124. Introduction of a New Class of Ligands for the Metal-Catalyzed Enantioselective Synthesis

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Protected thiosugars were prepared as ligands for the metal-catalyzed enantioselective synthesis. The protecting groups in these ligands were varied to test a proposed new concept for the metal-catalyzed enantioselective synthesis. This new concept centres on the use of a stair-like ligand with a large substituent on one side and a small substituent on the other rather than the commonly employed ligands which have C_2 symmetry (see *Fig. 3*). In such a ligand, both substituents should have a major influence on the coordination of a prochiral substrate. To test this proposal, 3-thio-α-D-glucofuranose derivatives with the following substituents were synthesized: 1,2-*O*-isopropylidene-5,6-*O*-methylidene (see **24**), 1,2:5,6-di-*O*-isopropylidene (see **2**), 5,6-*O*-cyclohexylidene-1,2-*O*-isopropylidene (see **23**), 1,2-*O*-cyclohexylidene-5,6-*O*-isopropylidene (see **14**), 1,2:5,6-di-*O*-cyclohexylidene (see **13**), 5,6-*O*-(adamantan-2-ylidene)-1,2-*O*-isopropylidene (see **21**), and 1,2:5,6-di-*O*-(adamantan-2-ylidene) (see **25**, *Table 2*). As a representative of the allofuranoses, 1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-allofuranose (**6**) was chosen. The following derivatives of 1,2-*O*-isopropylidene-α-D-xylofuranose were also synthesized: 1,2-*O*-isopropylidene-5-deoxy-3-thio-α-D-xylofuranose (**29**), 1,2-*O*-isopropylidene-3-thio-α-D-xylofuranose (**28**) and 5-*O*-[(*tert*-butyl)-diphenylsilyl]-1,2-*O*-isopropylidene-3-thio-α-D-xylofuranose (**15**, see *Table 2*). The proposed concept was tested using the copper-catalyzed 1,4-addition of BuMgCl to cyclohex-2-en-1-one. The enantioselectivity was very dependent on the ligand used and was up to 58%.

Introduction. – The enantioselective synthesis has become increasingly important in the last thirty years [1]. Many enantioselective syntheses use metal complexes with chiral C_2-symmetrical ligands as source of chirality (for a review, see [2]). This can be explained as follows (*Fig. 1*). A ligand with C_2-symmetry separates space into two identical half-spaces and, therefore, the number of possible competing diastereoisomeric transition states is reduced. As shown in *Fig. 1*, the coordination of the olefin occurs such that the smallest steric interaction results. This means the olefin coordinates with its smallest group close to the large group in the ligand.

Extension of the C_2 *Concept.* If the situation described in *Fig. 1* is examined more closely, it can be seen that only one side of the C_2-symmetrical ligand is used to induce the stereoselective coordination of the substrate. The other side of the C_2-symmetrical ligand simply makes the other potential coordination site equivalent to the first one. Hence only the proximate group of the ligand has a significant influence on the stereochemical coordination of the substrate. One example which shows this point very clearly is the asymmetric alkene hydroboration reported by *Masamune* [3] (*Scheme 1*) where he found that, with 1,1-disubstituted olefins, only low enantioselectivities were obtained. This result can be interpreted as resulting from coordination of the olefin such that the smallest

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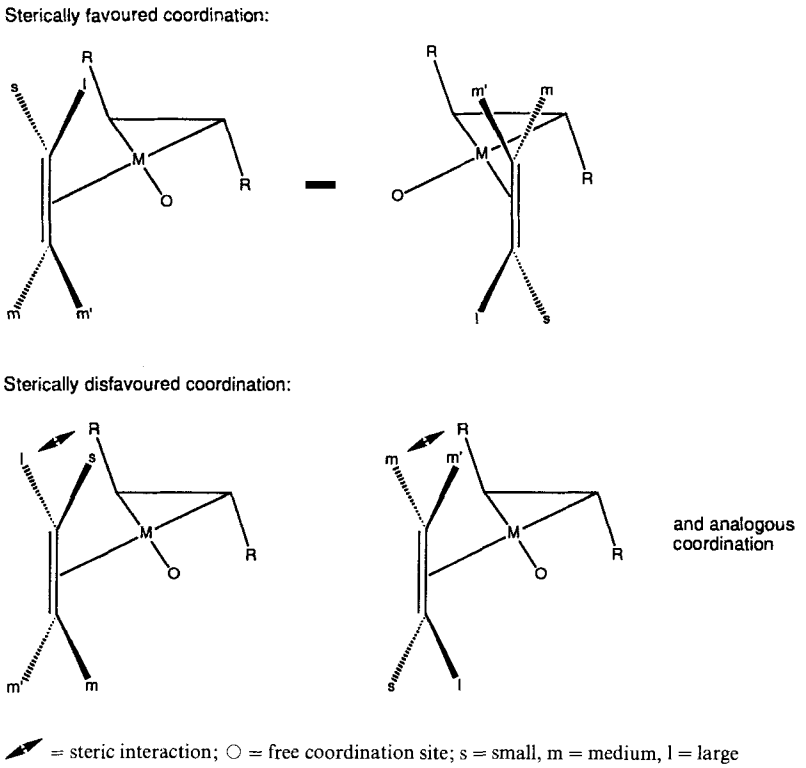
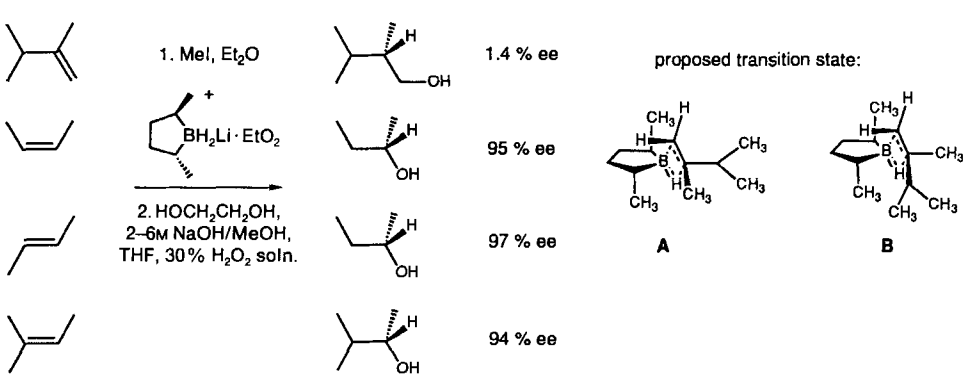


Fig. 1. *Stereochemical views of the use of a C_2-symmetrical ligand on a square planar complex and steric interaction of the coordination of an olefin*

group is opposite the Me group in the boron complex. If one terminus of the olefin is a methylene group, then the configuration of the complex formed depends only on the interaction of the other Me group with the olefin, which is small, and so the proposed transition states **A** and **B** in *Scheme 1* have comparable energy.

Scheme 1



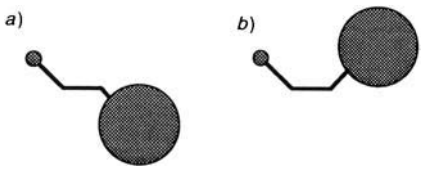


Fig. 2. a) *Structure of the stair-like ligand;* b) *structure of the U-shaped ligand*

The use of a stair-like ligand with one small substituent on one side and a large substituent on the other side (*Fig. 2a*), instead of a C_2-symmetrical ligand, produces a different situation.

In such a ligand both substituents have a major influence on the coordination of a prochiral substrate. The large substituent of the ligand directs the substrate to the coordination site *trans* to itself, and the small substituent is responsible for the discrimination of the enantiotopic sides of the substrate (*Fig. 3*). A further difference between the stair-like ligand and a C_2-symmetrical ligand is that, for all planar complexes, the

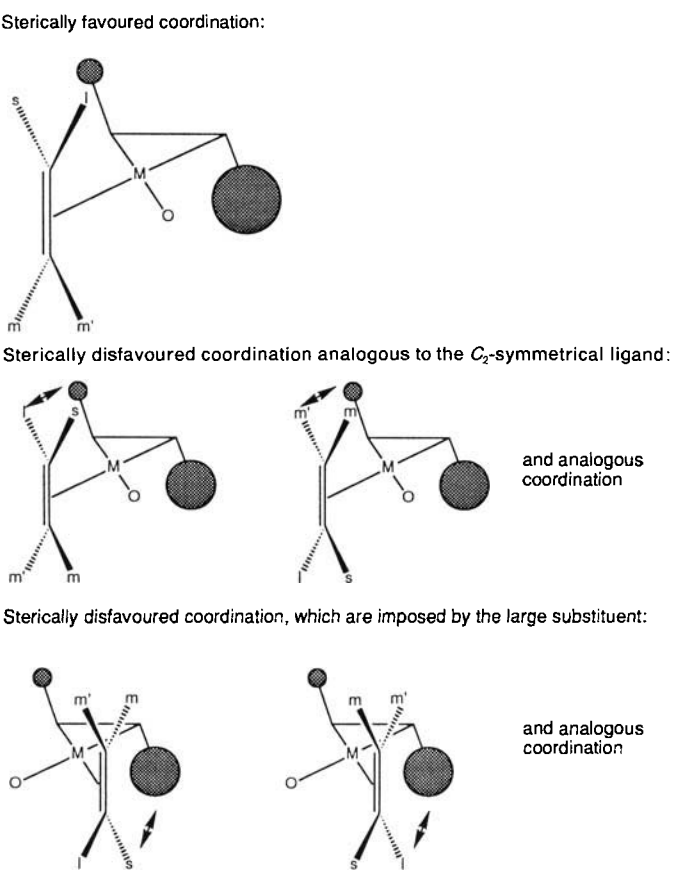


Fig. 3. *Stereochemical views of the use of a stair-like ligand on a square planar complex and steric interaction of the coordination of an olefin*

U-shaped ligand (*Fig. 2b*) should give similar results to those obtained for the related stair-like ligand.

The situation shown in *Figs. 1* and *3* can be extended to all commonly found coordination geometries. Further, the concept can be extended to similar ligands bound in a monodentate fashion (*e.g.* see *Fig. 4*). The advantage of a monodentate ligand is that there are no electronic effects due to the two different substituents because all electronic effects are concentrated on one donor atom. The 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (Glc1,2:5,6(Me_2C)$_2$[2]); **1**) was used as a ligand precursor for the testing of this new concept.

Fig. 4. *Comparison of a monodentate ligand with a bidentate ligand*

Results and Discussion. – *The Ligand System.* Glc1,2:5,6(Me_2C)$_2$ (**1**) was chosen as a ligand precursor because the 3-OH group can be substituted by all common donor atoms, both protecting groups can be varied independently, and because of the fixed geometry of the condensed five-membered rings. A disadvantage of **1** is the free rotation around the C(4)–C(5) bond, but there is some evidence that this free rotation is hindered by the coordination of a metal atom as proposed by *Kunz* and *Mohr* [4] (*Fig. 5*).

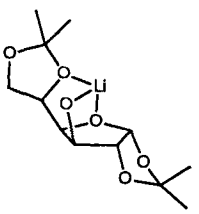


Fig. 5. *Postulated lithium complex of Glc1,2:5,6(Me_2C)$_2$* (**1**) [4]

The choice of **1** as a ligand precursor is further supported by some examples in the literature. *Inch* and coworkers [5] used this ligand for the enantioselective addition of *Grignard* reagents to ketones, and they produced alcohols with an optical purity of up to 70%. In another example, *Duthaler et al.* [6] used titanium complexes of **1** for the addition of C-nucleophiles to aldehydes and found ee's of up to 95%.

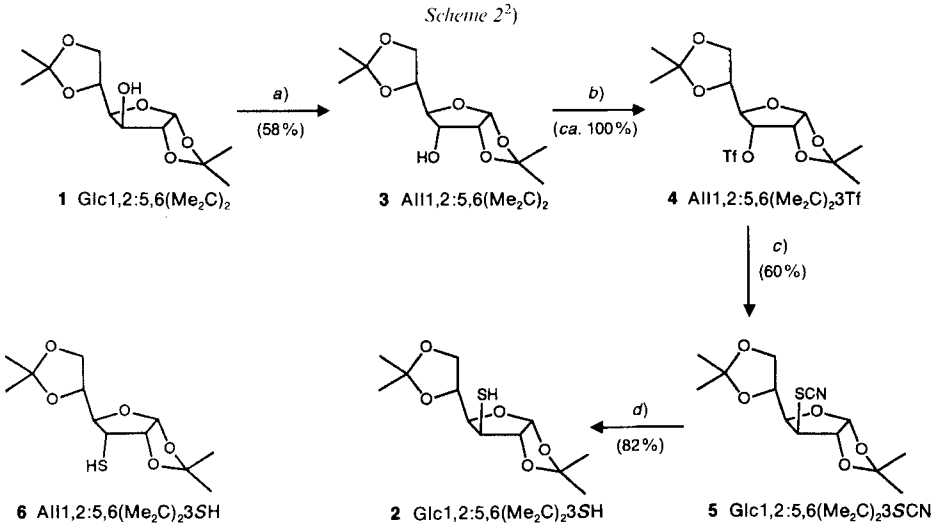
It is known that the O-atom tends to form stable complexes with hard metals such as Ti. If the O-atom at C(3) of **1** is substituted by an S-atom, then a ligand is produced which forms very stable complexes with soft metals such as Pd and Cu. We now synthesized several 3-thiosugars.

The 1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-glucofuranose (Glc1,2:5,6(Me_2C)$_2$3*S*H; **2**) was first described by *Freudenberg* and *Wolf* [7]. They transformed **1** to the 3-xanthogenate, which was then rearranged by pyrolysis to the 3-thio derivative. Reduction of

[2]) Abbreviations: All = allose, Glc = glucose, Rib = ribose, and Xyl = xylose; the sugar symbol is followed by the locants and symbols of the protecting groups, '3*S*' indicating a 3-thiosugar and 'CHO' an aldehyde; Ada = adamantan-2-ylidene, Chx = cyclohexylidene, CH_2 = methylidene, Me_2C = isopropylidene, (*t*-Bu)-Ph_2Si = (*tert*-butyl)diphenyl-silyl, and Tos = tosyl.

the product gave **2**. The problem with this synthesis is the rearrangement of the xanthogenate requiring temperatures above 300° and giving very low yields. For this reason, **2** was prepared by inversion of chirality at C(3) of **1** (→**3** (All1,2:5,6(Me_2C)$_2$)), trifluoromethanesulfonation (→**4** (All1,2:5,6(Me_2C)$_2$3Tf)), and substitution by thiocyanate to give 3-*S*-cyano-1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-glucofuranose (Glc1,2:5,6(Me_2C)$_2$3*S*CN; **5**) which was reduced with $NaBH_4$ to Glc1,2:5,6(Me_2C)$_2$3*S*H (**2**) in an overall yield of *ca.* 30% (*Scheme 2*).

Scheme 2[2])



a) 1. DMSO/Ac_2O, 2. $NaBH_4$ [18]. *b*) Triflic anhydride [19]. *c*) KSCN [8]. *d*) $NaBH_4$.

If step *a*) in *Scheme 2* is omitted, 1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-allofuranose (All1,2:5,6(Me_2C)$_2$3*S*H; **6**) results [8]. Although in this case, the nucleophilic substitution of the triflate by the thiocyanate does not proceed well because attack by the thiocyanate is sterically hindered.

Table 1. *Purification Method, Yield, Melting Points, and IR Frequencies for the Transformation of Glucoses to Alloses*[a]) *and of Triflates to Thiocyanates*[b])[2])

Product	Nr.	Purification	Yield [%]	M.p. [°C]	IR (SCN) [cm^{-1}]	Ref.
All1,2:5,6(Me_2C)$_2$	**3**	recrystallisation (hexane)	58	77		[18]
All1,2:5,6(Chx)$_2$	**7**	recrystallisation (hexane)	60	117		[21]
All1,2Chx5,6Me_2C	**8**	recrystallisation (hexane)	63	87		
Rib1,2Me_2C5(*t*-Bu)Ph_2Si	**9**	chromatography (hexane/AcOEt 4:1)	70	68		
Glc1,2:5,6(Me_2C)$_2$3*S*CN	**5**	chromatography (hexane/AcOEt 4:1)		44	2155*s*	[8]
Glc1,2:5,6(Chx)$_2$3*S*CN	**10**	chromatography (hexane/AcOEt 4:1)		90	2155*s*, 2067*m*	
Glc1,2Chx3*S*CN5,6Me_2C	**11**	recrystallisation (hexane)	65	110	2153*m*, 2033*w*	
d^5Xyl1,2Me_2C3*S*CN	**33**	chromatography (hexane/AcOEt 4:1)		57	2178*s*, 2125*w*	
Xyl1,2Me_2C3*S*CN5(*t*-Bu)Ph_2Si	**12**	chromatography (hexane/AcOEt 6:1)			2155*s*, 2075*m*	

[a]) 1. DMSO/Ac_2O, 2. $NaBH_4$. [b]) Triflic anhydride.

Table 2. *Solvents, Purification, Yield, Melting Points, and IR Frequencies for the Transformation of Thiocyanates to Thiols by $NaBH_4$ Reduction*[2])

Product	Nr.	Solvents EtOH/ H_2O/THF	Purification	Yield [%]	M.p. [°C]	IR (SH) [cm^{-1}]
Glc1,2:5,6(Me_2C)$_2$3*S*H	**2**	7:3:0	chromatography (hexane/AcOEt 3:1)	82		2563*w*
Glc1,2:5,6(Chx)$_2$3*S*H	**13**	3:1:0	chromatography (hexane/AcOEt 4:1)	65		2562*w*
Glc1,2Chx3*S*H5,6Me_2C	**14**	5:2:5	chromatography (hexane/AcOEt 4:1)	80	76	2553*w*
d^{5}Xyl1,2Me_2C3*S*H	**29**	3:1:3	chromatography (hexane/AcOEt 4:1)	61		2557*w*
Xyl1,2Me_2C3*S*H5(*t*-Bu)Ph_2Si	**15**	10:3:10	chromatography (hexane/AcOEt 4:1)	63		2568*w*
Glc1,2Me_2C3*S*H5,6CH_2	**24**	3:1:0	chromatography (hexane/AcOEt 3:1)	89		2561*w*
Glc1,2Me_2C3*S*H5,6Chx	**23**	3:1:0	chromatography (hexane/AcOEt 4:1)	50		2562*w*
Glc1,2Me_2C3*S*H5,6Ada	**21**	10:3:10	chromatography (hexane/AcOEt 6:1)	50[a])	87	2561*w*
Glc1,2:5,6(Ada)$_2$3*S*H	**25**	10:3:10	recrystallisation (hexane)	52	160	2591*w*
Xyl1,2Me_2C3*S*H	**28**	10:3:0	chromatography (hexane/AcOEt 5:1, then 2:1)	53	90	2544*m*

[a]) Estimated yield from ^{1}H-NMR spectrum.

The procedure outlined in *Scheme 2* also allowed the preparation of allose and ribose derivatives **7**–**9** and of 3-thiocyanates **10**–**12** (for abbreviated formulae, see *Table 1*). The latter were transformed to the corresponding 3-thiosugars **13**–**15** (*Table 2*; see also below).

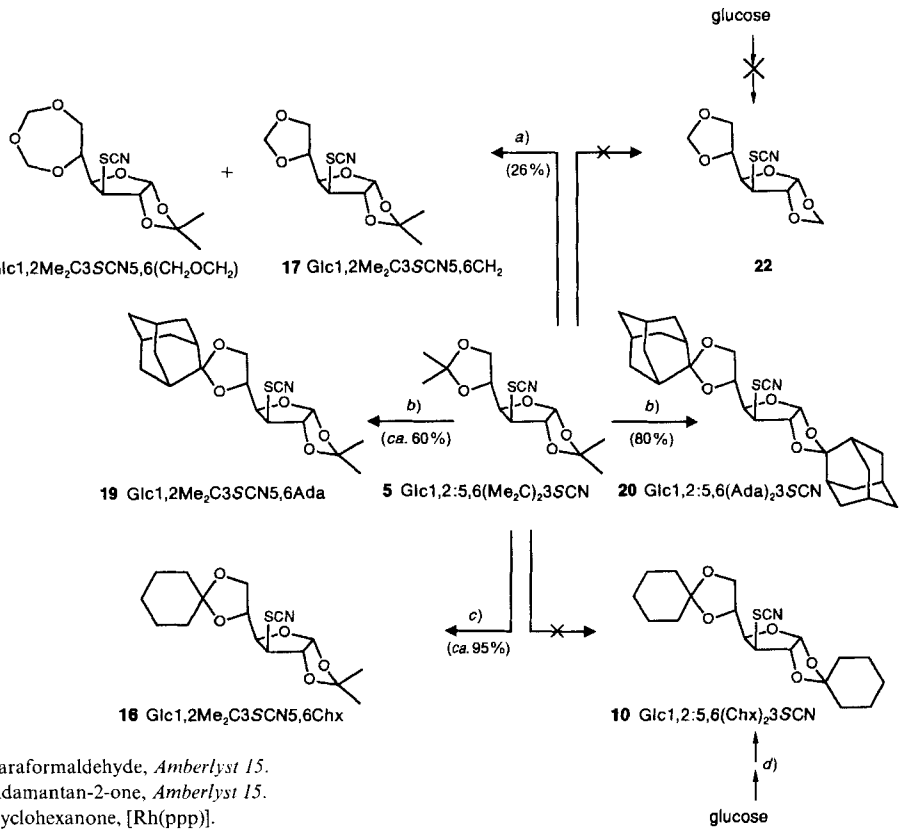
Acetal-Protected 3-Thio-α-D-glucoses. Only Glc1,2:5,6(Me_2C)$_2$3*S*CN (**5**) is described in [8]. It is a good precursor for the synthesis of different 1,2:5,6-protected 3-*S*-cyano-3-thio-α-D-glucofuranoses by transacetalization. Another way to prepare 1,2:5,6-protected 3-*S*-cyano-3-thio-α-D-glucofuranoses is to use the reaction sequence shown in *Scheme 2* for other glucose derivatives.

The transacetalization of Glc1,2:5,6(Me_2C)$_2$3*S*CN (**5**) with cyclohexanone and [Rh(MeCN)$_3${MeC(CH_2PPh_2)$_3$}](CF_3SO_3)$_3$ ([Rh(ppp)]) [10] in toluene (90°, 3 h) led to 3-*S*-cyano-5,6-cyclohexylidene-1,2-*O*-isopropylidene-3-thio-α-D-glucofuranose (Glc1,2Me_2C3*S*CN5,6Chx; **16**) in almost quantitative yield (*Scheme 3*). The structure of **16** was confirmed by a long-range ^{1}H-COSY-NMR (long range couplings between the acetal Me and H–C(1) and H–C(2)) and is also supported by the chemical behaviour of **1** and **5**.

In both Glc1,2:5,6(Me_2C)$_2$ (**1**) and Glc1,2:5,6(Me_2C)$_2$3*S*CN (**5**), the 5,6-protecting group can be removed without affecting the 1,2-protecting group [8] [10]. The transacetalization of **5** with paraformaldehyde also led to a monotransacetalized thiocyanate but in contrast to the transacetalization with cyclohexanone the reaction was problematic: refluxing a toluene solution of **5** in the presence of [Rh(ppp)] gave no product. However, the desired 3-*S*-cyano-1,2-*O*-isopropylidene-5,6-methylidene-3-thio-α-D-glucofuranose (Glc1,2Me_2C3*S*CN5,6CH_2; **17**; identified by ^{1}H-NMR similar to **16**) could be prepared in low yield in Et_2O at room temperature with *Amberlyst 15* as catalyst, besides three other products which could not be separated by chromatography. The structure of one of these by-products, **18**, was determined by ^{1}H-NMR spectroscopy (*Scheme 3*).

Adamantan-2-one was also used as a protecting reagent. With this ketone it was possible to prepare the mono- and di(adamantan-2-ylidene)-protected thiocyanates by transacetalization. The monotransacetalized 5,6-*O*-(adamantan-2-ylidene)-3-*S*-cyano-1,2-*O*-isopropylidene-3-thio-α-D-glucofuranose (Glc1,2Me_2C3*S*CN5,6Ada; **19**) was formed after 3 h reflux in toluene with *Amberlyst 15* as catalyst whereas the ditrans-

Scheme 3[2])



a) Paraformaldehyde, *Amberlyst 15*.
b) Adamantan-2-one, *Amberlyst 15*.
c) Cyclohexanone, [Rh(ppp)].
d) See text.

acetalized 1,2:5,6-di-*O*-(adamantan-2-ylidene)-3-*S*-cyano-3-thio-α-D-glucofuranose (Glc1,2:5,6(Ada)$_2$3*S*CN; **20**) was obtained after refluxing for 4 days (*Scheme 3*). It was not possible to separate the adamantan-2-one from product **19** by chromatography or by recrystallisation, but the structure of **19** was confirmed by ^{1}H-NMR (after reduction of **19** to the corresponding thiol **21** (see below), adamantan-2-one could easily be separated by chromatography).

The di(cyclohexylidene)- and di(methylidene)-protected thiocyanates **10** and **22**, respectively, could not be obtained from **5** by transacetalization (*Scheme 3*). Thus, **10** was prepared, without difficulties, by acetylization of glucose followed by the reaction sequence shown in *Scheme 2*; this procedure failed in the case of **22**.

The thiocyanates **10**, **16**, **17**, **19**, and **20** were reduced with $NaBH_4$ to the corresponding thiols **13**, **23**, **24**, **21**, and **25**, respectively (see *Table 2*).

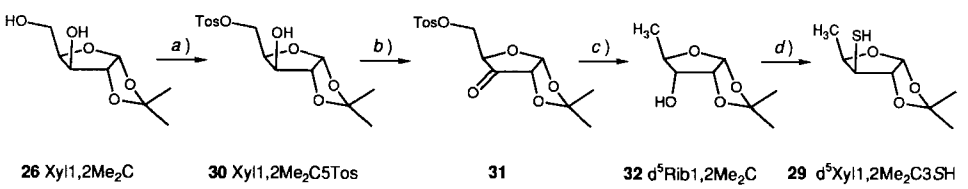
A further 3-thioglucose derivative, 1,2-*O*-cyclohexylidene-5,6-*O*-isopropylidene-3-thio-α-D-glucofuranose (Glc1,2Chx3*S*H5,6Me$_2$C; **14**), was prepared starting from 1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranose [11] (Glc1,2:5,6(Chx)$_2$ by transacetalizing with acetone *via* 3-thiocyanate **11** (see *Table 1*) according to the reaction sequence shown in *Scheme 2*.

1,2-O-Isopropylidene-3-thio-α-D-xylofuranoses. Three derivatives of 3-thio-α-D-xylofuranose were prepared, two of them from 1,2-*O*-isopropylidene-α-D-xylofuranose (Xyl1,2Me$_2$C; **26**). After protection of the more reactive, primary 5-OH group of **26** by a (*t*-Bu)Ph$_2$Si group (→Xyl1,2Me$_2$C5(*t*-Bu)Ph$_2$Si), the xylose derivative was transformed *via* 3-thiocyanate **12** (see *Table 1*) to the thiol **15** (see *Table 2*), according to *Scheme 2*. Unfortunately, the (*t*-Bu)Ph$_2$Si group, known to form stable silyl ethers, could not be removed from Xyl1,2Me$_2$C3*S*CN5 (*t*-Bu)Ph$_2$Si (**13**) with Bu$_4$NF; the isolated product still included the (*t*-Bu)Ph$_2$Si group, but no nitrogen could be detected.

The preparation of Xyl1,2Me$_2$C3*S*CN also failed by degradation of the 5,6-*O*-isopropylidene group in Glc1,2:5,6(Me$_2$C)$_2$3*S*CN (**5**) which gave 3-*S*-cyano-1,2-*O*-isopropylidene-3-thio-α-D-xylopentodialdo-1,4-furanose (Xyl1,2Me$_2$C3*S*CN5CHO; **27**) because no reducing agent was found which only reduced the aldehyde function in **27**. Instead 1,2-*O*-isopropylidene-3-thio-α-D-xylofuranose (Xyl1,2Me$_2$C3*S*H; **28**, see *Table 2*) was obtained by NaBH$_4$ reduction.

As a further 3-thioxylose derivative, 1,2-*O*-isopropylidene-5-deoxy-3-thio-α-D-xylofuranose (d^{5}Xyl1,2Me$_2$C3*S*H; **29**) was prepared. For this purpose the 5-OH group of **26** was tosylated (→**30**) and then the 3-OH group oxidized with DMSO/Ac$_2$O to ketone **31** (*Scheme 4*). Reduction with LiAlH$_4$ gave then 5-deoxy-1,2-*O*-isopropylidene-α-D-ribofuranose (d^{5}Rib1,2Me$_2$C; **32**) which could be transformed *via* the thiocyanate **33** (see *Table 1*) to the thiol **29** according to *Scheme 4*.

Scheme 4[2])

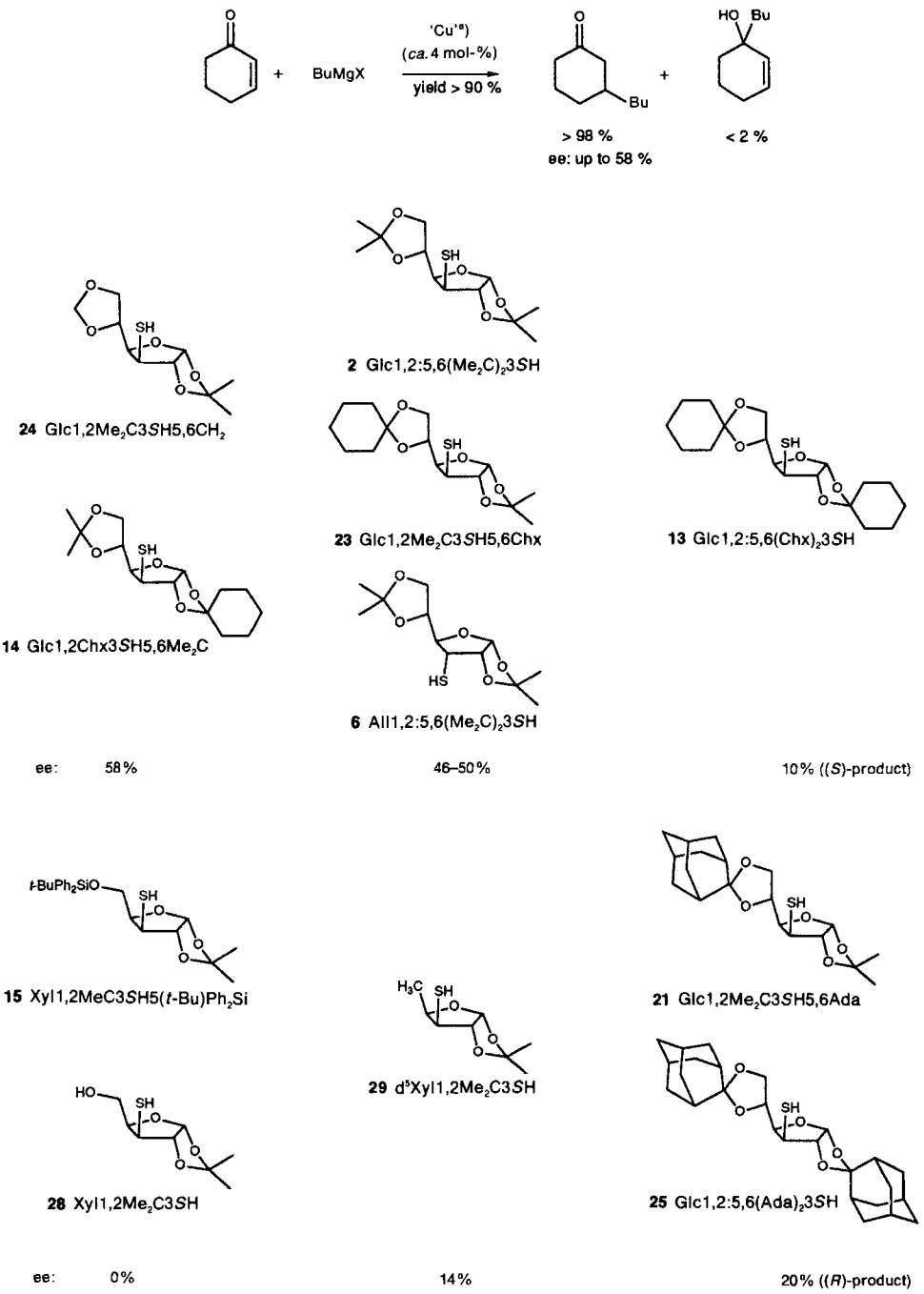


26 Xyl1,2Me$_2$C **30** Xyl1,2Me$_2$C5Tos **31** **32** d^{5}Rib1,2Me$_2$C **29** d^{5}Xyl1,2Me$_2$C3*S*H

a) 1. TosCl, 4-(dimethylamino)pyridine. *b*) DMSO/Ac$_2$O. *c*) LiAlH$_4$. *d*) 1. Triflic anhydride, 2. KSCN, 3. NaBH$_4$.

Enantioselective Copper-Catalyzed 1,4-Addition of Grignard *Reagents to α,β-Unsaturated Carbonyl Compounds.* This reaction is one of the most important and versatile C–C bond formation reactions (for reviews, see [12]). Because of our encouraging progress on the enantioselective and catalytic performance of this reaction [13], we decided to use it to test our new concept for metal-catalyzed enantioselective synthesis. The reported optimized reaction conditions for the addition of BuMgCl to 2-cyclohex-2-en-1-one were applied [13], and good chemical yields (> 90%) and very good regioselectivities (1,4-product > 98%) were found with all ligands used. The enantioselectivity was very dependent on the ligand, and was up to 58% (*Fig. 6*).

Considering these results in respect of our concept the following can be stated. The variation of the enantioselectivities is small, especially between ligands in which only one protecting group is changed. Further, the change of the sugar skeleton from glucose to xylose results in an unexpected decrease of the enantioselectivity. Nevertheless, if only the ligands which are derivatives of glucose are considered, it can be seen that there is some evidence that our concept is working. Thus, better or equivalent enantioselectivities are



[a]) 'Cu': [Cu(PBu$_3$)]I + 3 BuLi + 0.7 Tempo˙ + thiosugar

Fig. 6. *Test reaction and enantioselectivities found*[2])

found for each small/large combination of protecting groups compared to the appropriate large/large combination.

In a more general way, the results show that the groups on the central five-membered ring have to be of a certain size to reach an optimal enantioselectivity. Unfortunately, no correlation between the observed enantioselectivity and the 1,4-selectivity of the reaction is found. The 1,4-selectivities are equal for all of the ligands tested. This means that, in all cases, product formation proceeds *via* a copper-catalyzed process independent of the size of the ligand. A possible explanation for this could be: the larger the protecting groups, the greater is the amount of ligand-free copper in the reaction system, and the more readily the reaction proceeds *via* achiral ligand-free copper compounds. This means the amount of racemate formed becomes larger and the enantioselectivity correspondingly decreases.

The interpretation of the results obtained is rather difficult because of the superposition of at least two problems, unknown ligand geometry in the transition state and unknown reaction mechanism. One of these problems could be solved by the use of a stair-like ligand with a fixed geometry.

Conclusions. – A new class of ligands for the metal-catalyzed enantioselective synthesis was prepared by the use of protected 3-thio-α-D-glucofuranoses and 3-thio-α-D-xylofuranoses. These thiosugar derivatives are very suitable ligands for soft metal centres such as Pd or Cu. The protecting groups in the thiosugars were chosen so that a range of ligands useful for the examination of a new concept for the metal-catalyzed enantioselective synthesis was obtained. As the result of this investigation was not very clear, further work has to be done in this area.

The new class of ligands were tested in the copper-catalyzed 1,4-addition of *Grignard* reagents to α,β-unsaturated carbonyl compounds, and enantioselectivities of up to 58% were found, which represents one of the highest levels obtained for the catalytic version of this reaction.

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Experimental Part

General. All catalytic reactions were carried out using standard *Schlenk* techniques under Ar. Et_2O was dried over Na/benzophenone and distilled before use. BuLi and (*R,R*)-butane-2,3-diol were used as received from *Fluka*, while cyclohex-2-en-1-one (*Fluka*) was distilled before use. BuMgCl was a 2M soln. in Et_2O from *Aldrich*. Xyl1,2Me_2C5(*t*-Bu)Ph_2Si was prepared as described in [14] and All1,2:5,6(Me_2C)$_2$3*S*H (**6**) as described in [8]. TLC: LC plastic sheets of silica gel *60* F_{254} (layer thickness 0.2 mm) from *Merck*; detection with phosphomolybdic acid soln. (25 g of phosphomolybdic acid, 10 g of $Ce(SO_4)_2 \cdot 4H_2O$ and 10 ml of conc. H_2SO_4 soln. in 1 l of H_2O). Flash chromatography [14] (FC): silica gel *60* (particle size 0.035–0.070; 220–440 mesh ASTM) from *Fluka*. M.p.: open capillary; not corrected. IR Spectra: *Perkin-Elmer-883* spectrometer; KBr pellets or neat; range, 4000–200 cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker*-250-MHz instrument; in $CDCl_3$; see *Tables 3–5*. Microanalyses (*Table 6*) were performed at the micro elemental analytical laboratory of the Institute of Organic Chemistry at the ETH-Zürich.

*1,2-*O*-Cyclohexylidene-5,6-*O*-isopropylidene-α-*D*-glucofuranose* (Glc1,2Chx5,6Me_2C). A soln. of 2.0 g (5.88 mmol) of Glc1,2:5,6(Chx)$_2$ in 50 ml of acetone containing 3 drops of conc. H_2SO_4 soln. was stirred for 24 h at r.t. It was then neutralized with solid Na_2CO_3 and evaporated. The residue was dissolved in H_2O, the product extracted with Et_2O, the org. phase dried ($MgSO_4$) and evaporated, and the crude product recrystallized from Et_2O/hexane: 1.05 g (57%) of Glc1,2Chx5,6Me_2C. M.p. 125°.

Table 3. *^{1}H-NMR Chemical Shifts* (ppm] *and*

Compound	Nr.	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H′–C(6)	OH or SH
Glc1,2:5,6(Chx)$_2$		5.94 (*d*)	4.51 (*d*)		4.05 (*dd*)		3.95 (*dd*)	4.15 (*dd*)	2.64 (*d*)
Glc1,2Chx5,6Me$_2$C		5.94 (*d*)	4.52 (*d*)		4.07 (*dd*)		3.97 (*dd*)	4.17 (*dd*)	2.51 (*d*)
All1,2:5,6(Chx)$_2$	**7**	5.81 (*d*)	4.60 (*dd*)			4.29 (*m*)	3.79 (*dd*)	3.98 (*dd*)	2.57 (*d*)
All1,2Chx5,6Me$_2$C	**8**	5.82 (*d*)	4.59 (*dd*)			4.33 (*dt*)	3.79 (*dd*)		2.56 (*d*)
Glc1,2Me$_2$C3*S*CN5,6CH$_2$	**17**	6.01 (*d*)	4.95 (*d*)	3.81 (*d*)	4.25 (*dd*)	4.18 (*dt*)	4.03 (*d*)	4.03 (*d*)	
Glc1,2:5,6(Me$_2$C)$_2$3*S*CN	**5**	6.00 (*d*)	4.94 (*d*)	3.80 (*d*)		4.00 (*m*)			
Glc1,2Me$_2$C3*S*CN5,6Chx	**16**	5.99 (*d*)	4.93 (*d*)	3.81 (*d*)		3.97 (*m*)			
Glc1,2Chx3*S*CN5,6Me$_2$C	**11**	6.01 (*d*)	4.93 (*d*)	3.82 (*d*)	4.25 (*dd*)	3.99 (*m*)			
Glc1,2:5,6(Chx)$_2$3*S*CN	**10**	5.99 (*d*)	4.91 (*d*)	3.82 (*d*)		3.96 (*m*)			
Glc1,2Me$_2$C3*S*CN5,6Ada	**19**	5.99 (*d*)	4.93 (*d*)	3.82 (*d*)		3.96 (*m*)			
Glc1,2:5,6(Ada)$_2$3*S*CN	**20**	6.00 (*d*)	4.91 (*d*)	3.80 (*d*)		3.92 (*m*)			
Glc1,2Me$_2$C3*S*CN5,6(CH$_2$OCH$_2$)	**18**	6.00 (*d*)		3.84 (*d*)	4.30 (*dd*)	3.91 (*ddd*)	4.22 (*dd*)	3.68 (*dd*)	
Glc1,2Me$_2$C3*S*H5,6CH$_2$	**24**	5.88 (*d*)	4.64 (*d*)	3.55 (*dd*)	4.18 (*dd*)	4.31 (*dt*)	4.01 (*d*)	4.01 (*d*)	1.51 (*d*)
Glc1,2:5,6(Me$_2$C)$_2$3*S*H	**2**	5.79 (*d*)	4.55 (*d*)	3.46 (*dd*)	4.09 (*dd*)	4.25 (*ddd*)	3.92 (*dd*)	3.92 (*dd*)	1.47 (*d*)
Glc1,2Me$_2$C3*S*H5,6Chx	**23**	5.87 (*d*)	4.62 (*d*)	3.56 (*dd*)	4.16 (*dd*)	4.33 (*ddd*)	4.13 (*dd*)	3.98 (*dd*)	
Glc1,2Chx3*S*H5,6Me$_2$C	**14**	5.87 (*d*)	4.61 (*d*)	3.55(*dd*)	4.17 (*dd*)	4.34 (*ddd*)	4.15 (*dd*)	4.00 (*dd*)	
Glc1,2:5,6(Chx)$_2$3*S*H	**13**	5.87 (*d*)	4.60 (*d*)	3.57 (*dd*)	4.15 (*dd*)	4.33 (*ddd*)	3.98 (*dd*)	4.12 (*dd*)	
Glc1,2Me$_2$C3*S*H5,6Ada	**21**	5.83 (*d*)	4.56 (*d*)	3.53 (*dd*)		4.30 (*m*)		3.92 (*dd*)	
Glc1,2:5,6(Ada)$_2$3*S*H	**25**	5.89 (*d*)	4.58 (*d*)	3.60 (*dd*)		4.33 (*m*)		3.96 (*dd*)	

[a]) H–C(6) and H′–C(6) are isochronous.

Table 4. *^{1}H-NMR Chemical Shifts* [ppm] *and*

Compound	Nr.	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H′–C(5)	OH or SH
Xyl1,2Me$_2$C5Tos	**30**	5.88 (*d*)	4.52 (*d*)					2.22 (*d*)
d^{5}Rib1,2Me$_2$C	**32**	5.79 (*d*)	4.54 (*dd*)	3.50 (*ddd*)	3.81 (*dq*)			2.25 (*d*)
Rib1,2Me$_2$C5(*t*-Bu)Ph$_2$Si	**9**	5.84 (*d*)						2.29 (*d*)
d^{5}Xyl1,2Me$_2$C3*S*CN	**33**	5.96 (*d*)	4.90 (*d*)	3.75 (*d*)	4.60 (*dq*)			
Xyl1,2Me$_2$C3*S*CN5(*t*-Bu)Ph$_2$Si	**12**	6.00 (*d*)	4.93 (*d*)	3.94 (*d*)	4.48 (*m*)	3.80 (*dd*)	3.94 (*m*)	
d^{5}Xyl1,2Me$_2$C3*S*H	**29**	5.86 (*d*)	4.67 (*d*)	3.27 (*dd*)	4.51 (*dq*)			1.30 (*d*)
Xyl1,2Me$_2$C3*S*H	**28**	5.92 (*d*)	4.65 (*d*)	3.40 (*dd*)	4.48 (*ddd*)	3.89 (*dd*)	3.83 (*dd*)	1.46 (*d*)
Xyl1,2Me$_2$C3*S*H5(*t*-Bu)Ph$_2$Si	**15**	5.88 (*d*)	4.63 (*d*)	3.51 (*dd*)	4.44 (*ddd*)	3.89 (*dd*)	3.95 (*dd*)	1.42 (*d*)

[a]) $J(4,5) = J(4,\text{Me})$.

Coupling Constants J [Hz] *for the Glucose Derivatives*[2])

Other data	$J(1,2)$	$J(2,3)$	$J(3,4)$	$J(4,5)$	$J(5,6)$	$J(5,6')$	$J(6,6')$	$J(OH,3)$	$J(SH,3)$
4.43–4.29 (*m*, H–C(3), H–C(5)); 1.70–1.34 (*m*, Chx)	3.6		2.7	7.4	5.4	6.1	8.6	3.4	
4.38–4.30 (*m*, H–C(3), H–C(5)); 1.73–1.24 (*m*, Chx); 1.44, 1.36 (2*s*, Me)	3.6		2.8	7.5	5.5	6.2	8.6	3.6	
4.10–4.03 (*m*, H–C(3), H–C(4)); 1.80–1.31 (*m*, Chx)	3.8	5.2		4.6	4.6	6.7	8.5	8.3	
4.10–3.98 (*m*, H–C(3), H–C(4), H–C(6)); 1.80–1.20 (*m*, Chx); 1.46, 1.38 (2*s*, Me)	3.9	5.3			4.4		8.5	10.0	
5.88, 4.83 (2*s*, CH_2); 1.53, 1.35 (2*s*, Me)	3.7		3.5	8.5	4.5	4.5	[a])		
4.27–4.13 (*m*, H–C(4), 2 H–C(6)); 1.53, 1.43, 1.35, 1.34 (4*s*, Me)	3.6		3.4						
4.26–4.12 (*m*, H–C(4), 2 H–C(6)); 1.9–1.34 (*m*, Chx); 1.53, 1.34 (2*s*, Me)	3.6		3.4						
4.21–4.13 (*m*, 2 H–C(6)); 1.76–0.85 (*m*, Chx, Me)	3.6		3.5	9.0					
4.24–4.10 (*m*, H–C(4), 2 H–C(6)); 1.72–1.39 (*m*, Chx)	3.6		3.3						
4.27–4.13 (*m*, H–C(4), 2 H–C(6)); 2.11–1.67 (*m*, Ada); 1.53, 1.34 (2*s*, Me)	3.6		3.3						
4.24–4.11 (*m*, H–C(4), 2 H–C(6)); 2.50–1.22 (*m*, Ada)	3.6		3.3						
5.10–4.83 (*m*, 2 CH_2, H–C(2)); 1.51, 1.34 (2*s*, Me)	3.6		3.7	9.2	8.2	2.0	12.5		
5.05, 4.84 (2*s*, CH_2); 1.51, 1.31 (2*s*, Me)	3.7		3.7	8.7	5.6	5.6	[a])		8.7
1.43, 1.34, 1.28, 1.22 (4*s*, Me)	3.4		3.6	8.8	5.6	4.6	8.8		8.3
1.61–1.17 (*m*, SH, Chx); 1.51, 1.30 (2*s*, Me)	3.5		3.7	8.8	5.8	4.7	8.6		8.0
1.7–0.8 (*m*, SH, Chx); 1.42, 1.36 (2*s*, Me)	3.5		3.6	8.8	6.0	4.8	8.7		8.7
1.71–0.84 (*m*, SH, Chx)	3.4		3.4	8.8	4.8	6.0	8.6		8.0
4.11 (*m*, H–C(4), H′–C(6)); 2.0–1.52 (*m*, SH, Ada); 1.47, 1.27 (2*s*, Me)	3.5		3.6			4.9	8.6		7.5
4.13 (*m*, H–C(4), H′–C(6)); 2.05–1.51 (*m*, SH, Ada)	3.5		3.7			5.0	8.6		7.6

Coupling Constants J [Hz] *for the Xylose Derivatives*[2])

Other data	$J(1,2)$	$J(2,3)$	$J(3,4)$	$J(4,5)$	$J(4,5')$	$J(5,5')$	$J(3,OH)$	$J(3,SH)$
7.82–7.34 (MeC_6H_4); 4.35–4.08 (H–C(3), H–C(4), 2 H–C(5)); 2.45 (MeC_6H_4); 1.46, 1.30 (Me)	3.5						5.0	
1.56, 1.36 (Me); 1.33 (Me(5))	4.0	5.1	8.8	6.1			11.0	
7.72–7.67, 7.45–7.24 (arom. H); 4.19–4.08, 4.00–3.81 (H–C(3), H–C(4), 2 H–C(5)); 1.55, 1.38 (Me); 1.04 (*t*-Bu)	3.9	5.0					10.0	
1.38 (Me(5)); 1.52, 1.34 (Me)	3.8		3.6	6.3[a])				
7.73–7.23 (arom. H); 1.51, 1.35 (Me); 1.06 (*t*-Bu)	3.6		4.1	7.0		4.1	11.0	
1.34 (Me(5)); 1.51, 1.30 (Me)	3.7		3.8	6.3[a])				9.2
2.08 (OH); 1.51, 1.30 (Me)	3.5		4.0	6.6	5.3	11.8		9.6
7.75–7.25 (arom. H); 1.51, 1.32 (Me); 1.07 (*t*-Bu)	3.6		3.8	7.3	5.5	10.4		8.8

Table 5. *^{13}C-NMR Chemical Shifts for the Thiosugar Derivatives*[2])

Compound	Nr.	C(1)	C(3)	C(2), C(4), C(5)	C(6) or C(5)	Acetal-C's	Other data
Glc1,2Me$_2$C3*S*H5,6CH$_2$	**24**	104.6	45.2	87.6, 79.5, 73.5	68.3	112.1	95.3 (CH$_2$); 26.5, 26.18 (Me)
Glc1,2:5,6(Me$_2$C)$_2$3*S*H	**2**	104.8	45.4	87.7, 80.3, 74.1	67.8	112.2, 109.6	27.0, 26.7, 26.4, 25.3 (Me)
Glc1,2Me$_2$C3*S*H5,6Chx	**23**	104.7	45.4	87.3, 80.3, 73.7	67.4	112.1, 110.0	36.6, 34.6; 26.6, 26.2 (Me); 25.9, 24.0, 23.8
Glc1,2Chx3*S*H5,6Me$_2$C	**14**	104.3	45.5	87.1, 80.0, 74.2	67.4	112.8, 109.4	36.2, 35.7; 26.9, 25.2 (Me); 24.8, 23.8, 23.5
Glc1,2:5,6(Chx)$_2$3*S*H	**13**	104.4	45.4	86.9, 80.3, 73.4	67.7	112.8, 110.0	36.6, 36.1, 35.7, 34.6, 25.1, 24.9, 24.1, 23.9, 23.6
Glc1,2Me$_2$C3*S*H5,6Ada	**21**	104.8	45.5	87.1, 80.5, 73.8	67.5	112.3, 112.0	38.1, 37.0, 35.8, 35.0, 34.9, 34.7, 34.6, 26.9, 26.8, 26.6, 26.2
Glc1,2:5,6(Ada)$_2$3*S*H	**25**	104.4	45.8	86.6, 80.5, 73.8	67.6	115.3, 112.3	38.1, 37.7, 37.0, 37.0, 36.8, 35.7, 35.1, 35.0, 34.9, 34.7, 34.6, 34.31, 26.8, 26.6, 26.0
d^{5}Xyl1,2Me$_2$C3*S*H	**29**	103.9	47.6	88.3, 74.4		111.2	26.3, 26.1, 15.7 (Me)
Xyl1,2Me$_2$C3SH	**28**	104.4	44.6	88.4, 79.1	62.4	112.1	26.6, 26.3 (Me)
Xyl1,2Me$_2$C3*S*H5(*t*-Bu)Ph$_2$Si	**15**	104.5	45.2	87.6, 76.5	62.6	111.9	135.6, 135.5, 134.8, 133.2, 129.8, 129.6, 127.7 (Ar); 26.8, 26.6, 26.5, 26.3 (Me); 19.2

Table 6. *Microanalyses of the Sugar Derivatives*[2])

Compound	Nr.	Calc. [%]				Found [%]			
		C	H	N	S	C	H	N	S
Glc1,2:5,6(Chx)$_2$		63.51	8.29			63.38	8.51		
Glc1,2Chx5,6Me$_2$C		59.98	8.05			60.03	8.11		
All1,2:5,6(Chx)$_2$	7	63.51	8.29			62.97	7.51		
All1,2Chx5,6Me$_2$C	**8**	59.98	8.05			60.03	8.27		
Glc1,2Me$_2$C3*S*CN5,6CH$_2$	**17**	48.34	5.53	5.12	11.73	48.37	5.64	4.88	11.70
Glc1,2Me$_2$C3*S*CN5,6Chx	**16**	56.29	6.79	4.10	9.39	56.83	7.03	3.83	9.13
Glc1,2Chx3*S*CN5,6Me$_2$C	**11**	56.29	6.79	4.10	9.39	55.92	6.25	4.11	9.32
Glc1,2:5,6(Chx)$_2$3*S*CN	**10**	59.82	7.13	3.67	8.41	59.56	7.12	3.56	8.63
Glc1,2:5,6(Ada)$_2$3*S*CN	**20**	66.80	7.21	2.88		67.25	7.80	2.09	
Glc1,2Me$_2$C3*S*H5,6CH$_2$	**24**	48.37	6.49		12.91	48.57	6.64		11.77
Glc1,2Me$_2$C3*S*H5,6Chx	**23**	56.94	7.65		10.13	57.13	7.74		10.16
Glc1,2Chx3*S*H5,6Me$_2$C	**14**	56.94	7.65		10.13	56.90	7.81		10.18
Glc1,2:5,6(Chx)$_2$3*S*H	**13**	60.65	7.92		9.00	60.66	8.24		8.78
Glc1,2Me$_2$C3*S*H5,6Ada	**21**	61.93	7.66		8.70	61.74	7.49		8.49
Glc1,2:5,6(Ada)$_2$3*S*H	**25**	67.82	7.82		6.95	67.63	8.21		6.31
Xyl1,2Me$_2$C5Tos	**30**	52.31	5.85			52.18	5.88		
d^{5}Rib1,2Me$_2$C	**32**	55.17	8.04			54.70	7.75		
Rib1,2Me$_2$C5(*t*-Bu)Ph$_2$Si	**9**	67.26	7.53			67.00	7.66		
d^{5}Xyl1,2Me$_2$C3*S*CN	**33**	50.21	6.09	6.51	14.90	50.29	6.12	6.39	14.90
Xyl1,2Me$_2$C3*S*CN5(*t*-Bu)Ph$_2$Si	**12**	63.96	6.60	2.98		64.68	6.85	2.45	
d^{5}Xyl1,2Me$_2$C3*S*H	**29**	50.50	7.42		16.85	50.54	7.44		16.57
Xyl1,2Me$_2$C3*S*H	**28**	46.59	6.84		15.55	46.29	6.72		15.37
Xyl1,2Me$_2$C3*S*H5(*t*-Bu)Ph$_2$Si	**15**	64.83	7.25		7.21	65.41	7.48		6.27

1,2-O-Isopropylidene-5-O-tosyl-α-D-xylofuranose [16] (Xyl1,2Me$_2$C5Tos; **30**). A soln. of 5.0 g (26.2 mmol) of Xyl1,2Me$_2$C (**26**) and 3.21 g (26.2 mmol) of 4-(dimethylamino)pyridine in 50 ml of pyridine was treated at r.t. with 5.52 g (28.9 mmol) of TsCl. The resulting soln. was stirred for 7 h at r.t., and then extracted with sat. Na_2CO_3 soln. and AcOEt. The org. phase was dried ($MgSO_4$) and evaporated and the resulting oil purified by FC (hexane/AcOEt 1:1): 6.53 g (72%) of **30**. M.p. 130°.

1,2-O-Isopropylidene-5-deoxy-α-D-ribofuranose [17] (d^{5}Rib1,2Me$_2$C; **32**). A mixture of 40 ml of DMSO and 30 ml of Ac_2O was treated with 6.55 g (19.4 mmol) of **30** and stirred at r.t. for 36 h. Evaporation at *ca.* 40°/high vacuum gave an oil which was dissolved in 250 ml of dry Et_2O and treated with 1.41 g (36.8 mmol) of $LiAlH_4$. After

stirring overnight at r.t., excess $LiAlH_4$ was destroyed, first with AcOEt and then with H_2O. The aq. phase was extracted twice with Et_2O, the combined Et_2O phase dried ($MgSO_4$) and evaporated, and the resulting oil purified by FC (hexane/AcOEt 1:1): 1.03 g (30%) of **32**.

General Procedure for the Transformation of Glucoses to Alloses. The procedure of [18] was used in a slightly modified way. After the reduction of the ketone with $NaBH_4$, the reaction soln. was hydrolyzed with a small amount of AcOH and the EtOH evaporated. The resulting mixture was extracted with H_2O/AcOEt. The org. phase was dried ($MgSO_4$) and evaporated. For purification, yield, and melting points, see *Table 1*.

General Procedure for the Transformation of Alloses or Riboses to Triflates. The procedure of [19] was used in a slightly modified way. The crude product was extracted with petroleum ether (30–60°), and the solids were filtered off. The combined extracts were evaporated and used immediately without any further purification (the triflate decomposed slowly).

General Procedure for the Transformation of Triflates to Thiocyanates. The procedure of [8] was used in a slightly modified way. After workup, only Glc1,2Chx3*S*CN5,6Me_2C (**11**) could be crystallized. The other thiocyanates were used without any further purification. The crude yield was *ca.* 90% for each. Samples of each thiocyanate were purified by FC for characterization (*Table 1*).

3-S-Cyano-1,2-O-isopropylidene-5,6-O-methylidene-3-thio-α-D-glucofuranose (Glc1,2Me_2C3*S*CN5,6CH_2; **17**). A suspension of 6.72 g (22.2 mmol) of Glc1,2:5,6(Me_2C)$_2$3*S*CN (**5**), 13.0 g (144 mmol) of paraformaldehyde, and 5 g of *Amberlyst 15* in 80 ml of Et_2O was stirred at r.t. overnight. The solid was filtered off and washed 3 times with Et_2O. The resulting soln. was evaporated. TLC (hexane/AcOEt 3:1): R_f 0.33 (**18**), 0.36 (**17**), 0.45 (not identified), 0.50 (not identified). Only **17** (1.6 g, 26%) could be isolated in pure form by FC. IR: 2155*s*, 2103*w* (SCN).

3-S-Cyano-5,6-O-cyclohexylidene-1,2-O-isopropylidene-3-thio-α-D-glucofuranose (Glc1,2Me_2C3*S*CN5,6Chx; **16**). Two to five mg's of $[Rh(MeCN)_3\{MeC(CH_2PPh_2)_3\}](CF_3SO_3)_3$ [10] were added to a soln. of 1.92 g (6.31 mmol) of **5** and 1.9 g (19.3 mmol) of cyclohexanone in 20 ml of toluene. The resulting soln. was heated to 90° and the reaction followed by GC. After *ca.* 3 h (no **5** left), the soln. was evaporated and the resulting oil used without any further purification (^{1}H-NMR: only signals of **16** and cyclohexanone). A sample of *ca.* 200 mg was purified by FC. IR: 2154*s* (SCN).

5,6-O-(Adamantan-2-ylidene)-3-S-cyano-1,2-O-isopropylidene-3-thio-α-D-glucofuranose (Glc1,2Me_2C3*S*CN-5,6Ada; **19**). A suspension of 2.5 g (16.2 mmol) of adamantan-2-one, 1.2 g (4 mmol) of **5**, and 1 g of *Amberlyst 15* in 50 ml of toluene was refluxed for 3 h. Then *Amberlyst 15* was filtered off and washed 3 times with toluene. The combined filtrate was evaporated. Excess adamantan-2-one could not be separated from the product by FC or recrystallisation. ^{1}H-NMR: estimated yield of **19**, *ca.* 60%.

1,2:5,6-Di-O-(adamantan-2-ylidene)-3-S-cyano-3-thio-α-D-glucofuranose (Glc1,2:5,6(Ada)$_2$3*S*CN; **20**). As described for **19**, with 2.5 g (16.2 mmol) of adamantan-2-one, 1.2 g (4 mmol) of **5**, 1 g of *Amberlyst 15*, and 50 ml of toluene (reflux for 4 d). FC (hexane/AcOEt 4:1) gave 1.55 g (80%) of **20**. M.p. 102°. IR: 2152*s* (SCN).

3-S-Cyano-1,2-O-isopropylidene-3-thio-α-D-xylo-pentodialdo-1,4-furanose (Xyl1,2Me_2C3*S*CN5CHO; **27**). A soln. of 540 mg (2.61 mmol) of 3-*S*-cyano-1,2-*O*-isopropylidene-3-thio-α-D-glucofuranose [8] in 50 ml of MeOH was treated with a soln. of 560 mg (2.66 mmol) of $NaIO_4$ in *ca.* 2 ml of MeOH. It was stirred for 30 min at r.t. (→precipitate). The precipitate was filtered off and washed 3 times with acetone, the combined filtrate evaporated, and the resulting oil used without any further purification.

General Procedure for the Transformation of Thiocyanates to Thiols. A soln. of the thiocyanate in the appropriate solvent (*ca.* 100 ml/g thiocyanate, see *Table 2*) was treated with a *ca.* 7-fold excess of $NaBH_4$. The mixture was stirred for *ca.* 1 h at r.t. and then hydrolyzed with a small amount of AcOH. The EtOH was evaporated and the resulting mixture extracted with H_2O/AcOEt. The org. phase was dried ($MgSO_4$) and evaporated. For purification, yield, and melting points, see *Table 2*.

Typical Catalytic-Reaction Procedure. At r.t., 0.52 ml (0.088 mmol) of a 0.169 mM soln. of Glc1,2Me_2C3*S*H5,6CH_2 in Et_2O were added to a soln. of 34 mg (0.022 mmol) of tetrakis[iodo(tributylphosphine)copper(I)] [20] and 10 mg (0.064 mmol) of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (Tempo•) in 10 ml of Et_2O at r.t. The resulting soln. was cooled to −78°, 1.6M BuLi in hexane (0.17 ml, 0.27 mmol) added, and the resulting soln. stirred for 10 min at −78°. Two Et_2O solns. (8 ml each), one containing cyclohex-2-en-1-one (225 mg, 2.3 mmol) and the other containing BuMgCl (2.3 mmol), were added simultaneously *via* a syringe pump over 13 min. After the addition was complete, the mixture was quenched with sat. NH_4Cl soln. (*ca.* 15 ml). Then 30 µl of mesitylene (internal standard for GC analysis) were added. A sample of the org. layer was filtered through neutral Al_2O_3 and used for GC analysis (80–250°, 20° min; yield 92%). The org. phase of the remainder of the mixture was dried ($MgSO_4$) and evaporated and the crude product used for the determination of the enantiomeric excess (ee). With **24**, the ee was 58%.

*Determination of the Enantiomeric Excess by Acetalisation of 3-Butylcyclohexan-1-one with (*R,R*)-pentane-2,4-diol.* A suspension of 10 µl of 3-butylcyclohexan-1-one, 20 mg (0.2 mmol) of (*R,R*)-pentane-2,4-diol, 50 mg *Amberlyst 15* (activated at 130°), and 1 g of molecular sieves (*Union Carbide*, type 3 Å, activated at 250°/high vacuum) in 15 ml of Et_2O was stirred at r.t. overnight. The solids were separated by centrifugation, and the resulting soln. was used for the determination of the ee by GC (150°, isotherm). Traces of the starting material were found only.

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