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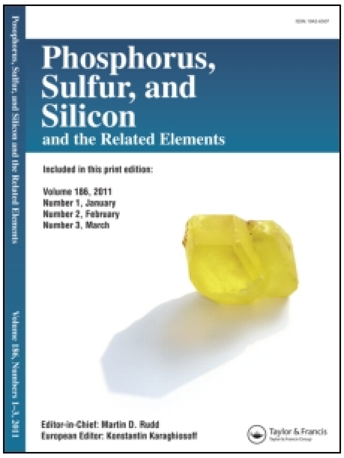

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Synthesis and Structure of 5-Carbaphosphatrane

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1-Hydro-5-carbaphosphatrane 4, the first 5-carbon analog of a phosphatrane, was synthesized. X-ray crystallographic analysis showed that it has a typical TBP structure and that it is a 10-P-5 phosphorane in a perfectly "*anti-apicophilic*" arrangement.

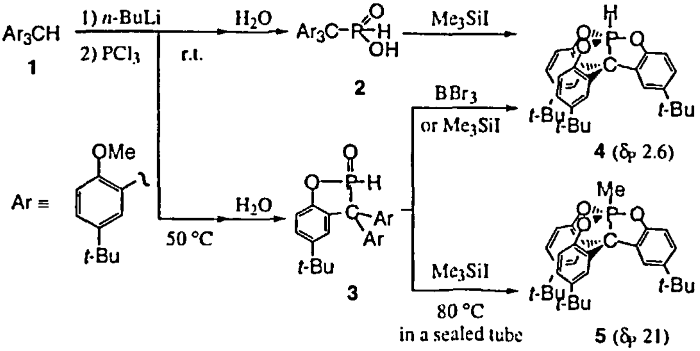
Keywords: anti-apicophilic arrangement; phosphatrane; hypervalent phosphorus

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. Here we report the synthesis and reactions of tribenzo-5-carbaphophatranes, representing the first example of 5-carbon analogs of main group atranes. These compounds are also of interest as 10-P-5 phosphoranes in the perfectly "*anti-apicophilic*" arrangement, where the equatorial positions are occupied with three oxygen atoms and apical positions with hydrogen or carbon atoms.

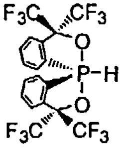
RESULTS AND DISCUSSION

Lithiation of triarylmethane **1** followed by the reaction with phosphorus trichloride at room temperature and hydrolysis afforded phosphinic acid **2**. On the other hand, when the reaciton mixture was heated at 50 °C, cyclic phophinate **3** was obtained as the result of intramolecular cyclization . 1-Hydro-5-carbaphosph-atrane **4** was synthesized by the reaction of cyclic phosphinate **3** with boron tribromide in $CHCl_3$. Treatment of **2** or **3** with iodotrimethylsilane at room temperature in $CDCl_3$ also afforded **4**. On the other hand, the reaction of **3** with iodotrimethylsilane at 80 °C in a sealed tube gave the 1-methyl derivative **5**.

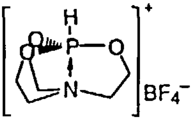


X-ray crystallographic analysis revealed that **4** has a typical trigonal bipyramidal structure. The apical bond lengths of **4** are 1.921(2) for the P-C bond and 1.38(2) Å for the P-H bond, respectively.

In ^{31}P NMR, 5-carbaphosphatranes **4** showed its signal at δ 2.6. The $^1J_{PH}$ value of **4** was 852 Hz. It is known that the coupling constant of an equatorial bond is usually larger than that of an apical bond. The $^1J_{PH}$ value of the H-equatorial phosphorane **6** is 733 Hz.[2] It is noteworthy that the $^1J_{PH}$ value of **4**, where the hydrogen atom is located at the apical position in **4**, is larger than that of **6** bearing an equatorial P-H bond. On the other hand, the $^1J_{PH}$ value of **4** is close to that of phosphatrane **7** ($^1J_{PH}$ = 791 Hz).[3]



6
$^1J_{PH}$ = 733 Hz

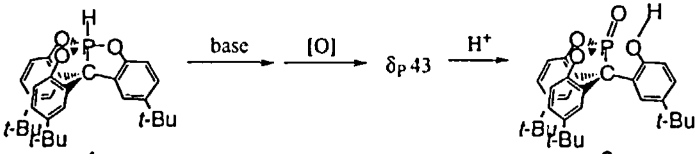


7
$^1J_{PH}$ = 791 Hz

When the $CDCl_3$ solution of **4** is allowed to stand for 2 months in the presence of D_2O, the H-D exchange in P-H bond was observed. This result indicates that there is tautomerization between the five-coordinate phosphatrane **4** and the three-coordinate phosphonite **8**.

4 **8**

It has been reported that phosphatranes bearing a 5-nitrogen do not react with bases such as NaOMe, proton sponge.[3] On the other hand, the reactions of carbaphosphatrane **4** with amino bases such as proton sponge, DBU, and triethylamine afforded a new compound which showed a signal at 43 ppm in ^{31}P NMR. Treatment of this compound with hydrochloric acid gave the cyclic phosphonate **9**.



4 **9**

In summury, we have succeeded in the first synthesis of 5-carbaphosphatrane, 5-carbon analog of phoshatrane, and revealed that it has a typical TBP structure. Its reactions involving tautomerization between carbaphosphatrane and cyclic phosphonite were also presented.

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