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X-Ray Structural Elucidation of a Novel Steric Effect of *o*-Methoxyl Substituents in 2,6-Dimethoxyphenylnickel(II) Complexes Mediated by *m*-Bromo Substitution

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Molecular structures of novel *trans*-[NiR_2L_2] complexes, *trans*-[$Ni\{C_6H_3(OMe)_2$-2,6$\}_2(PR_3)_2$] [PR_3=PMe_3 (**1a**), PMe_2Ph (**1b**)], and their *m*-brominated derivatives, *trans*-[$Ni\{C_6H(OMe)_2$-2,6-Br_2-3,5$\}_2(PR_3)_2$] [PR_3=PMe_3 (**2a**), PMe_2Ph (**2b**)], were determined by X-ray crystal structure analysis. A remarkable effect of *m*-substitution on the conformation of the *o*-methoxyl groups was found. This correlated well with the reactivity difference toward carbon monoxide. Crystal data: **1a**: monoclinic, space group $P2_1/c$, $a=8.737(2)$, $b=18.282(3)$, $c=16.319(4)$ Å, $\beta=105.06(2)°$, $Z=4$, $R=0.062$; **1b**: triclinic, space group $P\bar{1}$, $a=16.993(5)$, $b=10.180(3)$, $c=17.177(5)$ Å, $\alpha=112.44(2)$, $\beta=117.59(2)$, $\gamma=66.25(2)°$, $Z=3$, $R=0.060$; **2a**: monoclinic, space group $P2_1/c$, $a=9.294(2)$, $b=14.091(3)$, $c=10.770(2)$ Å, $\beta=92.06(3)°$, $Z=2$, $R=0.067$; **2b**: triclinic, space group $P\bar{1}$, $a=9.370(1)$, $b=11.387(2)$, $c=9.013(1)$ Å, $\alpha=94.52(2)$, $\beta=107.24(2)$, $\gamma=77.35(2)°$, $Z=1$, $R=0.058$.

Several 2,6-dimethoxyphenyl derivatives of transition metals are known. There seem to be at least three characteristic features caused by the *o*-methoxyl substituents. First, the steric effect allows the facile preparation of derivatives for Ni^{II},[1)] Cu^{I},[2)] Ag^{I},[3)] and Au^{I},[4)] which display greatly increased thermal and/or chemical stabilities, making their manipulation more facile than that of common phenyl derivatives. Secondly, the coordination properties through the oxygen lone-pair electrons have been demonstrated by the X-ray molecular structures of $V_2R_4\cdot 2THF$[5)] and Cr_2R_4,[6)] [R = $C_6H_3(OMe)_2$-2,6]. This functionality also explains the facile lithiation of the phosphine methyl groups in *trans*-[$NiR_2(PR'_3)_2$] [R = $C_6H_3(OMe)_2$-2,6; PR'_3 = PMe_3 (**1a**), PMe_2Ph (**1b**)].[1)] Thirdly, the mesomeric effect caused by the methoxyl oxygen atom affects the facile and stereospecific bromination (electrophilic substitution) on the 2,6-dimethoxyphenyl group, as observed for **1a** and **1b**.[1)] Interestingly, some of the resulting bromophenyl complexes *trans*-[$Ni\{C_6H(OMe)_2$-2,6-Br_2-3,5$\}_2(PR'_3)_2$] [PR'_3=PMe_3 (**2a**), PMe_2Ph (**2b**)] remarkably differed from the parent complexes **1a** and **1b** in the reactivity toward carbon monoxide, which catalyzes the intermolecular exchange of the PR'_3 ligands between **1a** and **1b** but not between **2a** and **2b**.[1)] In order to obtain more structural information to aid in understanding the difference, the detailed molecular structures of these complexes have now been determined by the X-ray crystal structure analysis.[7)] The results revealed the additional feature caused by the *o*-methoxyl substituents: their steric effect is highly influenced by the *m*-substituents and is associated with the rotational flexibility of the methoxyl group around the C(phenyl)–O bond.

Experimental

Crystallographic Data. Complexes **1a**, **1b**, **2a**, and **2b** were prepared by the procedures previously described.[1)] Single crystals were obtained by recrystallization from ethanol (**1a**, **1b**), ethyl methyl ketone (**2a**), or acetone (**2b**). Crystals of **1a**, **1b**, **2a**, and **2b** are all pale yellow in color with regular prismatic shapes. Preliminary oscillation and Weissenberg photographs taken with Cu*Kα* radiation showed that crystals of **1a** and **2a** are monoclinic, whereas those of **1b** and **2b** are triclinic. Accurate unit-cell parameters were determined at room temperature by the least-squares fit of 2θ values of 30, 25, 24, and 25 strong, higher angle reflections for **1a**, **1b**, **2a**, and **2b**, respectively. The density of each crystal was measured at room temperature by a flotation method in an aqueous solution of zinc bromide. Crystal data are summarized in Table 1.

Collection and Reduction of Intensity Data. Integrated intensities were measured on an Rigaku four-circle diffractometer by the θ-2θ scan technique at a 2θ scan rate of $4°\,\mathrm{min}^{-1}$ and a scan width of $\Delta 2\theta=(2.0+0.70\tan\theta)°$. The background intensities were measured for 7.5 s at both ends of a scan. Four standard reflections were measured after every 60 reflections in order to monitor the radiation damage and the change of the crystal orientations. No significant intensity decay of the standard reflections was observed for any of the crystals. The reflection intensities collected up to $2\theta=54°$ ($\sin\theta/\lambda=0.639$ Å^{-1}) were 5492, 3885, and 3904 for **1a**, **2a**, and **2b**, among which the observed reflections ($|F_o|>3\sigma(F_o)$) were 4138, 2284, and 3206, respectively. A total of 3394 (2397 non-zero) intensities for **1b** was first measured by adopting the small unit cell, which was later found to be a subcell of the true one. Reflections for **1b** based on the true unit cell were later collected up to $2\theta=50°$, and among the reflections measured 6006 were classed as observed ($|F_o|>3\sigma(F_o)$). The usual Lorentz and polarization effects were corrected for the intensity data, but no absorption correction was applied.

Determination and Refinement of the Structure. The crystal data of **2a** (space group $P2_1/c$ and $Z=2$) and **2b** (space group $P\bar{1}$ and $Z=1$) show that the **2a** and **2b** molecules must lie on a crystallographic center of symmetry. The crystal structures of **1a** and **2a** were solved by the heavy atom method. The heavy atoms located from the three-dimensional Patterson maps are: a nickel atom on a general position for **1a**, two bromine atoms on general positions in addition to a nickel atom on (0,0,0) for **2a**, respectively. The crystal structure of **2b** was solved by a combined use of the Patterson function and the direct method (*MULTAN*-78),[8)] and two bromine atoms were located on general positions in addition to a nickel atom on (0,0,0).

Non-hydrogen atoms for **1a**, **2a**, and **2b** were located on the subsequent Fourier maps based on the positions of the heavy atoms. These crystal structures were refined by the block-diagonal least-squares procedure (*HBLS*-V),[9)] the function minimized being $\sum w(|F_o|-|F_c|)^2$. All the hydrogen atoms

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TABLE 1. CRYSTAL DATA OF *trans*-[NiR_2L_2] COMPLEXES

	1a	**1b**	**2a**	**2b**
R	$C_6H_3(OMe)_2$-2,6	$C_6H_3(OMe)_2$-2,6	$C_6H(OMe)_2$-2,6-Br_2-3,5	$C_6H(OMe)_2$-2,6-Br_2-3,5
L	PMe_3	PMe_2Ph	PMe_3	PMe_2Ph
Formula	$C_{22}H_{36}O_4P_2Ni$	$C_{32}H_{40}O_4P_2Ni$	$C_{22}H_{32}Br_4O_4P_2Ni$	$C_{32}H_{36}Br_4O_4P_2Ni$
M	485.2	609.3	800.8	924.9
Crystal Size/mm^3	0.20×0.25×0.30	0.15×0.25×0.25	0.20×0.27×0.27	0.20×0.22×0.22
System	Monoclinic	Triclinic	Monoclinic	Triclinic
Absence of reflections	h01: 1≠2n 0k0: k≠2n	None	h01: 1≠2n 0k0: k≠2n	None
Space Group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	8.737(2)	16.993(5)	9.294(2)	9.370(1)
b/Å	18.282(3)	10.180(3)	14.091(3)	11.387(2)
c/Å	16.319(4)	17.177(5)	10.770(2)	9.013(1)
α/°		112.44(2)		94.52(2)
β/°	105.06(2)	117.59(2)	92.06(3)	107.24(2)
γ/°		66.25(2)		77.35(2)
U/Å^3	2517.1(9)	2339.8(13)	1409.6(5)	896.0(2)
Z	4	3	2	1
D_c/g cm^{-3}	1.280	1.297	1.886	1.714
D_m/g cm^{-3}	1.284	1.299	1.884	1.727
F(000)	1032	966	788	458
μ(Mo $K\alpha$)/cm^{-1}	7.2	5.8	36.2	31.4

TABLE 2. DETAILS OF THE REFINEMENT

	1a	**1b**	**2a**	**2b**
No. of reflections used[a)]	4138	6006	2284	3206
No. of parameters refined	407	773	219	272
Weighting parameters[b)]				
a[c)]	0.070	0.0365	0.1023	0.0201
b[c)]	0.0	0.0003	0.0003	0.0016
GOF[d)]	1.096	1.240	1.149	1.271
Final R value[e)]	0.062	0.060	0.067	0.058
Final Weighted R value (R_w)[f)]	0.068	0.063	0.077	0.073

a) $|F_o|>3\sigma(|F_o|)$. b) Weighting scheme used: $w=(\sigma^2_{cs}+a|F_o|+b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation obtained from counting statistics. c) Used in the final refinement. d) Goodness of fit, $\Sigma w(|F_o|-|F_c|)^2/(n-m)$, where n and m are the number of reflections used and number of parameters refined, respectively. e) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. f) $R_w=\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$

could be located on the difference Fourier maps, which were included in the successive refinement with isotropic temperature factors. At this stage of the refinement, the weighting schemes of the form $w=(\sigma_{cs}^2+a|F_o|+b|F_o|^2)^{-1}$ for $|F_o|>3\sigma(F_o)$ were applied. σ_{cs} is the standard deviation obtained from the counting statistics. The final weighted R values are (**1a**): 0.068; (**2a**): 0.077; (**2b**): 0.073. The values of a and b used in the final refinement are given in Table 2.

The structure analysis of **1b** was first carried out in a similar way to that for **1a**, **2a**, and **2b**, by adopting the subcell. Through the process of conventional refinement, a rather curious disordered structure was found: one of the methoxyl oxygen atoms takes two positions more than 1 Å apart from each other with half occupancy probability. After the anisotropic refinement of non-hydrogen atoms (R=0.103), hydrogen atoms were included in the refinement, but the convergence was not satisfactory. At this stage, a well-exposed Weissenberg photograph was taken around the b axis; additional reflections were thus found. This fact strongly indicated the possibility of a larger unit-cell for this crystal. The unit cell dimensions were redetermined, and reflection intensities were remeasured based on the true cell. Two interesting crystallographic features were found: (i) 2/3 of the total reflections measured based on the true cell are systematically weaker than the remaining 1/3 of the reflections, (ii) the subcell had been determined by using the stronger 1/3 reflections only. These two unit cells are related by these equations:

$$\boldsymbol{a}=\boldsymbol{a}_S-\boldsymbol{c}_S,$$
$$\boldsymbol{b}=\boldsymbol{b}_S,$$
$$\boldsymbol{c}=\boldsymbol{a}_S+2\boldsymbol{c}_S,$$

where the subscript shows the cell parameters of the subcell.

The crystal structure obtained by adopting the subcell, therefore, gives only the average structure. The true cell contains three molecules, and the space group is $P\bar{1}$. Therefore, one centrosymmetric molecule [**1b-1**] must lie on (0,0,0) and the other two molecules [**1b-2**] must lie on general positions. These two molecules [**1b-1** and **1b-2**] are crystallographically equivalent in the subcell. For the redetermination of the structure, the initial position of the **1b-2** could be easily deduced from the relationship between the true cell and the subcell. The coordinates of the nickel atom on the general position were refined by introducing an artificial bias of ±0.01 (in fraction) to the y parameter. The isotropic temperature factor of 3.0 Å^2 was applied for the nickel atom as the starting parameter. After two cycles of refinement, the temperature factors of the nickel atoms with the initial positions of (0,0,0) and (2/3, +0.01, 1/3) changed to large values of 10.1 and 3.2 Å^2 respectively and those with initial positions of (0,0,0) and (2/3, −0.01, 1/3) to 2.5 and 3.5 Å^2; the resulting atomic coordinates were (0.6657, 0.0209, 0.3258) from (2/3, +0.01, 1/3) and (0.6672, −0.0268, 0.3426)

TABLE 3. FINAL ATOMIC PARAMETERS, TOGETHER WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a)]

Atom	x	y	z	B_{eq}
(a) *trans*-$[\mathrm{Ni}\{\mathrm{C_6H_3(OMe)_2}\text{-}2,6\}_2(\mathrm{PMe_3})_2]$ (**1a**)				
Ni	0.29991(7)	0.10607(3)	0.22247(4)	2.75
P(1)	0.5314(2)	0.07764(7)	0.30317(9)	3.62
P(2)	0.0638(2)	0.14287(7)	0.15554(8)	3.43
C(11)	0.6497(8)	0.1541(4)	0.3561(4)	5.8
C(12)	0.6600(8)	0.0329(4)	0.2479(5)	6.1
C(13)	0.5466(8)	0.0162(4)	0.3929(4)	6.2
C(21)	−0.0739(7)	0.0731(4)	0.0999(4)	4.6
C(22)	−0.0433(7)	0.1852(4)	0.2257(4)	4.9
C(23)	0.0399(7)	0.2135(4)	0.0746(4)	5.4
C(31)	0.1999(6)	0.0374(3)	0.2823(3)	3.3
C(32)	0.1687(6)	0.0577(3)	0.3595(3)	3.6
C(33)	0.0961(7)	0.0118(4)	0.4056(4)	4.5
C(34)	0.0570(7)	−0.0578(4)	0.3765(4)	5.0
C(35)	0.0897(7)	−0.0826(3)	0.3031(4)	4.7
C(36)	0.1604(6)	−0.0344(3)	0.2576(3)	3.7
C(37)	0.1836(8)	0.1562(4)	0.4586(4)	5.9
C(38)	0.1535(9)	−0.1251(4)	0.1504(4)	6.1
C(41)	0.4035(6)	0.1768(3)	0.1648(3)	3.6
C(42)	0.4702(6)	0.1676(3)	0.0961(4)	4.2
C(43)	0.5487(7)	0.2247(4)	0.0666(4)	5.3
C(44)	0.5598(7)	0.2916(4)	0.1038(4)	5.9
C(45)	0.4932(7)	0.3049(3)	0.1692(4)	5.4
C(46)	0.4159(6)	0.2476(3)	0.1979(4)	4.2
C(47)	0.3484(9)	0.0534(4)	0.0458(5)	6.7
C(48)	0.354(1)	0.3237(4)	0.3069(6)	7.7
O(32)	0.2200(5)	0.1277(2)	0.3854(3)	4.5
O(36)	0.1991(5)	−0.0550(2)	0.1833(3)	4.9
O(42)	0.4750(5)	0.1018(3)	0.0559(3)	5.5
O(46)	0.3435(5)	0.2563(2)	0.2637(3)	5.5
(b) *trans*-$[\mathrm{Ni}\{\mathrm{C_6H_3(OMe)_2}\text{-}2,6\}_2(\mathrm{PMe_2Ph})_2]$ (**1b**)				
1b-1				
Ni	0	0	0	2.84
P(1)	0.08351(9)	−0.1875(2)	−0.06879(9)	3.53
C(111)	0.0237(4)	−0.2795(5)	−0.1845(4)	3.6
C(112)	−0.0114(4)	−0.3943(6)	−0.2024(4)	4.6
C(113)	−0.0583(4)	−0.4623(6)	−0.2904(5)	5.5
C(114)	−0.0700(4)	−0.4162(7)	−0.3614(4)	5.5
C(115)	−0.0362(5)	−0.3036(7)	−0.3448(4)	5.8
C(116)	0.0099(4)	−0.2350(6)	−0.2574(4)	4.6
C(12)	0.1462(4)	−0.3352(7)	−0.0094(4)	5.7
C(13)	0.1772(4)	−0.1638(7)	−0.0817(4)	5.3
C(31)	0.0828(4)	0.1156(5)	0.0360(3)	3.4
C(32)	0.0720(4)	0.2014(6)	−0.0168(4)	4.6
C(33)	0.1323(5)	0.2834(7)	0.0091(5)	6.4
C(34)	0.2043(5)	0.2808(7)	0.0876(5)	7.0
C(35)	0.2221(4)	0.1954(7)	0.1437(5)	6.0
C(36)	0.1605(4)	0.1122(6)	0.1156(4)	4.1
C(37)	−0.0301(7)	0.2862(9)	−0.1537(6)	9.2
C(38)	0.2325(5)	0.0358(8)	0.2539(5)	7.6
O(32)	−0.0041(3)	0.1917(5)	−0.0992(3)	6.5
O(36)	0.1711(3)	0.0201(5)	0.1632(3)	5.5
1b-2				
Ni	0.66785(4)	−0.02674(6)	0.34608(4)	2.75
P(1)	0.75716(9)	−0.2171(2)	0.2853(1)	3.80
P(2)	0.57664(9)	0.1721(2)	0.40187(9)	3.30
C(111)	0.6985(4)	−0.3047(5)	0.1682(4)	3.8
C(112)	0.6627(4)	−0.4194(6)	0.1472(4)	4.7
C(113)	0.6160(5)	−0.4825(6)	0.0593(4)	5.8
C(114)	0.6042(5)	−0.4334(7)	−0.0098(4)	6.6
C(115)	0.6375(5)	−0.3173(8)	0.0087(5)	6.6
C(116)	0.6853(4)	−0.2533(7)	0.0978(4)	5.4
C(12)	0.8160(4)	−0.3693(7)	0.3417(5)	6.1
C(13)	0.8547(4)	−0.1947(7)	0.2779(5)	6.4
C(211)	0.6328(4)	0.2912(5)	0.5083(4)	3.4
C(212)	0.6632(4)	0.3985(6)	0.5079(4)	4.4
C(213)	0.7106(4)	0.4839(6)	0.5882(5)	5.5
C(214)	0.7295(4)	0.4613(7)	0.6697(4)	6.0
C(215)	0.6999(5)	0.3559(7)	0.6710(4)	5.8
C(216)	0.6515(4)	0.2705(6)	0.5907(4)	4.6
C(22)	0.5070(4)	0.2949(6)	0.3257(4)	5.0
C(23)	0.4877(4)	0.1530(6)	0.4254(4)	4.9
C(31)	0.7444(3)	0.0922(5)	0.3696(3)	3.2
C(32)	0.7281(4)	0.1631(6)	0.3065(4)	3.8
C(33)	0.7805(5)	0.2524(7)	0.3219(4)	5.2
C(34)	0.8530(4)	0.2693(7)	0.4025(5)	5.5
C(35)	0.8748(4)	0.1981(6)	0.4674(4)	4.7
C(36)	0.8199(4)	0.1121(5)	0.4497(4)	3.6
C(37)	0.6263(5)	0.2129(9)	0.1605(5)	7.6
C(38)	0.9008(5)	0.0708(7)	0.5997(4)	5.8
C(41)	0.5883(4)	−0.1480(5)	0.3146(4)	3.5
C(42)	0.5954(4)	−0.2432(6)	0.3593(4)	4.1
C(43)	0.5323(5)	−0.3254(6)	0.3251(4)	5.5
C(44)	0.4613(5)	−0.3153(7)	0.2453(4)	6.1
C(45)	0.4488(4)	−0.2221(7)	0.1972(4)	4.9
C(46)	0.5118(4)	−0.1408(5)	0.2329(4)	3.7
C(47)	0.7050(5)	−0.1587(7)	0.5040(4)	5.7
C(48)	0.4462(5)	−0.0564(7)	0.0967(4)	6.2
O(32)	0.6560(3)	0.1344(4)	0.2258(3)	5.0
O(36)	0.8366(3)	0.0367(4)	0.5101(3)	4.4
O(42)	0.6668(3)	−0.2713(4)	0.4405(3)	5.9
O(46)	0.5051(3)	−0.0455(4)	0.1892(3)	4.8
(c) *trans*-$[\mathrm{Ni}\{\mathrm{C_6H(OMe)_2}\text{-}2,6\text{-}\mathrm{Br_2}\text{-}3,5\}_2(\mathrm{PMe_3})_2]$ (**2a**)				
Ni	0	0	0	2.22
Br(1)	0.43254(10)	−0.26991(8)	0.19628(13)	6.05
Br(2)	0.29983(12)	0.0598(1)	0.46699(10)	6.27
P(1)	−0.1878(3)	−0.0781(2)	0.07037(18)	2.84
C(11)	−0.2848(12)	−0.1530(8)	−0.0443(9)	5.2
C(12)	−0.3341(10)	−0.0047(7)	0.1260(10)	4.9
C(13)	−0.1594(10)	−0.1613(7)	0.1996(8)	4.1
C(31)	0.1313(8)	−0.0518(6)	0.1296(7)	2.8
C(32)	0.2177(9)	−0.1346(6)	0.1205(8)	3.4
C(33)	0.3180(9)	−0.1573(6)	0.2149(9)	3.8
C(34)	0.3408(9)	−0.1034(7)	0.3182(8)	4.3
C(35)	0.2571(9)	−0.0235(7)	0.3293(8)	3.8
C(36)	0.1535(8)	0.0007(6)	0.2394(7)	3.1
C(37)	0.1063(12)	−0.2080(8)	−0.0586(10)	5.5
C(38)	−0.0330(12)	0.0819(8)	0.3438(10)	5.5
O(32)	0.2188(8)	−0.1926(6)	0.0176(8)	6.7
O(36)	0.0745(7)	0.0832(5)	0.2509(6)	4.1
(d) *trans*-$[\mathrm{Ni}\{\mathrm{C_6H(OMe)_2}\text{-}2,6\text{-}\mathrm{Br_2}\text{-}3,5\}_2(\mathrm{PMe_2Ph})_2]$ (**2b**)				
Ni	0	0	0	2.19
Br(1)	0.54337(8)	−0.36534(7)	0.23880(8)	5.04
Br(2)	0.31851(8)	−0.28545(8)	−0.40566(8)	4.99
P(1)	0.1012(2)	0.1481(2)	−0.0450(2)	2.78
O(32)	0.2887(5)	−0.1445(4)	0.2457(5)	3.6
O(36)	0.0974(5)	−0.0827(4)	−0.3055(5)	3.8
C(111)	0.1096(6)	0.2727(5)	0.0976(7)	3.0
C(112)	−0.0225(7)	0.3554(5)	0.1014(8)	4.0
C(113)	−0.0224(8)	0.4439(6)	0.2146(10)	5.1
C(114)	0.1121(9)	0.4538(7)	0.3257(9)	5.7
C(115)	0.2455(9)	0.3734(8)	0.3244(9)	5.6
C(116)	0.2449(7)	0.2817(6)	0.2111(8)	4.1
C(12)	0.0018(8)	0.2239(6)	−0.2290(7)	4.2
C(13)	0.2950(7)	0.1088(6)	−0.0627(9)	4.2
C(31)	0.1756(6)	−0.1169(5)	−0.0286(6)	2.6
C(32)	0.2912(6)	−0.1763(5)	0.0949(6)	2.7
C(33)	0.4026(6)	−0.2734(5)	0.0695(6)	3.0
C(34)	0.4104(7)	−0.3079(5)	−0.0787(7)	3.3
C(35)	0.3045(6)	−0.2433(5)	−0.2005(6)	3.0
C(36)	0.1900(6)	−0.1495(5)	−0.1773(6)	2.9
C(37)	0.4007(9)	−0.0772(7)	0.3287(8)	4.9
C(38)	−0.0503(8)	−0.1012(7)	−0.3682(8)	4.7

a) Positional parameters are in fraction of cell edges and B_{eq} is the equivalent isotropic temperature factor calculated from the corresponding anisotropic factors.[11)]

from (2/3, −0.01, 1/3), respectively. The Fourier map based on phases of the former set of nickel positions includes many unreasonable supurious peaks especially around the methoxyl group, whereas the Fourier map calculated from the latter set of nickel positions could easily locate all the non-hydrogen atoms except two. The latter structure was then refined isotropically, and the next Fourier synthesis revealed the remaining two atoms. Refinement was then carried out in the same manner as those of **1a**, **2a**, and **2b**; it converged to a reasonable R value.

The details of the refinements for all the crystals are summarized in Table 2. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[10)] Final atomic coordinates of four crystals, together with equivalent isotropic temperature factors B_{eq}[11)] for non-hydrogen atoms are listed in Table 3.[||]

Computation. All the calculations were carried

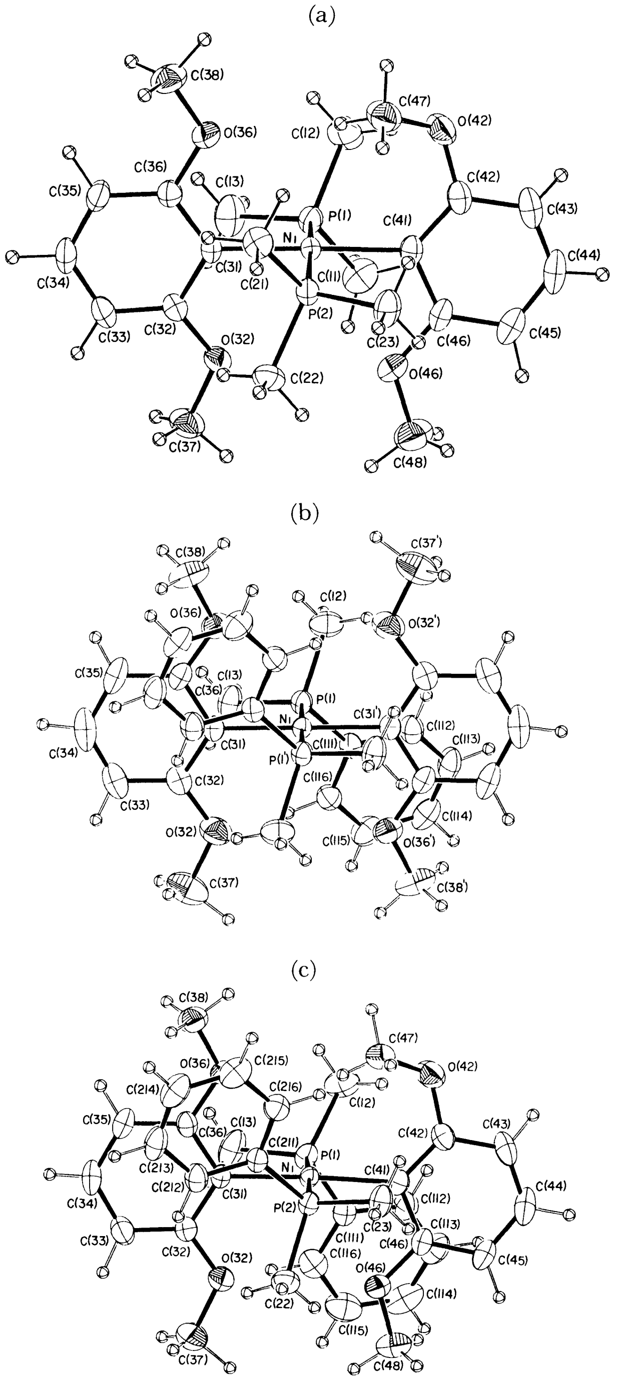
[||] Tables of anisotropic temperature factors for non-hydrogen atoms, the atomic coordinates and isotropic temperature factors for hydrogen atoms, and the observed and the calculated structure factors are deposited as Document No. 8415 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

out on an ACOS S900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

Molecular Structure. The molecular structures of **1a**, **1b-1**, **1b-2**, **2a**, and **2b** are shown in Fig. 1 by the *ORTEP* drawings,[12] together with the atomic numberings. The crystallographic molecular symmetries of **1b-1**, **2a**, and **2b** are C_i. The **1a** and **1b-2** molecules have no crystallographic symmetry, but the local center of symmetry is found in these structures when the conformations of methoxyl groups are ignored. The interatomic bond distances and angles observed in these complexes are summarized in Table 4.

Coordination Geometry of Nickel Atom: The important structural parameters needed to describe the coordination geometry of nickel atom are summarized in Table 5. The first structural feature commonly observed in these complexes is that the nickel atom takes a square-planar coordination with two phenyl and two phosphine ligands on *trans*-positions. As the **1b-1**, **2a**, and **2b** molecules occur on the center of symmetry, the five atoms defining the coordination plane of nickel atom are exactly coplanar. The least-squares planes of the coordination planes in **1a** and **1b-2** are listed in Table 6. The coplanality of the five atoms in **1a** is slightly lower than that of those in **1b-2**. However, the deformation geometry of the coordination planes is the same in both structures; that is, all the four atoms bonding to the nickel atom deviate toward the same direction from nickel atom, bending away from the C(47) atom, which is the only methoxyl methyl group approaching near to nickel atom in these complexes. It is noteworthy that the P(1)–Ni–P(2) bond angle [172.5(1)°] in **1a** shows an angular deviation of



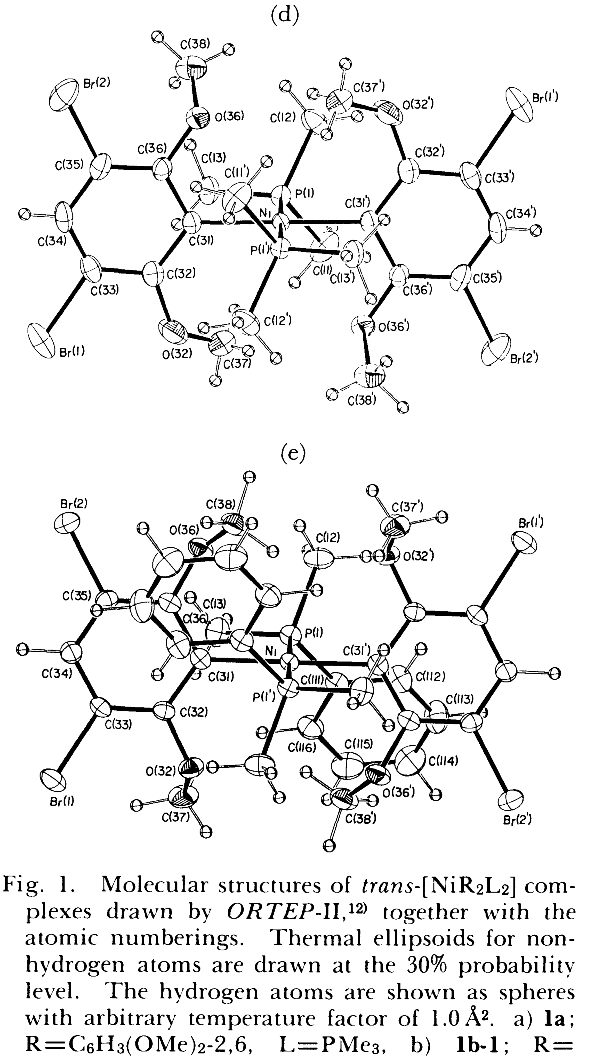


Fig. 1. Molecular structures of *trans*-[NiR_2L_2] complexes drawn by *ORTEP*-II,[12] together with the atomic numberings. Thermal ellipsoids for non-hydrogen atoms are drawn at the 30% probability level. The hydrogen atoms are shown as spheres with arbitrary temperature factor of 1.0 Å^2. a) **1a**; R=$C_6H_3(OMe)_2$-2,6, L=PMe_3, b) **1b-1**; R=$C_6H_3(OMe)_2$-2,6, L=PMe_2Ph, c) **1b-2**; R and L are same as those in **1b-1**, d) **2a**; R=$C_6H(OMe)_2$-2,6-Br_2-3,5, L=PMe_3, e) **2b**; R=$C_6H(OMe)_2$-2,6-Br_2-3,5, L=PMe_2Ph.

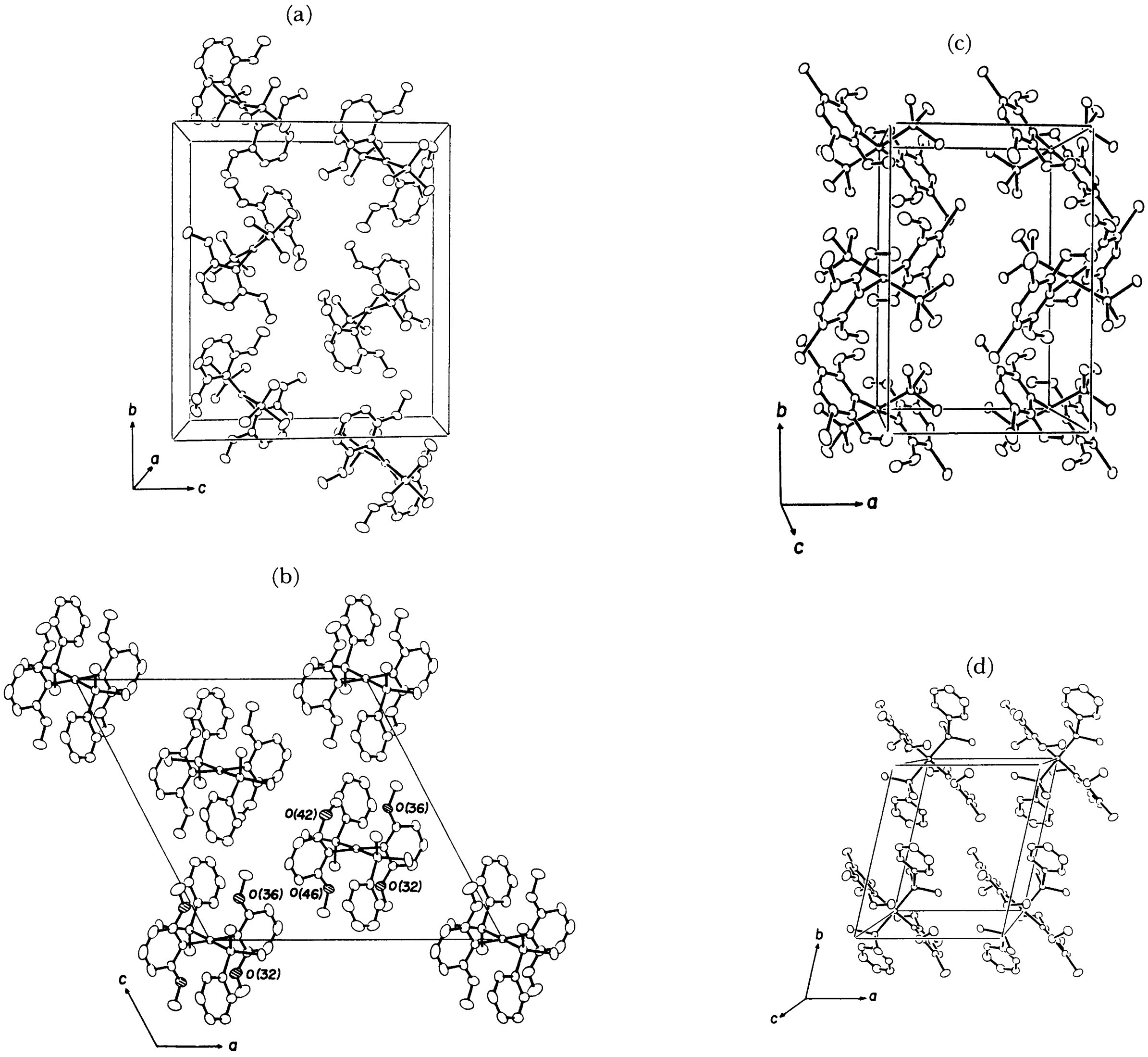


Fig. 2. Crystal structures of *trans*-[NiR_2L_2] complexes. a) **1a**, b) **1b**, c) **2a**, and d) **2b**.

Table 4. Interatomic bond distances and angles, together with their estimated standard deviations in parentheses*

Bond distance	*l*/Å				
	1a	**1b-1**	**1b-2**	**2a**	**2b**
Br(1) -C(33)				1.925(9)	1.902(5)
Br(2) -C(35)				1.922(9)	1.909(6)
P(1) -C(11)	1.818(6)			1.836(10)	
P(1) -C(12)	1.809(7)	1.819(7)	1.827(7)	1.828(10)	1.822(7)
P(1) -C(13)	1.822(7)	1.822(7)	1.828(8)	1.831(9)	1.824(8)
P(2) -C(21)	1.825(6)				
P(2) -C(22)	1.828(6)		1.815(6)		
P(2) -C(23)	1.820(6)		1.830(7)		
P(1) -C(111)		1.826(6)	1.824(6)		1.836(6)
P(2) -C(211)			1.829(6)		
C(111)-C(112)		1.390(8)	1.383(8)		1.389(9)
C(111)-C(116)		1.380(8)	1.387(9)		1.392(9)
C(112)-C(113)		1.389(9)	1.372(9)		1.376(11)
C(113)-C(114)		1.373(9)	1.362(10)		1.379(12)

*Important parameters are selected and summarized in Tables 5 and 7.

Table 4. (Continued)

Bond distance	l/Å				
	1a	1b-1	1b-2	2a	2b
C(114)-C(115)		1.361(10)	1.379(10)		1.380(12)
C(115)-C(116)		1.380(9)	1.394(10)		1.402(11)
C(211)-C(212)			1.387(9)		
C(211)-C(216)			1.380(8)		
C(212)-C(213)			1.389(9)		
C(213)-C(214)			1.373(10)		
C(214)-C(215)			1.368(10)		
C(215)-C(216)			1.394(9)		
C(31) -C(32)	1.405(7)	1.393(8)	1.389(8)	1.423(11)	1.397(7)
C(31) -C(36)	1.391(7)	1.393(8)	1.394(8)	1.404(11)	1.399(7)
C(32) -C(33)	1.385(7)	1.388(10)	1.393(9)	1.392(12)	1.400(7)
C(33) -C(34)	1.370(8)	1.338(11)	1.369(10)	1.358(13)	1.381(8)
C(34) -C(35)	1.380(8)	1.390(11)	1.385(9)	1.375(13)	1.376(8)
C(35) -C(36)	1.396(8)	1.408(9)	1.387(8)	1.384(12)	1.390(8)
C(41) -C(42)	1.402(7)		1.389(8)		
C(41) -C(46)	1.396(7)		1.405(7)		
C(42) -C(43)	1.403(8)		1.399(10)		
C(43) -C(44)	1.356(9)		1.349(10)		
C(44) -C(45)	1.364(9)		1.379(10)		
C(45) -C(46)	1.391(8)		1.387(8)		
C(32) -O(32)	1.385(6)	1.410(8)	1.383(7)	1.377(11)	1.385(7)
C(37) -O(32)	1.413(8)	1.400(11)	1.411(10)	1.324(13)	1.430(9)
C(36) -O(36)	1.392(6)	1.377(7)	1.379(7)	1.383(10)	1.386(7)
C(38) -O(36)	1.406(8)	1.407(9)	1.422(8)	1.440(12)	1.388(9)
C(42) -O(42)	1.376(7)		1.398(8)		
C(47) -O(42)	1.392(8)		1.384(9)		
C(46) -O(46)	1.390(7)		1.381(7)		
C(48) -O(46)	1.411(9)		1.421(8)		

Bond angle	φ/°				
	1a	1b-1	1b-2	2a	2b
Ni -P(1) -C(11)	115.4(2)			115.4(3)	
Ni -P(1) -C(12)	114.1(2)	112.0(3)	115.1(3)	115.8(3)	114.5(2)
Ni -P(1) -C(13)	119.8(2)	119.4(3)	119.3(3)	118.9(3)	117.6(2)
C(11) -P(1) -C(12)	103.6(3)			101.1(5)	
C(11) -P(1) -C(13)	100.3(3)			101.4(4)	
C(12) -P(1) -C(13)	101.3(3)	100.7(4)	100.5(4)	101.6(4)	100.0(3)
Ni -P(1) -C(111)		117.4(2)	114.4(2)		116.0(2)
C(111)-P(1) -C(12)		104.0(3)	103.6(3)		103.2(3)
C(111)-P(1) -C(13)		101.0(3)	101.6(4)		103.2(3)
Ni -P(2) -C(21)	116.8(2)				
Ni -P(2) -C(22)	112.9(2)		112.3(3)		
Ni -P(2) -C(23)	119.9(2)				
C(21) -P(2) -C(22)	103.2(3)				
C(21) -P(2) -C(23)	101.4(3)				
C(22) -P(2) -C(23)	100.0(3)		101.0(3)		
Ni -P(2) -C(211)			116.4(2)		
C(211)-P(2) -C(22)			103.7(3)		
C(211)-P(2) -C(23)			102.1(3)		
C(32) -C(31) -C(36)	114.8(4)	115.7(6)	115.2(5)	115.1(7)	116.0(5)

Table 4. (Continued)

Bond angle	ϕ/°				
	1a	**1b-1**	**1b-2**	**2a**	**2b**
C(31)-C(32)-C(33)	123.3(5)	122.8(7)	123.4(6)	120.2(7)	121.4(5)
C(31)-C(32)-O(32)	113.3(4)	112.8(6)	113.8(5)	124.3(7)	119.2(5)
C(33)-C(32)-O(32)	123.4(5)	124.4(7)	122.9(6)	115.3(7)	119.1(5)
C(32)-C(33)-C(34)	118.9(5)	119.5(8)	118.6(7)	123.4(8)	121.2(5)
C(33)-C(34)-C(35)	121.1(6)	121.9(8)	121.0(7)	117.2(9)	117.5(5)
C(34)-C(35)-C(36)	118.3(5)	117.5(7)	118.4(6)	121.5(8)	121.8(5)
C(31)-C(36)-C(35)	123.5(5)	122.6(6)	123.3(6)	122.5(7)	121.6(5)
C(31)-C(36)-O(36)	114.2(4)	113.8(5)	114.2(5)	117.1(7)	120.7(5)
C(35)-C(36)-O(36)	122.2(5)	123.7(6)	122.4(5)	120.2(7)	117.5(5)
C(32)-C(33)-Br(1)				118.1(6)	120.7(4)
C(34)-C(33)-Br(1)				118.5(7)	118.1(4)
C(34)-C(35)-Br(2)				117.7(7)	118.1(4)
C(36)-C(35)-Br(2)				120.6(6)	120.1(4)
C(32)-O(32)-C(37)	118.3(4)	118.8(7)	118.9(6)	124.6(8)	114.7(5)
C(36)-O(36)-C(38)	118.0(5)	118.1(6)	118.3(5)	115.8(7)	117.9(5)
C(42)-C(41)-C(46)	114.5(5)		114.0(5)		
C(41)-C(42)-C(43)	121.9(5)		122.6(6)		
C(41)-C(42)-O(42)	123.9(5)		124.3(6)		
C(43)-C(42)-O(42)	114.1(5)		113.0(6)		
C(42)-C(43)-C(44)	120.0(6)		120.3(7)		
C(43)-C(44)-C(45)	121.1(6)		120.6(7)		
C(44)-C(45)-C(46)	118.2(6)		118.0(6)		
C(41)-C(46)-C(45)	124.3(5)		124.4(6)		
C(41)-C(46)-O(46)	113.5(5)		113.6(5)		
C(45)-C(46)-O(46)	122.2(5)		121.9(5)		
C(42)-O(42)-C(47)	119.4(5)		119.2(6)		
C(46)-O(46)-C(48)	120.2(5)		118.6(5)		
P(1)-C(111)-C(112)		121.4(5)	121.2(5)		120.3(5)
P(1)-C(111)-C(116)		121.0(5)	120.5(5)		121.2(5)
C(112)-C(111)-C(116)		117.6(6)	118.3(6)		118.3(6)
C(111)-C(112)-C(113)		121.3(6)			121.8(7)
C(112)-C(113)-C(114)		119.6(7)	120.3(7)		119.8(8)
C(113)-C(114)-C(115)		119.7(7)	119.9(7)		119.7(8)
C(114)-C(115)-C(116)		120.9(7)	120.0(7)		120.5(7)
C(111)-C(116)-C(115)		121.0(6)	120.1(7)		119.8(6)
P(2)-C(211)-C(212)			120.4(5)		
P(2)-C(211)-C(216)			121.2(5)		
C(212)-C(211)-C(216)			118.3(6)		
C(211)-C(212)-C(213)			121.0(6)		
C(212)-C(213)-C(214)			120.1(7)		
C(213)-C(214)-C(215)			119.5(7)		
C(214)-C(215)-C(216)			120.8(7)		
C(211)-C(216)-C(215)			120.4(6)		

7.5 ° from the exact *trans* coordination, while the other P-Ni-C and P-Ni-P bond angles in Table 5 take the value near to 90 ° and 180 °, respectively. The second structural feature to note is that the ring planes of phenyl ligands are nearly perpendicular to the coordination plane of nickel atom. The dihedral angles between these planes in Table 5 show that almost all the phenyl ligands are normal to the coordination plane within several degrees, with one exception having the relatively large deviation of 13.9 ° from the right angle in the **2b** molecule. The third interesting feature is that the phosphine ligands take a very characteristic conformation, with one methyl group located roughly on the coordination plane of nickel atom regardless of the types of phosphine ligands, PMe_3 or PMe_2Ph. The torsional angles ϕ_1 and ϕ_2 in Table 5 are the measure to

TABLE 5. COORDINATION GEOMETRIES OF NICKEL ATOMS IN **1a**, **1b**, **2a**, AND **2b**

	1a	**1b-1**	**1b-2**	**2a**	**2b**
P(1) -Ni-C(31)	90.6(1)°	89.4(2)°	89.2(2)°	92.8(2)°	89.8(2)°
P(1) -Ni-C(41)	88.6(2)		89.5(2)		
P(2) -Ni-C(31)	87.7(1)		88.9(2)		
P(2) -Ni-C(41)	92.9(2)		92.3(2)		
P(1) -Ni-P(2)	172.5(1)		176.6(1)		
C(31)-Ni-C(41)	178.5(2)		176.6(3)		
ϕ_1 [a]	−6.0°	−8.5°	−1.4°	−4.6°	−7.2°
ϕ_2 [a]	3.2		14.4		
θ_1 [b]	92.3	89.2	90.6	91.0	103.9
θ_2 [b]	84.1		96.8		

a) Torsional angles around Ni-P bonds: $\phi_1=\phi_{C(31)\text{-}Ni\text{-}P(1)\text{-}C(13)}$, $\phi_2=\phi_{C(41)\text{-}Ni\text{-}P(2)\text{-}C(23)}$. b) Dihedral angles between Ni-coordination plane and phenyl ring planes: θ_1 and θ_2 correspond with the phenyl rings defined by C(31) to C(36) and by C(41) to C(46), respectively.

TABLE 6. COORDINATION PLANES OF NICKEL ATOMS IN **1a** AND **1b-2** MOLECULES

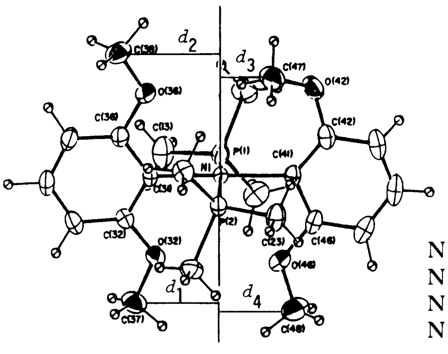
Least-squares plane through Ni, P(1), P(2), C(31), and C(41) atoms in the form of $AX+BY+CZ+D=0.0$, where X, Y, Z are the coordinates in the orthogonal unit cell in Å.

1a	$0.2192X-0.6949Y-0.6849Z+3.4467=0.0$
1b-2	$-0.0545X+0.4415Y-0.8956Z+5.6687=0.0$

Atomic deviations from the least-squares plane in Å.

	Ni	P(1)	P(2)	C(31)	C(41)
1a	0.066	−0.076	−0.070	0.044	0.040
1b-2	−0.043	0.010	0.011	0.011	0.012

TABLE 7. CONFORMATIONS OF METHOXYL GROUPS AND RELATED STRUCTURAL PARAMETERS IN **1a**, **1b**, **2a**, AND **2b**



1a

	1a	**1b-1**	**1b-2**	**2a**	**2b**
ϕ_1 [a]	175.0°	172.0°	173.0°	−31.8°	−106.7°
ϕ_2 [a]	−175.7	−164.4	−168.6	111.7	−79.3
ϕ_3 [a]	36.0		34.3		
ϕ_4 [a]	176.4		164.1		
d_1 [b]	2.365Å	2.516Å	2.403Å	1.339Å	2.286Å
d_2 [b]	2.801	2.467	2.706	2.249	1.312
d_3 [b]	1.425	2.516 [c]	1.447	1.339 [c]	2.286 [c]
d_4 [b]	2.069	2.467 [c]	2.009	2.249 [c]	1.312 [c]
$(d_1+d_4)/2$	2.217	2.492	2.206	1.794	1.799
$(d_2+d_3)/2$	2.113	2.492 [c]	2.077	1.794 [c]	1.799 [c]
Ni-C(31)-C(32)	120.0(3)°	123.0(5)°	121.8(4)°	126.5(6)°	122.9(4)°
Ni-C(31)-C(36)	125.2(4)	121.3(5)	122.9(4)	118.2(6)	121.1(4)
Ni-C(41)-C(42)	130.2(4)		130.5(5)		
Ni-C(41)-C(46)	115.3(4)		115.5(4)		
Ni-P(1)	2.170(2)Å	2.168(1)Å	2.168(2)Å	2.220(2)Å	2.224(1)Å
Ni-P(2)	2.175(1)		2.188(2)		
Ni-C(31)	1.933(5)	1.928(5)	1.931(5)	1.962(8)	1.945(5)
Ni-C(41)	1.954(5)		1.951(5)		

a) Torsional angles around C(phenyl)-O(methoxyl) bonds: $\phi_1=\phi_{C(31)\text{-}C(32)\text{-}O(32)\text{-}C(37)}$, $\phi_2=\phi_{C(31)\text{-}C(36)\text{-}O(36)\text{-}C(38)}$, $\phi_3=\phi_{C(41)\text{-}C(42)\text{-}O(42)\text{-}C(47)}$, and $\phi_4=\phi_{C(41)\text{-}C(46)\text{-}O(46)\text{-}C(48)}$. b) Distances from methoxyl methyl carbons to the normal of the coordination plane through Ni atom: d_1, d_2, d_3, and d_4 correspond with the C(37), C(38), C(47), and C(48) atoms, respectively. c) These parameters are not crystallographically unique but are listed for the sake of better understanding.

estimate the angular deviation of the unique methyl group of each phosphine ligand from the coordination plane; the maximum angular deviation observed is 14.4° of ϕ_2 in **1b-2** molecule.

Conformation of Methoxyl Group: The selected structural parameters for the conformations of methoxyl groups are listed in Table 7. The most interesting and important difference in the molecular structures of this series of complexes is the difference in the conformations of methoxyl groups, which are influenced very sensitively by the steric and/or electrostatic effect in the different types of phosphine ligands and/or the different substituents on *m*-positions.

The torsional angles around the O(methoxyl)–C(phenyl) bond (ϕ's in Table 7) were calculated as the measure to describe the conformation of methoxyl groups. When the methoxyl methyl groups are near the nickel atom, the ϕ angles become smaller, and when the methoxyl methyl groups are far from the nickel atom and near the substituents on *m*-positions, the ϕ angles become larger. Five independent molecules in Table 7 are divided into three conformers according to the conformations of methoxyl groups. The **1b-1** molecule gives one extreme case (Conformer A), in which all of the four methoxyl groups (only two are crystallographically independent) take the ϕ values near to 180°, indicating that all the methoxyl groups are located far from the nickel atom and near the *m*-substituents (H atoms). The molecules **1a** and **1b-2** have similar structures (Conformer B): one of the four methoxyl groups has the angle of 36.0° in **1a** and 34.3° in **1b-2** respectively, and the remaining three methoxyl groups have ϕ angles between 164.1° and 176.4°; this shows that only one methoxyl methyl is located near the nickel atom. The *m*-brominated derivatives, **2a** and **2b**, give the third conformer (Conformer C), in which all the ϕ angles are much smaller than 180°, the maximum value being 111.7° in the **2a** molecule.

The distances from the methoxyl carbons to the normal of the coordination plane passing through the nickel atom are calculated (*d*'s in Table 7) to estimate the free space of the 5th and/or 6th coordination sites of nickel atom. The average values of these distances on each coordination site of nickel atom are devided clearly into three types corresponding to the three types of conformers found in these complexes. The Conformer A [**1b-1**] gives the longest *d* distance of 2.492 Å on both sites of the coordination plane of nickel atom. Conformer B [**1a** and **1b-2**] takes a little shorter *d* distances, between 2.077 and 2.217 Å, than the Conformer A. On the other hand, Conformer C [the *m*-substituted derivatives **2a** and **2b**] takes the shortest *d* distances of 1.794 and 1.799 Å.

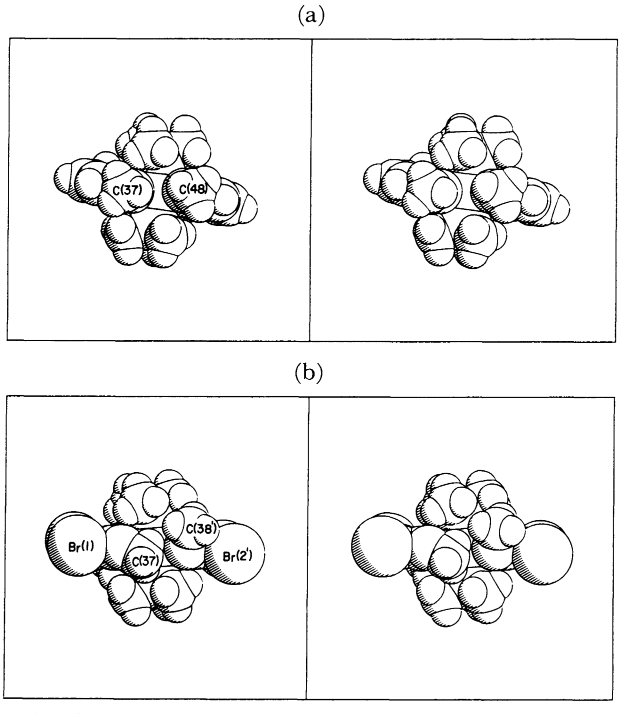


Fig. 3. Stereoscopic views of the molecular structures of **1a** and **2a** complexes shown by the space filling models drawn by *PLUTO*-78.[13] a) **1a**, b) **2a**.

The bond distances and angles included in the coordination plane of nickel atom show some interesting deformations which are correlated to the conformational differences of *o*-methoxyl groups and *m*-substituents. The Ni–C(phenyl) distances are divided into two types. The shorter ones are the Ni–C(31) bonds in *m*-unsubstituted molecules with two methoxyl groups near to the *m*-substituents: from 1.928(5) to, 1.933(5) Å. The longer ones are the the Ni–C(phenyl) bonds in *m*-unsubstituted molecules with one methoxyl group near to the nickel atom, and those in *m*-brominated molecules with two methoxyl groups near to the nickel atom: from 1.945(5) to 1.962(8) Å. Similar structural deformations are also found in Ni–P distances. The Ni–P distances in *m*-brominated molecules [**2a** and **2b**: 2.220(2) and 2.224(1) Å] are significantly longer than those in *m*-unsubstituted ones [**1a**, **1b-1**, and **1b-2**: from 2.168(2) to 2.188(2) Å]. The Ni–C(phenyl)–C(phenyl) angles also reflect the steric effect of methoxyl groups. The corresponding angles associated with the phenyl ligand with different conformations of methoxyl groups, one near to the *m*-substituent and another near to the nickel atom, show a remarkable difference: Ni–C(41)–C(42) angles [130.2(4) and 130.5(5)°] are much larger than the Ni–C(41)–C(46) ones [115.3(4) and 115.5(4)°] in **1a** and **1b-2**. These structural deformations are the causes of the slightly shorter *d* distances [$(d_1+d_4)/2$] in **1a** and **1b-2** molecules (2.217 Å in **1a** and 2.206 Å in **2b**) compared to that in **1b-1** (2.492 Å); this occurs in spite of the similar conformations of the methoxyl groups on the corresponding sites of the coordination plane. The structural deformations found in these molecules show that the Ni–C(phenyl), Ni–P distances and Ni–C(phenyl)–C(phenyl) angles are very flexible and sensitive to the steric effect of the methoxyl groups onto the nickel atom and its ligand molecules.

Crystal Structures. The crystal structures of **1a**, **1b**, **2a**, and **2b** complexes are shown in Fig. 2. No intermolecular distance shorter than the normal van der Waals contact is found in these structures. The molecular packing in **1b** crystal is projected the b* axis [Fig. 2(b)], which shows surprisingly identical molecular arrangement of crystallographically independent two molecules [**1b-1** and **1b-2**] in the unit cell. The only difference in these molecules is found in the conformation of the methoxyl group [O(42)–C(47)]. This specific packing structure in **1b** resulted in the systematically weak diffraction intensities of 2/3 of the total reflections observed from this crystal.

Concluding Remarks. The intermolecular exchange of the *t*-phosphine ligands are catalyzed by carbon monoxide between **1a** and **1b** but not between **2a** and **2b**.[1] The X-ray structure determinations of these complexes seem now to have revealed the structural evidence needed to understand the reactivity differences. We observed the largest structural difference between these complexes in spatial locations of methoxyl methyl group on *o*-positions, as shown by the space filling models of **1a** and **2a** complexes in Fig. 3.[13] Probably due to the relative lack of spatial restriction, the methoxyl methyl groups in **1a** and **1b** can adopt a variety of directions around the

C(phenyl)–O bond, both in the solid state as observed and in solution, too. It then can yield spatial free coordination sites on nickel atom both above and below the four-coordination plane by taking the conformations of methoxyl groups directed toward the *m*-substituents. Both such 5th and 6th coordination sites of nickel atom in *m*-brominated complexes **2a** and **2b** are completely confined by the four methoxyl methyl groups, at least in the solid state. Due to the spatial restriction caused by the large *m*-substituents, the rotational flexibility of the methoxyl groups must be highly restricted even in solution to the direction apart from the *m*-position, toward the phosphine ligands and closer to the nickel atom. The nickel atom there must be well protected from the attack of carbon monoxide.

Another structural feature related to the reactivity difference seems to exist in the flexibilities of C–Ni–C and P–Ni–P bond angles. The observed coplanality of these five atoms in **1a** and **1b** is poorer in the crystals than that in **2a** and **2b**, which suggests the flexibility of these bond angles in **1a** and **1b** in solution. If so, this flexibility enables the coordination of the fifth ligand such as carbon monoxide on the nickel to be more facile by bending one of these bonds (C–Ni–C and P–Ni–P) toward the opposite side of the fifth ligand. The observed coplanality for **2a** and **2b** are higher in the crystals. The deviational motions of these bonds in solution must be restricted by the steric interaction between the methoxyl methyl groups locating over and below the coordination plane.

An analogous effect may be expected from the observed deviations of Ni–C–C bond angles from 120° in **1a** and **1b**.

References

1) M. Wada, K. Nishiwaki, and Y. Kawasaki, *J. Chem. Soc., Dalton Trans.*, **1982**, 1443.

2) G. van Koten, A. J. Leusink, and J. G. Noltes, *J. Organomet. Chem.*, **85**, 105 (1975).

3) A. J. Leusink, G. van Koten, and J. G. Noltes, *J. Organomet. Chem.*, **56**, 379 (1973).

4) G. van Koten, C. A. Schaap, J. T. B. H. Jastrzebski, and J. G. Noltes, *J. Organomet. Chem.*, **186**, 427 (1980).

5) F. A. Cotton and M. Miller, *J. Am. Chem. Soc.*, **99**, 7886 (1977).

6) F. A. Cotton, S. A. Koch, and M. Miller, *Inorg. Chem.*, **17**, 2087 (1978)

7) D. Xu Y. Kai, K. Miki, N. Kasai, K. Nishiwaki, and M. Wada, *Chem. Lett.*, **1983**, 591.

8) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, M. M. Woolfson (1978). *MULTAN*-78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Bergium.

9) T. Ashida (1979). *HBLS*-V, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka Univ.

10) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, p. 71.

11) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

12) C. K. Johnson, *ORTEP*-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1974).

13) *PLUTO*-78, "User Manual for Cambridge Crystallographic Database," Crystallographic Data Center, University Chemical Labolatory, Cambridge (1978).