New Chiral N,S-Ligands Based on Oxazoline−Thioglucose Donors. Palladium(II)-Catalyzed Enantioselective Allylic Alkylation

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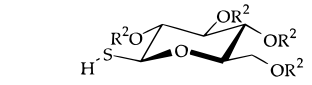
New bidentate ligands containing both chiral oxazoline and thiosugar elements, and also their 1,3-diphenylallyl Pd(II) complexes, have been prepared. The sugar is based on a 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranose moiety. These *N*,*S*-oxazoline−thioglucose ligands afford excellent ee's (90.2−96.9%) in the model enantioselective allylic alkylation reaction involving a 1,3-diphenylallyl precursor. ^{1}H and ^{13}C NMR spectra for the Pd compounds show that they exist in solution as a mixture of (syn/syn) exo and endo diastereomeric complexes. It is suggested that attack of the dimethyl malonate nucleophile pseudo-trans to the thioether donor is preferred for electronic reasons, whereas selective attack on the endo diastereomer, as opposed to the exo isomer, arises due to steric effects in combination with allyl rotation. The organic product is formed by preferential reaction of a minor component. Since the exo and endo isomers are shown to be in equilibrium, via 2-D exchange spectroscopy, the depleted endo diastereomer can be rapidly replaced.

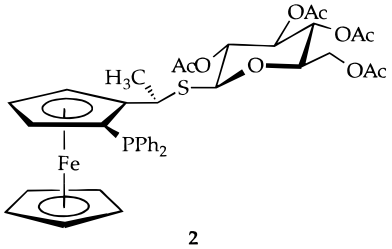
Introduction

There have been an increasing number of chiral auxiliaries for homogeneous catalysis. Although many of these contain tertiary phosphine donors,[1] there are several very successful chiral bidentate ligands based on nitrogen donors, with the bis(oxazoline) class pioneered by Pfaltz and co-workers among the best known.[2] There is relatively little reported with respect to chiral chelating ligands based on thioether and/or arene sulfur donors, with those developed by Williams[3] as notable exceptions.

We have become interested in using the thioglucose **1** as a source from which to prepare mixed-ligand donors.[4−6] This has led us to ligands **2**−**4**, which have been shown[4,5] to be good (but not excellent) auxiliaries for reaction 1, the enantioselective allylic alkylation of PhCH(OAc)CH=CHPh with the anion of dimethyl malonate.



1a R^2 = COMe, **1b** R^2 CO(t-Bu)



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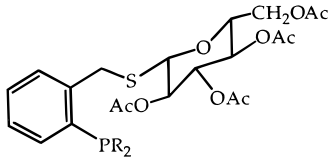

3, R = Ph **4**, R = Cy

$$\mathrm{PhCH(OAc)CH{=}CHPh} + \mathrm{CH(CO_2Me)_2^-} \xrightarrow{\text{chiral catalyst}} \mathrm{PhC^*H\{CH(CO_2Me)_2\}CH{=}CHPh} + \mathrm{OAc^-} \quad (1)$$

Interestingly, the ferrocene−phosphino−thiosugar bidentate species **2** afforded an enantiomeric excess (ee) of ca. 88%,[5] in this allylic alkylation using a dimethyl malonate anion. Moreover, X-ray diffraction[5] studies on its 1,3-diphenylallyl Pd complex, [Pd(η^3-PhCH-CHCHPh)(**2**)]CF_3SO_3, revealed an allyl moiety which was strongly rotated with respect to the P−Pd−S coord-

(1) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994. Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 6, 395. Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, Germany, 1993; p 325. Reiser, O. *Angew. Chem.* **1993**, *105*, 576. Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143. Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.

(2) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1.

(3) Williams, J. M. J. *Synlett* **1996**, 705. Frost, C. G.; Williams, J. M. J.; *Tetrahedron Lett.* **1993**, *34*, 2015.

(4) Barbaro, P.; Currao, A.; Herrmann, J.; Nesper, R.; Pregosin, P. S.; Salzmann, R. *Organometallics* **1996**, *15*, 1879.

(5) Albinati, A.; Pregosin, P. S.; Wick, K. *Organometallics* **1996**, *15*, 2419.

(6) Tschoerner, M.; Trabesinger, G.; Albinati, A.; Pregosin, P. S. *Organometallics* **1997**, *16* , 3447.

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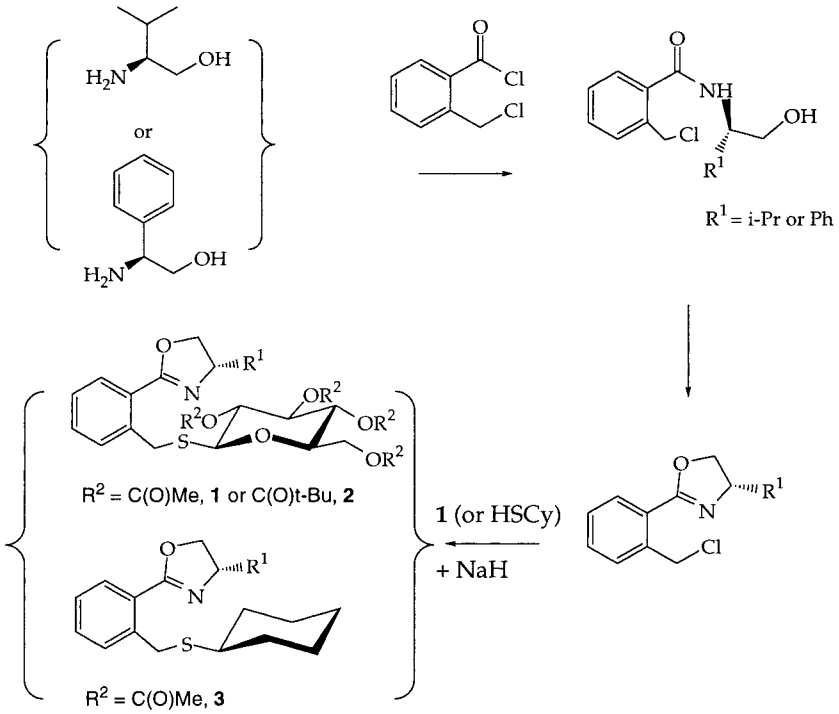
Scheme 1. Preparation of the Ligands



5, R^1 = i-Pr, R^2 = C(O)Me

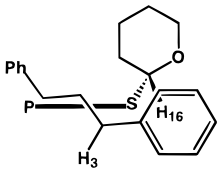
6, R^1 = i-Pr, R^2 = C(O)(t-Bu)

7, R^1 = Ph, R^2 = C(O)Me

8, R^1 = Ph, R^2 = C(O)(t-Bu)

9, R^1 = i-Pr, S-cyclohexyl complex

ination plane. This structural distortion, abbreviated as



abbreviated fragment of $[Pd(\eta^3\text{-PhCHCHCHPh})(\mathbf{2})]CF_3SO_3$

also exists in solution (based on NOE's and the marked anisotropic effect of the allyl aryl on H_{16})[7] and could be related to the allylation reaction coordinate, in that it was possible to predict the site of attack and thus the chirality of the organic product on the basis of the structure of the complex.

Analysis of X-ray structural data from diffraction studies[4,6,8] on P,S−Pd allyl complexes suggested that part of the problem might derive from the two fairly long M−L donor separations; e.g., both the Pd−P and Pd−S distances are usually >2.25 Å. These bond distances could lead to a more flexible (and thus less effective) chiral pocket. Consequently, it seemed reasonable to combine the thiosugar moiety with a fragment which would bring the entire chiral array closer to the substrate. To this end we have prepared several new ligands containing both chiral oxazoline (Pd−N typically ca. 2.1 Å[9,10]) and thiosugar elements, as well as their 1,3-diphenylallyl complexes, and report here on our preparative and catalytic results.

Results and Discussion

The new bidentate ligands **5**−**9** were prepared using standard methods. These reactions are shown in Scheme 1, and the details are given in the Experimental Section. The corresponding 1,3-diphenylallyl complexes were prepared from $[Pd(\mu\text{-Cl})(\eta^3\text{-PhCHCHCHPh})]_2$, as shown in Scheme 2. We have also synthesized several η^3-C_3H_5 complexes, and although these complexes will not be discussed, experimental details are provided.

Catalytic Results. The results from the catalytic experiments for the chemistry of eq 1, using the allyl

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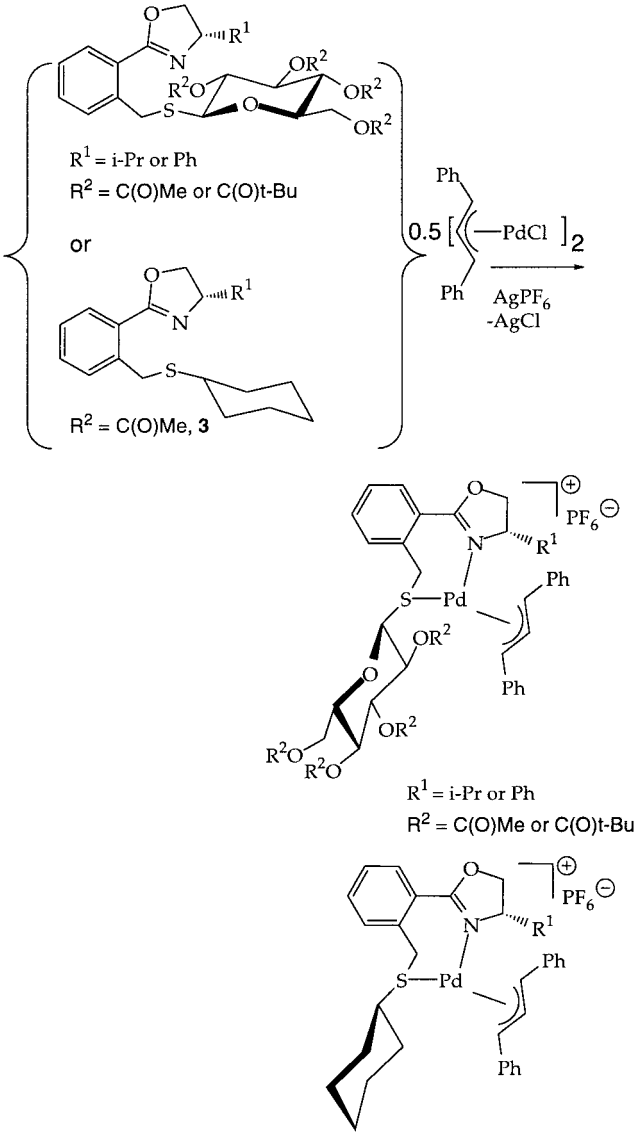
(10) Claridge, D. W.; Long, J. M. Brown, J. M.; Hibbs, D.; Hursthouse, M. B. *Tetrahedron* **1997**, *11* , 4035. Valk, J. M.; Claridge, D. W.; Brown, J. M.; Hibbs, D.; Hursthouse, M. B. *Tetrahedron: Asymmetry* **1995**, *6* , 2597. Bower, J. F.; Williams, J. *Synlett* **1996**, 685.

Scheme 2. Preparation of the 1,3-Diphenylallyl−Pd(II) Complexes



10, R^1 = i-Pr, R^2 = C(O)Me

11, R^1 = i-Pr, R^2 = C(O)(t-Bu)

12, R^1 = Ph, R^2 = C(O)Me

13, R^1 = Ph, R^2 = C(O)(t-Bu)

14, R^1 = i-Pr, S-cyclohexyl complex

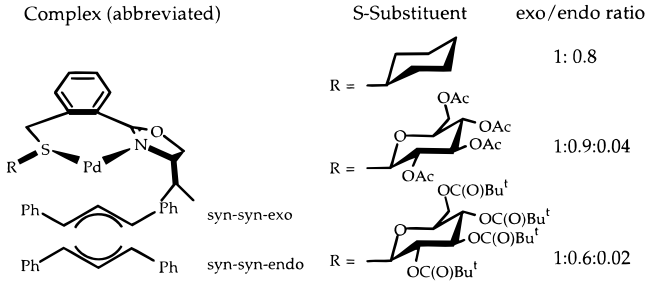
complexes **10**−**14** as precursors, are given in Table 1. It can be readily seen that *all four* of the *N*,*S*-oxazoline−thioglucose ligands result in excellent ee's (90.2−96.9%) with the *S* enantiomer predominating. The 96.9% result represents the best ee to date for an *N*,*S* ligand in allylic alkylation chemistry (although other donor combinations have achieved the same or even better[11−14]

Table 1. Data from the Pd-Catalyzed Allylic Alkylation of *rac*-1,3-Diphenylallyl Acetate with Dimethyl Malonate[a]

expt no.	time (h)[b]	precursor	yield (%)	ee[c] (%)
1	23	**14**	75	75.4 (*S*)
2	72	**10**	99	93.0 (*S*)
3	96	**11**	40	96.9 (*S*)
4	7	**12**	99	90.2 (*S*)
5	6	**13**	62	96.2 (*S*)

[a] Standard conditions: room temperature, 2 mol % *N*,*S*-complex precursor; CH_2Cl_2; room temperature; 2 equiv of dimethyl malonate; 2 equiv of BSA (*N*,*O*-bis(trimethylsilyl)acetamide); purification via chromatography (hexane/ethyl acetate, 5/1). [b] Time not optimized. [c] ee determined via HPLC (Chiralcel OD-H, hexane: ^{i}PrOH = 98:2, 0.5 mL/min).

Chart 1. Populations of the Diasteromeric Complexes[a]



[a] The structure of the third component was not determined. The endo isomer has the allyl Ph groups closer to the oxazoline i-Pr group.

results). The ee from **14**, with the *S*-cyclohexyl donor, ca. 75%, is much lower, indicating that the sugar moiety plays a role. It is worth noting that the ee values for the two pivaloyl derivatives are better than for the corresponding acetates, suggesting that the size of the substituent on the sulfur donor plays a small, but significant, role.

We believe that the *S* enantiomer arises due to preferential attack at the terminal allyl carbon pseudo-trans to the S donor in the syn/syn endo isomer. Assuming this to be correct, then the *S* enantiomer arises from attack at an allyl carbon from a minor, but not insignificant, component (*vide infra*). This point will be discussed in connection with the NMR.

NMR Spectroscopy. A discussion of the effectiveness of **10**−**14** requires some knowledge of their molecular structures. Unfortunately, for **10**−**14**, we have not been able to obtain crystals suitable for X-ray diffraction work. Consequently we turned to NMR spectroscopy to study the i-Pr complexes **10**, **11**, and (as model) **14**.

The ^{1}H NMR spectra for these three compounds show that they all exist in solution as a mixture of diastereomeric complexes in the ratios given in Chart 1. Figure 1 gives sections of the phase-sensitive NOESY spectra for **10**, **11**, and **14** at 293 K showing the central allyl proton H2. At this temperature the two major isomers in all three derivatives are in equilibrium (as indicated by the cross-peaks). As noted previously,[4,14−16] there is no correlation between the observed ee and the populations of the diastereomers in solution; however, since an equilibrium exists in all three derivatives, it is only

(11) Burckhardt, U.; Baumann, M.; Togni, A. *Tetrahedron: Asymmetry* **1997**, *8*, 155. Abbenhuis, H. C. L.; Burckhardt, U.; Gramlich, V.; Martelletti, A.; Spencer, J.; Steiner, I.; Togni, A. *Organometallics* **1996**, *15*, 1614. Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

(12) von Matt, Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T. Helmchen, G. *Tetrahedron: Asymmetry* **1994**, *5*, 573.

(13) Hayashi, T.; Yamane, M.; Ohno, A. *J. Org. Chem.* **1997**, *62*, 204.

(14) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493.

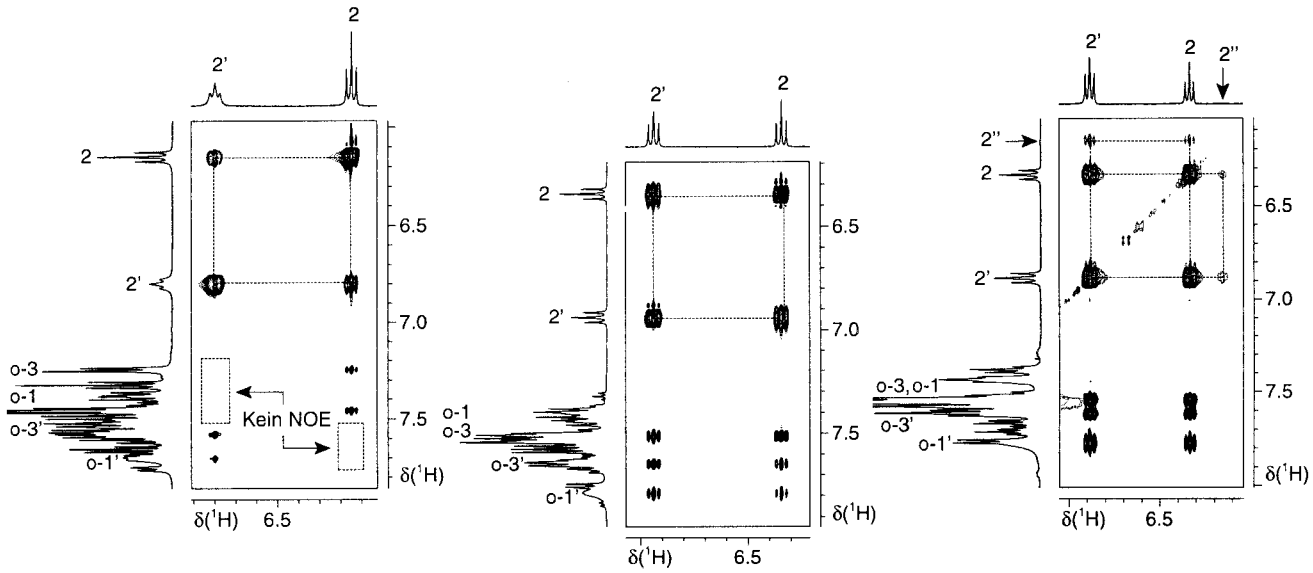
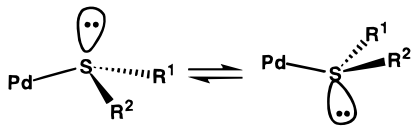


Figure 1. Sections of the NOESY spectra for **10**, **11**, and **14**. All three complexes show cross-peaks which arise due to exchange between the major diastereomers. The weaker cross-peaks stem from allyl−*o*-aryl interactions (500 MHz, mixing time 0.8 s, 293 K, CD_2Cl_2).

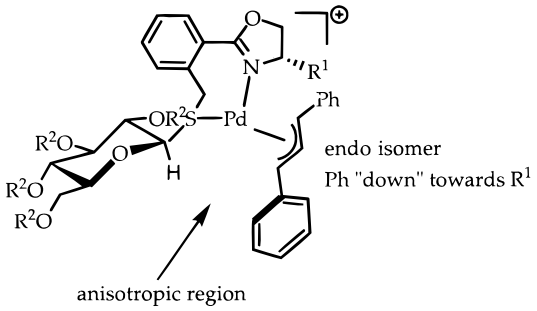
necessary for one of the diastereomers (including that which we have not properly characterized) to react considerably faster than the other(s) in order to explain the excellent enantioselectivity.

At 273 K (shown for **10** in Figure 2) the exchange is relatively slow, so that the cross-peaks reflect only the Overhauser effects. With these NOE data (and specifically the allyl anti/anti NOE's between the terminal protons[16] H1 and H3, one finds that the two major isomers both have the syn/syn structure with respect to the 1,3-diphenylallyl ligand. Consequently, we assign these two derivatives to the syn/syn exo and syn/syn endo structures, where exo and endo refer to the position of the central allyl proton with respect to the oxazoline i-Pr group (see Chart 1). The distinction between the endo and exo structures can be made using (a) NOE's from the oxazoline i-Pr group to the various allyl protons, as shown in Figure 3, and (b) anisotropic effects induced by the allyl phenyl groups; e.g., the ring oxazoline methine proton H13 appears at a relatively normal δ 3.67 in the exo isomer of **10** but at δ 2.52 in the endo isomer due to the proximate allyl Ph group. The analogous values for H13 in **11** are δ 3.65 and δ 2.48, respectively. Similar, but less pronounced, shift differences are also found for the i-Pr methyl protons (see Tables 2−4).

Relative Position of the Thiosugar Moiety. As the relative position of the thiosugar moiety is not defined, the shape of the chiral pocket offerred by our *N,S* auxiliaries remains uncertain. For phosphino−thioether complexes of Pd(II), e.g., **3**, our X-ray results[4,8] confirm a tendency for the S substituent to take up a pseudoaxial position; however, in solution it is generally known[17] that diastereomeric structures can arise due to inversion at the S center, i.e.



Regrettably, the NOE data do not allow us to unambiguously assign the position of the sugar ring with respect to the allyl ligand. However, several thiosugar proton chemical shifts are strongly influenced by the anisotropy arising from the allyl phenyl groups, and this provides a hint. In **10** the ^{1}H chemical shifts for the anomeric sugar protons H17, in the exo and endo isomers respectively, δ 4.14 and 1.97 (!), are markedly different. These data suggest that, at least for the endo



endo **10** showing H17, the anomeric proton, close to the Ph-group.

isomer, the sugar moiety and the i-Pr group are on the same side of the coordination plane defined by the S, Pd, and N atoms. This structural result is in agreement with the solid-state structure found for Pd(Cl)(Me)(**5**) (**15**; Me trans to N).[18] Complex **15** contains two modest-size donors apart from **5**, suggesting that the position

(15) A number of groups have observed and characterized mixtures of allyl diastereomers; for example, see: (a) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y. *J. Am. Chem. Soc.* **1994**, *116*, 775 (b) Ohkita, K.; Kurosawa, H.; Hasegawa, T.; Hirao, T.; Ikeda, I. *Organometallics* **1993**, *12*, 3211. (c) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelein, M.; Huttner, G.; Zsolnai, I. *Tetrahedron Lett.* **1994**, *35*, 1523.

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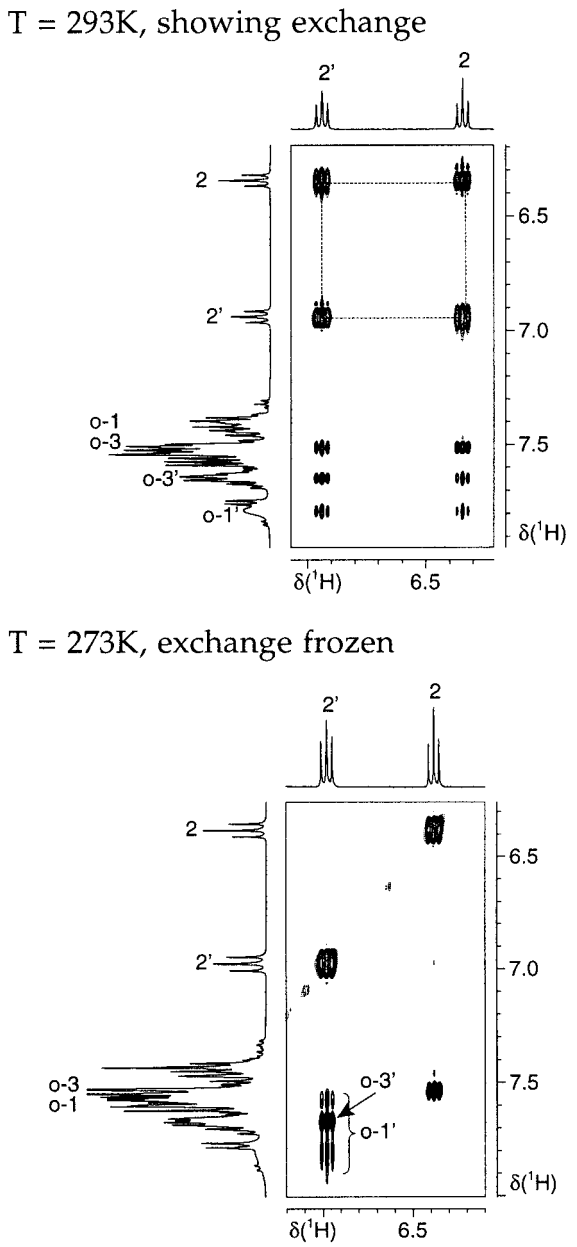
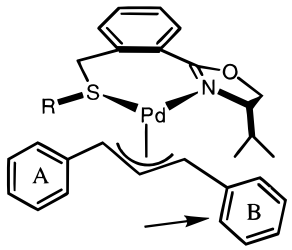


Figure 2. Temperature dependence of the NOESY spectrum for **10**.

for the sugar moiety does not arise from steric effects from the remaining ligands. Gillespie[19] has suggested that lone pairs may take up a substantial amount of space (an S lone pair in our case), so that it is not necessarily surprising to find the sugar and i-Pr groups on the same side of the coordination plane. The solid-state structure for Pd(benzoquinone)(**2**) suggests that the S lone pair requires considerable space.[6]

Dynamics within the 1,3-Diphenylallyl Ligand. Figure 4 shows proton resonances in the aromatic regions for **10**, **11**, and **14** and reveals some interesting dynamics. The proton o-1′ represents the ortho resonances of the allyl phenyl ring, B, proximate to the oxazoline i-Pr group, in the endo isomers (see arrow in **16**). These o-1′ protons show NOE's to the i-Pr group,



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thus distinguishing them from those of the second allyl phenyl ring, A. In the *S*-cyclohexyl complex **14** this resonance is somewhat broadened. In **10** it is quite broad, and in the t-Bu derivative, **11** it is even broader (see Figure 4). Since this line width change occurs for protons remote from the sulfur donor, these dynamics are unexpected. We interpret these data as suggested in Chart 2. The coordinated 1,3-diphenylallyl ligand in the endo isomer rotates such that allyl ring A moves up and away from the large sugar fragment. This rotation (for which there is now ample precedence[5,20]) moves ring B "down", closer to the i-Pr group. As it approaches the i-Pr group, the barrier to rotation increases and this interaction is reflected in the ^{1}H observations. Not surprisingly, this distortion has electronic consequences which can be monitored by ^{13}C NMR.

^{13}C NMR Allyl Chemical Shifts. Chart 2 also shows the ^{13}C chemical shifts for the two terminal allyl carbons in the syn/syn exo and endo isomers of **10**, **11**, and **14**. These values are in keeping with literature expectations, i.e., ^{13}C NMR and the trans influence in allyl complexes.[4,18,21] In all three cases the allyl signal pseudo-trans to the sulfur appears at considerably higher frequency than for the allyl carbon pseudo-trans to the nitrogen. Interestingly, the ^{13}C shifts for the allyl carbons trans to the S atom in the endo isomers all appear at higher frequency than those for the exo diastereomers. Further, for the endo isomers, with increasing size of the substituent on the sulfur donor the allyl signal pseudo-trans to the sulfur moves to even higher frequency (note the increased $\Delta\delta$ values in Chart 2). If we assume[7,9,15,16] that the higher frequency signal is "olefin-like" (less like an alkyl donor) and thus more electrophilic, then these data suggest the preferential attack of the endo isomer, trans to the S donor. The increased size of the sugar substituent induces a weakening of the Pd−C(allyl) bond proximate to the oxazoline moiety as a consequence of the rotation suggested above.

Put briefly, attack trans to the thioether is preferred for electronic reasons (trans influence), whereas attack on the endo isomer arises due to steric effects (which propagate themselves in the observed ^{13}C resonances). Since the two major isomers are in equilibrium, the depleted endo diastereomer can be rapidly re-formed. It is interesting (but not unprecedented[22]) that the

(18) Boog-Wick, K.; Pregosin, P. S. Unpublished results. Admittedly, this is an unrelated complex.
(19) Gillespie, R. J.; Spencer, J. N.; Moog, R. S. *J. Chem. Educ.* **1996**, *73*, 622.
(20) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031.
(21) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620. Clark, H. C.; Hampden-Smith, M. J.; Rüegger, H. *Organometallics* **1988**, *7*, 2085.

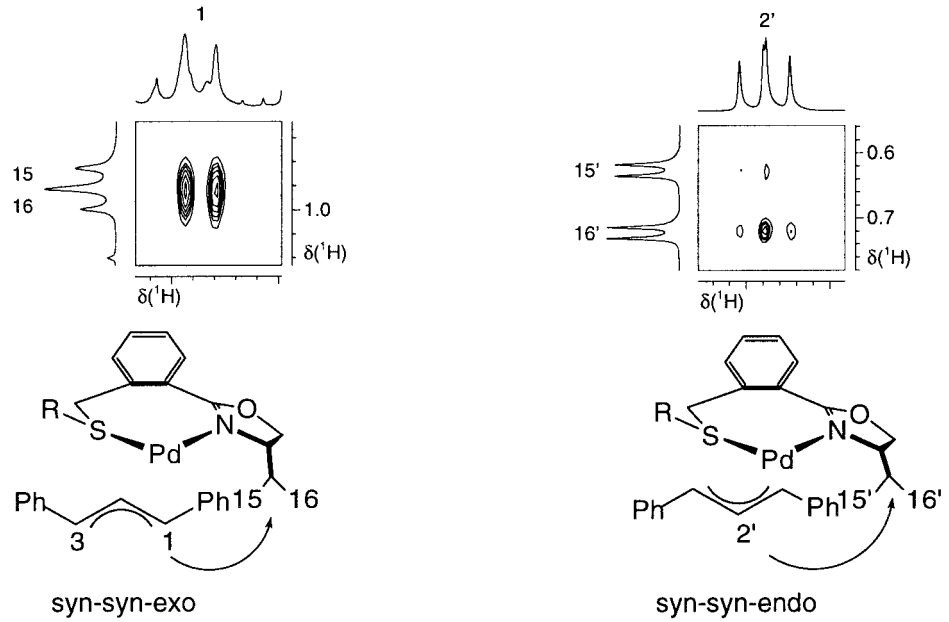

Figure 3. Sections of the NOESY spectrum of **10** showing the cross-peaks due to the interactions of the i-Pr methyl with (a, left) allyl H1, thus confirming the exo structure, and (b, right) allyl H2 (supporting the endo structure). Note that the latter NOE is much weaker, as expected, since H2 is further from the i-Pr group (400 MHz, mixing time 0.8 s, 273 K, CD_2Cl_2).

organic product is formed by preferential reaction of a minor component.

Experimental Section

(*S*)-2-Amino-3-methyl-1-butanol,[23] (*S*)-2-amino-2-phenylethanol,[23] and (chloromethyl)benzoyl chloride[24] were prepared according to the literature.

(2*S*)-(1-Hydroxy-2-isopropyl){*o*-(chloromethyl)benzoyl}-amine. (*S*)-Valinol (425.3 mg, 4.13 mmol, 1.2 equiv) was dissolved in 2 mL of absolute CH_2Cl_2. A 1.0 mL portion of freshly distilled NEt_3 was added using a syringe, followed by addition of (chloromethyl)benzoyl chloride (644.5 mg, 3.41 mmol) as a solution in 3 mL of CH_2Cl_2. After the mixture was stirred overnight, the resulting white suspension was extracted three times with CH_2Cl_2 and once with water, and then the organic layer was dried over Na_2SO_4. After removal of the solvent by distillation, the crude product was chromatographed using hexane/ethyl acetate (5/1) as eluent (R_f 0.20). The product amine was obtained as a yellow oil (531.1 mg, 61%). $[\alpha]_D = -41.8$ ($c = 0.9$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.87 (d, $J = 7.8$ Hz, 1 ar H), 7.33−7.49 (m, 3 ar H), 6.85 (t, $J = 7.8$, 1H), 4.61−4.74 (m, 2H), 4.42−4.53 (m, 1H), 4.13−4.23 (m, 2H), 1.85 (dq, $J = 19.9$, $J = 6.7$, 1H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 163.7 (C=O), 142.2 (C), 131.5, 130.4, 130.1, 127.7, 126.6 (C), 72.6 (CH), 70.2 (CH_2−O), 64.7 (CH_2−Cl), 33.0 (CH), 2 × 18.7 (CH_3). IR (CsI, cm^{-1}): 3232 br, 2962 s, 2867 m, 1635 s, 1198 m, 1065 m, 1048.

(4*S*)-2-{*o*-(Chloromethyl)benzoyl}-5,5-dihydro-4-isopropyloxazoline. Triphenylphosphine (5.0 g, 19.1 mmol, 3.7 equiv) was slowly dissolved in 30 mL of CH_3CN. To this solution was added (2*S*)-(1-hydroxy-2-isopropyl)−{*o*-(chloromethyl)benzoyl}amine (1.32 g, 5.2 mmol) dissolved in 15 mL of CH_3CN. The resulting yellow solution was treated sequentially with 3.3 mL of NEt_3 (23.2 mmol, 4.5 equiv) and 4.4 mL of CCl_4 (45.4 mmol, 8.8 equiv). Stirring overnight was followed by extraction with CH_2Cl_2 (175 mL) and then H_2O. The organic phase was washed with a saturated solution of NaCl and then dried over $MgSO_4$. After filtration and distillation of the solvent, the dark brown crude product was chromatographed using hexane/ethyl acetate (15/1) (R_f 0.28). The product (636.9 mg, 52%) was obtained as a colorless oil. $[\alpha]_D = -74.0$ ($c = 1.0$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.86 (d, $J = 7.5$ Hz, 1 ar H), 7.55 (d, $J = 7.7$, $J = 1.5$, 1 ar H), 7.46 (t, $J = 7.4$, $J = 1.6$, 1 ar H), 7.36 (t, $J = 7.6$, $J = 1.6$, 1 ar H), 5.25 (d, $J = 11.6$, 1H), 5.11 (d, $J = 11.6$, 1H), 4.34−4.45 (m, 1H), 4.07−4.20 (m, 2H), 1.81−1.94 (m, 1H), 1.06 (d, $J = 6.7$, 3H), 0.97 (d, $J = 6.7$, 3H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 162.3 (C=N), 137.7 (C), 130.9, 130.6, 130.1, 128.2, 126.8 (C), 73.3 (CH), 69.7 (CH_2−O), 44.7 (CH_2−Cl), 33.0 (CH), 18.9 (CH_3), 18.4 (CH_3). IR (CsBr pellet, cm^{-1}): 3032 m, 2958 s, 1709 s, 1640 s, 1202 m, 1116 s, 1046 s. EI$^+$-MS: *m*/*z* 237 (M^+), 194 (100%), 158, 139, 116, 89. Anal. Calcd for $C_{13}H_{16}NOCl$ (237.73): C, 65.68; H, 6.78; N, 5.89. Found: C, 65.38; H, 6.67; N, 5.78.

(4*S*)-2-{*o*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-thioglucopyranose)-methyl}benzoyl-5,5-dihydro-4-isopropyloxazoline (5). 1-Thio-*β*-D-glucose tetraacetate (670.1 mg, 1.84 mmol) was dissolved in 3 mL of absolute THF. NaH (220.7 mg, 5.52 mmol, 3 equiv) in 3 mL of absolute THF was added slowly at −65 °C. The suspension was stirred for 1 h at room temperature, after which time the oxazoline (437.2 mg, 1.84 mmol) dissolved in 4 mL of absolute THF was added. The reaction mixture was warmed to room temperature and then stirred at this temperature overnight. A thick-layer chromatography check (hexane/ethyl acetate, 2/1) of the orange-brown suspension revealed that starting material was still present. Consequently, the reaction mixture was warmed for 3 h at 50 °C. After the mixture was cooled to room temperature and the solvent was distilled, i.v., excess NaH was carefully destroyed with H_2O. The crude mass was extracted three times with with 50 mL of Et_2O (150 mL), after which the organic phase was washed with a saturated solution of NaCl and then dried over $MgSO_4$. After filtration and then distillation of the solvent, the crude product, as a yellow oil, was chromatographed (hexane/ethyl acetate, 2/1) (R_f 0.19). The product (443.3 mg, 43%) was obtained as a white crystalline compound, mp 91 °C. $[\alpha]_D = -179.0$ ($c = 1.0$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.84 (d, $J = 7.6$ Hz, 1 ar H), 7.27−7.41 (m, 3 ar

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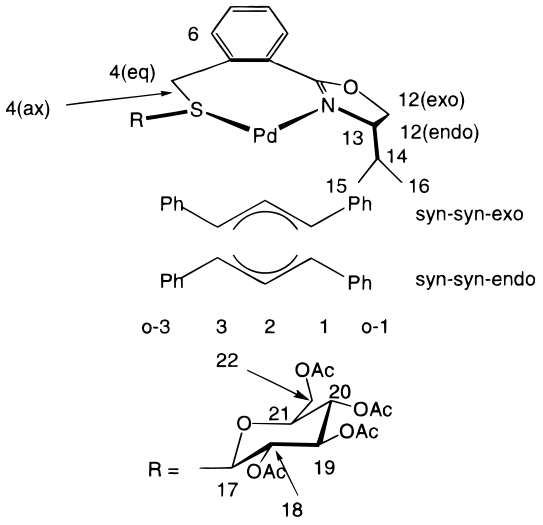
(23) Püntener, K. Ph.D. Thesis Number 10888, ETHZ, 1994.
(24) Burton, D. J.; Koppes, W. M. *J. Org. Chem.* **1975**, *40*, 3026.

Table 2. ^{1}H and ^{13}C NMR Data for 10[a]



2,3,4,6-tetra-O-Acetyl-
1-β-D-Glucopyranose

syn-syn-exo			syn-syn-endo		
	δ ^{1}H	δ ^{13}C		δ ^{1}H	δ ^{13}C
1	5.08	87.3	1	5.45	92.4
2	6.35	109.4	2	6.94	106.3
3	5.18	81.2	3	4.72	75.5
4(eq)	4.19	31.5	4(eq)	4.31	31.7
4(ax)	4.01	31.5	4(ax)	3.88	31.7
6	7.58		6	7.45	
12(endo)	4.14		12(endo)	4.17	70.7
12(exo)	3.36		12(exo)	3.95	70.7
13	3.67		13	2.52	
14	2.17		14	1.70	
15	0.98		15	0.64	
16	0.96		16	0.71	
17	4.14		17	1.97	80.3
18	5.19		18	5.06	
19	5.20		19	4.66	
20	5.13		20	4.94	
21	4.13		21	3.39	
22	4.21	61.5	22	4.00	61.8
22	4.49	61.5	22	4.27	61.8
o-1	7.50		o-1	7.79	
o-3	7.51		o-3	7.64	

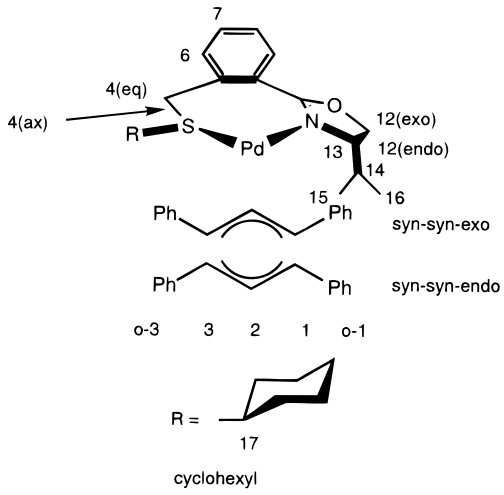
Table 3. Selected ^{1}H and ^{13}C NMR Data for 11[a]

syn-syn-exo			syn-syn-endo		
	δ (^{1}H)	δ (^{13}C)		δ (^{1}H)	δ (^{13}C)
1	5.03	87.5	1	5.54	93.4
2	6.33	109.7	2	6.88	106.3
3	5.16	81.1	3	4.67	74.3
13	3.65		13	2.48	
14	2.11		14	1.68	
15	0.99		15	0.70−0.75	
16	1.22		16	0.70−0.75	
o-1	7.53−7.55		o-1	7.78	
o-3	7.53−7.55		o-3	7.62	

[a] Numbering system as given in Table 2 (500 MHz, 293 K, CD_2Cl_2); o-1 and o-3 in the endo compound are distinguished.

H), 4.98−5.15 (m, 3H), 4.03−4.55 (m, 8H), 3.58−3.63 (m, 1H), 2.10 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.92 (s, 3H), 1.80−1.88 (m, 1H), 1.04 (d, J = 6.7, 3H), 0.96 (d, J = 6.7, 3H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 170.6 (C=O), 170.2 (C=O), 169.4 (C=O), 169.3 (C=O), 162.5 (C), 138.6, 130.7, 130.5, 130.2, 127.3, 126.9 (C), 82.6 (CH), 75.6 (CH), 73.9 (CH), 73.2 (CH), 69.9 (CH), 69.6 (CH_2−O), 68.3 (CH), 62.2 (CH_2), 33.0 (CH), 33.0 (CH_2−S), 20.8 (CH_3), 20.6 (2 × CH_3), 19.0 (CH_3), 18.6 (CH_3). IR (CsI, cm^{-1}): 2955 w, 2925 w, 1739 s, 1643 m, 1229 s, 1040

Table 4. Selected ^{1}H and ^{13}C NMR Data for 14[a]



syn-syn-exo			syn-syn-endo		
	δ ^{1}H	δ ^{13}C		δ ^{1}H	δ ^{13}C
1	4.93	86.6	1	5.22	89.9
2	6.15	109.8	2	6.79	105.5
3	4.77	79.5	3	4.72	76.0
4(eq)	3.98	34.7	4(eq)	3.94	32.2
4(ax)	3.72	34.7	4(ax)	3.67	32.2
6	7.37		6	7.49	
7	7.66		7	7.67	
12(endo)	3.45	71.6	12(endo)	4.00	
12(exo)	4.15	71.6	12(exo)	4.19	
13	3.56		13	2.50	
14	2.00		14	1.68	
15	1.10, 1.13		15	0.69, 0.73	
16	1.13, 1.10		16	0.73, 0.69	
17	2.01	32.3	17		
o-1	7.45		o-1	7.70	
o-3	7.24		o-3	7.57	

[a] Conditions: 500 MHz, 293 K, CD_2Cl_2. o-1 and o-3 in the endo compound are distinguished.

s. EI$^+$-MS: m/z 566 (M^+), 234 (100%), 201. Anal. Calcd for $C_{27}H_{35}NO_{10}S$ (565.64): C, 57.33; H, 6.24; N, 2.48. Found: C, 57.53; H, 6.50; N, 2.52.

(η^3-1,3-Diphenylpropenyl){(4*S*)-2-{*o*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-thioglucopyranose)methyl}benzoyl-5,5-dihydro-4-isopropyloxazoline}palladium(II) Hexafluorophosphate (10). The oxazoline **5** (30.0 mg, 5.3 × 10^{-2} mmol) was dissolved in 2 mL of CH_2Cl_2. The 1,3-diphenylallyl−Pd−chloro dimer (17.8 mg, 2.6 × 10^{-2} mmol, 0.5 equiv) was added. A yellow suspension resulted. KPF_6 (9.8 mg, 5.3 × 10^{-2} mmol) was dissolved in 2 mL of MeOH/Ac_2O and this solution added to the suspension. After the mixture was stirred for 30 min, the suspension was filtered through Celite, and then the solvent was distilled. The yellow residue was taken up in a minimum of CH_2Cl_2 and filtered again through Celite. The crude material which results after removal of the solvent can be crystallized slowly from CH_2Cl_2/pentane at −20 °C. After drying i.v., we obtain an orange, crystalline product (50.4 mg, 94%), mp 195 °C dec. $[\alpha]_D$ = −39.9 (c = 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): 2 isomers, δ 7.27−7.77 (m, 25H), 7.08 (t, J = 12.4 Hz, 0.5H), 6.26 (t, J = 11.7, 1H), 5.42 (d, J = 11.8, 1H), 4.88−5.33 (m, 6H), 4.45−4.67 (m, 3H), 4.01−4.31 (m, 8H), 3.84−3.91 (m, 1H), 3.67−3.74 (m, 1H), 3.55−3.59 (m, 0.5H), 3.23 (t, J = 9.2, 1H), 2.55−2.59 (m, 0.6H), 2.32−2.39 (m, 1.3H), 1.98−2.04 (4 × s, 18H), 1.73 (s, 3H), 0.84−0.96 (m, 9H), 0.63 (d, J = 6.6, 1.5 H), 0.57 (d, J = 6.9, 1.5H). ^{13}C NMR ($CDCl_3$, 250 MHz): 2 isomers, δ 170.2 (C=O), 170.1 (C=O), 170.0 (C=O), 169.8 (C=O), 169.7 (C=O), 169.5 (C=O), 169.4 (C=O), 168.1 (C=N), 167.2 (C=N), 126.4−137.7 (23 aromatics), 108.8 (CH), 106.8 (CH), 91.4 (CH), 87.0 (CH), 81.8 (CH), 81.2 (CH),

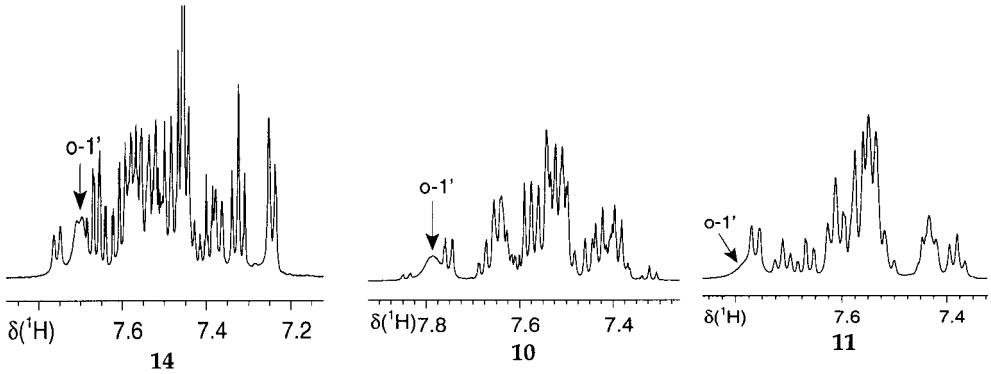
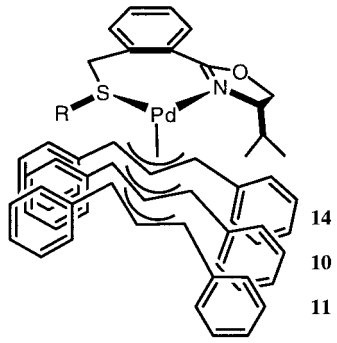


Figure 4. Sections of the aromatic region (500 MHz, CD_2Cl_2) for (from left to right) **14**, **10**, and **11**. The ortho protons of the allyl phenyl group proximate to the i-Pr group, o-1′, are indicated by arrows. It can be seen that this resonance becomes increasingly broad, indicating dynamics, as a function of the sulfur substituent (which lies on the other side of the cation).

Chart 2. Rotation of the Allyl as a Function of R and Allyl ^{13}C Data



	^{13}C trans to N	^{13}C trans to S	Δδ
	syn/syn endo		
14	76.0	89.9	13.9
10	75.5	92.4	16.9
11	74.3	93.4	19.1
	syn/syn exo		
14	79.5	86.6	7.1
10	81.2	87.3	6.1
11	81.1	87.5	6.4

77.2 (CH), 77.1 (CH), 76.3 (CH), 73.1 (CH), 73.0 (CH), 69.7 (CH_2−O), 69.4 (CH), 68.0 (CH), 67.2 (CH), 66.9 (CH), 66.8 (CH), 61.1 (CH_2), 34.1 (C), 30.9 (CH_2−S), 30.7 (CH), 30.2 (CH), 22.3 (C), 20.8 (C(CH_3)), 20.6 (C(CH_3)), 20.5 (C(CH_3)), 20.3 (C(CH_3)), 18.7 (CH_3), 18.4 (CH_3), 16.1 (CH_3), 15.3 (CH_3). IR (CsI, cm^{-1}): 3481 br, 2960 w, 1752 s, 1374 s, 1226 s, 1062 s, 1040 s. FAB^+-MS: *m*/*z* 864 (100%, $[M]^+ - PF_6$), 671, 566. Anal. Calcd for $C_{42}H_{48}NO_{10}F_6PSPd$ (1010.29): C, 49.93; H, 4.79; N, 1.39. Found: C, 49.87; H, 4.77; N, 1.34.

(4*S*)-2-{*o*-(Thiocyclohexyl)methyl}benzoyl-5,5-dihydro-4-isopropyloxazoline (9). Cyclohexyl mercaptan (0.4 mL, 3.26 mmol, 7.8 equiv) was dissolved in 2 mL of absolute THF. Na (40.0 mg, 1.74 mmol, 4.1 equiv) was carefully added. The oxazoline (100.0 mg, 0.42 mmol) in 2 mL of absolute THF was then added to the suspension. After the mixture was stirred for 4 h at room temperature and then overnight at 70 °C, the suspension was cooled in an ice bath. H_2O was carefully added to destroy excess Na. The crude mass was extracted three times with Et_2O (50 mL), after which the organic phase was washed with a saturated solution of NaCl and then dried over $MgSO_4$. After filtration and then distillation of the solvent, the crude product was obtained as a foul-smelling yellow oil. Column chromatography (hexane/ethyl acetate, 10/1) (R_f 0.27) afforded the product (66.3 mg, 50%) as a colorless oil. $[\alpha]_D = -55.5$ ($c = 0.9$, $CHCl_3$). ^1H NMR ($CDCl_3$, 250 MHz): δ 7.79 (d, $J = 7.2$ Hz, 1 ar H), 7.23−7.39 (m, 3 ar H), 4.05−4.45 (m, 5H), 2.51−2.60 (m, 1H), 1.54−1.97 (m, 5H), 1.15−1.38 (m, 6H), 1.07 (d, $J = 6.7$, 3H), 0.97 (d, $J = 6.7$, 3H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 163.2 (C=N), 139.8 (C), 130.5, 130.5, 130.4, 130.2, 126.6 (CH), 73.2 (CH), 69.7 (CH_2−O), 43.3 (CH), 33.6 (CH_2−S), 33.0 (CH), 32.7 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 19.1 (CH_3), 18.5 (CH_3). IR (CsBr film, cm^{-1}): 3059 w, 2927 s, 2849 s, 1640 s, 1246 m, 1042 s. EI^+-MS: *m*/*z* 317 (M^+), 234 (100%), 203. Anal. Calcd for $C_{19}H_{27}NOS$ (317.49): C, 71.88; H, 8.57; N, 4.41. Found: C, 71.79; H, 8.41; N, 4.57.

(η^3-1,3-Diphenylpropenyl){(4*S*)-2-{*o*-(thiocyclohexyl)-methyl}benzoyl-5,5-dihydro-4-isopropyloxazoline}-palladium(II)] Hexafluorophosphate) (14). This complex was prepared as described for **10**. From the bidentate cyclohexyl chelate (20.0 mg, 6.3×10^{-2} mmol), 1,3-diphenylallyl−Pd−chloro dimer (21.1 mg, 3.2×10^{-2} mmol, 0.5 equiv), and KPF_6 (11.7 mg, 6.3×10^{-2} mmol), we obtained 41.1 mg (86%) of the complex as a yellow powder, mp 197 °C dec. ^1H NMR ($CDCl_3$, 250 MHz): 2 isomers (1:0.8), δ 7.25−7.78 (m, 27H), 6.85 (t, $J = 12.0$ Hz, 0.8H), 6.06 (t, $J = 11.4$, 1H), 4.63−5.22 (m, 2H), 3.65−4.14 (m, 7H), 3.22−3.29 (m, 1H), 2.91 (br, 1H), 2.55 (br, 0.5H), 0.66−2.22 (m, 38H). IR (CsI, cm^{-1}): 3441 br, 2926 w, 2851 w, 1595 w, 1487 w, 1373 w, 1253 w, 1071 s. FAB^+-MS: *m*/*z* 616 (100%, $M^+ - PF_6$), 422, 307, 204. Anal. Calcd for $C_{34}H_{40}NOF_6PSPd$ (762.15): C, 53.58; H, 5.29; N, 1.84. Found: C, 53.48; H, 5.44; N, 1.74.

(4*S*)-2-{*o*-(2,3,4,6-Tetra-*O*-pivaloyl-β-D-thioglucopyranosyl)methyl}benzoyl-5,5-dihydro-4-isopropyloxazoline (6). 2,3,4,6-Tetra-*O*-pivaloyl-β-D-glucopyranosylmercaptan (141.0 mg, 0.26 mmol) was dissolved in 2 mL of absolute THF. NaH (40.0 mg, 0.79 mmol, 3 equiv) was carefully added at −65 °C, and 1 mL of absolute THF added. The suspension was stirred for 1 h, and then the oxazoline (62.9 mg, 0.26 mmol), dissolved in 4 mL of absolute THF, was added. The reaction mixture was warmed to room temperature and left to stand for 3 h. The reaction was then warmed with stirring to 60 °C overnight. The resulting brown suspension was cooled to room temperature and the solvent distilled. Careful addition of H_2O destroyed the excess NaH. Extraction with Et_2O (75 mL), washing with NaCl, drying over $MgSO_4$, filtration, and solvent distillation afforded a yellow-brown oil. Column chromatography (hexane/ethyl acetate, 7/1) (R_f 0.13) gave 85.6 mg (44%) of the colorless product **6**. $[\alpha]_D = -167.5$ ($c = 0.5$, $CHCl_3$). ^1H NMR ($CDCl_3$, 250 MHz): δ 7.85 (d, $J = 7.5$ Hz, $J = 1.4$, 1 ar H), 7.22−7.40 (m, 3 ar H), 5.00−5.28 (m, 3H), 4.65 (d, $J = 13.0$, 1 H), 4.30−4.41 (m, 2H), 4.00−4.24 (m, 5H), 3.69 (ddd, $J = 9.8$, $J = 5.5$, $J = 1.8$, 1H), 1.69−2.04 (m, 1H), 1.14 (s, 9H), 1.24 (s, 9H), 1.08 (s, 9H), 1.04 (d, $J = 6.7$, 3H), 0.99 (s, 9H),

0.95 (d, J = 6.7, 3H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 178.1 (C═O), 177.1 (C═O), 176.4 (C═O), 176.3 (C═O), 162.4 (C), 138.8, 130.6, 130.5, 130.3, 127.2, 126.7 (C), 82.6 (CH), 76.1 (CH), 73.4 (CH), 73.3 (CH), 69.6 (CH), 69.6 (CH_2−O), 67.9 (CH), 62.4 (CH_2), 38.9 ($C(CH_3)$), 38.7 ($C(CH_3)$), 38.7 ($C(CH_3)$), 38.4 ($C(CH_3)$), 33.2 (CH), 32.8 (CH_2−S), 27.2 ($C(CH_3)$), 27.1 ($C(CH_3)$), 27.0 ($C(CH_3)$), 26.9 ($C(CH_3)$), 19.1 (CH_3), 18.7 (CH_3). IR (CsI, cm^{-1}): 2971 s, 2872 s, 1741 s, 1641 m, 1281 s, 1143 s, 1038 s. FAB$^+$-MS: *m*/*z* 734 (100%, M$^+$), 234. Anal. Calcd for $C_{39}H_{59}NO_{10}S$ (565.64): C, 63.82; H, 8.10; N, 1.91. Found: C, 63.61; H, 8.22; N, 1.92.

(η^3-1,3-Diphenylpropenyl){(4*S*)-2-{*o*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-thioglucopyranosyl)methyl}benzoyl-5,5-dihydro-4-isopropyloxazoline}palladium Hexafluorophosphate (11). This complex was prepared as described for **10**. The ligand (20.0 mg, 2.7 × 10^{-2} mmol), 1,3-diphenylallyl−Pd−chloro dimer (9.2 mg, 1.3 × 10^{-2} mmol, 0.5 equiv), and KPF_6 (5.1 mg, 6.3 × 10^{-2} mmol) afforded **11** (29.0 mg, 90%) as a yellow powder, mp 165−173 °C dec. $[\alpha]_D$ = −29.0 (c = 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): 2 isomers (1:0.9), δ 7.27−7.90 (m, 28H), 6.97 (t, J = 11.9 Hz, 1H), 6.24 (t, J = 11.7, 1H), 5.45−5.54 (m, 2H), 4.97−5.29 (m, 3H), 4.64−4.75 (m, 2H), 3.72−4.50 (m, 13H), 3.66−3.74 (m, 1H), 3.49 (d, J = 9.7, 1H), 3.28 (t, J = 9.4, 1H), 2.51−2.54 (m, 1H), 2.25−2.30 (m, 1H), 2.07−2.11 (m, 1H), 1.74−1.81 (m, 1H), 0.89−1.24 (m, 78H), 0.68 (d, J = 6.7, 3H), 0.63 (d, J = 6.8, 3H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 177.9 (C═O), 177.7 (C═O), 177.0 (C═O), 176.5 (C═O), 176.3 (C═O), 176.2 (C═O), 168.5 (C═N), 167.4 (C═N), 126.4−137.6 (22 signals, aromatics), 109.4 (CH), 106.6 (CH), 92.8 (CH), 87.3 (CH), 82.2 (CH), 81.7 (CH), 79.3 (CH), 77.8 (CH), 74.9 (CH), 73.3 (CH), 72.7 (CH), 72.5 (CH), 70.1 (CH_2−O), 69.4 (CH), 67.6 (CH), 67.0 (CH), 66.2 (CH), 61.1 (CH_2), 38.8 ($C(CH_3)_3$), 38.7 ($C(CH_3)_3$), 31.1 (CH), 30.9 (CH_2−S), 30.7 (CH), 29.7 (CH), 27.2 ($C(CH_3)_3$), 27.1 ($C(CH_3)_3$), 27.0 ($C(CH_3)_3$), 18.9 (CH_3), 18.4 (CH_3), 16.8 (CH_3), 16.3 (CH_3). IR (CsI, cm^{-1}): 2971 w, 1741 s, 1477 w, 1367 w, 1279 w, 1138 m, 1087 w. FAB$^+$-MS: *m*/*z* 1032 (100%, M$^+$ − PF_6), 839. Anal. Calcd for $C_{54}H_{72}NO_{10}F_6PSPd$ (1178.61): C, 55.03: H, 6.16; N, 1.19. Found: C, 55.22; H, 6.17; N, 1.19.

(2*S*)-(1-Hydroxy-2-phenyl){*o*-(chloromethyl)benzoyl}-amine. (*S*)-Phenylglycinol (665.5 mg, 4.85 mmol, 1.2 equiv) was dissolved in 10 mL of absolute CH_2Cl_2, to afford an orange-yellow solution. A 1.2 mL portion of freshly distilled NEt_3 was injected via a syringe. The acid chloride (764.2 mg, 4.04 mmol) in 10 mL of absolute CH_2Cl_2 was then added. After the mixture was stirred overnight at room temperature, the yellow suspension was extracted three times with CH_2Cl_2 (100/75/50 mL) and then washed with H_2O. The organic phase was washed with a saturated solution of NaCl and then dried over Na_2SO_4. After filtration and then distillation of the solvent, the crude product, as a yellow oil, was chromatographed (hexane/ethyl acetate, 2/1) (R_f 0.17). The product (588.9 mg, 50%) was obtained as a white crystalline solid. $[\alpha]_D$ = −41.8 (c = 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.87 (d, J = 7.8 Hz, 1 ar H), 7.33−7.49 (m, 3 ar H), 6.85 (t, J = 7.8, 1H), 4.61−4.74 (m, 2H), 4.42−4.53 (m, 1H), 4.13−4.23 (m, 2H), 1.85 (dq, J = 19.9, J = 6.7, 1H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 163.7 (C═O), 142.2 (C), 131.5, 130.4, 130.1, 127.7, 126.6 (C), 72.6 (CH), 70.2 (CH_2−O), 64.7 (CH_2−Cl), 33.0 (CH), 2 × 18.7 (CH_3). IR (CsI, cm^{-1}): 3232 br, 2962 s, 2867 m, 1635 s, 1198 m, 1065 m, 1048 m.

(4*S*)-2-{(*o*-Chloromethyl)benzoyl}-5,5-dihydro-4-phenyloxazoline. Triphenylphosphine (PPh_3; 335.0 mg, 1.28 mmol, 3.7 equiv) was placed in a 20 mL Schlenk tube and then slowly dissolved in 8 mL of absolute CH_3CN. The amide (100.0 mg, 3.5 × 10^{-2} mmol) in 3 mL of absolute CH_3CN was added. Slow addition of NEt_3 (0.21 mL, 1.55 mmol, 4.5 equiv) and then CCl_4 (0.3 mL, 3.04 mmol, 8.8 equiv) gave a light yellow solution. Stirring overnight at room temperature was followed by extraction three times with CH_2Cl_2 (100 mL). The organic phase was washed with a saturated solution of NaCl and then dried over $MgSO_4$. After filtration and subsequent distillation of the solvent, the crude product, as a yellow-brown oil, was chromatographed (hexane/ethyl acetate, 7/1) (R_f 0.33). The product (65.4 mg, 70%) was obtained as a colorless oil. $[\alpha]_D$ = −0.8 (c = 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (dd, J = 7.8 Hz, J = 1.4, 1 ar H), 7.61 (dd, J = 7.7, J = 1.3, 1 ar H), 7.52 (ddd, J = 15.1, J = 7.6, J = 1.5, 1 ar H), 7.44 (dd, J = 7.7, J = 1.4, 1 ar H), 7.28−7.41 (m, 5 ar H), 5.49 (dd, J = 10.2, J = 8.5, 1H), 5.27 (d, J = 11.7, 1H), 5.24 (d, J = 11.7, 1H), 4.82 (dd, J = 10.2, J = 8.4, 1H), 4.27 (t, J = 8.4, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 164.5 (C═N), 142.9 (C), 138.6 (C), 132.0 (CH), 131.4 (CH), 131.1 (CH), 129.4 (CH), 129.0 (CH), 128.3 (CH), 127.4 (CH), 127.1 (C), 74.9 (CH_2−O), 71.3 (CH), 45.5 (CH_2−Cl). IR (CsI, cm^{-1}): 3059 m, 3027 m, 2964 m, 2895 m, 1637 s, 1296 s, 1272 s,1056 m, 1036 m. EI$^+$-MS: *m*/*z* 271 (100%, M$^+$), 235 (M$^+$ − HCl), 222. Anal. Calcd for $C_{16}H_{14}NOCl$ (271.75): C, 70.72; H, 5.19; N, 5.15. Found: C, 70.67; H, 5.19; N, 4.93.

(4*S*)-2-{*o*-(2,3,4,6-Tetra-*O*-acetyl-β-D-thioglucopyranose)-methyl}benzoyl-5,5-dihydro-4-phenyloxazoline (7). 1-Thio-β-D-glucose tetraacetate (110.4 mg, 0.30 mmol) was dissolved in 1 mL of absolute THF. NaH (36.4 mg, 0.91 mmol, 3 equiv) was carefully added at −65 °C and an additional 1 mL of absolute THF added. The resulting suspension was stirred for 1 h, and then the oxazoline (82.3 mg, 0.30 mmol) dissolved in 3 mL of absolute THF was added. Warming to room temperature was followed by stirring overnight. The solvent was distilled, i.v., and the excess NaH carefully destroyed using H_2O. The reaction mixture was extracted three times with diethyl ether. The organic phase was washed with a saturated solution of NaCl and then dried over $MgSO_4$. After filtration and distillation of the solvent, i.v., the crude product, as a yellow-brown oil, was chromatographed (hexane/ethyl acetate, 2/1) (R_f 0.34). The product, **7** (149.4 mg, 82%), was obtained as a white crystalline solid mp 112 °C. $[\alpha]_D$ = −124.4 (c = 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 7.4 Hz, 1 ar H), 7.28−7.44 (m, 8 ar H), 5.45 (t, J = 9.0, 1H), 5.01−5.15 (m, 3H), 4.79 (dd, J = 10.2, J = 8.4, 1H), 4.38−4.51 (m, 3H), 4.18−4.24 (m, 2H), 4.00 (dd, J = 12.3, J = 2.1, 1H), 2.09 (s, 3H), 3.56 (m, 1H), 2.03 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 171.3 (C═O), 170.9 (C═O), 170.0 (C═O), 164.8 (C═N), 142.9 (C), 139.5 (C), 131.6 (CH), 131.5 (CH), 131.4 (CH), 129.5 (CH), 128.3 (CH), 128.1 (CH), 127.4 (CH), 127.3 (C), 83.5 (CH), 76.2 (CH), 74.8 (CH_2−O), 74.6 (CH), 71.3 (CH), 80.6 (CH), 70.0 (CH), 62.8 (CH_2), 33.8 (CH_2−S), 21.3 (2 × CH_3). IR (CsI, cm^{-1}): 2934 br, 1741 s (C═O), 1633 m (C═N), 1247 s, 1228 s, 1037 s. EI$^+$-MS: *m*/*z* 599 (M$^+$), 268 (100%), 234. Anal. Calcd for $C_{30}H_{33}NO_{10}S$ (599.66): C, 60.09; H, 5.55; N, 2.34. Found: C, 59.86; H, 5.50; N, 2.35.

(η^3-1,3-Diphenylpropenyl){(4*S*)-2-{*o*-(2,3,4,6-tetra-*O*-acetyl-η-D-thioglucopyranose)methyl}benzoyl-5,5-dihydro-4-phenyloxazoline}palladium(II) Hexafluorophosphate (12). This complex was prepared analogously with **10**. From the ligand **7** (19.3 mg, 3.2 × 10^{-2} mmol), 1,3-diphenylallyl−Pd−chlorodimer (10.8 mg, 1.6 × 10^{-2} mmol, 0.5 equiv), and KPF_6 (6.0 mg, 3.2 × 10^{-2} mmol), one obtains **12** (25.8 mg, 77%) as a yellow powder, mp 129 °C (with sublimation). $[\alpha]_D$ = +37.6 (c = 1.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): 2 isomers, δ 8.00 (br, ar H, 2H), 7.19−7.70 (m, ar H, 25H), 6.92 (br, allyl H, 2H), 6.30 (t, J = 11.6 Hz, allyl H, 1H), 5.30 (dd, J = 18.7, J = 11.5, allyl H, 1H), 4.69−5.09 (br, m, 6H), 4.21−4.57 (br m, 4H), 3.84−4.14 (m, 6H), 3.17−3.43 (br m, 2H), 3.11 (br, 2H), 2.00 (br s, CH_3), 1.98 (br s, 3H), 1.97 (br s, 3H), 1.71 (br s, CH_3, 3H). ^{13}C NMR ($CDCl_3$, 250 MHz): 2 isomers, δ 167.0 (C), 169.7 (C), 169.5 (C), 168.2 (C), 139.0, 137.6, 136.5, 135.6, 133.7, 132.7, 132.6, 132.2, 131.9, 130.5, 130.3, 129.5, 129.3, 128.1, 128.0, 126.6, 126.1, 125.5, 109.2 (CH), 87.0 (CH), 81.6 (CH), 81.2 (CH), 76.8 (CH), 75.9 (CH_2), 73.0 (CH), 71.8 (CH), 68.0 (CH), 67.7 (CH), 67.2 (CH), 66.8 (CH), 61.2 (CH_2), 60.9 (CH_2), 31.6 (CH_2), 20.8 (CH_3), 20.5 (CH_3), 20.4 (CH_3). IR (CsI, cm^{-1}): 2924 br, 1751 s, 1623 m, 1228 s, 1037 m. FAB$^+$-

MS: *m*/*z* 898 (100%, $M^+ - PF_6$). Anal. Calcd for $C_{45}H_{46}NO_{10}F_6PSPd$ (1044.31): C, 51.76; H, 4.44; N, 1.34. Found: C, 51.75; H, 4.34, N, 1.50.

(4*S*)-2-{*o*-(2,3,4,6-Tetra-*O*-pivaloyl-*β*-D-thioglucopyranosyl)methyl}benzoyl-5,5-dihydro-4-phenyloxazoline (8). 2,3,4,6-tetra-*O*-pivaloyl-*β*-D-thioglucopyranosyl (144.5 mg, 0.27 mmol) was dissolved in 3 mL of absolute THF. NaH (32.6 mg, 0.81 mmol, 3 equiv) was carefully added at −65 °C and then 2 mL of absolute THF added. After the mixture was stirred for 1 h, the oxazoline (73.7 mg, 0.27 mmol) in 2 mL of absolute THF, was added. After it was warmed to room temperature, the reaction mixture was stirred for 3 h. The solvent was distilled from the brown suspension, i.v. Careful addition of H_2O, to destroy excess NaH, was followed by extraction three times with ether. The organic phase was washed with a saturated solution of NaCl and then dried over $MgSO_4$. After filtration and distillation of the solvent, i.v., the crude product, as a yellow oil, was chromatographed (hexane/ethyl acetate, 6/1) (R_f 0.12). The product, **8** (116.4 mg, 56%), is obtained as a viscous colorless oil. $[\alpha]_D = -112.1$ ($c = 1.1$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.96 (d, $J = 7.5$ Hz, 1 ar H), 7.27−7.46 (m, 8 ar H), 5.41 (dd, $J = 10.0$, $J = 8.9$, 1H), 5.01−5.27 (m, 3H), 4.76 (dd, $J = 10.2$, $J = 8.4$, 1H), 4.63 (d, $J = 13.1$, 1H), 4.44 (d, $J = 10.1$, 1H), 4.11−4.21 (m, 3H), 4.05 (dd, $J = 12.4$, $J = 5.4$, 1H), 3.63 (ddd, $J = 9.7$, $J = 5.3$, $J = 1.9$, 1H), 1.23 (s, 9H), 1.15 (s, 9H), 1.09 (s, 9H), 0.99 (s, 9H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 178.1 (C═O), 177.1 (C═O), 176.4 (C═O), 176.3 (C═O), 163.9 (C), 142.2 (C), 139.0 (C), 130.9 (CH), 130.8 (CH), 130.6 (CH), 128.8 (CH), 127.6 (CH), 127.3 (CH), 126.8 (CH), 126.3 (C), 82.5 (CH), 76.0 (CH), 74.0 (CH_2−O), 73.3 (CH), 70.6 (CH), 69.6 (CH), 67.8 (CH), 62.2 (CH_2), 38.8 ($C(CH_3)$), 38.7 ($C(CH_3)$), 38.7 ($C(CH_3)$), 38.4 ($C(CH_3)$), 32.8 (CH_2−S), 27.1 (C(CH_3)), 27.1 (C(CH_3)), 27.0 (C(CH_3)), 26.9 (C(CH_3)). IR (KBr solution cell, cm^{-1}): 2974 s, 1734 s, 1216 s, 1043 s. FAB$^+$-MS: *m*/*z* 768 (100%, M^+), 666, 499, 268. Anal. Calcd for $C_{42}H_{57}NO_{10}S$ (767.98): C, 65.69; H, 7.48; N, 1.82. Found: C, 64.95; H, 7.36; N, 1.81.

(η^3-1,3-Diphenylpropenyl){(4*S*)-2-{*o*-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-thioglucopyranosyl)methyl}benzoyl-5,5-dihydro-4-phenyloxazoline}palladium(II) Hexafluorophosphate (13). This complex was prepared analogouslyto the procedure described for **10**. From the oxazoline ligand **8** (21.6 mg, 2.8×10^{-2} mmol), the 1,3-diphenylallyl−Pd−chlorodimer (9.5 mg, 1.4×10^{-2} mmol, 0.5 equiv), and KPF_6 (5.3 mg, 2.8×10^{-2} mmol), one obtains 24.9 mg (73%) of **13** as a yellow powder, mp 99 °C. $[\alpha]_D = -37.1$ ($c = 1.1$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): 3 isomers detected, δ 7.94−8.07 (br m, ar H), 7.27−7.71 (br m, ar H), 6.87 (br m), 6.32 (br t, $J = 11.2$ Hz, allyl H), 5.75 (br d, $J = 12.3$), 5.41 (t, $J = 9.5$), 5.01−5.27 (m), 4.61−4.80 (br m), 3.87−4.46 (br m), 3.35−3.66 (br m), 3.04−3.08 (br d), 1.30 (s, CH_3), 1.26 (s, CH_3), 1.23 (s, CH_3), 1.21 (s, CH_3), 1.20 (s, CH_3), 1.15 (s, CH_3), 1.09 (s, CH_3), 0.99 (s, CH_3), 0.87 (s, CH_3). ^{13}C NMR ($CDCl_3$, 250 MHz): 3 isomers detected, δ 178.1 (C═O), 177.6 (C═O), 177.1 (C═O), 176.4 (C═O), 164.0 (C═N), 142.2 (C), 140.0 (C), 139.0 (C), 133.6, 132.3, 131.5, 130.9, 130.8, 130.7, 130.3, 129.9, 129.7, 129.1, 128.8, 128.4, 127.6, 127.3, 126.8, 126.3, 126.0, 106.3 (C), 82.5 (C), 78.2 (C), 76.0 (CH), 74.0 (CH_2), 73.3 (CH), 72.6 (CH), 70.6 (CH), 69.6 (CH), 67.8 (CH), 67.6 (CH), 62.8 (CH_2), 62.3 (CH_2), 38.9 (C), 38.7 (C), 38.6 (C), 38.4 (C), 32.8 (CH_2), 29.7 (CH_2), 27.3 (CH_3), 27.1 (CH_3), 27.1 (CH_3), 27.0 (CH_3), 26.9 (CH_3). IR (CsI, cm^{-1}): 2970 s, 2869 s, 1741 s, 1637 m, 1281 s, 1141 s, 1035 m. FAB$^+$-MS: *m*/*z* 1066 ($M^+ - PF_6$), 873. Anal. Calcd for $C_{57}H_{70}NO_{10}F_6PSPd$ (1212.61): C, 56.46; H, 5.82; N, 1.16. Found: C, 56.51; H, 5.90; N, 1.13.

(η^3-Propenyl){(4*S*)-2-{*o*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-thioglucopyranose)methyl}benzoyl-5,5-dihydro-4-isopropyloxazoline}palladium(II)] Hexafluorophosphate (17). The isopropyl oxazoline **5** (22.2 mg, 3.9×10^{-2} mmol) was dissolved in 2 mL of CH_2Cl_2, to afford a colorless solution. Addition of the η^3-C_3H_5-allyl−Pd−chloro dimer (7.2 mg, 1.9×10^{-2} mmol, 0.5 equiv) resulted in a yellow solution. A solution of KPF_6 (7.3 mg, 3.9×10^{-2} mmol) in 2 mL of MeOH/Ac_2O was then added to the oxazoline−Pd reaction mixture. After 30 min at room temperature, the suspension was filtered through Celite and the solvents removed i.v. The residue was dissolved in a small amount of CH_2Cl_2, the solution filtered through Celite, and the solvent removed i.v. The product was recrystallization from a small amount of CH_2Cl_2 and Et_2O overnight at −20 °C. The mother liquor was decanted and the off-white, crystalline product, **17** (31.0 mg, 92%), dried i.v., mp 157 °C. $[\alpha]_D = -60.2$ ($c = 1.2$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): 2 isomers, (1:0.7), δ 7.70−7.79 (m, 1 ar H), 7.44−7.60 (m, 3 ar H), 5.94−5.99 (m, allyl, 0.3 H), 5.49−5.62 (m, allyl, 0.5 H), 5.05−5.37 (m, 3H), 4.65−4.87 (m, 3H), 4.31−4.50 (m, 4H), 3.99−4.26 (m, 3H), 3.56−3.81 (m, 2H), 3.31 (d, $J = 12.2$ Hz, 0.6 H), 2.87 (d, $J = 12.5$, 0.4H), 2.28 (br), 2.17 (s, 3H), 2.02 (s, 9H), 1.02 (s, 3H), 1.00 (s, 3H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 170.3 (C═O), 170.2 (C═O), 169.7 (C═O), 169.5 (C═O), 169.2 (C), 168.9 (C), 133.0 (CH), 131.8 (CH), 131.2 (C), 130.9 (CH), 129.4 (CH), 126.2 (C), 120.5 (CH), 119.8 (CH), 83.9 (CH), 83.3 (CH), 76.9 (CH), 76.4 (CH), 76.1 (CH), 74.3 (CH_2), 73.1 (CH), 70.8 (CH_2), 70.3 (CH_2), 68.5 (CH), 67.0 (CH), 61.3 (CH_2), 61.0 (CH_2), 60.8 (CH_2), 60.5 (CH_2), 32.1 (CH_2−S), 31.6 (CH), 20.7 (CH_3), 20.6 (CH_3), 18.7 (CH_3), 18.3 (CH_3), 17.7 (CH_3), 16.8 (CH_3). IR (CsI, cm^{-1}): 2958 m, 2926 m, 1750 s, 1633 m, 1227 s, 1060 s, 1040 s. FAB$^+$-MS: *m*/*z* 712 ($M^+ - PF_6$), 672. Anal. Calcd for $C_{30}H_{40}NO_{10}F_6PSPd$ (858.08): C, 41.99; H, 4.70; N, 1.63. Found: C, 41.90; H, 4.77; N, 1.65.

(η^3-Propenyl){(4*S*)-2-{*o*-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-thioglucopyranosyl)methyl}benzoyl-5,5-dihydro-4-isopropyloxazoline}palladium(II) Hexafluorophosphate (18). This complex was prepared as for **17**. From the ligand **6** (21.6 mg, 2.9×10^{-2} mmol), η^3-C_3H_5-allyl−Pd−chloro dimer (5.4 mg, 1.5×10^{-2} mmol, 0.5 equiv), and KPF_6 (5.5 mg, 2.9×10^{-2} mmol) after recrystallization from CH_2Cl_2/pentane, 26.7 mg (88%) of the product as an off-white powder was obtained, mp 152 °C. $[\alpha]_D = -75.7$ ($c = 1.1$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.76 (d, $J = 7.4$ Hz, 1 ar H), 7.49−7.58 (m, 3 ar H), 5.21−5.48 (m, 4H), 4.19−4.83 (m, 10H), 2.56−3.92 (br, 2H), 1.80−2.56 (br, 1H), 1.20 (s, 9H), 1.17 (s, 9H), 1.14 (s, 18H), 1.02 (d, $J = 6.6$, 6H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 177.7 (C═O), 177.4 (C═O), 176.5 (C═O), 176.3 (C═O), 168.9 (C═N), 132.9 (CH), 131.7 (CH), 130.9 (CH), 129.3 (CH), 126.5 (C), 83.7 (br, CH), 72.4 (CH), 70.6 (br, CH_2), 68.4 (CH), 66.3 (CH), 61.1 (CH_2), 38.9 ($C(CH_3)_3$), 38.8 ($C(CH_3)_3$), 38.7 ($C(CH_3)_3$), 31.6 (CH), 27.1 (C(CH_3)$_3$), 27.0 (C(CH_3)$_3$), 18.6 (br, CH_3), 17.3 (br, CH_3). IR (CsI, cm^{-1}): 2970 m, 1739 s, 1633 m, 1281 s, 1139 s, 1087 m, 1035 s. FAB$^+$-MS: *m*/*z* 880 ($M^+ - PF_6$). Anal. Calcd for $C_{42}H_{64}NO_{10}F_6PSPd$ (1026.40): C, 49.15; H, 6.28; N, 1.36. Found: C, 48.45; H, 5.95; N, 1.36.

(η^3-Propenyl){(4*S*)-2-{*o*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-thioglucopyranose)methyl}benzoyl-5,5-dihydro-4-phenyloxazoline}-palladium(II) Hexafluorophosphate (19). This complex was prepared as for **17**. From the ligand **7** (23.4 mg, 3.9×10^{-2} mmol), η^3-C_3H_5-allyl−Pd−chloro dimer (7.2 mg, 2.0×10^{-2} mmol, 0.5 equiv), and KPF_6 (7.3 mg, 3.9×10^{-2} mmol) after recrystallization from CH_2Cl_2/pentane, one obtains 34.7 mg (quantitative) of the product **19** as an off-white powder, mp 142 °C. $[\alpha]_D = -64.2$ ($c = 1.5$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.48−7.76 (m, 4H), 5.12−5.34 (m, 3H), 4.78−4.87 (m, 3H), 4.44−4.50 (m, 5H), 4.07 (br, 4H), 2.01−2.17 (3 × s, 12H), 1.01 (d, $J = 6.6$, 6H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 170.3 (C═O), 170.2 (C═O), 169.7 (C═O), 169.5 (C═O), 169.0 (br, C═N), 133.0 (CH), 131.8 (CH), 130.9 (CH), 129.3 (CH), 126.3 (C), 119.8 (br, CH), 83.3 (br, CH), 73.1 (CH), 70.5 (br, CH_2), 68.5 (CH), 67.0 (CH_2), 61.1 (CH_2), 31.6 (CH), 20.7 (CH_3), 20.6 (CH_3). IR (CsI, cm^{-1}): 2960 m, 1751 s, 1633 m, 1229 s, 1060 m, 1038 m. FAB$^+$-MS: *m*/*z* 712 ($M^+ - PF_6$). Anal. Calcd for $C_{33}H_{38}NO_{10}F_6PSPd$ (892.09): C, 44.43; H, 4.29; N, 1.57. Found: C, 43.48; H, 5.35; N, 1.52.

(η^3-Propenyl){(4*S*)-2-{*o*-(2,3,4,6-tetra-*O*-pivaloyl-β-D-thioglucopyranosyl)methyl}benzoyl-5,5-dihydro-4-phenyloxazoline}palladium(II) Hexafluorophosphate (20). This complex was prepared as for **17**. From the ligand **8** (21.6 mg, 2.8×10^{-2} mmol), η^3-C_3H_5-allyl−Pd−chloro dimer (5.2 mg, 1.4×10^{-2} mmol, 0.5 equiv), and KPF_6 (5.3 mg, 2.8×10^{-2} mmol) after recrystallization from CH_2Cl_2/pentane, and then washing with hexane, 18.0 mg (60%) of the product **20** as an off-white powder was obtained, mp 156 °C dec. $[\alpha]_D = 1.7$ ($c = 0.9$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.41−7.72 (m, 9H), 2.78−5.64 (m, 17H), 1.11−1.21 (3 × s, 36H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 176.8 (C═O), 176.3 (C═O), 176.2 (C═O), 176.1 (C═O), 170.1 (br, C═N), 140.2 (br, C), 132.1 (br, CH), 130.5 (br, CH), 129.3 (CH), 127.3 (br, CH), 117.1 (br), 85.6 (br, CH), 72.8 (br, CH), 68.8 (br, CH), 66.5 (br, CH), 61.6 (br, CH_2), 60.2 (br, CH_2), 38.8 ($C(CH_3)_3$), 38.7 ($C(CH_3)_3$), 27.1 ($C(CH_3)_3$), 27.0 ($C(CH_3)_3$). IR (CsI, cm^{-1}): 2972 w, 1741 s, 1635 m, 1280 m, 1135 s, 1035 m. FAB$^+$-MS: *m*/*z* 914.3 ($M^+ - PF_6$). Anal. Calcd for $C_{45}H_{62}NO_{10}F_6PSPd$ (1060.41): C, 50.97; H, 5.89; N, 1.32. Found: C, 51.08; H, 5.86; N, 1.34.

The following sections describe the synthesis of the **2,3,4,6-tetra-*O*-pivaloyl-β-D-glucopyranosyl mercaptan** derivative.

Penta-*O*-pivaloyl-α-D-glucose. This compound was prepared according to the method of Mori et al.[25]

2,3,4,6-Tetra-*O*-pivaloyl-α-D-glucopyranosyl Bromide. This compound was also prepared according to the method of Mori et al.[25]

2-(2,3,4,6-Tetra-*O*-pivaloyl-β-D-glucopyranosyl)-2-thiourea Hydrobromide. 2,3,4,6-Tetra-*O*-pivaloyl-α-D-glucopyranosyl bromide (5.0 g, 8.64 mmol) and thiourea ($(NH_2)_2CS$; 723.7 mg, 9.5 mmol, 1.1 equiv) were dissolved in 7 mL of absolute Ac_2O. Stirring for 30 min at 65 °C afforded a brown suspension. Cooling to room temperature was followed by distillation of the solvent, i.v. The crude product was suspended in CH_2Cl_2, and unreacted thiourea was filtered out through Celite. The filtrate was concentrated to dryness and the resulting white powder dried i.v. to afford 3.03 g (71%) of colorless crystalline product, mp 161 °C. $[\alpha]_D = -19.6$ ($c = 1.1$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 9.62 (br, 2H), 8.13 (br, 2H), 5.46 (dd, $J = 23.4$ Hz, $J = 10.1$, 2H), 5.19 (m, 2H), 4.05−4.37 (m, 3H), 1.24 (s, 9H), 1.19 (s, 9H), 1.16 (s, 9H), 1.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 178.2 (C═O), 177.0 (C═O), 176.7 (C═O), 176.2 (C═O), 168.8 (C═N), 81.6 (CH), 72.2 (CH), 69.0 (CH), 66.6 (CH), 61.5 (CH_2), 38.9 ($C(CH_3)$), 38.8 ($C(CH_3)$), 38.8 ($C(CH_3)$), 38.7 ($C(CH_3)$), 27.2 ($C(CH_3)$), 27.1 ($C(CH_3)$), 27.0 ($C(CH_3)$), 27.0 ($C(CH_3)$). IR (CsI, cm^{-1}): 3379 br, 2973 m, 1741 s, 1644 m, 1281 m, 1138 s, 1043 s. FAB$^+$-MS: *m*/*z* 575, 499 (100%), 211. Anal. Calcd for $C_{27}H_{47}N_2O_9SBr$ (655.65): C, 49.46; H, 7.23; N, 4.27. Found: C, 49.36; H, 7.38; N, 4.50.

2,3,4,6-Tetra-*O*-pivaloyl-β-D-glucopyranosyl Mercaptan. The hydrobromide (2.03 g, 3.10 mmol) was suspended in 55 mL of H_2O. After the mixture was stirred for 1 h at room temperature, an aqueous solution of Na_2CO_3 (242.5 mg, 2.29 mmol, 3 equiv) was added. Stirring for 10 min was followed by cooling for 3 h at 5 °C. An off-white powder precipitated, which was filtered and washed with cold H_2O. The intermediate product was dried in the open air and then placed in a 50 mL flask together with $Na_2S_2O_4$ (2.90 g, 24.81 mmol, 8 equiv) and 15 mL of ethyl acetate. Stirring for 30 min at 80 °C, filtration to remove excess $Na_2S_2O_4$, and filtration through Celite and active charcoal gave a clear solution. After washing with ethyl acetate all of the solvent was removed. The crude product was purified by colum chromatography (hexane/ethyl acetate, 6/1) (R_f 0.41) to afford a colorless crystalline product (686.9 mg, 42%), mp 125 °C. $[\alpha]_D = +16.0$ ($c = 1.0$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 5.30 (t, $J = 9.3$ Hz, 1H), 5.18 (t, $J = 9.8$, 1H), 5.01 (t, $J = 9.6$, 1H), 4.54 (t, $J = 9.9$, 1H), 4.19 (dd, $J = 12.5$, $J = 2.1$, 1H), 4.10 (dd, $J = 12.5$, $J = 4.7$, 1H), 3.74 (ddd, $J = 9.9$, $J = 4.6$, $J = 2.1$, 1H), 2.26 (d, $J = 10.2$, 1H, SH), 1.23 (s, 9H), 1.18 (s, 9H), 1.14 (s, 9H), 1.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 178.0 (C═O), 177.0 (C═O), 176.8 (C═O), 176.3 (C═O), 79.0 (CH), 76.7 (CH), 73.4 (CH), 73.0 (CH), 67.5 (CH), 61.7 (CH_2), 38.8 ($C(CH_3)$), 38.7 ($C(CH_3)$), 38.7 ($C(CH_3)$), 27.1 ($C(CH_3)$), 27.1 ($C(CH_3)$), 27.1 ($C(CH_3)$), 27.0 ($C(CH_3)$). IR (KBr solution cells, cm^{-1}): 2970 s, 2935 m, 2870 m, 1741 s, 1478 m, 1279 m, 1158 s, 1134 s. EI$^+$-MS *m*/*z* 499, 431, 415, 328, 313, 226, 211 (100%). Anal. Calcd for $C_{26}H_{44}O_9S$ (532.69): C, 58.62; H, 8.33. Found: C, 58.43; H, 8.11.

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