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5-Carbaphosphatranes: The First Main Group Atrane Bearing a 1−5 Covalent Bond

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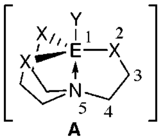
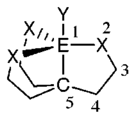
There have been extensive studies on a wide variety of main group atranes, generally depicted as **A**.[1] A number of their derivatives bearing different ring sizes and other building elements have also been reported so far. These studies established that the nature of the N→E dative bond has a great influence on their structures and reactivities. From such a viewpoint, it is particularly intriguing how their properties will change when the dative bond between the 5-nitrogen atom and the central atom is replaced by a covalent bond with a group 14 element like carbon as shown by a general formula **B**.



A



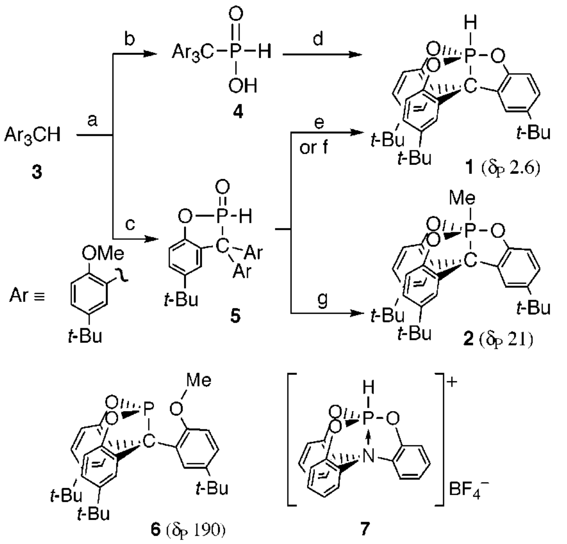
B

X = O, NR

However, there has been no example of such an atrane bearing a 1−5 covalent bond; the element at the 5-position of known atranes has been limited almost exclusively to nitrogen with a few exceptions of phosphorus.[2] Here we report the synthesis of 5-carbaphosphatranes **1** and **2**, presenting the first example of 5-carbon analogues of main group atranes. While they have an isoelectronic structure with usual phosphatranes bearing a 5-nitrogen atom, they are expected to be quite different in reactivities from usual ones reflecting the differences in the properties of the 1−5 bond.

Lithiation of triarylmethane **3** followed by the reaction with phosphorus trichloride at room temperature afforded phosphinic acid **4** after hydrolysis (Scheme 1). When the reaction was effected at 50 °C, the cyclic phosphinate **5** was obtained as a result of intramolecular cyclization with loss of chloromethane and hydrolysis.[3] 1-Hydro-5-carbaphosphatrane **1** was synthesized by treatment of **4** or **5** with iodotrimethylsilane at room temperature in $CDCl_3$.[4,5] In this reaction, the intermediary cyclic phosphonite **6** was observed by ^{31}P NMR (δ 190), which is considered to react with hydrogen iodide formed in situ to afford **1**. On the other hand, when the reaction of **5** with iodotrimethylsilane was carried out at 80 °C in a sealed tube, 1-methyl-5-carbaphosphatrane **2** was obtained instead of **1**, probably as a result of the reaction of the intermediate **6** with iodomethane generated in situ. Compound **1** was also obtained by the reaction of **5** with boron tribromide in $CHCl_3$. It was reported that the tribenzophosphatrane **7** bearing a 5-nitrogen is observable by NMR spectroscopy in solution, but too fragile to be isolated.[6] In contrast, 5-carbaphosphatrane **1** was obtained as stable crystals, showing the difference between a phosphatrane with an N→P dative bond and that with a C−P covalent bond.

Scheme 1[a]



[a] a) *n*-BuLi: b) PCl_3, rt, then H_2O, 11% (2 steps); c) PCl_3, 50 °C, then H_2O, 38% (2 steps); d) TMSI, rt, 38%; e) TMSI, rt, 39%; f) BBr_3, rt, then aq. $NaHCO_3$, 54%; g) TMSI, 80 °C, in a sealed tube, 29%.

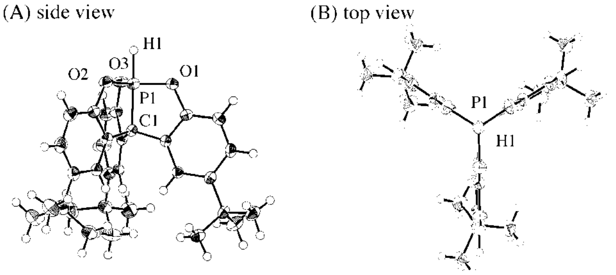

(A) side view (B) top view

Figure 1. ORTEP drawings of **1** with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) and angles (deg): P1−C1, 1.921(2); P1−H1, 1.38(2); O1−P1−O2, 121.96(9); O1−P1−O3, 118.14(9); O2−P1−O3, 119.62(9); C1−P1−O1, 91.65(9); C1−P1−O2, 91.69(9); C1−P1−O3, 91.99(9); H1−P1−C1, 178.7(9).

The structure of **1** was established by X-ray crystallographic analysis as shown in Figure 1.[7] 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 the apicophilicity of the elements.[8,9] The structure of **1** in the

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(1) For reviews, see: (a) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483−489. (b) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233−295. (c) Alder, R. W.; Read, D. *Coord. Chem. Rev.* **1998**, *176*, 113−133. For silatranes, see: Voronkov, M. G. *Pure Appl. Chem.* **1966**, *13*, 35−59.

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(3) For a similar reaction, see: Yoshifuji, M.; Nakazawa, M.; Sato, T.; Toyota, K. *Tetrahedron*, **2000**, *56*, 43−55.

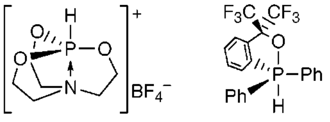
(4) For a demethylation reaction of anisole derivatives with iodotrimethylsilane, see: Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761−3764.

(5) **1**: colorless crystals, mp 272−274 °C. ^1H NMR (500 MHz, $CDCl_3$, 27 °C) δ 1.32 (s, 27H), 6.76 (d, 1H, $J_{PH} = 852$ Hz), 6.95 (d, 3H, $J = 8.4$ Hz), 7.14 (dd, 3H, $J = 8.4, 2.1$ Hz), 7.88 (brd, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 27 °C) δ 31.52 (s), 34.47 (s), 39.21 (d, $J_{PC} = 125$ Hz), 112.41 (d, $J_{PC} = 10.3$ Hz), 122.20 (d, $J_{PC} = 22.3$ Hz), 124.59 (s), 131.95 (d, $J_{PC} = 13.3$ Hz), 146.39 (s), 149.70(s); ^{31}P NMR (109 MHz, $CDCl_3$, 27 °C) δ 2.6. HRMS-(70 eV) *m/z* 488.2491, calcd for $C_{31}H_{37}O_3P$ 488.2480. Anal. Calcd for $C_{31}H_{37}O_3P$: C, 76.20; H, 7.63. Found: C, 76.48; H, 7.61.

(6) Müller, E.; Bürgi, H.-B. *Helv. Chim. Acta* **1987**, *70*, 1063−1069.

(7) Crystal data for **1**: monoclinic, $P2_1/c$, colorless, $a = 15.963(1)$ Å, $b = 11.278(1)$ Å, $c = 15.269(1)$ Å, $\beta = 93.842(4)°$, $V = 2742.7(3)$ Å^3, 123 K, $Z = 4$, $R = 0.055$, $R_W = 0.058$, GOF = 3.84.

10.1021/ja0056264 CCC: $20.00

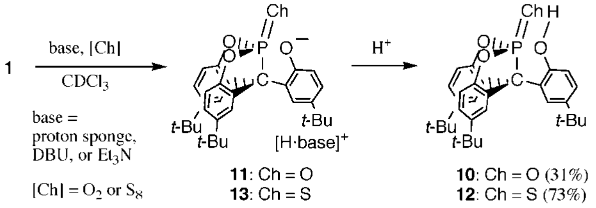


8 $^1J_{PH}$ = 791 Hz

9 $^1J_{PH}$ = 266 Hz

Figure 2. Coupling constants of the related compounds.

Scheme 2



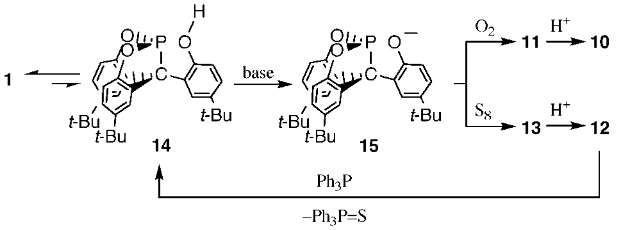
perfectly “anti-apicophilic”[10] arrangement is particularly noteworthy in this connection.

In ^{31}P NMR spectra, 5-carbaphosphatranes **1** and **2** showed their signals at δ 2.6 and 21, respectively. The $^1J_{PH}$ value of **1** and the $^1J_{PC}$(P−CH$_3$) value of **2** are 852 and 215 Hz, respectively, which are extraordinarily large for the apical P−H and P−C coupling constants of phosphoranes.[11] The $^1J_{PH}$ value of **1** is more than three times as large as that of the neutral phosphorane **9** ($^1J_{PH} = 266$ Hz) bearing an apical P−H bond,[12] whereas it is similar to those of phosphatranes **7** ($^1J_{PH} = 853$ Hz)[6] and **8** ($^1J_{PH} = 791$ Hz).[13] Although there is a difference that **1** is a neutral phosphorane and compounds **7** and **8** are ionic, these results indicate that the spectroscopic properties of **1** are similar to those of usual phosphatranes rather than to those of known neutral phosphoranes.

It has been reported that usual phosphatranes bearing a 5-nitrogen do not react with bases such as NaOMe and proton sponge.[14] In contrast, when 5-carbaphosphatrane **1** was treated with amino bases such as proton sponge, DBU, and triethylamine in the open atmosphere, the phenolate anion **11** (δ_P 43) was formed and converted to the cyclic phosphonate **10** after hydrolysis with hydrochloric acid (Scheme 2).

Similarly, the reaction of **1** with amino bases in the presence of elemental sulfur followed by treatment with hydrochloric acid afforded the cyclic phosphonothioate **12** via the corresponding anion **13**. These results can be reasonably explained by assuming the tautomerization between the five-coordinate carbaphosphatrane **1** and the three-coordinate phosphonite **14** (Scheme 3); the tautomer **14** is deprotonated with amines to give the ionic species **15**,[15] which is irreversibly oxidized or sulfurized to **11** or **13**, respectively. The tautomerization between **1** and **14** was further demonstrated by the desulfurization reaction of phosphonothioate **12**. Treatment of **12** with triphenylphosphine in CDCl$_3$ at 85 °C afforded the parent carbaphosphatrane **1** almost quantitatively, which is most probably formed via tautomerization of the three-coordinate species **14** first generated in the reaction (Scheme 3). Furthermore, the H−D exchange in the P−H bond of **1** was observed when the CDCl$_3$ solution of **1** was allowed to stand for 2 months in the presence of D$_2$O. This reaction was remarkably accelerated by acid, and in the presence of DCl/D$_2$O, the exchange was completed within 15 h at room temperature. These results are also consistent with the equilibrium between **1** and **14**. Phosphonite **14** was not observed in any spectroscopic measurement of **1**, and no significant change was observed in the variable temperature ^{1}H NMR spectra of **1** in the range of −80 to 80 °C. These observations are reasonable, however, if the tautomer **1** is thermodynamically much more favorable than **14**. While such tautomerization between five-coordinate and three-coordinate species has never been described for the usual phosphatranes with an N→P dative bond, it is no wonder that a neutral phosphorane **1** with a C−P covalent bond undergoes such isomerization. The reaction involving similar tautomerization was reported for an *o*-phosphinobenzoic acid.[16]

Scheme 3



In summary, we synthesized 5-carbaphosphatranes **1** and **2**, the first example of 5-carbon analogues of main group atranes. While the spectroscopic and structural properties of **1** are rather similar to those of usual phosphatranes, **1** showed characteristics as a neutral phosphoranes with respect to the reactivity. The present results revealed that 5-carbaphosphatranes constitute a novel class of highly coordinated phosphorus compounds bearing the properties both as a phosphatrane and as a neutral phosphorane.

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Supporting Information Available: Experimental procedure for the synthesis and reactions of **1** and **2** with physical properties of structural information on **1** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0056264

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(12) Ross, M. R.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 1234−1235.

(13) Clardy, J. C.; Milbrath, D. S.; Springer, J. P.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 623−624.

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(15) As for the structure of anion **15**, there is a possibility that it exists as a phosphoranide form. Theoretical study on the structure of **15** will be reported elsewhere.

(16) Kemp, R. A. *Phosphorus, Sulfur, and Silicon* **1994**, *87*, 83−92.