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Molecular Structures of Trichlorovinyl(*p*-tolyl)nickel(II) Complex, and Its Thermal and Photo Isomerization Products

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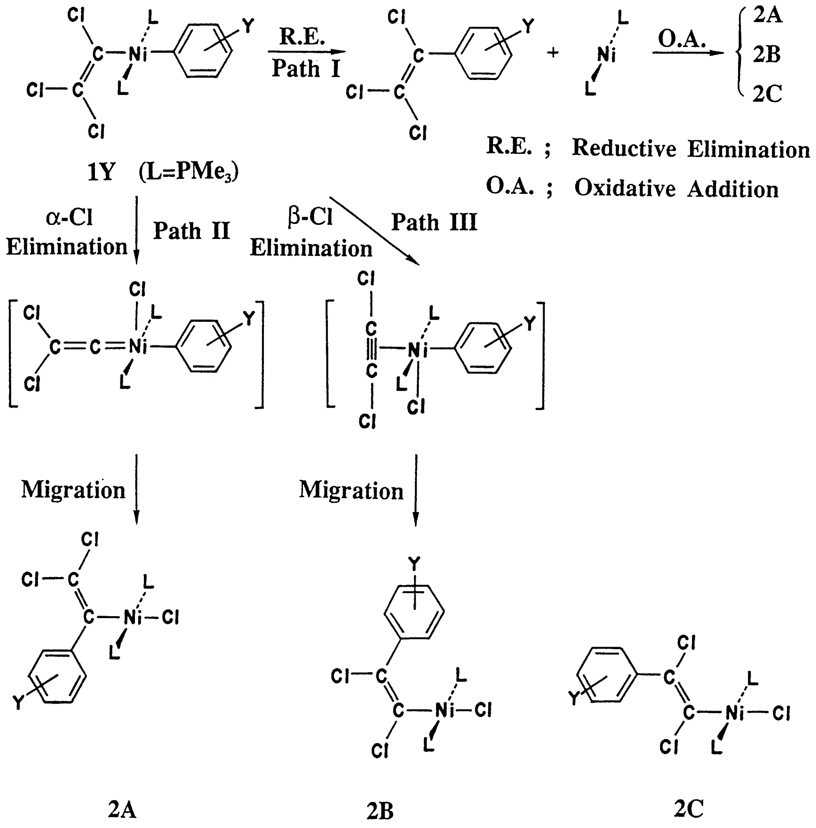
The molecular structure of the trichlorovinyl(*p*-tolyl)nickel(II) complex (*trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_4$Me-4)(PMe$_3$)$_2$] (**1**)), its thermal isomerization product (*trans*-[NiCl{C(C$_6$H$_4$Me-4)=CCl$_2$}(PMe$_3$)$_2$] (**2**)) and one of its photolysis products (*trans*-[NiCl{CCl=CCl(C$_6$H$_4$Me-4)}(PMe$_3$)$_2$] (**3**)) have been determined by an X-ray diffraction method. Crystal data: **1**; triclinic, space group $P\bar{1}$, a=8.768(1), b=9.347(1), c=13.029(2) Å, α=103.79(2), β=96.23(2), γ=86.90(3)°, V=1030.4(3) Å^3, Z=2, D_c=1.393 g cm^{-3}, **2**; orthorhombic, space group $P2_12_12_1$, a=13.884(2), b=14.505(3), c=10.272(2) Å, V=2068.6(6) Å^3, Z=4, D_c=1.388 g cm^{-3}, **3**; triclinic, space group $P\bar{1}$, a=11.628(4), b=8.975(3), c=10.437(4) Å, α=102.91(3), β=99.45(3), γ=89.91(4)°, V=1046.6(7) Å^3, Z=2, D_c=1.377 g cm^{-3}. Molecules **2** and **3** were found to contain *p*-tolyl group on the α-carbon and β-carbon atoms of the vinyl ligand, respectively. Intersting structural deformations were found in **1**.

Reductive elimination and oxidative addition are unit reactions used to obtain new substances through either the fission or formation of bonds using organometallic complexes as catalysts.[1)] The combined use of these reactions has been applied in the various fields of organic synthesis. One of the practical applications of these reactions is the formation of a monoorganometal complex from a diorganometal type. The thermolysis of a newly synthesized trichlorovinyl(aryl)nickel(II) complex (**1Y**), *trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_4$Y)(PMe$_3$)$_2$] (Y=OMe-2, Me-2, NMe$_2$-4, Me-4, Me-3, or Cl-4), resulted in the formation of isomeric monoorganonickel(II) complexes.[2)]

Three molecular structures (**2A**, **2B**, and **2C**) are possible for the thermal isomerization product of the trichlorovinyl(aryl)nickel(II) complex (**1Y**). A plausible reductive elimination of the trichlorovinyl and aryl groups, followed by an oxidative addition onto the nickel atom, may produce all of three possible isomers (Path I in Scheme 1). An α-chloro elimination of the tri-



Scheme 1.

chlorovinyl ligand followed by its coordination onto a nickel atom may give a vinylidene(chloro)(aryl)nickel intermediate (Path II). The migration of the aryl ligand onto the α-carbon atom of the vinylidene ligand may give an isomer, **2A**. β-Chloro elimination in a similar manner may give an acetylene(chloro)(aryl)nickel intermediate (Path III). The migration of the aryl ligand onto the acetylene carbon atom may give an isomer, **2B**. Isomer **2C** cannot be expected through α- or β-chloro elimination pathways. In order to obtain exact structural information concerning thermal isomerization in this system, X-ray crystal structure analyses of trichlorovinyl(*p*-tolyl)nickel(II) complex, *trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_4$Me-4)(PMe$_3$)$_2$] (**1**) and its thermal isomerization product, *trans*-[NiCl{C(C$_6$H$_4$Me-4)=CCl$_2$}(PMe$_3$)$_2$] (**2**) have been carried out.

The photolysis of **1Y** (Y=Me-4, Cl-4) has been studied in order to obtain little-known photochemical properties concenrning square-planar organonickel(II) complexes.[3] Two isomers were obtained in a mixture by irradiation, one of which was identical to the thermolysis product of **1Y**. The molecular structure of another Photolysis product of **1Y**, *trans*-[NiCl{CCl=CCl(C$_6$H$_4$-Me-4)}(PMe$_3$)$_2$] (**3**), was also determined in order to compare the stuctural characteristics with **1** and **2**.

Experimental

Crystal Data. Complexes **1**, **2**, and **3** were prepared by a procedure described previously.[2] Single crystals were obtained by recrystallization from ethanol. Crystals of **1**, **2**, and **3** are pale-yellow, brown, and dark-brown in color with regular prismatic shapes, respectively. Preliminary oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation showed that crystals **1** and **3** are triclinic, whereas **2** is orthorhombic. Unit-cell parameters were determined at room temperature by a least-squares fit of the 2θ values of 25 strong, higher-angle reflections for three complexes observed on a four-circle diffractometer. Crystal data are summarized in Table 1.

Collection and Reduction of Intensity Data. The integrated intensities were measured on a Rigaku four-circle diffractometer with graphite monochromatized Mo $K\alpha$ (λ=0.71069 Å) radiation. The θ–2θ scan technique was used at a 2θ scan rate of 4° min^{-1} with a scan width of $\Delta 2\theta$=(2.0+0.70 tan θ)°. The background intensities were measured for 7.5 s at both ends of each scan. Three standard reflections were measured after every 61 reflections in order to monitor the radiation damage and any change in the crystal orientation. No significant intensity decay of the standard reflections was observed for all crystals studied. The number of reflection intensities collected up to 2θ=55° for **1** ($\sin\theta_{\max}/\lambda$=0.650), 2θ=60° for **2** ($\sin\theta_{\max}/\lambda$=0.704), and 2θ=55° for **3** were 4327, 3387, and 4792, among which the observed reflections [$|F_o|>3\sigma(F_o)$] were 3482, 2745, and 3276, respectively. Although the usual Lorentz and polarization effects were

Table 1. Crystallographic and Experimental Data of *trans*-[Ni(CCl=Cl$_2$)(C$_6$H$_4$Me-4)(PMe$_3$)$_2$] **1**, and Its Isomerization Products **2** and **3**

Compound	1	2	3
Formula	$C_{15}H_{25}Cl_3P_2Ni$	$C_{15}H_{25}Cl_3P_2Ni$	$C_{15}H_{25}Cl_3P_2Ni$
Formula weight	432.4	432.4	432.4
System	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a/Å	8.768(1)	13.884(2)	11.628(4)
b/Å	9.347(1)	14.505(3)	8.975(3)
c/Å	13.029(2)	10.272(2)	10.437(4)
α/°	103.79(2)		102.91(3)
β/°	96.23(2)		99.45(3)
γ/°	86.90(3)		89.91(4)
V/Å^3	1030.4(3)	2068.6(6)	1046.6(7)
Z	2	4	2
D_c/g cm^{-3}	1.393	1.388	1.377
F(000)/e	448	896	448
μ(Mo $K\alpha$)/cm^{-1}	14.9	14.8	14.7
Temperature/° C	20	20	20
Crystal size/mm	0.3×0.25×0.25	0.3×0.3×0.3	0.25×0.3×0.3
Crystal color	Pale yellow	Brown	Dark brown
Crystal shape	Prismatic	Prismaic	Prismatic
2θ range/deg	$4<2\theta<55$	$4<2\theta<60$	$4<2\theta<55$
Reflections measured	4327	3387	4792
Reflections observed	3482	2745	3276
No. of variables	291	291	291
GOF[a]	1.014	1.002	1.028
R[b]	0.064	0.043	0.062
R_w[c]	0.094	0.062	0.084

a) $\Sigma w(|F_o|-|F_c|)^2/(n-m)$, where n and m are the number of reflections used and variables refined, respectively. b) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. c) $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w=[\sigma^2(F_o)+g(F_o)^2]^{-1}$, and g=0.003 for all the complexes.

Table 2. Final Atomic Parameters together with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}
(a) *trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_4$Me-4)(PMe$_3$)$_2$] (**1**)				
Ni	0.34958 (8)	0.05648 (7)	0.27470 (5)	3.4
Cl (1)	0.2101 (3)	0.2456 (2)	0.4821 (2)	6.0
Cl (2)	0.1270 (3)	0.2858 (2)	0.1619 (2)	5.7
Cl (3)	0.0116 (2)	0.4485 (2)	0.3606 (2)	5.8
P (1)	0.5432 (2)	0.2030 (2)	0.3088 (2)	4.5
P (2)	0.1684 (2)	−0.1037 (2)	0.2423 (2)	4.0
C (1)	0.2151 (8)	0.2122 (7)	0.3375 (6)	5.3
C (2)	0.1287 (8)	0.3029 (7)	0.2998 (6)	5.6
C (11)	0.5026 (10)	0.4025 (8)	0.3362 (9)	8.2
C (12)	0.6592 (9)	0.1813 (9)	0.4279 (6)	6.5
C (13)	0.6821 (9)	0.1801 (10)	0.2111 (7)	7.2
C (21)	0.0159 (9)	−0.0692 (10)	0.3325 (8)	7.2
C (22)	0.0626 (10)	−0.1139 (10)	0.1134 (6)	7.6
C (23)	0.2189 (9)	−0.2967 (7)	0.2387 (7)	6.4
C (31)	0.4863 (6)	−0.0992 (6)	0.2144 (4)	3.7
C (32)	0.4981 (7)	−0.1395 (7)	0.1040 (5)	4.4
C (33)	0.5897 (8)	−0.2557 (7)	0.0559 (5)	5.0
C (34)	0.6748 (7)	−0.3426 (7)	0.1158 (5)	4.8
C (35)	0.6679 (7)	−0.3053 (6)	0.2253 (5)	4.3
C (36)	0.5752 (7)	−0.1856 (6)	0.2714 (4)	3.9
C (37)	0.7728 (10)	−0.4730 (8)	0.0632 (7)	6.8
(b) *trans*-[NiCl{C(C$_6$H$_4$Me-4)=CCl$_2$}(PMe$_3$)$_2$] (**2**)				
Ni	0.19639 (5)	0.22907 (4)	0.03421 (6)	3.0
Cl (1)	0.22991 (13)	0.16763 (10)	0.22607 (14)	4.8
Cl (2)	−0.00759 (11)	0.29723 (14)	−0.0592 (3)	6.6
Cl (3)	0.05694 (14)	0.37699 (12)	−0.3000 (2)	6.2
P (1)	0.18605 (11)	0.09064 (8)	−0.05234 (13)	3.7
P (2)	0.20653 (13)	0.36621 (9)	0.12747 (14)	4.2
C (1)	0.1773 (4)	0.2834 (3)	−0.1333 (5)	3.4
C (2)	0.0908 (5)	0.3129 (4)	−0.1648 (6)	4.2
C (11)	0.1323 (6)	0.0742 (5)	−0.2133 (7)	5.5
C (12)	0.3056 (7)	0.0420 (5)	−0.0688 (10)	7.2
C (13)	0.1207 (8)	0.0075 (5)	0.0417 (8)	7.7
C (21)	0.1889 (8)	0.4700 (4)	0.0299 (8)	7.0
C (22)	0.1217 (7)	0.3804 (6)	0.2610 (8)	7.2
C (23)	0.3244 (7)	0.3864 (5)	0.2023 (8)	6.5
C (31)	0.2606 (4)	0.2922 (3)	−0.2214 (5)	3.2
C (32)	0.2548 (5)	0.2686 (4)	−0.3543 (5)	4.1
C (33)	0.3354 (5)	0.2763 (4)	−0.4339 (5)	4.3
C (34)	0.4227 (5)	0.3082 (4)	−0.3891 (6)	4.3
C (35)	0.4292 (5)	0.3288 (5)	−0.2539 (6)	4.5
C (36)	0.3498 (4)	0.3199 (5)	−0.1748 (6)	4.2
C (37)	0.5088 (6)	0.3208 (6)	−0.4763 (7)	6.6
(c) *trans*-[NiCl{CCl=CCl(C$_6$H$_4$Me-4)}(PMe$_3$)$_2$] (**3**)				
Ni	0.21246 (6)	0.16008 (8)	0.43907 (7)	3.7
Cl (1)	0.0090 (2)	0.3138 (3)	0.3315 (3)	6.6
Cl (2)	0.2702 (2)	0.0354 (3)	0.5957 (2)	6.7
Cl (3)	0.1103 (2)	0.4105 (2)	0.1084 (2)	6.3
P (1)	0.2847 (2)	0.3744 (2)	0.5794 (2)	4.4
P (2)	0.1544 (2)	−0.0603 (2)	0.3005 (2)	5.1
C (1)	0.1532 (5)	0.2658 (6)	0.3104 (6)	4.1
C (2)	0.1959 (5)	0.3095 (6)	0.2131 (6)	4.1
C (11)	0.2685 (7)	0.5536 (8)	0.5265 (7)	6.1
C (12)	0.2297 (7)	0.4133 (8)	0.7338 (7)	6.1
C (13)	0.4425 (6)	0.3679 (10)	0.6305 (9)	7.2
C (21)	0.0911 (8)	−0.0635 (10)	0.1308 (9)	8.2
C (22)	0.2761 (7)	−0.1869 (9)	0.2813 (10)	7.0
C (23)	0.0524 (7)	−0.1682 (8)	0.3597 (9)	8.4
C (31)	0.3147 (5)	0.2749 (6)	0.1810 (6)	4.2
C (32)	0.3550 (8)	0.3193 (10)	0.0752 (7)	6.6
C (33)	0.4659 (8)	0.2820 (11)	0.0461 (8)	7.6
C (34)	0.5399 (6)	0.1982 (8)	0.1173 (7)	5.6
C (35)	0.5008 (6)	0.1590 (8)	0.2229 (7)	5.1
C (36)	0.3914 (5)	0.1960 (7)	0.2537 (6)	4.7
C (37)	0.6577 (8)	0.1535 (11)	0.0825 (9)	8.3

corrected for the intensity data, no absorption correction was applied.

Determination and Refinement of the Structure. The three structures were all solved using the heavy-atom method. Successive Fourier syntheses phased by the nickel atoms found in Patterson maps clearly revealed the remaining nonhydrogen atoms. The structures were refined anisotropically by a full-matrix least-squares method (XRAY SYSTEM),[4] the function minimized being $\sum w(\Delta F)^2$. All of the hydrogen atoms were located on difference Fourier maps and were included in the refinement with isotropic temperature factors. The applied weighting function was $w=[\sigma_{cs}{}^2(F_o)+0.003\,(F_o)^2]^{-1}$, where σ_{cs} is the standard deviation estimated from the counting statistics. The final discrepancy factors, R (R_w), are 0.064 (0.094) for **1**, 0.043 (0.062) for **2**, and 0.062 (0.084) for **3**, respectively. The refinement parameters are summarized in Table 1.

The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[5] The final atomic coordinates of complexes (**1**, **2**, and **3**) together with the equivalent isotropic temperature factors (B_{eq}[6]) for nonhydrogen atoms are listed in Table 2.# All of the computations were processed on an ACOS 850 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Results and Discussion

Molecular and Crystal Structures. The molecular structures of complexes **1**, **2**, and **3** are shown in Figs. 1—3 by ORTEP drawings,[7] together with the atomic numberings. X-Ray structure analyses of complexes **1**, **2**, and **3** revealed that the thermolysis of complex **1** resulted in isomerization product **2A** (Scheme 1) through a displacement between the *p*-tolyl and *α*-chloro; photolysis gave **2B** through a displacement between the *p*-tolyl and *β*-chloro in the vinyl group. Postulated complex **2C** was not identified in the thermolysis and photolysis of **1Y**.

Coordination Geometry of Nickel Atom: Selected structural parameters around the nickel atoms in complexes **1**, **2**, and **3** are given in Table 3. The first structural feature observed commonly in these molecules is that the nickel atom takes a square-planar coordination with either two phosphine ligands and two carbon ligands or one carbon and one chlorine ligand at *trans*-positions; this is similar to those in a series of *trans*-[Ni(aryl)$_2$(PR$_3$)$_2$] and *trans*-[Ni(C$_6$Cl$_5$)(PMe$_3$)$_2${C(OMe)Me}BF$_4$ complexes.[8-10] In the complexes **1**, **2**, and **3**, five atoms defining the coordination plane of the nickel atom are nearly coplanar. The deviations from a mean plane defined by the inner co-coordination sphere, NiC$_2$P$_2$ or NiCClP$_2$, are: Ni, 0.025; P(1), −0.020; P(2), −0.020; C(1), 0.007; and C(31), 0.009 Å for **1**, Ni, 0.027; P(1), 0.037; P(2), 0.031; C(1), −0.050; and Cl(1),

Table 3. Coordination Geometries of Nickel Atoms in *trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_4$Me-4)(PMe$_3$)$_2$] **1** and Its Isomerization Products **2** and **3**

	1	**2**	**3**
P(1)-Ni-P(2)	175.6(1)°	178.2(1)°	175.5(1)°
P(1)-Ni-C(1)	91.6(2)	90.2(2)	91.5(2)
P(1)-Ni-C(31)	88.0(2)	—	—
P(1)-Ni-Cl(1)	—	90.3(1)	—
P(1)-Ni-Cl(2)	—	—	89.0(1)
P(2)-Ni-C(1)	92.1(2)	91.6(2)	90.9(2)
P(2)-Ni-C(31)	88.3(2)	—	—
P(2)-Ni-Cl(1)	—	87.9(1)	—
P(2)-Ni-Cl(2)	—	—	88.9(1)
C(1)-Ni-C(31)	178.9(3)	—	—
C(1)-Ni-Cl(1)	—	175.8(2)	—
C(1)-Ni-Cl(2)	—	—	175.9(2)
θ[a] (*Ni, Vinyl*)	88.2°	82.5°	88.7°
θ (*Ni, Tolyl*)	86.5	78.8	86.2
θ (*Vinyl, Tolyl*)	2.3	43.0	2.5

a) θ: Dihedral angle between the least-squares planes (*Ni, Vinyl, Tolyl*) composed of; *Ni*: Ni, P(1), P(2), C(1), and C(31) or Cl(1) or Cl(2). *Vinyl*: C(1), C(2), Cl(1), Cl(2), and Cl(3) in **1**. C(1), C(2), Cl(2), Cl(3), and C(31) in **2**. C(1), C(2), Cl(1), Cl(3), and C(31) in **3**. *Tolyl*: C(31)-C(36).

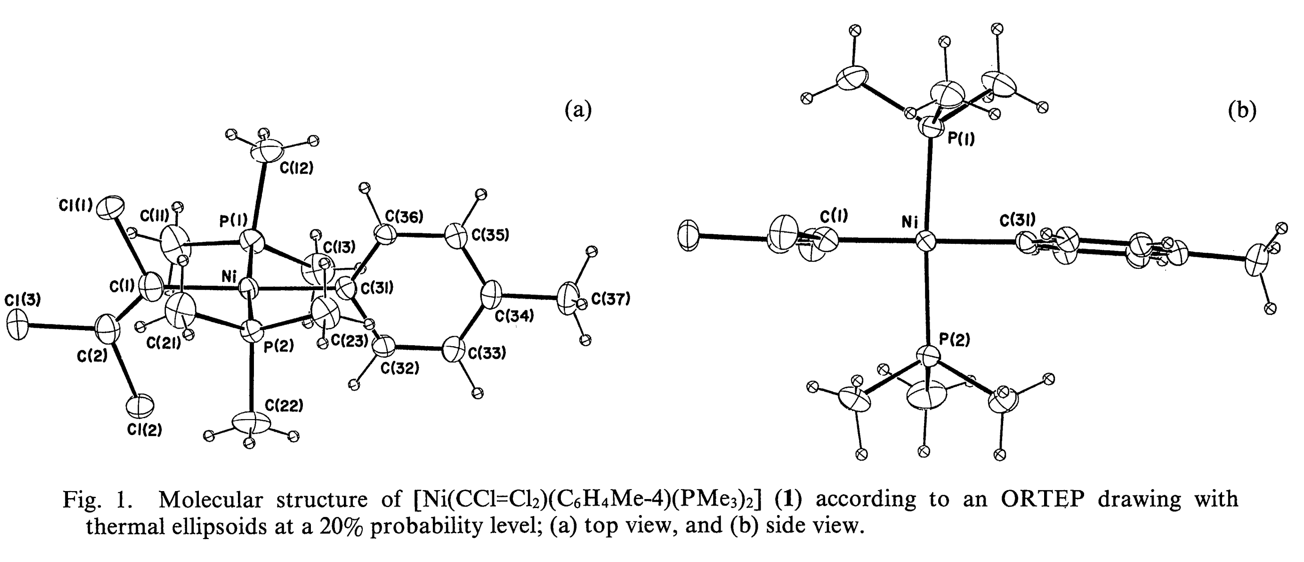


Fig. 1. Molecular structure of [Ni(CCl=Cl$_2$)(C$_6$H$_4$Me-4)(PMe$_3$)$_2$] (**1**) according to an ORTEP drawing with thermal ellipsoids at a 20% probability level; (a) top view, and (b) side view.

Tables of anisotropic temperature factors, coordinates of hydrogen atoms, and observed and calculated structure factors are kept as Document No. 8959 at the Office of the Editor of Bull. Chem. Soc. Jpn.

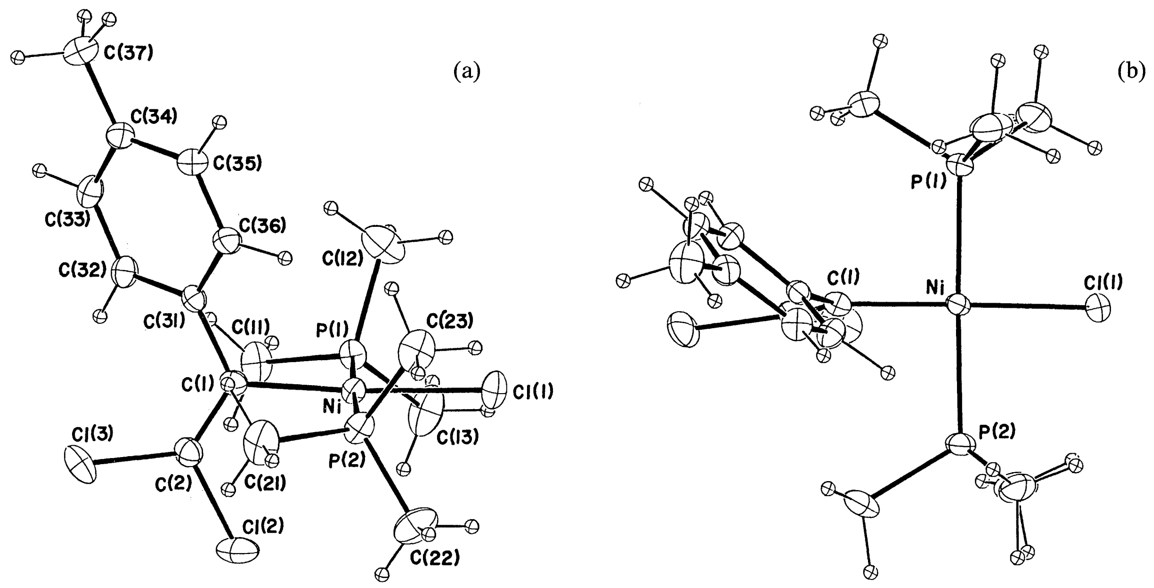


Fig. 2. Molecular structure of [NiCl{C(C_6H_4Me-4)=CCl_2}(PMe_3)$_2$] (**2**) according to an ORTEP drawing with thermal ellipsoids at a 20% probability level; (a) top view, and (b) side view.

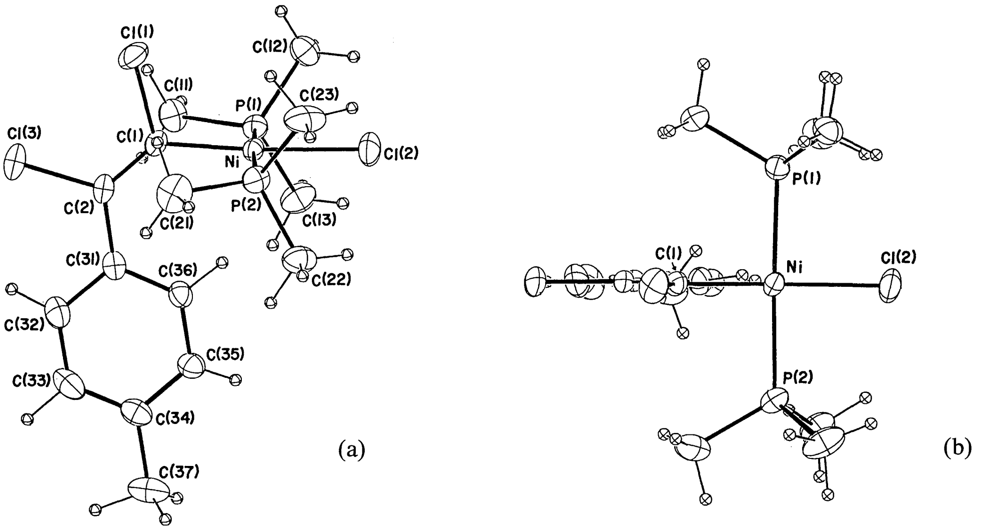


Fig. 3. Molecular structure of [NiCl{CCl=CCl(C_6H_4Me-4)}(PMe_3)$_2$] (**3**) according to an ORTEP drawing with thermal ellipsoids at a 20% probability level; (a) top view, and (b) side view.

−0.044 Å for **2**, Ni, 0.009; P(1), −0.091; P(2), −0.043; C(1), 0.107; and Cl(2), 0.049 Å for **3**, respectively. It is noteworthy that the P(1)–Ni–P(2) bond angles are 175.6(1)° and 175.5(1)° in complexes **1** and **3**, which show angular deviations of 4.4° and 4.5° from exact *trans* coordination; the bond angle in **2** [178.2(1)°] takes a value near to 180°. The bond angles C(1)–Ni–C(31) [178.9(3)°], C(1)–Ni–Cl(1) [175.8(2)°] and C(1)–Ni–Cl(2) [175.9(2)°] also deviate from the expected 180°, probably due to steric effects between the C or Cl and P atoms [mean C(1)···P 2.943 Å, 2.942 Å, 2.914 Å, and C(31)···P 2.850 Å, Cl(1)···P 3.100 Å, Cl(2)···P 3.088 Å for complexes **1**, **2**, and **3**, respectively]. The second feature is that the vinyl planes are approximately perpendicular to the Ni-coordination planes; the corresponding dihedral angles (θ) are 88.2° and 88.7° in complexes **1** and **3**, while that in complex **2** [82.5°] is slightly smaller. The *p*-tolyl plane in complexes **1** and **3** are also approximately perpendicular to the nickel coordination planes; the corresponding dihedral angles are 86.5° and 86.2°, respectively. The vinyl and *p*-tolyl planes in complex **2** are not coplanar with each other (dihedral angle; 43.0°) because of a nonbonded repulsion between the Cl(3) and H(32) atoms [Cl(3)···H(32); 2.82(6) Å, Cl(3)···C(32); 3.213(6) Å].

Conformation of Phosphine Ligand: Table 4 shows

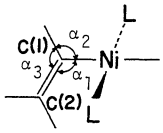
Table 4. Coordination Geometries of Phosphine Ligands in *trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_4$Me-4)(PMe$_3$)$_2$] **1** and Its Isomerization Products **2** and **3**

	1	**2**	**3**
ϕ[C(1)-Ni-P(1)-C(11)]	−19.1°	−17.9°	−2.0°
ϕ[C(1)-Ni-P(1)-C(12)]	98.7	102.4	120.8
ϕ[C(1)-Ni-P(1)-C(13)]	217.6	220.1	238.1
ϕ[C(1)-Ni-P(2)-C(21)]	−28.7	3.1	5.0
ϕ[C(1)-Ni-P(2)-C(22)]	89.4	125.2	124.1
ϕ[C(1)-Ni-P(2)-C(23)]	209.0	242.6	240.2
C(1)····C(11)	3.167 Å	3.204 Å	3.158 Å
C(1)····C(21)	3.219	3.188	3.139
C(31)····C(13)	3.213	—	—
C(31)····C(23)	3.148	—	—
Cl(n)[a]····C(12)	—	3.688	3.440
Cl(n)[a]····C(13)	—	3.359	3.431
Cl(n)[a]····C(22)	—	3.451	3.450
Cl(n)[a]····C(23)	—	3.443	3.514

ϕ: Torsional angle around Ni–P bonds. a) n=1 in **2**, 2 in **3**.

Table 5. Selected Structural Parameters in *trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_4$Me-4)(PMe$_3$)$_2$] **1** and Its Isomerization Products **2** and **3**

	1	**2**	**3**
Ni-P(1)	2.180(2) Å	2.201(2) Å	2.212(2) Å
Ni-P(2)	2.180(2)	2.212(2)	2.205(2)
Ni-C(1)	1.907(5)	1.911(5)	1.855(6)
Ni-C(31)	1.908(5)	—	—
Ni-Cl(1)	—	2.212(2)	—
Ni-Cl(2)	—	—	2.198(2)
C(1)-C(2)	1.258(10)	1.315(8)	1.333(8)
C(1)-Cl(1)	1.840(7)	—	1.767(6)
C(1)-C(31)	—	1.474(7)	—
C(2)-Cl(2)	1.763(7)	1.759(7)	—
C(2)-Cl(3)	1.746(7)	1.736(6)	1.758(6)
C(2)-C(31)	—	—	1.490(8)
α_1	132.5(6)°	118.8(4)°	134.1(5)°
α_2	116.3(4)	118.7(4)	107.8(3)
α_3	111.2(6)	122.5(5)	118.1(4)



the coordination geometries of the trimethylphosphine ligands in complexes **1**, **2**, and **3**. The ϕ's shows the torsional angles around the Ni–P bonds (taking the clockwise rotation as their positive direction). The ϕ's for the Ni–P(1) and Ni–P(2) bonds are −19.1°, −17.9°, −2.0°, and −28.7°, 3.1°, 5.0°, respectively. These values indicate that the first phosphine ligand [P(1), C(11), C(12), and C(13)] in complex **1** takes a similar conformation as that in complex **2**, while the second phosphine [P(2), C(21), C(22), and C(23)] in complex **2** has the similar conformation as that in complex **3**. In complex **1**, the two phosphine ligands are mutually related by nickel atom as an approximate center of symmetry. On the other hand, in complexes **2** and **3**, the phosphine ligands are related by an approximate mirror symmetry defined by a plane passing through the C(1), Ni, Cl(1) or Cl(2) atoms, which is normal to the coordination plane. The nonbonded intramolecular atomic distances between the C(1), C(31), or Cl(1), Cl(2) and nearby methyl groups in phosphine ligands are much shorter than the sum of Pauling's van der Waals radii [3.7 Å for C···C contact, and 3.8 Å for Cl···C]. Therefore, the conformations of these phosphine ligands are delicately modified by balancing the nonbonded atomic repulsions between the bulky methyl groups and the neighboring ligands.

Bonding Structure of Vinyl and *p*-Tolyl Ligands: Table 5 summarizes the selected structural parameters to describe the bonding geometries of the vinyl and *p*-tolyl ligands to the nickel atom. Almost the same Ni–P distances for the two phosphorus atoms of each molecule are observed [2.180(2) and 2.180(2) Å] for **1**, [2.201(2) and 2.212(2) Å] for **2**, and [2.212(2) and 2.205 Å] for **3**; the distances for three compounds, however, are slightly different from each other. The bond distance between the nickel and C(31) atoms in complex **1** [1.908(5) Å] has similar value as those between the nickel and vinyl α-carbon [C(1)], 1.907(5), 1.911(5), and 1.855(6) Å for complexes **1**, **2**, and **3**, respectively. These Ni–C distances are comparable with those reported in many organonickel complexes including C(sp^2)–Ni bonds.[11–14]

A remarkable structural feature is the unique structural deformations found in the vinyl ligand in complex **1**. First, the C(1)–C(2) bond distance of 1.258(10) Å is significantly shorter than the standard value for the C=C distance of 1.337 Å, while the corresponding distance in complex **2** [1.315(8) Å] and in complex **3** [1.337(8) Å] are equal to the standard C=C distance. Second, the C(1)–Cl(1) bond distance [1.840(7) Å] in complex **1** is longer than the C–Cl standard distance [1.72 Å in CH$_2$=CHCl, 1.767 Å in CH$_3$Cl or CH$_2$Cl$_2$], whereas the C(2)–Cl distances in **1**, **2**, and **3** complexes are in the range from 1.736 to 1.763 Å. A similar structural behavior has been observed for the vinyl ligand in [Ni(CCl=CCl$_2$)$_2$(PMe$_2$Ph)$_2$].[15] Third, the Ni–C(1)–C(2) bond angles (α_1) in complex **1** [132.5(6)°] and in complex **3** [134.1(5)°] are much larger than α_2 [**1**: 116.3(4), **3**: 107.8(3)°] and α_3 [**1**: 111.2(6), **3**: 118.1(4)°], while no angular deformation was found around the α-carbon atom of the vinyl ligand in complex **2**. The molecular structure of **1** shows an interesting trend toward linearity of the trichlorovinyl group.

Crystal Structure: No intermolecular distance shorter than the normal van der Waals contacts is found in the crystal structures of **1**, **2**, and **3**.

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