Carbohydratocarbene Complexes of Manganese and Rhenium☆

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The cationic carbyne complexes $[Cp(CO)_2M{\equiv}CR]^+$ $[BX_4]^-$ [M = Mn, X = F: R = Ph (**1**), Tol (**2**); M = Re, X = 3,5-$C_6H_2(CF_3)_2$: R = Ph (**3**)] add the anion of monodeprotonated protected mannofuranose (**4a**), glucofuranose (**4b**), and fructopyranose (**4c**) to the carbyne carbon atom to form the carbohydratocarbene complexes **5a–c**, **6a**, **b**, and **7a**. With **5b**, **5c**, and **6b** the addition proceeds with retention of configuration at the anomeric center. Due to inversion of configuration in the deprotonation step the complexes **5a**, **6a**, and **7a** are obtained as β-glycosides. The carbene ligand is oxidatively cleaved from the metal by trimethylamine *N*-oxide or air. Cleavage of the C(carbene)–O bond with reformation of the cation of the carbyne complex **2** is achieved by reaction of **6a** with BCl_3. Photolysis of $[Cp(CO)_2Mn{=}C(Ph)OEt]$ in the presence of L affords the carbene complexes $[Cp(CO)(L)Mn{=}C(Ph)OEt]$ [L = $P(OMe)_3$ (**11**), $P(Tol)_3$ (**12**)]. Ethoxide abstraction from **11** and **12** by BF_3 gives the chiral cationic carbyne complexes $[Cp(CO)(L)Mn{\equiv}CPh]^+[BF_4]^-$ (**13**, **14**) which add **4a** to form the corresponding mannofuranosylcarbene complexes (**15**, **16**). When 0.5 equivalents of **4a** are employed in the reaction with **13**, **14** the ratio of diastereomers is 3:2, both for **15** and **16**. Complex **11** was characterized by an X-ray structural analysis.

Chiral transition-metal complexes play a prominent role in enantioselective synthesis and catalysis. In these complexes either the metal or one or more ligands carry the chiral information. In most transformations complexes having chiral ligands are employed.

Transition metal-carbene complexes with a carbohydrate bound to the carbene carbon atom have been known until now only for gold and platinum[1]. These compounds are obtained by addition of amines or alcohols to the isocyanide functionality of the corresponding carbohydratoisocyano ligand. Recently, alkenylcarbene complexes with a carbohydrate in the β-position to the carbene carbon[2,3] were obtained by Aumann et al. by addition of sugar derivatives to alkynylcarbene complexes of chromium and tungsten.

The cationic carbyne complexes $[(CO)_5Cr{\equiv}C{-}NEt_2]^+$ and $[Cp(CO)_2M{\equiv}C{-}Aryl]^+$ (M = Mn, Re) add anionic and neutral nucleophiles such as alcoholates[4], amines[5,6], and isocyanides[7] to the carbyne carbon atom to form carbene complexes[8]. Analogously, it should be possible to also add carbohydrates via a hydroxy, an amino, or an isocyano group. In the resulting carbene complexes the carbohydrate should be attached directly to the carbene carbon atom. When carbyne complexes of the type $[Cp(CO)(L)M{\equiv}CR]^+$ are used the addition of carbohydrates gives diastereomers. Separation of the diastereomers should afford enantiomerically pure carbene complexes. These carbene complexes can be derivatized or easily be converted into other complexes, e.g. by displacement of the carbene ligand. Therefore, this route should render a great number of different types of chiral transition-metal complexes accessible. In this paper we report on the synthesis of the first carbohydratocarbene complexes of manganese and rhenium and the results of experiments concerning the addition of a protected mannofuranoside to the cation $[Cp(CO)(L)Mn{\equiv}CPh]^+$ [L = $P(OMe)_3$, $P(Tol)_3$].

Preparative Results

The cationic carbyne complexes **1–3** react at −78°C in dichloromethane with the sodium salts Na-**4a–c** of the protected carbohydrates mannofuranose (H-**4a**), glucofuranose (H-**4b**), and fructopyranose (H-**4c**) to afford the new carbene complexes **5–7**. (Prior to the reaction with **1–3**, the hydroxy group of the carbohydrates H-**4a–c** is deprotonated by sodium in THF. The resulting alcoholates Na-**4a–c** then add to the carbyne carbon as anionic nucleophiles.) Thus, chirality is easily introduced into the carbene ligand by starting from **1–3**. The IR spectra of **5–7** reveal that the $Cp(CO)_2Mn$ fragment of **1–3** remains intact on reaction with Na-**4**. From the ^{1}H-NMR spectra it follows that the carbene complexes **5–7** (Scheme 1) are obtained in enantiomerically pure form. The configuration of the carbohydrates H-**4b**, **c** is retained during addition. In contrast, inversion of configuration with exclusive formation of the β-anomer is observed with the carbohydrate functionality in **5a**, **6a**, and **7a** which is derived from the α-anomer of H-**4a**. However, the inversion of configuration presumably is not the result of the reaction of the alcoholate Na-**4a** with the carbyne complexes **1–3** but already occurs at the deprotonation stage. From previous investigations[9] it is known that Na^+ and the oxygen atoms of the carbohydrate form a complex. Formation of the β-anomer of Na-**4a** is favored since it can assume an almost ideal crown ether geometry. By analogy with the *O*-alkylation with

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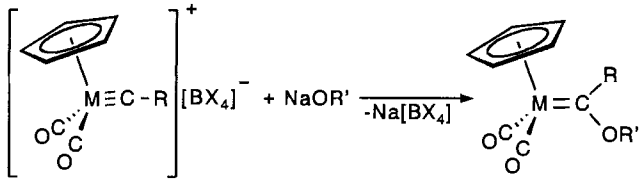
methyl iodide the β-glycoside is therefore formed exclusively in the reactions with **1**–**3**.

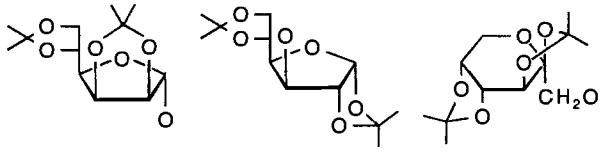
Scheme 1



1 - 3 Na-**4a-c** **5a-c, 6a-b, 7a**

	M	R	X
1, 5	Mn	Ph	F
2, 6	Mn	Tol	F
3, 7	Re	Ph	3,5-$C_6H_3(CF_3)_2$

OR' =



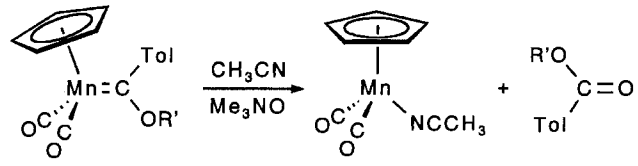
4a **4b** **4c**

The configuration of the furanosylcarbene complexes **5a**, **b**, **6a**, **b**, and **7a** is unambiguously established by their ^{1}H-NMR spectra. In contrast to the other resonances of the carbohydrate framework (δ = 3.60 to 5.04), the 1-H signal appears at rather low field (δ > 5.68) and is therefore easily detected just as the signals for the isopropylidene groups (δ = 1.16 to 1.49). For the α-anomer of the mannofuranosylcarbene complexes **5a**, **6a**, and **7a** a singlet is to be expected. The β-anomer, however, should give a doublet with a coupling constant of ca. 4 Hz[9]. The complexes **5a**, **6a**, and **7a** show a doublet each at δ = 5.68 (J = 4.3 Hz), 5.75 (J = 4.3 Hz), and 6.05 (J = 4.2 Hz), respectively. Consequently, they are present as β-anomers. The glucofuranosylcarbene complexes **5b** and **6b** show a doublet at δ = 6.06 [J = 3.1 (**5b**) and 3.4 Hz (**6b**)]. Since the configuration at the anomeric center is fixed by the isopropylidene group, **5b** and **6b** must be present as α-anomers. From the ^{13}C-NMR spectra of **5c**, **6a**, and **7a** it follows that the CO ligands are not equivalent. Two separate signals are observed. For **5a**, **5b**, and **6b** these resonances are not resolved.

The carbene ligand can be oxidatively cleaved from the metal. This has been shown with the example of **6a**. Compound **6a** reacts at room temperature with trimethylamine N-oxide in acetonitrile to form the acetonitrile complex **8** and the ester **9** (Scheme 2).

Similarly, the reaction of **6a** with trimethylamine N-oxide in THF affords [$Cp(CO)_2Mn(THF)$] and **9**. Apart from trimethylamine N-oxide, air can also serve as the oxidant. When compound **6a** adsorbed on silica gel is exposed to air for several hours the carbene ligand is oxidatively cleaved from the metal. The resulting ester **9** can be extracted with acetone. Chromatographic purification gives **9** and H-**4a** as by-product. Based on the ^{1}H-NMR spectrum the ratio **9**/H-**4a** is 5:1. Presumably, H-**4a** is formed by acid hydrolysis of the ester. The selective cleavage of the C(carbene)–O(carbohydrate) bond is achieved with boron trihalides. Complex **6a** reacts with e.g. BCl_3 to form [$Cp(CO)_2$-Mn≡CTol]$^+$, the cation in **2**.

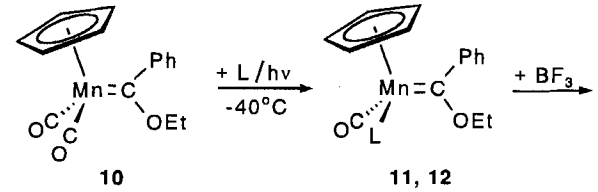
Scheme 2



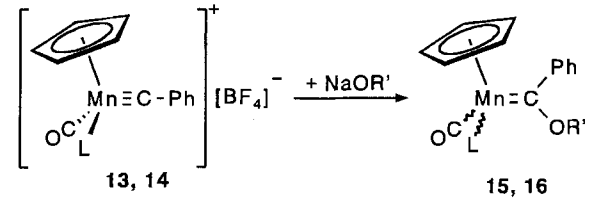
6a **8** **9**

By substitution of one CO ligand the prochiral $Cp(CO)_2Mn$ fragment is converted into the chiral Cp(CO)(L)Mn fragment. The reaction of the corresponding cationic carbyne complexes [Cp(CO)(L)Mn≡C-Ph]$^+$ with carbohydrates is expected to proceed diastereoselectively. The synthesis of racemic Cp(CO)(L)Mn carbene complexes has been reported[10–12]. The chiral carbene complexes **11** and **12** are obtained when solutions of the carbene complex **10** in toluene are irradiated at −40°C in the presence of $P(OMe)_3$ and $PTol_3$, respectively. Subsequent reaction with BF_3 gives the carbyne complexes **13** and **14**, which add Na-**4a** to form the carbene complexes **15** and **16** as a 1:1 mixture of diastereomers (Scheme 3). Surprisingly, when 0.5 equivalents of Na-**4a** are employed the ratio of diastereomers for **15** and **16** as determined by integration of the ^{1}H resonances is only 2:3. In contrast to **5a**, **6a**, and **7a** compound **16** is presumably present as α-anomer. Unfortunately, it was not possible to separate the diastereomers by column chromatography.

Scheme 3



10 **11, 12**



13, 14 **15, 16**

11, 13, 15: L = $P(OMe)_3$ OR' = **4a**

12, 14, 16: L = $PTol_3$

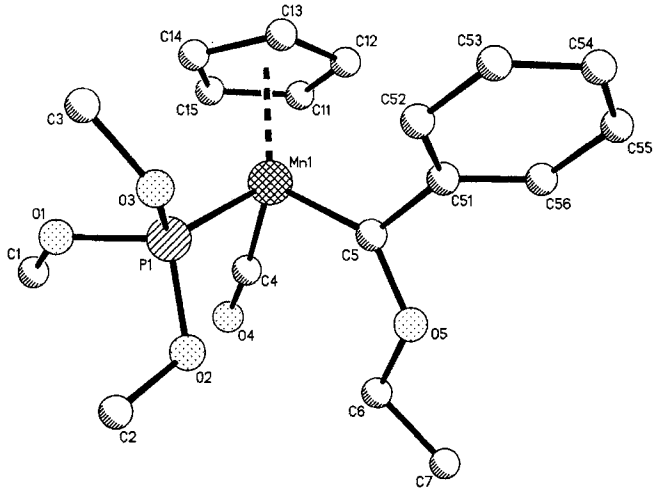
The CO absorptions of **11**–**16** establish that these compounds contain a Cp(CO)(L)Mn fragment. Since the σ-donor/π-acceptor ratio considerably increases from CO via

$P(OMe)_3$ to $P(Tol)_3$ the CO absorption significantly shift to lower wave numbers in the series **10**, **11**, **15** and **10**, **12**, **16**. Due to coupling with phosphorus the resonance of the OMe groups in **11** (δ = 3.61) is split into a doublet ($^3J_{PH}$ = 11.2 Hz). The signals of the cyclopentadienyl ring in **12**, **15**, and **16** appear as doublets obviously caused by coupling with the phosphorus of the ligand L ($^3J_{PH}$ = 1.4, 1.4, and 1.8 Hz, resp.). There is a double set of resonances in the ^{13}C-NMR spectra of **15** and **16**, due to the presence of pairs of diastereomers. When 0.5 equivalents of Na-**4a** are employed the ratio of diastereomers can be deduced from the ^{1}H-NMR spectrum of **16**. Both the hydrogen atoms of the Cp ligand and the methyl substituents of the $PTol_3$ ligand give rise to doublets. Integration of these doublets gives a ratio of diastereomers of 3:2. The 1-H resonance of both diastereomers of **15** and **16** appears as singlet each. From the integrals of these signals again a diastereomeric ratio of 3:2 can be deduced. The spectroscopic results also indicate that the mannofuranosyl substituent of the carbene ligand occupies the α-anomeric form which is in contrast to the observations with compounds **5a**, **6a**, and **7a**. The formation of the β-anomer is presumably disfavored by the bulky phosphite and phosphane ligand.

Structure of 11

Compound **11** was characterized by an X-ray structural determination. As expected and also observed with other CpL_2Mn(carbene) complexes, **11** exhibits a pseudo-octahedral geometry (Figure 1).

Figure 1. Structure of complex **11** in the crystal (without H atoms). Selected distances [A] and angles [°] (standard deviations in brackets) are: Mn(1)–P(1) 2.151(1), Mn(1)–C(5) 1.855(3), Mn(1)–C(4) 1.751(5), C(4)–O(4) 1.170(6), C(5)–O(5) 1.365(5), C(5)–C(51) 1.508(5); P(1)–Mn(1)–C(4) 91.4(2), C(4)–Mn(1)–C(5) 100.2(2), Mn(1)–C(5)–C(51) 124.4(3), Mn(1)–C(5)–O(5) 133.9(3), P(1)–Mn(1)–C(5) 90.6(1), O(5)–C(5)–C(51) 101.5(3)



The angles P–Mn–C are close to 90° [P(1)–Mn(1)–C(4) 91.4(2), P(1)–Mn(1)–C(5) 90.6(1)°]. The Mn–C(carbene) bond [1.855(3) Å] is comparable to that usually observed in other CpL_2Mn(carbene) complexes[11,13]. In comparison with the Mn–P bond in carbene complexes with triphenylphosphane ligands such as [Cp(CO)(PPh_3)Mn=C(OMe)Et] [2.229(2) Å][11], [Cp'(CO)(PPh_3)Mn=C–$OC(Me)_2CH_2CH$(Me)] [2.229(7) Å][11], and [Cp'(CO)(PPh_3)Mn=C–$OCH_2C(Me)_2CH_2CH$(Me)] [2.230(1) Å][11] that in carbene complexes with a trimethyl phosphite ligand is shorter, e.g. in [Cp(CO)[$P(OMe)_3$]-Mn=C–$SC(CO_2Me)$=$C(CO_2Me)$–S] [2.174(0) Å][14] or **11** [2.151(1) Å]. As expected for electronic reasons the carbene plane [C(5)/C(51)/O(5)] and the plane formed by the atoms C(4), Mn(1), and C(5) deviate only slightly from coplanarity. The dihedral angle C(4)–Mn(1)–C(5)–O(5) is 9.1°, the complex assumes the synclinal conformation. Probably for steric reasons the phenyl ring is strongly twisted against the carbene plane [dihedral angle Mn(1)–C(5)–C(51)–C(52) 58.2°] and is almost coplanar with the cyclopentadienyl ring.

Conclusion

The results demonstrate that carbene complexes of manganese with a carbohydrate as a carbene substituent are conveniently accessible by addition of carbohydrate anions to cationic carbyne complexes. Reaction of the resulting carbene complexes with strong Lewis acids such as BCl_3 reforms the carbyne complexes. Oxidative cleavage of the carbene ligand from the metal is easily achieved by e.g. exposure of the complex adsorbed on silica gel to air. Addition of carbohydrate anions to chiral carbyne complexes $[Cp(CO)(L)Mn{\equiv}CPh]^+$ gives carbohydratocarbene complexes. However, the kinetic resolution is only poor (de ca. 20%) and the separation of the diastereomers by chromatography is not possible. Preliminary results indicate that by modification of the reaction sequence in Scheme 3 considerably higher diastereoselectivities can be achieved. Substitution of phosphites or phosphanes for one CO ligand in the dicarbonyl complexes **5**–**7** proceeds faster than in **10** and with a de > 75%[15].

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Experimental

All manipulations were carried out under either nitrogen or argon 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 nitrogen-saturated. The yields refer to analytically pure compounds and were not optimized. The complexes **1**, **2**[16], and **10**[17], the carbohydrates **4**[18] and $P(Tol)_3$[19] were prepared according to literature procedures. $P(OMe)_3$ was purchased from Fa. Fluka. – IR: FT-IR-spectrophotometer, Fa. Bio-Rad. – ^{1}H and ^{13}C NMR: Bruker WM 250, Bruker AC 250, Jeol 400. If not specifically mentioned chemical shifts are reported relative to TMS. – MS: Varian MAT 312. – Photochemical reactions were carried out in a duran glas apparatus using a Hg high-pressure lamp (TQ 150, Fa. Heraeus).

Dicarbonyl(cyclopentadienyl)(phenylcarbyne)rhenium Tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (**3**): 900 mg (0.9 mmol) of $H(Et_2O)_2^+$ $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$[20] was added at –60°C to a stirred

solution of 400 mg (0.9 mmol) of dicarbonyl(cyclopentadienyl)-(ethoxyphenylcarbene)rhenium in 20 ml of CH_2Cl_2. After stirring of the mixture for 10 min the solvent was removed in vacuo at −40°C. Crystallization from 15 ml of CH_2Cl_2 at −30°C gave lemon-yellow crystals of **3**. Yield: 990 mg (87%). The compound was identified by a comparison of its IR data [ν(CO) = 2091 cm^{-1} s, 2041 s, in CH_2Cl_2] with those of the corresponding BCl_4^- salt[21].

Dicarbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-β-D-mannofuranosyloxy)phenylcarbene]manganese (**5a**): 400 mg (1.56 mmol) of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**H-4a**) in 25 ml of THF was deprotonated with Na. After the H_2 evolution had ceased the reaction mixture was decanted. The solvent of the liquid phase was removed in vacuo. The residue was dissolved in 10 ml of CH_2Cl_2 and the solution added slowly at −78°C to a solution of 500 mg (1.42 mmol) of **1** in 20 ml of CH_2Cl_2. The solution was warmed to room temp. and the solvent removed in vacuo. The residue was dissolved in 50 ml of pentane and the solution chromatographed at −20°C on a silica gel column. With pentane/CH_2Cl_2/Et_2O (10:5:1) a yellow-orange band was eluted and then an orange-brown band which contained **5a**. Evaporation of the solvent from the eluate in vacuo gave 240 mg of **5a** (32%, based on **1a**) as a yellow-brown sticky oil. − IR (pentane): ν(CO) = 1970 cm^{-1} s, 1908 s. − ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.29 (s, 3H, Me), 1.35 (s, 6H, Me), 1.49 (s, 3H, Me), 3.84−3.88 (m, 1H, 4-H), 4.02−4.09 (m, 2H, CH_2-6), 4.47 (m, 1H, 5-H), 4.79 (s, 5H, Cp), 4.79−4.88 (m, 2H, 2,3-H), 5.68 (d, ^3J = 4.3 Hz, 1H, 1-H), 7.07−7.38 (m, 5H, Ph). − ^{13}C NMR ([D$_6$]acetone, −30°C): δ = 25.2, 25.3, 26.0, 26.9, (4 Me), 66.9 (C-6), 73.6 (C-5), 79.2 (C-4), 79.6, 80.8 (C-2,3), 87.9 (Cp), 103.9 (C-1), 109.1, 114.2 (CMe_2), 124.0, 127.8, 128.4, 153.9 (Ph), 232.0 (CO), 332.4 (Mn=C). − MS (70 eV), *m/z* (%): 524 (8) [M^+], 468 (51) [M^+ − 2 CO], 265 (42) [M^+ − OR'], 197 (100) [M^+ − Ph − $Cp(CO)_2Mn$ − $OCMe_2O$], 120 (68) [M^+ − 2 CO − carbene ligand]. − $C_{26}H_{29}MnO_8$ (524.4): calcd. C 59.54, H 5.57; found C 59.41, H 5.57.

Dicarbonyl(cyclopentadienyl)[(1,2:5,6-di-O-isopropylidene-α-D-glucofuranosyloxy)phenylcarbene]manganese (**5b**): The reaction of 500 mg (1.42 mmol) of **1** with 400 mg (1.56 mmol) of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**H-4b**) and the purification of the reaction products were carried out analogously to those of **1**/H-**4a**. Yellow-brown powder of **5b**. Yield: 250 mg (34%, based on **1**), m.p. 42°C (dec.). − IR (pentane): ν(CO) = 1975 cm^{-1} s, 1915 s. − ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.26 (s, 3H, Me), 1.33 (s, 6H, Me), 1.37 (s, 3H, Me), 3.90−3.92 (m, 1H, 5-H), 4.12 (m, 2H, CH_2-6), 4.38−4.40 (m, 1H, 4-H), 4.67 (m, 1H, 2-H), 4.76 (s, 5H, Cp), 4.97 (m, 1H, 3-H), 6.06 (d, ^3J = 3.1 Hz, 1H, 1-H), 7.04−7.41 (m, 5H, Ph). − ^{13}C NMR ([D$_6$]acetone, 5°C): δ = 25.5, 26.3, 26.9, 27.1 (4 Me), 67.9 (C-6), 73.0 (C-5), 81.5 (C-4), 84.4, 86.5 (C-2,3), 88.2 (Cp), 106.2 (C-1), 109.5, 112.6 (2 CMe_2), 123.4, 128.1, 128.3, 153.3 (Ph), 232 (CO), 332 (Mn=C). − $C_{26}H_{29}MnO_8$ (524.4): calcd. C 59.54, H 5.57; found C 59.45, H 5.74.

Dicarbonyl(cyclopentadienyl)[(2,3:4,5-di-O-isopropylidene-β-D-fructopyranosyloxy)phenylcarbene]manganese (**5c**): The reaction of 500 mg of (1.42 mmol) of **1** with 400 mg (1.56 mmol) of 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**H-4c**) and the purification of the reaction products were carried out analogously to **1**/H-**4a**. Orange powder. Yield: 200 mg (27%, based on **1**), m.p. 88°C (dec.). − IR (pentane): ν(CO) = 1971 cm^{-1} s, 1909 s. − ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.16 (s, 3H, Me), 1.31 (s, 3H, Me), 1.35 (s, 3H, Me), 1.46 (s, 3H, Me), 3.60−4.67 (m, 7H, 1,2,3,4,5,6-H), 4.70 (s, 5H, Cp), 6.96−7.38 (m, 5H, Ph). − ^{13}C NMR ([D$_6$]acetone, −50°C): δ = 23.7, 25.0, 25.7, 26.4 (4 Me), 61.2, 70.0, 70.2, 70.9, 76.1 (C-1,3,4,5,6), 88.6 (Cp), 101.9 (C-2), 108.8, 109.2 (2 CMe_2), 123.2, 127.6, 127.9, 155.9 (Ph), 232.8, 233.2 (2 CO), 332.5 (Mn=C). − $C_{26}H_{29}MnO_8$ (524.4): calcd. C 59.54, H 5.57; found C 59.64, H 5.68.

Dicarbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-β-D-mannofuranosyloxy)tolylcarbene]manganese (**6a**): 390 mg (1.5 mmol) of H-**4a** in 25 ml of THF was deprotonated with Na. After cessation of the H_2 evolution the reaction mixture was decanted. The solvent was evaporated in vacuo and the residue dissolved in 10 ml of CH_2Cl_2. The solution was added slowly at −78°C to a solution of 500 mg (1.37 mmol) of **2** in 20 ml of CH_2Cl_2. With stirring the resulting solution was warmed to room temp. The solvent was removed in vacuo, the residue was dissolved in 50 ml of pentane and the solution chromatographed on silica gel at −20°C. First a yellow band containing [$Cp(CO)_2Mn$=C(OMe)(Tol)] was eluted with pentane/CH_2Cl_2/Et_2O (10:5:1) and then an orange-brown fraction containing **6a**. Yellow-brown powder. Yield: 370 mg (50%, based on **2**), m.p. 38°C (dec.). − IR (pentane): ν(CO) = 1972 cm^{-1} s, 1925 sh, 1911 vs, 1889 m. − ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.30 (s, 3H, Me), 1.36 (s, 6H, Me), 1.45 (s, 3H, Me), 2.33 (s, 3H, $C_6H_4CH_3$), 3.86−3.90 (m, 1H, 4-H), 4.02−4.13 (m, 2H, CH_2-6), 4.48−4.50 (m, 1H, 5-H), 4.78 (s, 5H, Cp), 4.81−4.84 (m, 1H, 3-H), 4.87−4.91 (m, 1H, 2-H), 5.75 (d, ^3J = 4.3 Hz, 1H, 1-H), 7.04−7.18 (m, 4H, C_6H_4). − ^{13}C NMR ([D$_6$]acetone, −45°C): δ = 21.0 ($C_6H_4CH_3$), 25.1, 25.3, 25.9, 26.9 (4 Me), 66.9 (C-6), 73.6 (C-5), 79.2 (C-4), 79.6 (C-2), 80.9 (C-3), 87.5 (Cp), 104.4 (C-1), 109.2, 114.3 (2 CMe_2), 124.8, 128.5, 138.9, 151.6 (C_6H_4), 231.9, 232.3 (CO), 333.6 (Mn=C). − $C_{27}H_{31}MnO_8$ (538.4): calcd. C 60.22, H 5.80; found C 60.20, H 5.86.

Dicarbonyl(cyclopentadienyl)[(1,2:5,6-di-O-isopropylidene-α-D-glucofuranosyloxy)tolylcarbene]manganese (**6b**): The reaction of 1.00 g (2.73 mmol) of **2** with 780 mg (3 mmol) of H-**4b** and the purification of the products were carried out analogously to **1**/H-**4a**. Yellow powder. Yield: 440 mg (30%, based on **2**), m.p. 43°C (dec.). − IR (pentane): ν(CO) = 1974 cm^{-1} s, 1957 sh, 1913 s, 1901 sh. − ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.26 (s, 3H, Me), 1.33 (s, 6H, Me), 1.38 (s, 3H, Me), 2.36 (s, 3H, $C_6H_4CH_3$), 3.91 (m, 1H, 5-H), 4.12 (m, 2H, CH_2-6), 4.37 (m, 1H, 4-H), 4.65 (m, 1H, 2-H), 4.75 (s, 5H, Cp), 5.04 (m, 1H, 3-H), 6.06 (d, ^3J = 3.4 Hz, 1H, 1-H), 6.97−7.24 (m, 4H, C_6H_4). − ^{13}C NMR ([D$_6$]acetone, 30°C): δ = 21.1 ($C_6H_4CH_3$), 25.6, 26.4, 27.0, 27.1 (4 Me), 68.1 (C-6), 73.2 (C-5), 81.7 (C-4), 84.6, 86.6 (C-2,3), 88.1 (Cp), 106.4 (C-1), 109.5, 112.6 (2 CMe_2), 123.8, 129.0, 138.2, 151.2 (C_6H_4), 232.3, 232.8 (2 CO), 334.4 (Mn=C). − $C_{27}H_{31}MnO_8$ (538.4): calcd. C 60.22, H 5.80; found C 60.24, H 6.02.

Dicarbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-β-D-mannofuranosyloxy)phenylcarbene]rhenium (**7a**): 100 mg (0.38 mmol) of H-**4a** and Na in 5 ml of THF were stirred until H_2 evolution had ceased. After decantation the solvent of the liquid phase was evaporated in vacuo. The residue was dissolved in 3 ml of CH_2Cl_2 and the solution added slowly at −78°C to a stirred solution of 250 mg (0.19 mmol) of **3** in 5 ml of CH_2Cl_2. The solution was warmed to room temp. and the solvent evaporated in vacuo. The residue was dissolved in 5 ml of pentane/Et_2O (2:1) and the solution chromatographed on silica gel at −20°C. With pentane/Et_2O (2:1) first a green band and then a yellow-orange band were eluted. The latter one contained **7a**. Orange powder. Yield: 100 mg (80%, based on **3**). − IR (pentane): ν(CO) = 1973 cm^{-1} s, 1897 s, 1883 sh. − ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.28, 1.29, 1.32, 1.36 (s, 12H, 4 Me), 3.95−3.99 (m, 1H, 4-H), 4.02−4.05 (m, 2H, CH_2-6), 4.37−4.41 (m, 1H, 5-H), 4.89−4.99 (m, 1H, 3-H), 5.01−5.04 (m, 1H, 2-H), 5.37 (s, 5H, Cp), 6.05 (d, ^3J = 4.2 Hz, 1H, 1-H), 7.07−7.32 (m, 5H, Ph). − ^{13}C NMR ([D$_6$]acetone, room

temp.): δ = 25.4, 25.5, 26.0, 27.0 (4 Me), 67.2 (C-6), 73.7 (C-5), 79.5 (C-4), 79.8 (C-2), 80.9 (C-3), 90.5 (Cp), 105.6 (C-1), 109.2, 114.1 (2 CMe_2), 123.9, 127.5, 128.0, 159.0 (Ph), 203.1, 204.1 (2 CO), 285.3 (Re=C). – MS (70 eV), *m/z* (%): 656 (15) [M^+], 413 (100) [$Cp(CO)_2Re(COTol)^+$]. – $C_{26}H_{29}O_8Re$ (655.7): calcd. C 47.62, H 4.46; found C 47.30, H 4.46.

(Acetonitrile)(dicarbonyl)(cyclopentadienyl)manganese (**8**) *and 2,3:5,6-Di-O-isopropylidene-1-O-(4-methylbenzoyl)-β-D-mannofuranose* (**9**): A solution of 120 mg (0.22 mmol) of **6a** and 17 mg (0.22 mmol) of trimethylamine *N*-oxide in 20 ml of acetonitrile was stirred for 1 h at room temp. The solvent was evaporated in vacuo. The residue was dissolved in 10 ml of pentane/CH_2Cl_2 (1:1) and the solution chromatographed at −20°C on silica gel. With pentane/CH_2Cl_2 (1:1) first a yellow band was eluted which gave, after removal of the solvent in vacuo, compound **8** as a yellow powder [yield: 30 mg (66.5%, based on **6a**)]. Complex **8** was identified by a comparison of its IR and ^{1}H-NMR data with those reported in ref.[22]. With pentane/CH_2Cl_2/Et_2O (1:1:0.1) another slightly yellow band was eluted which contained **9** [yield: 40 mg (48.2%, based on **6a**)]. – **9**: ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.31 (s, 6H, CMe_2), 1.36 (s, 3H, CMe_2), 1.39 (s, 3H, C*Me*), 2.40 (s, 3H, $C_6H_4CH_3$), 3.98–4.08 (m, 3H, 4-H, CH_2-6), 4.45 (m, 1H, 5-H), 4.92, 4.97 (m, 2H, 2,3-H), 6.11 (d, ^3J = 4.1 Hz, 1H, 1-H), 7.32–7.96 (m, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 378 (0.05) [M^+], 363 (15) [M^+ – Me], 305 (4) [M^+ – $OCMe_2$], 259 (5) [M^+ – OCTol], 119 (100) [OCTol].

Oxidative Cleavage of the Mn=C Bond by Air: 100 mg (0.19 mmol) of **6a** was dissolved in 30 ml of acetone and the solution adsorbed on silica gel. On exposure to air for 24 h the silica gel decolorized. The silica gel was extracted with 100 ml of acetone and the extract chromatographed on silica gel at room temp. The colorless band which was eluted with pentane/Et_2O (1:1) (R_f = 0.4) contained **9** and H-**4a** in a 5:1 ratio (based on the ^{1}H-NMR spectrum). Yield: 50 mg. The compounds were identified by their ^{1}H-NMR spectra.

Reaction of **6a** *with BCl_3:* 2.23 ml (2.23 mmol) of a 1 M solution of BCl_3 in hexane was added to a solution of 200 mg (0.37 mmol) of **6a** in 20 ml of pentane. A white precipitate formed. The solvent was decanted and the residue ($[Cp(CO)_2Mn{\equiv}CTol]BCl_4$) dried in vacuo. The complex was identified by its ν(CO) bands [IR (CH_2Cl_2): ν(CO) = 2084 cm^{-1} s, 2046 s] which were identical with those of the corresponding BF_4 salt **2**. Yield: 110 mg (70%, based on **6a**).

Carbonyl(cyclopentadienyl)(ethoxyphenylcarbene)(trimethyl phosphite)manganese (**11**): A solution of 2.00 g (6.45 mmol) of **10** and 0.95 ml (8.06 mmol) of trimethyl phosphite in 250 ml of toluene was irradiated for 2 h at −40°C while passing a slight stream of argon through the solution. The solvent was removed in vacuo at room temp. The orange residue was dissolved in pentane and the solution chromatographed on silica gel at −20°C. With pentane/CH_2Cl_2 (ratio slowly changing from 1:0 to 2:1) first a yellow band containing **10** [80 mg after recrystallization from pentane/CH_2Cl_2 (4:1)] and then an orange band were eluted. The solvent of the orange fraction was evaporated in vacuo, and the residue was recrystallized from 65 ml of pentane/CH_2Cl_2 (12:1). Orange crystals. Yield 1.80 g (69%, based on **10**), m.p. 75°C (dec.). – IR (CH_2Cl_2): ν(CO) = 1853 cm^{-1} s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.35 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 3.61 (d, $^3J_{PH}$ = 11.2 Hz, 9H, OMe), 4.31 (q, ^3J = 7.0 Hz, 2H, CH_2), 4.40 (s, 5H, Cp), 7.07–7.26 (m, 5H, Ph). – ^{13}C NMR ([D$_6$]acetone, 30°C): δ = 15.7 (OCH_2CH_3), 52.1 ($^2J_{PC}$ = 4.2 Hz, OCH_3), 70.5 (CH_2), 86.5 (Cp), 124.9, 126.8, 127.4, 157.1 (Ph), 236.9 ($^2J_{PC}$ = 44.0 Hz, CO), 325.7 ($^2J_{PC}$ = 42.6 Hz, Mn=C). – MS (70 eV), *m/z* (%): 406 (17) [M^+], 378 (8) [M^+ – CO], 254 (100) [M^+ – CO – $P(OMe)_3$]. – $C_{18}H_{24}MnO_5P$ (406.3): calcd. C 53.21, H 5.95; found C 53.28, H 5.98.

Carbonyl(cyclopentadienyl)(ethoxyphenylcarbene)(tritolylphosphane)manganese (**12**): The reaction of 2.00 g (6.45 mmol) of **10** with 2.45 g (8.06 mmol) of tritolylphosphane was carried out analogously to that with trimethyl phosphite. The chromatography was performed on silica gel with pentane/CH_2Cl_2 (4:1). First a yellow band containing **10** (120 mg) and then a red-brown fraction containing **12** were eluted. The solvent was removed in vacuo and the residue recrystallized at −35°C from 65 ml of pentane/CH_2Cl_2 (10:1). Orange powder. Yield 2.30 g (61%, based on **10**), m.p. 115°C (dec.). – IR (CH_2Cl_2): ν(CO) = 1836 cm^{-1} s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.19 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 2.35 (s, 9H, $C_6H_4CH_3$), 3.66 (q, ^3J = 7.0 Hz, 2H, OCH_2), 4.35 (d, $^3J_{PH}$ = 1.4 Hz, 5H, Cp), 6.62–7.06 (m, 5H, Ph), 7.15–7.33 (m, 12H, C_6H_4). – ^{13}C NMR (CD_2Cl_2, 5°C): δ = 20.3 ($C_6H_4CH_3$), 22.3 (CH_2CH_3), 85.5 (CH_2), 88.3 (Cp), 123.4–155.0 (Ph und C_6H_4), 237.9 (d, $^2J_{PC}$ = 31.5 Hz, CO), 325.0 (d, $^2J_{PC}$ = 25.7 Hz, Mn=C). – MS (70 eV), *m/z* (%): 586 (4) [M^+], 558 (17) [M^+ – CO], 424 (15) [M^+ – C(OEt)Ph], 304 (100) [$PTol_3$], 254 (64) [M^+ – $PTol_3$]. – $C_{36}H_{36}MnO_2P$ (586.6): calcd. C 73.71, H 6.19; found C 73.46, H 6.17.

Carbonyl(cyclopentadienyl)(phenylcarbyne)(trimethyl phosphite)manganese Tetrafluoroborate (**13**) *and Carbonyl(cyclopentadienyl)[(2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyloxy)phenylcarbene](trimethyl phosphite)manganese* (**15**): A vigorous stream of BF_3 was passed at −90°C through a stirred solution of 300 mg (0.70 mmol) of **11** in 15 ml of CH_2Cl_2 for 30 s. Then 200 ml of Et_2O cooled to −90°C was added to the solution. The carbyne complex **13** precipitated as an oil. After decantation the oil was washed with 25 ml of Et_2O cooled to −90°C and dried in vacuo at −40°C. Complex **13** was obtained as an orange oil [yield: 310 mg; 98%, based on **11**; IR (CH_2Cl_2): ν(CO) = 2025 cm^{-1} s] which was used for the subsequent reaction without further purification. 390 mg (1.50 mmol) of H-**4a** in 25 ml of THF was deprotonated with Na. The resulting alcoholate was dissolved in 10 ml of CH_2Cl_2, and the solution was slowly added at −78°C to the stirred solution of **13** in 15 ml of CH_2Cl_2. The reaction mixture was warmed to room temp., and the solvent was then removed in vacuo. Chromatography of the residue with pentane/CH_2Cl_2/Et_2O (10:5:1) at −20°C on silica gel gave after a light yellow band an orange band which contained **15**. Yield: 200 mg (44%, based on **11**). Viscous brown oil. – IR (pentane): ν(CO) = 1894 cm^{-1} sh, 1884 s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.28 (s, 6H, CMe_2), 1.33 (s, 3H, CMe_2), 1.37 (s, 3H, CMe_2), 3.56 (d, $^3J_{PH}$ = 11.2 Hz, 9H, OCH_3), 3.91–4.01, 4.30–4.33 (m, 4H, 4-H, CH_2-6, 5-H), 4.54 (d, $^3J_{PH}$ = 1.4 Hz, 5H, Cp), 4.89–4.94 (m, 2H, 2,3-H), 5.45, 5.65 (s, 1H, 1-H), 7.03–7.26 (m, 5H, Ph). – ^{13}C NMR ([D$_6$]acetone, 30°C): δ = 24.7, 25.7, 26.1, 27.0 [$C(CH_3)_2$], 52.0 (OCH_3), 67.0 (C-6), 73.6, 73.7 (C-5), 80.3, 80.4 (C-4), 82.0, 85.9, 86.1 (C-2,3), 86.6, 87.0 (Cp), 106.1, 106.5 (C-1), 109.2, 113.0 (CMe_2), 125.2, 125.4, 126.0, 127.0, 127.2, 127.4, 127.5, 154.6, 155.1 (Ph), 235.3 ($^2J_{PC}$ = 48.1 Hz, CO), 236.2 ($^2J_{PC}$ = 48.1 Hz, CO), 322.2 ($^2J_{PC}$ = 44.0 Hz, Mn=C), 322.7 ($^2J_{PC}$ = 44.0 Hz, Mn=C). – MS (70 eV), *m/z* (%): 620 (9) [M^+], 589 (2) [M^+ – OMe], 468 (97) [M^+ – CO – $P(OMe)_3$], 410 (5) [M^+ – CO – $P(OMe)_3$ – OC_3H_6], 93 (100) [$P(OMe)_2$]. – $C_{28}H_{38}MnO_{10}P$ (620.5): calcd. C 54.20, H 6.17; found C 54.11, H 6.29.

Carbonyl(cyclopentadienyl)(phenylcarbyne)(tritolylphosphane)manganese Tetrafluoroborate (**14**) *and Carbonyl(cyclopen-*

tadienyl)[(2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyloxy)-phenylcarbene](tritolylphosphane)manganese (**16**): The reaction was carried out analogously to that of **11**. Complex **14** [IR (CH_2Cl_2): ν(CO) = 2012 cm^{-1} s] was obtained from 660 mg (1.13 mmol) of **12** and BF_3. The subsequent reaction of **14** with 320 mg (1.24 mmol) of H-**4a** and chromatography gave **16** as a yellow powder. Yield: 450 mg (49%, based on **12**). – IR (pentane): ν(CO) = 1875 cm^{-1} sh, 1865 s. – ^{1}H NMR ([D$_6$]acetone, room temp.): δ = 1.25–1.45 (m, 12H, CMe_2), 2.33, 2.35 (s, 9H, $C_6H_4CH_3$), 3.90–4.04, 4.29–4.41 (m, 4H, 4,5-H, CH_2-6), 4.43, 4.54 (2 d, $^3J_{PH}$ = 1.8 Hz, 5H, Cp), 4.56–4.87 (m, 1H, 3-H), 4.94–5.06 (m, 1H, 2-H), 5.07, 5.31 (2 s, together 1H, 1-H), 6.64–7.34 (m, 17H, C_6H_5, C_6H_4). – ^{13}C NMR ([D$_6$]acetone, 30°C): δ = 21.2 ($C_6H_4CH_3$), 24.6, 24.8, 25.7, 25.8, 26.0, 26.2, 27.1, 27.2 [$C(CH_3)_2$], 66.9, 67.2 (C-6), 73.9, 74.0 (C-5), 80.5, 80.7 (C-4), 82.3, 82.9, 85.8, 86.4 (C-2,3), 87.9, 88.2 (Cp), 105.3, 106.8 (C-1), 109.2, 109.4, 112.8, 113.1 (CMe_2), 126.4, 126.8, 127.1, 129.2, 129.3, 129.4 (C_6H_5), 133.7, 133.8, 133.9, 134.0, 135.3, 135.7, 135.8, 136.2, 139.8 (C_6H_4), 153.4, 153.6 (C_6H_5), 236.8 ($^2J_{PC}$ = 31.6 Hz, CO), 237.8 ($^2J_{PC}$ = 31.6 Hz, CO), 321.3 ($^2J_{PC}$ = 31.6 Hz, Mn=C), 323.9 ($^2J_{PC}$ = 33.0 Hz, Mn=C). – ^{31}P NMR ([D$_6$]acetone, rel. H_3PO_4, 30°C): δ = 82.0, 84.6. – $C_{46}H_{50}MnO_7P$ (800.1): calcd. C 68.99, H 6.29; found C 69.10, H 6.66.

X-Ray Structural Analysis of **11**: $C_{18}H_{24}MnO_5P$, molecular mass 406.3, crystal size 0.6 × 0.6 × 0.6 mm^3 (obtained by crystallization from pentane/CH_2Cl_2, 12:1); crystal system hexagonal, space group $P6_5$, a = 9.770(3), c = 34.863(10) Å, V = 2884(2) Å^3, Z = 6, d_{calcd} = 1.404 g cm^{-1}; μ(Mo-$K_α$) = 0.764 mm^{-1}, F(000) = 1272; Wyckoff scan, 2Θ range 4.0–54.0°, scan rate variabel 2.0–29.3° min^{-1} in ω; 2524 independent reflections, 2268 reflections with $I > 4σ(I)$; 225 refined parameters; R = 0.032, R_w = 0.039. The refinement of the second enantiomer in the enantiomorphic space group $P6_1$ led to only R = 0.040 and R_w = 0.050. Largest difference peak (hole): +0.50 eÅ^{-3} (−0.37 eÅ^{-3}). – The measurements were performed at −26°C with a crystal of **11** mounted in a glass capillary on a Siemens R3m/V diffractometer (graphite monochromator, Mo-$K_α$ radiation, λ = 0.71073 Å). A semi-empirical absorption correction (based on 10 reflections) was carried out. The structure was solved by Patterson methods using the SHELXTL PLUS (VMS) program package. 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 "riding model". The positions of all other atoms were refined anisotropically by the full-matrix least-squares method. Complete lists of atom coordinates and thermal parameters were deposited[23].

☆ Dedicated to Prof. *Hans H. Brintzinger* on the occasion of his 60th birthday.

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