May, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (5), 1051—1055 (1977) 1051

The Crystal and Molecular Structures of *trans*-Dichlorobis(dimethylneomenthylphosphine)nickel(II), an Asymmetric Hydrosilylation Catalyst of Olefin*

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(Received November 18, 1976)

The molecular structure of $[\mathrm{NiCl_2\{Me_2}\textit{neo}\mathrm{Men)P\}_2}]$, an asymmetric hydrosilylation catalyst of olefin was determined by means of X-ray diffraction. This complex forms dark red monoclinic crystals; $a=9.527(1)$, $b=8.048(2)$, $c=19.461(3)$ Å, $\beta=99.12(1)°$, space group $P2_1$ with $Z=2$. The structure, determined by the heavy-atom method, has been refined anisotropically by a least-squares procedure to $R=0.099$ for 3023 non-zero reflections. The geometry around the nickel atom is *trans*-square planar [Ni–Cl 2.151(5) and 2.175(6) Å, Ni–P 2.239(5) and 2.230(5) Å]. Two neomenthyl groups are located above and below the co-ordination plane.

A variety of dihalodiphosphinenickel(II) complexes have been found to be effective catalysts for hydrosilylation of olefins and acetylene by Kumada and co-workers.[1–3] Dichlorobis(dimethylneomenthylphosphine)nickel(II) is a complex in which each phosphine has a chiral substituent, and is also a catalyst for the hydrosilylation of olefins.[4]

This paper describes the X-ray molecular structure of dichlorobis(dimethylneomenthylphosphine)nickel(II) $[\mathrm{NiCl_2\{Me_2}\textit{neo}\mathrm{Men)P\}_2}]$.*** Interest in the correlation between molecular structure and the catalytic activity for asymmetric hydrosilylation of olefins promoted this study.

Experimental

The crystals of $[\mathrm{NiCl_2\{Me_2}\textit{neo}\mathrm{Men)P\}_2}]$ used in this study were provided by Professor Kumada and co-workers of Kyoto University. They are dark red, long and prismatic and sublime gradually at room temperature. Preliminary oscillation and Weissenberg photographs taken with Cu*Kα* radiation showed that the crystal belongs to the monoclinic system. The systematic absence of reflections ($0k0$ for $k=2n+1$) indicated the space group to be $P2_1$ or $P2_1/m$. The correct space group was determined to be $P2_1$ on the basis of the optical activity of this complex since the molecule contains asymmetric carbon atoms.

The unit-cell dimensions were determined by a least-squares fit from 2θ values of 20 high-angle reflections measured on a G. E. single-crystal orienter mounted on a Rigaku SG-2 goniometer.

Crystal Data: $C_{24}H_{50}Cl_2NiP_2$, FW 530.2, monoclinic, space group $P2_1$, $a=9.527(1)$, $b=8.048(2)$, $c=19.461(3)$Å, $\beta=99.12(1)°$, $U=1473.3(4)$Å^3, $Z=2$, $D_c=1.20$ g cm^{-3}, μ(Mo)$=9.5$ cm^{-1}.

The intensity data were collected using a Rigaku automated, four-circle diffractometer using zirconium-filtered Mo*Kα* radiation. The $\theta-2\theta$ scan technique was employed. The integrated intensity of each reflection was determined by scanning over a peak at a rate of 4° min^{-1}, and subtracting the background obtained by averaging the two values measured for 5 s at both ends of the scan. The 2θ scan width was from $-1.0°$ for the $K\alpha_1$ peak to $1.0°$ for the $K\alpha_2$ peak. A total of 1508 reflections ($F(hkl)$'s, $\sin\theta/\lambda\leq0.482$) was measured at room temperature. At the same time an other set of data ($F(\bar{h}\bar{k}\bar{l})$'s) was also collected in order to determine the absolute configuration of the molecule. The crystal used had the dimensions of 0.20×0.18×0.10 mm and was coated with collodion. This crystal was too small, however, to give sufficient intensity for high-angle reflection measurements. Therefore, a second crystal of dimensions of 0.25×0.20×0.18 mm was chosen, and the remaining 1802 reflections ($0.48\leqq\sin\theta/\lambda\leqq0.63$) were measured. The intensities of three standard reflections, 020, 003, and 400 were measured after every 50 reflections. The intensities of these reflections decreased almost uniformly with time due to the gradual decomposition of the crystal. A linear correction was applied to each set of data, and then the relative scaling between two sets of data was carried out by comparing the intensities of standard reflections in the two sets. A total of 3310 independent intensity values within a 2θ sphere of 53°($\sin\theta/\lambda\leqq0.63$) was obtained. Lorentz and polarization corrections were made in the usual manner, while neither absorption nor extinction corrections were applied to the intensity data.

Solution and Refinement of the Structure

The structure was determined by the heavy-atom method. Approximate co-ordinates of the nickel, the two chlorine and the two phosphorus atoms were obtained from a three-dimentional Patterson function. The subsequent Fourier synthesis revealed positions of all the remaining non-hydrogen atoms.

The structure was refined by the block-diagonal least-squares procedure using the HBLS-V program.[5] The quantity minimized was $\sum(|F_o|-k|F_c|)^2$, where k is a scaling factor. The atomic scattering factors used were taken from those given by Hanson and co-workers.[6] Since the space group is $P2_1$, the y parameter of the nickel atom was fixed at 0.25 in order to define the origin of the unit-cell. The difference Fourier map did not clearly reveal any hydrogen atom positions. An attempt to find the positions of the hydrogen atoms by the technique of LaPlaca and Ibers[7] was also unsuccessful. Hydrogen atoms except for methyl hydrogen (20 out of the 50 hydrogen atoms) were then located assuming a C–H bond length of 1.08 Å and a tetrahedral angle for each carbon atom. In subsequent refinements, the contributions were included in the structure factor calculations, their parameters being fixed. The final R is 0.099 for 3023 non-zero reflections.

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* Read at the 21st symposium on Organometallic Chemistry Japan, Sendai, Oct. 4 (1973).

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*** *neo*Men: neomenthyl group.

In order to determine the absolute configuration of the molecule, a refinement was also carried out of the structure obtained and its enantiomorph. The R factors converged to 0.0689 and 0.0702, respectively, for the sets of $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ data ($\sin\theta/\lambda=0.48$), whereas for the enantiomorphic structure it converged to the slightly higher R values, 0.0697 and 0.0710, respectively. The former structure was, therefore, chosen as the final result (Fig. 1). This result confirmed the absolute configurations of both neomenthyl groups.

TABLE 1. POSITIONAL AND THERMAL PARAMETERS OF ATOMS
(e.s.d.'s in parentheses)

(a) Fractional co-ordinates.

Atom	x	y	z	Atom	x	y	z
Ni	−0.01391(17)	0.25000	0.24917(8)	C(19)	0.1447(14)	−0.0607(26)	0.1683(8)
Cl(1)	0.0086(5)	0.4215(5)	0.1668(2)	C(20)	0.0975(17)	−0.0803(26)	0.0363(11)
Cl(2)	−0.0358(5)	0.0791(5)	0.3334(2)	C(3)	0.2526(16)	0.2558(23)	0.3920(8)
P(1)	−0.2060(4)	0.1292(4)	0.1882(2)	C(4)	0.3242(14)	0.3862(20)	0.2628(8)
P(2)	0.1726(4)	0.3737(5)	0.3125(2)	C(31)	−0.0740(17)	0.5348(21)	0.4034(7)
C(1)	−0.2874(15)	0.2292(18)	0.1088(7)	C(32)	−0.0359(13)	0.5984(16)	0.3354(6)
C(2)	−0.3553(17)	0.1376(27)	0.2379(9)	C(33)	0.1246(12)	0.5899(15)	0.3314(5)
C(11)	−0.4187(13)	−0.2038(20)	0.1042(7)	C(34)	0.2105(13)	0.6902(16)	0.3918(6)
C(12)	−0.3066(13)	−0.2116(17)	0.1703(6)	C(35)	0.1697(18)	0.6315(21)	0.4637(6)
C(13)	−0.1785(10)	−0.0975(14)	0.1706(6)	C(36)	0.0098(18)	0.6304(21)	0.4633(7)
C(14)	−0.1043(15)	−0.1337(19)	0.1054(6)	C(37)	−0.2365(17)	0.5454(29)	0.4039(10)
C(15)	−0.2156(15)	−0.1291(20)	0.0384(7)	C(38)	0.3716(13)	0.7054(18)	0.3902(8)
C(16)	−0.3441(15)	−0.2431(26)	0.0423(7)	C(39)	0.4009(15)	0.7924(26)	0.3235(9)
C(17)	−0.5389(15)	−0.3233(24)	0.1081(10)	C(40)	0.4497(16)	0.8019(24)	0.4558(9)
C(18)	0.0318(14)	−0.0319(17)	0.1014(7)				

(b) Anisotropic temperature factors ($\times 10^4$) expressed in the form $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	139.6(18)	119.8(19)	18.6(3)	27.9(41)	7.0(12)	−0.1(14)
Cl(1)	245.3(65)	171.6(64)	24.1(9)	−44.4(109)	6.4(38)	18.4(40)
Cl(2)	283.5(74)	172.1(65)	22.7(8)	−68.9(117)	18.9(39)	30.8(41)
P(1)	124.2(40)	130.8(51)	27.7(9)	50.0(79)	−0.5(31)	−11.8(38)
P(2)	123.3(39)	139.9(54)	25.9(9)	71.0(80)	5.9(30)	16.6(38)
C(1)	184(20)	135(23)	46(5)	182(40)	−55(16)	8(19)
C(2)	157(21)	396(52)	55(6)	92(56)	104(20)	−76(31)
C(11)	104(15)	241(32)	38(4)	56(36)	−8(13)	1(20)
C(12)	146(17)	175(26)	29(4)	4(34)	14(12)	−39(16)
C(13)	81(12)	110(17)	28(3)	23(24)	7(10)	−12(13)
C(14)	170(19)	205(27)	20(3)	92(39)	17(12)	−25(16)
C(15)	182(21)	213(29)	29(4)	21(44)	−2(14)	−47(19)
C(16)	192(21)	297(37)	30(4)	52(60)	−35(14)	−55(24)
C(17)	133(19)	285(41)	64(7)	−86(48)	0(19)	−28(29)
C(18)	156(19)	138(22)	44(5)	52(35)	56(16)	−7(18)
C(19)	115(17)	340(45)	46(5)	44(48)	9(15)	−24(27)
C(20)	208(24)	331(44)	34(5)	−20(56)	89(17)	5(24)
C(3)	192(21)	221(30)	42(5)	−21(52)	−80(16)	50(24)
C(4)	136(18)	210(30)	58(8)	−37(40)	82(17)	−113(24)
C(31)	212(24)	219(30)	26(4)	−28(46)	35(15)	6(18)
C(32)	133(16)	140(21)	27(3)	34(31)	−8(11)	−24(15)
C(33)	123(14)	127(18)	17(3)	40(27)	6(9)	10(12)
C(34)	129(15)	143(21)	29(4)	58(30)	−14(12)	−21(15)
C(35)	258(27)	233(31)	17(3)	15(50)	−3(14)	−51(17)
C(36)	244(26)	234(33)	30(4)	49(51)	92(17)	−22(20)
C(37)	176(24)	369(51)	71(8)	−3(61)	153(24)	−16(36)
C(38)	113(16)	176(28)	56(6)	18(33)	−24(15)	−10(22)
C(39)	136(19)	338(48)	55(6)	0(50)	49(18)	65(30)
C(40)	159(21)	311(44)	56(7)	−17(48)	−9(18)	−154(29)

Table 1. (continued)

(c) Calculated co-ordinates and assigned isotropic temperature factors for hydrogen atoms.

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
H(11)	−0.464	−0.075	0.099	5.0	H(31)	−0.039	0.405	0.411	5.0
H(12A)	−0.269	−0.340	0.176	5.0	H(32A)	−0.071	0.727	0.329	5.0
H(12B)	−0.357	−0.183	0.215	5.0	H(32B)	−0.093	0.526	0.293	5.0
H(13)	−0.105	−0.127	0.218	5.0	H(33)	0.155	0.657	0·287	5.0
H(14)	−0.064	−0.262	0.110	5.0	H(34)	0.176	0.819	0.384	5.0
H(15A)	−0.167	−0.166	−0.006	5.0	H(35A)	0.223	0.707	0.506	5.0
H(15B)	−0.256	−0.004	0.031	5.0	H(35B)	0.208	0.502	0.474	5.0
H(16A)	−0.306	−0.372	0.047	5.0	H(36A)	−0.012	0.581	0.513	5.0
H(16B)	−0.418	−0.235	−0.006	5.0	H(36B)	−0.025	0.760	0.461	5.0
H(18)	−0.004	−0.098	0.098	5.0	H(38)	0.412	0.571	0.390	5.0

The positional and thermal parameters are given in Table 1.†

Results and Discussion

The molecular structure is illustrated in Fig. 1. A stereoscopic drawing of the molecule is given in Fig. 2. Bond lengths and bond angles are listed in Table 2.

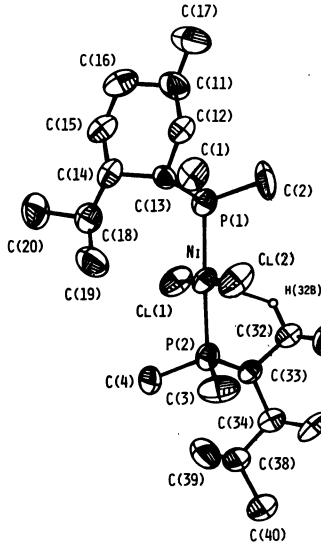

Fig. 1. An ORTEP drawing19) of the molecule with the numbering of atoms.

The co-ordination geometry around the nickel atom is *trans*-square planar, the deviations of Ni, Cl(1), Cl(2), P(1), and P(2) atoms from the co-ordination plane being 0.018, 0.009, 0.009, −0.018, and −0.018 Å, respectively.

The Ni–Cl bond lengths, 2.151(5) and 2.175(6) (av 2.163) Å are in agreement with the value 2.166(1) Å reported for [NiCl$_2$(C$_8$H$_{14}$PPh)$_2$],8) and are comparable to those of 2.175(2) and 2.167(2) Å found in [NiCl$_2${(MeO)$_2$C$_5$H$_8$PPh}$_2$].9) The Ni–P length are 2.239(5) and 2.230(5) (av 2.235) Å, which are equal to the values 2.227(1) and 2.232(3) Å reported for [NiCl$_2$(C$_8$H$_{14}$PPh)$_2$] and [NiBr$_2${(*t*-Bu)$_2$PF}$_2$],10) respectively. They are equal to or slightly shorter than the values 2.245(2) and 2.254(2) Å in [NiCl$_2${(MeO)$_2$C$_5$H$_8$PPh$_2$}]. They are significantly shorter than those of 2.251(3) and 2.263(7) Å found in diamagnetic *trans*-square planar [NiBr$_2$(Me$_2$PhP)$_2$]11) and [NiBr$_2$(PhCH$_2$PPh$_2$)$_2$],12) respectively, and are also shorter than those of 2.263(3) and 2.273(3) Å in distorted tetrahedral [Ni(N$_3$)(NO)(PPh$_3$)$_2$].13) However, they are slightly longer than the values 2.175(4) or 2.220(3) Å in *trans*-square planar [Ni(PhC≡C)$_2$(Et$_3$P)$_2$]14,15) and 2.221(1) Å in distorted tetrahedral [Ni(CO)$_2$(Ph$_3$P)$_2$].16)

The conformation about P(1)–Ni–P(2) shown in Fig. 3 is approximately staggered. Two neomenthyl groups bonded to the P(1) and P(2) atoms are located above and below the co-ordination plane. The conformations about the P(1)–C(13) and P(2)–C(33) bonds

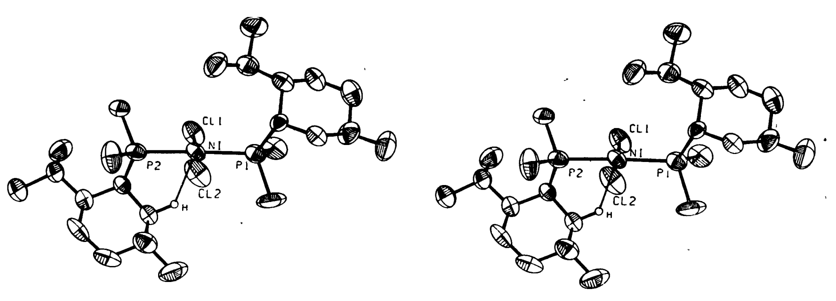

Fig. 2. A stereoscopic drawing19) of the molecule.

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† The table of observed and calculated structure factors is kept as Document No. 7705 at the Chemical Society of Japan.

TABLE 2. BOND LENGTHS AND BOND ANGLES (e.s.d.'s in parentheses)

(a) Bond lengths [l/Å]

Ni-Cl(1)	2.151(5)	Ni-Cl(2)	2.175(6)	C(14)-C(18)	1.546(21)	C(15)-C(16)	1.541(26)
Ni-P(1)	2.239(5)	Ni-P(2)	2.230(5)	C(18)-C(19)	1.569(25)	C(18)-C(20)	1.549(25)
P(1)-C(1)	1.805(15)	P(1)-C(2)	1.844(22)	C(31)-C(32)	1.516(21)	C(31)-C(36)	1.514(24)
P(1)-C(13)	1.883(12)	P(2)-C(3)	1.871(19)	C(31)-C(37)	1.551(29)	C(32)-C(33)	1.545(17)
P(2)-C(4)	1.864(17)	P(2)-C(33)	1.852(12)	C(33)-C(34)	1.549(19)	C(34)-C(35)	1.538(21)
C(11)-C(12)	1.537(21)	C(11)-C(16)	1.525(26)	C(34)-C(38)	1.544(20)	C(35)-C(36)	1.522(24)
C(11)-C(17)	1.507(25)	C(12)-C(13)	1.527(18)	C(38)-C(39)	1.538(26)	C(38)-C(40)	1.577(25)
C(13)-C(14)	1.573(19)	C(14)-C(15)	1.546(22)				

(b) Bond angles[φ/°]

Cl(1)-Ni-Cl(2)	179.2(2)	Cl(1)-Ni-P(1)	93.1(2)
Cl(1)-Ni-P(2)	87.7(2)	Cl(2)-Ni-P(1)	87.6(2)
Cl(2)-Ni-P(2)	91.7(2)	P(1)-Ni-P(2)	178.0(2)
Ni-P(1)-Cl(1)	117.7(5)	Ni-P(1)-C(13)	113.0(4)
Ni-P(2)-C(33)	109.2(4)	Ni-P(1)-C(2)	109.8(7)
Ni-P(2)-C(3)	110.6(5)	Ni-P(2)-C(3)	114.5(6)
C(13)-P(1)-C(2)	105.8(8)	C(13)-P(1)-Cl(1)	109.3(6)
C(33)-P(2)-C(3)	113.2(7)	C(11)-P(1)-C(2)	99.8(8)
C(3)-P(2)-C(4)	102.1(8)	C(33)-P(2)-C(3)	106.8(7)
C(12)-C(11)-C(17)	111.4(14)	C(12)-C(11)-C(16)	107.7(13)
C(11)-C(12)-C(13)	115.3(11)	C(16)-C(11)-C(17)	111.1(15)
C(12)-C(13)-C(14)	110.3(10)	P(1)-C(13)-C(12)	116.7(8)
C(13)-C(14)-C(15)	109.9(12)	P(1)-C(13)-C(14)	114.8(9)
C(15)-C(14)-C(18)	114.4(12)	C(13)-C(14)-C(18)	115.5(12)
C(15)-C(16)-C(11)	112.9(15)	C(14)-C(15)-C(16)	112.8(14)
C(14)-C(18)-C(20)	111.1(13)	C(14)-C(18)-C(19)	110.5(13)
C(32)-C(31)-C(36)	109.3(13)	C(19)-C(18)-C(20)	109.1(14)
C(36)-C(31)-C(37)	111.9(15)	C(32)-C(31)-C(37)	111.3(14)
C(32)-C(33)-C(34)	110.3(10)	C(31)-C(32)-C(33)	113.9(11)
C(34)-C(33)-C(35)	110.0(11)	P(2)-C(33)-C(32)	109.3(8)
C(33)-C(34)-C(38)	115.7(11)	P(2)-C(33)-C(34)	121.5(9)
C(34)-C(35)-C(36)	112.5(13)	C(35)-C(34)-C(38)	115.2(12)
C(34)-C(38)-C(39)	111.5(13)	C(35)-C(36)-C(31)	114.3(14)
C(39)-C(38)-C(40)	109.5(14)	C(34)-C(38)-C(40)	111.4(13)

(c) Short atomic contacts [l/Å] and angle [φ/°]

Ni⋯C(19)	3.431(21)	Ni⋯H(32B)[a]	2.54	P(2)-Ni-H(32B)[a]	71.1

a) Positional parameters of the H(32B) atom were calculated under the assumption that the C(sp^3)-H bond length is 1.08Å.

are intermediate between staggered and eclipsed conformations (Fig. 4). However, there is a significant difference in both conformations. The neomentyl group about the P(1)–C(13) bond is rotated by *ca.* 120° with respect to that about the P(2)–C(33) bond.

The steric hindrance between the neomenthyl and methyl groups on the phosphorus causes distortions of the P–C–C angles. The P(1)–C(13)–C(12), P(1)–C(13)–C(14), and P(2)–C(33)–C(34) angles, 116.7(8), 114.8(9), and 121.5(9)°, are considerably different from the normal value of 109.5°.

The C(19) and C(32) atoms are located in the vacant positions respectively above and below the nickel atom. An equatorial hydrogen atom, H(32B) attached to the C(32) atom has a short intramolecular atomic distance of 2.54 Å with the nickel atom. Although the position of this hydrogen atom is the calculated value, this short distance suggests the existence of a metal-hydrogen interaction in the present complex. Such short distances between metal and hydrogen atoms are also found in [PdI$_2${(Me$_2$Ph)P}$_2$] (Pd⋯H 2.84 and 2.85 Å (red isomer) and 3.28 Å (yellow isomer))[17] and [PdI$_2$(Ph$_3$P)$_2$](Pd⋯H 3.18 Å).[18]

The bond lengths and bond angles of both the neomenthyl groups appear to be normal for the sp^3 carbon (C–C(av) = 1.543 Å and C–C–C(av) = 111.9°), except for the bond angles given above.

Figure 5 shows a stereoscopic drawing of the molecular packing along the b axis. No abnormally short intermolecular atomic distance is present.

The calculations were carried out on the NEAC 2200-500 computer at Osaka University.

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 843005), for which the authors express their gratitude. The authors express their deep thanks to Professor Makoto Kumada and his co-workers of Kyoto University for kindly providing the crystals and for many helpful discussions.

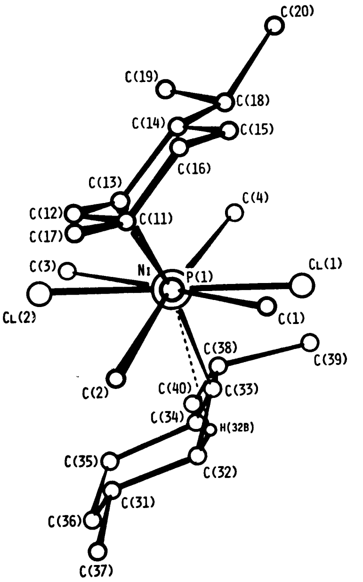

Fig. 3. The conformation about the P(1)–Ni–P(2) bond.

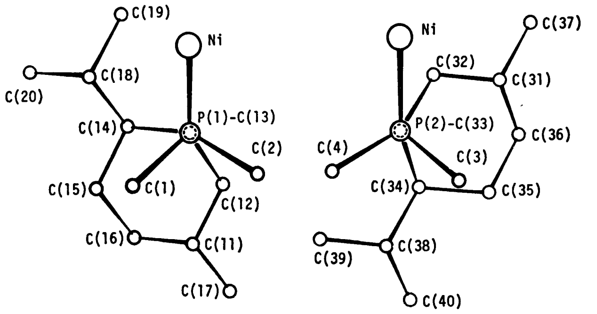

Fig. 4. The conformations about the P(1)–C(13) and P(2)–C(33) bonds.

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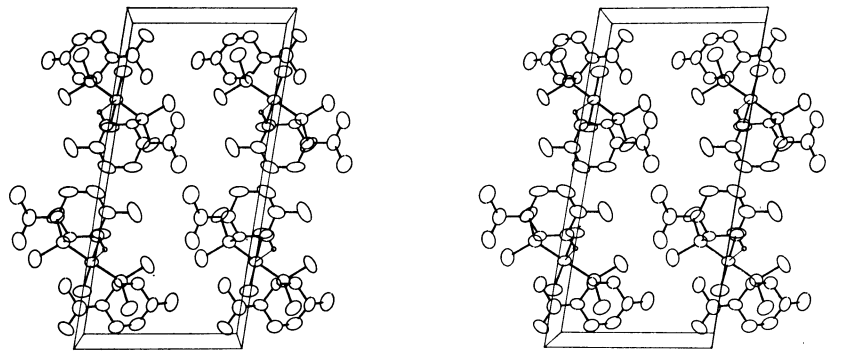

Fig. 5. A stereoscopic drawing[19] of the molecular packing viewed along the b axis.