. That is because the reaction of the (*S*)-glycerol **3d** gives the (2*R*)-2,3-dihydroxypropyloxycarbene complex **4d**. This is due to a change in the priority of the different groups at the stereogenic center.

[8] [8a] C. Kelley, N. Lugan, M. R. Terry, G. L. Geoffroy, B. S. Haggerty, A. L. Rheingold, *J. Am. Chem. Soc.* **1992**, *114*, 6735−6749. – [8b] U. Schubert, *Organometallics* **1982**, *1*, 1085−1088. – [8c] A. D. Redhouse, *J. Organomet. Chem.* **1975**, *99*, C29−C30. – [8d] W. A. Herrmann, J. L. Hubbard, I. Bernal, J. D. Korp, B. L. Haymore, G. L. Hillhouse, *Inorg. Chem.* **1984**, *23*, 2978−2983. – [8e] P. Friedrich, G. Besl, E. O. Fischer, G. Huttner, *J. Organomet. Chem.* **1977**, *139*, C68−C72. – [8f] C. Barbeau, K. S. Dichmann, L. Ricard, *Can. J. Chem.* **1973**, *51*, 3027−3031. – [8g] G. Le Borgne, E. Gentric, D. Grandjean, *Acta Crystallogr., Sect. B* **1975**, *31*, 2824−2829.

[9] The absolute configuration is assigned according to the modification of the Cahn-Ingold-Prelog priority rules proposed by Tirouflet et al. The η^5-C_5H_5 ligand is considered to be a pseudo-atom of atomic number 30, which gives the following sequence: η^5-C_5H_5 > PR_3 > CO > C(OR*)Ph. – [9a] C. Lecomte, Y. Dusausoy, J. Protas, J. Tirouflet, A. Dormond, *J. Organomet. Chem.* **1974**, *73*, 67−76. – [9b] T. E. Sloan, *Top. Stereochem.* **1981**, *12*, 1−36.

[10] K. Weissenbach, H. Fischer, unpublished results.

[11] [11a] C. G. Kreiter, E. O. Fischer, *XXIIIrd International Congress of Pure and Applied Chemistry*, Butterworths, London, vol. 6, **1971**, 151−168. – [11b] H. Brunner, J. Doppelberger, E. O. Fischer, M. Lappus, *J. Organomet. Chem.*, **1976**, *112*, 65−78.

[12] [12a] M. Brookhart, J. R. Tucker, G. R. Husk, *J. Organomet. Chem.* **1980**, *193*, C23−C26. – [12b] M. Brookhart, W. B. Studabaker, M. B. Humphrey, G. R. Husk, *Organometallics* **1989**, *8*, 132−140. – [12c] M. Brookhart, Y. Liu in *Advances in Metal Carbene Chemistry* (Ed.: U. Schubert), Kluwer Acadenic Publishers, Dordrecht, **1989**, 251−270.

[13] Examples for rotation around the Mn=C(carbene) bond: M. J. McGeary, T. L. Tonker, J. L. Templeton, *Organometallics* **1985**, *4*, 2102−2106 and ref.[8a]

[14] For hindered rotation around the C(carbene)−OR bond see e.g.: [14a] C. G. Kreiter, E. O.Fischer, *Angew. Chem.* **1969**, *81*, 780−781; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 761. – [14b] E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Müller, R. D. Fischer, *J. Organomet. Chem.* **1971**, *28*, 237−258. – [14c] E. O. Fischer, H.-J. Beck, C. G. Kreiter, J. Lynch, J. Müller, E. Winkler, *Chem. Ber.* **1972**, *105*, 162−172. – [14d] V. Guerchais, C. Lapinte, J.-Y. Thépot, L. Toupet, *Organometallics* **1988**, *7*, 604−612.

[15] [15a] N. M. Kostic, R. F. Fenske, *J. Am. Chem. Soc.* **1982**, *104*, 3879−3884. – [15b] D. S. Marynick, C. M. Kirkpatrick, *J. Am. Chem. Soc.* **1985**, *107*, 1993−1994.

[16] H. Brunner, W. Steger, *J. Organomet. Chem.* **1976**, *120*, 239−256.

[17] H. Brunner, M. Langer, *J. Organomet. Chem.* **1975**, *87*, 223−240.

[18] H. Brunner, J. A. Aclasis, *J. Organomet. Chem.* **1976**, *104*, 347−362.

[19] E. O. Fischer, A. Maasböl, *Chem. Ber.* **1967**, *100*, 2445−2456.

[20] M. L. Wolfrom, A. Thompson, *Meth. Carbohydr. Chem.* **1962**, vol. I/II, p. 334.

[21] M. Mikamo, *Carbohydr. Res.* **1989**, *191*, 150−153.

[22] C. E. Ballou, H. O. L. Fischer, *J. Am. Chem. Soc.* **1954**, *76*, 3188−3193.

[23] K. Sasse in *Methoden Org. Chem. (Houben-Weyl) 4th ed.*, **1963**, vol. XII/1, p. 32ff.

[24] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

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