

tolyl methyls to syn tolyl methyls to be 1.20 to 1.0.

A solution of sodium dimethyl malonate (1.0 mL, 0.044 M in degassed THF) was added dropwise to a suspension of $[\text{Pd}(S,S\text{-chiraphos})(\eta^3\text{-C}_3\text{H}_5)]\text{ClO}_4 \cdot 1/2\text{acetone}$ (0.030 g, 0.000042 mol) in degassed THF (9 mL) at 15–20 °C. The solution immediately turned yellow and all of the solid dissolved. After 10 min a solution of the π -allyl intermediate derived from acetate (I) (ratio of anti tolyl methyls to syn tolyl methyls 1.57 to 1.0) (0.030 g, 0.000042 mol) in degassed THF (10 mL) was added. The solution immediately darkened and became progressively blacker. After 1 h the deep brown reaction mixture was worked up in the usual manner yielding a brown solid (0.050 g) which was dissolved in THF (10 mL) and stirred vigorously with powdered Na_2SO_4 (0.50 g) for 2 h. The mixture was filtered and the filtrate worked up in the usual way yielding a yellow-brown solid (0.040 g). $^1\text{H NMR}$ (360 MHz, CDCl_3) showed the ratio of anti tolyl methyls to syn tolyl methyls to be 1.30 to 1.0.

Catalytic Allylation Reactions. A catalytic allylation reaction of *rac*-4,4-bis(4-methylphenyl)-3-buten-2-yl acetate under the standard conditions⁴ yielded after degradation (*S*)-methylsuccinic acid (64.0% ee). The reaction was repeated on acetate (I) (*S* to *R* ratio 95 to 5, *Z* to *E* ratio 85 to 15) and the allylation product examined. $^1\text{H NMR}$ (360 MHz, CDCl_3) in the tolyl methyl region showed peaks at δ 2.38 and 2.30 in the ratio of 1.57 to 1.0. The reaction run at one-half the catalyst concentration, [0.003 M], showed the same ratio.

Direct Allylation. A solution of acetate(I) (*S* to *R* ratio 95 to 5, *Z* to *E* ratio 60 to 40) (0.76 g, 0.003 mol) in THF (5 mL) was cooled to –70 °C and *n*-BuLi (2.25 mL, 1.4 M) added dropwise. After 0.25 h at –70 °C toluenesulfonyl chloride (0.522 g, 0.003 mol) was added in portions. The solution was stirred 1.25 h at –70 °C and then the temperature was raised to –20 °C over 0.75 h and kept there for 0.25 h. The solution was cooled to –70 °C and a solution of sodium dimethyl malonate (20 mL, 0.2 M in THF) was added dropwise. The solution was allowed to come to room temperature over 1 h, stirred for an additional 4 h and quenched by the addition of glacial HOAc (2 mL). The reaction mixture was poured into H_2O (500 mL) and then was extracted with Et_2O , and the combined Et_2O layers were washed with H_2O , aqueous NaHCO_3 , and brine and were dried over Na_2SO_4 . The volatiles were removed under reduced pressure yielding a yellow-green oil (1.0 g) which was chromatographed on Al_2O_3 (activity III, in hexane) and the malonic ester (VII) (0.060 g) was eluted with benzene. $^1\text{H NMR}$ (200 MHz, CDCl_3) in the tolyl methyl region showed peaks at δ 2.38 and 2.30 in the ratio of 44 to 56.

Competition Oxidation Addition Reaction. A mixture of $[\text{Pd}(S,S\text{-chiraphos})(\eta^3\text{-C}_3\text{H}_5)]\text{ClO}_4 \cdot 1/2\text{acetone}$ (0.100 g, 0.000142 mol) and 4,4-dimethyl-3-buten-2-yl acetate (0.403 g, 0.00284 mol) and 4,4-diphenyl-3-buten-2-yl acetate (0.755 g, 0.00284 mol) was suspended in degassed THF (20 mL) and a solution of sodium dimethyl malonate (0.75 mL, 0.215 M in THF) was added dropwise. The catalyst rapidly dissolved and after 0.5 h the amber-red solution was poured into H_2O . The usual workup yielded a yellow-orange solid (0.08 g): $^{31}\text{P NMR}$ (CDCl_3 , (peak intensity)) δ 56.74 (20.7), 54.70 (25.0), 52.84 (4.9), 51.23 (9.7), 50.75 (14.24), 50.66 (14.39), 47.66 (10.3), 47.42 (12.2), 47.38 (12.1), 46.06 (5.1), 43.16 (28.0), 41.12 (18.5). This is a mixture of π -allyls derived from both acetates (aryl to alkyl ratio 2.4:1).

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Structure of $[\text{Pd}(\eta^3\text{-C}(\text{Xyl})_2\text{CHCHPh})(S,S\text{-PPh}_2(\text{CHMe})_2\text{PPh}_2)]\text{BPh}_4$: A Catalyst for Asymmetric Allylic Alkylation Reactions

David H. Farrar*^{1a} and Nicholas C. Payne^{1b}

Contribution from the Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada, and the Department of Chemistry, University of Western Ontario, London, Ontario, Canada. Received June 6, 1984

Abstract: The crystal structure and absolute configuration of the major diastereomeric intermediate η^3 -allyl complex in $[\text{Pd}(\text{chiraphos})]^+$ catalyzed asymmetric allylic alkylations have been determined from a single-crystal X-ray structure determination. The $[\text{Pd}(\eta^3\text{-C}(\text{xylyl})_2\text{CHCHPh})(S,S\text{-chiraphos})]^+$ cation crystallizes as the tetraphenylborate salt with a molecule of ethyl acetate in a tetragonal unit cell of dimensions $a = 13.578$ (1) Å and $c = 76.261$ (3) Å, with $Z = 8$. Intensity data were collected with Cu radiation on an Enraf-Nonius CAD4F diffractometer, and 4007 observations with $I > 3\sigma(I)$ were used to refine 209 variables. With extensive rigid group constraints imposed, convergence was reached at $R = 0.079$. The known absolute configuration of the diphosphine ligand has been confirmed by measurements of anomalous scattering, and the space group was established as $P4_32_12$. The diphosphine chelate ring adopts a gauche conformation, configuration δ , which renders the phenyl substituents upon the P atoms quasi-axial and quasi-equatorial. The configuration which results for the η^3 -allyl ligand is that in which the two xylyl substituents on one terminal C atom of the η^3 -allyl ligand and the two phenyl rings on the adjacent P atom are staggered, thus minimizing steric interactions. The other terminal C atom, the chiral site at which nucleophilic attack occurs, is forced to adopt the *R* absolute configuration.

In the preceding two papers Mackenzie and Bosnich² have shown that asymmetric allylic alkylations take place through stereoselective nucleophilic attack on cationic complexes of the type $[\text{Pd}(\text{chiral-}\eta^3\text{-allyl})(\text{chiral diphosphine})]^+$. The chiral discrimination in the formation of these intermediates in the reactions has been linked to the structures of the starting Pd complexes by

an elegant series of kinetic and spectroscopic experiments. With such relationships firmly established, a crystallographic study of the intermediate η^3 -allyl complex would be a valuable source of information regarding the steric interactions between catalyst and substrate which are presumably the source of chiral induction. Whereas most of the complexes could only be obtained as amorphous solids, the major diastereomer of the $\text{Pd}(1,1\text{-bis}(3,5\text{-dimethylphenyl-3-phenyl-}\eta^3\text{-allyl)})(S,S\text{-chiraphos})$ cation does form poor crystals with a number of anions. Of these complexes, only those with the BPh_4^- anion were found to be even marginally

(1) (a) University of Toronto. (b) University of Western Ontario.

(2) Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.*, preceding two papers in this issue.

Table I. Crystal Data and Experimental Conditions Associated with Data Collection

molecular formula	C ₈₁ H ₈₁ BO ₂ P ₂ Pd
formula weight	1265.69
system	tetragonal
space group	P4 ₃ 2 ₁ 2
cell constants	
<i>a</i> , Å	13.578 (1)
<i>b</i> , Å	13.578 (1)
<i>c</i> , Å	76.261 (3)
cell volume, Å ³	14060.8
density, g·cm ⁻³	
calcd	1.21
obsd	1.2
Z	8
μ (Cu Kα), cm ⁻¹	29.4
radiation	Cu Kα, prefiltered by Ni foil
wavelength, Å	1.54056
temp, °C	23
approx crystal dimensions, cm	0.025 × 0.025 × 0.037
no. and 2θ range of centered reflctns	23; 20.2 < 2θ < 37.6°
data collected	<i>h</i> , <i>k</i> , <i>l</i>
scan mode	θ/2θ
scan width, deg	0.70 (corrected for dispersion)
max scan time, s	75
prescan rate, deg·min ⁻¹	10.7
acceptance ratio σ(<i>I</i>)/ <i>I</i>	0.04

suitable for X-ray analysis. We now report the crystal structure and absolute configuration of this salt as determined from an X-ray diffraction study.

Experimental Section

Collection and Reduction of X-ray Data. Yellow crystals of formula [Pd(CH(C₆H₅)CHC(C₆H₅)₂)(P₂(C₆H₅)₄C₂H₂(CH₃)₂)]B(C₆H₅)₄·CH₃C·H₂O₂CCH₃, grown from ethyl acetate solution, were provided by Mackenzie and Bosnich. Preliminary Weissenberg photography showed the crystals belonged to the tetragonal system. The systematic extinctions, *h*00 for *h* odd and 00*l* for *l* not equal to 4*n*, are consistent with the enantiomorphic space groups P4₃2₁2, *D*₄, No. 92³ and P4₃2₁2, *D*₄, No. 96.³ Preliminary cell constants were determined from the photographs, and a density of 1.2 g·cm⁻³, determined by flotation in carbon tetrachloride/ethylacetate, indicated 8 formula units per cell. No symmetry constraints are imposed on the ions.

Selection of a crystal from which intensity data might be recorded was greatly hampered by the fact that they effloresce immediately upon exposure to air. A number were sealed in Lindemann capillaries prefilled with mother liquor. After many tries a crystal of equant habit with adequate mosaicity (scan widths varying from 0.21° to 0.24°) was selected. Due to the unusually long *c* axis, 76.3 Å, Cu radiation was required for data collection. Cell constants and an orientation matrix were determined on an Enraf-Nonius CAD-4F diffractometer by using the search and index routines.⁴ Refinement of these parameters was carried out by using the setting angles of a number of carefully centered, high-angle reflections. Crystal data are summarized in Table I.

Prior to the collection of intensity data, a number of checks were made to ensure that overlap was not a serious problem. As a check on crystal mosaicity, several ω-scans of intense, low-angle reflections were recorded with a wide-open aperture. Scan widths were adequate.⁴ During data collection crystal quality and instrument stability were monitored by measuring three standard reflections every 3.3 h. Owing to the instability of the crystals, no attempt was made to measure more than a unique set of data. Conditions for these measurements are listed in Table I. In all, a total of 6388 reflections was measured. The recorded intensities were corrected for Lorentz and polarization effects and for decomposition (maximum correction 2.9%) during data collection, using the data reduction programs of the Enraf-Nonius SDP package.⁵ The value for *p* was 0.04.⁶ Since it was impossible to identify the crystal faces, an empirical absorption correction was applied to the data based on ψ scans

for nine reflections with varying 2θ values.⁷ Transmission coefficients varied from 0.883 to 0.998. Symmetry related reflections (*hk*0 and *kh*0) were averaged, (*R* = 0.1%) and finally 4007 unique data with *I* > 3σ(*I*) were available for determination of the structure.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques on *F*. Scattering factors for neutral non-hydrogen atoms were taken from Cromer and Waber,⁸ while those for H were from Stewart, Davidson and Simpson.⁹ The real and imaginary anomalous dispersion corrections of Cromer and Libermann¹⁰ were included for the Pd and P atoms. The quantity minimized in the refinements was Σ*w*(|*F*_o - |*F*_c||²), where *F*_o and *F*_c are the observed and calculated structure factors, and the weight *w* is defined as 4*F*_o²/σ²(*F*_o²).

The positional parameters for the Pd atom were determined from a Patterson synthesis assuming the space group to be P4₃2₁2. A series of structure factor and difference Fourier synthesis calculations revealed the positions for the remaining 80 non-hydrogen atoms associated with the two ions. Inspection of the diphosphine ligand chiraphos showed it was in the *R,R* configuration. The complex was known to contain *S,S*-chiraphos² and thus the model was inverted through the origin and the space group changed to P4₃2₁2.

Refinement was first attempted by using the SDP programs on the PDP11/23 computers at the Universities of Toronto and Western Ontario.⁵ The absence of a constrained least-squares program, the size of the model (87 independent, non-hydrogen atoms) and quality of the data were such that refinement did not proceed smoothly. In particular, unacceptable geometries resulted for the phenyl and xylyl rings. Future refinement was therefore carried out on the Cyber 835 at the University of Western Ontario¹¹ using the program WOCLS, imposing rigid group constraints wherever possible. The phenyl rings were assumed to have *D*_{6h} symmetry and a C-C bond length of 1.392 Å.¹² In the 3,5-dimethylphenyl groups the methyl C-ring C distance was assumed to be 1.485 Å.

After several cycles of refinement the model converged at *R*₁ = Σ||*F*_o - *F*_c||/Σ|*F*_o| = 0.118 and *R*₂ = (Σ*w*(|*F*_o - |*F*_c||²)/Σ*wF*_o²)^{1/2} = 0.185. NMR spectroscopy had indicated that the crystals contained 1 equiv of ethyl acetate in the lattice. A subsequent difference Fourier synthesis revealed a volume of electron density, in which seven peaks with values ranging from 1.3 to 3.6 eÅ⁻³ could be discerned. The positions and heights of these peaks suggested that the solvent molecule has at least two major orientations in the crystal lattice. Attempts to refine individual atoms were unsatisfactory, as were attempts to fit two idealized rigid groups in a disorder model. We finally settled on a rigid group model which incorporates seven atoms in chemically sensible positions and whose total number of electrons sums to one ethyl acetate molecule per equivalent position. A description of this model has been deposited.¹³ Although the geometry of the rigid group that resulted was unusual, we were able to refine this group, and it successfully accounted for the majority of the electron density in the region of the cell occupied by the solvent molecule.

Idealized positional parameters were computed for those hydrogen atoms in the cation and anion whose positions could be calculated, assuming either sp² or sp³ coordination geometries about the C atoms and bond distances of 0.95 and 1.0 Å, respectively. All 54 such H atoms were assigned isotropic thermal parameters 10% greater than those of the atoms to which they are bonded. Thereafter the contributions from the H atoms were included in the calculation of *F*_c, but no attempt was made to refine their parameters. We were unable to locate the remaining 27 H atoms which are associated with methyl groups and the disordered solvent molecule.

The final model involved isotropic thermal parameters assigned to all but the Pd and P atoms, for which anisotropic quantities were refined. Individual group atom thermal parameters were varied. As refinements proceeded the H atom parameters were recalculated, until convergence was reached at *R*₁ = 0.079 and *R*₂ = 0.094 (209 variables and 4007 observations with *I* > 3σ(*I*)). The chiral sense of the space group was checked by changing the sign of "*l*" for each reflection and again refining

(3) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England; Vol. I, 1969; Vol. IV, 1974.

(4) "Enraf-Nonius CAD4F Users Manual". Enraf-Nonius Delft, Delft, The Netherlands. 1982.

(5) The computer programs used in data reduction and preliminary structure solutions were from the Enraf-Nonius Structure Determination Package, SDP-PLUS version 1-0, 1982.

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(11) Structure refinement used modifications for the Cyber 835 at U.W.O. of the following: full-matrix least-squares, J. A. Ibers' NUCLS; Fourier syntheses, A. Zalkin's FORDAP; function and errors, W. R. Busing, K. O. Martin, and H. A. Levy's ORFFE; crystal structure illustration, C. K. Johnson's ORTEP.

(12) Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 773.

(13) Supplementary material.

Table II. Atomic Positional ($\times 10^4$) and Thermal ($\times 10^3$) Parameters^a

atom	x	y	z	U(eq)	atom	x	y	z	U(eq)
Pd	4368 (1)	3261 (1)	8003.8 (2)	48 (1)	Derived Group Atom Parameters (continued)				
P(1)	3491 (5)	1834 (5)	7943.6 (7)	50 (5)	C(53)	1730 (7)	5215 (8)	7904 (1)	65 (8)
P(2)	4500 (5)	2660 (4)	8282.7 (8)	54 (5)	C(54)	1878 (8)	6216 (7)	7875 (1)	78 (9)
C(1)	3293 (18)	1129 (17)	8153 (3)	62 (7)	C(55)	2778 (9)	6551 (8)	7811 (1)	77 (9)
C(2)	4156 (16)	1308 (15)	8279 (3)	51 (7)	C(56)	3530 (7)	5883 (10)	7776 (1)	78 (8)
C(3)	2970 (15)	68 (17)	8128 (3)	59 (8)	C(57)	769 (9)	4860 (11)	7972 (2)	80 (9)
C(4)	3980 (14)	828 (15)	8464 (2)	41 (7)	C(58)	2934 (13)	7620 (8)	7781 (2)	138 (13)
C(5)	4267 (17)	4254 (16)	7762 (3)	55 (7)	C(61)	4203 (10)	3700 (9)	7580 (1)	46 (7)
C(6)	5134 (14)	4344 (15)	7844 (3)	41 (6)	C(62)	4871 (9)	2960 (9)	7537 (1)	76 (9)
C(7)	5189 (14)	4702 (14)	8021 (3)	47 (7)	C(63)	4818 (7)	2498 (7)	7374 (1)	65 (8)
B	1133 (19)	660 (20)	6740 (3)	50 (9)	C(64)	4097 (8)	2774 (8)	7254 (1)	74 (8)
Derived Group Atom Parameters					C(65)	3428 (7)	3514 (7)	7297 (1)	67 (8)
O(1)	-607 (17)	1339 (20)	8837 (3)	219 (18)	C(66)	3481 (9)	3976 (8)	7460 (1)	63 (8)
O(2)	588 (13)	1664 (11)	9029 (2)	208 (10)	C(67)	5531 (10)	1709 (10)	7328 (2)	91 (9)
O(3)	1577 (19)	2105 (22)	9275 (3)	249 (23)	C(68)	2659 (10)	3808 (12)	7169 (2)	78 (8)
C(1)	386 (21)	2849 (14)	8901 (3)	271 (33)	C(71)	6201 (9)	4756 (14)	8106 (2)	49 (7)
C(2)	57 (15)	1879 (15)	8872 (2)	240 (21)	C(72)	6400 (12)	6510 (11)	8201 (2)	67 (8)
C(3)	1251 (13)	2280 (15)	9136 (3)	247 (22)	C(73)	7345 (15)	5781 (10)	8265 (2)	73 (8)
C(4)	1275 (20)	3170 (14)	9037 (4)	192 (17)	C(74)	8090 (9)	5099 (15)	8235 (2)	74 (9)
C(11)	2309 (10)	1927 (11)	7831 (2)	65 (8)	C(75)	7891 (12)	4245 (12)	8140 (2)	92 (9)
C(12)	1443 (14)	1942 (10)	7929 (1)	69 (8)	C(76)	6947 (15)	4073 (9)	8076 (2)	75 (8)
C(13)	545 (10)	2109 (11)	7846 (2)	86 (9)	C(81)	128 (11)	129 (12)	6669 (2)	52 (7)
C(14)	512 (10)	2261 (11)	7666 (2)	83 (9)	C(82)	-810 (15)	415 (9)	6722 (2)	81 (9)
C(15)	1377 (14)	2246 (10)	7568 (1)	77 (9)	C(83)	-1633 (10)	-93 (14)	6661 (2)	87 (9)
C(16)	2276 (10)	2079 (11)	7651 (2)	56 (8)	C(84)	-1518 (12)	-886 (12)	6547 (2)	80 (9)
C(21)	4214 (13)	955 (10)	7817 (2)	58 (7)	C(85)	-579 (17)	-1172 (9)	6494 (2)	119 (11)
C(22)	3742 (8)	314 (14)	7702 (2)	86 (9)	C(86)	244 (10)	-664 (14)	6555 (2)	79 (9)
C(23)	4288 (15)	-369 (11)	7607 (2)	87 (9)	C(91)	2129 (9)	365 (13)	6629 (2)	55 (7)
C(24)	5306 (14)	-410 (11)	7626 (2)	84 (9)	C(92)	2543 (12)	919 (9)	6494 (2)	63 (8)
C(25)	5779 (8)	231 (14)	7741 (2)	92 (10)	C(93)	3365 (12)	568 (13)	6405 (2)	63 (7)
C(26)	5232 (14)	914 (11)	7837 (2)	67 (8)	C(94)	3772 (9)	-338 (14)	6450 (2)	83 (9)
C(31)	3607 (10)	3233 (11)	8430 (2)	39 (6)	C(95)	3358 (13)	-892 (9)	6584 (2)	94 (9)
C(32)	2829 (13)	3728 (11)	8351 (1)	61 (8)	C(96)	2536 (13)	-541 (12)	6674 (2)	79 (8)
C(33)	2058 (10)	4093 (10)	8452 (2)	76 (9)	C(101)	918 (11)	1929 (8)	6712 (2)	55 (7)
C(34)	2065 (10)	3962 (11)	8633 (2)	84 (10)	C(102)	641 (11)	2257 (12)	6546 (2)	77 (9)
C(35)	2843 (13)	3467 (12)	8713 (1)	62 (8)	C(103)	547 (11)	3262 (14)	6514 (2)	87 (9)
C(36)	3614 (10)	3102 (10)	8612 (2)	82 (9)	C(104)	730 (12)	3938 (8)	6647 (3)	79 (9)
C(41)	5643 (9)	2773 (13)	8401 (2)	50 (7)	C(105)	1007 (12)	3610 (13)	6813 (2)	93 (10)
C(42)	5874 (11)	3628 (10)	8493 (2)	53 (7)	C(106)	1101 (11)	2606 (14)	6845 (2)	90 (10)
C(43)	6801 (14)	3735 (10)	8569 (2)	75 (9)	C(111)	1314 (13)	444 (12)	6950 (1)	57 (8)
C(44)	7496 (9)	2987 (15)	8553 (2)	92 (10)	C(112)	642 (9)	-120 (11)	7044 (2)	82 (9)
C(45)	7265 (12)	2132 (12)	8461 (2)	105 (11)	C(113)	811 (11)	-323 (10)	7221 (2)	92 (9)
C(46)	6338 (15)	2025 (9)	8385 (2)	80 (9)	C(114)	1653 (14)	37 (12)	7303 (1)	79 (9)
C(51)	3382 (8)	4881 (9)	7804 (2)	48 (7)	C(115)	2325 (9)	601 (12)	7208 (2)	76 (8)
C(52)	2482 (9)	4547 (7)	7868 (1)	57 (8)	C(116)	2156 (11)	805 (10)	7032 (2)	66 (8)

^aEstimated standard deviations are given in parentheses and correspond to the least significant digit(s). Positional parameters are given as fractional coordinates; U values are in \AA^2 . $U(\text{eq}) = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

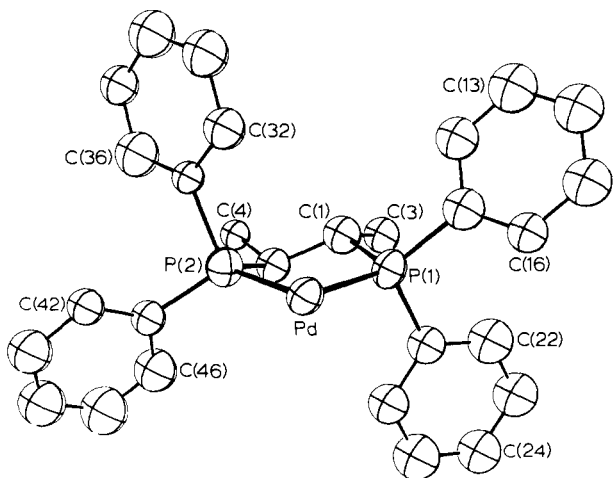
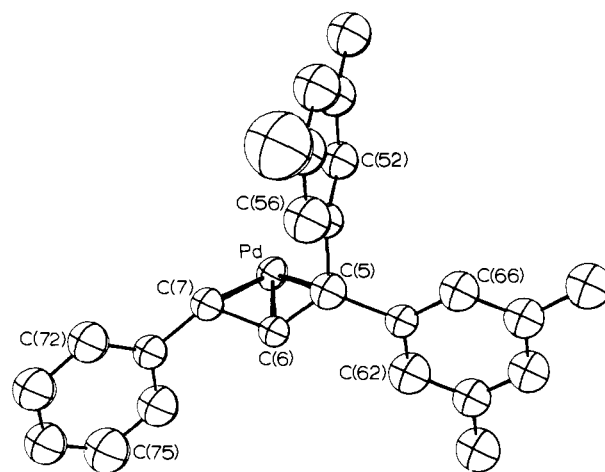


Figure 1. Chiraphos ligand bonded to Pd.

the model. The refinement resulted in values of $R_1 = 0.113$ and $R_2 = 0.10$ and thus the original indexing and choice of space group were taken as correct.

In the final cycle no shift exceeded 0.059 of its standard deviation. The error in an observation of unit weight is 3.65 electrons. A statistical

Figure 2. η^3 -Allyl ligand bonded to Pd.

analysis of R_2 over various ranges of F_o , $\lambda^{-1} \sin \theta$, and reflection parities showed no abnormal trends. A total difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance. The highest peak is of electron density 2.2 (1) $\text{e}\text{\AA}^{-3}$ at fractional coordinates (0.332, 0.332, -0.500). Final positional and U (equiv) thermal parameters for the non-H atoms are given in Table II,

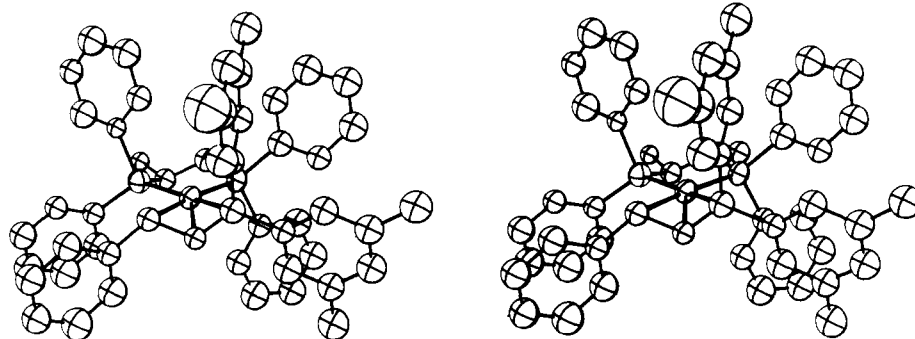


Figure 3. Stereoview of the cation, showing the steric interactions leading to chiral discrimination.

the values for the group atoms being derived parameters. Rigid group parameters, anisotropic thermal parameters for Pd and the two P atoms, and hydrogen atom parameters have been deposited, along with structure amplitudes as $10|F_o|$ and $10|F_c|$ in electrons.¹³

Structure Description

Several problems were encountered during this structure determination. The crystal is efflorescent and of barely adequate mosaicity, the tetragonal axis is unusually long, the solvent molecule is badly disordered, and there is a large number (87) of non-hydrogen atoms. However, we believe that these problems have been successfully dealt with and are confident that the results presented are reliable.

The crystals are built up from discrete ions, incorporating ethyl acetate in the crystal lattice. The shortest contact between the ions is 2.52 Å involving H1C(35) and H1C(86) at $(\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{4} + z)$; the closest contact to the solvent molecule is 2.67 Å between C(124) and H1C(35). Selected bond distances and angles are given in Table III. Figure 1 is an ORTEP drawing of the Pd atom and chiraphos ligand, Figure 2 is an illustration of the Pd and allyl ligand, both drawn as 50% probability thermal ellipsoids and showing the atom numbering scheme. Figure 3 is a combination of Figures 1 and 2, presenting a stereoview of the steric interactions between catalyst and substrate which result in the chiral discrimination observed.

The allyl group is η^3 -bonded to the Pd atom and can be considered as occupying two sites in a distorted square-planar coordination geometry. The remaining two sites contain the P atoms of the chiraphos ligand. A P-Pd-P angle of 85.8 (2)° is normal for a diphosphine ligand.¹⁴ The plane defined by the three allylic C atoms is at an angle of 106.1 (22)° to the plane defined by the Pd and two P atoms. In the chloro(η^3 -allyl)palladium dimer, $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$, the corresponding angle is 111.5 (9)°.¹⁵ The two Pd-P distances of 2.321 (6) and 2.285 (6) Å differ by 4.2σ with the longer distance being associated with the P atom that is *cis* to the disubstituted end of the allyl group. The P(1)-Pd-C(5) angle, 107.5 (6)°, is also larger (6.1σ) than the P(2)-Pd-C(7) angle, 102.5 (5)°. The central allylic C atom is slightly (3.7σ) closer to the Pd atom than the other two C atoms, 2.17 (2) Å compared to 2.29 (2) and 2.26 (2) Å. This pattern of distances has been previously noted¹⁵ for $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$.

The absolute configuration of the *S,S*-chiraphos ligand was known prior to undertaking the structure determination^{2,16} and has been confirmed by this analysis. All angles and distances associated with the P atoms are normal. When viewed from the Pd atom, the C(2) atom is 0.46 (2) Å below the plane defined by P(2), Pd, and P(1), and C(1) is 0.18 (2) Å above it. The disparity between these values is rather unusual, more normal displacements being 0.437 (5) and -0.363 (6) Å as observed in first structure determination of the chiraphos ligand.¹⁶ In each case the conformation of the chelate ring is δ , with the methyl substituents adopting equatorial dispositions. Such puckering

Table III. Selected Bond Distances (Å) and Angles (Deg)

bond	distance	bond	distance
Pd-P(1)	2.321 (6)	P(1)-C(11)	1.82 (2)
Pd-P(2)	2.285 (6)	P(1)-C(21)	1.82 (2)
Pd-C(5)	2.29 (2)	P(1)-C(1)	1.88 (2)
Pd-C(6)	2.17 (2)	P(2)-C(31)	1.83 (2)
Pd-C(7)	2.25 (2)	P(2)-C(41)	1.80 (2)
		P(2)-C(2)	1.89 (2)
C(5)-C(6)	1.34 (3)	C(1)-C(2)	1.53 (3)
C(5)-C(51)	1.51 (2)	C(1)-C(3)	1.52 (2)
C(5)-C(61)	1.58 (2)	C(2)-C(4)	1.57 (2)
C(6)-C(7)	1.44 (3)		
C(7)-C(71)	1.52 (2)	B-C(81)	1.64 (3)
		B-C(91)	1.65 (3)
		B-C(101)	1.76 (3)
		B-C(110)	1.65 (3)
atoms	angle	atoms	angle
P(1)-Pd-P(2)	85.8 (2)	Pd-P(1)-C(1)	109.3 (7)
P(1)-Pd-C(5)	107.5 (6)	Pd-P(1)-C(11)	119.2 (6)
P(2)-Pd-C(7)	102.5 (5)	Pd-P(1)-C(21)	112.0 (6)
C(5)-Pd-C(6)	34.8 (6)	C(1)-P(1)-C(11)	108.0 (9)
C(6)-Pd-C(7)	37.8 (6)	C(1)-P(1)-C(21)	101.1 (9)
		C(11)-P(1)-C(21)	105.7 (7)
Pd-C(5)-C(51)	102.2 (12)		
Pd-C(5)-C(61)	115.6 (12)	Pd-P(2)-C(2)	108.2 (7)
Pd-C(7)-C(71)	120.8 (12)	Pd-P(2)-C(31)	111.7 (5)
		Pd-P(2)-C(41)	120.3 (6)
C(6)-C(5)-C(51)	123.5 (18)	C(2)-P(2)-C(31)	105.0 (8)
C(6)-C(5)-C(61)	120.1 (17)	C(2)-P(2)-C(41)	107.6 (8)
C(7)-C(6)-C(5)	120.9 (19)	C(31)-P(2)-C(41)	103.0 (7)
C(71)-C(7)-C(6)	117.6 (16)		
C(81)-B-C(91)	113.9 (17)	P(1)-C(1)-C(2)	109.9 (16)
C(81)-B-C(101)	104.6 (16)	P(1)-C(1)-C(3)	114.4 (16)
C(81)-B-C(111)	111.7 (17)	C(2)-C(1)-C(3)	116.9 (19)
C(91)-B-C(101)	108.1 (16)	P(2)-C(2)-C(1)	110.6 (15)
C(91)-B-C(111)	109.6 (16)	P(2)-C(2)-C(4)	115.2 (14)
C(101)-B-C(111)	108.6 (16)	C(1)-C(2)-C(4)	112.2 (17)

renders the phenyl substituents upon the P atoms quasi-axial (rings 2 and 3) and quasi-equatorial (rings 1 and 4).

The dimensions of the allyl ligand are also in accord with structural determinations on Pd-allylic systems.^{15,17} The allyl ligand is coordinated to the metal atom in the orientation which results in the *R* configuration at C(7), with phenyl ring 7 being in the *syn* position. It is clear from Figure 3 that the phenyl substituent on P(2), ring 4, and the allylic phenyl group, ring 7, lie parallel to one another in the solid state. The angle between the normals to their planes is 6.6°; the distance between overlapping C atoms is approximately 3.65 Å.

The angles subtended at the B atom in the anion are in agreement with a tetrahedral geometry. Three of the B-C(α) distances group closely together at approximately 1.65 Å while the B-C(101) distance is 1.76 (3) Å. This difference is not significant statistically and the average B-C(α) bond length is 1.68 (3) Å.

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Discussion

This successful determination of the structure of an intermediate occurring during asymmetric allylic alkylations allows us to offer some suggestions as to the root cause of the chiral induction. It is generally accepted that chelating diphosphine ligands with an ability to form five-membered chelate rings will adopt a gauche conformation. This is particularly true in the case of first-row transition-metal complexes, in which the metal-phosphorus bond distances are comparatively short. In the case of the chiral *S,S*-chiraphos ligand, the asymmetry at the C atoms causes the ring to adopt the δ configuration, in which the two methyl substituents are disposed in the energetically favorable equatorial positions. The phenyl ring substituents upon the P atoms accordingly adopt quasi-axial and quasi-equatorial positions relative to the metal,P,P plane. Nonbonded steric interactions between the rings and the methyl groups result in an alternating face-edge profile presented to the two remaining coordination sites in the square-planar geometry at the metal. Examples are known in which either an attractive^{18,19} or repulsive²⁰ interaction has been postulated between substituents on P atoms in order to account for the observed geometry.

In the present study, the η^3 -allyl ligand contains three bulky substituents, one phenyl ring, and two even bulkier 3,5-di-

methylphenyl groups. Repulsive steric interactions between the substituents on P(1) and those on C(5) result in the adoption of a staggered arrangement. The earlier studies² confirmed that a major source of the discrimination occurs at the anti position of C(5). In the solid-state structure, ring six occupies this position. The phenyl ring on C(7) and the equatorial phenyl ring on P(2) lie parallel in the solid state; there may or may not be an attractive interaction between them. This interaction is not important in chiral discrimination.² If the alternative allyl ligand configuration were seen, the steric disposition at C(5) would consist of eclipsed substituents, and a presumably much higher energy species. Thus, as has been observed before, the chiral discrimination can be attributed to steric interactions between the substrate molecule and a chiral complex whose profile is fixed by the energetically favored conformation of the chiraphos chelate ring.

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Registry No. [Pd(η^3 -C(Xy)₂CHCHPh)(*S,S*-PPh₂(CHMe)₂PPh₂)]-BPh₄·CH₃CH₂O₂CCH₃, 95043-25-7.

Supplementary Material Available: A description of the solvent molecule, anisotropic thermal parameters for Pd, P(1), and P(2), rigid group parameters, hydrogen atom parameters, and structure amplitudes as 10|F_o| vs. 10|F_c| (21 pages). Ordering information is given on any current masthead page.

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Homogeneous Catalysis. Transition-Metal-Catalyzed Claisen Rearrangements

Terry G. Schenck and B. Bosnich*

Contribution from the Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1. Received July 19, 1984

Abstract: Palladium(0), palladium(II), rhodium(I), and iridium(I) complexes catalyze the rearrangement of allyl imidates to allyl amides under mild conditions. The palladium(II) catalysis is characterized by exclusive [3,3] regioselectivity and high stereoselectivity whereas the palladium(0), rhodium(I), and iridium(I) catalysts generally give both the [3,3] and [1,3] rearrangement products and although the palladium(0) catalyst can give high stereoselectivity, the rhodium(I) and iridium(I) catalysts are nonstereoselective. After a series of experiments using chiral substrates and substrates with specific deuterium labels, the mechanisms of these catalytic reactions have been elucidated. The palladium(II) catalysis is proposed to proceed via cyclic carbonium ion intermediates, and the mechanism resembles the thermal uncatalyzed Claisen rearrangement path. The palladium(0) catalysis is a form of catalytic allylation involving oxidative addition followed by nucleophilic attack on a π -allyl intermediate. The mechanism of the rhodium(I) and iridium(I) catalysis was not as fully investigated as the others, but it appears to involve carbonium ion intermediates formed by cleavage of the allyl-oxygen bond.

The Cope and Claisen [3,3]sigmatropic thermal rearrangements are of considerable synthetic utility. Mechanistic¹ and theoretical² studies show that these intramolecular reactions are subject to strong geometrical constraints governed by the intermediates that result from suprafacial cyclization so that there is nearly complete transfer of chirality from reactant to product. This stereocontrol has been ingeniously exploited in a number of synthetic strategies but generally the rearrangements have been embodied early in the synthesis because of the high temperatures (~200 °C) generally required. Because of this thermal restriction, a number of

attempts have been made to accelerate these reactions.³

The earliest attempts involved the use of protic (H₂SO₄)⁴ or Lewis acids (BF₃,⁵ BCl₃,⁶ alumina⁷). Although rate enhancements were observed, the yields were poor and the side products were numerous presumably because in all of these cases the reactions proceed via carbonium ions as evidenced by the diversity of products and the loss of stereocontrol. The most impressive rate acceleration of a Claisen rearrangement was reported by Ireland,⁸

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