Bioorganometallic Chemistry: Reactions of Methyltitanocene Cation Complexes with a Singly Deprotected Methyl Glucopyranoside

Birgit Meyer zu Berstenhorst,[a] Gerhard Erker,*[a] Gerald Kehr,[a] Julia-Christina Wasilke,[a] Jens Müller,[a] Hartmut Redlich,[a] and Jutta Pyplo-Schnieders[a]

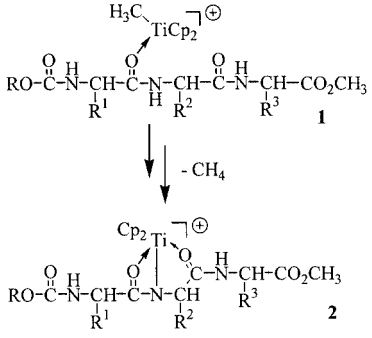
Keywords: Carbohydrate complexes / Titanocene / Zirconocene / Lewis acid / Chelate complexes / Bioorganometallic chemistry

The dimethyltitanocene/$B(C_6F_5)_3$ system reacts with the 4-unprotected methyl α-D-glucopyranoside derivative **5** ("HO-carb.") to yield the ionic complex $[Cp_2Ti(O\text{-carb.})]^+[MeB(C_6F_5)_3]^-$ (**10a**). Spectroscopic studies have led us to believe that **10a** is characterized by an internal ether-chelate structure in solution that involves coordination of the 6-OCH_2Ph oxygen atom. Treatment of **10a** with trimethylphosphane gives the open, non-chelated complex **11a**, in which the phosphane coordinates to the metal center. Reaction of the THF-stabilized salt $[Cp_2TiCH_3(THF)]^+[BPh_4]^-$ (**12a**) with **5** gave complex **13a**, with coordinated THF. Experiments with bis(methylcyclopentadienyl)titanium systems gave analogous results (complexes **10b**, **11b** and **13b**). Zirconocenes react differently. Addition of dimethylzirconocene (**14a**) or dimethylbis(methylcyclopentadienyl)zirconium (**14b**) to **5** gave the neutral complexes **15a**, **15b** and methane. Treatment of **15a** (**15b**) with $B(C_6F_5)_3$ again resulted in the formation of an ionic chelate complex **16a** (**16b**). A non-chelated complex **18** was formed by treating the THF-stabilized salt $[Cp_2ZrCH_3(THF)]^+[BPh_4]^-$ (**17**) with **5**.

Introduction

Titanocene dichloride is a potent anti-cancer agent.[1,2] In contrast to other metal-containing anti-cancer drugs, such as, for example, the "cisplatinum" derivatives, the mechanism of the biological action of $[Cp_2TiCl_2]$ and its congeners has remained less understood,[3a,3b] but it seems to be different from that of the cisplatinum cancerostatica.[3c−3f] Therefore, it is of interest to learn about the chemistry that titanocene derivatives and similar compounds undergo with typical "bio-molecules".[4] For carrying out such model reactions and for monitoring their mechanistic course, the use of the corresponding methyl-Group 4 metallocene derivatives have been of advantage, although they are not the actual biologically active in vivo species.

We have recently shown that, e.g., methyltitanocene cation reacts quite selectively with a variety of oligopeptide derivatives.[5,6] The $[Cp_2TiMe]^+$ molecule was shown to add preferentially to specific internal carbonyl positions of, e.g., a tripeptide under kinetic control (see Scheme 1). Under thermodynamic control it then migrates along the peptide chain. Eventually, it binds to specific favored positions at the chain by means of deprotonation with evolution of methane.[5]



Scheme 1

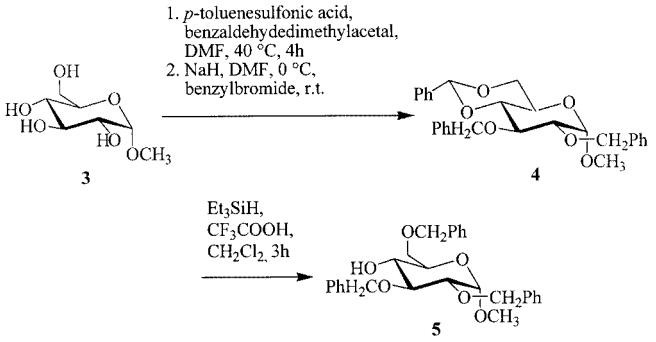
We have now begun to carry out similar studies on the reactions of methyl titanocenes and related compounds with another important class of biomolecules, the carbohydrates.[7] In an initial series of experiments we have treated a variety of methyltitanocene complexes with a suitably protected glucopyranoside derivative that contained a single active −OH group. Reactions were carried out with titanocene and zirconocene derivatives and were shown to feature some remarkable differences.

Results and Discussion

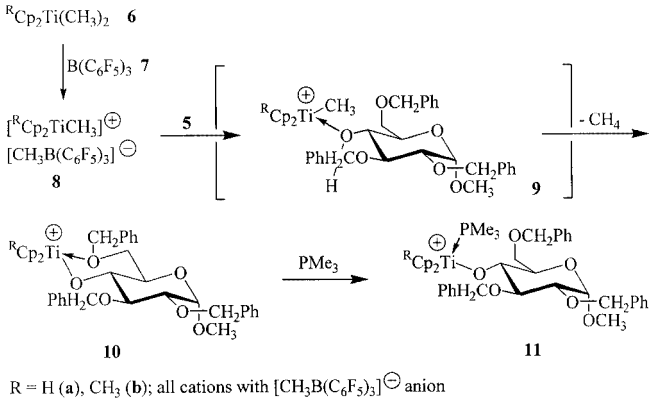
We have employed methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**5**) as the carbohydrate reagent for this study.

[a] Organisch-Chemisches Institut der Universität Münster, Corrensstr. 40, 48149 Münster, Germany
E-mail: erker@uni-muenster.de
Supporting information for this article is available on the WWW under http://www.eurjoc.eurjic.org or from the author.

  DOI: 10.1002/ejic.200400387



Scheme 2



R = H (**a**), CH_3 (**b**); all cations with $[CH_3B(C_6F_5)_3]^{\ominus}$ anion

Scheme 3

It was synthesized as depicted in Scheme 2.[8] Treatment of methyl α-D-glucopyranoside (**3**) with 2 equiv. of benzaldehyde dimethyl acetal and 0.2 equiv. of *p*-toluenesulfonic acid led to the 4,6-*O*-benzylidene acetal of glucose. The raw product was deprotonated by using sodium hydride in mineral oil at 0 °C for 2 h. Reaction with benzyl bromide, overnight at room temperature, gave the methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside **4**. Regioselective reductive cleavage of the acetal function to generate the 4-unprotected carbohydrate derivative was carried out by using triethylsilane in the presence of trifluoroacetic acid. Chromatographic workup eventually gave methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**5**) with an unprotected hydroxy group at C-4.

We used two pairs of titanocene and zirconocene reagents, namely the parent $[Cp_2M]$ derived compounds and their $[(MeC_5H_4)_2M]$ analogues, to ensure general reproducibility of our results. We first treated dimethyltitanocene (**6a**) with the carbohydrate derivative **5**. It turned out, however, that $[Cp_2TiMe_2]$ (**6a**) proved to be unreactive towards the free "4-OH sugar derivative" **5** in dichloromethane at room temperature. Similarly, the carbohydrate derivative **5** was recovered unchanged from the solution upon its attempted reaction with $[(CH_3-C_5H_4)_2TiMe_2]$ (**6b**).

The reaction conditions were, therefore, changed as follows: a solution containing **5** and 1 mol-equiv. of the strong Lewis acid $B(C_6F_5)_3$ (**7**)[9] was added dropwise to a dichloromethane solution of $[Cp_2TiMe_2]$ (**6a**). A rapid methane evolution was observed. Workup after 2 h at ambient temperature gave the salt $[Cp_2Ti(O\text{-carb.})]^+[MeB(C_6F_5)_3]^-$ (**10a**) as a red-brown solid in a yield of 70%. Under these conditions it can safely be assumed that the reagent $[Cp_2TiCH_3]^+[MeB(C_6F_5)_3]^-$ (**8a**) is generated in situ.[10] This is much more reactive than its neutral 16-electron precursor **6a** and is rapidly attacked by the free −OH group of **5**, potentially by involvement of a reactive coordinated intermediate **9a** to yield the product **10a** with liberation of 1 mol-equiv. of methane (see Scheme 3).

Complex **10a** features an optical rotation of $[\alpha]_D^{25} = +210$. It shows three separate ^1H NMR AB spin systems of the $-OCH_2Ph$ benzyl protective groups, and an AB part of an ABM spin system of the 6-H/H′ methylene hydrogen atoms (for the respective ^1H NMR chemical shifts see Table 1). The cyclopentadienyl groups at the titanium atom in **10a** are diastereotopic; they give rise to equal-intensity pairs of ^1H (δ = 6.60, 6.62 ppm) and ^{13}C (δ = 118.6, 121.4 ppm) NMR signals. This means that the titanium center in **10a** is pseudo-tetrahedrally coordinated by two η^5-Cp ligands, the carbohydrate 4-O oxygen atom and a fourth neutral donor ligand. In principle this could be the methyl group of the $[MeB(C_6F_5)_3]^-$ counteranion {tight ion pair formation between Group 4 metallocene $[Cp_2MR]^+$ cations and the $[MeB(C_6F_5)_3]^-$ anion is frequently observed}[11,12] or alternatively an internal ether oxygen coordination involving either the 3-OCH_2Ph or the 6-OCH_2Ph oxygen atom. A comparison with some typical ^{13}C NMR chemical shifts of related complexes (see below) enables us to assume that **10a** is characterized by an internal ether-chelate structure in solution that involves coordination of the 6-OCH_2Ph oxygen atom. The reaction between **5** and the in situ generated methylbis(methylcyclopentadienyl)titanium cation system **8a** gave analogous results (see Scheme 3 and Tables 1 and 2).

In order to answer this structural question, we treated both the complexes **10a** (R = H) and **10b** (R = CH_3) with PMe_3. It is known that trimethylphosphane serves as a stronger donor towards titanocene cation complexes than ethers. Thus, the formation of an open, non-chelate adduct is expected. The reaction of complex **10a** with PMe_3 in toluene at room temperature is instantaneous. The PMe_3 adduct **11a** was isolated as a brown solid in 67% yield ($[\alpha]_D^{25} = -44$). The ^1H NMR resonance of the PMe_3 ligand of **11a** occurs at δ = 0.78 ppm (d, $^2J_{H,P}$ = 9.1 Hz). Complex **11a** shows a pair of Cp resonances at δ = 5.31 and δ = 5.39 ppm, each of them is split into a doublet ($^3J_{H,P}$ = 2.8 Hz) by the *Ti*-coordinated PMe_3 ligand. The ^{31}P NMR resonance of the [Ti]−PMe_3 unit in **11a** was located at δ = 4.2 ppm. Complex **10b** reacts analogously with PMe_3 to yield the 1:1 addition product **11b** (63% isolated; $[\alpha]_D^{25} = -58$; ^{31}P NMR: δ = 3.2 ppm).[13]

For comparison we have also treated the THF-stabilized salt $[Cp_2TiCH_3(THF)]^+[BPh_4]^-$ (**12a**)[14] with **5**. This reaction does not proceed below room temperature. At room temperature evolution of methane is observed. The reaction is not as clean as the systems described above. Formation of a mixture of two major products in a 5:1 ratio is observed plus several minor components. Some further de-

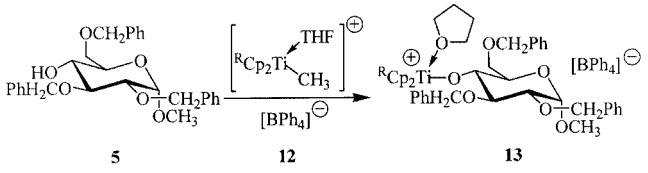
Table 1. Selected ^{1}H NMR spectroscopic data of the benzyl-protected titanocene- and zirconocene−*O*-glucopyranoside systems

	10a	**10b**	**11a**	**11b**	**13a**	**13b**	**15a**	**15b**	**16a**	**16b**	**18a**
1-*H*	4.67	4.70	4.59	4.59	4.85	4.77	4.70	4.71	4.66	4.62	4.81
2-*H*	3.58	3.66	3.42	3.44	3.76	3.71	3.51	3.50	3.49	3.50	3.68
3-*H*	3.79	3.93	3.54	3.61	3.70	3.67	3.45	3.51	3.69	3.73	3.65
4-*H*	4.88	4.94	4.34	4.51	4.89	4.68	3.84	3.84	4.19	4.26	4.28
5-*H*	3.58	3.65	3.38	3.48	3.56	3.50	3.37	3.51	3.51	3.52	3.51
6-*H*/6-H_a	3.52	3.65	3.14	3.20	3.29	3.57	3.43	3.41	3.74	3.77	3.40
6-*H′*/6-H_e	4.01	4.01	3.27	3.31	3.44	3.84	3.44	3.46	4.04	4.04	3.47
OCH_3	3.28	3.30	3.19	3.18	3.39	3.37	3.34	3.35	3.24	3.22	3.38
2-OCH_2	4.66, 4.75	4.65, 4.74	4.23, 4.29	4.18, 4.25	4.63, 4.63	4.65, 4.91	4.60, 4.64	4.60, 4.64	4.66, 4.74	4.59, 4.69	4.59, 4.61
3-OCH_2	4.56, 4.84	4.59, 4.92	4.03, 5.14	4.06, 5.08	4.34, 5.32	4.50, 5.24	4.57, 5.12	4.58, 5.08	4.66, 4.90	4.63, 4.85	4.39, 5.30
6-OCH_2	4.04, 4.40	4.07, 4.36	4.46, 4.58	4.53, 4.61	4.44, 4.76	4.47, 4.69	4.45, 4.53	4.42, 4.55	4.50, 4.67	4.48, 4.62	4.48, 4.69
Cp_A-*H*	6.60		5.31		5.93		5.86		6.53		6.03
Cp_B-*H*	6.62		5.39		5.99		5.89		6.67		6.03
Cp_A-CH_3		2.00		1.35		2.01		1.95		2.09	
α1-Cp_A-*H*		6.75		4.94		5.51		5.64		6.59	
α2-Cp_A-*H*		6.84		5.30		6.11		5.75		6.69	
β1-Cp_A-*H*		6.74		5.52		6.01		5.47		6.08	
β2-Cp_A-*H*		6.09		5.63		5.63		5.61		6.78	
Cp_B-CH_3		2.17		1.60		2.10		2.00		2.18	
α1-Cp_B-*H*		5.92		5.10		5.62		5.79		6.10	
α2-Cp_B-*H*		6.39		5.79		6.04		5.82		6.45	
β1-Cp_B-*H*		7.33		5.43		5.90		5.47		7.05	
β2-Cp_B-*H*		6.12		4.66		6.34		5.72		6.03	
Zr-CH_3							−0.08	−0.16			
α-THF-*H*					3.14	3.71					3.31
β-THF-*H*					1.63	1.82					1.66
P(CH_3)$_3$			0.78	0.77							
CH_3-BCF	0.48	0.52	1.37	1.39					0.56	0.45	

Table 2. Selected ^{13}C NMR spectroscopic data of the titanocene- and zirconocene-*O*-glucopyranoside complexes

	10a	**10b**	**11a**	**11b**	**13a**	**13b**	**15a**	**15b**	**16a**	**16b**	**18a**
C-1	98.6	98.6	97.1	97.2	96.3	97.3	97.4	97.3	98.3	98.1	96.6
C-2	78.9	80.5	80.7	80.7	80.0	80.6	80.1	80.2	78.5	79.0	79.6
C-3	81.1	82.5	81.1	81.5	80.7	83.1	82.4	82.6	80.3	81.1	80.2
C-4	95.2	93.7	88.4	88.4	89.2	86.0	79.0	79.2	87.1	85.7	82.5
C-5	66.8	67.4	71.9	72.2	69.2	71.4	71.3	71.5	67.2	67.1	69.6
C-6	73.8	74.1	68.7	68.6	67.9	68.8	68.9	69.0	74.8	74.7	68.1
OCH_3	55.9	56.0	55.3	55.3	55.2	55.0	54.9	54.9	55.5	55.5	55.3
2-OCH_2	73.4	73.5	72.2	72.1	72.2	72.5	72.4	72.4	74.8	73.0	71.6
3-OCH_2	75.2	75.8	73.7	73.3	73.3	75.2	75.1	75.1	73.1	75.4	73.0
6-OCH_2	79.7	80.1	74.7	74.8	73.9	72.3	73.2	73.1	80.0	80.0	73.9
Cp_A-*C*	121.4		113.9		118.1		110.3		118.0		115.2
Cp_B-*C*	118.6		114.0		118.5		110.4		116.5		115.2
Cp_A-*C*H_3		15.4		14.7		16.2		14.5		14.4	
ipso-Cp_A-*C*		139.2		129.2		131.3		122.6		137.3	
α1-Cp_A-*C*		115.6		114.4		116.6		112.4		111.9	
α2-Cp_A-*C*		117.0		114.8		123.4		108.0		113.0	
β1-Cp_A-*C*		116.0		111.8		113.2		106.0		118.4	
β2-Cp_A-*C*		123.0		115.4		107.9		112.0		114.6	
Cp_B-*C*H_3		16.6		14.8		15.7		14.7		15.3	
ipso-Cp_B-*C*		142.4		131.3		133.5		123.1		137.0	
α1-Cp_B-*C*		116.3		115.3		113.1		107.6		113.4	
α2-Cp_B-*C*		127.2		117.0		117.3		114.3		120.3	
β1-Cp_B-*C*		117.7		112.8		111.1		105.9		115.5	
β2-Cp_B-*C*		116.5		108.2		118.0		111.0		114.6	
Zr-*C*H_3							19.6	20.5			
α-THF-*C*					76.9	68.0					77.9
β-THF-*C*					24.4	25.5					25.4
P(*C*H_3)$_3$			15.4	16.2							
CH_3-BCF	9.9	10.4	11.4	11.6					9.9	9.8	

composition took place with time at ambient temperature. From the spectroscopic features we assign the structure of the "open" THF adduct **13a** to the main product of the reaction [^{1}H NMR: δ = 5.93/5.98 (Cp) ppm] (see Scheme 4 and Tables 1 and 2). It may be that the minor component [^{1}H NMR: δ = 5.76/5.79 (Cp) ppm] features an internal chelate, but this remains inconclusive at this time. The corresponding reaction of $[(MeC_5H_4)_2TiCH_3(THF)]^+[BPh_4]^-$ (**12b**) with **5** was only slightly cleaner. It gave the THF-stabilized product **13b**, which was characterized spectroscopically.



5 **12** **13**

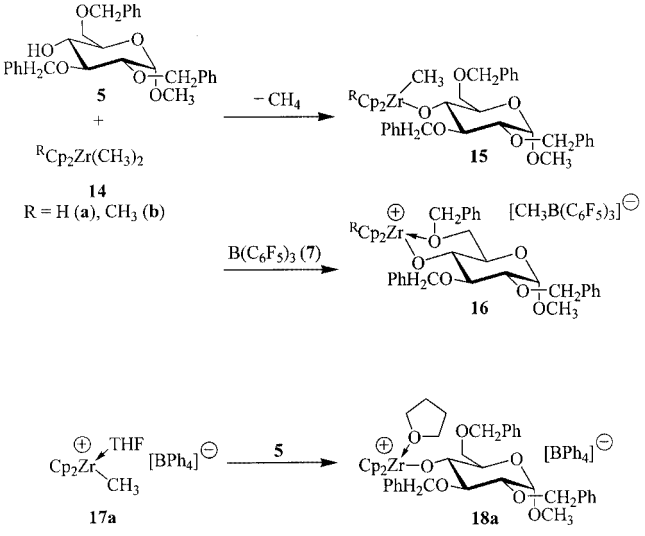
R = H (**a**), CH_3 (**b**)

Scheme 4

One obtains an indication of the essential structural differences between the (internal chelate) complexes **10** and their open counterparts **11/13** upon inspection of some of their characteristic spectroscopic data (see Tables 1 and 2). The ^{13}C NMR chemical shifts are especially useful for this structural assignment (see Table 2). As can be seen from the compilation of data in Table 2, the ^{13}C NMR chemical shifts of the core carbon atoms C-1, C-2 and C-3 are within a close range in the series of the complexes **10a**,**b**, **11a**,**b**, and **13a**,**b**. This also extends to the ^{13}C NMR shifts of the benzyl-CH_2 groups of the 2-OCH_2Ph units. The 3-OCH_2Ph ^{13}C NMR resonance shows a small, but unsystematic variation in this series. However, we note a marked shift ($\Delta\delta \approx 5-7$ ppm) to smaller δ values for the 6-OCH_2Ph resonance on going from the (chelate) **10a**,**b** systems to their (open) counterparts **11a**,**b** or **13a**,**b**. At the same time this change of the coordination pattern is revealed at the C-4 ($\Delta\delta \approx 5-6$ ppm) and the C-6 ($\Delta\delta \approx 5$ ppm) ^{13}C NMR chemical shifts. The C-5 ^{13}C NMR resonance actually features the reverse chemical shift variation ($\Delta\delta \approx -4$ to -5 ppm). Also an additional indication is given by the change of the magnitude of the 6/6′-H, 5-H coupling constants from $^3J_{ae}$ = 10.1 Hz and $^3J_{aa}$ = 3.9 Hz (**10a**) to $^3J_{H,H}$ = 3.8 Hz and 1.5 Hz in **11a**.

Similar structural and spectroscopic effects are noticed in the related zirconocene series. However, some of the chemistry of the reactions of **5** with the methylzirconocene derivatives is markedly different. The zirconocene−*O*-glucopyranoside complexes were much more sensitive than their titanocene analogues. In most cases they decomposed when kept above −10 °C. This severely hampered their isolation but some of these compounds could be characterized spectroscopically in solution at low temperatures.

In contrast to the titanocene system, dimethylzirconocene (**14a**) reacted readily with **5** to give the neutral system **15a** and methane. Complex **15a** shows the typical set of an open metallocene−*O*-glucopyranoside complex (e.g. ^{13}C NMR signals of the glucopyranoside atoms C-4 at δ = 79.5 ppm, C-5 at δ = 71.3, C-6 at δ = 68.9 and of the 6-OCH_2 group at δ = 73.2 ppm). Subsequent treatment of **15a** with $B(C_6F_5)_3$ (**7**) resulted in the abstraction of the σ-methyl group at the zirconium atom[10] with formation of the cation complex **16a** {with $[MeB(C_6F_5)_3]^-$ anion}. The cation of **16a** features a shifting of the respective ^{13}C NMR resonances that again indicates internal coordination of the oxygen atom from the 6-*O*-benzyl group to the now strongly electrophilic zirconium center [**16a**: ^{13}C NMR signals of C-4 at δ = 87.1 ppm ($\Delta\delta$ = +7.6 ppm), of C-5 at δ = 67.2 ppm ($\Delta\delta$ = −4.1 ppm), of C-6 at δ = 74.8 ppm ($\Delta\delta$ = +5.9 ppm) and 6-OCH_2−Ph at δ = 80.0 ppm ($\Delta\delta$ = +6.8 ppm)]. The reaction of $[(MeC_5H_4)_2Zr(CH_3)_2]$ (**14b**) with **5** proceeded analogously to generate **15b**, which was subsequently converted into the salt **16b** by treatment with $B(C_6F_5)_3$. The complexes **15b** and **16b** exhibit similar NMR features (see Scheme 5 and Tables 1 and 2). The [Zr]−*O*-glucopyranoside series was complemented by the in situ generation of (the very sensitive) complex **18a** by treatment of $[Cp_2ZrCH_3(THF)]^+[BPh_4]^-$ (**17a**) with **5**. It shows the typical NMR spectra of an open, THF-stabilized zirconocene−*O*-glucopyranoside cation complex (see Scheme 5, and Tables 1 and 2).



Scheme 5

Our study shows that titanocene cation complexes that bear an *O*-bonded carbohydrate σ-ligand seem to be rather robust molecules (as opposed to their very sensitive zirconium analogues). These titanocene cations are rather straightforwardly formed by our convenient one-pot synthesis using an in situ generated methyltitanocene cation. With the weakly coordinating $[CH_3B(C_6F_5)_3]^-$ counterion we obtained evidence for internal chelate coordination by the 6-*O*-benzyl group, but slightly stronger donors seem to very effectively compete with this internal ether coordination and add to the electrophilic titanocene cation.[15] This observation probably leaves some room for speculations about the potential use of carbohydrate-derived titanocene cation complexes as agents in medicinal chemis-

try.[2] Such systems might offer some advantages by adding transporting or target donor ligands to the titanocene unit in vivo, and one might envisage that suitably attached carbohydrate moieties might help to guide the titanocene towards its target structures.[16] We shall try to develop biocompatible derivatives of the titanocene systems presented in this paper in order to test their medicinal properties.

Experimental Section

General: All reactions were carried out under dry argon in Schlenk-type glassware or in a glove box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. NMR spectra were measured using a Bruker AC 200 P, a Varian Inova 500 or a Varian Unity Plus 600 NMR spectrometer. Most NMR assignments were made by carrying out a variety of 2D NMR experiments.[17] The coupling constants between vicinal hydrogen atoms at the carbohydrate moiety are designated as J_{aa} (i.e. axial-axial) and J_{ae} (axial-equatorial), respectively. The following instruments were used for additional physical characterization: IR spectroscopy: Nicolet 5DXC FT-IR spectrometer; melting points: DSC 2010 (TA instruments); elemental analyses: Foss Heraeus CHN-O-Rapid; mass spectrometry: Mircomass-Quatro LC-Z-electrospray mass spectrometer; optical rotation: Perkin−Elmer polarimeter 351.

Preparation of $[Cp_2Ti(O\text{-carb.})]^+[MeB(C_6F_5)_3]^-$ (10a): The carbohydrate **5** (464 mg, 1.00 mmol) and $B(C_6F_5)_3$ (**7**) (512 mg, 1.00 mmol) were dissolved in dichloromethane and added dropwise to a solution of dimethyltitanocene (**6a**) (208 mg, 1.00 mmol) in dichloromethane (25 mL). A change in the reaction color to deep red occurred and a gas was released. The reaction mixture was stirred for 2 h, the volatiles were removed in vacuo and the residue was washed with pentane resulting in 814 mg (70%) of the product as red-brown solid. M.p. (DSC): 131 °C (dec.). $[\alpha]_D^{25} = +210$ (c = 0.53, CH_2Cl_2). MS [ESI$^+$, $C_{38}H_{41}O_6Ti^+$ (641)]: m/z = 641 $[M]^+$, 209 $[Cp_2TiOMe]^+$. $C_{57}H_{44}BF_{15}O_6Ti$ (1168.7): calcd. C 58.58, H 3.80; found C 58.15, H 3.75. IR (KBr): $\tilde{\nu}$ = 3118, 2912, 1642, 1511, 1458, 1366, 1266, 1086, 952, 823, 738, 699 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 253 K, 600 MHz): δ = 0.48 (br. s, 3 H, CH_3−B$(C_6F_5)_3$], 3.28 (s, 3 H, OCH_3), 3.52 (t, $^2J = {}^3J_{aa}$ = 10.1 Hz, 1 H, 6-H$_a$), 3.58 (m, 2 H, 2-H, 5-H), 3.79 (t, $^3J_{aa}$ = 8.9 Hz, 1 H, 3-H), 4.01 (dd, ^2J = 10.1, $^3J_{ae}$ = 3.9 Hz, 1 H, 6-H$_e$), 4.04 (d, ^2J = 13.8 Hz, 1 H, 6-OCH_2Ph), 4.40 (d, ^2J = 13.8 Hz, 1 H, 6-OCH_2Ph), 4.56 (d, ^2J = 12.2 Hz, 1 H, 3-OCH_2Ph), 4.66 (d, ^2J = 11.7 Hz, 1 H, 2-OCH_2Ph), 4.67 (d, $^3J_{ae}$ = 3.5 Hz, 1 H, 1-H), 4.75 (d, ^2J = 11.7 Hz, 1 H, 2-OCH_2Ph), 4.84 (d, ^2J = 12.2 Hz, 1 H, 3-OCH_2Ph), 4.88 (t, $^3J_{aa}$ = 8.7 Hz, 1 H, 4-H), 6.60 (s, 5 H, Cp$_A$), 6.62 (s, 5 H, Cp$_B$), 7.22, 7.27, 7.32−7.39, 7.47 (each m, 15 H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 253 K, 151 MHz): δ = 9.9 [CH_3−B$(C_6F_5)_3$], 55.9 (OCH_3), 66.8 (C-5), 73.4 (2-OCH_2Ph), 73.8 (C-6), 75.2 (3-OCH_2Ph), 78.9 (C-2), 79.7 (6-OCH_2Ph), 81.1 (C-3), 95.2 (C-4), 98.6 (C-1), 118.6 (Cp$_B$), 121.4 (Cp$_A$), 127.9−130.0 (Ph), 130.9, 138.0, 138.9 (*ipso*-Ph), 136.3 [dm, $^1J_{C,F}$ = 247 Hz, *meta*-B$(C_6F_5)_3$], 137.4 [dm, $^1J_{C,F}$ = 243 Hz, *ortho*-B$(C_6F_5)_3$], 148.1 [dm, $^1J_{C,F}$ = 234 Hz, *para*-B$(C_6F_5)_3$] ppm [*ipso*-B$(C_6F_5)_3$ signal not observed]. ^{11}B{^{1}H} NMR (CD_2Cl_2, 298 K, 64 MHz): $\delta = -15$ ($\nu_{1/2}$ = 38.8 Hz) ppm.

Preparation of $[(MeC_5H_4)_2Ti(O\text{-carb.})]^+[MeB(C_6F_5)_3]^-$ (10b): Carbohydrate **5** (464 mg, 1.00 mmol) and $B(C_6F_5)_3$ (512 mg, 1.00 mmol) (**7**) were dissolved in dichloromethane and added dropwise to a solution of $[(MeC_5H_4)TiMe_2]$ (**6b**) (236 mg, 1.00 mmol) in dichloromethane (25 mL). A change in the reaction color to deep red occurred and a gas was released. The reaction mixture was stirred for 2 h, the volatiles were removed in vacuo and the residue was washed with pentane resulting in 1.09 g (91%) of the product as a brown solid. M.p. (DSC): 129 °C (dec.). $[\alpha]_D^{25} = +308$ (c = 0.53, CH_2Cl_2). MS [ESI$^+$, $C_{40}H_{45}O_6Ti^+$ (669)]: m/z = 669 $[M]^+$. $C_{59}H_{48}BF_{15}O_6Ti$ (1196.7): calcd. C 59.22, H 4.04; found C 58.86, H 3.91. IR (KBr): $\tilde{\nu}$ = 3450, 2908, 1642, 1511, 1458, 1367, 1267, 1086, 952, 832, 746, 699 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K, 600 MHz): δ = 0.52 [s, 3 H, CH_3−B$(C_6F_5)_3$], 2.00 (s, 3 H, Cp$_A$−CH_3), 2.17 (s, 3 H, Cp$_B$−CH_3), 3.30 (s, 3 H, OCH_3), 3.65 (m, 2 H, 5-H, 6-H$_a$*), 3.66 (dd, $^3J_{ae}$ = 3.6, $^3J_{aa}$ = 9.4 Hz, 1 H, 2-H), 3.93 (dd, $^3J_{aa}$ = 9.4, $^3J_{aa}$ = 8.7 Hz, 1 H, 3-H), 4.01 (m, 1 H, 6-H$_e$*), 4.07 (d, ^2J = 13.6 Hz, 1 H, 6-OCH_2Ph), 4.36 (d, ^2J = 13.6 Hz, 1 H, 6-OCH_2Ph), 4.59 (d, ^2J = 11.3 Hz, 1 H, 3-OCH_2Ph), 4.65 (d, ^2J = 11.7 Hz, 1 H, 2-OCH_2Ph), 4.70 (d, $^3J_{aa}$ = 3.6 Hz, 1 H, 1-H), 4.74 (d, ^2J = 11.7 Hz, 1 H, 2-OCH_2Ph), 4.92 (d, ^2J = 11.3 Hz, 1 H, 3-OCH_2Ph), 4.94 (t, $^3J_{aa}$ = 8.7 Hz, 1 H, 4-H), 5.92 (m, 1 H, α1-Cp$_B$), 6.09 (m, 1 H, β2-Cp$_A$*), 6.12 (m, 1 H, β2-Cp$_B$), 6.39 (m, 1 H, α2-Cp$_B$), 6.74 (m, 1 H, β1-Cp$_A$*), 6.75 (m, 1 H, α1-Cp$_A$), 6.84 (m, 1 H, α2-Cp$_A$), 7.33 (m, 1 H, β1-Cp$_B$), 7.25, 7.34, 7.51 (m, 15 H, Ph) ppm (* denotes a tentative assignment). ^{13}C{^{1}H} NMR CD_2Cl_2, 298 K, 151 MHz): δ = 10.4 [CH_3−B$(C_6F_5)_3$], 15.4 (Cp$_A$−CH_3), 16.6 (Cp$_B$−CH_3), 56.0 (OCH_3), 67.4 (C-5), 73.5 (2-OCH_2Ph), 74.1 (C-6), 75.8 (3-OCH_2Ph), 80.1 (6-OCH_2Ph), 80.5 (C-2), 82.5 (C-3), 93.7 (C-4), 98.6 (C-1), 115.6 (α1-Cp$_A$), 116.0 (β1-Cp$_A$), 116.3 (α1-Cp$_B$), 116.5 (β2-Cp$_B$), 117.0 (α2-Cp$_A$), 117.7 (β1-Cp$_B$), 123.0 (β2-Cp$_A$), 127.2 (α2-Cp$_B$), 128.1−128.9, 130.2, 130.6 (Ph), 129.8 [*ipso*-B$(C_6F_5)_3$], 131.3 (*ipso*-Ph), 136.8 [dm, $^1J_{C,F}$ = 246 Hz, *meta*-B$(C_6F_5)_3$], 137.8 [dm, $^1J_{C,F}$ = 243 Hz, *ortho*-B$(C_6F_5)_3$], 138.3, 138.8 (*ipso*-Ph), 139.2 (*ipso*-Cp$_A$), 142.4 (*ipso*-Cp$_B$), 148.6 [dm, $^1J_{C,F}$ = 241 Hz, *para*-B$(C_6F_5)_3$] ppm. ^{11}B{^{1}H} NMR (CD_2Cl_2, 298 K, 64 MHz): $\delta = -15$ ($\nu_{1/2}$ = 36 Hz) ppm.

Preparation of $[Cp_2Ti(O\text{-carb.})(PMe_3)]^+[MeB(C_6F_5)_3]^-$ (11a): Addition of 3 drops of trimethylphosphane to a solution of $[Cp_2Ti(O\text{-carb.})]^+[MeB(C_6F_5)_3]^-$ (**10a**) (250 mg, 0.214 mmol) in toluene (10 mL) led immediately to a yellow liquid. After removal of the volatiles in vacuo, the residue was washed twice with pentane resulting in 176 mg (66%) of the product as a dark brown solid. M.p. (DSC): 217 °C (dec.). $[\alpha]_D^{25} = -44.0$ (c = 0.59, CH_2Cl_2). MS [ESI$^+$, $C_{41}H_{50}O_6PTi^+$ (717)]: m/z = 717 $[M]^+$, 641 $[M - P(CH_3)_3]^+$. $C_{60}H_{53}BF_{15}O_6PTi$ (1244.7): calcd. C 57.90, H 4.29; found C 58.04, H 4.74. IR (KBr): $\tilde{\nu}$ = 3065, 2919, 1642, 1511, 1458, 1369, 1264, 1087, 952, 804, 736, 698 cm^{-1}. ^{1}H NMR (C_6D_6, 298 K, 600 MHz): δ = 0.78 [d, $^2J_{H,P}$ = 9.1 Hz, 9 H, P(CH_3)$_3$], 1.37 [br. s, 3 H, CH_3−B$(C_6F_5)_3$], 3.14 (dd, ^2J = 11.9, ^3J = 3.8 Hz, 1 H, 6-H), 3.19 (s, 3 H, OCH_3), 3.27 (dd, ^2J = 11.9, ^3J = 1.5 Hz, 1 H, 6-H′), 3.38 (ddd, ^3J = 1.5, ^3J = 3.8, $^3J_{aa}$ = 9.3 Hz, 1 H, 5-H), 3.42 (dd, $^3J_{aa}$ = 9.0, $^3J_{ae}$ = 3.7 Hz, 1 H, 2-H), 3.54 (dd, $^3J_{aa}$ = 8.4, $^3J_{aa}$ = 9.0 Hz, 1 H, 3-H), 4.03 (d, ^2J = 12.0 Hz, 1 H, 3-OCH_2Ph), 4.23 (d, ^2J = 11.6 Hz, 1 H, 2-OCH_2Ph), 4.29 (d, ^2J = 11.6 Hz, 1 H, 2-OCH_2Ph), 4.34 (dd, $^3J_{aa}$ = 8.4, $^3J_{aa}$ = 9.3 Hz, 1 H, 4-H), 4.46 (d, ^2J = 11.4 Hz, 1 H, 6-OCH_2Ph), 4.58 (d, ^2J = 11.4 Hz, 1 H, 6-OCH_2Ph), 4.59 (d, $^3J_{ae}$ = 3.7 Hz, 1 H, 1-H), 5.14 (d, ^2J = 12.0 Hz, 1 H, 3-OCH_2Ph), 5.31 (d, $^3J_{H,P}$ = 2.8 Hz, 5 H, Cp$_A$), 5.39 (d, $^3J_{H,P}$ = 2.8 Hz, 5 H, Cp$_B$), 7.07, 7.11−7.21, 7.24−7.28, 7.31, 7.32 (each m, 15 H, Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 151 MHz): δ = 11.4 [br. s, CH_3−B$(C_6F_5)_3$], 15.4 [d, $^1J_{C,P}$ = 24.5 Hz, P(CH_3)$_3$], 55.3 (OCH_3), 68.7 (C-6), 71.9 (C-5), 72.2 (2-OCH_2Ph), 73.7 (3-OCH_2Ph), 74.4 (6-OCH_2Ph), 80.7 (C-2), 81.1 (C-3), 88.4 (C-4), 97.3 (C-1), 113.9 (Cp$_A$), 114.0 (Cp$_B$), 127.7−128.9 (Ph), 137.2 [dm, $^1J_{C,F}$ = 247 Hz, *meta*-B$(C_6F_5)_3$], 138.2 [dm, $^1J_{C,F}$ = 239 Hz, *ortho*-B$(C_6F_5)_3$], 138.2, 138.2, 139.0 (*ipso*-Ph), 139.0 [*ipso*-B$(C_6F_5)_3$], 149.3 [dm, $^1J_{C,F}$ =

235 Hz, *para*-$B(C_6F_5)_3$] ppm. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 298 K, 64 MHz): $\delta = -15$ ($\nu_{1/2} = 33$ Hz) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 81 MHz): $\delta = 4.2$ (s) ppm.

Preparation of $[(MeC_5H_4)_2Ti(O\text{-carb.})(PMe_3)]^+[MeB(C_6F_5)_3]^-$ (11b): Addition of 3 drops of trimethylphosphane to a solution of $[(MeC_5H_4)_2Ti(O\text{-carb.})]^+[MeB(C_6F_5)_3]^-$ (**10b**) (250 mg, 0.209 mmol) in toluene (10 mL) led immediately to a yellow liquid. After removal of the volatiles in vacuo, the residue was washed twice with pentane resulting in 168 mg (63%) of the product as an orange solid. M.p. (DSC): 218 °C (dec.). $[\alpha]_D^{25} = -58$ ($c = 0.56$, CH_2Cl_2). MS [ESI$^+$, $C_{43}H_{54}O_6PTi^+$ (745)]: $m/z = 745$ $[M]^+$, 670 $[M - P(CH_3)_3]^+$. $C_{62}H_{57}BF_{15}O_6PTi$ (1272.7): calcd. C 58.51, H 4.51; found C 58.35, H 4.89. IR (KBr): $\tilde{\nu} = 3015, 2911, 1642, 1511, 1460, 1370, 1265, 1088, 953, 821, 738, 698$ cm^{-1}. ^1H NMR (C_6D_6, 298 K, 600 MHz): $\delta = 0.77$ [d, $^2J_{PH} = 2.3$ Hz, 9 H, $P(CH_3)_3$], 1.35 (s, 3 H, Cp_A-CH_3), 1.39 [s, 3 H, $CH_3-B(C_6F_5)_3$], 1.60 (s, 3 H, Cp_B-CH_3), 3.18 (s, 3 H, OCH_3), 3.20 (dd, $^2J = 11.8$, $^3J = 3.9$ Hz, 1 H, 6-H), 3.31 (dd, $^2J = 11.8$, $^3J = 1.5$ Hz, 1 H, 6-H′), 3.44 (dd, $^3J_{aa} = 9.1$, $^3J_{ae} = 3.4$ Hz, 1 H, 2-H), 3.48 (ddd, $^3J_{aa} = 9.4$, $^3J = 3.9$, $^3J = 1.5$ Hz, 1 H, 5-H), 3.61 (dd, $^3J_{aa} = 8.3$, $^3J_{aa} = 9.1$ Hz, 1 H, 3-H), 4.06 (d, $^2J = 11.9$ Hz, 1 H, 3-OCH_2Ph), 4.18 (d, $^2J = 11.5$ Hz, 1 H, 2-OCH_2Ph), 4.25 (d, $^2J = 11.5$ Hz, 1 H, 2-OCH_2Ph), 4.51 (dd, $^3J_{aa} = 8.3$, $^3J_{aa} = 9.4$ Hz, 1 H, 4-H), 4.53 (d, $^2J = 11.8$ Hz, 1 H, 6-OCH_2Ph), 4.59 (dd, $^3J_{ae} = 3.4$ Hz, 1 H, 1-H), 4.61 (d, $^2J = 11.8$ Hz, 1 H, 6-OCH_2Ph), 4.66 (m, 1 H, β2-Cp_B), 4.94 (m, 1 H, α1-Cp_A), 5.08 (d, $^2J = 11.9$ Hz, 1 H, 3-OCH_2Ph), 5.10 (m, 1 H, α1-Cp_B), 5.30 (m, 1 H, α2-Cp_A), 5.43 (m, 1 H, β1-Cp_B), 5.52 (m, 1 H, β1-Cp_A), 5.63 (m, 1 H, β2-Cp_A), 5.79 (m, 1 H, α2-Cp_B), 7.07, 7.12, 7.15, 7.26, 7.34 (m, 15 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 151 MHz): $\delta = 11.6$ [$CH_3-B(C_6F_5)_3$], 14.7 (Cp_A-CH_3), 14.8 (Cp_B-CH_3), 16.2 [br. s, $P(CH_3)_3$], 55.3 (OCH_3), 68.6 (C-6), 72.1 (2-OCH_2Ph), 72.2 (C-5), 73.3 (3-OCH_2Ph), 74.8 (6-OCH_2Ph), 80.7 (C-2), 81.5 (C-3), 88.4 (C-4), 97.2 (C-1), 108.2 (β2-Cp_B), 111.8 (β1-Cp_A), 112.8 (β1-Cp_B), 114.4 (α1-Cp_A), 114.8 (α2-Cp_A), 115.3 (α1-Cp_B), 115.4 (β2-Cp_A), 117.0 (α2-Cp_B), 127.3−128.8 (Ph), 129.2 (*ispo*-Cp_A), 131.3 (*ispo*-Cp_B), 137.2 [dm, $^1J_{C,F} = 245$ Hz, *meta*-$B(C_6F_5)_3$], 138.1, 138.2, 139.0 (*ipso*-Ph), 138.2 [dm, $^1J_{C,F} = 247$ Hz, *ortho*-$B(C_6F_5)_3$], 149.3 [dm, $^1J_{C,F} = 240$ Hz, *para*-$B(C_6F_5)_3$] ppm [*ipso*-$B(C_6F_5)_3$ not observed]. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 298 K, 64 MHz): $\delta = -15$ ($\nu_{1/2} = 31$ Hz) ppm. ^{31}P NMR (CD_2Cl_2, 298 K, 81 MHz): $\delta = 3.2$ (s) ppm.

Preparation of $[Cp_2Ti(O\text{-carb.})(THF)]^+[BPh_4]^-$ (13a): NMR spectroscopic experiment: A solution of $[Cp_2TiMe(THF)]^+[BPh_4]^-$ (**12a**) (47 mg, 0.08 mmol) in [D_2]dichloromethane was combined with the carbohydrate **5** (37 mg, 0.08 mmol) at −60 °C. The reaction was warmed to room temperature resulting in a red color. NMR spectroscopic studies showed that the reaction started at room temperature but the start of decomposition was also noticed, hence the solution was immediately cooled to −40 °C. The product obtained was a mixture of 5:1. Main product: ^1H NMR (CD_2Cl_2, 243 K, 600 MHz): $\delta = 1.52$ (m, 2 H, β-THF), 1.63 (m, 2 H, β′-THF), 1.81 (m, 4 H, β-THF_{free}), 3.09 (m, 2 H, α-THF), 3.14 (m, 2 H, α′-THF), 3.29 (dd, $^2J = 10.9$, $^3J = 2.6$ Hz, 1 H, 6-H), 3.39 (s, 3 H, OCH_3), 3.44 (dd, $^2J = 10.4$, $^3J = 1.9$ Hz, 1 H, 6-H′), 3.56 (m, 1 H, 5-H), 3.69 (m, 4 H, α-THF_{free}), 3.70 (m, 1 H, 3-H), 3.76 (dd, $^3J_{aa} = 9.2$, $^3J_{ae} = 3.3$ Hz, 1 H, 2-H), 4.34 (d, $^2J = 12.3$ Hz, 1 H, 3-OCH_2Ph), 4.44 (d, $^2J = 11.8$ Hz, 1 H, 6-OCH_2Ph), 4.63 (m, 2 H, 2-OCH_2Ph), 4.76 (d, $^2J = 11.8$ Hz, 1 H, 6-OCH_2Ph), 4.85 (d, $^3J_{ae} = 3.3$ Hz, 1 H, 1-H), 4.89 (dd, $^3J_{aa} = 8.4$, $^3J_{aa} = 9.7$ Hz, 1 H, 4-H), 5.32 (d, $^2J = 12.3$ Hz, 1 H, 3-OCH_2Ph), 5.93 (s, 5 H, Cp_A), 5.99 (s, 5 H, Cp_B), 6.21, 6.93, 7.07, 7.32 −7.50, 7.62 (each m, 35 H, Ph, BPh_4) ppm. $^{13}C\{^1H\}$ NMR (from ghsqc[17]) (CD_2Cl_2, 243 K, 151 MHz): $\delta = 24.4$ (β-THF, β′-THF), 25.1 (β-THF_{free}), 55.2 (OCH_3), 67.8 (α-THF_{free}), 67.9 (C-6), 69.2 (C-5), 72.2 (2-OCH_2Ph), 73.3 (3-OCH_2Ph), 73.9 (6-OCH_2Ph), 76.9 (α-THF, α′-THF), 80.0 (C-2), 80.7 (C-3), 89.2 (C-4), 96.3 (C-1), 118.1 (Cp_A), 118.5 (Cp_B), 125.2 −139.1 (Ph, BPh_4), 137.7, 137.8, 138.4 (*ipso*-Ph), 163.7 (1:1:1:1 q, $^1J_{CB} = 44$ Hz, *ipso*-BPh_4) ppm. Due to the ratio of the isomers the minor product was determined by the Cp resonances. Minor product: ^1H NMR (CD_2Cl_2, 243 K, 600 MHz): $\delta = 5.76$ (s, 5 H, Cp_A), 5.79 (s, 5 H, Cp_B) ppm.

Preparation of $[(MeC_5H_4)_2Ti(O\text{-carb.})(THF)]^+[BPh_4]^-$ (13b): $[(MeC_5H_4)_2TiMe(THF)]^+[BPh_4]^-$ (**12b**) (337 mg, 0.550 mmol) and the carbohydrate **5** (255 mg, 0.549 mmol) were each dissolved in dichloromethane (25 mL) and then combined in a flask at room temperature. The reaction mixture was stirred for 2 h, the volatiles were removed in vacuo and the residue was washed with pentane resulting in 512 mg (88%) of the product as an ocher solid, obtained in 95% purity. M.p. (DSC): 161 °C (dec.). MS [ESI$^+$, $C_{44}H_{53}O_7Ti^+$ (741)]: $m/z = 669$ $[M - THF]^+$, 237 $[(MeC_5H_4)_2TiOMe]^+$, 186 $[C_9H_{14}O_4]^+$. ^1H NMR (CD_2Cl_2, 243 K, 600 MHz): $\delta = 1.82$ (m, 4 H, β-THF), 2.01 (s, 3 H, Cp_A-CH_3), 2.10 (s, 3 H, Cp_B-CH_3), 3.37 (s, 3 H, OCH_3), 3.50 (dd, $^3J_{aa} = 9.6$, $^3J = 2.6$ Hz, 1 H, 5-H), 3.57 (m, 1 H, 6-H), 3.67 (d, $^3J_{aa} = 9.0$ Hz, 1 H, 3-H), 3.71 (m, 1 H, 2-H), 3.71 (m, 4 H, α-THF), 3.84 (dd, $^2J = 10.3$, $^3J = 2.6$ Hz, 1 H, 6-H′), 4.47 (d, $^2J = 11.4$ Hz, 1 H, 6-OCH_2Ph), 4.50 (d, $^2J = 11.5$ Hz, 1 H, 3-OCH_2Ph), 4.65 (d, $^2J = 11.4$ Hz, 1 H, 2-OCH_2Ph), 4.68 (m, 1 H, 4-H), 4.69 (d, $^2J = 11.4$ Hz, 1 H, 6-OCH_2Ph), 4.77 (d, $^3J_{ae} = 2.4$ Hz, 1 H, 1-H), 4.91 (d, $^2J = 11.4$ Hz, 1 H, 2-OCH_2Ph), 5.24 (d, $^2J = 11.5$ Hz, 1 H, 3-OCH_2Ph), 5.51 (m, 1 H, α1-Cp_A), 5.62 (m, 1 H, α1-Cp_B), 5.63 (m, 1 H, β2-Cp_A), 5.90 (m, 1 H, β1-Cp_B), 6.01 (m, 1 H, β1-Cp_A), 6.04 (m, 1 H, α2-Cp_B), 6.11 (m, 1 H, α2-Cp_A), 6.34 (m, 1 H, β2-Cp_B), 7.08, 7.26−7.49, 7.58, 7.62 (m, 35 H, Ph, BPh_4) ppm. $^{13}C\{^1H\}$ NMR (*ipso*-C of BPh_4^- not found) (CD_2Cl_2, 243 K, 151 MHz): $\delta = 15.7$ (Cp_B-CH_3), 16.2 (Cp_A-CH_3), 25.5 (β-THF), 55.0 (OCH_3), 68.0 (α-THF), 68.8 (C-6), 71.4 (C-5), 72.3 (6-OCH_2Ph), 72.5 (2-OCH_2Ph), 75.2 (3-OCH_2Ph), 80.6 (C-2), 83.1 (C-3), 86.0 (C-4), 97.3 (C-1), 107.9 (β2-Cp_A), 111.1 (β1-Cp_B), 113.1 (α1-Cp_B), 113.2 (β1-Cp_A), 116.6 (α1-Cp_A), 117.3 (α2-Cp_B), 118.0 (β2-Cp_B), 123.4 (α2-Cp_A), 127.0−128.8, 135.7−142.8 (m, Ph, BPh_4), 131.3 (*ipso*-Cp_A), 133.5 (*ipso*-Cp_B), 138.2, 138.7, 139.4 (*ipso*-Ph), 164.4 (1:1:1:1 q, $^1J_{CB} = 49$ Hz, *ipso*-BPh_4) ppm. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 298 K, 64 MHz): $\delta = -7$ ($\nu_{1/2} = 12.5$ Hz) ppm.

Preparation of $[Cp_2Zr(O\text{-carb.})Me]$ (15a): Dimethylzirconocene (**14a**) (540 mg, 2.15 mmol) and the carbohydrate **5** (1.00 g, 2.15 mmol) were both dissolved in dichloromethane (25 mL) and then combined in a flask, after which methane immediately evolved. The volatiles were removed in vacuo and the residue was twice washed with pentane resulting in 1.02 g (68%) of the product as a viscous yellow solid. $[\alpha]_D^{25} = +9$ ($c = 0.46$, CH_2Cl_2). IR (film, CH_2Cl_2): $\tilde{\nu} = 3062, 2987, 2928, 2690, 2306, 1422, 1368, 1249, 1156, 1086, 1048, 896, 804, 782, 713, 693$ cm^{-1}. ^1H NMR (CH_2Cl_2, 243 K, 600 MHz): $\delta = -0.08$ (s, 3 H, $Zr-CH_3$), 3.34 (s, 3 H, OCH_3), 3.37 (ddd, $^3J_{aa} = 8.8$, $^3J = 3.8$, $^3J = 1.8$ Hz, 1 H, 5-H), 3.43 (dd, $^2J = 10.2$, $^3J = 3.8$ Hz, 1 H, 6-H), 3.44 (dd, $^2J = 10.2$, $^3J = 1.8$ Hz, 1 H, 6-H′), 3.45 (t, $^3J_{aa} = 9.6$ Hz, 1 H, 3-H), 3.51 (dd, $^3J_{aa} = 9.6$, $^3J_{ae} = 3.4$ Hz, 1 H, 2-H), 3.84 (dd, $^3J_{aa} = 9.6$, $^3J_{aa} = 8.8$ Hz, 1 H, 4-H), 4.45 (d, $^2J = 11.5$ Hz, 1 H, 6-OCH_2Ph), 4.53 (d, $^2J = 11.5$ Hz, 1 H, 6-OCH_2Ph), 4.57 (d, $^2J = 11.5$ Hz, 1 H, 3-OCH_2Ph), 4.60 (d, $^2J = 11.7$ Hz, 1 H, 2-OCH_2Ph), 4.64 (d, $^2J = 11.7$ Hz, 1 H, 2-OCH_2Ph), 4.70 (d, $^3J_{ae} = 3.4$ Hz, 1 H, 1-H), 5.12 (d, $^2J = 11.5$ Hz, 1 H, 3-OCH_2Ph), 5.86 (s, 5 H, Cp_A), 5.89 (s, 5 H, Cp_B), 7.27−7.48 (m, 15 H, Ph) ppm. $^{13}C\{^1H\}$ NMR

(CD_2Cl_2, 243 K, 151 MHz): δ = 19.6 (Zr−*C*H_3), 54.9 (O*C*H_3), 68.9 (C-6), 71.3 (C-5), 72.4 (2-O*C*H_2Ph), 73.2 (6-O*C*H_2Ph), 75.1 (3-O*C*H_2Ph), 79.5 (C-4), 80.1 (C-2), 82.4 (C-3), 97.4 (C-1), 110.3 (Cp_A), 110.4 (Cp_B), 111.4, 112.0, 127.0−128.4 (Ph), 138.1, 138.2, 139.5 (*ipso*-Ph) ppm.

Preparation of [(MeC_5H_4)$_2$Zr(O-carb.)Me] (15b): (MeC_5H_4)$_2$ZrMe_2 (**14b**) (559 mg, 2.00 mmol) and the carbohydrate **5** (929 mg, 2.00 mmol) were both dissolved in dichloromethane (20 mL) and then combined in a flask, after which methane immediately evolved. A color change of the solution from colorless to yellow was noticed. The volatiles were removed in vacuo and the residue was washed twice with pentane resulting in 1.15 g (79%) of the product as a viscous light yellow solid. $[\alpha]_D^{25}$ = +49 (*c* = 0.53, CH_2Cl_2). IR (film, CH_2Cl_2): $\tilde{\nu}$ = 3067, 2983, 2932, 2690, 2303, 1420, 1366, 1244, 1158, 1084, 1047, 894, 802, 785, 716, 691 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 243 K, 600 MHz): δ = −0.16 (s, 3 H, C*H*$_3$−Zr), 1.95 (s, 3 H, Cp_A−C*H*$_3$), 2.00 (s, 3 H, Cp_B−C*H*$_3$), 3.35 (s, 3 H, OC*H*$_3$), 3.41 (dd, ^2J = 10.4, ^3J = 4.8 Hz, 1 H, 6-H), 3.44 (m, 1 H, 5-H), 3.46 (dd, ^2J = 10.4, ^3J = 1.5 Hz, 1 H, 6-H′), 3.50 (m, 1 H, 2-H), 3.51 (m, 1 H, 3-H), 3.84 (dd, $^3J_{aa}$ = 8.6, $^3J_{aa}$ = 9.4 Hz, 1 H, 4-H), 4.42 (d, ^2J = 11.6 Hz, 1 H, 6-OC*H*$_2$Ph), 4.55 (d, ^2J = 11.6 Hz, 1 H, 6-OC*H*$_2$Ph), 4.58 (d, ^2J = 11.3 Hz, 1 H, 3-OC*H*$_2$Ph), 4.60 (d, ^2J = 11.7 Hz, 1 H, 2-OC*H*$_2$Ph), 4.64 (d, ^2J = 11.7 Hz, 1 H, 2-OC*H*$_2$Ph), 4.71 (d, $^3J_{ae}$ = 2.4 Hz, 1 H, 1-H), 5.08 (d, ^2J = 11.3 Hz, 1 H, 3-OC*H*$_2$Ph), 5.47 (m, 2 H, β1-Cp_A, β1-Cp_B), 5.61 (m, 1 H, β2-Cp_A), 5.72 (m, 2 H, α1-Cp_A, β2-Cp_B), 5.75 (m, 1 H, α2-Cp_A), 5.79 (m, 1 H, α1-Cp_B), 5.82 (m, 1 H, α2-Cp_B), 7.30, 7.36, 7.42, 7.45 (m, 15 H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 243 K, 151 MHz): δ = 14.5 (Cp_A−*C*H_3), 14.7 (Cp_B−*C*H_3), 20.5 (*C*H_3−Zr), 54.9 (O*C*H_3), 69.0 (C-6), 71.5 (C-5), 72.4 (2-O*C*H_2Ph), 73.1 (6-O*C*H_2Ph), 75.1 (3-O*C*H_2Ph), 79.0 (C-4), 80.2 (C-2), 82.6 (C-3), 97.3 (C-1), 105.9 (β1-Cp_B), 106.0 (β1-Cp_A), 107.6 (α1-Cp_B), 108.0 (α2-Cp_A), 111.0 (β2-Cp_B), 112.0 (β2-Cp_A), 112.4 (α1-Cp_A), 114.3 (α2-Cp_B), 122.6 (*ipso*-Cp_A), 123.1 (*ipso*-Cp_B), 127.2−128.3 (Ph), 138.2, 138.2, 139.4 (*ipso*-Ph) ppm.

Preparation of [Cp_2Zr(O-carb.)]$^+$[$MeB(C_6F_5)_3$]$^-$ (16a): NMR spectroscopic experiment: Complex **15a** (21 mg, 0.029 mmol) and $B(C_6F_5)_3$ (**7**) (15 mg, 0.03 mmol) were each dissolved in [D_2]dichloromethane (0.5 mL) and combined at −78 °C. The reaction color changed from colorless to yellow. NMR studies showed that the product is stable up to 10 °C. ^{1}H NMR (CD_2Cl_2, 233 K, 600 MHz): δ = 0.56 [s, 3 H, C*H*$_3$−$B(C_6F_5)_3$], 3.24 (s, 3 H, OC*H*$_3$), 3.49 (m, 1 H, 2-H), 3.51 (m, 1 H, 5-H), 3.69 (t, $^3J_{aa}$ = 8.9 Hz, 1 H, 3-H), 3.74 (t, ^2J = $^3J_{aa}$ = 10.2 Hz, 1 H, 6-H_a), 4.04 (d, ^2J = 10.2 Hz, 1 H, 6-H_e), 4.19 (t, $^3J_{aa}$ = 8.9 Hz, 1 H, 4-H), 4.50 (d, ^2J = 13.2 Hz, 1 H, 6-OC*H*$_2$Ph), 4.66 (d, ^2J = 12.1 Hz, 1 H, 2-OC*H*$_2$Ph), 4.66 (d, ^2J = 11.8 Hz, 1 H, 3-OC*H*$_2$Ph), 4.66 (d, $^3J_{ae}$ = 3.4 Hz, 1 H, 1-H), 4.67 (d, ^2J = 13.2 Hz, 1 H, 6-OC*H*$_2$Ph), 4.74 (d, ^2J = 12.1 Hz, 1 H, 2-OC*H*$_2$Ph), 4.90 (d, ^2J = 11.8 Hz, 1 H, 3-OC*H*$_2$Ph), 6.53 (Cp_A), 6.67 (Cp_B), 7.23−7.44, 7.52 (m, 15 H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K, 151 MHz): δ = 9.9 [*C*H_3−$B(C_6F_5)_3$], 55.5 (O*C*H_3), 67.2 (C-5), 73.1 (3-O*C*H_2Ph), 74.8 (C-6, 2-O*C*H_2Ph), 78.5 (C-2), 80.0 (6-O*C*H_2Ph), 80.3 (C-3), 87.1 (C-4), 98.3 (C-1), 116.5 (Cp_B), 118.0 (Cp_A), 126.9−128.3, 130.6 (Ph), 129.7 (*ipso*-Ph), 136.1 [dm, $^1J_{C,F}$ = 246 Hz, *meta*-$B(C_6F_5)_3$], 137.2 [dm, $^2J_{C,F}$ = 245 Hz, *ortho*-$B(C_6F_5)_3$], 137.8, 139.0 (*ipso*-Ph), 147.9 [dm, $^1J_{C,F}$ = 238 Hz, *para*-$B(C_6F_5)_3$] ppm [*ipso*-$B(C_6F_5)_3$ not observed].

Preparation of [(MeC_5H_4)Zr(O-carb.)]$^+$[$MeB(C_6F_5)_3$]$^-$ (16b): NMR spectroscopic experiment: Complex **15b** (73 mg, 0.100 mmol) and $B(C_6F_5)_3$ (**7**) (51 mg, 0.100 mmol) were each dissolved in [D_2]dichloromethane (0.5 mL), combined at −78 °C and warmed to room temperature. A change of the reaction color from colorless to yellow was noticed. ^{1}H NMR (CD_2Cl_2, 233 K, 600 MHz): δ = 0.45 [s, 3 H, C*H*$_3$−$B(C_6F_5)_3$], 2.09 (s, 3 H, Cp_A−C*H*$_3$), 2.18 (s, 3 H, Cp_B−C*H*$_3$), 3.22 (s, 3 H, OC*H*$_3$), 3.50 (dd, $^3J_{aa}$ = 9.2, $^3J_{ae}$ = 3.5 Hz, 1 H, 2-H), 3.52 (m, 1 H, 5-H), 3.73 (dd, $^3J_{aa}$ = 8.9, $^3J_{aa}$ = 9.2 Hz, 1 H, 3-H), 3.77 (t, ^2J = 10.5, $^3J_{aa}$ = 9.9 Hz, 1 H, 6-H_a), 4.04 (dd, ^2J = 10.5, $^3J_{ae}$ = 2.7 Hz, 1 H, 6-H_e), 4.26 (t, $^3J_{aa}$ = 8.9 Hz, 1 H, 4-H), 4.48 (d, ^2J = 13.1 Hz, 1 H, 6-OC*H*$_2$Ph), 4.59 (d, ^2J = 11.4 Hz, 1 H, 2-OC*H*$_2$Ph), 4.62 (d, $^3J_{ae}$ = 3.5 Hz, 1 H, 1-H), 4.62 (d, ^2J = 13.1 Hz, 1 H, 6-OC*H*$_2$Ph), 4.63 (d, ^2J = 11.0 Hz, 1 H, 3-OC*H*$_2$Ph), 4.69 (d, ^2J = 11.4 Hz, 1 H, 2-OC*H*$_2$Ph), 4.85 (d, ^2J = 11.0 Hz, 1 H, 3-OC*H*$_2$Ph), 6.03 (m, 1 H, β2-Cp_B), 6.08 (m, 1 H, β1-Cp_A*), 6.10 (m, 1 H, α1-Cp_B), 6.45 (m, 1 H, α2-Cp_B), 6.59 (m, 1 H, α1-Cp_A), 6.69 (m, 1 H, α2-Cp_A), 6.78 (m, 1 H, β2-Cp_A*), 7.05 (m, 1 H, β1-Cp_B), 7.26−7.35, 7.51 (each m, 15 H, Ph) (* denotes a tentative assignment). ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K, 151 MHz): δ = 9.8 [*C*H_3−$B(C_6F_5)_3$], 14.4 (Cp_A−*C*H_3), 15.3 (Cp_B−*C*H_3), 55.5 (O*C*H_3), 67.1 (C-5), 73.0 (2-O*C*H_2Ph), 74.7 (C-6), 75.4 (3-O*C*H_2Ph), 79.0 (C-2), 80.0 (6-O*C*H_2Ph), 81.1 (C-3), 85.7 (C-4), 98.1 (C-1), 111.9 (α1-Cp_A), 113.0 (α2-Cp_A), 113.4 (α1-Cp_B), 114.6 (β2-Cp_A, β2-Cp_B), 115.5 (β1-Cp_B), 118.4 (β1-Cp_A), 120.3 (α2-Cp_B), 127.2−128.3, 129.8, 130.7 (Ph), 129.6 (*ipso*-Ph), 136.0 [dm, $^1J_{C,F}$ = 249 Hz, *meta*-$B(C_6F_5)_3$], 137.0 (*ipso*-Cp_B), 137.2 [dm, $^1J_{C,F}$ = 245 Hz, *ortho*-$B(C_6F_5)_3$], 137.3 (*ipso*-Cp_A), 137.7, 138.2 (*ipso*-Ph), 147.8 [dm, $^1J_{C,F}$ = 236 Hz, *para*-$B(C_6F_5)_3$] ppm [*ipso*- $B(C_6F_5)_3$ not observed].

Preparation of [Cp_2Zr(O-carb.)(THF)]$^+$[BPh_4]$^-$ (18): NMR spectroscopic experiment: A solution of [Cp_2ZrMe(THF)]$^+$[BPh_4]$^-$ (**17**) (31 mg, 0.05 mmol) in [D_2]dichloromethane was combined with the carbohydrate **5** (23 mg, 0.05 mmol) at −60 °C resulting in a yellow color. The reaction mixture was warmed to room temperature. ^{1}H NMR (CD_2Cl_2, 233 K, 600 MHz): δ = 1.66 (br. s, 4 H, β-THF), 3.31 (br. s, 4 H, α-THF), 3.38 (s, 3 H, OC*H*$_3$), 3.40 (dd, ^2J = 10.9, ^3J = 3.4 Hz, 1 H, 6-H), 3.47 (dd, ^2J = 10.9, ^3J = 1.5 Hz, 1 H, 6-H′), 3.51 (ddd, $^3J_{aa}$ = 9.6, ^3J = 3.4, ^3J = 1.5 Hz, 1 H, 5-H), 3.65 (dd, $^3J_{aa}$ = 9.0, $^3J_{aa}$ = 8.0 Hz, 1 H, 3-H), 3.68 (dd, $^3J_{aa}$ = 9.0, $^3J_{ae}$ = 3.0 Hz, 1 H, 2-H), 4.28 (dd, $^3J_{aa}$ = 9.6, $^3J_{aa}$ = 8.0 Hz, 1 H, 4-H), 4.39 (d, ^2J = 12.2 Hz, 1 H, 3-OC*H*$_2$Ph), 4.48 (d, ^2J = 11.8 Hz, 1 H, 6-OC*H*$_2$Ph), 4.59 (d, ^2J = 11.8 Hz, 1 H, 2-OC*H*$_2$Ph), 4.61 (d, ^2J = 11.8 Hz, 1 H, 2-OC*H*$_2$Ph), 4.69 (d, ^2J = 11.8 Hz, 1 H, 6-OC*H*$_2$Ph), 4.81 (d, $^3J_{aa}$ = 3.0 Hz, 1 H, 1-H), 5.30 (d, ^2J = 12.2 Hz, 1 H, 3-OC*H*$_2$Ph), 6.03 (s, 10 H, Cp), 6.91, 7.06, 7.32−7.44 (each m, 35 H, Ph, BPh_4) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K, 151 MHz): δ = 25.4 (β-THF), 55.3 (O*C*H_3), 68.1 (C-6), 69.6 (C-5), 71.6 (2-O*C*H_2Ph), 73.0 (3-O*C*H_2Ph), 73.9 (6-O*C*H_2Ph), 77.9 (α-THF), 79.6 (C-2), 80.2 (C-3), 82.5 (C-4), 96.6 (C-1), 115.2 (Cp), 121.8, 126.6−128.8, 131.0, 135.5, 138.5 (Ph, BPh_4), 137.0, 137.4, 138.8 (*ipso*-Ph), 163.6 (1:1:1:1 q, $^1J_{CB}$ = 49 Hz, *ipso*-BPh_4) ppm.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

[1] [1a] H. Köpf, P. Köpf-Maier, *Angew. Chem.* **1979**, *91*, 509; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 477−488. [1b] P. Köpf-Maier, W. Wagner, H. Köpf, *Cancer Chemother. Pharmacol.* **1981**, *5*, 237−241. [1c] M. M. Harding, G. Mokdsi, *Curr. Med. Chem.* **2000**, *7*, 1289−1303.

[2] [2a] B. K. Keppler, *Metal Complexes in Cancer Chemotherapy*, Wiley-VCH, Weinheim, **1993**, p. 260−323.

[3] [3a] B. Rosenberg, L. VanCamp, J. E. Troska, V. H. Mansour, *Nature (London)* **1969**, *222*, 385−392. [3b] M. Rozencweig, D. D. von Hoff, M. Slavik, F. M. Muggia, *Ann. Intern. Med.* **1977**,

86, 803−812. [3c] H. Sun, H. Li, R. A. Weir, P. J. Sadler, *Angew. Chem.* **1998**, *110*, 1622−1625; *Angew. Chem. Int. Ed.* **1998**, *37*, 1577−1579. [3d] M. Guo, P. J. Sadler, *J. Chem. Soc., Dalton Trans.* **2000**, 7−9. [3e] M. Guo, Z. Guo, P. J. Sadler, *J. Biol. Inorg. Chem.* **2001**, *6*, 698−707. [3f] S. Top, E. B. Kaloun, A. Vessières, I. Laios, G. Leclercq, G. Jaouen, *J. Organomet. Chem.* **2002**, *643*/*644*, 350−356.

[4] [4a] A. D. Ryabov, *Angew. Chem.* **1991**, *103*, 945−955; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 931−941. [4b] K. Severin, R. Bergs, W. Beck, *Angew. Chem.* **1998**, *110*, 1722−1743; *Angew. Chem. Int. Ed.* **1998**, *37*, 1653−1654. [4c] K. Haas, W. Ponikwar, H. Nöth, W. Beck, *Angew. Chem.* **1998**, *110*, 1200−1203, *Angew. Chem. Int. Ed.* **1998**, *37*, 1086−1089.

[5] D. Harmsen, G. Erker, R. Fröhlich, G. Kehr, *Eur. J. Inorg. Chem.* **2002**, *1*, 3156−3171.

[6] J. Wonnemann, M. Oberhoff, G. Erker, R. Fröhlich, K. Bergander, *Eur. J. Inorg. Chem.* **1999**, *584*, 318−322.

[7] [7a] M. Riediker, P. Herold, S. Wyler-Helfer, R. O. Duthaler, *Helv. Chim. Acta* **1990**, *73*, 659−73. [7b] M. Riediker, A. Hafner, U. Piantini, G. Rihs, A. Togni, *Angew. Chem.* **1989**, *101*, 493−495; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 494−500. [7c] L. Jessen, E. T. K. Haupt, J. Heck, *Chem. Eur. J.* **2001**, *7*, 3791−3797. [7d] C. Gack, P. Klüfers, *Acta Crystallogr., Sect. C* **1996**, *52*, 2972−2975. [7e] P. Klüfers, T. Kunte, *Angew. Chem.* **2001**, *113*, 4356−4358; *Angew. Chem. Int. Ed.* **2001**, *40*, 4210−4212. [7f] S. Herdin, G. Kettenbach, P. Klüfers, *Z. Naturforsch., Teil B* **2004**, *59*, 134−139. [7g] T. Matsumoto, H. Maeta, K. Suzuki, *Tetrahedron Lett.* **1988**, *29*, 3567−3570.

[8] [8a] J. J. Patroni, R. V. Stick, B. W. Skelton, A. H. White, *Austral. J. Chem.* **1988**, *41*, 91−102. [8b] R. C. Bernotas, *Tetrahedron Lett.* **1990**, *31*, 469−472. [8c] M. P. DeNinno, J. B. Etienne, K. C. Duplantier, *Tetrahedron Lett.* **1995**, *36*, 669−672.

[9] [9a] A. G. Massey, A. J. Park, F. G. A. Stone, *Proc. Chem. Soc.* **1963**, 212. [9b]A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245−250.

[10] [10a] X. Yang, C. L. Stern, J. T. Marks, *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625. [10b] M. S. W. Chan, K. Vanka, C. C. Pye, T. Ziegler, *Organometallics* **1999**, *18*, 4624−4636.

[11] [11a] S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927. [11b] S. Beck, M. H. Prosenc, H. H. Brintzinger, R. Goretzki, N. Herfert, G. Fink, *J. Mol. Catal. A: Chem.* **1996**, *111*, 67−79. [11c] P. A. Deck, C. L. Beswick, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 1772−1784. [11d] I. A. Guzei, R. A. Stockland, Jr., R. F. Jordan, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *C56*, 635−636. [11e] M.-C. Chen, J. A. S. Roberts, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 4605−4625. [11f] C. Zuccaccia, N. G. Stahl, A. Macchioni, M.-C. Chen, J. A. Roberts, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 1448−1464.

[12] [12a] J. Zhou, S. J. Lancester, D. A. Walker, S. Beck, M. Thornton-Pett, M. Bochmann, *J. Am. Chem. Soc.* **2001**, *123*, 233−237. [12b] F. Song, R. D. Cannon, M. Bochmann, *Chem. Commun.* **2003**, 542−543. [12c] A. Rodriguez-Delgado, M. D. Hannant, S. J. Lancaster, M. Bochmann, *Macromol. Chem. Phy.* **2004**, *205*, 334−346. [12d] V. Busico, V. Van Axel Castelli, P. Aprea, R. Cipullo, A. Segre, G. Talarico, M. Vacatello, *J. Am. Chem. Soc.* **2003**, *125*, 5451−5460. [12e] J. W. Strauch, J.-L. Fauré, S. Bredeau, C. Wang, G. Kehr, R. Fröhlich, H. Luftmann, G. Erker, *J. Am. Chem. Soc.* **2004**, *126*, 2089−2104.

[13] [13a] L. B. Kool, M. D. Rausch, *J. Organomet. Chem.* **1985**, *297*, 159−169. [13b] M. Bochmann, L. M. Wilson, M. B. Hursthouse, R. L. Short, *Organometallics* **1987**, *6*, 2556−2563. [13c] J. C. Green, M. L. H. Green, G. C. Taylor, J. Saunders, *J. Chem. Soc., Dalton Trans.* **2000**, 317−327. [13d] M. Dahlmann, R. Fröhlich, G. Erker, *Eur. J. Inorg. Chem.* **2000**, *8*, 1789−1793.

[14] [14a] R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325−387. [14b] R. Taube, L. Krukowka, *J. Organomet. Chem.* **1988**, *347*, C9−C11. [14c] S. L. Borkowsky, R. F. Jordan, G. D. Hinch, *Organometallics* **1991**, *10*, 1268−1274.

[15] [15a] K. Döppert, *J. Organomet. Chem.* **1987**, *319*, 351−354. [15b] J. H. Toney, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 947−953. [15c] U. Thewalt, G. Schleußner, *Angew. Chem.* **1978**, *90*, 559−560; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 531.

[16] M. Guo, H. Sun, H. J. McArdle, L. Gambling, P. J. Sadler, *Biochemistry* **2000**, *39*, 10023−10033.

[17] S. Braun, H.-O. Kalinowski, S. Berger, *150 and More NMR Experiments*, Wiley-VCH, Weinheim, **1995**.

Received May 11, 2004
Early View Article
Published Online November 10, 2004

