Diastereoselective Substitution of PR_3 for CO in Carbohydrato- and Menthyloxycarbene Complexes of Manganese – Synthesis of Chiral-at-Metal Carbene and Carbyne Complexes

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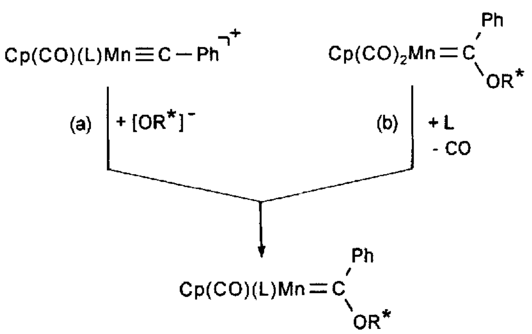
The substitution of PR_3 (R = $C_6H_4CH_3$-*p*, C_6H_4Cl-*p*, C_6H_{11}, OCH_3) for a CO ligand in chiral carbohydratocarbene complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C(OR^*)Ph]$ [OR* = α- (**1α**) and β-mannofuranosyl (**1β**), (−)-menthyloxy (**9**)] proceeds diastereoselectively. The diastereoselectivity depends on PR_3 and on the OR* substituent and ranges from 12% de (R = OCH_3) to 80% (R = $C_6H_4CH_3$-*p*). In contrast, the reaction of **1β** with $P(OPh)_3$ is non-selective. The diastereoselectivity generally increases with increasing nucleophilicity of PR_3 and decreases in the series **1β** > **1α** > **9**. The highest diastereoselectivity was observed in the reaction of **1β** with $P(C_6H_4CH_3\text{-}p)_3$. Predominantly, the isomer with the (*S*) configuration at the metal [(S_{Mn})-**2β**] was formed which could be separated from the diastereomeric mixture by chromatography and be obtained in a pure form. Subsequent reaction of (S_{Mn})-**2β** with BF_3 afforded the carbyne-manganese complex (S_{Mn})-$[(\eta^5\text{-}C_5H_5)\{P(C_6H_4CH_3\text{-}p)_3\}(CO)Mn{\equiv}CPh]BF_4$.

Chiral transition-metal complexes play a prominent role in enantioselective synthesis and catalysis. Although carbohydrates are available in a great variety from the chiral pool, the number of reports on their use as chiral auxiliaries in transition-metal-mediated transformations of organic molecules is rather restricted. There are only very few transition-metal carbene complexes known carrying carbohydrate substituents at the carbene carbon atom[1–5].

Recently, we reported on the synthesis of the first carbohydratocarbene complexes of manganese and rhenium[4]. These chiral carbene complexes, $[Cp(CO)_2M{=}C(Aryl)OR^*]$ (M = Mn, Re; OR* = mannofuranosyl, glucofuranosyl, fructopyranosyl; Aryl = Ph, Tol), are obtained by addition of the anion of the corresponding protected carbohydrate to the cationic carbyne complexes $[Cp(CO)_2M{\equiv}C{-}Aryl]^+$. The carbohydrate is attached directly to the carbene carbon atom and thus in close proximity to the metal. Therefore, transfer of the chiral information of the carbohydrate substituent should render the substitution of a nucleophile for CO in the prochiral $Cp(CO)_2Mn$ fragment diastereoselective. Separation of the diastereomers by column chromatography and subsequent OR* elimination by electrophiles such as boron trihalides should afford enantiomerically pure carbyne complexes which then could easily be transformed into other carbene complexes. In addition, oxidative displacement of the carbene ligand in the presence of a potential ligand L′ should readily make a great variety of chiral-at-metal complexes of the type $[Cp(CO)LMn{-}L']$ accessible.

Two different routes to diastereomerically enriched $[Cp(CO)LMn{=}C(Aryl)OR^*]$ compounds are conceivable: (a) addition of carbohydrate anions $[OR^*]^-$ to an excess of $[Cp(CO)LMn{\equiv}C{-}Aryl]^+$ cations and (b) replacement of a CO ligand in $[Cp(CO)_2Mn{=}C(Aryl)OR^*]$ by L (Scheme 1).

Scheme 1



We recently observed that the kinetic resolution of $[OR^*]^-$ addition to the carbyne carbon atom of $[Cp(CO)LMn{\equiv}C{-}Ph]^+$ [L = $P(OMe)_3$, $PTol_3$] (route a) is disappointingly poor (de ca. 20%)[4]. In this paper we report on the diastereoselectivity of the CO/PR_3 exchange in $[Cp(CO)_2Mn{=}C(Ph)OR^*]$, on the synthesis of a diastereomerically pure carbohydratocarbene complex $[Cp(CO)(PTol_3)Mn{=}C(Ph)OR^*]$ and on its subsequent transformation into the first enantiomerically pure chiral-at-metal carbyne complex of manganese.

Results and Discussion

Substitution of a phosphane or phosphite for CO in $[Cp(CO)_2MnL']$ complexes can be usually achieved by both thermolysis and photolysis. The photolytical synthesis of

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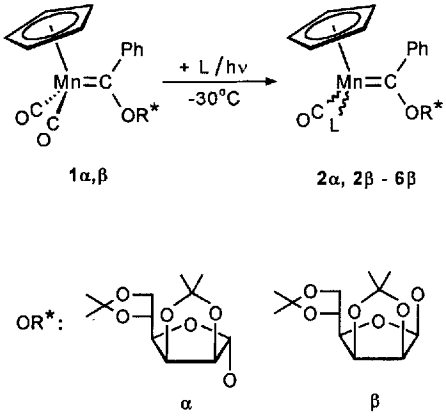
racemic [Cp(CO)LMn(carbene)] complexes was reported[6–8].

When solutions of **1α,β** and tritolyl phosphane in toluene were refluxed for several hours, no reaction was observed. The starting complexes were recovered unchanged. However, irradiation of the carbohydratocarbene complex **1β**[4] in toluene in the presence of phosphanes or phosphites for 20 minutes at −30 °C afforded the carbene complexes **2β**–**6β** in moderate to high yield (Scheme 2).

Scheme 2



L = $P(C_6H_4CH_3\text{-}p)_3$ (**2**), $P(C_6H_4Cl\text{-}p)_3$ (**3**)

$P(C_6H_{11})_3$ (**4**), $P(OCH_3)_3$ (**5**)

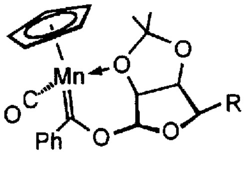
$P(OC_6H_5)_3$ (**6**)

The compounds **2β**,**3β** and **5β**,**6β** are stable under these photochemical conditions. In contrast, complex **4β** slowly decomposed already during irradiation, thus reducing its yield. After chromatography and recrystallization from pentane **2β**–**6β** were obtained as red crystals (**2β**) or yellow-brown powders (**3β**–**6β**) which are stable in air at room temperature. Similarly, photolysis of **1α** in toluene in the presence of tritolylphosphane afforded **2α** in 82% yield (Scheme 2).

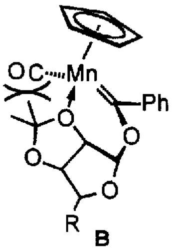
All complexes were obtained as mixtures of diastereomers. The ratio of diastereomers was determined by ^{1}H-NMR spectroscopy. The resonances of the 1-H atom at the anomeric center, of the 4-H atom and of the isopropylidene groups were easily detected. Whereas compound **2α** exhibits two singlets for the 1-H atom, for **2β**, **3β**, **5β**, and **6β** two doublets each are observed for the same atom: δ = 4.95, 5.02 (^3J = 3.5 Hz, 3.6 Hz, **2β**), 4.89, 5.00 (^3J = 3.2 Hz, 3.0 Hz, **3β**), 5.28, 5.52 (^3J = 3.8 Hz, 3.5 Hz, **5β**), and 5.18, 5.26 (^3J = 3.5 Hz, **6β**).

The diastereoselectivity of PR_3 substitution for CO varies considerably. The de of **2β**–**6β** in the reaction mixture is 80% (**2β**), 56% (**3β**), 66% (**4β**), 12% (**5β**), and 0% (**6β**). In general, the diastereomeric excess decreases with decreasing nucleophilicity of PR_3. There is roughly an inverse correlation between the diastereomeric excess and the energy of the ν(CO) absorption in **2**. The slightly lower diastereoselectivity when $P(C_6H_{11})_3$ is used instead of $PTol_3$ is probably due to steric factors.

Since **1α,β** did not react with $PTol_3$ when solutions were heated at 110 °C but only under photolytic conditions, Mn–CO dissociation can be assumed to be the initiating and rate-limiting step. A reaction sequence involving photo-induced η^5/η^3 isomerization and addition of PR_3 followed by CO extrusion and η^3/η^5 rearrangement is very unlikely. Due to the chiral carbene ligand loss of a CO group from **1β** should proceed stereoselectively. The resulting coordinatively unsaturated intermediate is presumably stabilized by interaction with the carbohydrate substituent. Molecular models show that the carbene ligand can adopt a conformation in which the oxygen atom at C-2 of the carbohydrate substituent is in close proximity to the metal. Therefore, the intermediate is easily stabilized through intramolecular coordination of the carbohydrate substituent and chelation. From the molecular model it also follows that the metallacycle **A**[9] with (*S*) configuration at the metal (S_{Mn}) should be slightly more stable than the diastereomer **B** (R_{Mn}). In **A** unfavorable steric interactions between the isopropylidene protecting group and the remaining carbonyl ligand are avoided.



A



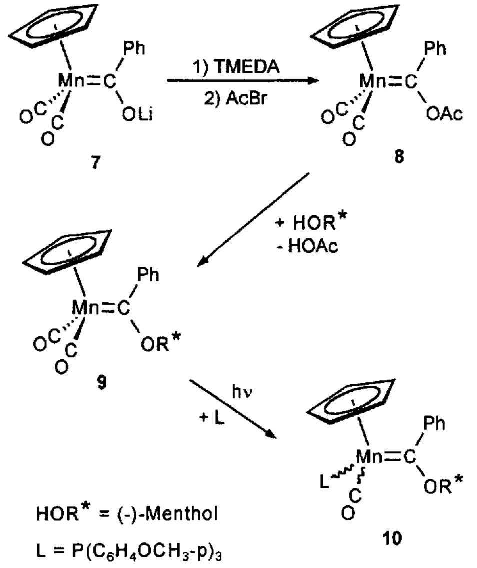
B

Subsequent dechelation and addition of PR_3 should afford diastereoselectively the product complexes. Alternatively, dechelation and racemization followed by addition of PR_3 would afford a mixture of the diastereomers with a ratio of ca. 1.5. The diastereomeric ratio of **2α** and **5α** formed by reaction of the anion of monodeprotonated protected mannofuranose to $[Cp(CO)LMn{\equiv}CPh]^+$ [L = $PTol_3$, $P(OMe)_3$] is 3:2 in both cases[4]. Therefore, the strong dependence of the diastereoselectivity on the nucleophile indicates that the rate of PR_3 addition is comparable to that of racemization. The increasing diastereoselectivity with increasing nucleophilicity of PR_3 is easily rationalized by an increase in the rate of PR_3 addition.

The intermediate obtained by loss of CO from the α-mannofuranosylcarbene complex **1α** cannot be stabilized by chelation to the same extent as the *β* isomer. Therefore, a lower diastereoselectivity for the CO/PR_3 exchange in **1α** is to be expected. This conclusion was confirmed by the considerable drop in diastereoselectivity from 80 to 20% when **1β** was replaced by its *α* isomer **1α** in the reaction with tritolylphosphane.

To further test the influence of the OR* substituent on the diastereoselectivity the (−)-menthyloxycarbene complex **9** was prepared. Deviating from the preparative sequence for **1α,β**, complex **9** was obtained from the lithium manganate 7[10] in a "one-pot" synthesis (Scheme 3). Successive reactions of 7 with tmeda and acetyl bromide gave the thermolabile acetoxycarbene complex **8**. The same method was employed for the preparation of some pentacarbonyl(carbene) complexes of chromium and tungsten[11–14]. Treatment of **8** with (−)-menthol afforded after chromatography pure (−)-menthyloxy(phenyl)carbene complex **9** in an overall yield of 40%. Photolysis of a solution of **9** in toluene at −30 °C for 20 minutes in the presence of $P(C_6H_4OCH_3\text{-}p)_3$ gave **10** (Scheme 3).

Scheme 3

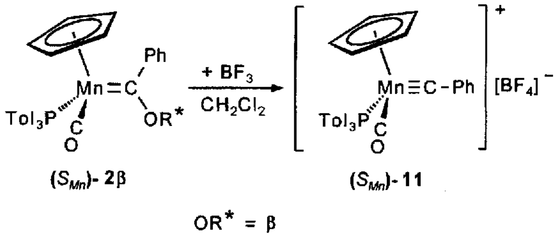


The monocarbonyl complex **10** was formed as a mixture of diastereomers in a ratio of 5:4 as determined by integration of the ^{1}H-NMR resonances of the Cp rings. The presence of two diastereomers was also evident from the appearance of two sets of ^{13}C-NMR resonances for the carbonyl carbon [δ = 238.2 and 239.4 ($^2J_{PC}$ = 31.7 Hz, 30.5 Hz)] and the carbene carbon atom [δ = 323.3 and 326.4 ($^2J_{PC}$ = 29.3 Hz)] of almost equal intensity. The diastereoselectivity was even lower than that of the reaction of $P(C_6H_4CH_3\text{-}p)_3$ with **1α** confirming the assumption that the isopropylidene group of the carbohydrate substituent exerts a significant intermediate-destabilizing and product-determining influence on the CO/PR$_3$ exchange. Similarly, only a low asymmetric induction was observed in the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C(OR^*)Ph]$ (OR* = (−)-bornyloxy) with $P(C_6H_4CH_3\text{-}p)_3$[15].

The major diastereomer of **2β** was separated from the isomeric mixture by a second chromatography of the 9:1 mixture of **2β**. According to the ^{1}H-NMR spectrum the major diastereomer of **2β** was thus obtained with a de >95%. The X-ray structural analysis unambiguously established (*S*) configuration at manganese of the major isomer. Due to the poor quality of the crystals, a detailed discussion of the bond lengths and angles was not feasible. The preferential formation of the (S_{Mn}) diastereomer agrees with the expectations on the basis of the molecular model. Very likely, the (S_{Mn}) diastereomer is also preferentially formed in the reactions of **1β** with $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_{11})_3$, and $P(OCH_3)_3$.

Treatment of (S_{Mn})-**2β** with BF$_3$ gave the chiral cationic carbyne complex (S_{Mn})-**11** via [OR*]$^-$ abstraction (Scheme 4)[16].

Scheme 4



Compound (S_{Mn})-**11** was isolated in 81% yield. The enantiomeric purity of (S_{Mn})-**11** (ee >95%) was established by its reaction with the sodium salt of mannofuranose to quantitatively regenerate (S_{Mn})-**2α**[4] with a de >95%. The synthesis of *racemic* cationic carbyne complexes of manganese was reported[17].

These results demonstrate that non-racemic chiral-at-metal [(Cp)(CO)LM(carbyne)] complexes with high enantiomeric excess can conveniently be prepared by proper choice of L by using carbohydrates as chiral auxiliaries. Since the stereochemistry at the manganese atom does not change on addition of nucleophiles to the carbyne carbon atom in e.g. **11**, a large number of enantiomerically pure carbene complexes are readily accessible by reaction of **11** with nucleophiles (e.g. OR$^-$, SR$^-$, NR$_2^-$, halides etc.)[16,18]. Therefore, the diastereoselective substitution of PR$_3$ for CO in [Cp(CO)$_2$Mn(carbene)] complexes, OR$^-$ abstraction and addition of nucleophiles offer a simple route to non-racemic chiral-at-metal carbyne and carbene complexes. Other chiral complexes, [Cp(CO)(PR$_3$)MnL], should be accessible via oxidative decomplexation of the carbene ligand and addition of a nucleophile L[19].

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Experimental

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 (Fa. J. T. Baker, silica gel for flash chromatography) was argon-saturated. The yields refer to analytically pure compounds and were not optimized. The complexes **1β**[4], **7**[10], $[Cp(CO)_2Mn{\equiv}CPh]^+[BF_4]^-$ (**12**)[20], 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose[21], and $P(C_6H_4CH_3\text{-}p)_3$, $P(C_6H_4OCH_3\text{-}p)_3$, $P(C_6H_4Cl\text{-}p)_3$[22] were prepared according to literature procedures. $P(C_6H_{11})_3$ was purchased from Strem Chemicals, Inc. P(OPh)$_3$ was obtained from Fa. Janssen, tmeda from Fa. Merck. P(OMe)$_3$ and acetyl bromide were purchased from Fa. Fluka. – IR: FT-IR spectrophotometer, Fa. Bio-Rad. – ^{1}H NMR and ^{13}C NMR: Bruker WM 250, Jeol JNX 400. Chemical shifts are reported relative to TMS. – MS: Varian MAT 312. – Photochemical reactions were carried out in a duran glas apparatus by using a Hg high-pressure lamp (TQ 150, Fa. Heraeus).

Dicarbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyloxy)phenylcarbene]manganese (**1α**): 1.68 g (6.46 mmol) of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose in 50 ml of THF was deprotonated with 0.16 g (6.46 mmol) of NaH. After the H_2 evolution had ceased the solvent was evaporated in vacuo. The residue was dissolved in 20 ml of CH_2Cl_2 and the solution added slowly at −65°C to a solution of 1.13 g (3.23 mmol) of $[Cp(CO)_2Mn{\equiv}CPh]^+[BF_4]^-$ (**12**)[20] in 50 ml of CH_2Cl_2. The solution was warmed to room temp. and the solvent removed in vacuo. The residue was dissolved in 45 ml of pentane/CH_2Cl_2 (8:1) and the solution chromatographed at −30°C on silica gel. With pentane/CH_2Cl_2/Et_2O (8:1:1) first a small yellow-orange band and then a yellow-brown band (which contained **1α**) and a red-brown band (which contained **1β**) were eluted. Evaporation of the solvent of the second fraction in vacuo gave **1α** as a yellow-brown sticky oil [Yield: 360 mg (21%, based on **12**)] and of the third fraction gave **1β** as a gold-brown powder [Yield: 490 mg (29%, based on **12**), m.p. 39°C (dec.)]. Complex **1β** was identified by a comparison of its IR and ^{1}H-NMR spectra with those reported in ref.[4]. – **1α**: IR (pentane): ν(CO) = 1978 cm^{-1} s, 1918 s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.30 (s, 3H, Me), 1.31 (s, 3H, Me), 1.32 (s, 3H, Me), 1.36 (s, 3H, Me), 3.90–4.03 (m, 2H, CH_2-6), 4.31 (m, 2H, 4,5-H), 4.75 (s, 5H, Cp), 5.02 (m, 2H, 2,3-H), 5.61 (s, 1H, 1-H), 6.99–7.03 (m, 2H, Ph), 7.27–7.41 (m, 3H, Ph). – ^{13}C NMR ([D$_6$]acetone, room temp.): δ = 24.6, 25.7, 26.0, 27.0 [2 $C(CH_3)_2$], 67.1 (C-6), 73.6 (C-5), 80.4 (C-4), 83.0, 86.0 (C-2,3), 88.6 (Cp), 107.2 (C-1), 109.4, 113.3 (2 CMe_2), 123.9, 128.1, 128.2, 153.9 (Ph), 232.1, 232.5 (2 CO), 333.7 (Mn=C). – MS (70 eV), *m/z* (%): 524 (3.5) [M$^+$], 509 (6) [M$^+$ − Me], 468 (20) [M$^+$ − 2 CO], 410 (1) [M$^+$ − 2 CO − Me_2CO], 265 (5) [M$^+$ − OR], 225 (25) [M$^+$ − 2 CO − R], 120 (20) [CpMn$^+$], 55 (100) [Mn$^+$]. – $C_{26}H_{29}MnO_8$ × 1/4 pentane (524.4): calcd. C 60.33, H 5.95; found C 60.23, H 6.03.

Carbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-β-D-mannofuranosyloxy)phenylcarbene](tritolylphosphane)manganese (**2β**): A solution of 300 mg (0.57 mmol) of **1β** and 210 mg (0.69 mmol) of tritolylphosphane in 25 ml of toluene was irradiated for 20 min at −30°C while passing a slight stream of argon through the solution. The solvent was removed in vacuo at room temp. The brown residue was dissolved in 50 ml of pentane and the solution chromatographed at −20°C on silica gel. With pentane/CH_2Cl_2/Et_2O (10:5:1) first a light yellow band containing $CpMn(CO)_3$ (10 mg) and then a brown band were eluted. The solvent of the brown fraction was evaporated in vacuo. Compound **2β** was obtained as a yellow-brown powder in a 9:1 ratio of diastereomers (determined by ^{1}H-NMR spectroscopy). Yield: 370 mg (81%, based on **1β**).

Complex **2β** was dissolved in pentane and chromatographed again at −20°C. With pentane/CH_2Cl_2/Et_2O (8:1:1) two orange-brown bands were eluted. The first band contained the major diastereomer. Crystallization from pentane at −30°C gave red crystals of (S_{Mn})-**2β** [Yield: 240 mg (53%, based on **1β**), m.p. 143°C (dec.)]. The second fraction consisted of a 3:2 mixture of (S_{Mn})- and (R_{Mn})-**2β** [Yield: 100 mg (22%, based on **1β**)]. – **2β**: IR (pentane): ν(CO) = 1862 cm^{-1} s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.27 (s, 3H, Me), 1.31 (s, 3H, Me), 1.46 (s, 3H, Me), 1.67 (s, 3H, Me), 2.32 (s, 9H, $C_6H_4CH_3$), 3.39 (dd, ^3J = 6.0 Hz, 3.5 Hz, 1H, 4-H), 4.01–4.05 (m, 2H, CH_2-6), 4.37–4.39 (m, 1H, 5-H), 4.55–4.59, 4.66–4.68 (m, 2H, 2,3-H), 4.69 (d, $^3J_{PH}$ = 1.8 Hz, 5H, Cp), 4.95 (d, ^3J = 3.5 Hz, 1H, 1-H), 6.72–6.75, 6.86–6.93, 7.05–7.08, 7.19–7.26 (m, 17H, aromat.). – ^{13}C NMR ([D$_6$]acetone, room temp.): δ = 21.2 ($C_6H_4CH_3$), 25.5, 25.7, 26.8, 26.9 [2 $C(CH_3)_2$], 67.0 (C-6), 74.1 (C-5), 76.8 (C-4), 80.1, 80.6 (C-2,3), 89.1 (Cp), 101.3 (C-1), 108.9, 113.2 (2 CMe_2), 126.5, 127.1, 127.4, 129.1, 129.2 (C_6H_5), 133.6, 133.7, 134.3, 134.8, 135.2, 139.6 (C_6H_4), 153.4 (C_6H_5), 237.8 ($^2J_{PC}$ = 33.0 Hz, CO), 323.2 ($^2J_{PC}$ = 33.0 Hz, Mn=C). – MS (FAB, NBOH), *m/z* (%): 800 (1.4) [M$^+$], 772 (20) [M$^+$ − CO], 541 (30) [M$^+$ − OR], 513 (43) [M$^+$ − CO − OR], 468 (65) [M$^+$ − CO − $PTol_3$], 421 (100) [M$^+$ − CO − carbene ligand], 304 (17) [$PTol_3^+$], 120 (31) [CpMn$^+$]. – $C_{46}H_{50}MnO_7P$ (800.8): calcd. C 68.99, H 6.29; found C 68.92, H 6.50.

Carbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyloxy)phenylcarbene](tritolylphosphane)manganese (**2α**): Irradiation of a solution of 320 mg (0.61 mmol) of **1α** and 230 mg (0.76 mmol) of tritolylphosphane in 25 ml of toluene and purification of the raw products were carried out as described for **2β**. The brown residue was dissolved in pentane and chromatographed at −20°C. With pentane/CH_2Cl_2/Et_2O (8:1:1) first a light yellow band [$CpMn(CO)_3$] was eluted. The brown band eluted next contained **2α** in a 3:2 ratio of diastereomers. Yield: 400 mg (82%, based on **1α**). Complex **2α** was identified by a comparison of its IR and ^{1}H-NMR spectra with those reported in ref.[4].

Carbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-β-D-mannofuranosyloxy)phenylcarbene](tri-p-chlorophenylphosphane)manganese (**3β**): The photolysis of 370 mg (0.81 mmol) of **1β** in the presence of 320 mg (0.88 mmol) of tri-*p*-chlorophenylphosphane and the purification of the reaction products were carried out as described for **1β**/tritolylphosphane. Yellow-brown powder of **3β** as a 7:2 mixture of diastereomers. Yield: 430 mg (62%, based on **1β**), m.p. 60°C (dec.). – IR (pentane): ν(CO) = 1865 cm^{-1} s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.27, 1.31, 1.34, 1.36, 1.47, 1.49, 1.62, 1.66 (s, 12H, 4 Me), 3.42–3.47 (m, 1H, 4-H), 3.98–4.13 (m, 2H, CH_2-6), 4.35–4.44 (m, 1H, 5-H), 4.59–4.72 (m, 2H, 2,3-H), 4.75 (d, $^2J_{PC}$ = 1.6 Hz, 5H, Cp), 4.89, 5.00 (2 d, ^3J = 3.2 and 3.0 Hz, 1H, 1-H), 6.78–7.38 (m, 17H, Ph, C_6H_4Cl). – ^{13}C NMR ([D$_6$]acetone, room temp.): δ = 25.4, 25.7, 26.8, 27.0 [$C(CH_3)_2$], 67.0 (C-6), 74.2 (C-5), 77.2 (C-4), 80.2, 80.7 (C-2, C-3), 88.4, 89.2 (Cp), 101.3, 101.5 (C-1), 109.1, 109.3, 113.3 (CMe_2), 126.9, 127.7, 127.8, 129.0, 129.1, 129.9, 135.2, 135.3, 136.1, 136.2, 136.6, 137.1, 153.1 (Ph, C_6H_4Cl), 237.2 ($^2J_{PC}$ = 31.7 Hz, CO), 324.7 ($^2J_{PC}$ = 32.9 Hz, Mn=C). – $C_{43}H_{41}Cl_3MnO_7P$ (862.0): calcd. C 59.91, H 4.79; found C 59.76, H 5.14.

Carbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-β-D-mannofuranosyloxy)phenylcarbene](tricyclohexylphosphane)manganese (**4β**): The synthesis of **4β** from 490 mg (0.94 mmol) of **1β** and 330 mg (1.18 mmol) of tricyclohexylphosphane and the purification of the reaction products were carried out as described for **1β**/tritolylphosphane. Brown powder of **4β** as a 5:1 mixture of diastereomers. Yield: 450 mg (62%, based on **1β**), m.p. 58°C (dec.). – IR (pentane): ν(CO) = 1852 cm^{-1} s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 0.87–2.00 (m, 45H, 4 Me, PCy_3), 3.28, 3.44 (2 dd, ^3J = 6.1 Hz, 3.4 Hz, 1H, 4-H), 4.05–4.08 (m, 2H, CH_2-6), 4.38–4.41 (m, 1H, 5-H), 4.55–4.56, 4.65–4.67 (m, 2H, 2,3-H), 4.82, 4.88 (2 d, $^3J_{PH}$ = 1.4 Hz, 5H, Cp), 4.91 (d, ^3J = 3.6 Hz, 1H, 1-H), 7.18–7.23 (m, 3H, Ph), 7.25–7.39 (m, 2H, Ph). – ^{13}C NMR (CD_2Cl_2, room temp.): δ = 25.3, 25.6, 26.3, 26.7 [2 $C(CH_3)_2$], 27.8, 27.9, 28.0, 28.1, 29.7, 29.8, 31.3, 31.4, 31.7, 31.9, 39.0, 39.2 (PCy_3), 67.0 (C-6), 73.4 (C-5), 76.2 (C-4), 79.5, 80.2 (C-2, C-3), 86.5, 87.3 (Cp), 101.1 (C-1), 108.8, 113.0 (2 CMe_2), 126.5, 126.8, 127.4, 153.8 (Ph), 240.1 ($^2J_{PC}$ = 31.7 Hz, CO), 315.9 ($^2J_{PC}$ = 30.5 Hz, Mn=C). – MS (FAB, NBOH), *m/z* (%): 776 (0.6) [M$^+$], 748 (2) [M$^+$ − CO], 517 (26) [M$^+$ − OR], 489 (13) [M$^+$ − OR − CO], 468 (13) [M$^+$ − CO − PCy_3], 400 (19) [M$^+$ − CO − carbene ligand], 297 (100). – $C_{43}H_{62}MnO_7P$ × 1/8 CH_2Cl_2 (787.5): calcd. C 65.80, H 8.23; found C 65.77, H 7.97.

Carbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-β-D-mannofuranosyloxy)phenylcarbene](trimethylphosphite)manganese (**5β**): The synthesis of **5β** from 500 mg (0.95 mmol) of **1β** and 0.14 ml (1.20 mmol) of trimethyl phosphite and the purification of the reaction products were carried out analogously to those of **1β**/tritolylphosphane. Yellow-brown powder of **5β** as a 9:7 mixture of diastereomers. Yield: 460 mg (78%, based on **1β**), m.p. 42°C (dec.). – IR (pentane): ν(CO) = 1889 cm^{-1} sh, 1879 s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.29 (s, 3H, Me), 1.34, 1.36 (2 s, 6H, Me), 1.51, 1.52 (2 s, 3H, Me), 3.49, 3.51 [2 d, $^{3}J_{PH}$ = 11.3 Hz, 9H, P(OMe)$_3$], 3.56–3.58 (m, 1H, 4-H), 3.96–4.08 (m, 2H, CH$_2$-6), 4.35–4.42 (m, 1H, 5-H), 4.58–4.62 (m, 1H, 3-H), 4.66, 4.67 (2 d, $^{3}J_{PH}$ = 1.6 and 1.3 Hz, 5H, Cp), 4.71–4.79 (m, 1H, 2-H), 5.28, 5.52 (2 d, ^{3}J = 3.8 and 3.5 Hz, 1H, 1-H), 7.18–7.30 (m, 5H, Ph). – ^{13}C NMR ([D$_6$]acetone, room temp.): δ = 25.6, 25.7, 26.5, 27.0 [C(*C*H$_3$)$_2$], 51.9 [$^{2}J_{PC}$ = 4.9 Hz, P(OMe)$_3$], 52.0 [$^{2}J_{PC}$ = 4.9 Hz, P(OMe)$_3$], 67.3, 67.4 (C-6), 74.0, 74.2 (C-5), 77.7, 77.8 (C-4), 80.3, 80.6, 80.9 (C-2, C-3), 86.6, 87.3 (Cp), 102.5, 102.9 (C-1), 109.2, 109.3, 113.6, 113.7 (*C*Me$_2$), 126.1, 126.8, 126.9, 127.4, 127.5, 127.6, 155.2 (Ph), 236.0 (CO), 324.0 (Mn=C). – MS (FAB, NBOH), *m/z* (%): 620 (17) [M$^+$], 589 (5) [M$^+$ – OMe], 468 (100) [M$^+$ – CO – P(OMe)$_3$], 361 (48) [M$^+$ – OR], 333 (30) [M$^+$ – CO – OR], 244 (40) [M$^+$ – CO – carbene ligand], 120 (22) [CpMn$^+$]. – $C_{28}H_{38}MnO_{10}P$ (620.5): calcd. C 54.20, H 6.17; found C 54.51, H 6.21.

Carbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-β-D-mannofuranosyloxy)phenylcarbene](triphenylphosphite)manganese (**6β**): The synthesis of **6β** from 420 mg (0.80 mmol) of **1β** and 0.26 ml (1.00 mmol) of triphenyl phosphite and the purification of the reaction products were carried out analogously to those of **1β**/tritolylphosphane. Yellow-brown powder of **6β** as a 1:1 mixture of diastereomers. Yield: 470 mg (74%, based on **1β**), m.p. 45°C (dec.). – IR (pentane): ν(CO) = 1901 cm^{-1} s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.27, 1.31, 1.34, 1.42, 1.58, 1.64 (6 s, together 12H, 4 Me), 3.46–3.49 (m, 1H, 4-H), 3.96–4.12 (m, 2H, CH$_2$-6), 4.25 (s, 5H, Cp), 4.39–4.66 (m, 1H, 5-H), 4.68–4.73 (m, 2H, 2,3-H), 5.18, 5.26 (2 d, ^{3}J = 3.5 Hz, 1H, 1-H), 7.15–7.45 (Ph, OC$_6$H$_5$). – ^{13}C NMR ([D$_6$]acetone, room temp.): δ = 25.5, 25.7, 26.6, 27.0 [C(*C*H$_3$)$_2$], 67.2, 67.3 (C-6), 74.0, 74.1 (C-5), 77.7, 77.8 (C-4), 80.0, 80.2, 80.5, 80.8 (C-2, C-3), 86.9, 87.3 (Cp), 102.1 (C-1), 109.2, 109.3, 113.5, 113.7 (*C*Me$_2$), 120.8, 120.9, 121.5, 121.6, 122.7, 122.8, 125.1, 125.3, 125.9, 126.1, 126.5, 127.3, 127.8, 128.1, 129.5, 130.2, 130.3, 130.7, 130.8, 151.5, 152.8, 152.9, 153.0, 153.7, 154.5 (Ph, O*C*$_6$H$_5$), 235.7 ($^{2}J_{PC}$ = 48.8 Hz, CO), 324.5 ($^{2}J_{PC}$ = 42.7 Hz, Mn=C), 325.2 ($^{2}J_{PC}$ = 43.9 Hz, Mn=C). – $C_{43}H_{44}MnO_{10}P$ × 1/4 pentane (824.7): calcd. C 64.44, H 5.74; found C 64.48, H 5.60.

Dicarbonyl(cyclopentadienyl){[(–)menthyloxy]phenylcarbene}-manganese (**9**): 1.13 g (3.92 mmol) of **7** was suspended in 50 ml of CH$_2$Cl$_2$. After cooling of the suspension to –40°C 0.58 ml (3.92 mmol) of TMEDA and 0.29 ml of acetyl bromide were slowly added. The color of the solution immediately changed from orange to brown. The IR spectrum of the solution indicated formation of complex **8** [IR (CH$_2$Cl$_2$): ν(CO) = 1986 cm^{-1} s, 1921 s]. The solution was stirred for 15 min at –40°C. Then a solution of 0.92 g (5.88 mmol) of (–)-menthol in 15 ml of CH$_2$Cl$_2$ was slowly added. The resulting solution was allowed to warm to room temp. within 2 h. The solvent was evaporated in vacuo. The brown residue was dissolved in 200 ml of pentane and the solution chromatographed at –20°C. With pentane/CH$_2$Cl$_2$ (10:1) an orange band containing **9** was eluted. Evaporation of the solvent in vacuo gave **9** as a yellow powder. Recrystallization from 20 ml of pentane afforded yellow crystals. Yield: 660 mg (40%, based on **7**), m.p. 48°C (dec.). – IR (pentane): ν(CO) = 1971 cm^{-1} vs, 1966 s, 1959 s, 1913 vs, 1906 s, 1888 s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 0.69 (d, ^{3}J = 6.9 Hz, 3H, Me), 0.86–0.97 (m, 9H, 2 Me and menthyl H), 1.22–1.28 (m, 3H, menthyl H), 1.62–1.75 (m, 3H, menthyl H), 4.33–4.34 (m, 1H, 1-H), 4.64 (s, 5H, Cp), 6.92–6.96 (m, 2H, Ph), 7.22–7.40 (m, 3H, Ph). – ^{13}C NMR ([D$_6$]acetone, room temp.): δ = 16.7 (C-9), 21.5 (C-10), 22.3 (C-7), 23.6 (C-3), 26.4 (C-8), 32.0 (C-5), 34.6 (C-4), 42.9 (C-6), 48.9 (C-2), 86.9 (C-1), 87.9 (Cp), 123.0, 127.7, 128.1, 154.3 (Ph), 232.9, 233.3 (2 CO), 332.7 (Mn=C). – MS (70 eV), *m/z* (%): 420 (6) [M$^+$], 364 (23) [M$^+$ – 2 CO], 282 (2) [Cp(CO)$_2$Mn=C(Ph)OH$^+$], 226 (100) [CpMn=C(Ph)OH$^+$], 120 (51) [CpMn$^+$]. – $C_{24}H_{29}MnO_3$ × 1/4 pentane (438.4): calcd. C 69.17, H 7.36; found C 69.19, H 7.16.

Carbonyl(cyclopentadienyl){[(–)menthyloxy]phenylcarbene}-[tris(anisyl)phosphane]manganese (**10**): The synthesis of **10** from 320 mg (0.76 mmol) of **9** and 330 mg (0.95 mmol) of tris(anisyl)-phosphane and the purification of the reaction products were carried out as described for **1β**/tritolylphosphane. Compound **10** was obtained as a copper-colored powder consisting of a 5:4 mixture of diastereomers. Yield: 470 mg (83%, based on **9**), m.p. 102°C (dec.). – IR (pentane): ν(CO) = 1884 cm^{-1} sh, 1854 s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 0.16–0.19, 0.63–0.65, 0.74–0.93, 1.07–1.10, 1.24–2.00 (m, 18H, menthyl-H), 3.80, 3.83 (2 s, 9H, C$_6$H$_4$OC*H*$_3$), 4.33, 4.39 (2 d, $^{2}J_{PH}$ = 1.5 and 1.7 Hz, 5H, Cp), 6.85–7.34 (m, 17H, Ph, C$_6$*H*$_4$OCH$_3$). – ^{13}C NMR ([D$_6$]acetone, room temp.): δ = 16.4, 16.6 (C-9), 21.7, 22.1 (C-10), 22.4, 22.5 (C-7), 23.2, 23.4 (C-3), 25.6, 25.8 (C-8), 32.1, 32.2 (C-5), 34.7, 34.9 (C-4), 43.6, 43.8 (C-6), 49.1, 49.6 (C-2), 55.5 (C$_6$H$_4$O*C*H$_3$), 81.8, 83.1 (C-1), 87.5, 88.0 (Cp), 113.8, 113.9, 114.9, 115.0, 126.1, 126.2, 127.1, 131.1, 131.5, 135.3, 135.4, 135.5, 135.7, 153.2, 153.4, 161.0, 161.1 (Ph, *C*$_6$H$_4$OCH$_3$), 238.2 ($^{2}J_{PC}$ = 31.7 Hz, CO), 239.4 ($^{2}J_{PC}$ = 30.5 Hz, CO), 323.3 ($^{2}J_{PC}$ = 29.3 Hz, Mn=C), 326.4 ($^{2}J_{PC}$ = 29.3 Hz, Mn=C). – MS (FAB, NBOH): *m/z* (%): 744 (1.5) [M$^+$], 716 (18) [M$^+$ – CO], 589 (3) [M$^+$ – menthyl], 561 (4) [M$^+$ – CO – menthyl], 472 (34) [M$^+$ – CO – carbene ligand], 364 (100) [M$^+$ – CO – P(C$_6$H$_4$OMe-*p*)$_3$], 226 (94) [CpMn=C(Ph)OH$^+$], 120 (42) [CpMn$^+$]. – $C_{44}H_{50}MnO_5P$ × 1/8 CH$_2$Cl$_2$ (755.4): calcd. C 70.16, H 6.71; found C 70.09, H 6.72.

Carbonyl(tritolylphosphane)(phenylcarbyne)manganese Tetrafluoroborate [(S_{Mn})-**11**]: At –70°C a vigorous stream of BF$_3$ was passed for 30 s through a stirred solution of 470 mg (0.59 mmol) of (S_{Mn})-**2β** in 15 ml of CH$_2$Cl$_2$. Then 150 ml of pentane precooled to –70°C was added. The carbyne complex (S_{Mn})-**11** precipitated as a yellow-orange powder. After decanting, the residue was washed with 20 ml of Et$_2$O and several times with 20-ml portions of pentane, both precooled to –70°C. Complex (S_{Mn})-**11** was dried in vacuo at –40°C. Orange powder. Yield: 300 mg [81%, based on (S_{Mn})-**2β**]. – Complex (S_{Mn})-**11** was identified by a comparison of its IR [IR (CH$_2$Cl$_2$): ν(CO) = 2012 cm^{-1} s] and ^{1}H-NMR spectra [([D$_6$]acetone, room temp.): δ = 2.41 (s, 9H, C$_6$H$_4$C*H*$_3$), 5.56 (d, $^{3}J_{PH}$ = 1.7 Hz, 5H, Cp), 7.39–7.82 (m, 17H, C$_6$H$_5$, C$_6$H$_4$)] with those of racemic **11** reported in ref.[4]. The ee >95% of (S_{Mn})-**11** was established by quantitative reaction with the Na salt of di-*O*-isopropylidene-β-D-mannofuranose to reform (S_{Mn})-**2α**[4] with de >95%.

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