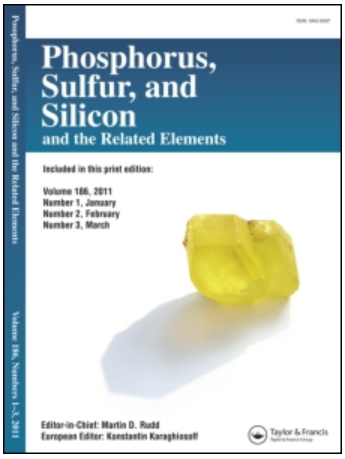

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Solution and Crystal Structure of a Hexacoordinate Phosphoranate Bearing Two Martin Ligands and Two Methyl Groups

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A hexacoordinate phosphoranate bearing two Martin ligands and two methyl groups was synthesized by the reaction of the monocyclic phosphorane bearing a hydroxy group with KH, and was crystallized in the presence of 18-crown-6 ether. The crystal structure of the phosphoranate could be regarded as an intermediate model in the reaction of the O-equatorial methylphosphorane with a methyl anion.

Keywords Hexacoordinate; hypervalent; phosphorus; X-ray analysis

INTRODUCTION

The reaction of a nucleophile with a pentacoordinate molecule having a trigonal bipyramidal structure is thought to take place within the equatorial plane to afford a hexacoordinate phosphoranate, resulting from the interaction of the nucleophile with the most reactive antibonding orbital.[1] In our recent article , the *O*-equatorial spirophosphoranes **1** having an apical carbon–equatorial oxygen arrangement, i.e., anti-apicophilic phosphoranes, were found to be more reactive toward nucleophiles, such as MeLi and TBAF (n-Bu_4N^+ F^-), than the corresponding

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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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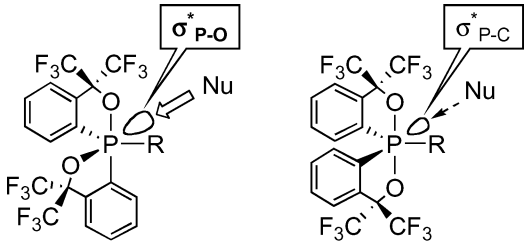
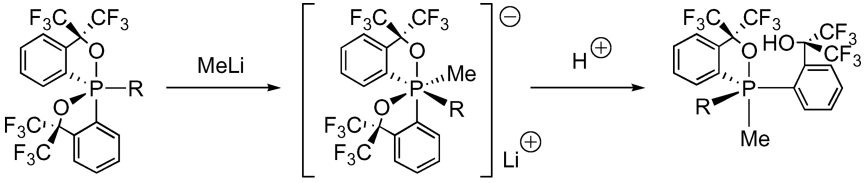


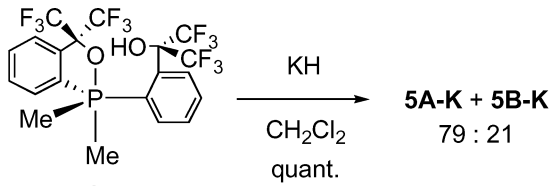
FIGURE 1 Enhanced electrophilicity of the *O*-equatorial spirophosphoranes.

O-apical isomers **2** (Figure 1).[2] Density functional theory (DFT) calculations for the methylphosphoranes (**1a** and **2a**) showed that the σ^*_{P-O} orbital of **1a** was lower in energy than the σ^*_{P-C} orbital of **2a** by 18.7 kcal mol^{-1}, which was in good agreement with the greater reactivity of the *O*-equatorial phosphoranes.

The reaction of the spirocyclic *O*-equatorial phosphoranes **1a** and **1b** with MeLi afforded the corresponding monocyclic phosphoranes **4a** and **4b**,[2,3] respectively, after the addition of aqueous ammonium chloride (Scheme 1). The reaction was somewhat complex for **1a** due to the concomitant deprotonation of the methyl group, as well as the rather rapid stereomutations of **1a** to **2a** compared to **1b** to **2b**; therefore, we could not definitely identify the intermediates **3** in the reaction of **1** with MeLi. In this article, we report the solution and crystal structure of a hexacoordinate phosphoranate prepared from the monocyclic phosphorane **4a**, which can be regarded as an intermediate model for the reaction of **1a** with MeLi, and which shows a considerable stability of the phosphoranate anion.[4]



SCHEME 1



4a

	5A-K	**5B-K**
^{31}P NMR (CD_3CN, δ)	–148.0	–144.2
^{19}F NMR (CD_3CN, δ)	–71.7 (q, 3F, $^4J_{F\text{-}F}$ = 10.0 Hz)	–70.9 (br s, 6F)
	–72.3 (q, 3F, $^4J_{F\text{-}F}$ = 11.2 Hz)	–72.8 (br m, 6F)
	–72.5 (q, 3F, $^4J_{F\text{-}F}$ = 11.2 Hz)	
	–73.0 (q, 3F, $^4J_{F\text{-}F}$ = 10.0 Hz)	

SCHEME 2

RESULTS AND DISCUSSION

The monocyclic phosphorane **4a** (δ_P = –26.6 ppm in CD_3CN)[3] was treated with KH in CH_2Cl_2 for 20 min at room temperature, then the ^{31}P, ^{19}F, and ^{1}H NMR spectra were measured in CD_3CN. In the ^{31}P NMR spectrum, two singlets at –148.0 ppm (**5A–K** major) and –144.2 ppm (**5B–K** minor) were observed (Scheme 2). The highly upfield-shifted signals corresponded to the formation of hexacoordinate species.[2,4,5] The two observed signals indicated the presence of two hexacoordinate phosphoranate anions **5-K** in the reaction mixture, which was also supported by the ^{1}H and ^{19}F NMR spectra. No change was observed in these spectra upon heating at 60°C for 4 h.

For the major isomer **5A–K**, two distinct methyl signals at δ = 1.35 (d, $^3J_{PH}$ = 13.7 Hz, 3H) and 1.26 (d, $^3J_{PH}$ = 5.1 Hz, 3H) and four CF_3 signals at δ = –71.7, –72.3, –72.5, and –73.0 were observed in the ^{1}H and the ^{19}F NMR spectrum, respectively. Therefore, among the five possible stereoisomers **I**–**V**, the major isomer **5A–K** is assigned to isomer **I** (Figure 2). On the other hand, for the minor isomer **5B–K,** only two CF_3 signals (δ = –70.9 and –72.8) were observed in the ^{19}F NMR spectrum, thus the structure of **5B–K** can be assigned to the isomers **II** or **III**. We believe that isomer **II** is more favorable than **III** since a hexacoordinate dioxaphosphirane species having a structure similar to **II** has been isolated and showed only two CF_3 signals.[5a] Based on the above-described assignments, the ratio **5A–K**:**5B–K** was calculated to be 79:21 based on the integral values in the ^{19}F NMR spectrum.

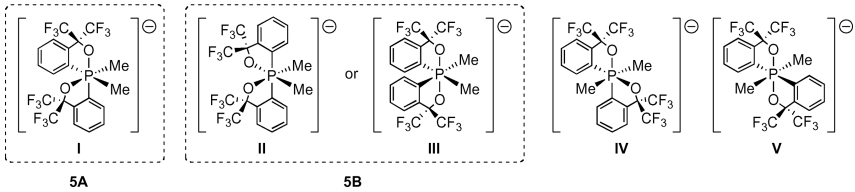
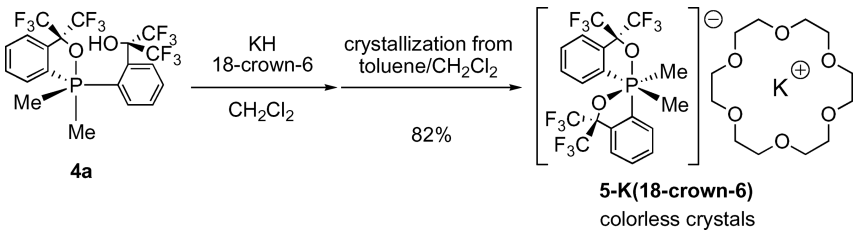


FIGURE 2 Five possible isomeric forms for phosphoranate **5**.

In the presence of 18-crown-6 ether the phosphoranate **5-K(18-crown-6)** was isolated as colorless crystals in 82% yield by crystallization from a toluene/CH_2Cl_2 solution under an Ar atmosphere (Scheme 3). A single crystal X-ray analysis unambiguously determined the structure of **5-K(18-crown-6)**, showing that the molecular structure of the anionic moiety corresponded to the major isomer **5A** (i.e., isomeric form **I** in Figure 2) as assigned on the basis of the NMR spectra. The ORTEP drawing of the anionic moiety of **5A-K(18-crown-6)** is shown in Figure 3. It is noted that the ligand configuration around the phosphorus atom of **5A-K(18-crown-6)** is quite similar to that in the fluoroantimonate **7**,[6] and the phosphoranate with an oxaphosphetane ring **8** (Figure 4).[2] It is important that **5A-K(18-crown-6)** can be regarded as an intermediate model for the reaction of the *O*-equatorial methylphosphorane **1a** with a methyl anion.

The bond distances around the phosphorus atom of **5A–K(18-crown-6)** are summarized in Table I along with those of the *O*-equatorial *n*-butylphosphorane **1b** and the monocyclic phosphorane **4a**. Comparing **5A–K(18-crown-6)** and the starting material **4a**, the two P–C(methyl) distances (P–C3 and P–C4) of the former are almost the same, whereas for the latter, the equatorial P–C4 (1.818(5) Å) is apparently shorter than the apical P–C3 distance (1.856(4) Å). When compared to the *O*-equatorial **1b**, the P–O2 distance of **5A–K(18-crown-6)** is 0.26 Å longer than that of **1b**. This trend is very similar to the case of the



SCHEME 3

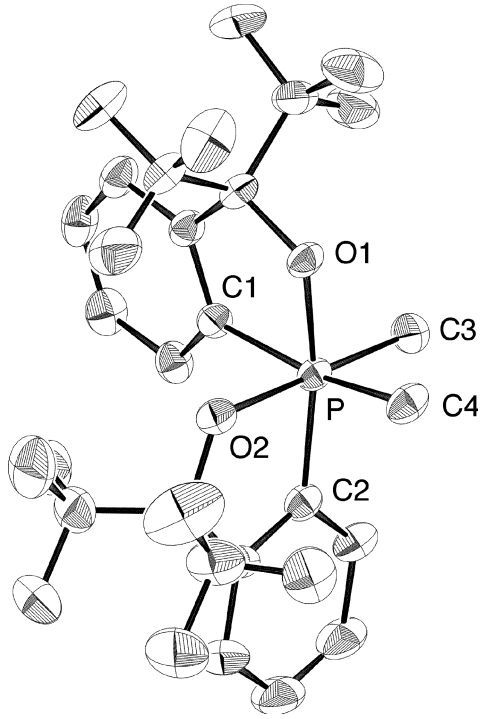


FIGURE 3 ORTEP drawing of the anion in **5A-K(18-crown-6)** showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms and the cation moiety are omitted for clarity.

phosphoranate **8**, i.e., the hexacoordinate phosphoranates derived from the *O*-equatorial phosphoranes are stabilized by the trans influence.

When several crystals of **5A–K(18-crown-6)** were dissolved in CD_3CN, two signals were again observed in the ^{31}P NMR spectrum

TABLE I Selected Bond Distances (Å) for 5A–K(18-crown-6), 1b and 4a

	5A–K(18-crown-6)	1b	4a
P–O1	1.841(5)	1.773(3)	2.030(2)
P–O2	1.917(5)	1.658(3)	—
P–C1	1.888(6)	1.806(4)	1.832(4)
P–C2	1.901(7)	1.860(4)	1.853(4)
P–C3	1.876(8)	1.830(5)	1.856(4)
P–C4	1.873(7)	—	1.818(5)

at δ = –148.8 (**5A–K(18-crown-6)** and –146.6 (**5B–K(18-crown-6)**. According to the the ^{19}F and ^{1}H NMR spectra, the isomer ratio (**5A–K(18-crown-6)**:**5B–K(18-crown-6)** = 81:19) was the same as for **5-K** (**5A–K**:**5B–K** = 79 : 21) (Scheme 2), implying that the phosphoranate isomers **5A** and **5B** show a relatively rapid equilibrium at room temperature regardless of the counter cation.

EXPERIMENTAL

General

Melting points were measured using a Yanaco micro melting point apparatus. The ^{1}H (400 MHz), ^{19}F (376 MHz), and ^{31}P (162 MHz) NMR spectra were recorded using a JEOL EX-400 spectrometer. The ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, as determined by residual acetonitrile (δ = 1.90). The ^{19}F NMR chemical shifts (δ) are given in ppm downfield from the external $CFCl_3$. The ^{31}P NMR chemical shifts (δ) are given in ppm downfield from the external 85% H_3PO_4. The elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. Toluene was freshly distilled from Na/benzophenone, and the other solvents were distilled over CaH_2.

Synthesis of 5-K(18-crown-6)

Under Ar, a CH_2Cl_2 (0.5 mL) solution of **1a** (117 mg, 0.213 mmol) was treated with an excess of KH in the presence of 18-crown-6 ether (67 mg, 0.25 mmol) for 10 min at room temperature. The mixture was filtered through Celite under Ar, and dry toluene was added to the mixture. The mixed solution was allowed to stand for several days to afford colorless crystals of **5A–K(18-crown-6)** (148 mg, 0.174 mmol, 82%). The NMR spectra showed the presence of two isomeric phosphoranates, i.e., the major isomer **5A–K(18-crown-6)** and minor isomer **5B–K(18-crown-6)** (major:minor = 81:19). ^{1}H NMR (CD_3CN): δ = 7.84 (dd, J = 7.5, 4.8 Hz, 1H, **A**), 7.73 (dd, J = 11.9, 7.9 Hz, 2H, **B**), 7.51-7.40 (m, 2H, **A**, 2H, **B**), 7.37-7.22 (m, 2H, **A**, 2H, **B**), 6.95 (t, J = 7.5 Hz, 1H, **A**), 6.80 (dd, J = 13.1, 7.5 Hz, 1H, **A**), 5.96 (dd, J = 13.1, 7.5 Hz, 1H, **A**), 3.53 (s, 24H), 1.39–1.35 (6H, overlapped,**B**), 1.35 (d, $^{2}J_{PH}$ = 12.7 Hz, 3H, **A**), 1.26 (d, $^{2}J_{PH}$ = 5.5 Hz, 3H, **A**). ^{19}F NMR (CD_3CN): δ = –70.8 (br s, 6F, **B**), –71.6 (q, $^{4}J_{FF}$ = 11.2 Hz, 3F, **A**), –72.3 (q, $^{4}J_{FF}$ = 9.7 Hz, 3F, **A**), –72.5 (q, $^{4}J_{FF}$ = 9.7 Hz, 3F, **A**), –72.7 (br m, 6F,**B**), –73.0 (q, $^{4}J_{FF}$ = 11.2 Hz, 3F, **A**). ^{31}P NMR (CD_3CN): δ = –146.6 (**B**), –148.8 (**A**); mp 205–208°C

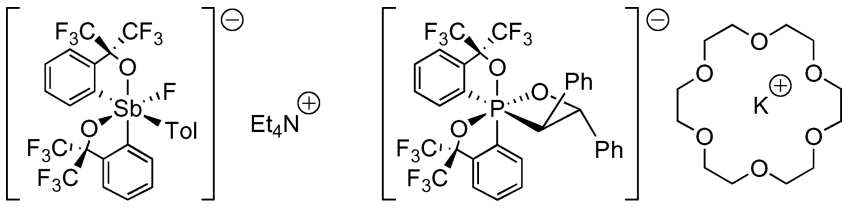


FIGURE 4 Isolated hexacoordinate antimony (**7**) and phosphorus (**8**) compounds.

(decomp.); Anal. calcd for $C_{32}H_{38}F_{12}KO_8P$: C, 45.29; H, 4.51. Found: C, 45.40; H, 4.81%.

X-Ray Analysis of 5A–K(18-crown-6)

A single crystal of **5A–K(18-crown-6)** suitable for X-ray diffraction (crystal size: 0.60 × 0.50 × 0.20) was mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 293 K for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (MAC Science).[7] For each data set, the rotation images were collected in 3-degree increments with a total rotation of 180 deg about the ϕ axis. The data were processed using SCALEPACK. The structure was solved by direct methods using the SHELX-97 program.[8] Refinement on F^2 was carried out using full-matrix least-squares by the SHELX-97 program.[8] All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters. Crystallographic data: crystal system = monoclinic, space group = $P2_1$, $a = 9.6610(5)$ Å, $b = 19.6900(10)$ Å, $c = 9.9880(5)$ Å, $\beta = 97.522(3)^\circ$, $V = 1883.62(17)$ Å^3, $Z = 2$, $D_{calc} = 1.496$ g cm^{-3}, $F(000) = 872$, data/param = 4357/487, R_1 ($I > 2\sigma(I)$) = 0.0812, wR_2 (all data) = 0.2591, $GOF = 1.179$. CCDC-670330 contains the supplementary crystallographic data for this article. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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