ASYMMETRIC HYDROGENATION IN THE PRESENCE OF BISDIPHENYLPHOSPHINE COMPLEXES OF RHODIUM.

3. MOLECULAR STRUCTURE OF 2R-3-PHENYL-2-(N-METHYLDIPHENYLPHOSPHINAMINO)-1-DIPHENYLPHOSPHINOXYPROPANE (1,5-CYCLOOCTADIENE)RHODIUM(I) PERCHLORATE AND ITS EFFECTIVENESS AS AN ENANTIOSELECTIVE CATALYST

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In the asymmetric hydrogenation of substrates of the α-acylaminoacrylic acid type in the presence of bisdiphenyl-phosphine complexes of rhodium an empirical relationship was obtained between the configuration (R, S) of the product and the conformation (δ, λ) of the complex. This relationship was obtained for complexes containing the $Ph_2PX-Rh-XPPh_2$ fragment, which can possess a C_2 symmetry axis, and the conformation of the chelate ring can be determined by means of models [1]. In the case of complexes with unsymmetrical ligands, such as 2R-3-phenyl-2-(N-methyldiphenylphosphinamino)-1-diphenylphosphinoxypropane R-PheNOP, the conformation can only be determined reliably by x-ray crystallographic analysis (XCA). We therefore investigated the molecular structure of the complex $[Rh(R\text{-PheNOP})(COD)]ClO_4$ (I) (where COD is 1,5-cyclooctadiene), which effectively catalyzes asymmetric hydrogenation [2], by XCA.

DISCUSSION OF RESULTS

The geometric parameters of the cation (I) (Fig. 1) are similar to those observed in the structures of the perchlorates of (COD)-S-N-(diphenylphosphine)-2-(diphenyl-phosphinoxymethylpyrrolidine)rhodium (II) [3] and (COD)-(trans-1,2-bisdiphenylphosphinaminocyclohexane) rhodium (III) [4], where the seven-membered chelate ring is linked directly to the pyrrolidine and cyclohexane rings. As in (II), the configuration of the metal ring in (I) is asymmetric (Fig. 2); its conformation can be described conditionally as a "boat," in which the P^2, O^1, and N atoms deviate from the average plane $RhP^1C^9C^{10}$, realized with an accuracy of 0.15 Å, by 1.598, 0.680, and 1.105 Å respectively on one side.

As a rule, the structures of the bis(diphenylphosphine) chelate complexes of rhodium, which are the precursors of catalysts for the asymmetric hydrogenation of olefins [3, 4], are characterized by the chiral orientation of the Ph groups at the phosphorus atoms coordinated with the metal. In such systems in at least one of the two Ph_2P groups the orientation of the Ph substituents in relation to the RhP_2 plane is usually substantially nonequivalent. The complex (I) is no exception in this sense.

As seen from Fig. 2, the phenyl rings attached to the P^1 atom are more or less symmetrically placed in relation to the RhP_2 plane; the inclination of the P^1-C^{13} and P^1-C^{19} bonds to this plane amounts to 44.7 and 58.6° respectively. At the same time the phenyl rings at the P^2 atom are differently oriented; the P^2-C^{31} bond forms an angle of 63.7° with the RhP_2 plane, while P^2-C^{25} bond hardly deviates from it at all (the corresponding angle amounts to 3.8°). The planes of the two phenyl rings $C^{25}-C^{30}$ and $C^{31}-C^{36}$ at the P^2 atoms are in fact perpendicular to the RhP_2 plane [dihedral angles 86.3(2) and 83.4(2)° respectively] and form a dihedral angle of 115.6(3)° between them, but in relation to the plane of the projection in Fig. 2 the first of the phenyl rings is almost parallel while the second is almost perpendicular.

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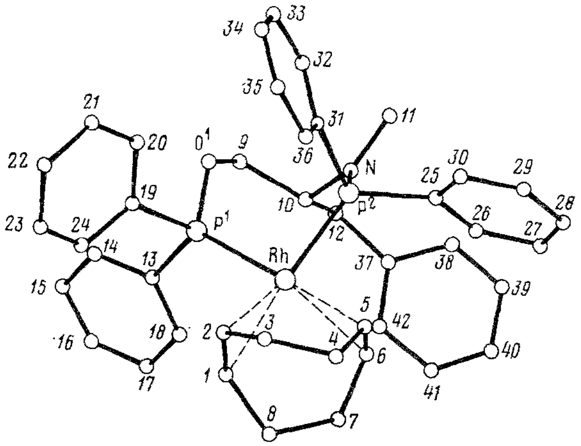


Fig. 1. The structure of the complex cation $[Rh(R\text{-}PheNOP)(COD)]^+$ (I).

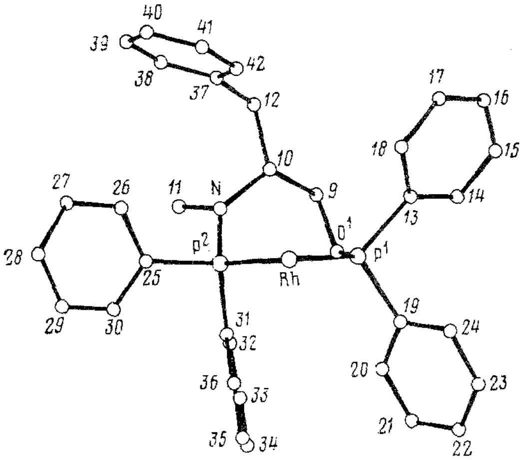


Fig. 2. A projection of the cation (I) from the side of the rhodium atom along the P^2-Rh-P^1 plane. The cyclooctadiene ligand is not shown.

The typical square-plane coordination of the rhodium atom for 16-electron complexes undergoes extremely significant tetrahedral distortion in the cation (I); the dihedral angle between the RhP_2 and RhA(1.2)A(5.6) planes amounts to 18.0° [A(1,2) and A(5,6) are the centers of the double bonds coordinated with the metal atom]. It should be noted that similar tetrahedral distortion of the square-planar coordination of the rhodium is typical of molecules of the investigated group of diene complexes of rhodium — precursors of the catalysts for asymmetric hydrogenation. For instance, in the complexes (II) [3] and (III) [4] the dihedral angles which characterize the tetrahedral distortion of the coordination of the metal atom amount to 23 and 20° respectively. This confirms the suggestion in [5] about the generality of the steric factors which on the one hand give rise to some rotation of the diene ligand, leading to distortion of the square-planar coordination of the rhodium atom, and on the other secure the enantioselectivity of the catalytic action of the complex.

The bond lengths Rh—P^1 2.296(2) and Rh—P^2 2.299(2) Å lie in the range of values 2.27-2.34 Å characteristic of 16-electron diolefins and in particular, the norbornadiene and COD complexes of rhodium with bis(diphenylphosphine) ligands [3-5]. At the same time these bonds are somewhat elongated compared with the Rh—P bonds (2.237 and 2.252 Å) in the 18-electron rhodium complex with the η^6-arene ligand (η^6-hexadeuterobenzene)[1R, 2R-trans-1,2-bis(diphenylphosphinomethyl)cyclobutane]rhodium perchlorate [6].

The COD ligand in the cation of (I) has an extremely complex form; the Cremer—Pople parameters (q_2 = 1.420, q_3 = 0.014, q_4 = −0.160 Å, φ_2 = 118.83, φ_3 = 300.13°) correspond to the intermediate conformation with the most substantial contribution from the canonical "boat" form and a less significant contribution from the "boat—boat" form (B ← BB according to the nomenclature employed in [7]).

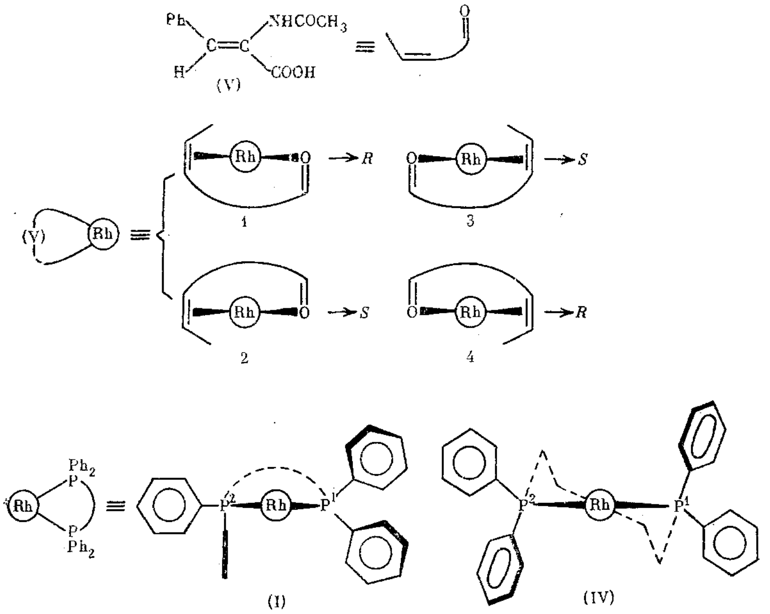
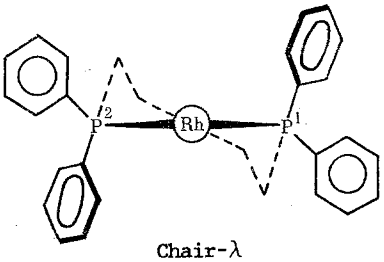


Fig. 3. The possible structure of the intermediate compounds from asymmetric catalytic hydrogenation of α-N-acetylaminocinnamic acid.

The η^2-coordinated double bonds $C^1 = C^2$ 1.38(1) and $C^5 = C^6$ 1.33(1) Å are not entirely perpendicular to the average coordination plane of the metal atom or to the line joining their centers. [The inclination of the bond to the above-mentioned plane amounts to 79.8 and 81.6, and the angles with the $P^1P^2RhA(1.2)A(5.6)$ direction are 87.0 and 85.4° respectively.] This leads to an appreciable increase in the distances $R{-}C^1$ 2.275(7) and $Rh{-}C^5$ 2.278(7) Å compared with $Rh{-}C^2$ 2.227(7) and $Rh{-}C^6$ 2.202(6) Å. A substantial difference in the Rh—C(COD) distances due to the above-mentioned reasons is also observed in the other COD complexes of rhodium and, in particular, in (II) and (III), where the difference in the respective Rh—C distances amounts on the average to 0.04 and 0.06 Å [3, 4].

Thus, from the projection of the cation (I) (Fig. 2) it is seen that the arrangement of the phosphine phenyl groups is characterized by the lack of symmetry. Comparison of their asymmetric arrangement with the arrangement typical of seven-membered chelate complexes of the type [Rh-S,S-DIOP](IV), which possess a C_2 symmetry axis, reveals the folowing feature: with the difference in the conformations of the metal ring the chiral arrangement of the phenyl groups at P^2 in [Rh-PheNOP] is similar to the arrangement of the phenyl groups at the corresponding phosphorus atom in (Rh-S, S-DIOP).



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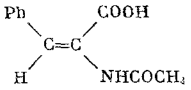
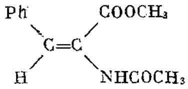
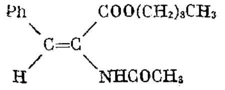
It has been considered [8] that the asymmetry of the product is determined by the chiral arrangement of the phosphine phenyl groups of the catalytic complex. Therefore, if we consider not the conformation but the position of the Ph groups characteristic of this conformation, we can expect that the general relationship between the conformation of the catalyst and the configuration of the product in the hydrogenation of N-acetylaminocinnamic acid (V) [1] will also be fulfilled for the complex (I).

Four modes of orientation in (V) are possible during the formation of the complex—substrate adduct (Fig. 3) [1, 9]. Through two of these four diastereomeric intermediate complexes of rhodium(I) (1,4 or 2,3, leading to different isomers of the product) the reaction

TABLE 1. The Asymmetric Hydrogenation of α-N-Acetylaminocinnamic Acid and Its Esters in the Presence of [Rh(R-PheNOP)(COD)]ClO_4 (100% conversion, the product with the S configuration)

Substrate	T., °C	Reaction time, min	Av. rate, mole/sec· 10^7	p, ±10 rel.%
	25 50	47 27	3,5 6,2	6,5 3,5
	25 50	90 37	1,85 4,5	14,5 8,3
	25 50	140 60	1,2 2,8	25,6 19,5

Note: pH_2 = 1 atm, [I] = 0.2 M, [I]/[Rh] = 100, MeOH 5 ml.

takes place at a higher rate, and it is this which gives rise to the enantioselectivity of the process [10]. It can be supposed that the stability and the reactivity of these diastereomeric intermediate complexes, which depends in the final count on their structure, is responsible for the difference in the rates. In the case of the complex (IV) an enantiomeric excess of 81% [11] of S-acetylphenylalanine (VI) was obtained. Consequently, the reaction here takes place through the intermediate complexes (2-IV) and (3-IV) to the extent of 90.5% and through the complexes (1-IV) and (4-IV) to the extent of 9.5%. There is a C_2 symmetry axis in the complex (IV), and the intermediate complexes (1-IV) and (4-IV) are therefore perfectly equivalent, like (2-IV) and (3-IV) (Fig. 3). This equivalence is lost in the unsymmetric complex (I). The steric hindrances in the intermediate complexes are determined by interaction between the PPh groups and the $\mathrm{Ph{-}C{=}\underset{|}{C}COOH}$ fragment of the coordinated substrate (V) [1]. Since the chirality of these groups at P^2 in (I) and (IV) is of the same sign (see Fig. 3), it can be supposed that the ratio of (1-I) and (2-I) in the reaction (which determines the enantioselectivity) does not differ significantly from that of (1-IV) and (2-IV), and the enantioselectivity will not consequently change. The P^1 group in (I) is characterized by an arrangement of the Ph groups close to symmetrical, and the ratio of (3-I) and (4-I) in the relation is therefore closer to the racemic product than in the case of (3-IV) and (4-IV). By means of such an analysis it is possible to explain the formation of the product with the S configuration during the hydrogenation of (V) in the presence of (I) [2]. An analogous approach gives a product configuration which coincides with experiment in the case of the cationic complexes with the PPPM and BPPM ligands [12], and the exception is the complex with S-Prolophos [3].

It can be expected that the increase in the steric hindrance of the intermediate complexes (1-I) and (4-I), due to the steric interaction between the $\mathrm{Ph\underset{|}{C}{=}\underset{|}{C}COOH}$ fragment of the coordinated substrate and the PPh_2 groups, will increase the differences between (1-I) and (2-I) and, accordingly, between (3-I) and (4-I) (to a lesser degree), further increasing the optical yield. Such an increase can be achieved by the introduction of radicals which increase the volume of the interacting fragments into the substrate molecule, e.g., by substitution of the COOH group in $\mathrm{Ph\underset{|}{C}{=}\underset{|}{C}COOH}$ by the COOR fragment. In fact, the optical yield increases (Table 1) synchronously with the volume of the radical, and the reaction rate here decreases. This corresponds to the general increase of the steric hindrance in the intermediate complexes and, consequently, to a decrease in their reactivity.

EXPERIMENTAL

The crystals of the complex (I) were obtained according to [2]. The crystals of (I) are monoclinic; at 20°C a = 10.587 (1), b = 14.256 (1), c = 13.435(2) Å, β = 102.57(9)°, V = 1979.1(4) Å^3, d_{calc} = 1.416 g/cm^3, Z = 2, space group $P2_1$. The unit cell parameters and the intensities of 3143 unique reflections with $F^2 \geq 3\sigma$ were measured on a Hilger-Watts four-circle automatic diffractometer (20°C, MoK_α radiation, graphite monochromator, θ/2θ-scan, $\theta \lesssim 30°$).

TABLE 2. The Coordinates of the Nonhydrogen Atoms ($\times 10^4$; for the Rh atom $\times 10^5$)

Atom	X	Y	Z	Atom	X	Y	Z
Rh	−15867(4)	0	−32057(3)	C^{17}	−3402(8)	1688(6)	−481(6)
P^1	−2116(1)	−626(1)	−1775(1)	C^{18}	−2908(6)	1114(5)	−1145(5)
P^2	507(1)	−514(1)	−2649(1)	C^{19}	−3180	−1639(5)	−2041(5)
Cl	−3355(2)	−6071(1)	−2258(2)	C^{20}	−2642(6)	−2523(5)	−2070(5)
O^1	−966(4)	−1079(3)	−915(3)	C^{21}	−3425(7)	−3278(5)	−2343(6)
O^2	−3732(11)	−5695(8)	−1456(7)	C^{22}	−4736(8)	−3188(5)	−2606(6)
O^3	−3140(26)	−5534(8)	−2912(12)	C^{23}	−5293(7)	−2306(6)	−2594(6)
O^4	−4097(14)	−6740(11)	−2786(10)	C^{24}	−4519(6)	−1539(5)	−2300(6)
O^5	−2443(12)	−6675(11)	−1818(12)	C^{25}	1677(5)	−188(5)	−3411(4)
N	1253(4)	−181(4)	−1485(4)	C^{26}	2225(6)	692(6)	−3267(6)
C^1	−3599(6)	612(7)	−3780(5)	C^{27}	2997(6)	1040(6)	−3894(6)
C^2	−3519(6)	−257(5)	−4219(5)	C^{28}	3215(6)	477(7)	−4675(6)
C^3	−3321(8)	−421(7)	−5259(6)	C^{29}	2692(8)	−413(7)	−4829(6)
C^4	−2348(7)	195(8)	−5607(5)	C^{30}	1947(7)	−726(6)	−4189(6)
C^5	−1206(6)	438(6)	−4745(5)	C^{31}	433(6)	−1804(5)	−2735(5)
C^6	−1095(7)	1176(6)	−4123(5)	C^{32}	983(7)	−2398(5)	−1966(6)
C^7	−2109(8)	1905(6)	−4146(8)	C^{33}	813(8)	−3369(5)	−2060(7)
C^8	−3507(8)	1535(7)	−4281(7)	C^{34}	71(8)	−3709(6)	−2943(8)

TABLE 3. The Coordinates of the Hydrogen Atoms (10^3)

Atom	X	Y	Z	Atom	X	Y	Z
H^1	−382(7)	67(6)	−326(6)	H^{17}	−333(7)	227(5)	−64(5)
H^2	−357(7)	−91(5)	−399(5)	H^{18}	−262(7)	142(5)	−190(5)
H$^{3.1}$	−311(7)	−98(5)	−535(5)	H^{20}	−179(7)	−272(5)	−190(6)
H$^{3.2}$	−423(7)	−43(5)	−567(5)	H^{21}	−259(7)	−381(6)	−244(6)
H$^{4.1}$	−197(6)	5(7)	−610(5)	H^{22}	−512(7)	−378(6)	−279(5)
H$^{4.2}$	−284(7)	83(5)	−583(5)	H^{23}	−614(7)	−217(5)	−279(6)
H^5	−42(6)	−4(7)	−475(5)	H^{24}	−477(7)	−112(6)	−235(5)
H^6	−12(7)	148(5)	−368(5)	H^{26}	239(7)	103(5)	−263(5)
H$^{7.1}$	−191(7)	238(6)	−359(5)	H^{27}	343(7)	172(5)	−377(6)
H$^{7.2}$	−191(7)	232(6)	−467(5)	H^{28}	364(7)	74(5)	−501(6)
H$^{8.1}$	−376(7)	203(5)	−389(5)	H^{29}	252(7)	−77(5)	−556(5)
H$^{8.2}$	−405(7)	145(5)	−499(5)	H^{30}	141(7)	−124(5)	−439(5)
H$^{9.1}$	−61(6)	−20(5)	27(5)	H^{32}	155(7)	−214(5)	−131(6)
H$^{9.2}$	53(7)	−87(5)	23(5)	H^{33}	98(7)	−371(6)	−163(5)
H^{10}	−28(7)	67(5)	−127(5)	H^{34}	−8(7)	−419(5)	−303(5)
H$^{11.1}$	312(6)	4(7)	−87(5)	H^{35}	−104(7)	−329(5)	−435(5)
H$^{11.2}$	255(7)	−79(5)	−35(5)	H^{36}	−101(7)	−163(5)	−434(5)
H$^{11.3}$	309(7)	−92(5)	−131(5)	H^{38}	331(7)	169(5)	−39(6)
H$^{12.1}$	85(7)	118(6)	39(5)	H^{39}	384(7)	287(5)	−150(5)
H$^{12.2}$	193(7)	77(5)	32(6)	H^{40}	254(7)	352(5)	−222(5)
H^{14}	−344(7)	−75(6)	−15(5)	H^{41}	32(7)	345(5)	−243(5)
H^{15}	−412(6)	21(5)	94(5)	H^{42}	−30(7)	219(5)	−130(5)
H^{16}	−411(7)	176(5)	69(6)				

The structure was interpreted by the heavy-atom method; the coordinates of the rhodium atoms were determined from the Patterson function, and the remaining nonhydrogen atoms were found by successive approximations of the electron density syntheses. The structure was refined by the method of least squares first in isotropic and then in anisotropic approximation. The high temperature factors of the oxygen atoms in the ClO_4^- anion are clearly due to the strong thermal motion or to the disordering of the anion in the crystal. However, attempts to localize the possible additional positions of the O atoms were unsuccessful. All the hydrogen atoms were localized in the difference synthesis and were included in the final refinement with fixed $B_{iso} = 6.5$ Å^2. The final R value was 0.0368, and the weighted R_w factor was 0.0414.

The absolute configuration of the complex was established by the Hamiltonian test on the basis of allowance for the anomalous scattering by the Rh, Cl, and P atoms. (The divergence factors for the inverted structure amounted to R = 0.0376 and $R_W = 0.0425$, which corresponds to 99.5% probability of accuracy in the determination of the absolute configuration.) The absolute configuration of the complex obtained in this way corresponds to the known absolute configuration of the diphosphine ligand (obtained from R-phenylalanine) contained in it.

The coordinates of the nonhydrogen and hydrogen atoms are given in Tables 2 and 3. The temperature factors of the nonhydrogen atoms can be obtained from the authors. All the calculations were performed on a Eclipse S/200 computer by means of the INEXTL programs [13].

The methyl and n-butyl α-N-acetylaminocinnamates were obtained according to [14]. The hydrogenation, the isolation of the product, and its analysis were conducted as described earlier [2]. The optical yield was determined from the $[\alpha]_D$ value of the sample [S-N-acetylphenylalanine methyl ester, $[\alpha]_D^{25}$ + 21.4 (C 1.9, MeOH) [15]; S-N-acetylphenylalanine butyl ester was obtained according to [2]; mp 78.5–79.5°C, $[\alpha]_D^{25}$ +9.9 (C 0.36, EtOH).

CONCLUSIONS

1. The structure of 2R-3-phenyl-2-methyl-diphenylphosphinamino-1-diphenylphosphinoxypropane(1,5-cyclooctadiene)rhodium (I) perchlorate was determined by x-ray crystallographic analysis, and the asymmetric arrangement of the phosphine phenyl groups was established.

2. Examination of the established structure of the complex in comparison with the previously investigated structures of asymmetric hydrogenation catalysts showed the existence of a correlation between the configuration of the phosphorus atoms in the catalytic complexes and the configuration of the hydrogenation product.

LITERATURE CITED

1. V. A. Pavlov and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2015 (1983).
2. V. A. Pavlov, A. A. Voloboev, L. S. Gorshkova, and E. I. Klabunovskii, Dokl. Akad. Nauk SSSR , 283, 1206 (1985).
3. E. Cesarotti, A. Chiesa, and A. Ciani, J. Organomet. Chem., 251, 79 (1983).
4. K. Onuma and A. Nakamura, Bull. Chem. Soc. Jpn., 54, 761 (1981).
5. E. P. Kyba, R. E. Davis, R. N. Yuri, and K. R. Shirley, Inorg. Chem., 20, 3616 (1981).
6. J. M. Townsend and J. F. Blount, Inorg. Chem., 20, 269 (1981).
7. V. A. Palyulin, N. S. Zefirov, V. E. Shklover, and Yu. T. Struchkov, J. Mol. Struct., 70, 65 (1981).
8. B. Bosnich and M. K. Roberts, Adv. Chem. Ser. Catal. Aspects Metal Phosphine Complexes, 337 (1982).
9. K. E. Koenig, M. K. Sabacky, G. L. Bachman, W. C. Christopfel, H. D. Barnstorf, R. B. Friedman, W. S. Knowles, B. R. Stults, B. D. Vineyard, and D. J. Weinkauff, in: Transition Metal Mediated Organic Synthesis, D. W. Slocun and O. R. Hughes, eds., Ann. N. Y. Acad. Sci., 333, 16 (1980).
10. J. Halpern, Science, 217, No. 4558, 401 (1982).
11. E. Gelbard, H. B. Kagan, and R. Stern, Tetrahedron, 32, 233 (1976).
12. I. Ojima, T. Kogure, and N. Yoda, J. Org. Chem., 45, 4728 (1980).
13. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, 1029 (1983).
14. A. H. Cook, G. Harris, and J. Heilborn, J. Chem. Soc., 1060 (1948).
15. H. B. Kagan and T. P. Dang, J. Am. Chem. Soc., 94, 6429 (1972).