ORGANOMETALLICS

Volume 15, Number 10, May 14, 1996

© Copyright 1996
American Chemical Society

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on May 14, 1996 on http://pubs.acs.org | doi: 10.1021/om950983m

Communications

A New P,S-Chiral Auxiliary Derived from Thioglucose. X-ray Structure of a Palladium 1,3-Diphenylallyl Complex with a Strongly Rotated Allyl Ligand

Alberto Albinati,* Paul S. Pregosin,* and Karin Wick

Laboratorium für Anorganische Chemie, ETH Zentrum, Zürich 8092, Switzerland

Received December 27, 1995[⊗]

Summary: The new ferrocene-based P,S-chiral auxiliary **1***, derived from thioglucose, has been prepared and used in the palladium-catalyzed enantioselective allylic alkylation reaction. The X-ray structure of the allyl cationic complex* $[Pd(\eta^3\text{-}PhCHCHCHPh)(\mathbf{1})]CF_3SO_3$ *(***2***) reveals a markedly rotated 1,3-diphenylallyl ligand such that the terminal allyl carbon C(3), trans to the phosphorus donor, is ca. 0.85(3) Å below the coordination plane. This distortion is pertinent to the Pd(0) transition state complex expected in the allylic alkylation reaction.*

The palladium-catalyzed enantioselective allylic alkylation reaction continues to develop, with an increasing variety of chiral auxiliaries achieving enantioselectivities (ee's) at or above the 90% level.[1−7] Whereas interest initially centered on the model 1,3-diphenylallyl acetate (or carbonate) substrate, with diphosphine-type auxiliaries, recent reports have extended the reaction to various synthetically attractive cyclic organic substrates[4,6] using P,N and P,O bidentate chiral ligands.[4]

A mechanistic point remains unsettled. The Pd(0) transition state (TS), which develops as the new C−C bond is made, may be structurally close to the ground state (early TS) as noted by Pfaltz and co-workers[1] or, alternatively, farther along the reaction coordinate (late TS) as suggested by Brown and co-workers.[2] If the latter were correct, ground-state considerations such as the ^{13}C shifts of the terminal allyl carbons or X-ray data, although informative in their own way, might have no predictive value.

We have prepared[8a] the new ferrocene-based chiral P,S-bidentate ligand **1**, along with several of its Pd(II) allyl complexes. This new auxiliary affords an 88% ee[8b] in the enantioselective allylic alkylation of the racemic test substrate PhCH═CHCH(OAc)Ph using the CH$(CO_2Me)_2$ anion. Moreover, **1** is interesting in the following ways.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) 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. Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339. von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. Leutenegger, U.; Umbricht, C.; Fahrni, P.; von Matt, A.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143. Mueller, D.; Umbricht, B.; Weber, A.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232.

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

(3) Gamez, P.; Dunjic, B.; Fache, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1417. Andersson, P. G.; Harden, A.; Tanner, D.; Norrby, P. O. *Chem. Eur. J.* **1995**, *1*, 12.

(4) Knühl, G.; Sennhenn, P.; Helmchen, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1845. Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelein, M.; Huttner, G.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523. Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, 1769.

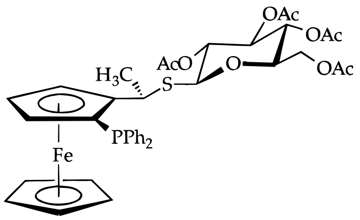
(5) Hiraswa, K.; Kawamata, M.; Hiroi, K. *Yakugaku Zasshi* **1994**, *114*(2), 111. Yamaguchi, M.; Shima, T.; Hida, M. *Tetrahedron Lett.* **1990**, *31*, 5049. Yamaguchi, M.; Shima, T.; Yamagishi, T.; Hida, M. *Tetrahedron: Asymmetry* **1991**, *2*, 663.

(6) Trost, B. M.; Breit, B.; Peukert, S.; Zambrano, J.; Ziller, J. W. *Angew. Chem.* **1995**, *107*, 2577. Trost, B. M.; Lee, C. B.; Weiss, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7247. Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 4089. Trost, B. M.; Organ, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 10320.

(7) Togni, A.; Venanzi, L. M. *Angew. Chem.* **1994**, *33*, 497. Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

S0276-7333(95)00983-6 CCC: $12.00 © 1996 American Chemical Society

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on May 14, 1996 on http://pubs.acs.org | doi: 10.1021/om950983m



1

(a) This result represents a rare example[9,10] of the use of a sugar moiety in homogeneous catalysis and the first involving thioglucose.

(b) The solid-state structure[11] of the intermediate $[\mathrm{Pd}(\eta^3\text{-PhCHCHCHPh})(\mathbf{1})]\mathrm{CF_3SO_3}$ (**2**) reveals a strongly rotated 1,3-diphenylallyl ligand (see Figure 1). This rotation removes the allyl phenyl group on C(3) from the space occupied by the relatively large sugar moiety, thus avoiding unfavorable steric effects. The terminal allyl carbon C(3), trans to the phosphorus donor, is found ca. 0.85(3) Å below the coordination plane so that the allyl can be considered as having experienced a strong clockwise rotation.[12−14] The allyl carbons C(1) and C(2) now lie almost in the P−Pd−S coordination plane, and thus the molecule is "prepared" for a TS having a Pd(0) olefin structure. Interestingly, all three allyl carbons are on one side of the coordination plane, away from the sugar substituent, as indicated in the fragment

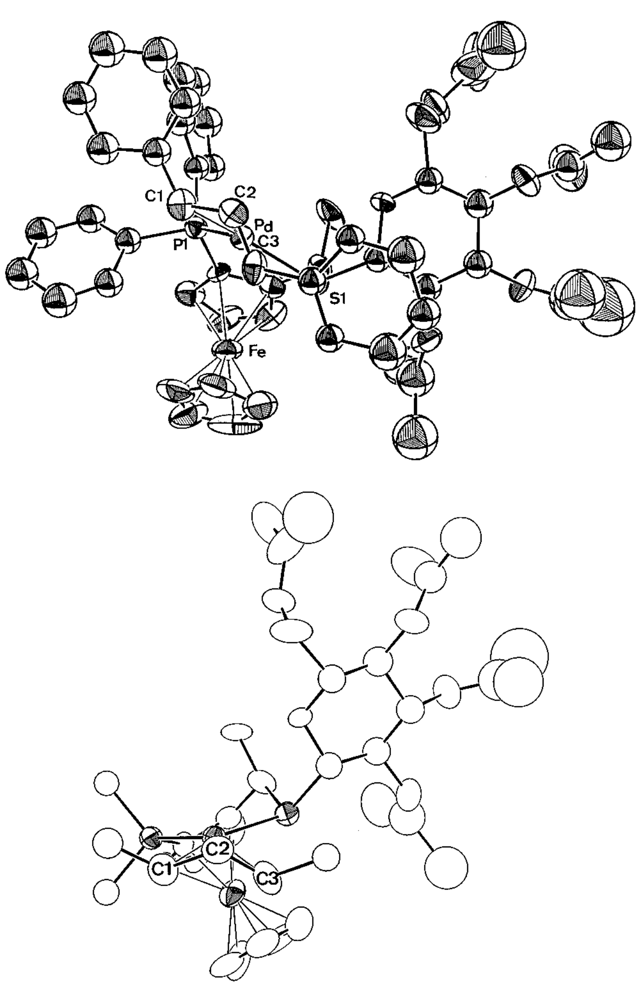
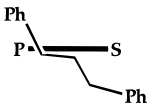


Figure 1. Two views of the cation **2**. In the bottom view, seen from behind the allyl and looking toward the metal, four phenyl groups (the two allyl and the PPh_2) have been omitted. This allows one to better see the allyl clockwise rotation and the strong displacement of C(3), ca. 0.85(3) Å away from the P−Pd−S plane (these three atoms and the Fe are shaded). The allyl plane makes an angle of ca. 125.9(3)° with the P−Pd−S coordination plane. Selected distances (Å) and angles (deg): Pd−S(1) = 2.383(5), Pd−P = 2.328(4), Pd−C(1) = 2.20(2), Pd−C(2) = 2.15(2), Pd−C(3) = 2.31(2); S(1)−Pd−P(1) = 96.5(2), S(1)−Pd−C(1) = 161.8(5), S(1)−Pd−C(3) = 96.8(5), P(1)−Pd−C(1) = 100.9(4), P(1)−Pd−C(3) = 154.7(5), C(1)−C(2)−C(3) = 120(2).



This is an abbreviated fragment showing approximate positions of the allyl carbons (values (Å) from the P−Pd−S plane: C(1) = 0.04(3); C(2) = 0.30(3); C(3) = 0.85(3)). Detailed solution NOE studies[15] show that, although there are two isomers in equilibrium in solution (2-D exchange NMR), the major isomer has essentially the same structure as in the solid state.

(c) As can be seen from the ORTEP plot for complex **2**, ligand **1** affords a six-membered chelate ring with the

---

(8) (a) **1** was prepared by dissolving (*R*)-*N*,*N*-dimethyl-1-[(*S*)-(diphenylphosphino)ferrocenyl]ethylamine (200 mg, 0.453 mmol) in 1.5 mL of HOAc and adding this to *β*-(D)-thioglucose (330 mg, 0.906 mmol) in 2 mL of HOAc. The mixture was refluxed for 2 h at 80 °C and the resulting solution poured into a saturated solution of sodium carbonate. Extraction with methylene chloride, drying ($MgSO_4$), and concentration affords a crude product. This was chromatographed on silica gel (methylene chloride/ethyl ether, 9:1) to give 184 mg (53%) of **1**. Complex **2** was prepared as described previously,[14] starting from [Pd-(μ-Cl)(η^3-PHCHCHCHPh)]$_2$ and 2 equiv of **1**. Suitable crystals of **2** were obtained from $CHCl_3$/pentane. (b) The catalytic runs were carried out as described by Pfaltz and co-workers.[1] The ca. 88% ee (HPLC) is *not* an optimized result in that we have made no attempt to change temperature, solvent, or base.

(9) Michalik, M.; Freier, T.; Schwarze, M.; Selke, R. *Magn. Reson. Chem.* **1995**, *33*, 835. Selke, R.; Facklam, C.; Foken, H.; Heller, H. *Tetrahedron: Asymmetry* **1993**, *4*, 369.

(10) Rajanbabu, T. V.; Ayers, T. A.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 4101.

(11) Crystal data for $\mathbf{2}\cdot2CHCl_3$: $C_{56}H_{54}Cl_6F_3FeO_{12}PPdS$, M_r = 1446.11, orthorhombic, space group $P2_12_12_1$, a = 14.345(3) Å, b = 14.795(3) Å, c = 30.221(3) Å, V = 6414(2) Å^3, Z = 4, ρ = 1.497 g cm^{-3}, μ = 9.044 cm^{-1}, T = 23 °C, λ(Mo Kα) = 0.710 69 Å). A suitable crystal of compound **2**, obtained by crystallization from $CHCl_3$/pentane, was mounted on a glass fiber and covered with epoxy resin for protection. The intensities were measured on an Enraf-Nonius CAD4 diffractometer. Three standard reflections were measured every 3600 s, with an intensity variation <21%. Both an empirical absorption correction (Ψ scans) and a decay correction were applied to the reduced data. Of the 6182 independent data collected, 4097 reflections (with $F^2 > 3.0\sigma(F^2)$) were used for the refinement. The structure was solved by direct and Fourier methods and refined by full-matrix least squares using the MOLEN package. From the Fourier difference maps two clathrated solvent molecules were found and included in the refinement. Models for the disordered triflate and solvent molecules were based on the positions of the strongest peaks in the Fourier maps, and only the displacement parameters were allowed to vary during the refinement. The Pd, P, Fe, and S atoms and those of the acetate and cyclopentadienyl groups were refined anisotropically, while the others were treated isotropically. The contribution of the hydrogen atoms (in idealized positions) was not refined. Final agreement factors were (for the enantiomorph giving the statiscally lower values): R = 0.073, R_w = 0.101, GOF = 2.994. Upon convergence the final Fourier difference showed no significant features.

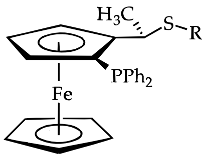
(12) One expects[2] and finds (via the observed enantiomer) that the attack of the nucleophile occurs at the allyl terminus trans to phosphorus, so that it is germane that C(3), trans to phosphorus, is the carbon below the coordination plane. The carbon atoms C(1) and C(2) will eventually develop the double bond.

(13) During the preparation of this paper we learned of structural studies from the groups of A. Pfaltz, M. Zehnder, and A. Togni describing rotated 1,3-diphenylallyl Pd complexes. None of these has a terminal allyl carbon as far below the coordination plane as does **2**. The differences are at least several tenths of an angstrom, thus making **2** an extreme case.

(14) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031.

methyl group in a pseudo-axial position. In earlier studies involving related ferrocene auxiliaries it was found[16,17] that the six-membered chelate conformation was relatively invariant, with the methyl group preferring a pseudo-equatorial orientation.

(d) **1** is an auxiliary which demonstrates interesting structural cooperativity. The *S*-cyclohexyl and *S*-ethyl ligands **3** and **4**, respectively, with the same chirality at the ferrocene α-CH, afford significantly reduced ee's (67% and 34%, respectively). Clearly, the thioglucose plays a role; however, related *β*-(D)-thioglucose diphenylphosphino P,S-chiral auxiliaries, which also form six-membered rings but have a CH_2S(glucose) fragment, are relatively ineffective in terms of ee.[18] The combination of the two stereogenic fragments affords an improved result.



R = ethyl, **3**

R = cyclohexyl, **4**

Although it is obvious that the structure of **2** has some resemblance to a possible TS, it is likely that the special nature of the auxiliary dictates this structure so that it is too soon to generalize; further studies are in progress.

Acknowledgment. P.S.P. thanks the Swiss National Science Foundation as well as the ETH for support, the Johnson-Matthey Research Foundation, Reading, England, for the loan of precious metals, and Prof. A. Togni for helpful discussion.

Supporting Information Available: Experimental data for the diffraction study (Table S1), positional and isotropic displacement parameters (Table S2), positional parameters for the hydrogen atoms (Table S3), anisotropic displacement parameters (Table S4), and an extended list of bond distances and bond angles (Table S5) (9 pages). Ordering information is given on any current masthead page.

OM950983M

---

(15) These are exo and endo isomers, where these descriptors refer to the orientation of the central allyl C−H vector with respect to the substituted Cp ring. These diastereomeric complexes exchange slowly on the NMR time scale. For structural details on related isomers and applications of the 2-D exchange methodology see: Barbaro, P.; Pregosin, P. S.; Salzmann, R.; Albinati, A.; Kunz, R. W. *Organometallics* **1995**, *14*, 5160. Herrmann, J.; Pregosin, P. S.; Salzmann, R.; Albinati, A. *Organometallics* **1995**, *14*, 3311. Pregosin, P. S.; Salzmann, R.; Togni, A. *Organometallics* **1995**, *14*, 842. Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067 and references therein.

(16) Burckhardt, U.; Hintermann, L.; Schnyder, A.; Togni, A. *Organometallics* **1995**, *14*, 5415 and references therein.

(17) An allyl complex of Pd(II) derived from a new chiral P,S,O-chiral ligand has just been prepared and also shows a pseudo-axial methyl group: Spencer, J.; Gramlich, V.; Haeusel, R.; Togni, A. *Tetrahedron: Asymmetry* **1996**, *7*, 41.

(18) Pregosin, P. S. Unpublished results.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on May 14, 1996 on http://pubs.acs.org | doi: 10.1021/om950983m