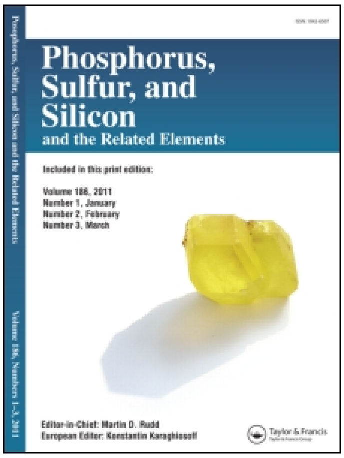

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Chemistry of Carbaphosphatranes

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Chemistry of Carbaphosphatranes

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A 5-carbaphosphatrane and a 6-carbaphosphatrane were synthesized by utilizing triarylmethyl-type tetradentate ligands. Their structures were determined by X-ray crystallographic analysis to reveal that they have nealy ideal trigonal bipyramidal structures with a perfectly anti-apicophilic arrangement. $^1J_{PH}$ *and* $^1J_{PC}$ *values of carbaphosphatranes were shown to be extraordinarily large as an apical coupling constant. The reactivities of carbaphosphatranes based on the tautomerization with their corresponding phosphonites were demonstrated in some reactions.*

Keywords Anti-apicophilic; hypervalent; phosphorane; tautomerism; trigonal bipyramidal; X-Ray crystallography

INTRODUCTION

While a variety of main group atranes have been reported so far,[1] there has been no example of an atrane bearing a carbon atom at 5-position instead of a group 15 element such as nitrogen or phosphorus. Recently, we have reported the synthesis and structure of 5-carbaphosphatrane **1**, the first example of 5-carbon analogues of phosphatranes. Beside of its thermodynamically disfavored anti-apicophilic arrangement, 5-carbaphosphatrane **1** showed remarkably thermal stability.[2] In the course of our study, we also synthesized ring-expanded analog, 6-carbaphosphatrane **2** as the mixture of its trivalent tautomer.[3] Herein we report the syntheses, structures and reactivities of carbaphosphatranes.

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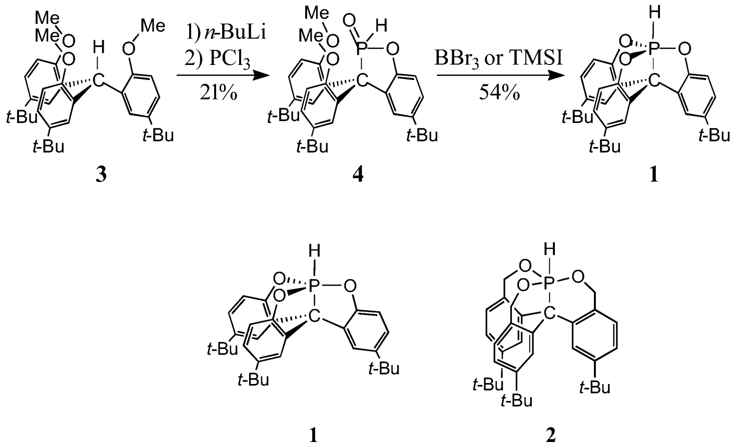
RESULTS AND DISCUSSIONS

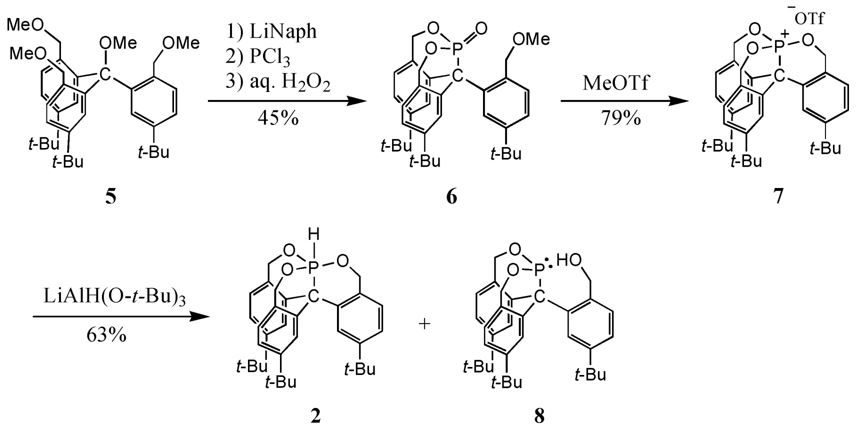
Lithiation of triarylmethane **3** followed by the reaction with phosphorus trichloride at 50°C gave cyclic phosphinate **4** via intramolecular cyclization and hydrolysis. 1-Hydro-5-carbaphosphatrane **1** was synthesized by the reaction of cyclic phosphinate **4** with tribromoborane in $CHCl_3$. Treatment of **4** with iodotrimethylsilane at room temperature in $CDCl_3$ also afforded **1** (Scheme 1).



SCHEME 1

On the other hand, lithiation of methyl ether **5** with 2 equiv. of lithium naphthalenide (LiNaph) and subsequent treatment with phosphorus trichloride under refluxing condition gave a bicyclic phosphonite as a result of two intramolecular cyclization reactions with loss of chloromethane, which was oxidized to bicyclic phosphonate **6** by aqueous H_2O_2. Phosphonium salt **7** was obtained by the reaction of **6** with 5 equiv. of methyl triflate. Treatment of **7** with 1 equiv. of lithium tri(*t*-butoxy)aluminum hydride gave a mixture of 1-hydro-6-carbaphosphatrane **2** and its tautomer, phosphonite **8** (Scheme 2).

The structure of **1** was established by X-ray crystallographic analysis (Figure 1a). The apical bond lengths of **1** are 1.921(2) and 1.38(2) Å for the P—C and P—H bonds, respectively, and the sum of the angles between equatorial bonds is 359.7°. The figure clearly shows that **1** has a nearly ideal trigonal bipyramidal structure, where the apical positions are occupied by hydrogen and carbon atoms while three oxygen atoms are located at the equatorial positions. It is well known that phosphoranes usually bear electronegative atoms at the apical positions and electropositive atoms at the equatorial positions according to



SCHEME 2

the apicophilicity of the elements. The structure of **1** in the perfectly "anti-apicophilic" arrangement is particularly noteworthy in this connection.

Single crystals of **2** and **8** were obtained by the slow evaporation of saturated solutions of a mixture of **2** and **8** in ether or benzene, for **2** and **8**, respectively. To the best of our knowledge, this is the first example of isolation and structural determination of both tri- and pentavalent tautomers. It is interesting to point out that the ratios of **2**/**8** are 0.4/1 and 0.64/1 in ether and in benzene, respectively, and **8** exists mainly in both solvents. The reason why solvent-dependent crystallization occurred in this system remains unclear. The structures of **2** and **8** were definitively determined by X-ray crystallographic analysis (Figures 1b and 1c). **2** has a slightly distorted trigonal bipyramidal geometry with an anti-apicophilic arrangement similar to that of **1** around the

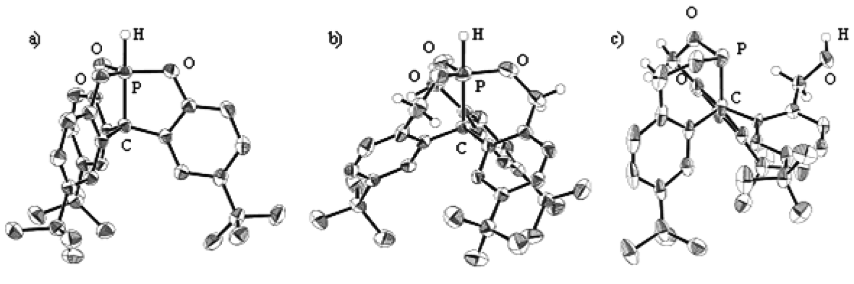
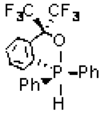


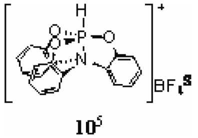
FIGURE 1 ORTEP drawings of a) 1-hydro-5-caraphosphatrane **1**, b) 1- hydro-6-carbaphosphatrane **2**, c) trivalent tautomer **8**.

TABLE I $^1J_{PH}$ and $^1J_{PC}$ Coupling Constants of Various Pentacoordinated Phosphorus Compounds

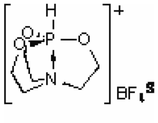
	1	2	9	10	11	12	13	14	15
$^1J_{PH}$	852	882	266	853	791	733			
$^1J_{PC}$	125	121					116 (P-Bu^n)	125	122



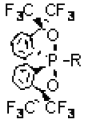
9[4]



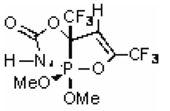
10[5]



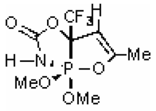
11[6]



12[4] (R = H)
13[7] (R = Bu^n)



14[8]



15[8]

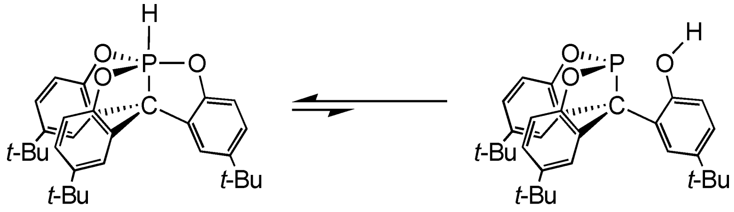
phosphorus. Unlike the C_{3v} structure of **1**, **2** has a propeller-like C_3 structure due to three six-membered rings. While the P—H and P—O bond lengths of **2** are typical lengths, as was the case for **1**, the P—C bond length is slightly longer than typical values for the apical P—C bond of a phosphorane.

^{31}P NMR spectra of **2** and **8** showed the signals at δ_P –58 and 123, respectively. The signal of **2** was observed at a higher field region than that of **1** (δ_P 2.7), attributable to the strong electron-donating ability of benzyloxy groups to the phosphorus center. The $^1J_{PH}$ and $^1J_{PC}$ values of **1**, **2**, and the related compounds are summarized in Table I.

These values of **1** and **2** are extraordinarily large for the coupling constants of apical bonds in usual phosphoranes. It is well-known that the coupling constants are dominated by the *s* character of each bond, increasing as the *s* character increases. It is widely recognized that the coupling constant of an apical bond of a phosphorane is smaller than that of an equatorial bond since the apical bond is a three-center four-electron bond formed from the *p* orbital of a phosphorus atom. Indeed, the $^1J_{PH}$ value of phosphorane **9** bearing an apical hydrogen is much smaller than that of phosphorane **12** bearing an equatorial hydrogen.[4] Similarly the apical $^1J_{PC}$ value of a usual phosphorane is also smaller than that for an equatorial P—C bond. However, the $^1J_{PH}$ values of **1** and **2**, where the hydrogen atom is located at the apical position, are much larger than that of the equatorial P—H bond of phosphorane **12**

($^{1}J_{\mathrm{PH}} = 733$ Hz).[4] The $^{1}J_{\mathrm{PH}}$ values of **1** and **2** are more than three times as large as that of the neutral phosphorane **9** ($^{1}J_{\mathrm{PH}} = 266$ Hz) bearing an apical P-H bond, whereas it is similar to those of phosphatranes **10**[5] ($^{1}J_{\mathrm{PH}} = 853$ Hz) and **11** [6] ($^{1}J_{\mathrm{PH}} = 791$ Hz). Although there is a difference that **1** and **2** are neutral compounds and **10** and **11** are ionic, these results indicate that the spectroscopic properties of **1** and **2** are more similar to those of usual phosphatranes than to those of known neutral phosphoranes. The $^{1}J_{\mathrm{PC}}$ values of **1** and **2** are also larger than that of phosphorane **13** [7] ($^{1}J_{\mathrm{PC}}(\mathrm{P{-}CH_2}) = 116$ Hz) bearing an equatorial P—C bond. It was reported that, in some phosphoranes such as **14** and **15**, where all the equatorial positions are occupied by oxygen and nitrogen atoms, the apical P—C coupling constants are as large as 117–128 Hz.[8] These reports associated with the results given in Table II suggest that anomalously large apical coupling constants are one of the characteristics of pentacoordinate phosphorus compounds where all the equatorial positions are occupied by electronegative atoms.

Usually, alkoxy- or aryloxy-substituted hydrophosphoranes showed tautomerization with the trivalent tautomer. The tautomerization of 1-hydro-5-carbaphosphatrane **1** was not observed by NMR even at the higher temperature (Scheme 3), while 1-hydro-6-carbaphosphatrane exists as the mixture of the pentavalent and trivalent tautomers.



1 (not observed)

SCHEME 3

Variable temperature NMR in various solvents was measured in order to investigate the dynamic equilibrium between **2** and **8**. The K_{eq} value for eq. 1 was determined over a temperature range of 307–342 K and thermodynamic parameters were estimated from a van't Hoff plot. They were also obtained by theoretical calculations on the model compounds **16** and **17** (without *t*-Bu groups) at the B3LYP/6-31G(d) level (Table II).

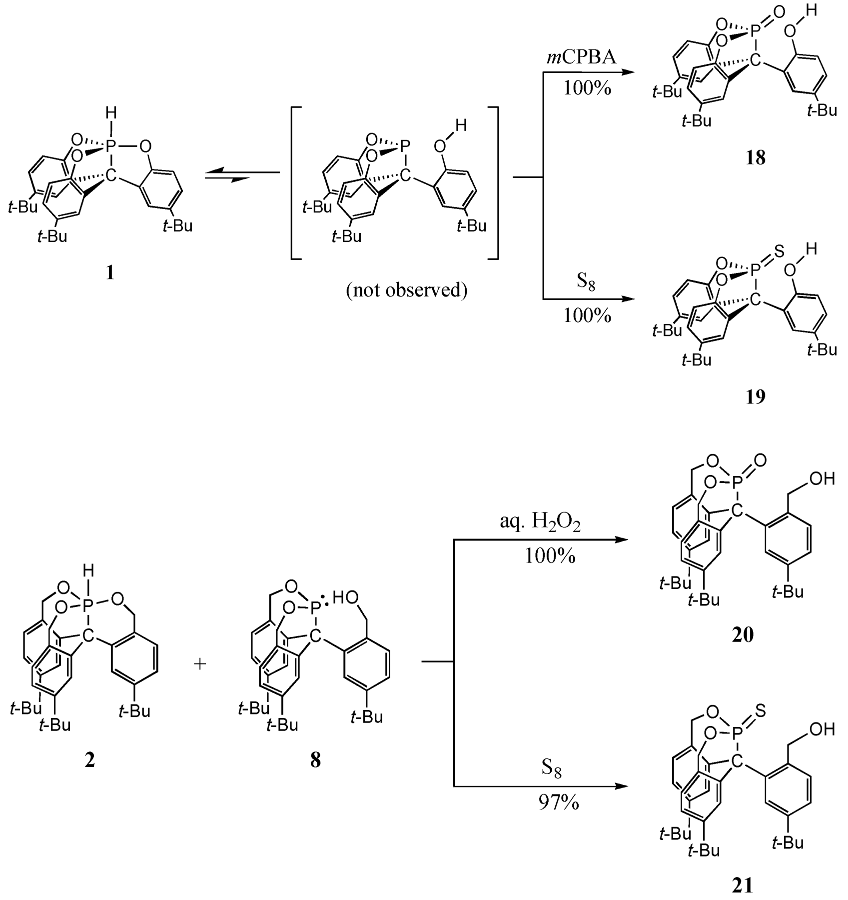
While **2** is enthalpicly favorable, **8** is more stable due to entropy effects. Taking into consideration that an analogous trivalent species was not observed in the case of **1**, ring expansion from five-membered ring

TABLE II Thermodynamic Parameters for eq (1) at 298K

$$\mathbf{2(16)} \overset{K_{eq}}{\rightleftharpoons} \mathbf{8(17)} \qquad (1)$$

	solvent	*K*eq	ΔG°	ΔH°	ΔS°
Exp.	benzene	1.3	−0.2	3.4	50
	$CHCl_3$	2.4	−0.5	2.8	46
	THF	4.5	−0.8	2.5	46
Calcd.		12	−1.5	0.9	34

to six-membered ring destabilizes the "anti-apicophilic" phosphorane form. In addition, the ratio of **2** to **8** depends on the polarities of solvents. The tautomer **8**, which has a larger dipole moment than **2** as predicted by theoretical calculations, is preferred to **2** in a more polar



SCHEME 4

solvent. Hydrogen bonding between **8** and THF may contribute to its stability in THF.

Although tautomerization between 1-hydro-5-carbaphosphatrane **1** and the trivalent tautomer was not observed by NMR spectroscopy, oxidation and sulfurization of **1** to give cyclic phosphonate **18** and thioxophosphonate **19** suggest the existence of tautomerization (Scheme 4). On the other hand, 1-hydro-6-carbaphosphatrane **2** was oxidized or sulfurized more easily than in the case of **1**. These results consist with the direct observation of tautomerization between the pentavalent and trivalent species in the case of 1-hydro-6-carbaphosphatrane.

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