Inorganica Chimica Acta, *112* (1986) 65–70

Asymmetric Catalysis.
8*. X-ray Structure Analysis of the Asymmetric Hydrosilylation Catalyst *Cyclo*-octa-1,5-diene-pyrrol-2-carbald-(s)-1-phenylethyliminato–rhodium(I)

HENRI BRUNNER**, GEORG RIEPL

Institut für Anorganische Chemie, Universität Regensburg, Universitätsstrasse 31, D-8400 Regensburg, F.R.G.

IVAN BERNAL and WOLFGANG H. RIES

Department of Chemistry, University of Houston, Houston, Tex. 77004, U.S.A.

Received June 11, 1985

Abstract

Complex $(-)_{578}$-I was prepared by reaction of $[(COD\text{-}1,5)RhCl]_2$ with the Na derivative of the Schiff base, derived from pyrrol-2-carbaldehyde and (s)-1-phenylethylamine. An X-ray structure analysis for $(-)_{578}$-I, an enantioselective catalyst for the hydrosilylation of acetophenone, was carried out. The (s)-1-phenylethyl group, responsible for the optical induction, adopts the following conformation: the phenyl and methyl substituents of the asymmetric carbon atom C13 stagger the C21–H bond in the chelate plane, and the C–H bond of the asymmetric carbon atom C13 is oriented towards the mid-point of the coordinated double bond Cl–C2 of the COD–1,5 ligand.

Introduction

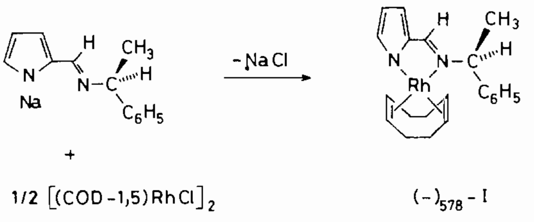
In homogeneous enantioselective catalysis most chelate ligands used contain a chiral backbone for optical induction and two diphenylphosphine groups for coordination [2–4]. Some examples of that design are Diop [5], Prophos [6], Chiraphos [7], Norphos [8], BPPM [9] and BPPFA [10]. The phenyl substituents of the $P(C_6H_5)_2$ groups are thought to act as chirality transmitters from their location in the ligand backbone to the metal coordination sites where prochiral precursors are converted to optically active products [11–13]. Though ligands of that type are very effective in asymmetrically catalyzed reactions, e.g. hydrogenation, hydrosilylation and cross coupling [2–4], it has been argued that it cannot he the best solution to the challenging problems of enantioselective catalysis to conduct these different specific chiral informations of the ligand backbones by the same transmitter $P(C_6H_5)_2$ [13–15]. It has been suggested that the inducing chirality be moved from the ligand backbone to the area where the phenyl transmitters are bonded to the phosphorus atoms. Then a direct interaction of the inducing chirality with the relevant metal coordination sites could take place [13–15]. A possible approach to this concept is the synthesis of chelate ligands, which contain imino groups and coordinate with the imine nitrogen atom. If optically active amines $H_2N–R^*$ are used in the preparation of such chelate imines, the optically active groups R^* are in the location of the phenyl transmitters in diphenyl phosphine chelates. Even if the chelate ring is made rigid, an effect known to be favorable in asymmetric catalysis, one problem remains: the free rotation around $N–R^*$. By rotation around $N–R^*$, and R^* such as CH(Me)(Ph) could in principle adopt a variety of different conformations, each of which would have another influence on the metal coordination positions where the prochiral substrates are converted to optically active products. However, a series of conformational analyses demonstrated that, due to intramolecular repulsions and attractions, a substituent $R^* = CH(Me)(Ph)$ at the imine nitrogen in a metal-bonded chelate imine prefers specific conformations [14–22], a fact promising for asymmetric catalysis. Furthermore, imines derived from pyridine- and pyrrol-2-carbaldehyde and (S)-1-H_2N–CH(Me)(Ph) have been used successfully as ligands in rhodium complexes to catalyze the asymmetric hydrosilylation of acetophenone in optical yields exceeding those obtained with chelating diphosphines [23, 24]. To determine especially the conformation of the N–CH(Me)(Ph) substituent with respect to the rest of the molecule in such a hydrosilylation catalyst, an X-ray structure analysis of the rhodium–cyclooctadiene-1,5 complex of the anion of pyrrol-2-carbald-(S)-1-phenylethylimine $(-)_{578}$-I was carried out. $(-)_{578}$-I was prepared by reaction of

---

*Part 7 is ref. 1.

**Author to whom correspondence should be addressed.

0020-1693/86/$3.50



Scheme 1.

$[(COD-1,5)RhCl]_2$ with the Na derivative of the Schiff base pyrrol-2-carbald-(s)-1-phenylethylimine, derived from pyrrol-2-carbaldehyde and (s)-1-phenylethylamine, as shown in Scheme 1.

Experimental

Synthesis of $(-)_{578}$-I

0.4 ml (2.1 mmol) pyrrol-2-carbald-(s)-1-phenylethylimine in 100 ml ether is treated with 240 mg (10 mmol) NaH. After 2 h the filtered solution at −70 °C is added to a solution of 500 mg (1.0 mmol) $[(COD-1,5)RhCl]_2$ in 40 ml THF. After slow warming to room temperature, the solvent is evaporated and the petrol ether/benzene 1:1 solution of the residue is chromatographed at SiO_2: yellow band giving orange crystals, yield 720 mg (88%); recrystallization from 6 ml benzene/40 ml petrol ether at −30 °C, m.p. 151 °C. *Anal.* Found: C, 61.59; H, 5.97; N, 6.84. Calc.: C, 61.77; H, 6.17; N, 6.86. Optical rotation: $[\alpha]_{18}^{578}$ −450°, $[\alpha]_{18}^{546}$ −610° (4.54 mg I/ml benzene). ^{1}H NMR (90 MHz, $CDCl_3$/TMS, δ-values): $\underline{CH_3}$, 1.56(d, 7 Hz); $\underline{CH}CH_3$, 4.37(q, 7 Hz); $\underline{CH}$=N, 7.55(d, 3 Hz); H3, 6.47(m); H4, 6.12(m); H5, 7.3(m); COD-1,5, 1.8–2.4 and 3.8–4.6(broad).

X-ray Data Collection, Solution and Refinement of the Structure

An orange crystal of **I** of suitable size was mounted on an Enraf-Nonius CAD-4 diffractometer operating with OS/4 software. Details of our methods of data collection are available in ref. 24. The specifics of this case are summarized in Table I. The unique Rh atom was found in the Patterson function and all non-hydrogen atoms in subsequent Fourier maps. After these were refined, all the hydrogen atoms appeared in a difference Fourier map. Refinement was finished with anisotropic thermal parameters for the heavier atoms and isotropic thermal parameters for the hydrogens, as summarized in Table II. Table III gives the positions of the atoms in their correct absolute configuration. Bond lengths and angles are given in Tables IV and V; least-squares planes and deviations of selected atoms therefrom are listed in Table VI, together with some dihedral angles (Table VI is deposited as supplementary material with the Editor-in-Chief). All data processing was carried out with SHELX-76 [26]. The molecule (Fig. 1) and the packing diagram (Fig. 2) were drawn with ORTEP2 [27]. In both of these figures $(-)_{578}$-I appears in its correct absolute configuration.

TABLE I. Summary of Data Collection and Processing Parameters for $(-)_{578}$-I

Space group	$P2_12_12_1$
Cell constants	
a	9.259(10) Å
b	11.722(5) Å
c	16.868(7) Å
Cell volume (*V*)	1830.599 Å^3
Molecular formula	$C_{21}H_{25}N_2Rh$
Molecular weight	408.358
Density (calc.) (δ)	1.48148 g cm^{-3}
Radiation	Mo Kα (λ = 0.71069 Å)
Absorption coefficient (μ)	8.78 cm^{-1}
Data collection range	$4° \leq 2\theta \leq 65.0°$
Scan width (Δθ)	$(1.0 + 0.35 \tan\theta)°$
Maximum scan time	240 s
Scan speed range	0.38 to 10.06° min^{-1}
Total data collected	3721
Data with $I > 3\sigma(I)$	2585
Total variables	230
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0310
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.0352
Weights	$w = [1.0000/\sigma(F_o)]^2$
Goodness-of-fit	2.09

Description of the Molecule

If we define as Cen1 and Cen2 the mid points of the two olefinic bonds (half way between C1 and C2 and between C5 and C6, respectively), the geometry of the fragment Cen1, Cen2, Rh, N1, N2 is planar to within a maximum deviation of 0.016 Å (plane A of Table VI). This is in good agreement with the fact that **I** is a Rh(I) complex in a valence state in which the square planar geometry is common. The distances of the aliphatic carbon atoms C3, C4, C7 and C8 from plane A demonstrate that the COD ligand in its standard boat conformation is almost perfectly bisected by this plane. This is further documented by the fact that the least-squares planes E, containing the four olefinic carbon atoms C1, C2, C5 and C6, and F, calculated for C3, C4, C7 and C8, show only minor deviations from the ideal perpendicular orientation towards plane A.

The pyrrole ring is exactly planar; the maximum deviation of any atom from the least-squares plane defined by the five ring atoms is only 0.007(7) Å (plane B; Table VI), with a dihedral angle of 6.7° to plane A. Therefore plane D calculated for the atoms of the conjugated π-system of the Schiff base ligand and the centers of the olefinic bonds shows bigger deviations from the ideal geometry.

TABLE II. Atomic Coordinates and Thermal Parameters (×1000, Rh × 10 000) of $(-)_{578}$-I

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.08556(5)	0.23788(3)	0.16005(3)	378(2)	318(2)	369(2)	15(2)	11(3)	−47(2)
N1	0.2692(5)	0.1409(4)	0.1751(3)	39(3)	39(2)	36(3)	0(2)	−4(3)	3(2)
N2	0.0724(6)	0.1273(3)	0.0610(3)	40(3)	31(2)	39(3)	1(3)	−6(3)	−6(2)
C1	−0.0582(8)	0.3644(5)	0.1133(4)	65(5)	42(3)	60(4)	20(4)	9(4)	5(3)
C2	−0.1343(6)	0.2931(5)	0.1616(5)	40(3)	58(4)	77(5)	18(3)	−1(4)	−15(4)
C3	−0.1830(9)	0.3239(8)	0.2480(5)	73(6)	113(7)	64(6)	40(5)	25(5)	−1(5)
C4	−0.0731(9)	0.3222(7)	0.3066(4)	74(6)	90(5)	64(5)	−3(6)	27(5)	−28(4)
C5	0.0822(9)	0.2993(5)	0.2787(3)	65(4)	52(4)	51(4)	−6(4)	5(4)	−16(3)
C6	0.1581(8)	0.3743(6)	0.2329(4)	61(5)	48(4)	54(4)	−10(4)	10(4)	−22(3)
C7	0.1019(9)	0.4888(5)	0.2046(5)	91(6)	38(4)	91(6)	−8(5)	9(6)	−10(4)
C8	−0.0095(10)	0.4840(6)	0.1370(5)	129(8)	36(4)	105(7)	13(5)	−18(6)	−11(4)
C9	0.3853(7)	0.1315(6)	0.2241(4)	51(5)	60(4)	47(4)	−7(4)	−17(4)	9(3)
C10	0.4818(8)	0.0528(6)	0.1950(4)	44(4)	59(4)	65(5)	9(4)	−18(4)	9(4)
C11	0.4244(7)	0.0133(5)	0.1244(4)	42(4)	42(3)	69(4)	6(4)	−2(4)	3(3)
C12	0.2949(6)	0.0684(5)	0.1135(4)	30(3)	31(3)	44(3)	0(3)	−2(3)	0(3)
C13	−0.0411(6)	0.1213(5)	−0.0017(4)	31(3)	42(3)	43(4)	5(3)	−8(3)	−3(3)
C14	0.0154(7)	0.1748(6)	−0.0781(4)	55(4)	54(4)	52(4)	−10(4)	−13(4)	14(4)
C15	−0.0969(7)	0.0005(5)	−0.0108(3)	31(3)	43(3)	33(3)	1(3)	−9(3)	−3(2)
C16	−0.0550(8)	−0.0706(5)	−0.0722(4)	54(5)	57(4)	46(4)	−4(4)	0(4)	−9(3)
C17	−0.1084(9)	−0.1806(6)	−0.0780(4)	78(6)	59(4)	58(5)	−4(5)	−9(5)	−18(4)
C18	−0.2032(8)	−0.2203(6)	−0.0228(5)	57(5)	49(5)	106(7)	−7(4)	−36(5)	0(5)
C19	−0.2448(8)	−0.1495(6)	0.0411(5)	55(5)	66(5)	67(5)	−21(4)	−7(4)	11(4)
C20	−0.1944(7)	−0.0403(6)	0.0453(4)	46(4)	64(5)	48(4)	−8(4)	0(4)	−4(4)
C21	0.1848(6)	0.0633(5)	0.0551(3)	37(3)	33(3)	42(4)	3(3)	4(3)	−7(3)
H1	−0.0366(8)	0.3368(5)	0.0584(4)	127(17)					
H2	−0.1610(6)	0.2156(5)	0.1415(5)	127(17)					
H3A	−0.2708(9)	0.2694(8)	0.2664(5)	138(12)					
H3B	−0.2200(9)	0.4112(8)	0.2454(5)	138(12)					
H4A	−0.0733(9)	0.4016(7)	0.3391(4)	138(12)					
H4B	−0.1006(9)	0.2531(7)	0.3461(4)	138(12)					
H5	0.1309(9)	0.2267(5)	0.2948(3)	127(17)					
H6	0.2578(8)	0.3520(6)	0.2162(4)	127(17)					
H7A	0.1930(9)	0.5412(5)	0.1881(5)	138(12)					
H7B	0.0455(9)	0.5280(5)	0.2536(5)	138(12)					
H8A	−0.1012(10)	0.5375(6)	0.1506(5)	138(12)					
H8B	0.0466(10)	0.5179(6)	0.0861(5)	138(12)					
H9	0.3970(7)	0.1739(6)	0.2751(4)	74(12)					
H10	0.5756(8)	0.0305(6)	0.2200(4)	74(12)					
H11	0.4697(7)	−0.0429(5)	0.0875(4)	74(12)					
H13	−0.1323(50)	0.1641(40)	0.0196(27)	28(15)					
H14A	0.1030(7)	0.1246(6)	−0.1019(4)	64(11)					
H14B	0.0535(7)	0.2599(6)	−0.0651(4)	64(11)					
H14C	−0.0710(7)	0.1793(6)	−0.1210(4)	64(11)					
H16	0.0130(8)	−0.0409(5)	−0.1134(4)	59(9)					
H17	−0.0753(9)	−0.2315(6)	−0.1219(4)	59(9)					
H18	−0.2447(8)	−0.2986(6)	−0.0287(5)	59(9)					
H19	−0.3109(8)	−0.1795(6)	0.0830(5)	59(9)					
H20	−0.2277(7)	0.0109(6)	0.0891(4)	59(9)					
H21	0.1947(6)	0.0099(5)	0.0092(3)	30(15)					

The phenyl ring C15 → C20 (plane G; Table VI) is planar with a maximum deviation of −0.016(7) Å for C19 and makes dihedral angles of 83.3° and 81.8° with planes A and D, respectively.

The most appropriate compound for comparison with our structural results is (COD-1,5)$_2$Rh$_2$(biimidazolate) [28], hereafter referred to as **II**. The relationship of the structural parameters of **II** to other literature data has been discussed by Rasmussen *et al.* [28]. **I** and **II** contain the same fragment (COD-1,5)Rh(N1–C–C–N2) but differ somewhat in the nature of the 5-membered chelate ring. This is shown by the Rh–N distances, which are shorter in **I** (2.061 and 2.119 Å) than in **II** (average 2.134 Å),

TABLE III. Determination of Absolute Configuration of $(-)_{578}$-I

Reflection number	Indices	Calculated F^a ratio	Measured F^b ratio
1	1 1 4	0.96	0.95
2	1 3 1	1.03	1.04
3	2 1 2	0.96	0.96
4	2 1 3	0.94	0.93
5	2 1 4	0.97	0.99
6	3 2 4	0.98	0.99
7	2 3 3	0.97	0.97
8	4 4 3	0.97	0.98
9	1 6 1	0.97	0.97
10	4 1 3	1.04	1.02
11	1 4 2	1.02	1.04
12	1 4 4	1.02	1.04
13	1 4 3	1.03	1.03
14	2 2 6	0.97	0.99
15	1 4 6	1.03	1.03
16	4 4 2	1.03	1.04
17	5 1 4	1.04	1.02
18	4 2 6	1.02	1.02
19	3 7 7	1.02	1.02
20	4 4 7	0.98	0.99
21	3 7 5	1.04	1.03
22	4 7 6	1.02	1.04
23	5 7 3	0.98	0.99

^{a}Calculated $F(hkl)$/calculated $F(\bar{h}\bar{k}\bar{l})$. ^{b}Ratio of experimentally measured $F(hkl)/F(\bar{h}\bar{k}\bar{l})$ as $[I(hkl)/I(\bar{h}\bar{k}\bar{l})]^{1/2}$.

TABLE IV. Intramolecular Bond Distances (Å) for $(-)_{578}$-I

Rh–N1	2.061(5)	C9–C10	1.375(8)
Rh–N2	2.119(4)	C10–C11	1.384(8)
Rh–C1	2.143(6)	C11–C12	1.374(8)
Rh–C2	2.136(5)	C12–C21	1.419(7)
Rh–C5	2.127(6)	N2–C21	1.287(6)
Rh–C6	2.125(6)	N2–C13	1.492(7)
C1–C2	1.363(8)	C13–C14	1.525(8)
C2–C3	1.569(9)	C13–H13	1.04(5)
C3–C4	1.42(1)	C13–C15	1.515(7)
C4–C5	1.54(1)	C15–C16	1.385(7)
C5–C6	1.366(8)	C15–C20	1.393(8)
C6–C7	1.516(9)	C16–C17	1.384(8)
C7–C8	1.54(1)	C17–C18	1.362(9)
C8–C1	1.527(9)	C18–C19	1.412(9)
N1–C9	1.361(7)	C19–C20	1.365(8)
N1–C12	1.363(7)		

TABLE V. Intramolecular Bond Angles (°) for $(-)_{578}$-I

C1–Rh–C2	37.2(2)	N2–Rh–C5	161.5(2)
C5–Rh–C6	37.5(2)	N2–Rh–C6	159.1(2)
C1–Rh–C5	95.9(3)	Rh–N1–C9	140.4(4)
C2–Rh–C6	93.8(3)	Rh–N1–C12	113.2(4)
C1–Rh–C6	83.6(3)	Rh–N2–C13	128.9(4)
C2–Rh–C5	82.7(3)	Rh–N2–C21	111.8(4)
C8–C1–C2	124.0(7)	N1–C12–C21	115.5(5)
C1–C2–C3	124.2(6)	C12–C21–N2	120.2(5)
C2–C3–C4	116.0(6)	C9–N1–C12	106.0(5)
C3–C4–C5	117.4(6)	N1–C9–C10	110.5(6)
C4–C5–C6	122.8(7)	C9–C10–C11	106.3(6)
C5–C6–C7	124.9(7)	C10–C11–C12	107.1(6)
C6–C7–C8	115.5(6)	C11–C12–N1	110.0(5)
C7–C8–C1	115.2(6)	C11–C12–C21	134.5(6)
Rh–C1–C8	110.8(5)	C13–N2–C21	119.2(5)
Rh–C1–C2	71.1(3)	N2–C13–C14	109.7(5)
Rh–C2–C3	110.8(5)	N2–C13–H13	108(3)
Rh–C2–C1	71.7(4)	N2–C13–C15	110.9(5)
Rh–C5–C4	111.1(5)	C14–C13–H13	112(3)
Rh–C5–C6	71.2(4)	C14–C13–C15	114.5(5)
Rh–C6–C7	112.1(5)	C15–C13–H13	102(3)
Rh–C6–C5	71.3(3)	C13–C15–C16	123.0(6)
N1–Rh–C1	159.9(2)	C13–C15–C20	118.2(5)
N1–Rh–C2	162.1(2)	C16–C15–C20	118.9(6)
N1–Rh–C5	94.8(2)	C15–C16–C17	120.9(7)
N2–Rh–C6	94.8(2)	C16–C17–C18	120.0(7)
N2–Rh–N1	78.9(2)	C17–C18–C19	119.7(7)
N2–Rh–C1	95.6(2)	C18–C19–C20	119.9(7)
N2–Rh–C2	98.1(2)	C19–C20–C15	120.5(7)

and by the difference in ligand bite (in **I**, N–Rh–N 78.9°; in **II**, 82.4°). The slightly shorther Rh–N bonds in **I** compared to **II** are associated with slightly longer Rh–C bonds (average Rh–C in **I** 2.133; in **II** 2.114 Å). Consistent with this fact, the average value of the C=C bonds in **I**, 1.364(8) Å, is in excellent agreement with those found for double bonds coordinated to rhodium in (COD)Rh(chiraphos)$^+$ [29], 1.359(8), and in (NBD)Rh(Norphos)$^+$ [30], 1.367(10) Å. It is shorter than the average value of 1.396(9) Å for **II** [28].

The range of length for C–C σ-bonds, 1.516(9) Å to 1.569(9) Å, in the COD moiety does not differ from those found for other accurate studies [29–35]. Therefore the short C3–C4 distance of 1.42(1) Å in connection with long C4–C5 and C2–C3 bonds, respectively, should be due to malcompensated thermal motion. Similar results can be observed in a number of structures for COD rhodium complexes [29, 31–35].

Conformational Analysis of the 1-Phenylethyl Group

The conformation of an 1-phenylethyl substituent with respect to a planar chelate ring has been analyzed in a number of cases, and rules to differentiate between more and less stable conformations have been established [14–22, 36]. The interaction of the 1-phenylethyl group with the substituent at the imine carbon atom, which for $(-)_{578}$-I is the hydrogen atom at C21, turned out to be the conformation-determining effect; specific intramolecular attractions and repulsions make only minor contributions.

In the present X-ray structure analysis, a completely different conformation is found (Fig. 1) from

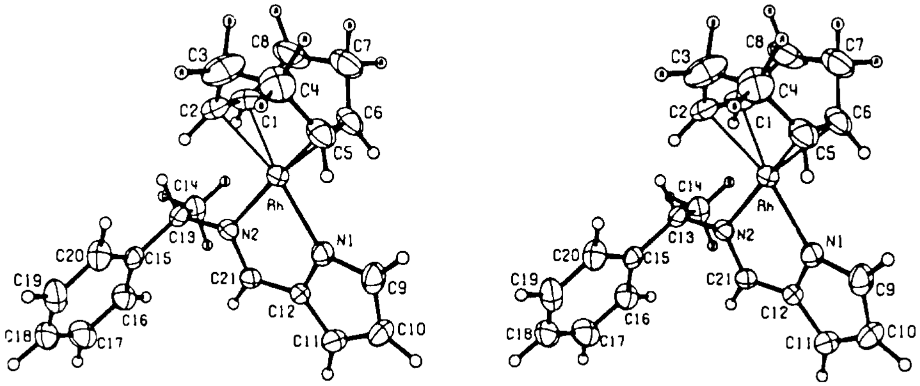


Fig. 1. Stereopair of (–)$_{578}$-I showing the numbering system used.

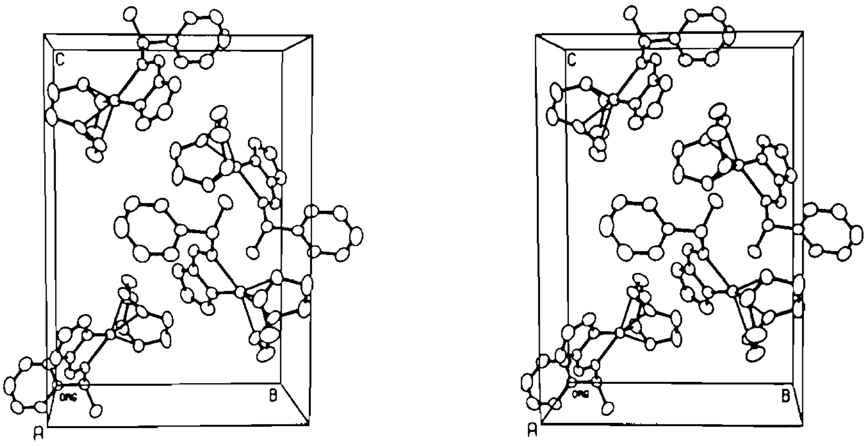


Fig. 2. Packing diagram of (–)$_{578}$-I.

those reported earlier. Methyl C14 and phenyl C15–C20 exactly stagger the C–H bond at C21 and the ligand plane, which is a sterically favorable arrangement, and the C–H bond at the asymmetric carbon C13 eclipses the chelate plane, pointing towards the Rh atom. This is demonstrated by the fact that atoms H13, C13, C14 and C15 deviate from plane C, defined by Rh, N1, N2, C12, C21 (Table VI), by −0.328, −0.050, 1.330, and −1.185 Å, respectively. In this way the hydrogen atom at C13 is located between the two hydrogens of the coordinated double bond C1–C2, as is the C–H bond at C9 with respect to the olefinic bond C5–C6 on the other side of the molecule*. Conformers, which by rotation around N2–C13 would have methyl C14 or phenyl C15–C20 or both on the rhodium olefin side, would suffer from extreme steric hindrance with the C–H bonds of the olefin C1–C2. Thus, for the conformation of the 1-phenylethyl group in (–)$_{578}$-I, the intramolecular contacts of the substituents at the asymmetric C13 with the coordinated olefin C1–C2 are much larger than with the hydrogen substituent at the imino carbon C21; the arrangement found is a good compromise for both interactions. In a previous paper we had proposed a set of measures [36] to describe the conformation of an 1-phenylethyl group in a chelate ligand which for (–)$_{578}$-I are given by the following parameters: Rh–N2, 2.119; N2–C13, 1.492 Å. N1–Rh–N2, 78.9; Rh–N2–C13, 128.9°. N1–Rh–N2–C13, 179.2; Rh–N2–C13–C15, −128.1; Rh–N2–C13–C14, 104.5; Rh–N2–C13–H, −17.3; N2–C13–C15–C20, 77.6°.

Absolute Configuration Determination

When the structure refinement was complete, we calculated structure factor tables for $F(h,k,l)$ and $F(\bar{h},\bar{k},\bar{l})$ and obtained a set of 23 reflections, listed in Table III, for which the differences, $\Delta[F(hkl) - F(\bar{h}\bar{k}\bar{l})]$, due to the anomalous scattering are large and have $\Delta > 3\sigma(F_o)$. The reflections in question were measured and their ratios $[F(hkl)/F(\bar{h}\bar{k}\bar{l})]_{obs}$ and $[F(hkl)/F(\bar{h}\bar{k}\bar{l})]_{calc}$ compared. The ratios calculated in Table III are in excellent agreement with

---

*Intramolecular nonbonding distances: H(C13)–H(C1) 2.31, H(C13)–H(C2) 2.16, H(C9–H(C5) 2.56, H(C9)–H(C6) 2.65 Å.

the observed ratios, and the coordinates in Table II led to a better *R*-value at the isotropic stage of refinement than those for the opposite enantiomer ($R_{W,S} = 6.24$, $R_{W,R} = 6.34$); thus the absolute configuration of the $(-)_{578}$ enantiomer of **I** at the carbon atom C13 is (s), a fact not known in advance to the X-ray crystallographers.

Acknowledgement

H.B. and G.R. thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG for support of this work. W.H.R. thanks NATO for a grant to spend a year in Houston, I.B. thanks the Alexander von Humboldt-Stiftung for a U.S. Senior Scientist Award to spend the Summer of 1982 in Regensburg.

References

1 H. Brunner and M. Pröbster, *Inorg. Chim. Acta, 61*, 129 (1982).
2 K. E. König, M. J. Sabacky, G. L. Bachmann, W. C. Christopfel, H. D. Barnstorff, R. B. Friedman, W. S. Knowles, B. R. Stults, B. D. Vineyard and D. J. Weinkauff, *Ann. N.Y. Acad. Sci.*, 333, 16 (1980).
3 V. Caplar, G. Comisso and V. Sunjic, *Synthesis, 2*, 85 (1981).
4 L. Marko and J. Bakos, 'Aspects of Homogeneous Catalysis, Vol. 4', Reidel, Dordrecht/Boston/London, 1981, p. 145.
5 H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc., 94*, 6429 (1972).
6 M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc., 100*, 5491 (1978).
7 M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc., 99*, 6262 (1977).
8 H. Brunner and W. Pieronczyk, *Angew. Chem., Int. Ed. Engl., 18*, 620 (1979).
9 K. Achiwa, *J. Am. Chem. Soc., 98*, 8265 (1976).
10 T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto and M. Kumada, *Tetrahedron Lett.*, 1133 (1976).
11 W. S. Knowles, B. D. Vineyard, M. J. Sabacky and B. R. Stults, 'Fundamental Research in Homogeneous Catalysis, Vol. 3', Plenum, New York/London, 1979, p. 537.
12 A. D. Slack, I. Greveling and M. C. Baird, *Inorg. Chem., 18*, 3125 (1979).
13 H. Brunner, A. F. M. M. Rahman and I. Bernal, *Inorg. Chim. Acta, 83*, L93 (1984).
14 H. Brunner, G. Agrifoglio, I. Bernal and M. Creswick, *Angew. Chem., Int. Ed. Engl., 19*, 641 (1980).
15 H. Bunner, in A. Müller and E. Diemann (eds.), 'Transition Metal Chemistry', Verlag Chemie, Weinheim/Deerfield Beach/Basle, 1981, p. 265.
16 H. Brunner, J. Lukassek and G. Agrifoglio, *J. Organomet. Chem., 195*, 63 (1980).
17 I. Bernal, M. Creswick, H. Brunner and G. Agrifoglio, *J. Organomet. Chem., 198*, C4 (1980).
18 H. Brunner and G. Agrifoglio, *J. Organomet. Chem., 207*, C43 (1980).
19 H. Brunner, G. Agrifoglio, R. Benn and A. Rufińska, *J. Organomet. Chem., 217*, 365 (1981).
20 H. Brunner and D. K. Rastogi, *Inorg. Chem., 19*, 891 (1980).
21 H. Brunner and D. K. Rastogi, *Bull. Soc. Chim. Belg., 89*, 883 (1980).
22 H. Brunner, *Angew. Chem., Int. Ed. Engl., 22*, 897 (1983).
23 H. Brunner and G. Riepl, *Angew. Chem. Suppl.*, 769 (1982).
24 H. T. Johnson, K. C. Klein and S. Thomen, *J. Mol. Catal., 12*, 37 (1981).
25 G. M. Reisner, I. Bernal and G. R. Dobson, *J. Organomet. Chem., 157*, 23 (1978).
26 G. M. Sheldrick, 'SHELX-76', (A program for crystal structure determination), University of Cambridge, 1976.
27 C. K. Johnson, 'ORTEP 2', (A fortran ellipsoid plotting program for crystal structure illustration, Rep. ORNL-5138), Oak Ridge, Tenn., 1972.
28 W. S. Kaiser, R. B. Saillant, W. M. Butler and P. G. Rasmussen, *Inorg. Chem., 15*, 2681 (1976).
29 R. G. Ball and N. C. Payne, *Inorg. Chem., 16*, 1187 (1977).
30 E. P. Kyba, R. E. Davis, P. N. Juri and K. R. Shirley, *Inorg. Chem., 20*, 3616 (1981).
31 M. P. Anderson and L. H. Pignolet, *Inorg. Chem., 20*, 4101 (1981).
32 J. G. Leipoldt, S. S. Basson, G. J. Lamprecht, L. D. C. Bok and J. J. J. Schlebusch, *Inorg. Chim. Acta, 40*, 43 (1980).
33 P. A. Tucker, W. Scutcher and D. R. Russel, *Acta Crystallogr., Sect. B:, 31*, 592 (1975).
34 M. Arthurs, S. M. Nelson and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 779 (1977).
35 M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 11, 2243 (1972).
36 I. Bernal, W. H. Ries, H. Brunner and D. K. Rastogi, *J. Organomet. Chem., 290*, 353 (1985).