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Crystal structures of *anti* and *syn* isomers of *trans*-bis(dimethylphenylphosphine)bis(2-tolyl)nickel(II)

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Abstract

The molecular structures of both *anti* and *syn* isomers of *trans*-bis(dimethylphenylphosphine)bis(2-tolyl)nickel(II), *trans*-[Ni(C_6H_4Me-2)$_2$(PMe_2Ph)$_2$] have been determined by single-crystal X-ray diffraction studies. Crystals of the *anti* isomer are monoclinic, space group $P2_1/n$ with $Z = 2$ in a unit cell of dimensions, a 12.288(3), b 7.345(2), c 15.930(3) Å, β 103.49(2)°, where the molecule has a centrosymmetric structure. Crystals of the *syn* isomer are monoclinic, space group $P2_1$ with $Z = 4$ in a unit cell of dimensions, a 9.492(2), b 17.540(4), c 16.825(3) Å, β 94.77(2)°, where two crystallographically independent molecules exist. Structures were refined to $R = 0.036$ (2581 reflections) and $R = 0.079$ (4056 reflections) for the *anti* and *syn* isomers, respectively. The coordination geometry around the Ni atom is typically square-planar in each complex. All the structural parameters, including the Ni–C(2-tolyl) bond lengths, are normal when compared with those hitherto reported. The non-bonded distances between two adjacent methyl carbon atoms of 2-tolyl groups are not less than 3.9 Å in the *syn* isomer.

Introduction

Up to now, only the *anti* isomer had been reported for *trans*-bis(dimethylphenylphosphine)bis(2-tolyl)nickel(II), *trans*-[Ni(C_6H_4Me-2)$_2$(PMe_2Ph)$_2$] [1], but recently both *anti* and *syn* isomers of this complex have been isolated in the solid state [2]. The crude product of the complex prepared by the known procedure was obtained as a mixture of two isomers, but careful fractional recrystallizations enabled us to separate both pure isomers, crystals of which were suitable for an X-ray diffraction study [2]. We carried out the crystal structure studies on both isomers of this

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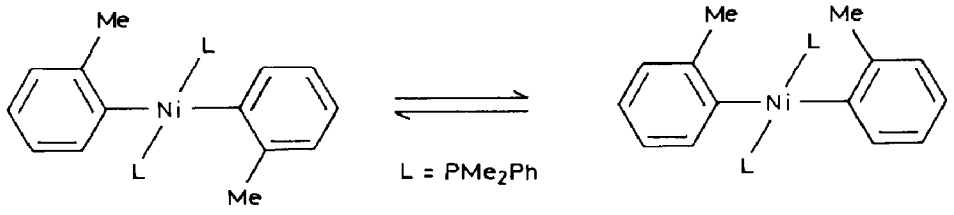
complex in order to compare their structures and to examine the degree of steric hindrance by the two methyl groups on the tolyl ligands in the *syn* isomer, and thus had been regarded as the reason why this isomer was difficult to isolate.



anti isomer

syn isomer

Experimental

The yellow prismatic crystals of the *anti* and *syn* isomers were obtained by the procedure previously reported [2]. After crystals of the *anti* isomer had been isolated from the mixture in methanol solution, the *syn* isomer began to crystallize from the methanol filtrate, to which water was being added. Crystal data are summarized in Table 1. The accurate unit-cell dimensions were determined by the least-squares fit of 2θ values of 25 reflections. The crystal data indicated that the nickel atom of the *anti* isomer is located at the center of symmetry, while two crystallographically independent molecules exist in the *syn* isomer. Well-shaped crystals of approximate dimensions $0.30 \times 0.35 \times 0.45$ and $0.20 \times 0.25 \times 0.40$ mm for the *anti* and *syn* isomers, respectively, were mounted on a Rigaku automated, four-circle diffractometer. The quality of each crystal was established from diffraction profiles examined by the ω-scan of several strong reflections. Integrated intensities of Mo-K_α radiation (λ 0.71069 Å), graphite-monochromatized for the *anti* isomer and Zr-filtered for the *syn* isomer, were collected by the θ–2θ scan

Table 1

Crystal data for *anti* and *syn* isomers of *trans*-[Ni(C_6H_4Me-2)$_2$(PMe_2Ph)$_2$]. Formula $C_{30}H_{32}NiP_2$, M.W. 517.28

	anti isomer	*syn* isomer
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1$
a (Å)	12.288(3)	9.492(2)
b (Å)	7.345(2)	17.540(4)
c (Å)	15.930(3)	16.825(3)
β (°)	103.49(2)	94.77(2)
U (Å^3)	1398.0(5)	2792.2(8)
Dc (g cm^{-3})	1.229	1.231
Dm (g cm^{-3})	1.23	1.23
Z	2	4
F(000)	548	1096
μ (Mo-$K\alpha$) (cm^{-1})	8.22	8.23

Table 2

Conditions during refinements

	anti isomer	*syn* isomer
No. of reflections used	2581	4056
No. of atoms refined	35	138
No. of parameters refined	227	884
Weighting parameters (See text)		
a	0.0100	0.0648
b	0.0002	0.0013
Final R value [a]	0.036	0.079
Final R_w value [b]	0.044	0.090
Δ/σ [c]	0.11	0.82
$\Delta\rho$ [d] maximum ($e\text{Å}^{-3}$)	0.3	1.4
minimum ($e\text{Å}^{-3}$)	−0.2	−0.4

[a] $R = \Sigma\| F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w = \{\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2\}^{1/2}$. [c] Maximum shift to esd ratio for non-hydrogen atoms. [d] Residual peak of electron density in the final difference Fourier map. The highest peak in each isomer appeared in the region around the Ni atom.

technique. The scan speed was 4° min^{-1} in 2θ and the scan width was $\Delta 2\theta = (2.0 + 0.70 \tan\theta)°$. Background intensities were measured for 5 s at each end of a scan. Three or four standard reflections were measured at regular intervals to monitor the stability and orientation of the crystals, and showed no significant decay throughout the data collection. Totals of 3059 and 6303 independent reflections were collected within 2θ up to 54° ($\sin\theta/\lambda = 0.639$ Å^{-1}) for the *anti* and *syn* isomers, respectively. Corrections for Lorentz and polarization effects were applied to the intensity data. No absorption corrections were made, which may limit the accuracy of the present structure determination.

Table 3

Final atomic coordinates and B_{eq} for the *anti* isomer

Atom	x	y	z	$B_{eq}(\text{Å}^2)$
Ni	0.5	0.5	0.5	2.8
C(1)	0.3440(2)	0.4274(4)	0.4794(2)	3.2
C(2)	0.2604(2)	0.5366(4)	0.5012(2)	3.5
C(3)	0.1491(3)	0.4777(4)	0.4820(2)	4.9
C(4)	0.1172(3)	0.3157(5)	0.4417(2)	5.7
C(5)	0.1966(3)	0.2057(4)	0.4194(2)	5.3
C(6)	0.3078(3)	0.2621(4)	0.4382(2)	4.3
C(7)	0.2884(3)	0.7191(4)	0.5433(2)	5.0
P	0.46889(5)	0.64605(9)	0.37806(4)	3.4
C(11)	0.5314(3)	0.8720(4)	0.3789(2)	5.8
C(12)	0.3245(3)	0.6941(5)	0.3206(2)	5.8
C(13)	0.5207(2)	0.5228(4)	0.2961(2)	3.6
C(14)	0.6143(3)	0.5774(5)	0.2689(3)	5.7
C(15)	0.6505(4)	0.4762(6)	0.2061(3)	8.1
C(16)	0.5940(4)	0.3225(6)	0.1727(3)	8.0
C(17)	0.5020(4)	0.2667(5)	0.2002(3)	7.1
C(18)	0.4653(3)	0.3653(4)	0.2619(2)	5.1

Table 4

Final atomic coordinates and B_{eq} for the *syn* isomer

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
molecule 1				
Ni(1)	0.35322(14)	0.25	0.29761(8)	2.9
C(11)	0.4940(15)	0.3281(9)	0.2865(8)	4.8
C(12)	0.5331(15)	0.3535(10)	0.2103(10)	5.6
C(13)	0.6388(17)	0.4098(11)	0.2073(13)	8.2
C(14)	0.7060(18)	0.4437(11)	0.2748(15)	9.2
C(15)	0.6654(19)	0.4218(12)	0.3514(13)	8.3
C(16)	0.5612(17)	0.3640(9)	0.3568(12)	6.2
C(17)	0.4692(19)	0.3200(13)	0.1386(10)	7.6
C(21)	0.2122(13)	0.1713(7)	0.3115(6)	2.9
C(22)	0.1410(15)	0.1310(8)	0.2441(8)	4.4
C(23)	0.0406(15)	0.0778(9)	0.2560(9)	4.9
C(24)	−0.0019(16)	0.0599(9)	0.3267(11)	5.9
C(25)	0.0621(16)	0.0967(11)	0.3917(9)	5.7
C(26)	0.1720(15)	0.1544(8)	0.3861(8)	4.3
C(27)	0.1805(16)	0.1508(11)	0.1600(9)	5.8
P(11)	0.5213(4)	0.1670(3)	0.3134(2)	3.8
C(31)	0.6944(15)	0.1871(11)	0.2775(11)	6.8
C(32)	0.4894(16)	0.0734(10)	0.2685(9)	5.7
C(33)	0.5637(12)	0.1463(7)	0.4211(7)	3.5
C(34)	0.4980(17)	0.0846(11)	0.4560(11)	6.6
C(35)	0.5242(18)	0.0715(12)	0.5369(10)	6.6
C(36)	0.6228(22)	0.1165(15)	0.5797(12)	9.2
C(37)	0.6932(27)	0.1738(10)	0.5453(12)	9.7
C(38)	0.6569(19)	0.1883(9)	0.4638(11)	7.0
P(12)	0.1861(4)	0.3345(3)	0.2949(2)	3.6
C(41)	0.0134(14)	0.3110(11)	0.2422(9)	5.4
C(42)	0.2163(15)	0.4294(10)	0.2547(10)	5.8
C(43)	0.1416(12)	0.3577(8)	0.3975(8)	4.0
C(44)	0.2218(17)	0.4047(13)	0.4447(11)	7.6
C(45)	0.1893(19)	0.4195(14)	0.5211(11)	8.4
C(46)	0.0768(20)	0.3818(13)	0.5520(9)	8.0
C(47)	−0.0010(23)	0.3361(14)	0.5076(13)	8.8
C(48)	0.0275(19)	0.3223(11)	0.4270(12)	7.6
molecule 2				
Ni(2)	0.89282(14)	0.25698(11)	0.88276(8)	2.9
C(51)	0.7562(11)	0.1799(7)	0.8973(9)	3.8
C(52)	0.7195(15)	0.1556(8)	0.9679(10)	4.9
C(53)	0.6179(16)	0.0971(10)	0.9806(11)	6.3
C(54)	0.5436(15)	0.0639(9)	0.9128(12)	6.5
C(55)	0.5693(15)	0.0845(11)	0.8399(12)	7.5
C(56)	0.6773(14)	0.1457(10)	0.8295(10)	5.5
C(57)	0.7946(16)	0.1871(10)	1.0462(9)	5.4
C(61)	1.0336(11)	0.3354(8)	0.8716(8)	3.7
C(62)	1.0882(13)	0.3781(7)	0.9395(8)	4.1
C(63)	1.1946(14)	0.4337(9)	0.9293(10)	5.2
C(64)	1.2420(15)	0.4479(9)	0.8549(11)	6.1
C(65)	1.1914(16)	0.4068(9)	0.7878(10)	6.0
C(66)	1.0860(14)	0.3508(8)	0.7981(9)	4.4
C(67)	1.0474(18)	0.3622(9)	1.0203(8)	5.4
P(21)	1.0592(4)	0.1726(2)	0.8821(2)	3.3
C(71)	1.0224(19)	0.0723(9)	0.9132(9)	6.2
C(72)	1.2211(15)	0.1930(9)	0.9401(9)	4.8

Table 4 (continued)

Atom	x	y	z	B_{eq}(Å^2)
molecule 2				
C(73)	1.1104(15)	0.1571(8)	0.7826(8)	4.2
C(74)	1.0140(14)	0.1279(14)	0.7253(11)	9.2
C(75)	1.0430(19)	0.1143(15)	0.6460(11)	8.6
C(76)	1.1772(20)	0.1308(12)	0.6237(10)	7.7
C(77)	1.2763(18)	0.1593(12)	0.6817(10)	6.8
C(78)	1.2410(14)	0.1694(10)	0.7576(9)	5.2
P(22)	0.7248(4)	0.3410(3)	0.8672(2)	3.7
C(81)	0.7550(19)	0.4418(10)	0.8944(10)	6.8
C(82)	0.5598(17)	0.3205(12)	0.9119(11)	7.4
C(83)	0.6647(14)	0.3509(8)	0.7631(8)	4.3
C(84)	0.7500(14)	0.3965(9)	0.7135(9)	5.0
C(85)	0.7067(17)	0.4065(12)	0.6317(10)	6.9
C(86)	0.5813(19)	0.3765(11)	0.5994(8)	6.3
C(87)	0.5002(24)	0.3351(12)	0.6492(11)	9.1
C(88)	0.5415(18)	0.3215(12)	0.7278(11)	7.4

Both structures were solved by the heavy atom method. All the non-hydrogen atoms were located satisfactorily on the Fourier maps that were based on positions of the Ni and P atoms determined from each Patterson function. The structures were refined by the block-diagonal least-squares procedure by use of the HBLS-V program[3], the function minimized was $\Sigma\, w(|F_o| - |F_c|)^2$. The electron densities assigned for all the hydrogen atoms were found at essentially the same positions on the difference Fourier maps after anisotropic refinement as calculated from stereochemical considerations. These hydrogen atoms were included in further refinements. The weighting scheme used was $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics, and a and b are constants which were adjusted during the refinement cycles. Table 2 summarizes the conditions for the course of refinements including the final R and R_w values. The atomic scattering factors were taken from International Tables for X-ray Crystallography [4]. The final atomic positional parameters, together with the B_{eq} values[6], for the *anti* and *syn* isomers are listed in Tables 3 and 4, respectively. Tables of anisotropic temperature factors, atomic parameters for hydrogen atoms, and observed and calculated structure factors (Tables S1–S6) are available from the authors upon request.

All the computations were carried out on an ACOS 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and discussion

Crystal structures of both isomers are presented in Fig. 1. No unusually short contacts between adjacent molecules are observed for either isomers, the shortest intermolecular distances between non-hydrogen atoms were found to be 3.716(5) Å [C(18)(x, y, z)...C(12)$(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$] and 3.62(3) Å [C(55)$(x, y, z)$... C(78)$(-1+x, y, z)$] for the *anti* and *syn* isomers, respectively.

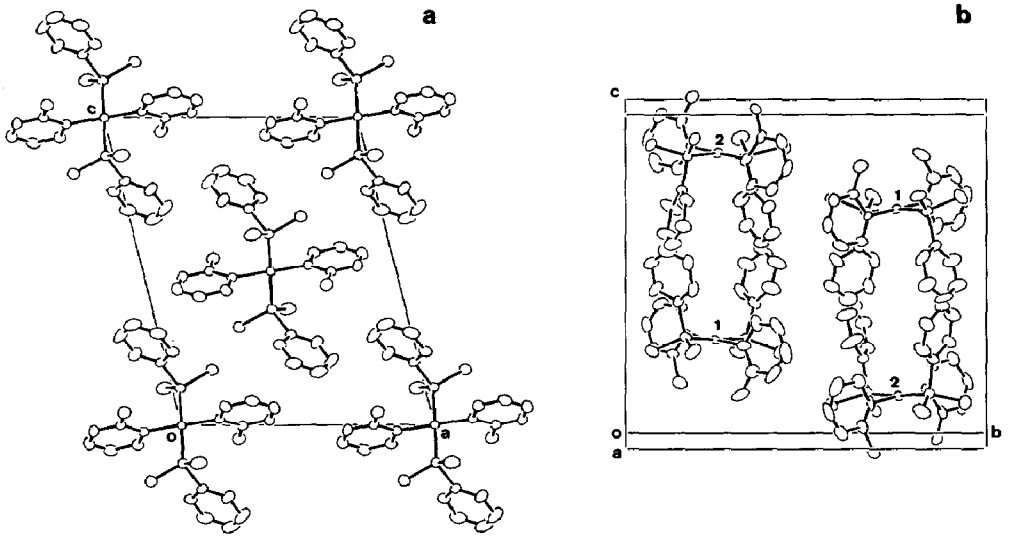


Fig. 1. ORTEP [6] drawings of the crystal strucutre of *trans*-[Ni(C_6H_4Me-2)$_2$(PMe_2Ph)$_2$]. Non-hydrogen atoms are thermal ellipsoids at 30% probability levels, and hydrogen atoms are omitted for clarity. (a) *anti* isomer as viewed along the *b* axis. (b) *syn* isomer as viewed along the a^* axis, there are two crystallographically independent molecules (labelled as 1 and 2) in the unit cell.

Molecular structures of *anti* and *syn* isomers are presented in Fig. 2 along with the atomic numbering scheme. Bond distances and angles are listed in Tables 5 and 6. Figure 3 shows a perspective view down the P–Ni–P axis of each molecule.

The molecule of the *anti* isomer has *Ci* symmetry. The phenyl and methyl groups of the phosphine ligands, therefore, take on an antiperiplanar staggered conformation about the P–Ni–P axis, each phenyl group is located on the side opposite that of the coordination plane. In the *syn* isomer, two crystallographically independent molecules (1 and 2) are very similar to each other. In contrast to the *anti* isomer, the phosphine substitutents take on a synperiplanar eclipsed conformation about the P–Ni–P axis, where phenyl groups are on the same side of the coordination plane. There is only a slight difference in the phosphine conformation of two independent molecules of the *syn* isomer. As depicted in Fig. 3, the phosphine ligands are more completely eclipsed in molecule 1 (torsion angle 0.1°) than in molecule 2 (13.5°).

The coordination geometry around the Ni atom is typically square-planar in each isomer. The Ni, two P(phosphine) and two C(2-tolyl) atoms are completely coplanar because the center of symmetry is located at the Ni atom in the *anti* isomer, whereas the maximum atomic deviations from the least-squares plane are 0.057 and 0.095 Å for molecules 1 and 2 of the *syn* isomer, respectively. The 2-tolyl planes of each isomer are almost perpendicular to the coordination plane of Ni, the dihedral angles between these planes being 87.2° for the *anti* isomer and 88.0 and 88.9° for molecule 1, and 85.9 and 82.6° for molecule 2 of the *syn* isomer.

The Ni–C(phenyl) bond lengths in the known square-planar nickel(II) complexes lie in between 1.81 and 1.98 Å [7–17]. This includes those bond lengths whose *trans*-position is the carbon atom, which are in the range 1.905 to 1.978 Å [12–17]. The present Ni–C(2-tolyl) bond lengths, not only in the *anti* isomers but also in the *syn* isomer, fall in the same range with no lengthening of the Ni–C bond being observed because of repulsion by the 2-tolyl groups in the *syn* isomer.

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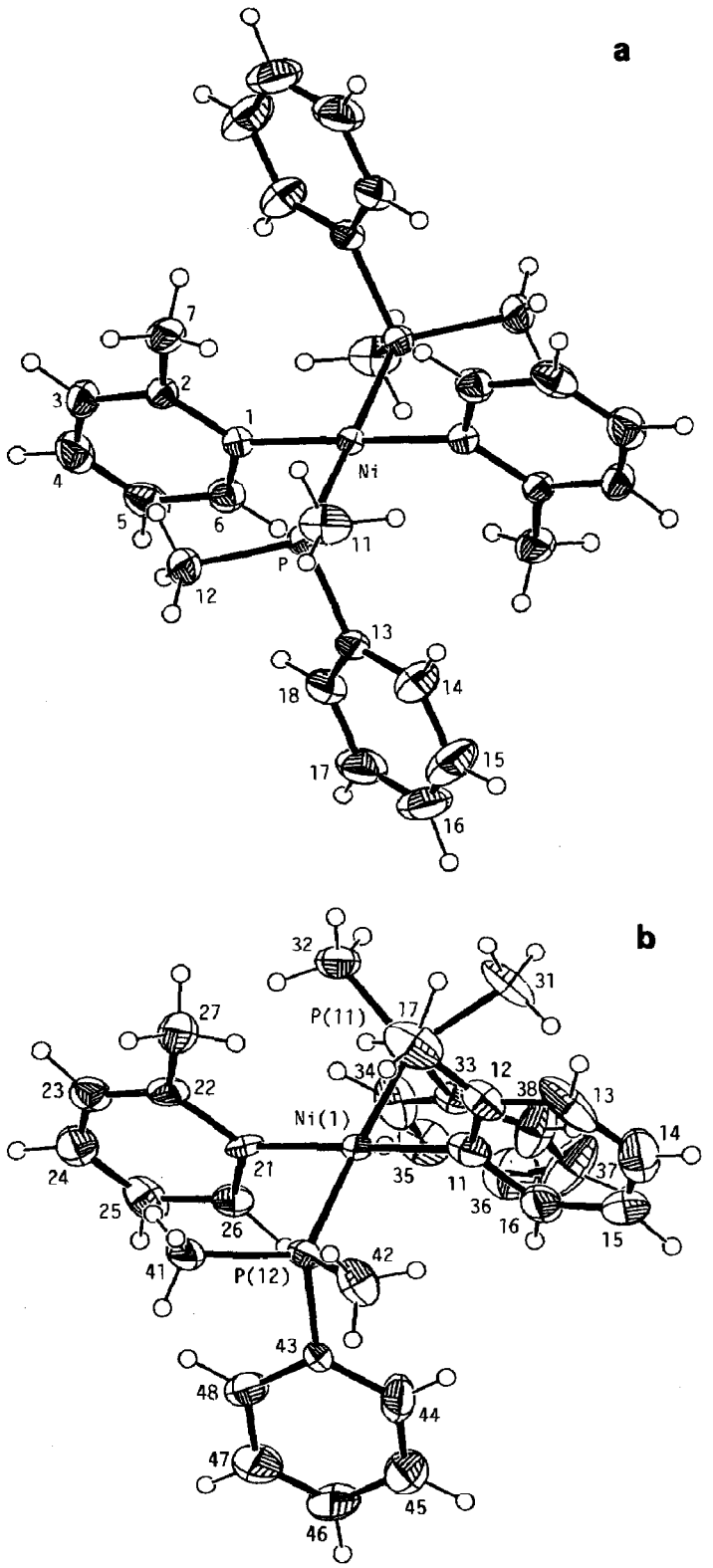

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Fig. 2. ORTEP [6] drawings of the molecular structures of *trans*-[Ni(C_6H_4Me-2)$_2$(PMe_2Ph)$_2$] showing the atomic numbering. Non-hydrogen atoms are thermal ellipsoids at 30% probability levels, whereas hydrogen atoms are drawn as spheres with B 1.0 Å^2. In order to clarify numbering systems, only atomic numbers are shown for carbon atoms. (a) *anti* isomer, (b) *syn* isomer (molecule 1), (c) *syn* isomer (molecule 2).

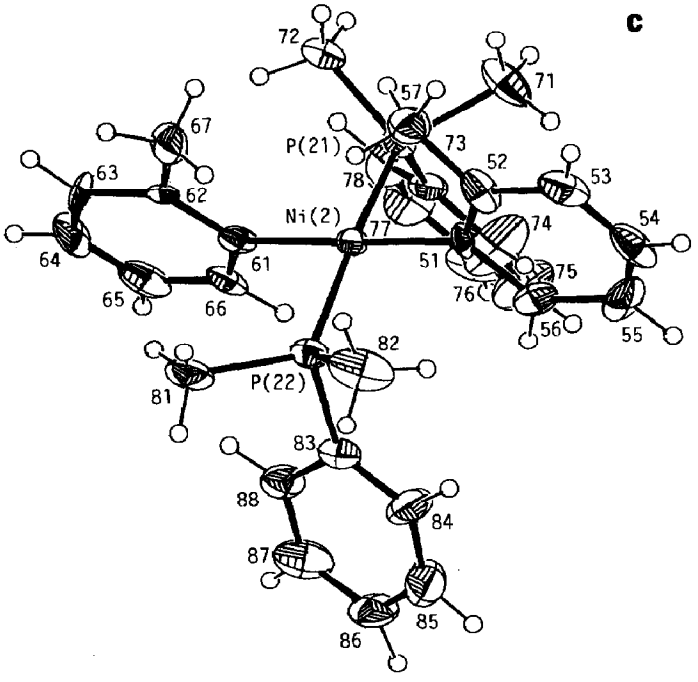

Fig. 2. (continued).

Table 5

Bond distances(Å) and angles(°) for the *anti* isomer

Ni–C(1)	1.942(3)	Ni–P	2.173(1)
C(1)–C(2)	1.409(4)	C(1)–C(6)	1.403(4)
C(2)–C(3)	1.399(4)	C(2)–C(7)	1.503(4)
C(3)–C(4)	1.366(5)	C(4)–C(5)	1.376(5)
C(5)–C(6)	1.392(4)		
P–C(11)	1.827(4)	P–C(12)	1.831(4)
P–C(13)	1.821(3)		
C(13)–C(14)	1.380(4)	C(13)–C(18)	1.387(4)
C(14)–C(15)	1.400(6)	C(15)–C(16)	1.366(7)
C(16)–C(17)	1.368(6)	C(17)–C(18)	1.378(5)
C(1)–Ni–P	91.4(1)		
Ni–C(1)–C(2)	123.3(2)	Ni–C(1)–C(6)	120.6(2)
C(2)–C(1)–C(6)	116.0(3)	C(1)–C(2)–C(3)	120.2(3)
C(1)–C(2)–C(7)	120.9(3)	C(3)–C(2)–C(7)	118.9(3)
C(2)–C(3)–C(4)	122.0(3)	C(3)–C(4)–C(5)	119.4(4)
C(4)–C(5)–C(6)	119.3(3)	C(1)–C(6)–C(5)	123.2(3)
Ni–P–C(11)	117.1(2)	Ni–P–C(12)	119.3(2)
Ni–P–C(13)	112.2(1)	C(11)–P–C(12)	100.7(2)
C(11)–P–C(13)	103.9(2)	C(12)–P–C(13)	101.4(2)
P–C(13)–C(14)	122.5(3)	P–C(13)–C(18)	118.4(2)
C(14)–C(13)–C(18)	119.2(3)	C(13)–C(14)–C(15)	119.8(4)
C(14)–C(15)–C(16)	120.0(4)	C(15)–C(16)–C(17)	120.4(5)
C(16)–C(17)–C(18)	120.2(4)	C(13)–C(18)–C(17)	120.4(3)

Table 6

Bond distances (Å) and angles (°) for the *syn* isomer

molecule 1			
Ni(1)–C(11)	1.933(16)	Ni(1)–C(21)	1.950(12)
Ni(1)–P(11)	2.160(5)	Ni(1)–P(12)	2.169(5)
C(11)–C(12)	1.44(3)	C(11)–C(16)	1.44(3)
C(12)–C(13)	1.41(3)	C(12)–C(17)	1.43(3)
C(13)–C(14)	1.39(4)	C(14)–C(15)	1.43(4)
C(15)–C(16)	1.43(3)		
C(21)–C(22)	1.46(2)	C(21)–C(26)	1.38(2)
C(220–C(23)	1.36(3)	C(22)–C(27)	1.53(3)
C(23)–C(24)	1.33(3)	C(24)–C(25)	1.37(3)
C(25)–C(26)	1.46(3)		
P(11)–C(31)	1.831(19)	P(11)–C(32)	1.823(18)
P(11)–C(33)	1.858(13)		
C(33)–C(34)	1.40(3)	C(33)–C(38)	1.32(3)
C(34)–C(35)	1.38(3)	C(35)–C(36)	1.38(4)
C(36)–C(37)	1.36(4)	C(37)–C(38)	1.41(4)
P(12)–C(41)	1.844(19)	P(12)–C(42)	1.828(18)
P(12)–C(43)	1.856(15)		
C(43)–C(44)	1.34(3)	C(43)–C(48)	1.38(3)
C(44)–C(45)	1.37(4)	C(45)–C(46)	1.39(4)
C(46)–C(47)	1.29(4)	C(47)–C(48)	1.43(4)
molecule 2			
Ni(2)–C(51)	1.903(15)	Ni(2)–C(61)	1.939(13)
Ni(2)–P(21)	2.166(4)	Ni(2)–P(22)	2.172(4)
C(51)–C(52)	1.34(3)	C(51)–C(56)	1.44(3)
C(52)–C(53)	1.44(3)	C(52)–C(57)	1.55(3)
C(53)–C(54)	1.42(3)	C(54)–C(55)	1.32(3)
C(55)–C(56)	1.50(3)		
C(61)–C(62)	1.43(2)	C(61)–C(66)	1.40(2)
C(62)–C(63)	1.42(3)	C(62)–C(67)	1.47(3)
C(63)–C(64)	1.39(3)	C(64)–C(65)	1.39(3)
C(65)–C(66)	1.42(3)		
P(21)–C(71)	1.876(19)	P(21)–C(72)	1.788(15)
P(21)–C(73)	1.802(14)		
C(73)–C(74)	1.37(3)	C(73)–C(78)	1.36(3)
C(74)–C(75)	1.41(4)	C(75)–C(76)	1.39(4)
C(76)–C(77)	1.39(3)	C(77)–C(78)	1.36(3)
P(22)–C(81)	1.843(18)	P(22)–C(82)	1.828(21)
P(22)–C(83)	1.804(15)		
C(83)–C(84)	1.45(3)	C(83)–C(88)	1.37(3)
C(84)–C(85)	1.41(3)	C(85)–C(86)	1.37(3)
C(86)–C(87)	1.39(3)	C(87)–C(88)	1.37(4)
molecule 1			
C(11)–Ni(1)–C(21)	178.7(6)	C(11)–Ni(1)–P(11)	88.8(5)
C(11)–Ni(1)–P(12)	91.4(5)	C(21)–Ni(1)–P(11)	90.9(4)
C(21)–Ni(1)–P(12)	88.7(4)	P(11)–Ni(1)–P(12)	174.2(2)
Ni(1)–C(11)–C(12)	122.6(12)	Ni(1)–C(11)–C(16)	119.5(13)
C(12)–C(11)–C(16)	117.8(15)	C(11)–C(12)–C(13)	119.2(16)
C(11)–C(12)–C(17)	120.2(16)	C(13)–C(12)–C(17)	120.6(17)
C(12)–C(13)–C(14)	123.3(20)	C(13)–C(14)–C(15)	118.8(22)
C(14)–C(15)–C(16)	119.4(20)	C(11)–C(16)–C(15)	121.4(17)
Ni(1)–C(21)–C(22)	122.0(9)	Ni(1)–C(21)–C(26)	120.5(10)
C(22)–C(21)–C(26)	117.4(12)	C(21)–C(22)–C(23)	120.3(13)
C(21)–C(22)–C(27)	118.4(13)	C(23)–C(22)–C(27)	121.3(14)

Table 6 (continued)

molecule 1			
molecule 1			
C(22)–C(23)–C(24)	124.3(15)	C(23)–C(24)–C(25)	117.2(17)
C(24)–C(25)–C(26)	123.2(16)	C(21)–C(26)–C(25)	117.5(13)
Ni(1)–P(11)–C(31)	120.2(7)	Ni(1)–P(11)–C(32)	117.4(6)
Ni(1)–P(11)–C(33)	110.5(5)	C(31)–P(11)–C(32)	99.2(9)
C(31)–P(11)–C(33)	104.1(7)	C(32)–P(11)–C(33)	103.4(8)
P(11)–C(33)–C(34)	119.5(11)	P(11)–C(33)–C(38)	120.2(12)
C(34)–C(33)–C(38)	120.3(14)	C(33)–C(34)–C(35)	119.5(16)
C(34)–C(35)–C(36)	118.5(19)	C(35)–C(36)–C(37)	122.4(23)
C(36)–C(37)–C(38)	117.2(22)	C(33)–C(38)–C(37)	121.9(18)
Ni(1)–P(12)–C(41)	118.5(6)	Ni(1)–P(12)–C(42)	119.5(6)
Ni(1)–P(12)–C(43)	110.6(5)	C(41)–P(12)–C(42)	100.8(8)
C(41)–P(12)–C(43)	103.5(8)	C(42)–P(12)–C(43)	101.5(8)
P(12)–C(43)–C(44)	121.7(13)	P(12)–C(43)–C(48)	118.9(12)
C(44)–C(43)–C(48)	119.4(16)	C(43)–C(44)–C(45)	120.8(20)
C(44)–C(45)–C(46)	119.9(22)	C(45)–C(46)–C(47)	120.0(22)
C(46)–C(47)–C(48)	120.9(22)	C(43)–C(48)–C(47)	118.9(18)
molecule 2			
C(51)–Ni(2)–C(61)	178.2(6)	C(51)–Ni(2)–P(21)	91.2(5)
C(51)–Ni(2)–P(22)	89.8(5)	C(61)–Ni(2)–P(21)	88.6(4)
C(61)–Ni(2)–P(22)	90.7(4)	P(21)–Ni(2)–P(22)	172.8(2)
Ni(2)–C(51)–C(52)	124.9(12)	Ni(2)–C(51)–C(56)	120.6(11)
C(52)–C(51)–C(56)	114.5(14)	C(51)–C(52)–C(53)	126.0(15)
C(51)–C(52)–C(57)	120.5(14)	C(53)–C(52)–C(57)	113.4(14)
C(52)–C(53)–C(54)	118.1(16)	C(53)–C(54)–C(55)	121.1(18)
C(54)–C(55)–C(56)	118.9(18)	C(51)–C(56)–C(55)	121.2(15)
Ni(2)–C(61)–C(62)	120.1(10)	Ni(2)–C(61)–C(66)	121.5(10)
C(62)–C(61)–C(66)	118.4(12)	C(61)–C(62)–C(63)	118.4(13)
C(61)–C(62)–C(67)	122.4(13)	C(63)–C(62)–C(67)	119.0(13)
C(62)–C(63)–C(64)	121.2(15)	C(63)–C(64)–C(65)	121.5(17)
C(64)–C(65)–C(66)	117.2(15)	C(61)–C(66)–C(65)	123.2(13)
Ni(2)–P(21)–C(71)	119.1(6)	Ni(2)–P(21)–C(72)	117.0(5)
Ni(2)–P(21)–C(73)	111.2(5)	C(71)–P(21)–C(72)	102.0(8)
C(71)–P(21)–C(73)	100.9(8)	C(72)–P(21)–C(73)	104.6(7)
P(21)–C(73)–C(74)	119.5(14)	P(21)–C(73)–C(78)	126.0(12)
C(74)–C(73)–C(78)	114.5(16)	C(73)–C(74)–C(75)	124.0(22)
C(74)–C(75)–C(74)	118.5(22)	C(75)–C(76)–C(77)	117.9(20)
C(76)–C(77)–C(78)	120.0(18)	C(73)–C(78)–C(77)	125.0(16)
Ni(2)–P(22)–C(81)	121.5(6)	Ni(2)–P(22)–C(82)	117.6(7)
Ni(2)–P(22)–C(83)	110.6(5)	C(81)–P(22)–C(82)	102.0(9)
C(81)–P(22)–C(83)	100.3(8)	C(82)–P(22)–C(83)	101.9(9)
P(22)–C(83)–C(84)	117.7(11)	P(22)–C(83)–C(88)	125.1(13)
C(84)–C(83)–C(88)	117.1(15)	C(83)–C(84)–C(85)	119.9(15)
C(84)–C(85)–C(86)	120.6(17)	C(85)–C(86)–C(87)	118.0(18)
C(86)–C(87)–C(88)	123.0(20)	C(83)–C(88)–C(87)	121.3(19)

In the two independent molecules of the *syn* isomer, the interatomic distances between the two methyl carbon atoms of the 2-tolyl groups are C(17)–C(27) 4.08(3) Å for molecule 1 and C(57)–C(67) 3.94(3) Å for molecule 2; the closest distances between methyl hydrogen atoms are 2.2(3) and 2.6(3) Å, respectively. The slightly bent C(2-tolyl)–Ni–C(2-tolyl) angles of 178.7(6) and 178.2(6)° for molecules 1 and

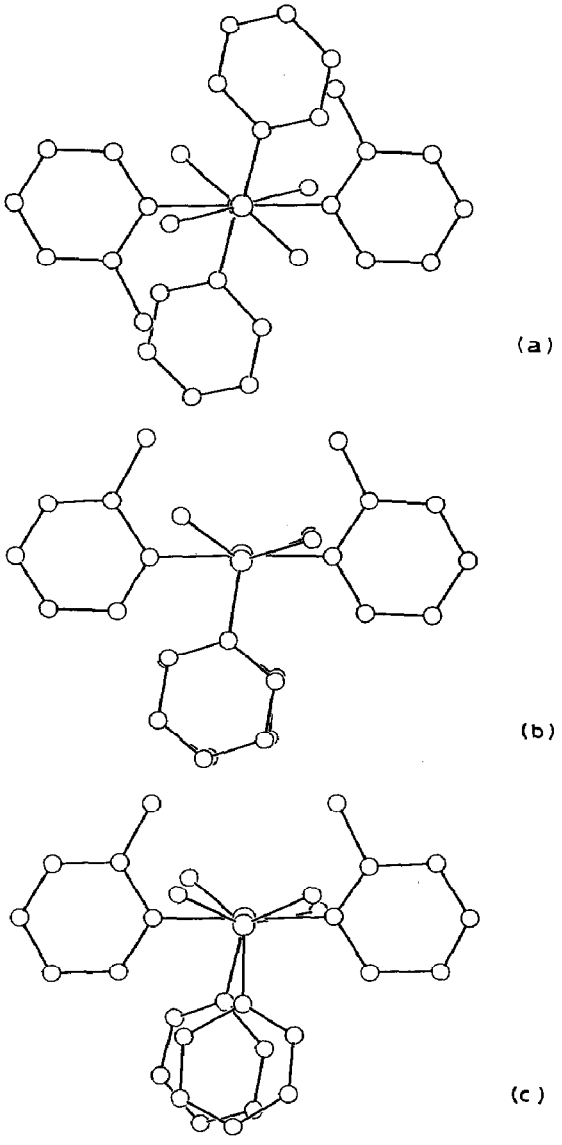

Fig. 3. Perspective drawing of molecules of trans-[Ni(C_6H_4Me-2)$_2$(PMe_2Ph)$_2$] as viewed down the P–Ni–P axis. (a) *anti* isomer, (b) *syn* isomer (molecule 1), (c) *syn* isomer (molecule 2).

2 may be due to the contact between 2-tolyl methyl groups, but no unusually short distances between methyl groups were observed in the crystal structure. In conclusion, the *syn* isomer has only negligibly little intramolecular repulsive forces caused by the adjacent 2-tolyl methyl groups.

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