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META-SUBSTITUTION EFFECT ON THE MOLECULAR STRUCTURES OF BIS(*ORTHO*-DIMETHOXYPHENYL)NICKEL(II) COMPLEXES

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Molecular structures of novel *trans*-[NiR_2L_2] complexes [L=PMe_3, R=$C_6H_3(OMe)_2$-2,6 (<u>1a</u>) and $C_6H(OMe)_2$-2,6-Br_2-3,5 (<u>2a</u>)] were determined by the X-ray crystal structure analysis, which revealed a remarkable effect of *meta*-bromo-substitution on the conformation of the *ortho*-methoxy groups, correlating well with the reactivity difference between <u>1a</u> and <u>2a</u> toward carbon monoxide.

It is well-known that σ-bonded organonickel(II) complexes of types *trans*-[Ni(aryl)X$(PR_3)_2$] and *trans*-[Ni$(aryl)_2(PR_3)_2$] are more stable when the aryl is an *ortho*-substituted aromatic group than when an *ortho*-unsubstituted,[1)] while the detailed role of such *ortho*-substituents has not well understood.[2)] In continuation of our own studies in this area, we have recently investigated the preparation and reaction of bis(2,6-dimethoxyphenyl)nickel(II) complexes, *trans*-[Ni{C_6H_3-$(OMe)_2$-2,6}$_2(PR_3)_2$] [PR_3=PMe_3 (<u>1a</u>), PMe_2Ph (<u>1b</u>)], and their *meta*-brominated derivatives, *trans*-[Ni{$C_6H(OMe)_2$-2,6-Br_2-3,5}$_2(PR_3)_2$] [PR_3=PMe_3 (<u>2a</u>), PMe_2Ph (<u>2b</u>)].[3)] These two types of complexes remarkably differed in the reactivity toward carbon monoxide, which catalyzed the intermolecular exchange of the PR_3 ligands between <u>1a</u> and <u>1b</u> but not between <u>2a</u> and <u>2b</u>.[3)] In order to obtain the structural informations for understanding the difference, the molecular structures of <u>1a</u> and

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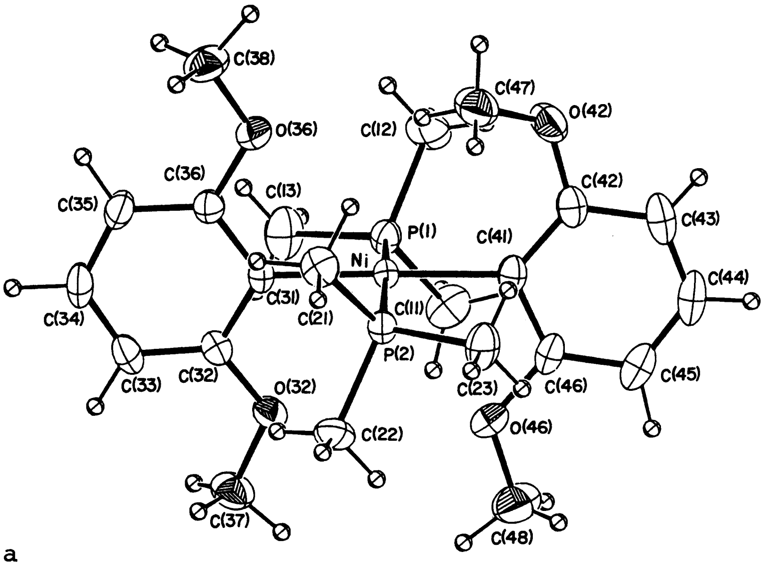
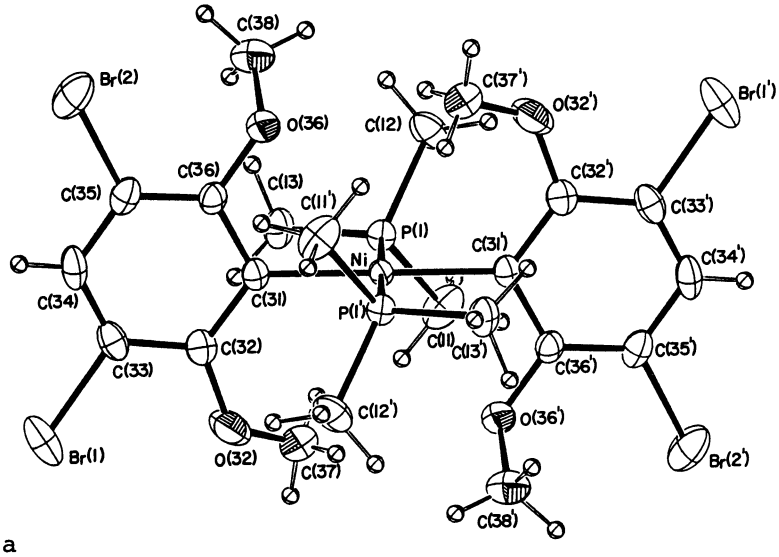
2a have been determined by the X-ray crystal structure analysis.

Crystal Data: 1a, $C_{22}H_{36}O_4P_2Ni$, M=485.2, monoclinic, $P2_1/c$, a=8.737(2), b=18.282(3), c=16.319(4) Å, β=105.06(2)°, U=2517.1(9) Å^3, Z=4, D_c=1.280, D_m=1.284 g cm^{-3}, 2a, $C_{22}H_{32}Br_4O_4P_2Ni$, M=800.8, monoclinic, $P2_1/c$, a=9.264(2), b=14.091(3), c=10.770(2) Å, β=92.06(3)°, U=1409.6(5) Å^3, Z=2, D_c=1.886, D_m=1.884 g cm^{-3}. The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with graphite-monochromatized Mo*K*α radiation. 5492 and 3885 reflections were collected up to 2θ=54° by the θ-2θ scan method, of which 4355 and 2280 were considered significant [$|F_o|>3\sigma(F_o)$] and were used for the structure refinements for 1a and 2a complexes, respectively. The crystal structures were solved by the conventional heavy atom method and refined by the block-diagonal least-squares (*HBLS*-V),[4)] (non-hydrogen atoms anisotropic, hydrogen atoms isotropic) to the R indices of 0.062 and 0.052 for 1a and 2a, respectively.

The molecular structures of 1a and 2a are shown in Figure 1 together with atomic numberings.[5)] The 2a molecule has a crystallographic C_i symmetry. The common features in these structures are as follows: (i) the nickel atom takes a square-planar coordination with two phenyl and two phosphine ligands on *trans* positions, (ii) the phenyl ligands are almost perpendicular to the nickel coordination plane, (iii) the phosphine ligands take a conformation locating one methyl group roughly on the coordination plane. The most interesting difference in these structures is seen in the location of methoxy methyl groups. In 1a molecule, three methoxy methyl groups [C(37), C(38), and C(48)] locate away from the nickel atom and close to the hydrogen atoms on *meta*-positions, the corresponding interatomic distances being 2.56(5), 2.48(5), and 2.39(5) Å, respectively. On the other hand, the remaining methoxy group [C(47)] locates above the nickel atom and close to a methyl group [C(12)] of phosphine ligand, C(47)...C(12) being 3.710(10) Å. In 2a molecule, all the methoxy methyl groups are pushed toward the nickel atom by sterically bulky bromine atom on *meta*-position. The C(38) atom is close to Br(2) [3.327(11) Å], C(37') [3.600(16) Å], and C(12) [3.781(15) Å], while C(37) is close to C(12') [3.750(15) Å] and C(13) [3.838(14) Å] as well as to C(38'). These conformations result in that the distances from methoxy carbons to the normal of coordination plane through nickel atom are 2.365, 2.801, 1.425 and 2.069 Å (av. 2.165 Å) in 1a and 2.249 and 1.346 Å (two carbons, respectively) (av. 1.798 Å) in 2a. Related to these results, some other differences are found between the



1a

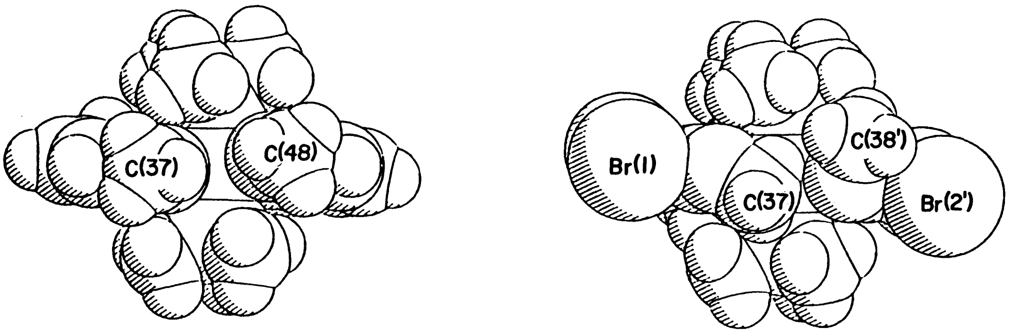


2a

Fig. 1. Molecular structures of *trans*-[NiR_2L_2] complexes [L=PMe_3, R=$C_6H_3(OMe)_2$-2,6 (1a) and $C_6H(OMe)_2$-2,6-Br_2-3,5 (2a)]. Thermal ellipsoids are drawn at the 30% probability level.

structural parameters in these molecules; the Ni-P and Ni-C(Ph) distances are shorter in 1a [Ni-P(1)=2.170(2), Ni-P(2)=2.175(1), Ni-C(31)=1.933(5), and Ni-C(41) =1.954(5) Å] than those in 2a [Ni-P(1)=2.216(2) and Ni-C(31)=1.958(8) Å]. The Ni-C-C angles distribute in a wide range; Ni-C(31)-C(32)=120.0(3), Ni-C(31)-C(36) =125.2(4), Ni-C(41)-C(42)=130.2(4), and Ni-C(41)-C(46)=115.3(4)° in 1a and Ni-C(31)-C(32)=126.5(6) and Ni-C(31)-C(36)=118.2(6)° in 2a, suggesting the flexibility of the Ni-phenyl bond.

The space-filling models of these structures (Fig. 2)6) revealed that the nickel atom in 2a is completely confined by the four methoxy groups, while that the nickel atom in 1a has a free space on one side of its coordination plane.



1a 2a

Fig. 2. Space-filling models of 1a and 2a complexes.

As a molecule of carbon monoxide approaches, the free space in 1a can further expand due to the flexibility of Ni-phenyl bonds and due to the presence of enough room for the methoxy groups to rotate about the C-OMe bond. In 2a molecule, the presence of bulky bromine atoms at the *meta*-positions prevent such intramolecular motions, and this molecule presents an interesting example of remote substitution effect on the reactivity of nickel atom.

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