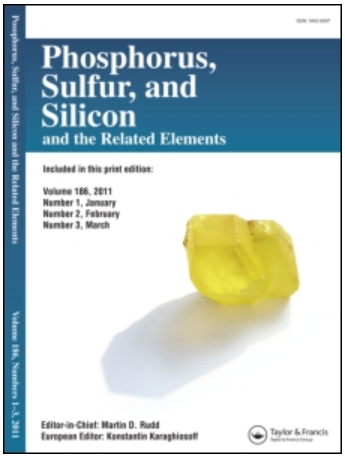

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SYNTHESES OF NEW BIDENTATE THIOETHYLPHOSPHINE LIGANDS AND THEIR RHODIUM (I) COMPLEXES WITH CARBOHYDRATES AS CHIRAL GROUPS

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SYNTHESES OF NEW BIDENTATE THIOETHYLPHOSPHINE LIGANDS AND THEIR RHODIUM (I) COMPLEXES WITH CARBOHYDRATES AS CHIRAL GROUPS

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Substitution-, addition- and rearrangement reactions on easily available derivatives of carbohydrates (**1**, **2** and **4**) with diphenylvinylphosphine or 2-mercaptoethyldiphenylphosphine gave chiral bidentate β-thioethylphosphine ligands (**5–9**). These compounds form complexes with rhodium (I) in which ligands are coordinated to the metal centre by both the phosphine and the thioether function (**10–12**). Ligands as well as complexes were examined by Circular Dichroism (CD) spectroscopy.

Key words: Bidentate ligands, circular dichroism, Rh-complexes, carbohydrates, chelate.

INTRODUCTION

In asymmetric catalysis, chiral diphosphines represent the most abundant ligand building groups.[1] The interest in synthesis and application of mixed chelating ligands, in which one donor atom is phosphorus and the second sulfur, nitrogen and oxygen, respectively, increased appreciably for some years.[2-4]

Thus chelating thiophosphine ligands have proven efficient in a number of catalytic processes. Bressan[5] and co-workers hydrogenated alkenes and ketones with the help of Rh (I) complexes containing thiophosphine ligands. These catalyst systems are also useful for homogeneous oxidation reactions at terminal olefins.[6]

In enantioselective synthesis thiophosphine ligands also have proven successful. Gladiali and co-workers prepared S—P-binaphthyls and used them in asymmetric hydroformylation of styrene.[7]

A short time ago, Pd (II) complexes coordinated with *exo*-8-((*o*-(diphenylphosphino)benzyl)thio)borneol were employed in allylic alkylations.[8]

On the other hand, carbohydrates, the most common chiral natural products, are ligands of interest in the synthesis of catalyst systems showing enantioselective effects.[9] Now the combination of carbohydrates with thiophosphines described in this paper offers a source of new chiral thiophosphines for use in asymmetric reactions. Three possible ways of synthesizing these ligands are shown below.

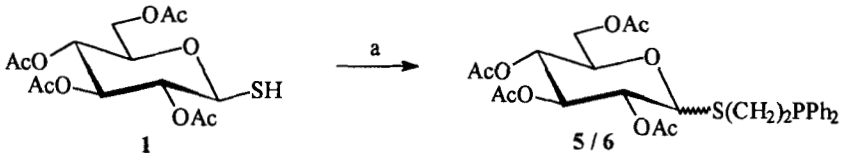
RESULTS AND DISCUSSION

β-Thioethylphosphine can be synthesized starting from thiols in Michael-analogous addition reactions to vinylphosphines.[10] β-D-thioglucose-tetraacetate (**1**) was caused

to react with diphenylvinylphosphine in THF at room temperature without the need of any catalyst. Under these conditions the products **5** and **6** were formed, which were characterized as an α/β-mixture (3/1) of 2,3,4,6-tetra-O-acetyl-1-(2-thioethyl-diphenylphosphine)-D-glucopyranoside (Scheme I).

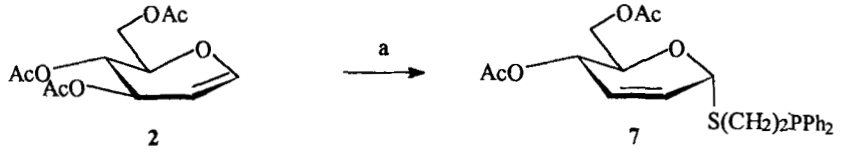
Another possible procedure is a rearrangement reaction of glycals with S-nucleophiles catalyzed by a Lewis-acid (Ferrier-I-reaction).[11] In this connection the 2-mercaptoethyldiphenylphosphine proved itself to be an excellent S-nucleophile. Mono- and also disaccharides can be transformed stereoselectively as well as regioselectively.

3,4,6-Tri-O-acetyl-D-glucal (**2**) converts into 4,6-di-O-acetyl-1-(2-thioethyldiphenylphosphine)-2,3-didesoxy-α-D-erythro-hex-2-eno-pyranoside (**7**), catalyzed by BF_3-etherate. Formation of only one of the anomers was observed. It was not possible to determine the kind of anomer on 2,3-unsaturated glycosides by means of NMR-



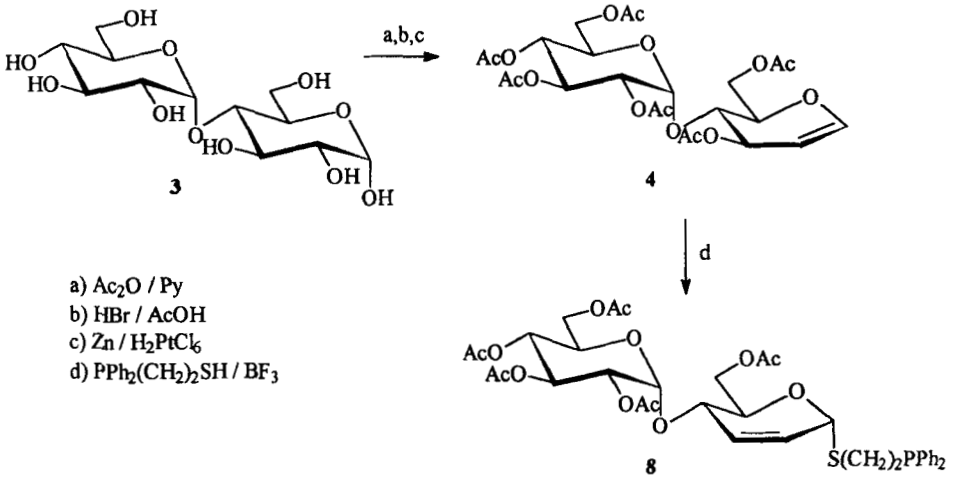
a) $CH_2{=}CHPPh_2$ / THF

SCHEME I Michael-analogous addition reaction.



a) $HS(CH_2)_2PPh_2$ / $BF_3 \cdot Et_2O$

SCHEME II Ferrier-Reaction of glucal.



a) Ac_2O / Py
b) HBr / AcOH
c) Zn / H_2PtCl_6
d) $PPh_2(CH_2)_2SH$ / BF_3

SCHEME III Ferrier-reaction of maltal.

spectroscopy. Considering the anomer effect and the steric conditions, we conclude that the α-anomer was formed (Scheme II). With S-nucleophiles, even the 3-substituted product could be expected, but this product was not observed.[12]

Disaccharides could be converted under these conditions as well. Scheme III shows the reaction sequence with maltose.

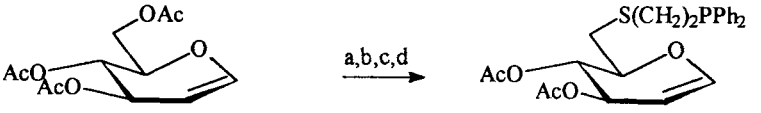
These two alternatives show convenient syntheses of β-thioethylphosphines. The S—P-arrangement is linked with the anomer centre in both cases. To add the 2-thioethylphosphine at another position on the carbohydrate, there is the opportunity to perform a nucleophilic substitution reaction between the nucleophile and a 6-tosyl-glycoside.[13] This variation should lead to different catalytic effects. 3,4-Di-O-acetyl-6-O-(*p*-toluylsulfonyl)-1,2-didesoxy-D-arabino-hex-1-eno-pyranoside can be derived from tri-O-acetyl-D-glucal.[14] After substitution of the tosyl group the 3,4-di-O-acetyl-6-(2-thioethyldiphenylphosphine)-1,2-didesoxy-D-*arabino*-hex-1-eno-pyranoside (**9**) was formed (Scheme IV).

The cationic rhodium (I)-complexes were prepared starting from the (1/5-cis,cis-cyclooctadiene) rhodium (I) acetylacetonate complex (Scheme V).

The ^{31}P-NMR spectra show a P/Rh coupling of 145 Hz. Therefore the complexes contain the compounds **7–9** as bidentate ligands.[2] Another indication is the investigation by CD spectroscopy.

Circular Dichroism (CD) spectroscopy in general is useful for the examination of the properties of optically active substances.[15] CD spectra were taken from the ligands **7–9** and the corresponding Rh-complexes **10–12**. The main fact that can be extracted from the CD spectra of ligands and complexes is the similarity between the spectra of compounds **7** and **8** (complexes **10** and **11**, respectively) on one side and the dissimilarity of these spectra to the ones derived from compounds **9** and **12**.

The UV spectra of the ligands are dominated by the absorption bands of the diphenylphosphine chromophore, while in the CD spectra in the region of this chromophore no CD effects can be observed. This is clearly caused by the long distance and the high conformational flexibility of the linking linear chain between this chro-



2 **9**

a) $NaOCH_3$ / CH_3OH
b) TosCl / Py
c) Ac_2O / AcOH
d) $PPh_2(CH_2)_2SH$ / DMF

SCHEME IV Preparation of **9**.

$$[Rh(COD)(acac)] + HBF_4 + L \longrightarrow [(Rh(COD)(L)]BF_4$$

L: **7**, **8** or **9**

10: L = **7**
11: L = **8**
12: L = **9**

SCHEME V Preparation of the cationic rhodium (I)-complexes.

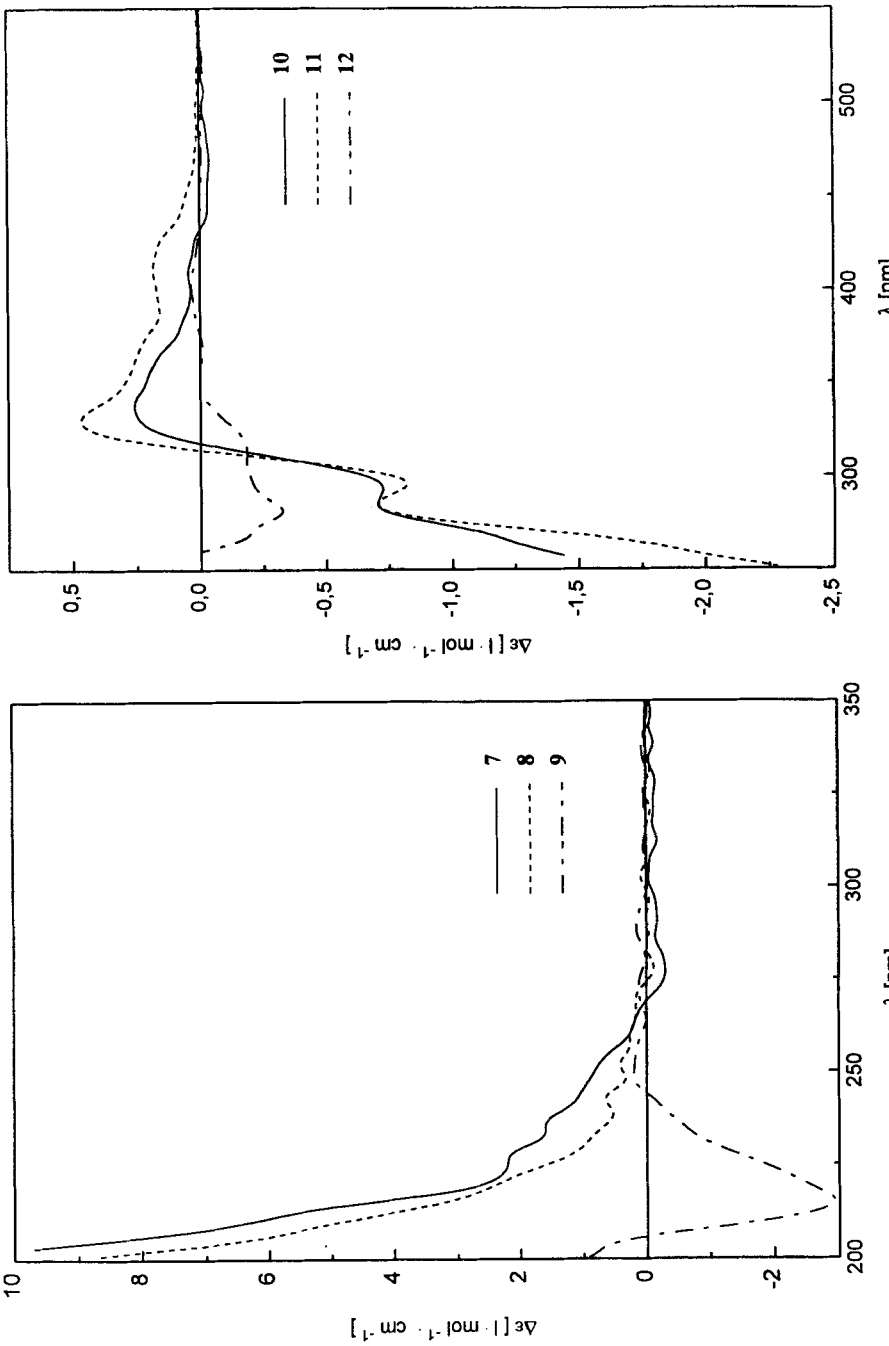


Figure 1 CD spectra of left: ligands **7–9**; concentration = $2.3 \cdot 10^{-4}$ mol·l^{-1} in methanol for all samples; right: complexes **10–12**; concentration = $1.9 \cdot 10^{-4}$ mol·l^{-1} in methanol for all samples.

mophore and the saccharide ring containing the chiral information. In the CD spectrum of compound **9** the clearly expressed negative band with a minimum at 215 nm can be attributed to the enolether chromophore —CH=CH—O—, the sign of the effect follows the rule stated by Snatzke.[16] In the spectra of the other ligand compounds **7** and **8** lacking the enol ether function the observed featureless positive effects presumably are the sum effects of the acetyl group $n \rightarrow \pi^*$ and the thioether $n \rightarrow \sigma^*$ transitions.

In the complex compounds **10–12**, the chromophore is built up by the rhodium central ion and its ligands. According to the "sphere" rule by Snatzke[17] sign and strength of CD effects depend on the chiral influence (group, substituent) which is closest to the chromophore itself. So it is understandable that the influence of the additional sugar ring in the compound **11** (disaccharide ligand) compared to compound **10** is minimal in the spectral region of the rhodium chromophore. This leads to the obvious similarity between the spectra of compounds **10** and **11**. Additionally, this fact gives a further strong hint that the rhodium is chelated by sulfur and phosphino group. If this would not be the case and rhodium would be bound only to the phosphino group, one would expect a much smaller or even zero chiral influence of the ligand onto the CD effect in the rhodium absorption bands.

CONCLUSION

In this work, three different reaction paths to new chiral β-thiophosphine ligands are shown. In every case the basic synthons are carbohydrate derivatives. Regarding the high applicability (useful for mono- and disaccharides), the excellent regio- and stereoselectivity and the good yields, the lewis-acid catalysed allyl rearrangement reaction at 1,2-unsaturated carbohydrates represents the best synthetic variant.

The new P—S-ligands **7**, **8** and **9** act as chelating ligands in the prepared rhodium complexes. In addition to the characteristic Rh/P coupling constants for P—S-chelates in ^{31}P-NMR, for the first time CD spectroscopy gives a strong hint for the proposed structural assignments. The existence of CD effects in the spectral region of the rhodium chromophore allows the conclusion that rhodium must be coordinated by sulfur and phosphorus. The new ligands and rhodium complexes will be used in enantioselective synthesis, e.g. in hydroformylation and in the Heck reaction.

EXPERIMENTAL

General Methods

All syntheses were performed in dry and oxygen-free solvents. 3,4,6-Tri-O-acetyl-D-glucal and 1-thio-β-D-glucose-tetraacetate were obtained from Aldrich. Column chromatography was performed on Merck silicagel 60. The ^{1}H, ^{31}P and ^{13}C NMR spectra were measured on a Bruker AC 250 or ARX 400 and are reported in ppm (δ), coupling constants are given in Hertz (Hz). The mass spectrometry was performed on an AMD 402/3. The syntheses of rhodium complexes were performed using standard Schlenk techniques under an argon atmosphere. CD spectra were recorded on a JASCO J-710 spectropolarimeter at 25°C using methanol as solvent.

2,3,4,6-tetra-O-acetyl-1-(2-thioethyldiphenylphosphine)-α-D-glucopyranoside (**5**) *and 2,3,4,6-tetra-O-acetyl-1-(2-thioethyldiphenylphosphine)-β-D-glucopyranoside* (**6**): 1-Thio-β-D-glucose-tetraacetate (364 mg, 1 mmol) and diphenylvinylphosphine (200 mg, 1 mmol) were dissolved in dry THF (10 ml) and the

solution was stirred at room temperature. After 30 min, evaporation of the solvent and purification by column chromatography with toluene/ethylacetate = 4/1 gave **5** and **6**. They were isolated as a mixture of anomers (α/β = 3/1). Yield: 216 mg (40%), viscous liquid.

Compound **5**: ^{1}H-NMR ($CDCl_3$): δ = 7.38 (m, 10H, H-phenyl), 5.68 (d, 1H, $J_{1,2}$ = 5.8, H-1), 5.36 (dd, 1H, $J_{3,4}$ = 9.2, $J_{4,5}$ = 10.4, H-4), 5.10–4.90 (m, 2H, H-2, 3), 4.35 (ddd, 1H, $J_{5,6a}$ = 6.4, $J_{5,6b}$ = 2.1, H-5), 4.20 (dd, 1H, $J_{6a,6b}$ = 12.2 H-6a), 3.85 (dd, 1H, H-6b), 2.80–2.20 (m, 4H, H-CH_2), 2.05–1.97 (4·s, 12H, H-acetyl); ^{31}P-NMR ($CDCl_3$): δ = −16.21 ppm.

Compound **6**: ^{1}H-NMR ($CDCl_3$): δ = 7.40 (m, 10H, H-phenyl), 5.18 (d, 1H, $J_{3,4}$ = 9.1, H-4), 3.69 (ddd, 1H, $J_{4,5}$ = 9.5, $J_{5,6a}$ = 4.9, $J_{5,6b}$ = 2.4, H-5), 5.08–4.90 (m, 2H, H-2, 3), 4.48 (d, 1H, $J_{1,2}$ = 10.0, H-1), 4.18 (dd, 1H, $J_{6a,6b}$ = 12.2, H-6a), 4.07 (dd, 1H, H-6b), 2.80–2.20 (m, 4H, H-CH_2), 2.05–1.97 (4·s, 12H, H-acetyl); ^{31}P-NMR ($CDCl_3$): δ = −16.06 ppm.

4,6-di-O-acetyl-1-(2-thioethyldiphenylphosphine)-2,3-didesoxy-α-D-erythro-hex-2-eno-pyranoside (**7**): 3,4,6-Tri-O-acetyl-D-glucal (2 g, 7 mmol) and 2-mercaptoethyldiphenylphosphine[18] (2 g, 8 mmol) were dissolved in dry acetonitrile (50 ml). The solution was stirred at 0°C. The reaction was started with 1 ml (8 mmol) borotrifluoride-etherate. After 1 h, neutralisation with K_2CO_3 (1 g), evaporation of the solvent and purification by column chromatography (toluene/ethylacetate = 8/1) gave pure **7**. Yield: 1.4 g (71%), viscous liquid.

$[\alpha]_D^{23}$ = +208.9° (c = 1, $CHCl_3$); 1H-NMR ($CDCl_3$): δ 7.40–7.00 (m, 10H, H-phenyl), 5.90 (ddd, 1H, $J_{1,3}$ = 1.8, $J_{2,3}$ 10.1, $J_{3,4}$ 3.6, H-3), 5.75 (td ~ ddd, 1H, $J_{1,2}$ 1.5, $J_{2,4}$ 1.5, H-2), 5.55 (m, 1H, H-1), 5.35 (dd, 1H, $J_{4,5}$ 9.1, H-4), 4.30 (m, 1H, H-5), 4.20 (dd, 1H, $J_{5,6a}$ 5.5, $J_{6a,6b}$ 11.6, H-6a), 4.10 (dd, 1H, $J_{5,6b}$ = 2.4, H-6b), 2.75 (m, 2H, H-CH_2), 2.40 (m, 2H, H-CH_2), 2.10, 2.00 (s, 3H, H-acetyl);

^{13}C-NMR ($CDCl_3$): δ 170.68, 170.21 ($\underline{C}OCH_3$), 137.81 (Ph1-C1, Ph2-C1), 132.83 (Ph1-C2, Ph2-C2), 128.83 (Ph1-C3, Ph2-C3), 128.63 (C2), 128.52 (Ph1-C4, Ph2-C4), 127.05 (C3), 80.32 (C1), 67.16 (C4), 67.68 (C5), 63.05 (C6), 29.00 (CH_2), 28.60 (CH_2), 20.94, 20.63 ($CO\underline{C}H_3$); ^{31}P-NMR ($CDCl_3$): δ −16.14 ppm; Anal. Calcd. for $C_{24}H_{27}O_5PS$ (458.51 g/mol): C, 62.87; H, 5.93; S, 6.99; Found: C, 62.83; H, 5.88; S, 7.10.

6-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-1-(2-thioethyldiphenylphosphine)-2,3-didesoxy-α-D-erythro-hex-2-eno-pyranoside (**8**): Hexa-O-acetyl-D-maltal (**4**)[19] (200 mg, 0.3 mmol) and 2-mercaptoethyldiphenylphosphine (75 µl, 0.35 mmol) were dissolved in acetonitrile (10 ml) at 0°C. The reaction was started with 0.1 ml BF_3-etherate. After 1 h, neutralisation with K_2CO_3 (1 g), evaporation of the solvent and purification by column chromatography (toluene/ethylacetate 8/1) gave pure **8**. Yield: 250 mg (93%), viscous liquid; $[\alpha]_D^{23}$ = +104.1° (c 1, $CHCl_3$), ^{1}H-NMR ($CDCl_3$): δ = 7.4–7.0 (m, 10H, H-phenyl), 5.82 (ddd, 1H, $J_{1,2}$ = 3.0, $J_{2,3}$ = 10.1, $J_{2,4}$ = 1.5, H-2), 5.70 (m, 1H, H-3), 5.45 (m, 1H, H-1), 5.35 (t ~ dd, 1H, $J_{3',4'}$ = 9.8, $J_{2',3'}$ = 9.4, H-3'), 5.21 (d, 1H, $J_{1',2'}$ = 3.7, H-1'), 5.00 (t ~ dd, 1H, $J_{4',5'}$ = 9.8, H-4'), 4.78 (dd, 1H, H-2'), 4.25–4.15 (m, 5H, H-6a,b, 6'a,b, 5'), 4.05–3.95 (m, 2H, H-4 5), 2.8–2.5 (m, 2H, H-CH_2), 2.40–2.30 (m, 2H, H-CH_2), 2.01, 1.98, 1.94, 1.90 (s, 3H, H-acetyl); ^{13}C-NMR ($CDCl_3$): δ = 170.54, 170.47, 170.12, 169.90, 169.48 ($\underline{C}OCH_3$), 137.81 (Ph1, Ph2-C1), 132.83 (Ph1, Ph2-C2), 132.53 (Ph1, Ph2-C3), 128.77 (C2), 128.57 (Ph1, Ph2-C4), 126.28 (C3), 94.18 (C1), 80.15 (C1'), 70.74 (C4'), 69.95 (C2'), 69.80 (C3'), 68.24 (C4), 68.14 (C5), 67.37 (C5'), 63.34 (C6), 61.70 (C6'), 29.00 (CH_2), 28.60 (CH_2), 20.94 − 20.63 ($CO\underline{C}H_3$);

^{31}P-NMR ($CDCl_3$): δ = −16.24 ppm; Anal. Calcd. for $C_{36}H_{43}O_{13}PS$ (746.6 g/mol): C, 57.81; H, 5.80; S, 4.29; Found: C, 57.42; H, 5.82; S, 3.84.

3,4-di-O-acetyl-6-(2-thioethyldiphenylphosphine)-1,2-didesoxy-D-arabino-hex-1-eno-pyranoside (**9**): To a stirred mixture of 2-mercaptoethyldiphenylphosphine (0.5 g, 2 mmol) and K-*t*-butanolate (227 mg, 2 mmol) in dry N,N-dimethylformamide (5 ml) was added dropwise 3,4-di-O-acetyl-6-O-(*p*-toluylsulfonyl)-1,2-didesoxy-D-*arabino*-hex-1-eno-pyranoside[10] (770 mg, 2 mmol) in dry N,N-dimethylformamide (10 ml). The reaction mixture was stirred for 30 min at room temperature. Then the mixture was taken up in CH_2Cl_2 (20 ml) and washed with water. The organic layer was dried over $MgSO_4$. The purification was carried out with column chromatography (toluene/ethylacetate = 8:1). Yield: 350 mg (70 %), viscous liquid.

$[\alpha]_D^{23}$ = −22.9° (c = 0.5, $CHCl_3$), ^{1}H-NMR ($CDCl_3$): δ = 7.2–7.0 (m, 10H, H-phenyl), 6.30 (dd, 1H, $J_{1,2}$ = 6.1, $J_{1,3}$ = 1.2, H-1), 5.20 (m, 1H, H-4), 5.15 (t ~ dd, 1H, $J_{2,3}$ 12.4, H-2), 4.07 (ddd, 1H, $J_{3,4}$ = 5.8, H-3), 4.72 (ddd, 1H, $J_{4,5}$ = 3.4, $J_{5,6a}$ = 0.6, $J_{5,6b}$ = 6.1, H-5), 2.30 (dd, 1H, $J_{6a,6b}$ = 11.6, H-6a), 2.25 (m, 1H, H-6b), 2.74 (m, 2H, H-CH_2), 2.60 (m, 2H, H-CH_2), 1.98, 1.94 (s, 3H, H-acetyl); ^{13}C-NMR ($CDCl_3$): δ = 170.30, 169.57 ($\underline{C}OCH_3$), 145.56 (C1), 137.90 (Ph1, Ph2-C1), 132.84 (Ph1, Ph2-C2), 128.80–128.51 (Ph1, Ph2-C3, Ph1, Ph2-C4), 98.74 (C2), 75.85 (C3), 69.50 (C4), 67.06 (C5), 31.99 (C6), 29.55 (CH_2), 28.78 (CH_2), 21.04, 20.86 ($CO\underline{C}H_3$).

^{31}P-NMR ($CDCl_3$): δ = −16.17 ppm; Anal. Calcd. for $C_{24}H_{27}O_5PS$ (458.51 g/mol): C, 62.87; H, 5.93; P, 6.75; S, 6.99; Found: C, 62.27; H, 6.11; P, 7.19; S, 6.98.

General Preparation of the Complexes **10**–**12**

(1,5-cyclooctadiene)-rhodium (I)-acetylacetonate (77.5 mg, 0.25 mmol) was dissolved in diethylether (4 ml) after which HBF_4-etherate (19.5 µl, 0.24 mmol) was added. The mixture was stirred for 30 min at room temperature. **7**, **8** or **9** (0.21 mmol), respectively, was dissolved in diethylether (2 ml) and given to the rhodium-solution. The resulting precipitation was filtered, washed with diethylether and dried *in vacuo*.

(1,5-cyclooctadiene)-[4,6-di-O-acetyl-1-(2-thioethyldiphenylphosphine)-2,3-didesoxy-α-D-erythro-hex-2-eno-pyranoside]-rhodium (I)-tetrafluoroborate (**10**). Yield: 97 mg (73%), yellow solid, decomposition point: 80.2°C; ^{31}P-NMR ($CDCl_3$): δ = 58.9 (d, $J_{Rh,P}$ = 145.9 Hz); FAB-MS (sulfolan as matrix): [M^+] = 699 (representing the cationic part of the compound); Anal. Calcd. for $C_{32}H_{39}$ BF_4O_5 PRhS (756.4): C, 50.81; H, 5.19; P, 4.09; Rh, 13.60; S, 4.23; Found: C, 50.01; H, 5.23; P, 4.36; Rh, 13.32; S, 4.25.

(1,5-cyclooctadiene)-[6-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-1-(2-thioethyldiphenylphosphine)-2,3-didesoxy-α-D-erythro-hex-2-eno-pyranoside]-rhodium(I)-tetrafluoroborate (**11**). Yield: 100 mg (76%), yellow solid, mp: 111.4°C; ^{31}P-NMR ($CDCl_3$): δ = 58.5 (d, $J_{Rh,P}$ = 146.4 Hz); FAB-MS (sulfolan as matrix): [M^+] = 957 (representing the cationic part of the compound); Anal. Calcd. for $C_{40}H_{55}$ BF_4O_{13}PRhS (1044.66): C, 48.70; H, 5.62; P, 3.14; Rh, 10.43; S, 3.25; Found: C, 48.52; H, 5.67; P, 3.18; Rh, 11.11; S, 3.13.

(1,5-cyclooctadiene)-[3,4-di-O-acetyl-6-(2- thioethyldiphenylphosphine)-1,2-didesoxy-D-arabino-hex-1-eno-pyranoside]-rhodium (I)-tetrafluoroborate (**12**). Yield: 85 mg (62%), yellow solid, decomposition point: 140.6°C; ^{31}P-NMR ($CDCl_3$): δ = 58.5 ppm (d, $J_{Rh,P}$ = 146.6 Hz); FAB-MS (sulfolan as matrix): [M^+] = 699 (representing the cationic part of the compound); Anal. Calcd. for $C_{32}H_{39}$ BF_4O_5PRhS (756.4).: C, 50.81; H, 5.19; P, 4.09; Rh, 13.60; S, 4.23; Found: C, 49.00; H, 5.26; P, 4.11; Rh, 13.66; S, 4.10.

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