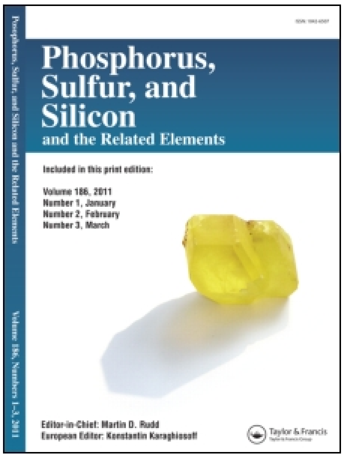

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COCRYSTALLIZATION OF TWO DIFFERENT PSEUDOROTAMERS OF MONOCYCLIC PHOSPHORANE BEARING TWO MARTIN LIGANDS

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Solution and crystal structures of monocyclic pentacoordinate phosphoranes bearing two Martin ligands and two carbon substituents are described. When the two carbon substituents are different, relative apicophilicity of the two monodentate carbon substituents could be determined based on the equilibrium ratio of the pseudorotamers. In some cases, x-ray structural analysis could be carried out and the crystallized structure from CH_3CN is consistent with the major pseudorotamer in solution (CD_3CN). Furthermore, when the equilibrium ratio of pseudorotamers is almost unity, novel cocrystallization of two pseudorotamers in a single crystal was observed.

Keywords: Apicophilicity; hypervalent; phosphorus; pseudorotamer; solvent effect; x-ray structure

We have reported on synthesis, structure, and stereomutation of spirophosphoranes exhibiting reversed apicophilicity (*O-cis*) **1**[1,2] (Figure 1). *O-cis*-phosphorane **1** could be converted to the corresponding *O-trans*-phosphorane **2** irreversibly by heating in solution. Kinetic measurements revealed that **1b** was less stable than **2b** by >12 kcal/mol. Reactivities of *O-cis*- and *O-trans*-phosphoranes toward nucleophiles such as MeLi or n-$Bu_4N^+F^-$: tetra-n-butyl ammonium fluoride (TBAF) were also investigated to find out whether there was enhanced electrophilicity of the former in comparison with the latter. In the course of

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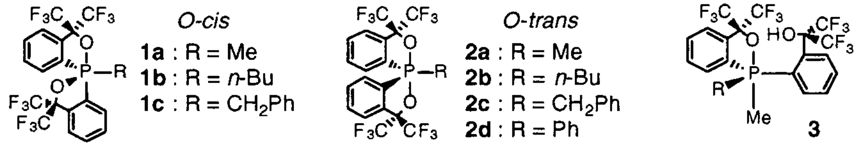


FIGURE 1

these studies, the resulting monocyclic phosphoranes **3** were found to have unique structural characteristics in the liquid and the solid phase. Here we describe structural details of **3** by means of nuclear magnetic resonance (NMR) spectroscopy and x-ray crystallographic analysis.

RESULTS AND DISCUSSION

Synthesis

Monocyclic phosphoranes bearing an alkyl substituent and a methyl group **3a–3c** were synthesized by the reaction of corresponding *O-cis*-phosphorane **1a–1c** with MeLi in 9.6, 82, and 30% yield, respectively (Figure 2). It is noteworthy that **3a–3c** could not be synthesized from corresponding *O-trans* isomer **2a–2c** due to its reduced electrophilicity on phosphorus in comparison with **1a–1c**. However, an aryl derivative **3d** could be prepared from *O-trans*-phosphorane **2d**, which could be more electrophilic than **2a–2c**. Monocyclic phosphoranes **3** were stable in air at room temperature.

Solution Structure

Phosphorane **3a** (R = Me) showed one singlet in ^{31}P-NMR (δ −34.8) and two methyl signals in ^{1}H-NMR [δ 2.57 (d, 3H, $^{2}J_{\text{P–H}} = 13.7$ Hz), 1.46 (d, 3H, $^{2}J_{\text{P–H}} = 5.9$ Hz)] in $CDCl_3$ (Figure 3). Since coupling constants between an equatorial ligand and the central atom have been known to be larger than those between an apical ligand and the central atom,[3]

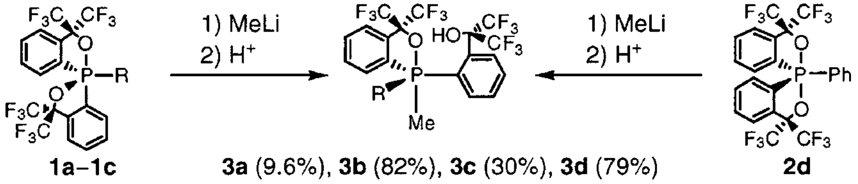


FIGURE 2

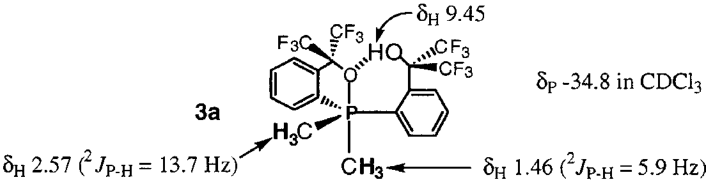


FIGURE 3

the two methyl signals in ^{1}H-NMR correspond to the equatorial and the apical one, respectively. That is, an interchange of the apical and the equatorial methyl group by Berry pseudorotation is frozen in the NMR time scale due to the intramolecular hydrogen bond between the hydroxy proton and the apical oxygen of the Martin ligand. The slow pseudorotation is rarely observed for monocyclic phosphoranes.

The aryl derivative **3d** (R = Ph) showed one singlet in ^{31}P-NMR $\{\delta\ -22.5\}$ and one methyl signal in ^{1}H-NMR [δ 2.75 (d, 3H, $^2J_{\mathrm{P-H}} =$ 13.7 Hz)] in $CDCl_3$. These signals indicated that only methyl-equatorial phenyl-apical pseudorotamer (**3dB**) was observed in solution (Figure 4). On the other hand, **3b** (R = *n*-Bu) showed two singlets in ^{31}P-NMR $\{\delta\ -24.2, -26.2\}$ and two sets of methyl and *n*-butyl group in ^{1}H- and ^{13}C-NMR. That is, **3b** exists as an equilibrium mixture of the two pseudorotamers (**3bA** and **3bB**) (Figure 4). The equilibrium ratio (**3bA:3bB** = 5:1) can be explained based on steric and electronic factors according to the apicophilicity concept:[4] that is, the methyl group is less bulky and more electron withdrawing than the *n*-butyl group, and therefore the former is more apicophilic than the latter. In the case of

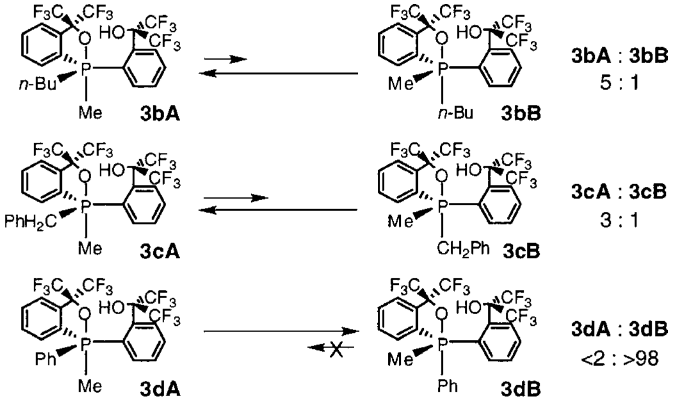
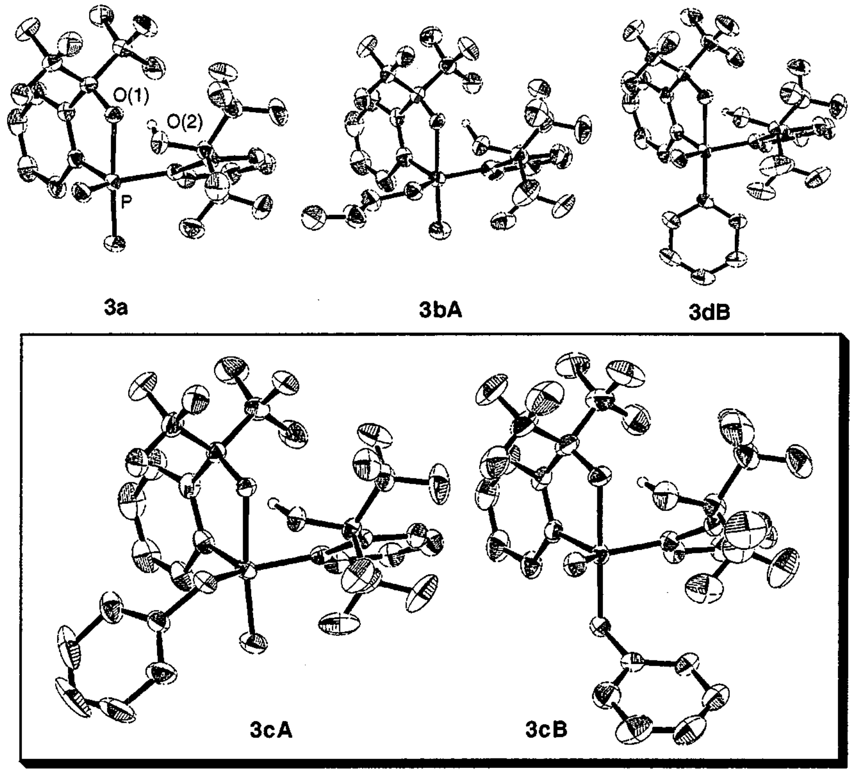


FIGURE 4

3c (R = CH_2Ph), **3cA:3cB** was 3:1 in $CDCl_3$. Interestingly, the ratio **3cA:3cB** became 1:1.2 in CD_3CN.

Crystal Structure

All monocyclic phosphoranes **3** were crystallized out from CH_3CN solution, and were successfully analyzed by x-ray crystallography (Figure 5). The crystal structure of **3a** was a slightly distorted TBP structure, and was consistent with that expected from NMR studies. One of the two methyl groups occupied the apical position [P—C(apical), 1.856(4) Å], and the other was located at the equatorial site [P—C(equatorial), 1.818(5) Å]. The distance between the apical oxygen [O(1)] and the hydroxy oxygen [O(2)] was 2.5 Å, and the distance indicated presence of the intramolecular hydrogen bond. In **3d**, the phenyl group occupied the apical position exclusively. In the case of **3b**, only pseudorotamer **3bA**, which was predominant in the equilibrium



3a **3bA** **3dB**

3cA **3cB**

FIGURE 5

in solution, was obtained as crystals. Surprisingly, **3c** existed as a 1:1 mixture of **3cA** and **3cB** in the solid state. This phenomenon might be due to the close equilibrium ratio (**3cA:3cB** = 1:1.2) in CD_3CN. To the best of our knowledge, this is the first example of cocrystallization of two different pseudorotamers in one single crystal.

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