Asymmetric Catalysis. Part 19 [1]. X-Ray Structure Analysis of (renorphos)$NiCl_2$ and (renorphos)$_2$Ni, renorphos = *trans*-2.3-bis(diphenylphosphino)-bicyclo[2.2.1]heptane

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Abstract

Renorphos, *trans*-2,3-bis(diphenylphosphino)-bicyclo[2.2.1]heptane, has been used as a ligand to prepare the complexes (renorphos)$NiCl_2$, **I**, and (renorphos)$_2$Ni, **II**. X-ray structure analyses of which have been carried out. For square-planar **I** there is an optical self-resolution on crystallization, whereas the crystal of tetrahedral **II** consists of pairs of enantiomers, whose components contain identical renorphos ligands. Two of the four phenyl rings of each renorphos ligand, responsible for the chirality transmission in asymmetric catalysis, are of the equatorial and axial type respectively. For the orientation of the phenyl planes a new measure, the setting angle, is proposed.

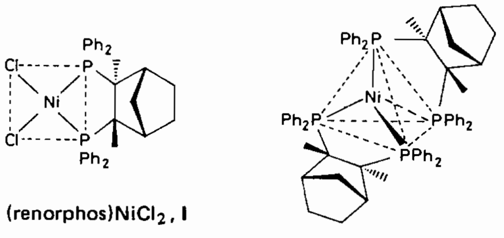
Introduction

In asymmetric catalysis with transition metal complexes chelating phosphanes are the optically active ligands most frequently used [3]. One of these ligands, (+)- and (–)-norphos, (2*S*, 3*S*)- and (2*R*, 3*R*)-*trans*-2.3-bis(diphenylphosphino)-bicyclo[2.2.1]hept-5-ene, has been developed recently [4, 5]. It has been shown to give excellent optical yields in a diversity of reactions [4–9], and it will be commercially available in the near future [10]. Fe- and Rh-complexes of norphos and renorphos, and a derivative hydrogenated at the norbornene double bond, have already been structurally characterized [11, 12]. In the present paper we describe the X-ray structure analyses of the Ni-complexes (renorphos)$NiCl_2$, **I**, and (renorphos)$_2$Ni, **II**, the first of which has proved to be a catalyst for the hydrogenation of α[N-acetamido]-cinnamic acid by $NaBH_4$ [13].

Results and Discussion

Preparation of Complexes and Isomer Situation

The ligand used for all preparations was racemic norphos, (±)-$C_7H_8(PPh_2)_2$. During the synthesis of **II** starting from $NiCl_2 \cdot 6H_2O$, (±)-norphos, and $NaBH_4$, a hydrogenation of the double bond in the norbornene skeleton of norphos takes place to give renorphos, (±)-$C_7H_{10}(PPh_2)_2$. So, in (renorphos)$_2$Ni, **II**, and in (renorphos)$NiCl_2$, **I**, obtained from **II** by treatment with chloroform, renorphos is the actual ligand.



(renorphos)$NiCl_2$, **I**

(renorphos)$_2$Ni, **II**

Scheme I

In the synthesis of (renorphos)$_2$Ni, **II**, using racemic renorphos, a number of different isomers is possible. The unit cell of the crystal of **II** used for the X-ray structure analysis is centric (space group $P2_1/n$).

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Therefore, enantiomers are present. As in the (renorphos)$_2$Ni molecules there are two identical renorphos ligands, the crystal consists of a racemic mixture [(+)-renorphos]$_2$Ni/[(−)-renorphos]$_2$Ni, from which in Figs. 2, 3, and 5 only the [(+)-renorphos]$_2$-Ni molecule with ligand configuration 2*S*, 3*S* is shown.

Complex **I** formed from a racemic mixture of **II** on crystallization could give a crystal of [(+)-renorphos]NiCl$_2$, a crystal of [(−)-renorphos]NiCl$_2$, or a crystal of a racemic mixture of [(+)-renorphos]-NiCl$_2$/[(−)-renorphos]NiCl$_2$. As the unit cell of the crystal of **I** used for the X-ray structure determination is acentric (space group $P2_12_12_1$) only one enantiomer is present. There is self-resolution on crystallization [14]. The absolute configuration of the renorphos ligand in **I** has not been determined. The 2*S*, 3*S*-configuration was arbitrarily chosen in Figs. 1 and 4.

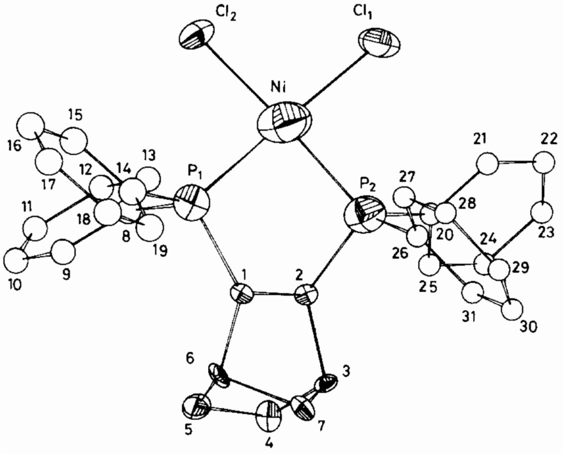


Fig. 1. ORTEP of (renorphos)NiCl$_2$, I.

Structure of I and II

The structure of **I** consists of discrete molecules of $NiCl_2(PPh_2)_2C_7H_{10}$ of approximate C_2 symmetry. The coordination geometry is almost square planar (Fig. 1). The structure of **II** consists of discrete molecules of $Ni(P_2Ph_4C_7H_{10})_2$, of approximate C_2 symmetry. The coordination geometry is closely tetrahedral (Figs. 2, 3). For both no packing distance is smaller than the commonly accepted Van der Waals radii. In **I** and **II** the renorphos ligand exhibits the expected exo/endo configuration.

The Ni–P distances in **I** and **II** are close to 2.20 Å, similar to comparable compounds [15, 16]. The norbornane skeleton in **II** exhibits the normal geometry with the angles C3–C7–C6 and C10–C14–C13 (91.9°(7) and 91.2°(7) respectively) being significantly smaller than the tetrahedral angles found in other cases [11, 12, 17]. The torsion angles for the three different (renorphos)Ni parts in **I** and **II** are given in Table VII. They are remarkably similar, deviating from each other by no more than 8°. Also, the corresponding torsion angles of the (norphos)Rh moiety in (norbornadiene)Rh(norphos) link up with them [12] (Table VII).

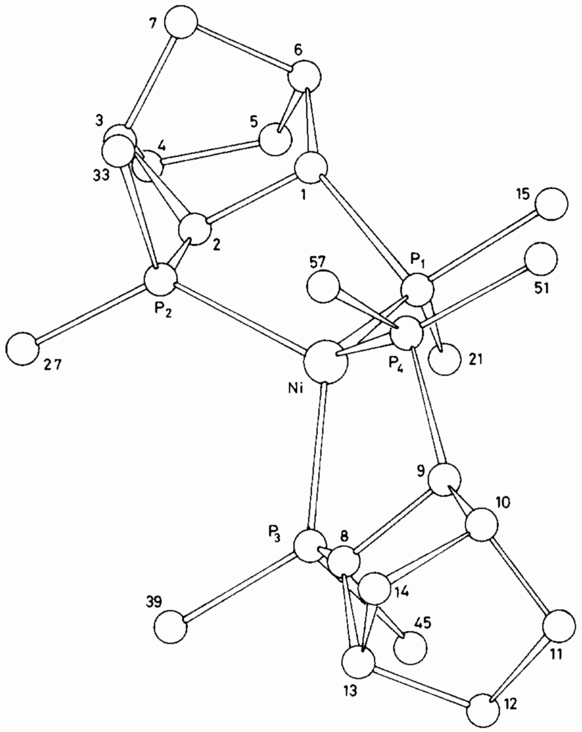


Fig. 2. ORTEP of (renorphos)$_2$Ni, II, excluding the 8 phenyl groups except the *ipso* carbon atoms.

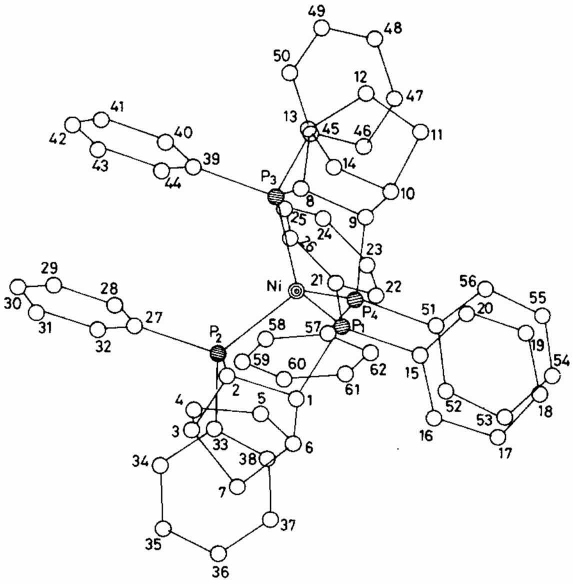


Fig. 3. ORTEP of (renorphos)$_2$Ni, II, including the carbon atoms of the 8 phenyl groups.

TABLE I. Crystal Data for I and II and Working Conditions.

	I	II
Space Group	$P2_12_12_1$	$P2_1/n$
Cell Constants	a = 9.444(3) b = 16.407(4) c = 17.921(8) Å	a = 20.292(9) b = 14.388(4) c = 18.067(7) Å β = 104.03(4)
Cell Volume	V = 2776.8 Å^3	V = 5120.6 Å^3
Molecules in the Unit Cell	Z = 4	Z = 4
Molecular Formula	$NiCl_2P_2C_{31}H_{30}$	$NiP_4C_{62}H_{60}$
Molecular Weight	594.15	983.74
Density (calc)	1.421 g cm^{-3}	1.27 g cm^{-3}
Absorption Coefficient	$\mu_{CuK\alpha}$ = 39.50 cm^{-1} F(000) = 1232 e/cell	$\mu_{MoK\alpha}$ = 5.42 cm^{-1}
Scan Mode	0–2θ	ω
Scan Speed	0.6 deg/min	2.7 deg/min
Scan Width	1.5 deg	1.35 deg
θ Range (d_{min})	2–60° (0.89 Å)	2–22° (0.95 Å)
Background Time	2 × 75 s	2 × 10 s
Reciprocal Space Explored	h, k, l ⩾ 0	k, l ⩾ 0
Measured Reflections	2409	6256
Observed Reflections	911	2464
σ^2 = Peak Counts + Total Background Counts	$I > 2.5\ \sigma$	$I > 3.0\ \sigma$
Wavelength	1.54184 Å	0.71069 Å
(Graphite-monochromated	CuKα Radiation)	MoKα Radiation)
Power used	40 kV × 32 mA	50 kV × 30 mA
Approximate Crystal Size	0.10 × 0.08 × 0.07 mm^3	0.20 × 0.15 × 0.10 mm^3

TABLE II. Atomic Fractional Coordinates[a] with E.s.d. s in Parentheses. Compound I.

Atom	x/a	y/b	z/c
Ni	3107(6)	330(3)	7781(6)
Cl(1)	1896(11)	−729(6)	7388(4)
Cl(2)	3393(11)	831(6)	6673(4)
P(1)	4569(9)	1276(5)	8176(4)
P(2)	2698(8)	−35(5)	8937(4)
C(1)	483(2)	104(1)	917(1)
C(2)	332(3)	83(2)	947(1)
C(3)	358(3)	92(2)	1036(1)
C(4)	346(3)	178(2)	1050(2)
C(5)	465(4)	217(2)	1011(2)
C(6)	550(4)	146(2)	983(2)
C(7)	509(4)	78(2)	1042(2)
C(8)	390(3)	229(1)	810(1)
C(9)	478(2)	295(2)	822(1)
C(10)	424(3)	374(1)	819(1)
C(11)	281(3)	386(1)	804(1)
C(12)	193(2)	320(2)	792(1)
C(13)	247(3)	241(1)	794(1)
C(14)	636(2)	128(2)	778(1)
C(15)	655(2)	166(2)	710(1)
C(16)	786(3)	163(2)	674(1)
C(17)	897(2)	121(2)	707(1)
C(18)	878(2)	82(2)	775(1)
C(19)	747(3)	86(2)	811(1)
C(20)	86(2)	−17(2)	925(1)
C(21)	15(2)	−86(1)	898(1)
C(22)	115(2)	−106(1)	923(1)
C(23)	−183(3)	−56(2)	974(1)
C(24)	−115(2)	14(1)	1001(1)
C(25)	20(2)	33(1)	976(1)
C(26)	372(3)	−91(1)	924(1)
C(27)	469(2)	−128(1)	876(1)
C(28)	546(2)	−195(1)	900(1)
C(29)	526(3)	−226(1)	972(1)
C(30)	428(2)	−189(1)	1019(1)
C(31)	351(2)	−122(1)	995(1)

[a] The values are × 10^4 for Ni, Cl, P atoms and × 10^3 for C atoms.

In asymmetric catalysis the distance between the inducing chirality, usually located in the backbone of chelating phosphane ligands, and the metal coordination sites, where the prochiral precursors are converted to chiral products, is 3 to 4 bonds (5 to 6 Å [18]). It is commonly accepted that due to this large distance there has to be a transmission of the chiral information. This transmission is thought to be brought about by the chiral arrangement of the phenyl rings of the $P(C_6H_5)_2$ groups, which most of the ligands used in asymmetric catalysis contain. According to Knowles, the phenyl groups in such a

TABLE III. Atomic Fractional Coordinates[a] with E.s.d. s in Parentheses. Compound **II**.

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ni	24142(5)	22818(7)	−856(5)
P(1)	28026(10)	9844(16)	−4797(13)
P(2)	14043(10)	20863(16)	−8452(12)
P(3)	24245(10)	25441(16)	11095(12)
P(4)	30324(11)	35131(16)	−1509(13)
C(1)	2135(4)	736(6)	−1359(5)
C(2)	1442(4)	864(6)	−1127(4)
C(3)	938(4)	346(7)	−1783(5)
C(4)	1005(7)	−645(8)	−1562(7)
C(5)	1706(6)	−895(7)	−1588(6)
C(6)	1980(5)	−90(6)	−1937(6)
C(7)	1261(5)	349(6)	−2459(5)
C(8)	2728(4)	3783(6)	1220(4)
C(9)	3362(4)	3811(6)	879(4)
C(10)	3691(4)	4750(7)	1205(6)
C(11)	4132(5)	4512(8)	1933(6)
C(12)	3669(5)	4184(8)	2391(6)
C(13)	2966(5)	4438(8)	1934(5)
C(14)	3151(5)	5315(6)	1473(6)

[a] The values are $\times 10^5$ for Ni and P atoms and $\times 10^4$ for C atoms.

TABLE IV. Atomic Fractional Coordinates[a] of Phenyl Group C Atoms, with E.s.d. s in Parentheses. Compound **II**.

Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(15)	3587(4)	936(5)	−804(4)
C(16)	3596(4)	794(6)	−1554(5)
C(17)	4233(5)	738(7)	−1765(6)
C(18)	4811(5)	856(7)	−1243(5)
C(19)	4829(5)	1017(7)	−496(5)
C(20)	4195(4)	1062(6)	−291(5)
C(21)	2878(4)	−112(5)	47(4)
C(22)	2501(4)	−217(6)	592(5)
C(23)	2494(5)	−3074(8)	957(6)
C(24)	2891(5)	−1800(7)	823(6)
C(25)	3274(5)	−1692(7)	308(6)
C(26)	3253(4)	−863(6)	−86(5)
C(27)	596(4)	2142(6)	−529(4)
C(28)	441(5)	2991(7)	−289(5)
C(29)	−199(5)	3108(8)	−37(6)
C(30)	−590(5)	2343(8)	−64(6)
C(31)	−430(5)	1529(8)	−302(6)
C(32)	184(5)	1392(7)	−540(5)
C(33)	1156(4)	2636(6)	−1798(4)
C(34)	486(4)	2587(6)	−2240(5)
C(35)	350(5)	2874(7)	−3018(5)
C(36)	870(5)	3166(7)	−3319(5)
C(37)	1508(5)	3231(7)	−2875(5)
C(38)	1647(4)	2973(6)	−2132(5)
C(39)	1644(4)	2564(6)	1456(5)
C(40)	1395(5)	3353(7)	1730(6)
C(41)	785(6)	3274(8)	2012(7)
C(42)	462(5)	2445(7)	1957(6)
C(43)	666(5)	1695(7)	1660(5)
C(44)	1290(4)	1741(6)	1410(5)
C(45)	2988(4)	1922(6)	1898(5)
C(46)	2926(5)	1946(7)	2640(5)
C(47)	3386(5)	1481(7)	3219(6)
C(48)	3899(5)	996(7)	3049(6)
C(49)	3952(5)	948(8)	2331(6)
C(50)	3512(4)	1384(6)	1740(5)
C(51)	3830(4)	3468(6)	−464(5)
C(52)	3779(5)	3193(7)	−1228(5)
C(53)	4372(5)	3137(7)	−1523(6)
C(54)	4969(5)	3329(7)	−1049(6)
C(55)	5037(5)	3581(7)	−315(6)
C(56)	4454(5)	3639(8)	2(6)
C(57)	2647(4)	4610(6)	−587(5)
C(58)	1973(5)	4753(7)	−650(5)
C(59)	1653(6)	4753(7)	−942(6)
C(60)	2065(6)	5602(8)	−1121(6)
C(61)	2729(6)	6172(8)	−1058(6)
C(62)	3048(5)	5338(7)	−779(6)

[a] The values are $\times 10^4$.

chiral array can be described as axial or equatorial and face-exposed or edge-exposed [12, 18–22].

The axial/equatorial character of a phenyl substituent is defined by the angle of the P–C (phenyl) bond with respect to the P–M–P plane, which the chelating phosphane forms with the metal atom. The axial and equatorial arrangement of the two phenyl rings of a $P(C_6H_5)_2$ group is a direct consequence of the puckering of the metal/phosphane chelate ring. For the three different Ni(renorphos) systems of the present X-ray structure analyses of **I** and **II** this puckering of the chelate ring and the axial/equatorial position of the phenyl rings are evident from Figs. 4 and 5, in which the projection of the P–Ni–P plane forms a horizontal line.

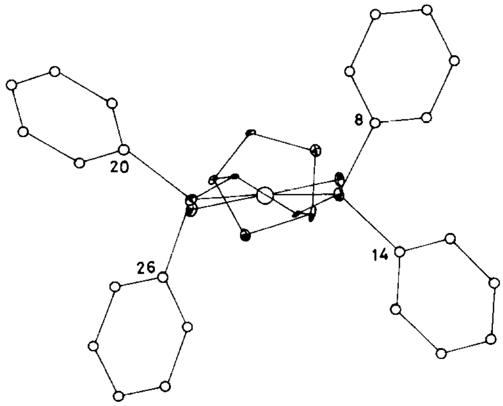


Fig. 4. Perspective view of (renorphos)NiCl$_2$, **I**, along the bisector of the P2–Ni–P1 system (horizontal), showing the deviation of the Cl atoms from the plane P2–Ni–P1 and the arrangement of the phenyl rings.

X-ray analyses [12, 18–22] show that the two phenyl rings of a $P(C_6H_5)_2$ group usually are almost

TABLE V. Selected Bond Distances (A) and Angles (deg) with E.s.d. s in Parentheses for Compound I.

Ni–Cl(1)	2.196(11)	C(1)–C(2)	1.56(4)
Ni–Cl(2)	2.166(9)	C(1)–C(6)	1.52(4)
Ni–P(1)	2.195(10)	C(2)–C(3)	1.61(3)
Ni–P(2)	2.190(9)	C(3)–C(4)	1.45(4)
P(1)–C(1)	1.84(3)	C(3)–C(7)	1.45(4)
P(1)–C(8)	1.78(2)	C(4)–C(5)	1.47(5)
P(1)–C(14)	1.83(2)	C(5)–C(6)	1.51(5)
P(2)–C(2)	1.81(3)	C(6)–C(7)	1.58(5)
P(2)–C(20)	1.82(2)		
P(2)–C(26)	1.81(2)		
Cl(1)–Ni–Cl(2)	94.1(4)	Ni–P(1)–C(1)	104.1(8)
Cl(1)–Ni–P(1)	172.1(4)	Ni–P(1)–C(8)	114.2(8)
Cl(1)–Ni–P(2)	89.7(4)	Ni–P(1)–C(14)	117.3(8)
Cl(2)–Ni–P(1)	87.1(4)	Ni–P(2)–C(2)	103.4(8)
Cl(2)–Ni–P(2)	173.1(4)	Ni–P(2)–C(20)	119.3(6)
P(1)–Ni–P(2)	90.0(3)	Ni–P(2)–C(26)	113.9(6)

TABLE VI. Selected Interatomic Distances (Å) and Angles (deg) with E.s.d. s in Parentheses for Compound II.

Ni–P(1)	2.210(3)	P(1)–C(1)	1.856(7)
Ni–P(2)	2.191(2)	P(2)–C(2)	1.837(9)
Ni–P(3)	2.187(2)	P(3)–C(8)	1.880(9)
Ni–P(4)	2.190(3)	P(4)–C(9)	1.869(8)
$(P{-}C_{phenyl})_{Av}$	1.841(13)	$(C{-}C_{phenyl})_{Av}$	1.382(38)
P(1)–Ni–P(2)	92.4(1)	Ni–P(1)–C(1)	101.3(3)
P(1)–Ni–P(3)	123.0(1)	Ni–P(2)–C(2)	101.6(2)
P(1)–Ni–P(4)	114.4(1)	Ni–P(3)–C(8)	101.2(2)
P(2)–Ni–P(3)	115.1(1)	Ni–P(4)–C(9)	101.7(3)
P(2)–Ni–P(4)	122.1(1)	$(Ni{-}P{-}C_{phenyl})_{Av}$	122.8(8)
P(3)–Ni–P(4)	92.6(1)	$(C{-}C{-}C_{phenyl})_{Av}$	120.0(19)

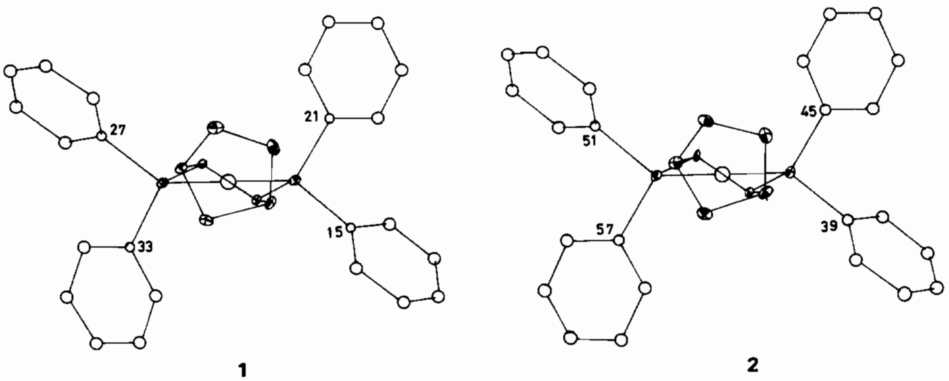
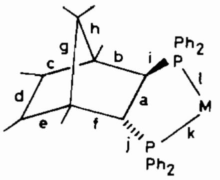


Fig. 5. Perspective view of (renorphos)$_2$Ni, **II**, along the bisector of the P2–Ni–P1 system, 1 (horizontal), and along the bisector of the P4–Ni–P3 system, 2 (horizontal). 1 and 2 show the arrangement of the phenyl rings omitting the other renorphos ligand for the sake of clarity.

perpendicular to each other. On the basis of representations similar to Figs. 4 and 5, they are classified as face-exposed (phenyl ring parallel to plane of paper) and edge-exposed (phenyl ring perpendicular to plane of paper). In the present paper we introduce a new structural parameter to describe this phenyl orientation. We propose to define a 'setting angle' as the dihedral angle between the phenyl plane and the

TABLE VII. Torsion Angles for the (renorphos)Ni Parts of I and II and for the norphos Derivative (Norbornadiene)Rh(norphos) [12]. A Positive Sign is Attributed to the Torsion Angle abc, if Looking Along Bond b, the Near Bond is Rotated Clockwise with Respect ot the Far Bond.



	(renorphos)$NiCl_2$, I	$(renorphos)_2Ni$, II		(norbornadiene)Rh(norphos)
		renorphos P2P1	renorphos P4P3	
abc	56	53	48	49
afe	−82	−82	−88	−75
abh	−50	−49	−55	−56
afg	25	24	17	30
bcd	−75	−73	−74	−65
fed	66	66	65	67
bhg	65	61	61	68
fgh	−54	−52	−49	−61
hcd	27	27	27	34
ged	−41	−45	−47	−37
cde	7	9	11	3
baf	17	18	24	15
lia	43	47	49	48
kja	49	47	48	47
iaj	−60	−63	−63	−64
ibc	−72	−74	−75	−79
ibh	−177	−176	−177	−177
jfe	156	156	154	160
jfg	−97	−98	−101	−94
iaf	162	162	164	156
jab	155	153	156	155
hib	170	173	170	175
hkj	−17	−14	−14	−14
kjf	169	167	164	170
kli	−12	−15	−15	−15
ghc	−50	−51	−52	−47
hge	55	57	60	50

M–P–C(Ph) plane, always choosing for it a value ≤90°. Table VIII shows that these setting angles have two typical ranges of values: not far from zero for the axial phenyls and not far from 90° for the equatorial phenyls. For the three Ni(renorphos) systems of structures **I** and **II**, the setting angles of axial phenyls are between 2 and 18.8° and of equatorial phenyls between 64.7 and 85.9° (Table VIII).

It is interesting to note that the setting angles of the four equatorial phenyl rings of the (renorphos)Ni systems of $(renorphos)_2Ni$, **II**, ranging between 64.7 to 69.5, are smaller than those of the (renorphos)Ni system of (renorphos)$NiCl_2$, **I** (71, 85.9°). The reason for this is a packing requirement in **II**. The equatorial phenyls in **II** form couples of face-to-face oriented rings, resulting in a graphite-like juxtaposition for Ph(15–20) and Ph(51–56) and for Ph(27–32) and Ph(39–44). This face-to-face arrangement, obvious from Figs. 3 and 6, causes the decrease in the setting angles of equatorial phenyls in **II** compared to **I** where this graphite-like arrangement is missing. Such a graphite-like packing of phenyl rings with distances of *ca.* 3.7 Å has also been observed in complexes containing triphenylphosphine [23].

Figure 6 shows that all four of these graphite-like packed phenyls exhibit an interesting 'stretching'. Whereas the average of the distances of the 16 bonds C_{ipso}– C_{ortho} and C_{para} – C_{meta} is 1.355(23) Å, the 8 bonds C_{ortho} – C_{meta} show an average distance of 1.443(20) Å.

The graphite-like juxtaposition of the four equatorial phenyl rings in **II** also has an influence on the

TABLE VIII. Orientation of Phenyl Rings in I and II.

	Setting angle (°)	Angle between P–C(Ph) bond and P–Ni–P plane (°)
(renorphos)NiCl$_2$, I		
Ni–P(1)–C(8)– – –Ph(8–13)	11.4	60.6 (axial)
Ni–P(1)–C(14)– – –Ph(14–19)	85.9	45.6 (equatorial)
Ni–P(2)–C(20)– – –Ph(20–25)	71.0	40.7 (equatorial)
Ni–P(2)–C(26)– – –Ph(26–31)	2.0	64.9 (axial)
(renorphos)$_2$Ni, II		
Ni–P(1)–C(15)– – –Ph(15–20)	69.5	40.9 (equatorial)
Ni–P(1)–C(21)– – –Ph(21–26)	18.8	55.3 (axial)
Ni–P(2)–C(27)– – –Ph(27–32)	66.4	40.1 (equatorial)
Ni–P(2)–C(33)– – –Ph(33–38)	16.0	57.5 (axial)
Ni–P(3)–C(39)– – –Ph(39–44)	64.7	40.9 (equatorial)
Ni–P(3)–C(45)– – –Ph(45–50)	12.7	55.9 (axial)
Ni–P(4)–C(51)– – –Ph(51–56)	65.9	43.0 (equatorial)
Ni–P(4)–C(57)– – –Ph(57–62)	5.3	56.9 (axial)

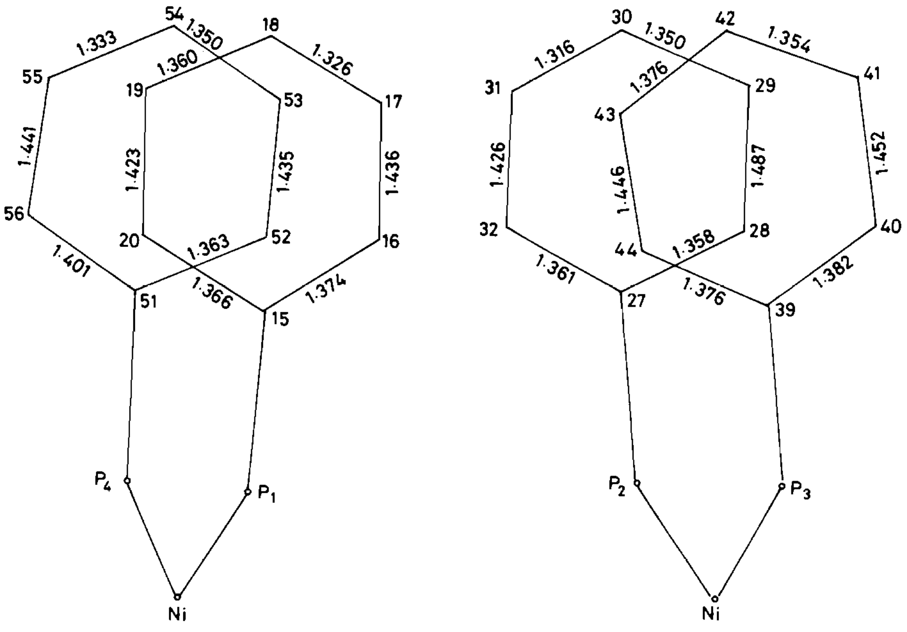


Fig. 6. The graphite-like packing of the equatorial phenyls Ph(51–56)/Ph(15–20) and Ph(27–32)/Ph(39–44), showing the 'stretching' of the four phenyl rings in II.

orientation of the four axial phenyl rings due to close contacts of *ortho*-carbon atoms (Table IX). C38 of Ph(33–38) at P2, *e.g.*, approaches C(58) of Ph(57–62) at P1 of the same norphos ligand to a distance of 3.65 Å, whilst its hydrogen H(38) is only 2.45 Å away from H(1) at C(1) of the norbornane skeleton. So a rotation of Ph(33–38) from the position found in the X-ray analysis would increase one of these two interactions. The other axial phenyls in **II** are blocked by similar interactions (Table IX). A model of **II** shows that the 8 phenyl rings and the 2 norbornane skeletons give the molecule almost perfectly the shape of a sphere. In (renorphos)NiCl$_2$ the two axial phenyl rings experience the same kind of interactions with the norbornene skeleton and the equatorial phenyl rings (Table IX), the setting angles of which however are closer to 90°, since their orientation is not imposed by the requirements of the graphite-like packing with a second renorphos ligand. For **I** there are also close contacts of *ortho*-C–H bonds of the phenyl rings with C–H bonds of the norbornane skeleton other than C1–H1 and C2–H2,

TABLE IX. Interactions Fixing the Orientations of the Axial Phenyl Rings not Packed in a Graphite-like Manner in II and the Phenyl Rings in I.

(renorphos)$_2$Ni, II					
			H38	2.45 Å	H1
Ph(33–38)	C58	3.65 Å	C38		
			H22	2.54 Å	H2
Ph(21–26)	C50	3.43 Å	C22		
			H50	2.91 Å	H9
Ph(45–50)	C22	3.43 Å	C50		
			H58	2.41 Å	H8
Ph(57–62)	C38	3.65 Å	C58		
(renorphos)NiCl$_2$, I					
			H9	2.78 Å	H5
Ph(8–13)	C15	3.36 Å	C9		
			H19	2.07 Å	H1
Ph(14–19)	C6	3.75 Å	C19		
			H25	2.25 Å	H2
Ph(20–25)	C3	3.50 Å	C25		
			H27	2.98 Å	H1
Ph(26–31)	C3	3.57 Å	C31		

the substituents of the chelate ring (Table IX). For Ph(14–19) the calculated distance of 2.07 Å between H1 and H19 is so short that a distortion of the C1–H1 bond has to be assumed, diminishing as a consequence the H1–H27 distance to a value smaller than the 2.98 Å listed in Table IX.

H27 and H13, the *ortho*-hydrogens of the axial phenyls in I, are very close to the Ni atom (Ni–H13 = 2.86 Å and Ni–H27 = 2.89 Å). One can speculate that these positive Ni–H interactions complete the square planar coordination around Ni to octahedral and help keep both Ph(8–13) and Ph(26–31) close to a setting angle of 0 in spite of the short contacts between H9 and H5 as well as H27 and H1 (Table IX).

Experimental

Preparation of (renorphos)$_2$Ni, II

1.8 g (3.9 mmol) (±)-norphos were added under N_2 to a solution of 950 mg (4 mmol) $NiCl_2 \cdot 6H_2O$ in 60 ml EtOH. The mixture was stirred for 2 h, then 450 mg (14.5 mmol) $NaBH_4$ were added during 1 h. The yellow–brown solution was evaporated to dryness. Extraction with 120 ml benzene/pentane 1:1 gave a yellow solution, which was passed through a short Al_2O_3 column (activity II–III). The solvent was removed and the orange solid obtained was recrystallized from benzene/EtOH 2:1. Yield of II: 1.2 g.

Preparation of (renorphos)NiCl$_2$, I

The solution of 50 mg (renorphos)$_2$Ni, II, in 5 ml benzene was treated with 0.05 ml $CHCl_3$. The yellow solution was kept at room temperature for 2 days, after which time the color had changed to red. Red crystals and orange crystals deposited; one of the red crystals of I was used for the X-ray structure analysis.

Crystallographic Studies

Three-dimensional intensity data, collected on a Philips PW-1100 four circle diffractometer with a randomly oriented crystal of I, were corrected for Lorentz and polarization effects and also for absorption using the procedure suggested by North *et al.* [24]. The structure was solved by Patterson and Fourier methods, and refined by least squares in the block diagonal approximation. The phenyl rings were treated as rigid bodies. In the last four least-squares cycles the contribution of the calculated structure factors of hydrogen atoms was taken into account. The final value for the conventional *R*-factor was 0.085 for I. Three dimensional intensity data for II were collected similarly but not corrected for absorption in view of the small transmittance range (<0.05) in the crystal. Refinement as described above but without the rigid body approximation gave a final value for the conventional *R*-factor of 0.069 for II.

Details on crystal data and working conditions are given in Table I. The atomic fractional coordinates and thermal parameters for I and II are given in Tables II–IV, selected interatomic distances and angles are reported in Tables V, VI.

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