Chiral P,S-Ligands Based on β-D-Thioglucose Tetraacetate. Palladium(II) Complexes and Allylic Alkylation

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The new chelating P,S-ligands 2,3,4,6-tetra-*O*-acetyl-1-((2-(diphenylphosphino)benzy)lthio)-β-D-glucopyranose, [(2-$Ph_2PC_6H_4CH_2$)SCHCH(OAc)CH(OAc)CH(OAc)CH(CH_2OAc)O, **2**] and 2,3,4,6-tetra-*O*-acetyl-1-((2-(dicyclohexylphosphino)benzyl)thio)-β-D-glucopyranose [(2-Cy_2-$PC_6H_4CH_2$)SCHCH(OAc)CH(OAc)CH(OAc)CH(CH_2OAc)O,, **3**] as well as their (1,3-diphenylallyl)palladium(II) cationic complexes [Pd(η^3-PhCHCHCHPh)(**2**)]PF_6, **6**, and [Pd(η^3-PhCHCHCHPh)(**3**)]PF_6, **7**, and one η^3-C_3H_5 complex [Pd(η^3-C_3H_5)(**2**)]PF_6, **5**, have been prepared. The solid-state structure of [Pd(η^3-C_3H_5)(**2**)]PF_6, **5**, has been determined by X-ray diffraction methods and found to have the *S*-sugar substituent and one of the *P*-phenyl rings in pseudo-axial positions on the same side of the P−Pd−S coordination plane. Detailed NMR measurements for **6** reveal the presence of two diastereomeric isomers whereas for **7** four diastereomers are found. 2-D exchange NMR is used to characterize several of the selective equilibria within **6** and **7**. On the basis of the observed ee in the enantioselective homogeneous allylic alkylation of **7**, it is suggested that the reaction kinetics for the four isomers are not all the same.

Introduction

The chemistry of Pd(II) allyl complexes remains an active research theme with a variety of organic substrates capable of allylation in the presence of catalytic amounts of palladium salts.[1] In recent years, the Pd-catalyzed enantioselective allylic alkylation[2,3] and amination[4] have preempted much of the limelight. These reactions are often modeled using the 1,3-diphenylallyl acetate precursor given in eq (1). The chiral catalyst

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

often consists of a precursor palladium complex containing a chiral chelating ligand; however, the catalyst can be generated *in situ* from, e.g., [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ or via the Pd(0) benzylidene acetone complex Pd_2{(PhCH=CH)$_2$CO)}$_3$·$CHCl_3$, and a suitable number of equivalents of the chiral auxiliary. Several different donor combinations within the chelating chiral auxiliary have been used, e.g., P−P,[5] P−N,[6a−c] P−O,[6d] N−N,[7,8] and N−S[9] compounds have all been successfully used.

The mechanism[10] of this palladium-mediated allylation reaction is reasonably well understood. A chiral Pd(0) olefin complex oxidatively adds the prochiral allylic acetate to afford an isolable η^3-allyl cationic compound of the form [Pd(η^3-PhCHCHCHPh)(chiral chelate)]$^+$, which is then attacked, in the rate-determining step, by the carbon or nitrogen nucleophile. The nucleophile attacks from the side remote from the metal, and since the initial oxidative addition proceeds with inversion, the complete reaction is often found to go with retention of configuration at carbon. The complications arising from the possibility that the Pd(0) complex acts

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(1) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley and Sons, Inc.: New York, 1994. Hayashi, T. In *Catalytic Asymmetry Synthesis*; Ojima, I., Ed.; VCH Publishers, Inc.: New York, 1993; p 325. Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257. Trost, B. M. *Chemtracts Org. Chem.* **1988**, *1*, 415.

(2) Hiraswa, K.; Kawamata, M.; Hiroi, K. *Yakugaku Zasshi* **1994**, *114* (2), 111. Yamaguchi, M.; Shima, T.; Hida, M. *Tetrahedron Lett.* **1990**, *31*, 5049. Yamaguchi, M.; Shima, T.; Yamagishi, T.; Hida, M. *Tetrahedron Asymm.* **1991**, *2*, 663.

(3) Reiser, O. *Angew. Chem.* **1993**, *105*, 576.

(4) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301. Bäckvall, J.; Nordberg, R. E.; Zetterberg, K.; Åkermark, B. *Organometallics* **1983**, *2*, 1625.

(5) (a) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062. (b) Hayashi, T.; Yamamoto, A. *Tetrahedron Lett.* **1988**, *29*, 669.

(6) (a) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493. (b) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelein, M.; Huttner, G.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523. (c) Sprinz, J.; Helmchen, G.; *Tetrahedron Lett.* **1993**, 1769. (d) Knühl, G.; Sennhenn, P.; Helmchen, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1845.

(7) Togni. A.; Venanzi, L. M. *Angew. Chem.* **1994**, *33*, 497. Andersson, P. G.; Harden, A.; Tanner, D.; Norrby, P. O. *Chem. Eur. J.* **1995**, *1*, 12. Gamez, P.; Dunjic, B.; Fache, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1417. Togni, A. *Tetrahedron Asym.* **1991**, *2*, 683.

(8) (a) von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rüegger, H, Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265. (b) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339. (c) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (d) Leutenegger, U.; Umbricht, C.; Fahrni, P.; von Matt, A.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143. (e) Mueller, D.; Umbricht, B.; Weber, A.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232.

(9) Dawson, G.; Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 3149.

(10) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046. Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033.

(11) Granberg, K. L.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 6858. Nilsson, Y. I. M.; Andersson, P. G.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 6609.

(12) Herrmann, J.; Pregosin, P. S.; Salzmann, R.; Albinati, A. *Organometallics* **1995**, *14*, 3311.

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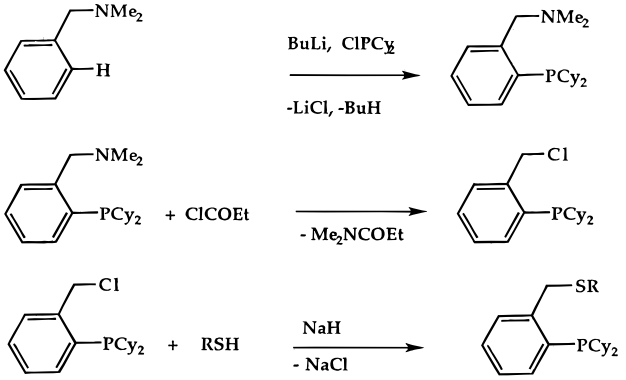
Scheme 1. Preparation of the Ligands



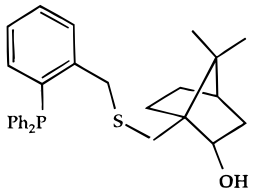
The synthesis for the PPh_2 analog follows identical lines.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 5

molecule A		molecule B	
Pd−C(1A)	2.15(1)	Pd−C(1B)	2.11(1)
Pd−C(2A)	2.17(2)	Pd−C(2B)	2.11(2)
Pd−C(3A)	2.25(1)	Pd−C(3B)	2.22(1)
Pd−S(A)	2.364(3)	Pd−S(B)	2.340(2)
Pd−P(A)	2.297(2)	Pd−P(B)	2.279(3)
S(A)−C(4)	1.85(1)	S(B)−C(4)	1.83(1)
S(A)−C(5)	1.79(1)	S(B)−C(5)	1.81(1)
P(A)−C(21)	1.82(1)	P(B)−C(21)	1.83(1)
P(A)−C(31)	1.84(1)	P(B)−C(31)	1.80(1)
P(A)−C(41)	1.81(1)	P(B)−C(41)	1.83(1)
P(A)−Pd−S(A)	94.6(1)	P(B)−Pd−S(B)	95.5(1)
P(A)−Pd−C(1A)	100.8(3)	P(B)−Pd−C(1B)	98.2(5)
P(A)−Pd−C(3A)	166.7(4)	P(B)−Pd−C(3B)	166.0(3)
S(A)−Pd−C(1A)	164.4(3)	S(B)−Pd−C(1B)	165.8(5)
S(A)−Pd−C(3A)	98.5(4)	S(B)−Pd−C(3B)	98.4(3)

as a nucleophile have been discussed by Bäckvall and co-workers.[11]

We have recently become interested in chiral bidentate ligands with phosphorus and sulfur donors, e.g., the *exo*-norborneol derivative **1**. In contrast to other



1

chelating ligands, the chirality of **1** is not located in the phosphine backbone. Complexes of Pd(II) with **1** proved to be disappointing precursors for the enantioselective allylic alkylation,[12] with ee's ≤22%; however, the allyl complexes [Pd(η^3-C_3H_5)(**1**)](CF_3SO_3) and [Pd(η^3-PhCHCHCHPh)(**1**)](BF_4) showed unexpected and novel allyl dynamics.[12] In the former, the η^3-C_3H_5 ligand isomerization is selective ($\eta^3-\eta^1$ opens *trans* to the P-donor) and controlled by electronic effects. In the latter the $\eta^3-\eta^1$ opening of the η^3-PhCHCHCHPh is also selective ($\eta^3-\eta^1$ opens *trans* to the S-donor, away from the P-donor) but controlled by steric effects. Selectivity in

(13) Pregosin, P. S.; Salzmann, R.; Togni, A. *Organometallics* **1995**, *14*, 842.

(14) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067.

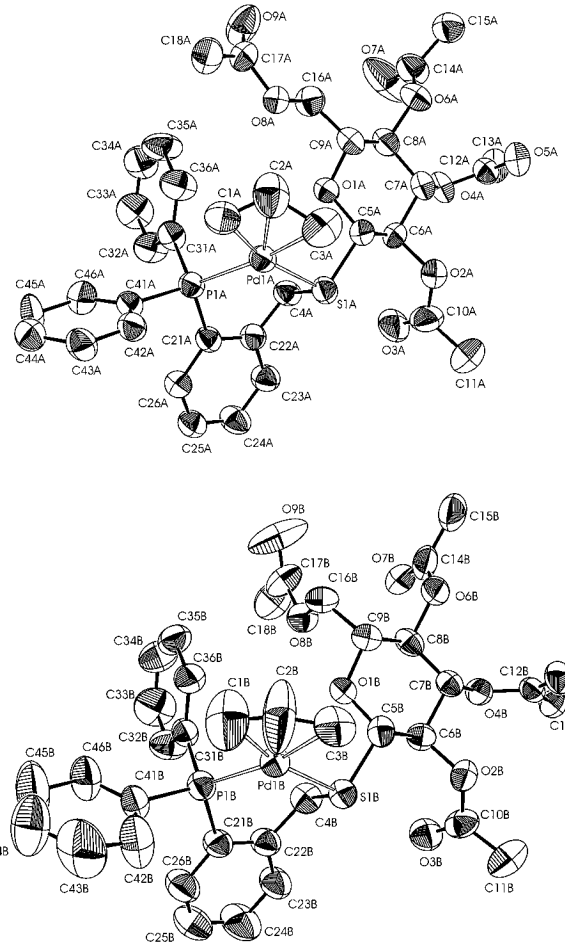
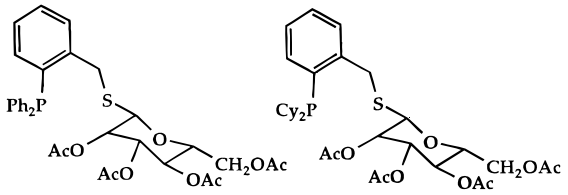


Figure 1. ORTEP plot for the two cations of [Pd(η^3-C_3H_5)-(**2**)]PF_6, **5** (anions not shown).

allyl isomerization has also been observed in several JOSIPHOS complexes.[13,14]

We considered that the intervening SCH_2 group, between the donor and the norborneol moiety of **1**, placed the chiral centers of the borneol fragment too far from the palladium coordination sphere to effectively transfer the chiral information. To improve on this situation we have now prepared two new chiral bidentate P,S-ligands, **2** and **3**, derived from β-D-thioglucose tetraacetate, **4**, together with several palladium(II) complexes and present here our results.



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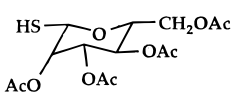

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Results and Discussion

Both **2** and **3** were prepared by the reaction of the thiolate anion of **4** with the known chloro-methyl phosphine compound as shown in Scheme 1. It is worth

Table 2. Experimental Data for the X-ray Diffraction Study of 5

composn	$C_{36}H_{40}O_9P_2SF_6Pd + 3H_2O + 0.5CH_2Cl_2$
fw	1027.59
cryst size	0.45 × 0.45 × 0.25 mm
color	orange
lattice consts (Å, deg)	$a = 17.122(3)$; $b = 14.098(3)$; c = 22.316(5) α = 90; $\beta = 104.53(2)$; $\gamma = 90$
V (Å^3)	5215(2)
cryst system	monoclinic
space group	$P21$ (No. 4)
formula units/cell	$Z = 4$
ρ(calcd) (g/cm^3)	1.309
abs coeff μ (mm^{-1})	0.58
F(000)	2100.0
T (K)	200
data collcn	scanner STOE IPDS
monochromator	graphite monochromator
wavelength (Å)	λ(MoKa) = 0.71073
detector dist; φ(start) − φ(end); $\Delta\varphi$	$d = 80$ mm; $\varphi = 0-175$ °; $\Delta\varphi = 1.0$ °
data collcn; irradiaton time; images	oscillation; $t = 6$ min; $n = 175$
θ range for data collcn	3.8° < θ < 24.2°
h(min), h(max); k(min), k(max); l(min), l(max)	−19, 17; −16, 16; −25, 25
collcd reflcns	29 271
indepdt reflcns	15 566 (R(int) = 0.041)
indepdt reflcns with $\|F\|^2 > 2\sigma(\|F\|^2)$	14 504
abs corr	
struct solution	SHELXS-86 (Patterson methods)
struct refinement	SHELXL-93 (full-matrix least-squares on F^2)
no. of params	1012
no. of param restraints	1
max shift/std dev	$<10^{-3}$
mean shift/std dev	$<10^{-3}$
resid electron density (electrons/Å^3)	min = −0.66; max = 1.62
wR for $\|F\|^2 > 2\sigma(\|F\|^2)$	0.218 ($a = 0.1627$; $b = 9.33$)
wR for all indepdt reflcns	0.229
R for $\|F\|^2 > 2\sigma(\|F\|^2)$	0.077
R for all indepdt reflcns	0.082
goodness of fit (GooF) for $\|F\|^2 > 2\sigma(\|F\|^2)$	1.051
goodness of fit (GooF) for all indepdt reflcns	1.067
absolute struct param	0.01(4)

[a] w$R = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{1/2}$. $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$. $P = F_o^2(\geq 0) + 2F_c^2/3$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] GooF = $(\sum w(F_o^2 - F_c^2)^2/n - p)^{1/2}$. n = number of reflections. p = number of parameters.

noting that the chirality is introduced in the last step from a commercially available source.

Three Pd(II) complexes of ligand **2** were prepared, $PdCl_2$(**2**), [Pd(η^3-C_3H_5)(**2**)]PF_6 , **5**, and [Pd(η^3-PhCHCHCHPh)(**2**)]PF_6, **6**, in order to obtain a feeling for the coordination characteristics of **2**. The dichloride was useful in that it provided a simple model for the ^{1}H NMR spectroscopy of a thioglucose coordinated to Pd(II). The ^{1}H NMR spectrum of **4** is known.[15] As **3** was only of interest in connection with the catalytic chemistry, we have restricted its coordination chemistry to [Pd(η^3-PhCHCHCHPh)(**3**)]PF_6, **7**. The allyl complexes were prepared as described previously.[12]

Solid-State Structure of [Pd(η^3-C_3H_5)(2)]PF_6, 5. To assist in the characterization of the new ligand **2** and its complexes, we have determined the solid-state structure of **5** via X-ray diffraction methods. Suitable crystals could be obtained from a CH_2Cl_2/pentane solution at 4 °C. The data were collected at 200 K as the crystal appears not to be very stable over extended periods.

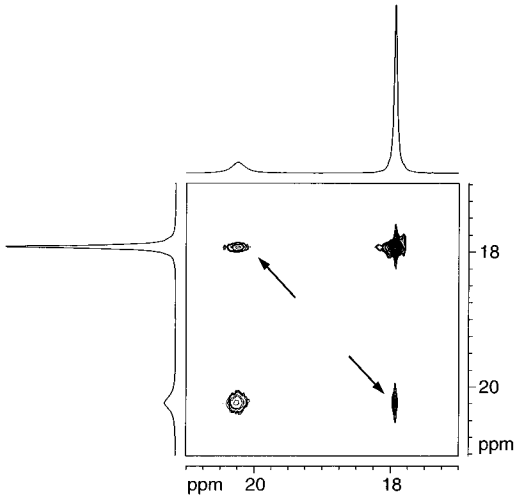


Figure 2. ^{31}P NMR exchange spectrum for **6**. The cross-peaks indicate clearly show that **6a**,**b** are in equilibrium ($CDCl_3$, 202 MHz).

The complex has two nonequivalent molecules, A and B, in the unit cell, and selected bond lengths and bond angles for both of these are given in Table 1. The two molecules are not significantly different in terms of their Pd−P and Pd−S separations, with the observed bond lengths and angles consistent with literature expectations.[16−18] However, between the two molecules, there are marked conformational differences at the ester functions, C(12), C(14), and C(17), in addition to some conformational changes at the phenyl rings. Molecule A exhibits an allyl ligand with somewhat less displacement than the allyl in molecule B so that the discussion which follows is based on A. ORTEP plots for cations A and B are shown in Figure 1 and Tables 2 and 3 provide experimental parameters for the structure determination and atomic coordinates and equivalent isotropic displacement parameters, respectively.

The geometry about the metal is distorted square-planar with the allyl carbons and the P- and-S-donor atoms comprising the immediate coordination sphere. As expected, the Pd−C(3) separation, 2.25(1) Å in pseudo-*trans* position to the P-donor atom, is somewhat longer than the corresponding Pd−C(1) contact, 2.15(1) Å, as a consequence of the larger *trans* influence of a tertiary phosphine relative to a thioether.[19] The literature range[20−25] for Pd−C separations in allylpalladium complexes is ca. 2.1−2.3 Å. The Pd−S and Pd−P distances, 2.364(3) and 2.297(2) Å, respectively, in [Pd-

(15) Pregosin, P. S.; Becker, E. D. *Helv. Chim. Acta* **1984**, *66*, 1436.
(16) Grant, G. J.; Sanders, K. A.; Setzer, W. N.; Van Derveer, D. G. *Inorg. Chem.* **1991**, *30*, 4053.
(17) Abel, E. A.; Dormer, J. C.; Ellis, D.; Orrell, K. G.; Sik, V.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1073.
(18) Chooi, S. Y.; Andy Hor, T. T.; Leung, P.; Mok, K. F. *Inorg. Chem.* **1992**, *31*, 1494. Giesbrecht, G. R.; Hanan, G. S.; Kickham, J. E.; Loeb, S. L. *Inorg. Chem.* **1992**, *31*, 3286.
(19) Appleton, T.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.
(20) Ozawa, F.; Son, T.; Ebina, S.; Osakada, K.; Yamamoto, A. *Organometallics* **1992**, *11*, 171.
(21) Grassi, M.; Meille, S. V.; Musco, A.; Pontellini, R.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1990**, 251; **1989**, 615.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 5

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Pd(1A)	8054(1)	−2(1)	110(1)	48(1)	C(26B)	4127(7)	1621(10)	6026(6)	78(3)
Pd(1B)	1388(1)	1397(1)	5716(1)	50(1)	C(31B)	2455(6)	3448(7)	5715(4)	53(2)
S(1A)	8292(1)	−889(2)	−725(1)	51(1)	C(32B)	3146(7)	3992(9)	5983(6)	77(3)
P(1A)	6922(1)	−843(2)	159(1)	47(1)	C(33B)	3094(11)	4950(11)	6030(9)	106(5)
C(1A)	8100(7)	1039(8)	814(5)	68(3)	C(34B)	2365(9)	5391(9)	5835(7)	85(4)
C(2A)	8457(9)	1412(3)	434(7)	95(4)	C(35B)	1690(8)	4909(9)	5592(5)	74(3)
C(3A)	9134(7)	962(9)	276(8)	90(4)	C(36B)	1707(7)	3893(8)	5523(5)	65(3)
C(4A)	7305(6)	−1424(7)	−1089(4)	53(2)	C(41B)	2691(7)	2026(8)	4839(5)	62(3)
C(21A)	6954(5)	−2048(7)	−124(4)	48(2)	C(42B)	2655(11)	1100(13)	4613(8)	108(5)
C(22A)	7161(6)	−2193(7)	−677(4)	53(2)	C(43B)	2658(15)	1000(17)	3961(9)	141(8)
C(23A)	7218(7)	−3137(7)	−886(5)	62(2)	C(44B)	2874(15)	1777(18)	3660(8)	131(7)
C(24A)	7091(8)	−3890(7)	−517(5)	69(3)	C(45B)	2954(18)	2614(18)	3901(10)	155(10)
C(25A)	6903(7)	−3740(8)	40(5)	62(2)	C(46B)	2836(10)	2781(12)	4501(6)	90(4)
C(26A)	6833(6)	−2838(7)	230(5)	60(2)	C(5B)	1065(6)	1762(7)	7052(4)	52(2)
C(31A)	5989(6)	−346(8)	−332(4)	56(2)	C(6B)	1230(6)	1843(7)	7746(4)	52(2)
C(32A)	5342(7)	−876(10)	−572(6)	74(3)	C(7B)	540(5)	2377(6)	7929(4)	45(2)
C(33A)	4599(8)	−469(12)	−927(7)	92(4)	C(8B)	407(5)	3299(7)	7610(4)	51(2)
C(34A)	4589(8)	501(11)	−1020(6)	86(4)	C(9B)	294(6)	3202(6)	6903(4)	50(2)
C(35A)	5257(8)	1064(10)	−782(7)	91(4)	O(1B)	981(4)	2696(4)	6801(3)	49(1)
C(36A)	5966(8)	612(10)	−431(7)	82(4)	O(2B)	1256(4)	890(5)	8015(3)	56(2)
C(41A)	6719(5)	−956(6)	916(4)	45(2)	C(10B)	1983(8)	544(8)	8315(5)	66(3)
C(42A)	7368(6)	−935(7)	1427(5)	55(2)	O(3B)	2624(5)	999(6)	8360(4)	73(2)
C(43A)	7255(7)	−1016(8)	2032(4)	61(2)	C(11B)	1908(10)	−406(10)	8560(7)	92(4)
C(44A)	6452(7)	−1085(8)	2095(5)	65(3)	O(4B)	9203(4)	−2473(5)	1408(3)	53(1)
C(45A)	5834(7)	−1132(10)	1599(5)	72(3)	C(12B)	9606(5)	−2924(6)	1041(4)	47(2)
C(46A)	5961(6)	−1041(8)	994(5)	62(2)	O(5B)	9789(4)	1602(5)	−1247(3)	60(2)
C(5A)	8353(5)	61(7)	−1247(4)	53(2)	C(13B)	9219(6)	−2777(8)	384(4)	59(2)
C(6A)	−1686(6)	−264(7)	8094(5)	54(2)	O(6B)	10327(4)	−1284(5)	2309(3)	59(2)
C(7A)	−1663(6)	601(7)	7672(4)	52(2)	C(14B)	10278(8)	−365(9)	2086(5)	72(3)
C(8A)	7707(6)	1323(7)	−2259(4)	57(2)	O(7B)	9662(6)	64(7)	1925(5)	93(3)
C(9A)	7734(6)	1561(7)	−1578(4)	54(2)	C(15B)	110077(8)	−55(11)	2056(7)	86(4)
O(1A)	7676(4)	689(4)	−1273(3)	51(1)	C(16B)	252(6)	4132(7)	6574(5)	58(2)
O(2A)	9047(5)	−811(5)	−1883(4)	64(2)	O(8B)	970(4)	4677(5)	6877(3)	62(2)
C(10A)	8968(11)	−1773(9)	−1923(7)	86(4)	C(17B)	890(9)	5634(8)	6871(6)	79(3)
O(3A)	8324(7)	−2189(6)	−2041(5)	92(3)	O(9B)	296(8)	6012(7)	6583(6)	136(6)
C(11A)	9778(11)	−2232(13)	−1845(10)	113(6)	C(18B)	1592(10)	6107(10)	7237(7)	96(4)
O(4A)	−1868(4)	294(5)	7048(3)	58(2)	P(1)	10993(2)	−789(3)	336(2)	82(1)
C(12A)	−1453(6)	618(7)	6672(5)	57(2)	F(11)	11580(6)	−514(9)	−84(5)	128(1)
O(5A)	−824(4)	1081(6)	6844(3)	65(2)	F(12)	11771(7)	−908(9)	885(6)	128(1)
C(13A)	−1833(8)	408(10)	6010(5)	75(3)	F(13)	10215(7)	−570(8)	−208(5)	128(1)
O(6A)	7871(5)	2157(5)	−2571(3)	64(2)	F(14)	10435(6)	−985(9)	784(5)	128(1)
C(14A)	7330(8)	2445(10)	−3074(6)	82(4)	F(15)	11010(7)	295(8)	551(6)	128(1)
O(7A)	6726(8)	2044(13)	−3267(8)	173(8)	F(16)	10985(7)	−1822(9)	162(5)	128(1)
C(15A)	7587(8)	3242(9)	−3408(6)	77(3)	P(2)	1485(2)	−1731(2)	4978(2)	73(1)
C(16A)	7033(7)	2165(8)	−1537(4)	61(2)	F(21)	1431(6)	−2476(6)	5505(4)	102(1)
O(8A)	7101(4)	2382(5)	−892(3)	53(2)	F(22)	1756(6)	−903(7)	5479(4)	102(1)
C(17A)	6602(7)	3085(8)	−807(5)	64(3)	F(23)	554(6)	−1467(6)	4926(4)	102(1)
O(9A)	6156(6)	3481(9)	−1195(4)	96(3)	F(24)	2373(6)	−1985(6)	5040(4)	102(1)
C(18A)	6722(8)	3289(10)	−124(6)	78(3)	F(25)	1192(6)	−2503(6)	4466(4)	102(1)
S(1B)	1852(1)	1175(2)	6786(1)	49(1)	F(26)	1495(6)	−979(6)	4453(4)	102(1)
P(1B)	2507(2)	2183(2)	5606(1)	52(1)	C(1)	222(10)	−1745(10)	6389(7)	95(4)
C(1B)	678(10)	1501(18)	4797(7)	134(8)	Cl(1)	222(10)	−1745(10)	6389(7)	95(4)
C(2B)	285(12)	1088(21)	5079(7)	164(12)	Cl(2)	−785(4)	−1760(6)	6449(4)	180(3)
C(3B)	179(6)	737(9)	5582(6)	75(3)	O(1)	3773(4)	4336(6)	2897(4)	74(2)
C(4B)	2677(6)	2034(8)	7033(5)	58(2)	O(2)	3540(5)	7367(6)	6750(4)	77(2)
C(21B)	3422(6)	1827(7)	6184(5)	56(2)	O(3)	4926(6)	−3598(7)	−1013(5)	116(4)
C(22B)	3396(6)	1790(8)	6792(5)	58(2)	O(4)	3220(5)	−21(10)	2332(5)	103(3)
C(23B)	4103(7)	1547(11)	7234(11)	77(3)	O(5)	6640(6)	2261(7)	1483(5)	93(3)
C(24B)	4805(8)	1355(15)	7069(7)	104(5)	O(6)	3336(6)	−819(7)	7309(7)	129(5)
C(25B)	4805(8)	1355(15)	7069(7)	104(5)					

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(η^3-C_3H_5)(**2**)]PF_6 are in good agreement with the values for the Pd−S and Pd−P separations determined[12] for [Pd(η^3-C_3H_5)(**1**)]CF_3SO_3, 2.350(2) and 2.287(2) Å, respectively. The angle P−Pd−S, at 94.6(1)°, is suggestive of a relatively large ligand. The analogous angle in [Pd(η^3-C_3H_5)(**1**)]CF_3SO_3 is 95.41(7)°. The pseudo-*trans* angles P−Pd−C(1) and P−Pd−C(3), 164.3 and 166.7°, respectively, suggest no special displacement of the allyl ligand.

The terminal carbons of the allyl ligand are not symmetrically placed with respect to a coordination

(22) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1899. Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1979**, 670.

(23) Knierzinger, A.; Schoholzer, P. *Helv. Chim. Acta* **1992**, *75*, 1211.

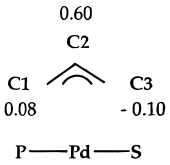
(24) Fernandez-Galan, R.; Manzano, B. R.; Otero, A.; Lanfranchi, M.; Pellingelli, A. *Inorg. Chem.* **1994**, *33*, 2309.

(25) Albinati, A.; Kunz, R. W.; Ammann, C.; Pregosin, P. S. *Organometallics* **1991**, *10*, 1800. Musco, A.; Pontellini, R.; Grassi, M.; Sironi, A.; Meille, S. V.; Ruegger, H.; Ammann, C.; Pregosin, P. S. *Organometalics* **1988**, *7*, 2130.

(26) Abel, E. W.; Ellis, D.; Orrell. K. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1992**, 3497.

(27) Abel, E. W.; Coston, T. P. J.; Higgins, K. M.; Ellis, D.; Orrell, K. G.; Sik, V.; Cameron, T. S. *J. Chem. Soc., Dalton Trans.* **1989**, 701.

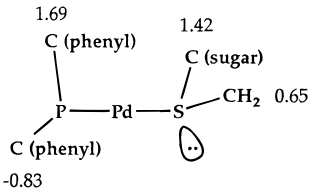
plane defined by the P, Pd, and S atoms. One carbon is slightly below and the other slightly above this plane as indicated



Distances in Å from the P-Pd-S coordination plane for the three allyl carbon atoms.

so that one can think of the allyl as slightly rotated.

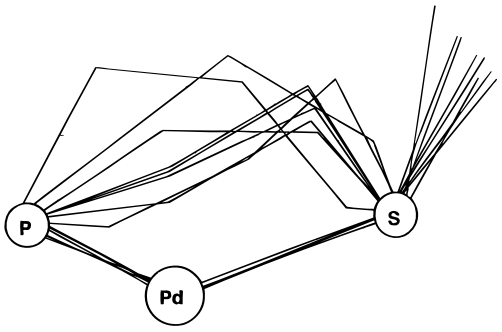
The PPh_2 moiety has one pseudo-equatorial phenyl (−0.83 Å from the coordination plane) and one pseudo-axial phenyl group (+1.69Å from the coordination plane). If this placement were strictly axial, one would expect a value of ca. 1.8 Å. Interestingly, both adjacent thioether carbons are on the same side of the plane as the axial *P*-phenyl, with the anomeric sugar carbon in pseudo-axial and the benzyl carbon in pseudo-equatorial positions:



Distances in Å from the P-Pd-S coordination plane

From this sketch it is clear that there is a substantial amount of space for the sulfur lone pair.

A literature search using the Cambridge data base revealed structural data for seven P,S−palladium complexes (see Experimental Section). A perspective for these seven (together with [Pd(η^3-C_3H_5)(**1**)]CF_3SO_3 and [Pd(η^3-C_3H_5)(**2**)]PF_6) is shown as follows:

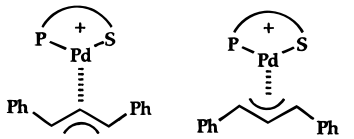


As can be seen, there is a strong tendency for the sulfur substituent to be pseudo-axial.

NMR Studies on [Pd(η^3-PhCHCHCHPh)(2)]PF_6, 6. The ligands **2** and **3** proved to be somewhat better than **1** in the enantioselective allylic alkylation in that one finds ee's of 64% and 53%, respectively. These ee's are not special as it is known that values in excess of 90% can be obtained.[5−8] It was somewhat surprising to us that the cyclohexyl analog was less selective than the phenyl derivative. To further our understanding of this chemistry we studied the two 1,3-diphenylallyl intermediates [Pd(η^3-PhCHCHCHPh)(**2**)]PF_6, **6**, and [Pd(η^3-PhCHCHCHPh)(**3**)]PF_6, **7**, using multinuclear, multidimensional NMR methods.

Complex **6** in $CDCl_3$ reveals the presence of two diastereomeric complexes, **6a** and **6b**, with ^{31}P chemical shifts of 18.1 and 19.9 ppm, respectively. These can be shown to be exchanging with each other via 2-D ^{31}P exchange spectroscopy (see Figure 2). We consider the difference in ^{31}P line widths between **6a** and **6b** to stem from differences in the rate of sulfur inversion[26−28] between these two diastereomers (note that the coordinated S atom is a stereogenic center). At ambient temperature the ratio **6a**:**6b** is ca. 4:1, and at 323 K, this ratio is ca. 3:1.

A NOESY measurement at ambient temperature was informative but somewhat ambiguous;[29] however, at 323 K, with increased molecular motions, it was possible to unambiguously assign a sufficient number of protons such that, together with the allyl ^3J(H,H) values, one could assign **6a**,**b** as both having the syn/syn geometry, i.e., as abbreviated as follows:

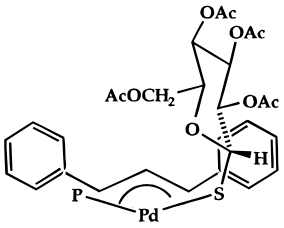


6a syn/syn exo major isomer

6b syn/syn endo minor isomer

Exo and endo are somewhat arbitrary descriptors and refer to the relative position of the central allyl proton. The two cationic complexes are rotational isomers and arise, presumably, via $\eta^3-\eta^1-\eta^3$ isomerization. For the major isomer, **6a**, we note some interesting structural details derived from the presence (or absence) of NOE's:

(a) The sugar moiety on sulfur occupies a pseudo-axial position. Several NOE's define its position; however, in addition, we note that the sugar anomeric methine SC**H**O proton in **6a** appears at relatively low frequency, δ = 2.48, due to the shielding of the proximate allyl phenyl group, i.e.



structural fragment of **6a** showing the screening of the sugar methine proton via the proximate allyl phenyl group.

The analogous proton in **6b** has δ = 4.38, a normal position for such a signal.

(28) Abel, E. W.; Moss, I.; Orrell. K. G.; Sik, V.; Stephanson, D.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 521 and references therein.

(29) When molecular motions become slow, perhaps due to a relatively large molecular weight, NOE's can be either positive or negative; see: Hull, W. E. In *Two-Dimensional NMR Spectroscopy. Applications for Chemists and Biochemists*; VCH: New York, 1987.

(30) Barbaro, P.; Pregosin, P. S.; Salzmann, R.; Albinati, A.; Kunz, R. *Organometallics* **1995**, *14*, 5160.

(31) Cozzi, F.; Ponzini, F.; Annunziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem.* **1995** , *107*, 1092.

(32) Åkermark, B.; Krakenberger, B.; Hansson S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620.

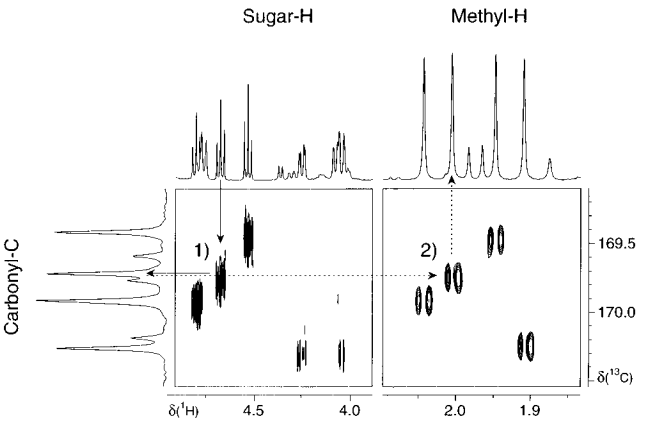
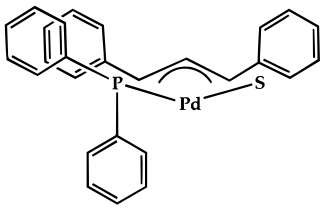


Figure 3. Section of the selective $^{13}C,^{1}H$ correlation for **6**. A soft pulse in the range of the carbonyl groups selects these C═O resonances and correlates these with the ring protons (show as (1)). Simultaneously, one observes the corresponding C═O methyl proton cross-peaks (shown as (2)), thereby assigning all of these signals ($CDCl_3$, 500 MHz).

(b) Relative to the allyl phenyl, the PPh_2 moiety has the following structure:

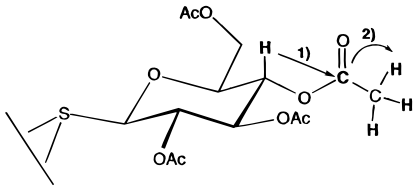


fragment of **6a**

with one axial phenyl (down, on the opposite side from the sugar) and an equatorial phenyl.

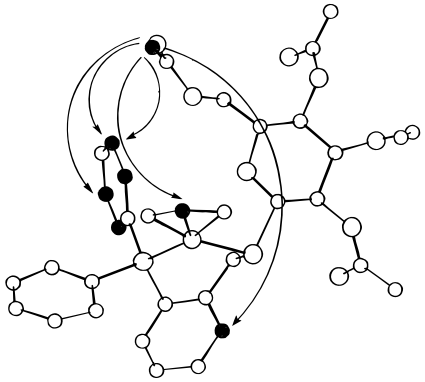
(c) The equatorial *P*-phenyl ring and the proximate allyl phenyl ring are stacking; i.e., they move together. This conclusion derives from the absence of NOE's between the two sets of *ortho* phenyl protons, and we have described this stacking phenomenon previously[30] for $[Pd(\eta^3\text{-PhCHCHCHPh})(P,P)]^+$ cations, with P,P = (*R*)-1,2-bis(diphenylphospino)cyclopentane and (*S*)-MeO-BIPHEMP (BIPHEMP = (2,2′-bis(diphenylphosphino)-6,6′-dimethoxybiphenyl)), among others. We consider the stacking of these rings to be a necessary compromise and most likely repulsive in nature, although for 1,8-diarylnaphthalenes it is known[31] that, in special cases, ring-stacking can be attractive.

Conclusion (a), with respect to the pseudo-axial position of the sugar moiety, is based on NOE data together with a selective long-range C,H correlation. This latter is not routine in coordination chemistry; rather this was dictated by the special nature of the sugar ligand. Initially, the NOESY (and COSY) experiments assigned all five thio-sugar-ring protons. After these, the coupled ^{13}C *long-range* experiment, using a soft pulse in the range of the carbonyl groups to select these ^{13}C═O resonances, correlates these ^{13}C signals with the sugar ring protons (which relationship we show as (1))



thus completing this assignment. Simultaneously, one observes the corresponding ^{13}C═O to methyl proton correlations (shown as (2)), thereby assigning all of these signals. Sections of this spectrum are given in Figure 3.

With all of the assignments in hand, the NOE's from the acetate **methyl** group to the rest of the compound determine the axial position of the sugar fragment (the phenyl groups on the allyl are omitted for clarity):



The terminal allyl ^{13}C chemical shifts[30,32] in **6a**,**b** for the carbon *trans* to sulfur, δ = 86.3 and 89.0, respectively, are at lower frequency than those observed for the allyl terminus *trans* to the P-donor, δ = 97.6 and 95.4, respectively. The analogous ^{13}C chemical shifts for the terminal allyl carbons of the two syn/syn isomers in the *exo*-norborneol analog are 83.4 and 84.0 and 97.5 and 98.0, respectively. The ^{13}C values for carbon termini *trans* to the S-donor in **6** are at slightly higher frequency, suggesting a larger trans influence. Interestingly, these 86.3 and 89.0 values (trans to sulfur) are not too different from those found previously[30] for the (1,3-diphenylallyl)palladium complex of (*S,S*)-CHIRAPHOS, δ = 90.1 and 88.1. We do *not* suggest that the thioether S-donor ligand in **6** exercises the same electronic *trans* influence as a tertiary phosphine P-donor; however, the combination of the thioether electronic *trans* influence and *cis* PPh_2 *steric effects* creates an environment which weakens the Pd−allyl interaction.

NMR Studies on $[Pd(\eta^3\text{-PhCHCHCHPh})(3)]PF_6$, 7. For $CDCl_3$ solutions of complex **7**, at ambient temperature, we find *four* isomers in solution, **7a**−**d**, in the ratio 45:46:6:3, with ^{31}P chemical shifts of 19.4, 17.0 (broad), 16.9, and 15.5 ppm, respectively. Although the ^{1}H assignment is not as complete as for **6**, due to signal overlap, there is enough detail from the $^{31}P,^{1}H$ correlation, the $^{13}C,^{1}H$ correlation, and the NOESY measurements to assign **7a,b**, the two major components, as syn/syn geometric isomers and **7c,d** as syn/anti geometric isomers. Unfortunately, the data were insufficient to allow us to draw detailed conclusions with respect to their 3-D solution structures.

Figure 4 shows two sections of the 2-D ^{1}H exchange spectrum for **7**. The upper trace, which shows the

(33) Faller, J. W. In *Determination of Organic Structures by Physical Methods*; Nachod, F. C., Zuckerman, J. J., Eds.; Academic Press: New York, 1973; Vol. 5, p 75. Faller, J.; Thomsen, M. E. *J. Am. Chem. Soc.* **1969**, *91*, 6871. Faller, J.; Incorvia, M. J.; Thomsen, M. E. *J. Am. Chem. Soc.* **1969**, *91*, 518. Faller, J.; Incorvia, M. J. *J. Organomet. Chem.* **1969**, *19*, 13.

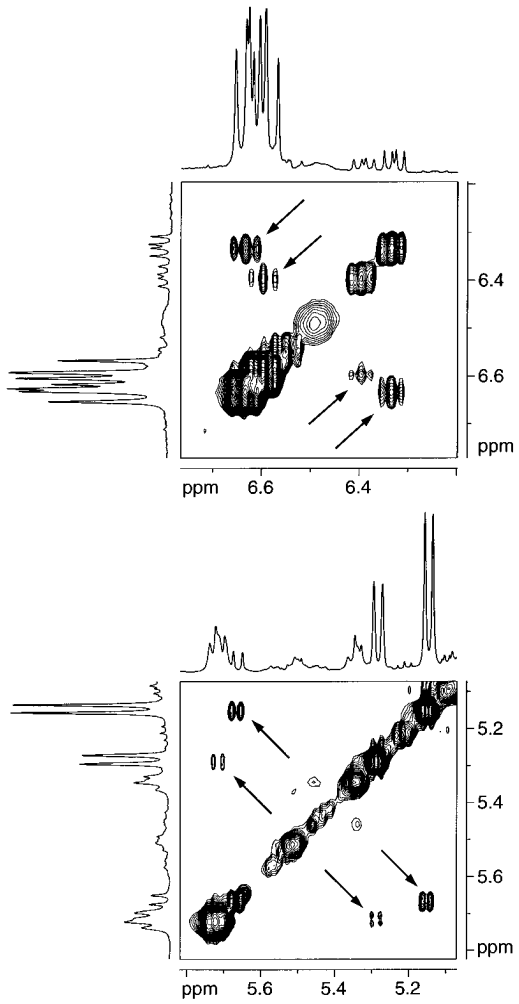
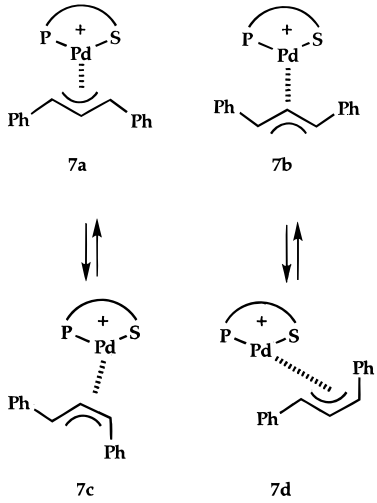


Figure 4. Sections of the ^{1}H exchange spectrum for **7**. The top trace shows the four different central allyl protons (two major, both syn/syn, and two minor, both syn/anti) and the selective excchange between these. The bottom trace shows the resonances of the terminal allyl protons *trans* to the sulfur donor. The exchange is selective, and the cross-peaks indicated allow an accurate determination of the allyl ^3J(H,H) spin−spin interactions in the minor isomers ($CDCl_3$, 500 MHz).

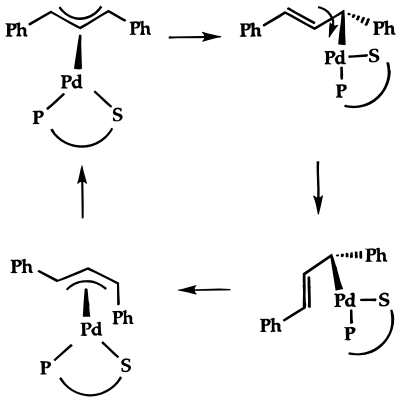
region of the central allyl protons, reveals that each of the two major syn/syn isomers is in *selective exchange with one of the minor components but not with each other*. This is in contrast to what we observed for **6a,b**. The lower trace shows the region of the terminal allyl protons *trans* to the sulfur donor. Apart from the obvious selectivity, noted above, one can use the cross-peaks indicated in the lower trace to obtain the ^3J(H,H) values and thus determine that the terminal allyl protons *trans* to the S-donor in the minor isomers are anti to their respective central protons; i.e., the phenyl groups are still syn. Together with other NMR data, we can assign the correct syn/anti structures (there are two possibilities) as shown in Scheme 2. With these assignments, we can now rationalize the selective dynamics. The η^3-η^1 isomerization[33−36] proceeds by dissociation of the carbon *trans* to sulfur and *cis* to

Scheme 2. Isomers of 7



fragments of abbreviated **7a-7d** showing the syn/syn and syn/anti geometric isomers. Complex **7a** is the endo isomer, complex **7b** the exo isomer. The exo isomer has the central allyl proton on the same side as the sugar moiety.

phosphorus and is thus under steric control; i.e., the allyl chooses to open away from the larger PPh_2 fragment. This is in agreement with observations for the analogous complexes with the *exo*-norborneol ligand **1**. After dissociation, rotation around the sp^3-sp^2 carbon, followed by $\eta^1-\eta^3$ complexation, gives the product and explains the selectivity, i.e.

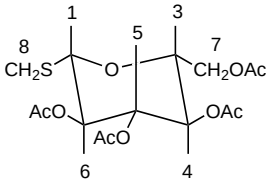


In Tables 4 and 5 we give some ^{1}H and ^{13}C details for both **6** and **7**.

For the two syn/syn isomers of **7a,b**, the terminal allyl ^{13}C chemical shifts are $\delta = 99.7$ and 81.4, **7a**, and $\delta =$ 103.6 and 76.5, **7b**, with the low-frequency resonances again assigned to the allyl carbon *trans* to the S-donor. A comparison of the ^{13}C values for **7** with those for **6** is informative. Specifically, for **7**, the signals *trans* to the PCy_2 and *S*-sugar moieties are at higher and lower frequency, respectively, than for **6**. Consequently, substituting Cy for Ph affects *both* the *cis* and *trans* positions. If the *cis* effect of changing Ph for Cy were only steric in nature, the large Cy groups might be expected to weaken the proximate allyl−Pd bond. One would then expect the 86.3 and 89.0 ppm values for **6** to move to even higher frequency, and this is the

(34) Vrieze, K.; Volger, H. C.; van Leeuwen, P. S. N. M. *Inorg. Chim. Acta Rev.* **1969**, 109.
(35) Cesarotti, E.; Grassi, M.; Prati, L.; Demartin, F. *J. Chem. Soc., Dalton Trans.* **1991**, 2073. Cesarotti, E.; Grassi, M.; Prati, L.; Demartin, F. *J. Organomet. Chem.* **1989**, *370*, 407. Grassi, M.; Meille, S.; Musco, A.; Pontellini, R. *J. Chem. Soc., Dalton Trans.* **1989**, 615.
(36) Gogoll, A.; Ornebro, J.; Grennberg, H.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.

Table 4. Selected ^{1}H Data[a] for 3 and 7



	3	7a	7b	7c	7d
H_c		6.55	6.57	6.32	6.37
		$J_{H_cH_{tp}} = J_{H_cH_{ts}} = 13.4$	$J_{H_cH_{tp}} = 13.5$, $J_{H_cH_{ts}} = 10.0$	$J_{H_cH_{tp}} = 8.2$, $J_{H_cH_{ts}} = 12.1$	$J_{H_cH_{tp}} = 8.4$, $J_{H_cH_{ts}} = 12.2$
H_{tp}[b]		5.77	5.93	7.64	7.36
		$J_{HP} = 9.0$	$J_{HP} = 7.6$	$J_{HP} = 5.5$	
H_{ts}[c]		5.21	5.08	5.67	5.71
H_1	4.42	4.3	3.95		
	$J_{H_2H_3} = 10.1$				
H_3	3.67	3.55	3.32		
	$J_{H_2H_3} = 10.4$[d]	$J_{H_2H_3} = 10.0$	$J_{H_2H_3} = 9.9$		
H_4	5.03	4.68	4.91		
	$J_{H_3H_4} = 9.0$	$J_{H_3H_4} = 10.0$	$J_{H_3H_4} = 9.9$		
H_5	5.09	4.93	4.58		
	$J_{H_4H_5} = 7.9$	$J_{H_4H_5} = 9.5$	$J_{H_4H_5} = 9.5$		
H_6	5.13	4.99	4.97		
	$J_{H_5H_6} = 10.1$	$J_{H_5H_6} = 9.0$	$J_{H_5H_6} = 9.9$		
H_7'	4.25	4.15	4.40		
	$J_{H_7H_7'} = 12.3$, $J_{H_1H_2} = 2.3$	$J_{H_7H_7'} = 13.3$, $J_{H_1H_2} = 3.0$	$J_{H_7H_7'} = 13.0$, $J_{H_1H_2} = 3.0$		
H_7	4.15	3.78	4.11		
	$J_{H_1H_2}$ =5. 1	$J_{H_1H_2} = 1.9$	$J_{H_1H_2} = 3.0$		
H_8'	4.32	4.44	4.22		
	$J_{H_8H_8'} = 12.3$, $J_{H_8P} = 1.4$	$J_{H_8H_8'} = 14.9$	$J_{H_8H_8'} = 12.0$		
H_8	4.2	3.68	3.99		
	$J_{H_8P} = 1.4$		$J_{H_8P} = 2.0$		

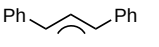
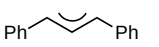
[a] Chemical shifts (ppm) and coupling constants (Hz), in $CDCl_3$, 296 K, 500.13 MHz. [b] Trans to phosphorus; H_c is the central allyl proton. [c] Trans to sulfur. [d] Eight-line multiplet.

Table 5. Selected ^{13}C Data[a] for 3 and 7

nucleus	3	7a	7b	7c	7d
C_c		110.8	109.6	108.1	108.5
C_{tp}[b]		99.7	103.6		
		J(C,P) = 19	J(C,P) = 17		
C_{ts}[c]		81.4	76.5	77.4	77.9
C_1	82.2	76.	82.2		
C_3	75.5	76.9	76.5		
C_4	70.0	66.7	67.1		
C_5	68.4	73.8	73.2		
C_6	73.9	68.3	68.3		
C_7	62.2	60.6	61.3		
C_8	32.9	36.0	35.0		
	J(C,P) = 28	J(C,P) = 8			
C_{1a}[d]	34.2	34.9	35.7		
	J(C,P) = 12	J(C,P) = 22	J(C,P) = 23		
C_{1b}[d]	34.1				
	J(C,P) = 12				

[a] Chemical shifts (ppm) and coupling constants (Hz), in $CDCl_3$, 296 K, 125.8 MHz; see ^{1}H table for numbering scheme. [b] Trans to phosphorus; H_c is the central allyl proton. [c] Trans to sulfur. [d] Methine cyclohexyl carbons.

Table 6. Selected ^{1}H and ^{13}C NMR Data for the Two Isomers of 6

	 a (exo)		 b (endo)	
	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$
1a[a]	4.91	86.3	6.65	89.0
2	7.12	111.1	5.91	110.0
3a[b]	5.79	97.6	5.96	95.4
allyl-*o*-CH[a]	7.00	127.7	6.95	129.2
allyl-*o*-CH[b]	7.84	128.0	7.72	128.3
Ph*CH*$_2$S	4.06	31.8	4.01	32.5
Ph*CH*$_2$S	3.63	31.8	3.69	32.5
S*CH*(sugar)	2.48	78.2	4.38	82.0
SCH*CH*(sugar)	4.86	67.1	4.96	68.1

[a] Trans to S. [b] Trans to P, $CDCl_3$, 323 K.

opposite of what we observe. Therefore, the change from phenyl to cyclohexyl phosphorus substituents is also accompanied by a *cis electronic effect*, in addition to other electronic and steric effects.

Comments on the Catalytic Results. The allyl complexes **5** and **7**, containing ligands **2** and **3**, respectively, were used in the catalytic experiments. On the basis of HPLC results, the *R* enantiomer is produced in excess in both cases with the observed ee's being 64% and 53%, respectively. These ee's are interesting in connection with the observed solution populations for the intermediates **6** and **7**. If we assume for **6** that **6a**,**b** react at ca. the same rate, then the observed 4:1 ratio in solution would afford an ee of ca. 60%, in reasonable agreement with the experiment. Moreover, starting from **5** the *R* enantiomer can be rationalized by assuming that the nucleophile attacks at the allylic terminus which is *trans* to the P-donor. This is in agreement with several recent reports on mixed donor P,N auxiliaries and is based on the concept of relative *trans* influence.[6,8] If we make the same reaction rate assumption for **7** then (a) we would expect little or no ee as the two major isomers have almost identical populations and (b) it is not clear which enantiomer should be preferred even assuming that attack takes place preferentially at the terminus *trans* to the phosphorus moiety. The observed 53% ee is a clear sign that, for **7**, this assumption is wrong and that the reaction kinetics for these four isomers are not the same. A proposal concerning selective steric effects in the transition state has been made previously by several authors[6,8a,9] and may well be correct for **7**.

Conclusions. Our new P,S ligands are potentially useful auxiliaries. One need not have the chirality built

into the chelate backbone to achieve moderate ee's; however, keeping the chiral substituent close to the coordination sphere seems a prerequisite; i.e., **2** and **3** are better than **1**. In **6** and **7** a change from a PPh_2 moiety to a PCy_2 analog has a marked effect both on the nature and number of observed diastereomers as well as their allyl dynamics. There is a significant electronic cis-effect on changing from the PPh_2 to the PCy_2 moiety. There is not necessarily a correlation between observed enantiomeric excess and population of the diastereomers in solution. The crystal structure for **5** suggests there is quite a lot of open space around the sulfur atom, and we believe that this facilitates inversion at this stereogenic center (broad ^{31}P and ^{1}H resonances in some, but not all, of the diastereomers). A logical extension to our existing sugar-based ligands would involve suppressing the S-inversion by a suitable choice of carbon backbone. We have preliminary evidence, from ferrocene-based β-D-thioglucose tetraacetate ligands, that this is the correct approach and plan to report on these shortly.

Experimental Section

IR spectra (values in cm^{-1}) were measured on a Perkin-Elmer 883 instrument. FAB mass spectra (*m/e*) and microanalyses were performed in the analytical laboratories of the ETH Zürich. The chloride-bridged complexes were prepared as described in the literature.

The NMR experiments were carried out using a Bruker AMX 500 spectrometer on 0.02 mmol samples in $CDCl_3$. The frequencies 500.13, 202.47, and 125.75 MHz were employed for ^{1}H, ^{13}C, and ^{31}P, respectively. Standard-pulse sequences were employed for the ^{1}H-2D-NOESY,[37] $^{13}C-^{1}H$,[38] and $^{31}P-^{1}H$ [39] correlation studies. The phase-sensitive NOESY experiments used mixing times of 0.8 s.

The following codes represent the seven palladium−P,S structures taken from the Cambridge data base. List of compounds: BAKKAZ, IMTOPD, LELSOK, LELTEB, PAFKOW, KEJTEC, and JORTOZ.

Materials and Methods. All manipulations were performed under a nitrogen atmosphere. Diethyl ether, *n*-hexane, THF, CH_2Cl_2, and benzene were distilled over Na−benzophenone. (*rac*)-(*E*)-3-Acetoxy-1,3-diphenyl-1-propene was prepared as previously described.[5a] All the other chemicals were commercial products and were used as received without further purification. Dicyclohexylchlorophosphine was obtained from Strem, whereas *N*,*N*-dimethyl-2-bromobenzylamine and 1-thio-β-D-glucose-tetraacetate were purchased from Aldrich.

Synthesis of the Ligands. *N*,*N*-Dimethyl-*o*-lithiobenzylamine. This compound can be either obtained by the following procedure or by the method described by Van Koten and co-workers.[40] A 1.6 M solution of *n*-butyllithium (3.36 mL, 5.37 mmol) in hexane was added dropwise at 0 °C to a stirred solution of *N*,*N*-dimethyl-2-bromobenzylamine (1.0 g, 4.67 mmol) in diethyl ether (15 mL). A white compound precipitated immediately. The solution was decanted off and the solid washed with *n*-hexane (30 mL) and again decanted. This procedure was repeated twice, and the solid was dried under vacuum. Yield: 527 mg (80%). Anal. Calcd for $C_9H_{12}NLi$: C, 76.59; H, 8.57; N, 9.92. Found: C, 76.63; H, 8.32; N, 9.87.

N,N-Dimethyl-o-(dicyclohexylphosphino)benzylamine. Solid *N*,*N*-dimethyl-*o*-lithiobenzylamine was added at −78 °C under vigorous stirring to a solution of dicyclohexylchlorophosphine (1.0 mL, 4.34 mmol) in diethyl ether (15 mL) (673 mg, 4.77 mmol). The mixture was then allowed to slowly warm to room temperature and stirred for 1 h. After the addition of water (30 mL), the organic phase and the ether extract (3 × 30 mL) from the aqueous solution were combined and dried over Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue held under vacuum at 70 °C for 1 h to give pure **2** as a colorless viscous liquid in 93% yield. Anal. Calcd for $C_{21}H_{34}NP$: C, 76.09; H, 10.34; N, 4.23. Found: C, 76.02; H, 10.41; N, 4.33. ^{31}P NMR (101 MHz, $CDCl_3$): δ −17.32 (s). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta(CH_2)$ 3.83 (d, 2H, J_{HP} = 2.7 Hz); $\delta(CH_3)$ 2.26 (s, 6H); δ(Cy) 0.87−1.90 (m, 22H); δ(Ph) 7.15−7.55 (m, 4H).

***o*-(Dicyclohexylphosphino)benzyl Chloride.** A solution of ethyl chloroformate (0.54 mL, 5.64 mmol) and *N*,*N*-dimethyl-*o*-(dicyclohexylphosphino)benzylamine (1.44 g, 4.34 mmol) in benzene (20 mL) was refluxed for 6 h under stirring. The mixture was then cooled to room temperature and the solvent removed under high vacuum. Purification of the crude yellow residue by short-column chromatography (silica, hexane:benzene = 3:1) gave 0.73 g (52%) of a colorless viscous liquid. Anal. Calcd for $C_{19}H_{28}ClP$: C, 70.68; H, 8.74. Found: C, 70.53; H, 8.68. ^{31}P NMR (101 MHz, $CDCl_3$): δ −16.50 (s). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta(CH_2)$ 5.03 (d, 2H, J(P,H) = 2.2 Hz); δ(Cy) 0.93−2.00 (m, 22H); δ(Ph) 7.24−7.53 (m, 4H).

2,3,4,6-Tetra-*O*-acetyl-1-((*o*-(diphenylphosphino)benzyl)thio)-β-D-glucopyranose, 2. Compound **4** (736 mg, 2.02 mmol) was dissolved in 20 mL of THF and cooled to 203 K. NaH (80.8 mg, 2.02 mmol) in paraffin oil was added and the mixture stirred for 1 h. *o*-(Dicyclohexylphosphino)benzyl chloride (680 mg, 2.02 mmol) was added and the reaction mixture warmed to 40 °C for another 1 h. The THF was removed *i.v.* and the product dissolved in ether. The ether layer was washed three times with 20 mL portions of water and then dried over $MgSO_4$. Distillation of the ether and chromatography through silica gel using 1:1 hexane:ethyl acetate, R_f 0.59, afforded 1.07 g (80%) of the product as a white powder. Mp: 109 °C. $[\alpha]_D$ = −75.1° (*c* = 0.47, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 7.5−6.8 (14H, arom. H), 5.10 (dxd, J = 9,1, J = 9.1, 1H, H−C(3)), 5.06 (dxd, J = 9.1, J = 9.1, 1H, H−C(4)), 5.00 (dxd, J = 9.1, J = 9.3, 1H, H−C(2)), 4.38 (dxd, J = 9.3, 1H, H−C(1)), 4.29 (dxd, J = 13.6, J = 1.9, 1H, H−C(7)), 4.23 (dxd, J = 12,3, J = 4.8, 1H, 1H, H−C(6)), 4.08 (dxd, J = 12,3, J = 2,1, 1H, H−C(6)), 4.04 (d, J = 13.6, 1H, 1H, H−C(7)), 3.2 (dxdxd, J = 2.1, J = 4.8, J = 9.1, 1H, H−C(5)), 2.02 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H), 1.84 (s, 3H). ^{31}P NMR ($CDCl_3$): −17.3. ^{13}C NMR ($CDCl_3$): 170.8, 170.3, 169.5, 143−127 (arom. C), 82.7, 75.7, 74.0, 70.1, 68.4, 62.3, 32.9 (d, J = 25.5), 20.9, 20.7. IR (CsI pellet): 1741 (br, C=O). FAB-MS: 639.1 (M^+). Anal. Calcd for $C_{33}H_{35}O_9PS$ (638.71): C, 62.01; H, 5.52. Found: C, 61.84; H, 5.53.

2,3,4,6-Tetra-*O*-acetyl-1-((*o*-(dicyclohexylphosphino)-benzyl)thio)-β-D-glucopyranose, 3. A solution of 72 mg of an NaH dispersion (55% in oil, 1.67 mmol) and 1-thio-β-D-glucose tetraacetate (553 mg, 1.52 mmol) in THF (40 mL) was added to *o*-(dicyclohexylphosphino)benzyl chloride (490 mg, 1.52 mmol) in THF (40 mL). The mixture was allowed to react at 40 °C for 29 h with stirring. The solvent was then evaporated under vacuum and the residue purified by column chromatography (silica, hexane:ethyl acetate = 1:1, R_f = 0.60) to give the product as a white solid. Yield: 400 mg (62%). Anal. Calcd for $C_{33}H_{47}O_9PS$: C, 60.91; H, 7.28. Found: C, 60.76; H, 7.51. ^{31}P NMR (101 MHz, $CDCl_3$): δ −16.80 (s).

$PdCl_2$(2). Ligand **2** (30 mg, 0.05 mmol) was dissolved in 2 mL of benzene and then treated with $PdCl_2(NCCH_3)_2$ (12.2 mg, 0.05 mmol). After the mixture was stirred for 2 h, the yellow solid which resulted was collected by filtration and recrystallized from dichloromethane/ether to afford the product, 28.4 mg (74.1%). ^{1}H NMR ($CDCl_3$): δ 8.0−6.7 (m, 14H, arom. H),

(37) Jeener, J.; Meier, G. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4545.
(38) Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285.
(39) Sklener, V.; Miyashiro, H.; Zon, G.; Miles, H. T.; Bax, A. *FEBS Lett.* **1986**, *208*, 94.
(40) Van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1979**, *174*, 367.

5.87 (d, 2H, J = 9.9), 5.4−5.1 (m, 2H), 4.89 (t, 1H, J = 9.3), 4.3−3.9 (m, 4H), 3.79 (d, 1H, J = 11.3), 2.09 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H). ^{31}P NMR ($CDCl_3$): δ 25.3. ^{13}C NMR ($CDCl_3$): δ 170.7, 170.5, 169.6, 169.4, 136−125 (arom. C), 84.5, 77.3, 73.1, 68.2, 68.0, 62.1, 31.3 (d, $J(^{13}C,^{31}P)$ = 11), 21.0, 20.6, 20.6. IR (CsI Pellet): 1750 (s, br, C═O), 1435 m, 1369 m, 1222 s, 1096 s, 1062 m, 1035 m, 692 m, 529 m, 517 m, 327 m, 318 sh, 294 m, 279 sh. FAB-MS: 779 (M^+ − Cl). Anal. Calcd for $C_{33}H_{35}O_9PSCl_2Pd$ (816.00): C, 48.57; H, 4.32. Found: C, 48.79; H, 4.62.

[Pd(η^3-C_3H_5)(2)]PF_6), 5. [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ (22.1 mg, 0.061 mmol) in 2 mL methanol was treated with $Ag(CF_3SO_3)$ (31.1 mg, 0.12 mmol). After removal of AgCl by filtration, the filtrate was treated with a solution of **2** (80.4 mg, 0.12 mmol) in 2 mL of dichloromethane. After 0.5 h the solvents were distilled and the crude product was crystallized from dichloromethane/ether. The product, 110.8 mg (93%), is a white powder. Due to the dynamic nature of this complex, no detailed assignments were made. ^{1}H NMR ($CDCl_3$): δ 7.8−6.7 (m, 14H, arom. H), 5.85 (m, 1H), 5.45−4.80 (m, 5H), 4.5−3.2 (m, 8H), 2.06 (s, 3H), 1.93 (s, 6H), 1.91 (s, 3H). ^{31}P NMR ($CDCl_3$): δ 17.5 (br). ^{13}C NMR ($CDCl_3$): δ 170.6, 170.1, 169.8, 169.4, 138−127 (arom. C), 122.4 (J = 6), 84.8, 84.0, 76.1, 75.1, 73.4, 73.3, 68.8, 67.4, 67.3, 61.9, 61.6, 20.7, 20.6 (2 signals), 20.6. The three allyl carbons appear at δ 121.8, 69.8 (*trans* to S), and 78.8 (*trans* to P). IR (CsI Pellet): 1749 (br, C═O). FAB-MS: 784.9 (M^+ − triflate). Anal. Calcd for $C_{37}H_{40}O_{12}F_3PS_2Pd$ (935.25): C, 47.52; H, 4.31. Calcd for $C_{37}H_{40}O_{12}F_3PS_2Pd{\cdot}H_2O$ (953.22): C, 46.62; H, 4.44. Found: C, 46.79; H, 4.59. The thiosugar readily H-bonds 1 equiv of water.

Bis[(μ-chloro)(η^3-1,3-diphenylallyl)palladium(II)]. $PdCl_2$ (350 mg, 1.95 mmol) and LiCl (350 mg, 8.3 mmol) were stirred in H_2O (2.3 mL) for 45 min. Ethanol (3.9 mL) and (*rac*)-(*E*)-3-acetoxy-1,3-diphenyl-1-propene (1 g, 3.97 mmol) in THF (11 mL) were then added, and the brown solution was cooled to 0 °C. After the addition of 1.2 mL of concentrated HCl, carbon monoxide was slowly bubbled through the solution for 15 min. Another 0.8 mL of concentrated HCl was added and CO bubbled for 1.5 h. The stream of CO was then stopped and the solution stirred under CO atmosphere for 7 h at room temperature. The yellow-orange suspension obtained was filtered over a G4 glass frit, washed with mother liquors, MeOH (100 mL), and diethyl ether (30 mL), and dried under high vacuum. Yield: 643 mg (98.4%). Anal. Calcd for $C_{30}H_{26}Cl_2Pd_2$: C, 53.76; H, 3.91. Found: C, 53.65; H, 4.09. ^{1}H NMR (CD_2Cl_2, 250 MHz): $\delta(H_{anti})$ 4.64 (d, 4H, J(H,H) = 11.21 Hz); $\delta(H_{cent})$ 6.16 (t, 2H).

[Pd(η^3-1,3-diphenylallyl)(3)]PF_6, 7. Solid Bis[(μ-chloro)(η^3-1,3-diphenylallyl)palladium(II)] (46 mg, 0.07 mmol) was added to a solution of ligand **3** (94 mg, 0.14 mmol) in acetone (10 mL). After the addition of $TlPF_6$ (49 mg, 0.14 mmol) the mixture was decanted and TlCl filtered off over Celite. The solution was concentrated to $^1/_3$ under a stream of nitrogen, and *n*-pentane (30 mL) was added causing the precipitation of a yellow solid. The pure compound were obtained in a 83% yield after recrystallization from CH_2Cl_2/*n*-pentane under a stream of nitrogen. Anal. Calcd for $C_{48}H_{60}F_6O_9P_2PdS$: C, 52.63; H, 5.52. Found: C, 52.51; H, 5.49.

[Pd(η^3-1,3-diphenylallyl)(2)]PF_6, 6. This complex was prepared in an analogous fashion to that described for **7** except that $AgPF_6$ was employed. The product could be obtained in 73% yield. Anal. Calcd for $C_{48}H_{48}F_6O_9P_2PdS$: C, 56.24; H, 4.72. Found: C, 56.11; H, 5.09.

Enantioselective Allylic Alkylation Reactions. The reactions were carried out under the conditions reported by Pfaltz and co-workers.[8] Complex **7** (5 mg, 0.005 mmol) was used as a catalyst with a substrate:catalyst ratio of 100:1. The reaction was complete in 3 days with a 73% chemical yield and 53.4% ee (determined by HPLC).

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Supporting Information Available: Tables S1−S3, listing interatomic distances and bond angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (9 pages). Ordering information is given on any current masthead page.

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