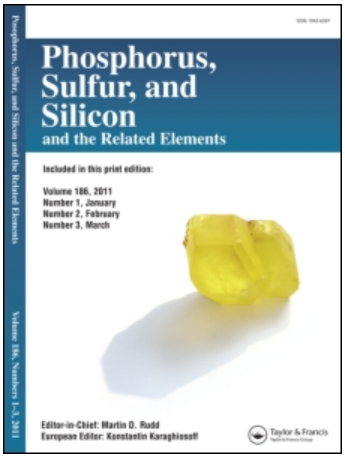

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Perfectly "Anti-Apicophilic" Phosphoranes: Conversion of a 1-Hydro-5-carbaphosphatrane into 1-Alkyl- and 1-Aryl-5-carbaphosphatranes

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1-Alkyl- and 1-aryl-5-carbaphosphatranes were prepared by the reaction of 1-hydro-5-carbaphosphatrane with nucleophiles and subsequent intramolecular oxidative cyclization. X-ray crystallographic investigation of the t*-butyl derivative revealed that it has a perfectly "anti-apicophilic" arrangement. The apical* $^{1}J_{PC}$ *coupling constants of the 5-carbaphosphatranes were extraordinarily large.*

Keywords Apicophilicity; carbaphosphatrane; coupling constant; trigonal bipyramidal structure

INTRODUCTION

Usually 10-P-5 phosphoranes assume trigonal bipyramidal structures in the ground state in which there are two distinctive sites: the apical and the equatorial positions.[1] It is well known that site preference of the substituents is dominated by their electronegativity and π-donating ability, as well as steric hindrance in the pentacoordinate species. In pentacoordinate phosphoranes, electronegative and small groups prefer the apical positions, whereas electropositive and bulky groups have a tendency to occupy the equatorial positions; this preference is called the apicophilicity.[2] The apical bond is known to be a three-centered four-electron bond involving a *p* orbital of the central

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Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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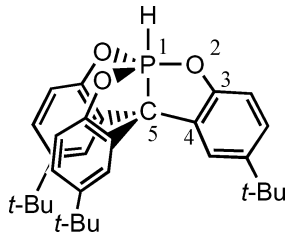


FIGURE 1 1-Hydro-5-carbaphosphatrane **1**.

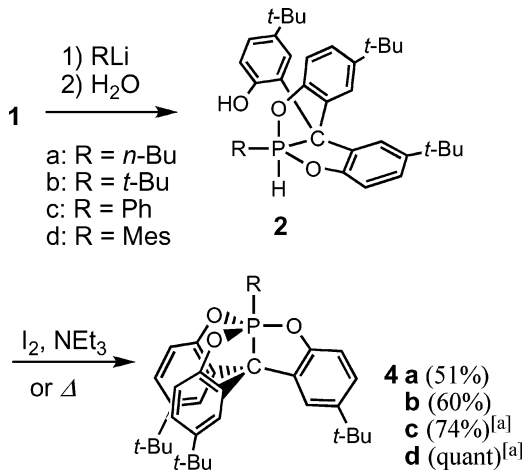
element. It has unique characteristics, being a weaker and more polar bond. Coupling constants to the central element are smaller when compared to those involving usual σ bonds. Recently, it was reported that a specially designed tetraoxyphosphorane, in which a carbon substituent occupies the apical position due to steric hindrance, could be isolated as the only detectable isomer.[3] Moreover, a spirophosphorane having an apical carbon and equatorial oxygen five-membered ring structure was synthesized as a kinetically favored isomer.[4] Here we report the synthesis of the perfectly "anti-apicophilic" phosphorane, in which all equatorial positions are occupied with electronegative oxygen atoms and apical positions with electropositive carbon atoms, by the reaction of 1-hydro-5-carbaphosphatrane with various nucleophiles and subsequent oxidation.

RESULTS AND DISCUSSION

Recently we have reported the synthesis of 1-hydro-5-carbaphospahtrane **1** (Figure 1), a five-carbon analog of phosphatranes bearing the tetradentate ligand based on the triarylmethyl framework with three oxygen atoms at 2,2′,2″-positions.[5,6]

1-Hydro-5-carbaphosphatrane **1** showed similar characteristics to known phosphatranes in the spectroscopic and structural aspects in spite of the difference of the bond properties, whereas the reactivity of **1** is based on tautomerization with the trivalent isomer and is quite different from those of known phosphatranes. **1** is also regarded as an example of an anti-apicophilic phosphorane, in which all equatorial positions are occupied with three oxygen atoms. It has been reported that the reactivity towards nucleophiles such as fluoride anion and alkyllithiums is enhanced in the *O*-equatorial spirophosphoranes compared to the *O*-apical ones.[7]

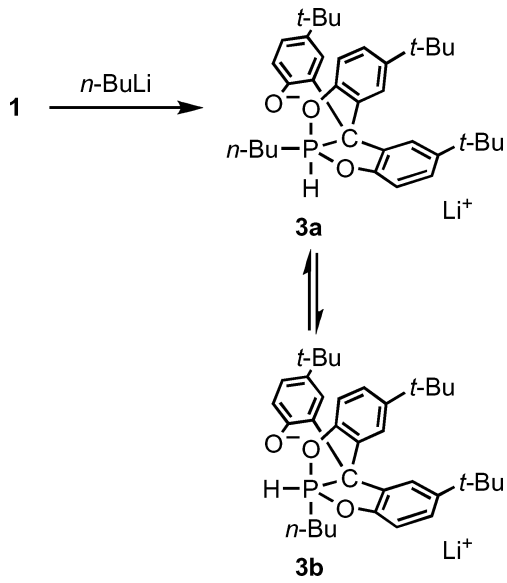
Treatment of **1** with alkyllithium reagents in THF followed by hydrolysis gave the bicyclic hydrophosphoranes **2a** and **2b** (Scheme 1). In



SCHEME 1 Reactions of **1** with nucleophiles and the synthesis of 1-alkyl- and 1-aryl-5-carbaphosphatranes **4**. [a]Yields are estimated by ^{1}H NMR.

the ^{1}H NMR spectra of **2a** and **2b**, three aromatic rings were observed with a ratio of 2:1, strongly suggesting that the carbaphosphatrane framework is not maintained and one five-membered ring is cleaved by nucleophilic substitution. When the reaction was monitored by ^{31}P NMR spectroscopy, a new signal was observed at δ_P −67 with one bond P—H coupling ($^1J_{PH}$ = 567 Hz). This signal can be assigned to phenolate **3** formed by nucleophilic substitution at the central phosphorus atom, and the structure of **3** can be considered to be similar to that of **2a**, since $^1J_{PH}$ value of **3** is close to that of **2a** (645 Hz). The reactions of an *H*-equatorial spirophosphorane with nucleophiles are reported to proceed via deprotonation at the phosphorus atom and subsequent nucleophilic attack.[8] In the case of **1**, however, the presence of a P-H proton was still observable during the reaction of **1** with *n*-BuLi. This different reactivity is derived from the structural difference. Because the hydrogen atom in **1** is fixed at the apical position, its acidity is lower than that of the *H*-equatorial spirophosphoranes, and thus nucleophilic substitution is preferred over deprotonation in the case of **1**. Variable temperature ^{31}P NMR experiments showed that a new signal appeared at δ_P −89 at −80°C in the presence of an excess amount of 12-crown-4 ether. These observations must be attributable to pseudorotation between the *H*-apical isomer **3a** and the *H*-equatorial isomer **3b**, but the exact reason why two signals were observed in VT-NMR is unclear.

Phosphoranes **2a** and **2b** were slowly oxidized to 1-alkyl-5-carbaphosphatranes **4a** and **4b** in air, respectively, and the reaction



SCHEME 2 Plausible structures of the intermediates.

was accelerated by treatment with I_2. These reactions proceeded quantitatively, judging from ^1H and ^{31}P NMR spectra, and isolated by HPLC in the yields described in Scheme 1. The structure of **4b** was confirmed by the result of single-crystal X-ray diffraction studies. An ORTEP drawing of the molecular structure of **4b** is shown in Figure 2.[9]

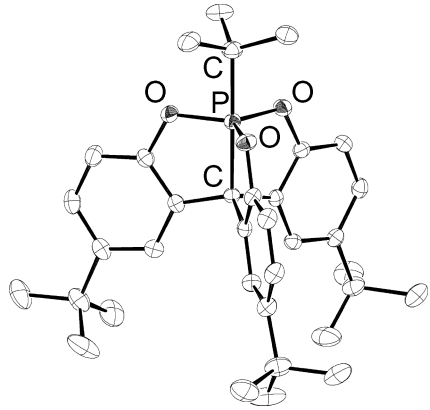


FIGURE 2 ORTEP drawing of the molecular structure of 1-*t*-butyl-5-carbaphosphatrane **4b** in the crystal; ellipsoids are drawn at 50% probability level.

The apical P—C bond length for P-*t*-Bu is 1.877(2) Å, which is slightly longer than the sum of the covalent radii of carbon and phosphorus (1.83 Å), while that for P—CAr_3 (1.959(2) Å) is much longer, because of the steric bulkiness and rigidity. The equatorial P—O bond lengths fall within the normal range of P—O bond lengths in pentacoordinate phosphoranes. The axial C—P—C bond angle is 179.27(7)°, and equatorial O—P—O bond angles are 118.95(6)–121.16(6)°, the sum of equatorial bond angles being 360°. These structural parameters indicate that **4b** has a nearly ideal trigonal bipyramidal structure; nevertheless **4b** displays a perfect anti-apicophilic arrangement. Usually, bulky and electropositive substituents prefer the equatorial positions. However, in the case of **4b**, a *t*-butyl group is located at the apical position in spite of its steric hindrance and electropositive character. The formation of **4a** and **4b** in good yields can be attributed to the conformation of their precursors **2a** and **2b**. Because the *t*-butyl group is the most equatophilic substituent in **2b**, the *t*-butyl group is located in equatorial position, and one of the apical positions is occupied with the hydrogen atom. The hydrogen atom at the apical position has hydridic character and is easily eliminated with phenolic proton as hydrogen molecule. Similar reactions have been reported by Akiba et al.,[8] and the same type of reaction was also observed using aromatic nucleophiles. When **1** was treated with aryllithium reagents, PhLi and MesLi (Mes = 2,4,6-trimethylphenyl), phosphoranes **2c** and **2d** were obtained quantitatively. Thermolyses of **2c** and **2d** in a sealed tube readily gave 1-aryl-5-carbaphosphatranes **4c** and **4d**, respectively. The yields were estimated by ^{1}H NMR of crude materials, and **4c** was obtained in 74% yield with the recovery of **1**, while **4d** was obtained quantitatively. Unfortunately isolation of **4c** and **4d** failed due to their instability against air. The difference of yields of these reactions can be rationalized by the structural difference of the reaction intermediate, as described above. The apicophilicity of the mesityl group is smaller than that of the phenyl group due to its steric hindrance. In **2d**, *H*-apical isomer is much more favorable than *H*-equatorial isomer, and the hydrogen atom is thought to be located in the apical position. However, the apicophilicity of the phenyl group is reported to be almost the same as that of the hydrogen atom. The *H*-apical isomer and the *H*-equatorial isomer are in the equilibrium in the case of **2c**. When elimination of the hydrogen molecule proceeds from the *H*-apical isomer, 1-phenyl-5-carbaphosphatrane **4c** is obtained. If the reaction proceeds from the *H*-equatorial isomer with elimination of a benzene molecule, 1-hydro-5-carbaphosphatrane **1** is recovered. Therefore, when the equatophilicity of the introduced substituent is large, anti-apicophilic phosphoranes are readily formed via a dehydrogenation process in our system.

TABLE I $^1J_{PC}$ Values in 5-Carbaphosphatranes

		$^1J_{PC}$[Hz]	
	R	R-P	P—CAr_3
1	H	(853)[a,b]	124[b]
4a	*n*-Bu	207	135
4b	*t*-Bu	208	137
4c	Ph	--[c]	137
4d	Mes	248	124
4e	Me	215[b]	133[b]

[a] $^1J_{PH}$ value. [b] ref. 5. [c] not determined.

NMR spectroscopy reveals unique characteristics of **4a–d**. The ^{31}P NMR signals of **4a–d** were observed at δ_P 22, 22, 8, and 29, respectively. Usually, chemical shifts of pentacoordinate phosphorus atom are observed at δ_P –100 to 0.[1] The downfield shifts observed for **4a–d** indicate that the central phosphorus atom is deshielded because the electronegative oxygen atoms occupied all equatorial positions. We have already reported that the apical coupling constants of 1-hydro-5-carbaphosphatrane **1** are extremely large for apical coupling constants in a pentacoordinate phosphorane. It has widely been recognized that the magnitude of the coupling constant is dominated by the *s* character of the corresponding bond.[10] Since the apical bonds of a phosphorane involve a *p* orbital of the central phosphorus atom, the apical coupling constants are usually smaller than the equatorial coupling constants. However, the apical $^1J_{PC}$ values in **4a–d** are much larger than the equatorial P—C coupling constants of usual *C*-equatorial phosphoranes, as shown in Table I, and similar to those of 1-hydro derivative **1** and its ring-expanded analogs.[6] One possible explanation for the extraordinarily large apical coupling constants is that the contribution of the positive charge to the Fermi term[11] is expected to be larger in the apical coupling of **4a–d** since the central phosphorus atom of **4a–d** is positively charged as indicated by the ^{31}P NMR shifts.

In summary, we have presented the synthesis of perfectly anti-apicophilic phosphoranes by nucleophilic addition to 1-hydro-5-carbaphosphatrane and subsequent oxidation. In our system, when the apicophilicity of nucleophiles decreases, perfectly anti-apicophilic phosphoranes are formed more easily due to the rigid framework, which is designed to stabilize anti-apicophilic trigonal bipyramidal structure. The *t*-butyl derivative was found to have a nearly ideal trigonal

bipyramidal structure in spite of its thermodynamically disfavored arrangement around the central phosphorus atom.

EXPERIMENTAL

4b: To a solution of **1** (35.4 mg, 72.5 μmol) in THF (5 mL), a solution of *t*-BuLi in pentane (1.77 M, 0.22 mmol) at −78°C was added. After stirring for 1 h at −78°C, the mixture was treated with H_2O and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, **2b** (37.1 mg) was obtained as a colorless oil. To a solution of **2b** in $CDCl_3$ (0.5 mL), iodine (10.3 mg, 40.6 μmol) was added in the presence of Et_3N (0.05 mL). The mixture was stirred for 30 min at ambient temperature and treated with a Na_2SO_3 solution and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the crude reaction products were separated by HPLC to give **4b** (23.5 mg, 60%). **4b**: colorless crystals; mp 187–190°C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 27°C): $\delta = 1.32$ (s, 27H), 1.43 (d, $J_{PH} = 19.2$ Hz, 9H), 6.91 (d, $J = 8.4$ Hz, 3H), 7.12 (dd, $J = 8.4$, 2.1 Hz, 3H), 7.87 (br s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 27°C): $\delta = 29.2$ (d, $J_{PC} = 4.4$ Hz), 31.6 (s), 34.4 (s), 40.3 (d, $J_{PC} = 136.9$ Hz), 42.2 (d, $J_{PC} = 207.5$ Hz), 111.9 (d, $J_{PC} = 8.8$ Hz), 122.0 (d, $J_{PC} = 22.0$ Hz), 124.2 (d, $J_{PC} = 11.6$ Hz), 132.6 (d, $J_{PC} = 11.2$ Hz), 145.6 (s), 149.8 (d, $J_{PC} = 2.9$ Hz). ^{31}P NMR (109 MHz, $CDCl_3$, 27°C): $\delta = 22$. HRMS (EI 70 eV): *m/z* 502.2637, Calcd for $C_{32}H_{39}O_3P$ 502.2606.

4a, **4c**, and **4d** were prepared by a similar procedure.

4a: colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 27°C): $\delta = 1.00$ (t, $J = 7.4$ Hz, 3H), 1.32 (s, 27H), 1.48–1.51 (m, 2H), 1.83–1.85 (m, 2H), 2.00–2.06 (m, 2H), 6.90 (d, $J = 8.5$ Hz, 3H), 7.12 (dd, $J = 8.5$, 2.1 Hz, 3H), 7.87 (br s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 27°C): $\delta = 14.0$ (s), 24.5 (d, $J_{PC} = 24.8$ Hz), 28.2 (d, $J_{PC} = 7.9$ Hz), 31.5 (s), 34.4 (s), 35.9 (d, $J_{PC} = 207.3$ Hz), 40.2 (d, $J_{PC} = 134.5$ Hz), 111.9 (d, $J_{PC} = 9.5$ Hz), 122.0 (d, $J_{PC} = 22.3$ Hz), 124.0 (s), 132.5 (d, $J_{PC} = 12.0$ Hz), 145.7 (s), 149.6 (d, $J_{PC} = 3.7$ Hz). ^{31}P NMR (109 MHz, $CDCl_3$, 27°C): δ 22.

4d: colorless solid. ^{1}H NMR (500 MHz, toluene-d_8, TMS, 27°C): $\delta = 1.28$ (s, 27H), 2.16 (s, 3H), 2.65 (d, $J_{PH} = 1.4$ Hz, 6H), 6.78 (d, $J = 8.4$ Hz, 3H), 6.82 (d, $J_{PH} = 6.4$ Hz, 2H), 6.90 (dd, $J = 8.4$, 2.1 Hz, 3H), 8.19 (br s, 3H). ^{13}C{^{1}H} NMR (125 MHz, toluene-d_8, 27°C): $\delta = 20.7$ (s), 25.8 (d, $J_{PC} = 4.4$ Hz), 31.5 (s), 34.4 (s), 46.0 (d, $J_{PC} = 123.8$ Hz), 112.8 (d, $J_{PC} = 9.5$ Hz), 121.8 (d, $J_{PC} = 22.0$ Hz), 124.5 (s), 130.1 (d, $J_{PC} = 19.9$ Hz), 132.6 (d, $J_{PC} = 12.5$ Hz), 137.1 (s), 137.9 (d, $J_{PC} = 11.0$ Hz), 141.9 (d, $J_{PC} = 248.0$ Hz), 145.5 (s), 151.0 (d, $J_{PC} = 4.8$ Hz). ^{31}P NMR (109 MHz, toluene-d_8, 27°C): $\delta = 29$.

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[9] Crystal data for **4b**: monoclinic, $P2_1/n$, colorless, $a = 11.3312(9)$ Å, $b = 17.9837(10)$ Å. $c = 15.6717(17)$ Å, $\beta = 88.6517(8)^\circ$, $V = 3192.6(5)$ Å^3, 123 K, $Z = 4$, $R_1 = 0.0394$, w$R_2 = 0.1047$, GOOF $= 1.046$. Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 671988. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk).

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