

Synthesis, Structure, and Bonding Properties of 5-Carbaphosphatranes: A New Class of Main Group Atrane

Junji Kobayashi,[†] Kei Goto,[†] Takayuki Kawashima,^{*,†} Michael W. Schmidt,^{*,‡} and Shigeru Nagase^{§,||}

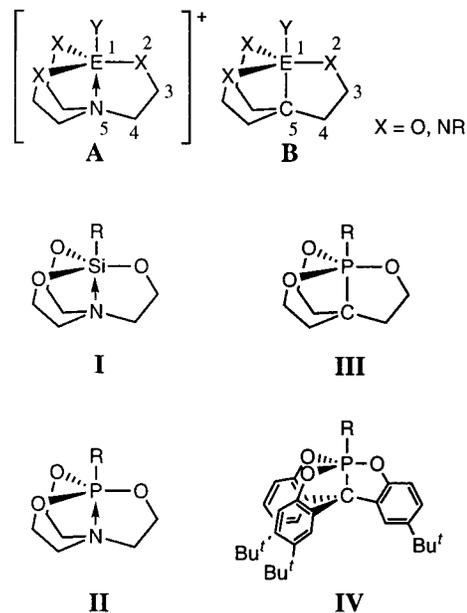
Contribution from the Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

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Abstract: 1-Hydro-5-carbaphosphatrane (**1**) and 1-methyl-5-carbaphosphatrane (**2**), the first 5-carbon analogues of phosphatranes, were synthesized by a demethylation reaction of cyclic phosphinate **3**. X-ray analysis revealed that **1** has a typical trigonal bipyramidal structure with hydrogen and carbon atoms at the apical position and three oxygen atoms at the equatorial positions, indicating that **1** is a phosphorane in the perfectly "anti-apicophilic" arrangement. The P–C and P–H bond lengths were 1.921(2) and 1.38(2) Å, respectively. The $^1J_{\text{PH}}$ value of **1** and the $^1J_{\text{PC}}$ (P–CH₃) value of **2** were 852 and 215 Hz, respectively, which are extraordinarily large for the apical coupling constants of phosphoranes, but close to those of the reported phosphatranes with a 5-nitrogen atom. IR and Raman spectra are also reported. Force constant calculations indicate the transannular bond in carbaphosphatrane is 3 times stronger than in silatrane, due to its covalent character.

Introduction

There have been extensive studies on a wide variety of main group atranes, generally depicted as **A**.^{1,2} A number of their derivatives bearing different ring sizes, and other building elements have also been reported so far. A silatrane (**I**) was first reported by Frye and co-workers³ and has been widely investigated. Voronkov reported the chemical properties of silatranes as well as their biological activities.^{2a} Verkade investigated phosphorus-centered atranes, phosphatranes (**II**), and revealed that they have unique structure, physical properties, and reactivities.^{1a} Pro-phosphatranes, that is, the conjugated bases of phosphatranes, are known as very strong neutral bases and have been utilized as catalysts in organic synthesis.^{4a} These unique features of phosphatranes are considered to be caused by the N→P dative bond. From such a viewpoint, it is



particularly intriguing how their properties will change when the N→P dative bond is replaced by a covalent bond with group 14 elements such as carbon (**III**). Very recent work has shown that the protonated atrane containing P→P has a short P→P

[†] The University of Tokyo.

[‡] Present address: 201 Spedding Hall, Iowa State University Ames, IA 50011

[§] Tokyo Metropolitan University.

^{||} Present address: Department of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan.

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distance and is highly resistant to deprotonation.^{4b,c} 5-Carbaphosphatranes are expected to have structural properties similar to reported phosphatranes since they have an isoelectronic structure. On the other hand, they are expected to have reactivities different from those of phosphatranes, reflecting the difference in their bonding properties. Such comparisons between 5-carbaphosphatranes and phosphatranes will give important information about the relationship between bonding properties and reactivities of hypervalent compounds. Here we report the synthesis of the first carbon analogues of a phosphatranane, 5-carbaphosphatranes (**IV**), and the elucidation of their structural and spectroscopic properties by both experimental data and theoretical calculations. Parts of this work have been communicated.⁵

The present compound is being described as an atrane since it is a substituted tricyclo[3.3.3.0]undecane with a highly coordinated bridgehead atom. The superficially related systems with N substituted for P⁶ are typically formulated as salts $\overline{C[-(CH_2)_3-]_3N^+X^-}$, $X^- = Br^-,^{6a} Cl^-,^{6b} I_3^-,^{6c} BPh_4^-.$ ^{6d,e} Since the available structural data for these do not indicate the presence of an NX bond, these compounds are named azoniapropellanes and are not generally regarded as atranes.

Experimental Section

General Information. 2-Bromo-4-*tert*-butylanisole was synthesized by a reported procedure in two steps.⁷ Solvents were purified according to standard procedures. All the reactions were carried out in a dry argon atmosphere. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX500 FT-NMR spectrometer, and ³¹P NMR spectra were recorded on a JEOL EXcalibur270 spectrometer. All ¹H and ³¹P NMR spectra were recorded in CDCl₃ unless otherwise mentioned. Chemical shifts are reported in parts per million, downfield positive, and relative to tetramethylsilane for ¹H NMR or 85% H₃PO₄ for ³¹P NMR. High-pressure liquid chromatography (HPLC) was performed by LC-918 and LC-908 C60 with JAIGEL 1H+2H columns (Japan Analytical Industry) with chloroform as solvent. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, the University of Tokyo.

Preparation of 5,5',5''-Tri-*tert*-butyl-2,2',2''-trimethoxytriphenylmethanol (4). To Mg turnings (1.01 g, 41.5 mmol) was added a solution of 2-bromo-4-*tert*-butylanisole (10.1 g, 41.5 mmol) in THF (10 mL), and the mixture was refluxed for 4 h. To the mixture was added a solution of diethyl carbonate (1.5 mL, 13 mmol) in THF (5 mL), and the mixture was refluxed overnight. The mixture was treated with H₂O and extracted with CHCl₃. The extracts were dried over anhydrous MgSO₄. After removal of the solvent, the residue was recrystallized from hexane to give **4** (6.44 g, 99% yield). **4**: colorless crystals; mp 113–115 °C; ¹H NMR (270 MHz, CDCl₃) δ 1.20 (s, 27H), 3.45 (s, 9H), 5.49 (s, 1H), 6.76 (d, 3H, *J* = 8.4 Hz), 7.18–7.23 (m, 6H); ¹³C-¹H NMR (125 MHz, CDCl₃, 27 °C) δ 31.28 (s), 34.10 (s), 55.44 (s), 81.19 (s), 111.22 (s), 124.19 (s), 127.49 (s), 132.64 (s), 142.06 (s), 155.17 (s). Anal. Calcd for C₃₄H₄₆O₄: C, 78.72; H, 8.94. Found: C, 78.43; H, 8.92.

Preparation of 5,5',5''-Tri-*tert*-butyl-2,2',2''-trimethoxytriphenylmethane (5). To a solution of **4** (8.92 g, 17.2 mmol) in acetic acid (100 mL) was added triethylsilane (40 mL, 26 mmol), and the mixture was stirred at 80 °C overnight. The mixture was neutralized with aqueous NaOH and extracted with CHCl₃. The extracts were dried over anhydrous MgSO₄. After removal of the solvent, the residue was reprecipitated from CHCl₃/EtOH to give **5** as colorless crystals (7.24 g, 84% yield). **5**: colorless crystals; mp 122–125 °C; ¹H NMR (270 MHz, CDCl₃) δ 1.15 (s, 27H), 3.67 (s, 9H), 6.50 (s, 1H), 6.75 (d, 3H, *J* = 8.5 Hz), 6.84 (d, 3H, *J* = 2.4 Hz), 7.14 (dd, 3H, *J* = 8.5, 2.4 Hz); ¹³C-¹H NMR (125 MHz, CDCl₃, 27 °C) δ 31.41 (s), 33.96 (s), 36.78 (s), 56.08 (s), 110.43 (s), 122.94 (s), 127.48 (s), 132.07 (s), 142.16 (s), 155.23 (s). Anal. Calcd for C₃₄H₄₆O₃: C, 81.23; H, 9.22. Found: C, 80.56; H, 9.21.

Preparation of Phosphinic Acid 6. To a solution of **5** (1.05 g, 2.09 mmol) in benzene (50 mL) was added *n*-BuLi (1.60 M hexane solution, 9.9 mmol) at 50 °C. The mixture was stirred at 50 °C for 24 h. To this solution was added PCl₃ (2.0 mL, 23 mmol), and the mixture was stirred at room temperature for 5 days. After removal of the solvent, the residue was subjected to wet column chromatography (WCC) (SiO₂/CHCl₃) and dry column chromatography (DCC) (SiO₂/CHCl₃) to give a fraction containing **6**, which was further purified by HPLC to give **6** (116.4 mg, 12% yield). **6**: colorless solids; mp 276–278 °C; ¹H NMR (500 MHz, CDCl₃, 27 °C) δ 1.02 (s, 27H), 3.66 (s, 9H), 6.29 (brs, 3H), 6.82 (d, 3H, *J* = 8.3 Hz), 7.22 (br d, 3H, *J* = 8.3 Hz), 7.34 (d, 1H, *J*_{PH} = 610 Hz); ¹³C-¹H NMR (125 MHz, CDCl₃, 27 °C) δ 31.15 (s), 33.87 (s), 55.15 (s), 62.00 (d, *J*_{PC} = 86 Hz), 110.36 (s), 124.32 (s), 128.19 (s), 128.69 (br s), 142.67 (s), 155.55 (s); ³¹P NMR (109 MHz, CDCl₃, 27 °C) δ 44.5; LRMS (EI 70 eV) *m/z* 567, calcd for C₃₄H₄₇O₃P 567. Anal. Calcd for C₃₄H₄₇O₃P·0.5H₂O: C, 70.93; H, 8.40. Found: C, 70.72; H, 8.19.

Preparation of Cyclic Phosphinate 3. To a solution of **5** (5.06 g, 11.0 mmol) in benzene (250 mL) was added *n*-BuLi (1.67 M hexane solution, 50 mmol) at 50 °C. The mixture was stirred at 50 °C for 24 h. To the mixture was added PCl₃ (10 mL, 0.11 mmol), and the mixture was stirred at 50 °C for 2 days and 80 °C for 5 days. After removal of the solvent, the residue was subjected to WCC (SiO₂/CHCl₃) and DCC (SiO₂/CHCl₃) to give a fraction containing **3**, which was further purified by HPLC to give **3** (1.22 g, 21% yield). **3**: colorless solids; mp 218–219 °C; ¹H NMR (500 MHz, CDCl₃, 27 °C) δ 1.12 (s, 9H), 1.19 (s, 9H), 1.23 (s, 9H), 3.42 (s, 3H), 3.77 (s, 3H), 6.60 (br s, 1H), 6.77 (d, 1H, *J* = 8.5 Hz), 6.86 (d, 1H, *J* = 1.9 Hz), 6.93 (d, 1H, *J* = 8.5 Hz), 7.00 (d, 1H, *J* = 8.5 Hz), 7.14 (br s, 1H), 7.21 (br d, 1H, *J* = 8.4 Hz), 7.27 (dd, 1H, *J* = 8.4, 2.2 Hz), 7.27 (d, 1H, *J*_{PH} = 624 Hz), 7.40 (d, 1H, *J* = 8.4 Hz); ¹³C-¹H NMR (125 MHz, CDCl₃, 27 °C) δ 31.35 (s), 31.41 (s), 31.56 (s), 34.02 (s), 34.35 (s), 34.39 (s), 55.19 (s), 56.04 (s), 56.77 (d, *J*_{PC} = 77 Hz), 110.44 (s), 111.92 (d, *J*_{PC} = 9.0 Hz), 112.28 (s), 125.08 (s), 125.13 (s), 125.17 (s), 125.38 (s), 125.80 (d, *J*_{PC} = 5.1 Hz), 126.17 (s), 126.54 (s), 127.51 (d, *J*_{PC} = 8.3 Hz), 129.39 (d, *J*_{PC} = 6.6 Hz), 142.49 (s), 144.18 (s), 145.00(s), 152.57 (d, *J*_{PC} = 5.6 Hz), 154.55 (d, *J*_{PC} = 6.4 Hz), 155.41 (d, *J*_{PC} = 3.6 Hz); ³¹P NMR (109 MHz, CDCl₃, 27 °C) δ 58.1; HRMS (EI 70 eV) *m/z* 534.2930, calcd for C₃₃H₄₃O₄P 534.2899. Anal. Calcd for C₃₃H₄₃O₄P: C, 74.13; H, 8.11. Found: C, 74.05; H, 8.04.

Reaction of Cyclic Phosphinate 3 with Iodotrimethylsilane. To a solution of cyclic phosphinate **3** (34.9 mg, 0.0653 mmol) in CDCl₃ (0.5 mL) in a 5-mm-diameter Pyrex glass tube was added iodotrimethylsilane (0.02 mL, 0.16 mmol). The solution was allowed to stand at room temperature, and the reaction was monitored by ³¹P NMR. After 22 h, a signal was observed at δ = 190 by ³¹P NMR and elemental sulfur (17.2 mg, 0.536 mmol) was added to the reaction mixture. After removal of the solvent under reduced pressure, the crude products were subjected to HPLC to give phosphonothioate **13** (8.9 mg, 26%). **13**: ¹H NMR (270 MHz, CDCl₃, 27 °C) δ 1.25 (s, 18H), 1.26 (s, 9H), 3.44 (s, 3H), 6.85 (d, 1H, *J* = 8.4 Hz), 6.96 (d, 2H, *J* = 8.4 Hz), 7.18–7.40

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(m, 6H); ^{31}P NMR (109 MHz, CDCl_3 , 27 °C) δ 126.9; LRMS (FAB 70 eV) m/z 535, calcd for $\text{C}_{32}\text{H}_{40}\text{O}_3\text{PS}$ 535.

Synthesis of 1-Hydro-5-carbaphosphatrane 1 (Method A). To a solution of phosphinic acid **6** (55.1 mg, 0.0971 mmol) in CDCl_3 (0.5 mL) in a 5-mm-diameter Pyrex glass tube was added iodotrimethylsilane (0.07 mL, 0.50 mmol). The solution was allowed to stand at room temperature for 1 week. After removal of the solvent under reduced pressure, the crude products were subjected to HPLC to afford **1** (17.9 mg, 38%), which was further purified by recrystallization from $\text{CHCl}_3/\text{EtOH}$. **1**: colorless crystals; mp 272–274 °C; ^1H NMR (500 MHz, CDCl_3 , 27 °C) δ 1.32 (s, 27H), 6.76 (d, 1H, $J_{\text{PH}} = 852$ Hz), 6.95 (d, 3H, $J = 8.4$ Hz), 7.14 (dd, 3H, $J = 8.4$, 2.1 Hz), 7.88 (br d, 3H, $J = 0.8$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 27 °C) δ 31.52 (s), 34.47 (s), 39.21 (d, $J_{\text{PC}} = 125$ Hz), 112.41 (d, $J_{\text{PC}} = 10.3$ Hz), 122.20 (d, $J_{\text{PC}} = 22.3$ Hz), 124.59 (s), 131.95 (d, $J_{\text{PC}} = 13.3$ Hz), 146.39 (s), 149.71 (s); ^{31}P NMR (109 MHz, CDCl_3 , 27 °C) δ 2.7; HRMS (EI 70 eV) m/z 488.2491, calcd for $\text{C}_{31}\text{H}_{37}\text{O}_3\text{P}$ 488.2480. Anal. Calcd for $\text{C}_{31}\text{H}_{37}\text{O}_3\text{P}$: C, 76.20; H, 7.63. Found: C, 76.48; H, 7.61.

Synthesis of 1-Hydro-5-carbaphosphatrane 1 (Method B). To a solution of cyclic phosphinate **3** (1.18 g, 2.21 mmol) in CHCl_3 (50 mL) was added a solution of boron tribromide (1.0 M in CH_2Cl_2 , 10 mL, 10 mmol). The solution was stirred at room temperature for 60 h, treated with aqueous NaHCO_3 , and extracted with CHCl_3 . The extracts were dried over anhydrous MgSO_4 . After removal of the solvent under reduced pressure, the crude products were subjected to HPLC to afford **1**, which was further purified by reprecipitation from $\text{CHCl}_3/\text{EtOH}$ and obtained as colorless crystals (0.58 g, 54%).

Synthesis of 1-Methyl-5-carbaphosphatrane (2). To a solution of cyclic phosphinate **3** (31.2 mg, 0.0584 mmol) in CDCl_3 (0.5 mL) in a 5-mm-diameter Pyrex glass tube was added iodotrimethylsilane (0.05 mL, 0.35 mmol). After a few freeze–pump–thaw cycles, the tube was sealed in vacuo and the solution was heated at 80 °C for 63 h. After confirmation of disappearance of **3** by ^{31}P NMR, the sealed tube was opened and the solvent was removed under reduced pressure. The crude products were separated by HPLC to afford **2** (8.5 mg, 29%). **2**: colorless crystals; mp 187–190 °C; ^1H NMR (500 MHz, CDCl_3 , TMS, 27 °C) δ 1.32 (s, 27H), 1.66 (d, 3H, $J_{\text{PH}} = 18.3$ Hz), 6.89 (d, 3H, $J = 8.4$ Hz), 7.11 (dd, 3H, $J = 8.4$, 2.2 Hz), 7.86 (br s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 27 °C) δ 20.26 (d, $J_{\text{PC}} = 215$ Hz), 31.54 (s), 34.43 (s), 40.08 (d, $J_{\text{PC}} = 133$ Hz), 111.92 (d, $J_{\text{PC}} = 9.9$ Hz), 121.96 (d, $J_{\text{PC}} = 22.1$ Hz), 124.38 (s), 132.54 (d, $J_{\text{PC}} = 12.5$ Hz), 145.78 (s), 149.49 (d, $J_{\text{PC}} = 4.1$ Hz); ^{31}P NMR (109 MHz, CDCl_3 , 27 °C) δ 21.1; HRMS (EI 70 eV) m/z 502.2637, calcd for $\text{C}_{32}\text{H}_{39}\text{O}_3\text{P}$ 502.2606.

X-ray Studies. Single crystals of **1** were grown from their benzene solution. The intensity data were collected at 123 K on a MAC Science DIP-2030 imaging plate area detector with Mo $K\alpha$ radiation ($\lambda = 0.710$ 69 Å). Reflection data were corrected for Lorentz and polarization factors and for absorption using the multiscan method. Crystallographic and experimental data are listed in Table 1. The structures were solved by the direct method (SIR97) and refined by full-matrix least squares on F^2 (SHELXL-97).⁸ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms without the hydrogen directly bonding to phosphorus atom were idealized by using the riding model.

Computational Method. To understand bonding and assist in the identification of structures, a variety of calculational methods were used: closed-shell SCF (RHF),⁹ second-order Møller–Plesset perturbation (MP2),¹⁰ and density functional theory using the B3LYP func-

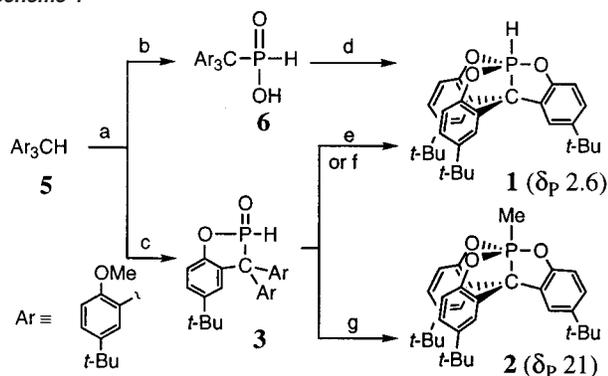
Table 1. Crystallographic Data for **1**

formula	$\text{C}_{34}\text{H}_{37}\text{O}_3\text{P}$
temperature (K)	123
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	15.9630(10)
b (Å)	11.2780(10)
c (Å)	15.2690(10)
β (deg)	93.842(4)
V (Å ³)	2742.7(3)
Z	4
calculated density (g cm ⁻³)	1.183
reflection collected	16 713
unique	5236
R_{int}	0.021
F_{000}	1048.00
goodness of fit (F)	1.059
R indices ($I > 2\sigma(I)$)	$R1 = 0.0571$ $wR2 = 0.1453$

tional.¹¹ Most structural optimizations were performed with the 6-31G(d) basis set.¹² For the study of transannular bonding, improved structures were obtained using a basis set containing triple- ζ quality sets and two sets of d orbitals on the hypervalent center but only one d on the other heavy atoms, which is termed 6-311G(2d,d).¹³ All calculations used Cartesian Gaussians rather than spherical harmonics. Bond orders were computed using Mayer's RHF formula¹⁴ with the MP2 density matrix. MP2 Raman intensities were computed by a finite difference technique.¹⁵ A vibrational decomposition due to Boatz and Gordon¹⁶ was used for normal-mode analysis and force constant extraction, using Pulay's natural internal coordinates,¹⁷ which include the transannular bond as an individual symmetry-adapted coordinate. Additional bonding comparisons were made using RHF localized orbitals¹⁸ and Mulliken population analysis.¹⁹ Most calculations were performed using the parallel computing procedures²⁰ contained in the GAMESS program,²¹ except the B3LYP computations which were made using GAUSSIAN98.²²

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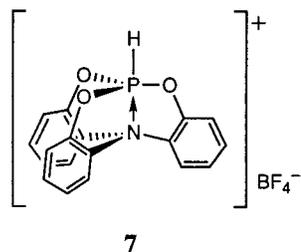
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Scheme 1^a

^a Conditions: (a) *n*-BuLi; (b) PCl₃, room temperature, then H₂O, 11% (two steps); (c) PCl₃, 50 °C, then H₂O, 38% (two steps); (d) TMSI, room temperature, 38%; (e) TMSI, room temperature, 39%; (f) BBr₃, room temperature, then aqueous NaHCO₃, 54%; (g) TMSI, 80 °C, in a sealed tube, 29%.

Results and Discussion

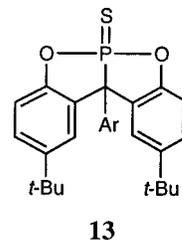
Synthesis. Scheme 1 outlines the synthetic pathways for 5-carbaphosphatranes. A triarylmethyl group was employed for the synthesis of 5-carbaphosphatranes for the following reasons: (a) it can be easily synthesized from an aryl halide and diethyl carbonate; (b) it has a rigid structure and so is suitable for the multidentate ligand which suppresses pseudorotation. Triarylmethane **5** was prepared according to the typical procedure. Lithiation of **5** followed by reaction with phosphorus trichloride at room temperature afforded phosphinic acid **6** after hydrolysis. When the reaction was effected at 50 °C, the cyclic phosphonate **3** was obtained as a result of intramolecular cyclization with loss of chloromethane and hydrolysis.²³ 1-Hydro-5-carbaphosphatrane (**1**) was synthesized by treatment of **3** or **6** with iodotrimethylsilane at room temperature in CDCl₃.²⁴ On the other hand, when the reaction of **3** with iodotrimethylsilane was carried out at 80 °C in a sealed tube, 1-methyl-5-carbaphosphatrane (**2**) was obtained instead of **1**. Compound **1** was also obtained by the reaction of **3** with boron tribromide in CHCl₃. It was reported that the tribenzophosphatrane **7** bearing



a 5-nitrogen atom is observable by NMR spectroscopy in solution but too fragile to be isolated.²⁵ In contrast, **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.

Reaction Mechanism. When the reaction of **3** with iodotrimethylsilane was carried out in CDCl₃ and the reaction was monitored by ³¹P NMR, a compound giving a signal at 190 ppm was observed as an intermediate. This compound is considered to be the cyclic phosphonite **12**, because the chemical shift is a reasonable value for a cyclic phosphonite²⁶ and this

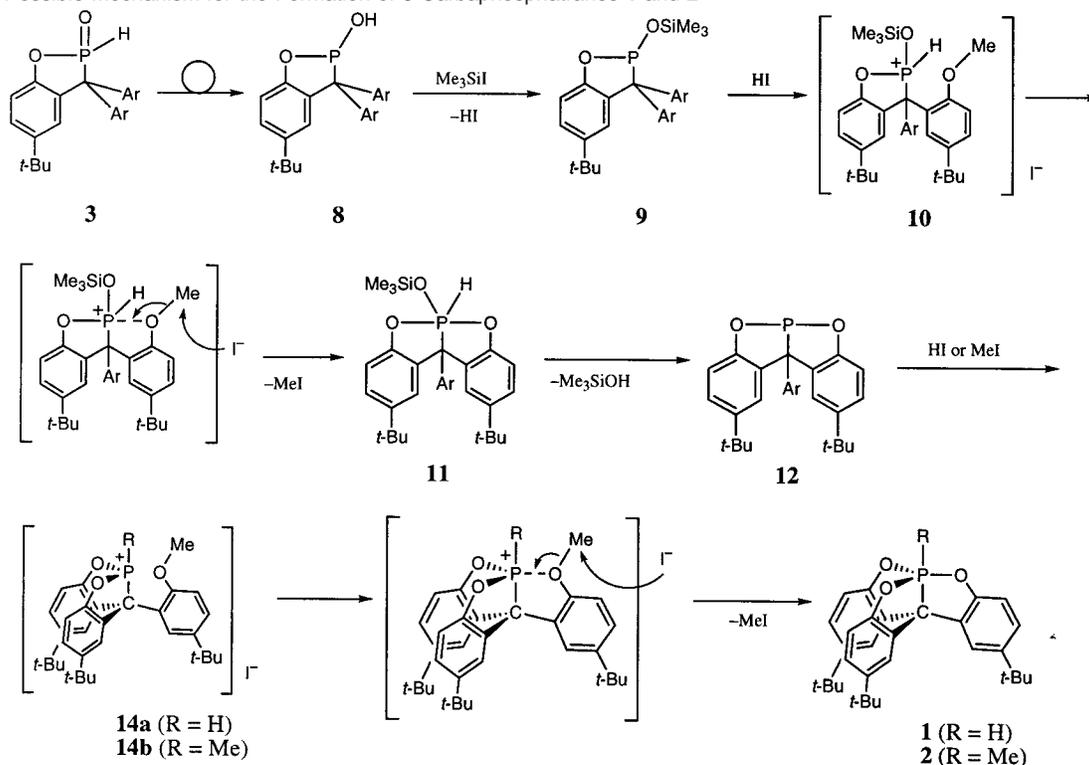
compound was converted to phosphonothioate **13** (δ_P 126) by



addition of elemental sulfur. A possible mechanism for the formation of 5-carbaphosphatranes is shown in Scheme 2. The reaction of iodotrimethylsilane with cyclic phosphonite **8**, which is a tautomer of cyclic phosphinate **3**, affords silyl phosphonite **9** with generation of hydrogen iodide. However, these species were not observed by ³¹P NMR. This is probably because phosphonium salt **10** is formed by the protonation of silyl phosphonite **9** with hydrogen iodide. The demethylation process proceeds via the attack of iodide anion on the methyl group of phosphonium salt **10**. The intermediate **12**, which was observed by ³¹P NMR (δ_P 190) during the reaction, is formed by the reductive elimination of trimethylsilanol from phosphorane **11**. The phosphonium salts **14a** and **14b** were formed by the reaction of cyclic phosphonite **12** with hydrogen iodide or methyl iodide in a way similar to the phosphonium salt **10**. In the case of phosphonium salts **14a** and **14b**, the demethylation reaction is considered to proceed similarly to afford 5-carbaphosphatranes **1** and **2**, respectively.

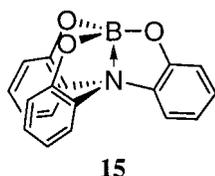
Structure. The structure of **1** was definitively determined by X-ray crystallographic analysis. Single crystals of **1** were grown by the slow evaporation of a saturated benzene solution at room temperature. The side and top views of **1** are shown in Figure 1. It is clearly shown that **1** has a nearly ideal trigonal bipyramidal structure around the central phosphorus atom. The apical positions are occupied by hydrogen and carbon atoms while three oxygen atoms are located at the equatorial positions, indicating that **1** is a 10-P-5 phosphorane in the perfectly “anti-apicophilic” arrangement.²⁷ Selected bond lengths and angles are summarized in Table 2. The sum of bond angles between equatorial bonds is 359.7°, while the bond angle between apical bonds and those between apical and equatorial bonds are 178.7(9)° and 87.2(9)–91.99(9)°, respectively. These parameters indicate the trigonal bipyramidal geometry around the central phosphorus atom. The P–H and P–O bond lengths are 1.38(2) and 1.648(2)–1.649(2) Å, respectively, which are typical lengths for P–H and P–O bonds. On the other hand, the P–C bond length is 1.921(2) Å, slightly longer than the typical value for the apical P–C bond of a phosphorane.²⁸ Such an elongation is attributable to the rigidity of the tetradentate ligand based on

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Scheme 2. Possible Mechanism for the Formation of 5-Carbaphosphatranes **1** and **2**

the triarylmethyl unit, as discussed in the literature for tribenzosilatrane.²⁹

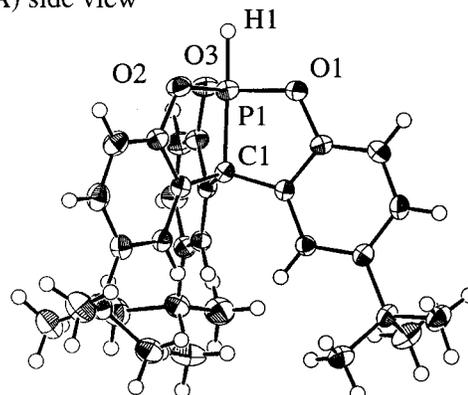
NMR Spectra. In the ³¹P NMR spectra, 5-carbaphosphatranes **1** and **2** showed signals at 2.7 and 21.1 ppm, respectively. The ¹³C NMR signals for the central carbon of the triarylmethyl ligand of **1** and **2** were observed at 39.2 and 40.8 ppm, respectively, which are high-field shifted by ~20 ppm from phosphinic acid **6** (62.0 ppm). These observations can be explained by assuming that the carbon atom located at the apical position is shielded due to the electronic property of the three-center four-electron apical bond.³⁰ In the ¹H NMR spectrum of **1**, the aromatic protons at positions ortho to the central carbon atom (δ 7.88) showed a low-field shift by ~1.5 ppm from the usual position. Such a low-field shift of the ortho protons was also reported for tribenzo-1-hydrophosphatranes **7** (δ 8.49) and boratranes **15** (δ 8.10–7.80),³¹ suggesting a structural similarity



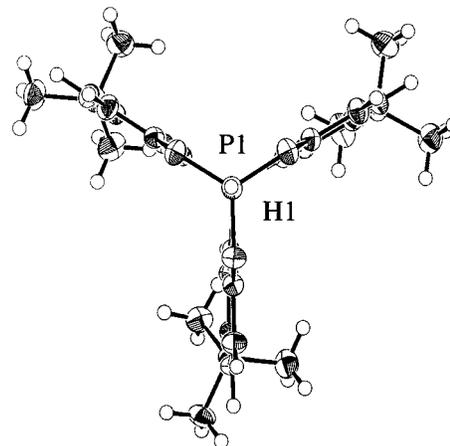
between 5-carbaphosphatranes **1** and the usual phosphatranes **7** and boratranes **15**. The rest of the aromatic protons of **1** were observed in the usual region (6.95, 7.14 ppm).

The ¹J_{PH} value of **1** and the ¹J_{PC}(P–CH₃) value of **2** are 852 and 215 Hz, respectively, which are extraordinarily large for

(A) side view



(B) top view

**Figure 1.** Ortep drawings of **1** with thermal ellipsoid plot (50% probability).

(A) Side view; (B) top view.

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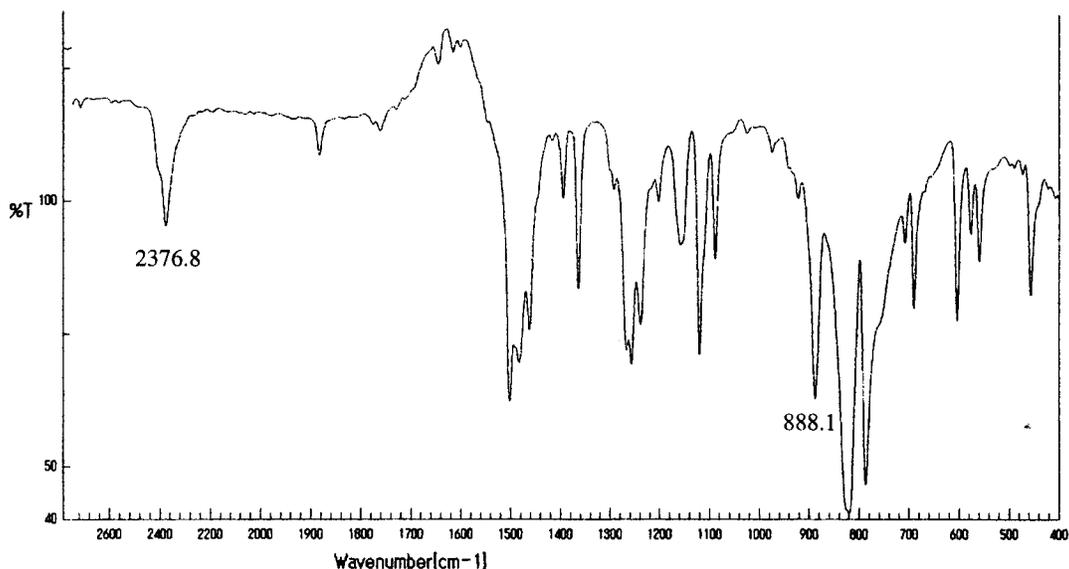


Figure 2. IR spectrum of 1-hydro-5-carbaphosphatrane (1).

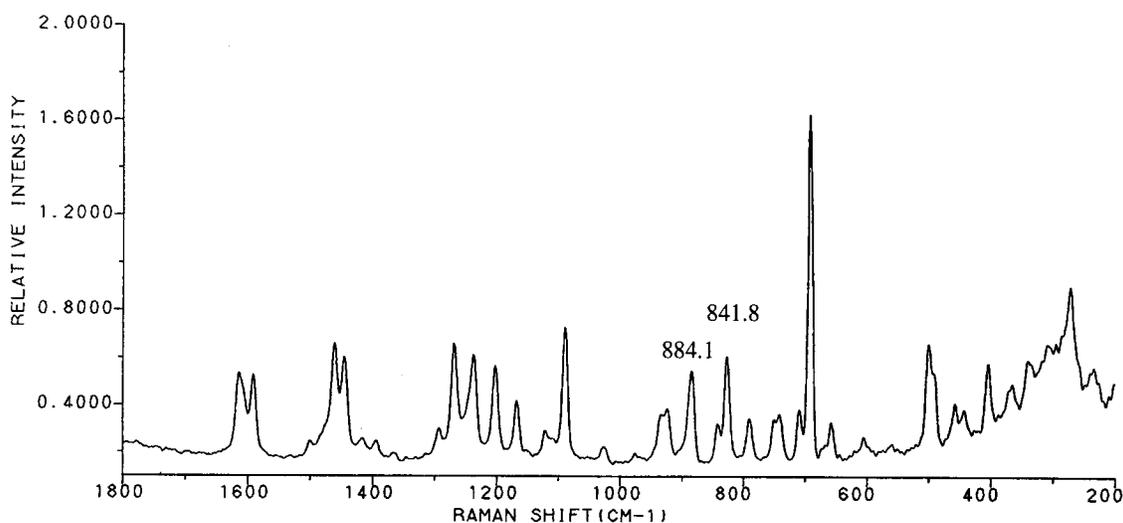


Figure 3. Raman spectrum of 1-hydro-5-carbaphosphatrane (1).

Theoretical Calculation of Transannular Bond Distance of Alkyl Atranenes. An early surprise in silatrane chemistry was the recognition that the Si–N bond distance was not only capable of varying over the range 2.02–2.18 Å for halogen, OR, or R substituents in X-ray studies,^{2e} it also changes according to the state of the compound. Thus, the X-ray distance for methylsilatrane of 2.18 Å³⁹ is considerably shorter than the gas-phase value of 2.45 Å.⁴⁰ Later experiments showed the same behavior for fluorosilatrane, with an X-ray structure of 2.04 Å⁴¹ compared to 2.32 Å in the gas phase.⁴² An NMR and IR study suggested that Si–N distances take on intermediate values in solution.⁴³ Recent X-ray experiments have further broadened the range of known Si–N distances: two very short values are 2.01 Å for SCN substitution,⁴⁴ 2.01 Å for an OR ligand

containing cobalt,⁴⁵ and an extremely long 3.00 Å for an osmium substituent.⁴⁶ This wide range is indicative of only a weak Si–N bond, with a low force constant.

Of course, a number of theoretical studies have attempted to reproduce and therefore understand this wide range of silatrane distances. A large number of substituted silatranes and phosphatranes were previously considered by us at the RHF/6-31G-(d) level, but no comparisons between these two families of atrane were made.⁴⁷ However, this level of computation gave silatrane bond distances ~0.25 Å longer than the two available gas-phase structures. Probe calculations were reported indicating that the structures were sensitive both to the basis set and to the inclusion of electron correlation. Our earlier study included pertinent references to prior calculations, but new theoretical

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Table 4. Computed Atrane Structures (in Å)^a

	I			II	III	IV
	R = F	R = Me	R = H	R = H	R = H	R = R' = H
RHF/6-31G(d)	2.534	2.734	2.648	2.444	1.902	1.940
RHF/6-311G(2d,d)	2.572	2.771	2.690	2.463	1.900	
MP2/6-31G(d)	2.269	2.384	2.302	2.110	1.907	1.951
MP2/6-311G(2d,d)	2.300	2.443	2.327	2.122	1.902	
B3LYP/6-31G(d)	2.424	2.642	2.475	2.188	1.928	1.958
B3LYP/6-311G(2d,d)	2.484	2.719	2.576	2.219	1.927	
ED experiment	2.324 ^d	2.45 ^c				
X-ray experiment	2.042 ^d	2.175 ^e	2.146 ^f	1.986 ^g		1.921 ^h

^a Computed values with the 6-31G(d) basis differ slightly from ref 46e due to use of a different 6-31G(d) basis set for Si. ^b Reference 42. ^c Reference 40. ^d Reference 41. ^e Reference 39. ^f Reference 52. ^g Reference 36. ^h Present work; the experiment is for R' = *t*-Bu.

reports have appeared since.⁴⁸ One of these^{48c} contains a first attempt to provide a theoretical force field for four silatranes, but the results given focus on zero point energies and skeleton modes. Most importantly, Anglada and co-workers demonstrated that full MP2/6-31G(d) geometry optimization on methylsilatrane gave a Si–N distance of 2.40 Å,^{48e} in good agreement with the gas-phase value 2.45 ± 0.05 Å, although B3LYP/6-31G(d) does not (2.69 Å). The present work will show that MP2 computations also give a similar good result for the gas-phase geometry of fluorosilatrane and, furthermore, that this level of theory is in good agreement with the available vibrational experiments on the parent silatrane.

Table 4 compares computed transannular distances for various theoretical methods using two basis sets. As Anglada and co-workers showed, MP2/6-31G(d) gives good results for methylsilatrane, and the present calculation for fluorosilatrane is similar. Both MP2/6-31G(d) results are ~0.06 Å shorter than the gas-phase structures, which is a marked improvement over the 0.25-Å elongation from RHF/6-31G(d). Improvements in the basis set lead to MP2/6-311G(2d,d) values that are in essentially perfect agreement with experiment. Note that B3LYP, which is the only DFT functional that was considered, gives results shorter than RHF but deteriorates considerably with basis set improvement.

Unfortunately, there is no experimental data regarding the gas-phase structure of the phosphatrane cation **II** (R = H), but the MP2 results indicate some fraction of the difference between solid and gas phase observed in silatrane persists in this compound. Again, the RHF and B3LYP values seem too long.

For 5-carbaphosphatrane, all methods give very similar bond distances, and improving the basis does not change the result. Furthermore, the computations for **IV** (R = R' = H) are in good agreement with the present solid-state experimental PC bond distance of **I**, hinting that the transannular bond in 5-carbaphosphatrane possesses a steeper potential well than silatrane or phosphatrane.

From Table 4, it is clear that MP2/6-31G(d) is the minimal level of theory needed to obtain reasonable structures for the simple atranes **I–III**. Accordingly, this method is used to obtain vibrational frequencies for these simple atranes, to allow comparison of their transannular stretching force constants. For subsequent calculations on 5-carbaphosphatranes and related

species, which include the three benzene rings, it appears that the RHF/6-31G(d) method will give acceptable results in much shorter computer time.

Vibrational Analysis. Several experimental studies of the vibrational spectroscopy of parent and substituted silatranes have been conducted.⁴⁹ Early experiments often used samples in KBr pellets (which absorb below ~400 cm⁻¹), which complicated their assignments, but modes in the range 540–590 cm⁻¹ are now considered to be skeletal breathing rather than transannular stretches.^{2b} Lukevics and co-workers assigned a mode in the range 320–390 cm⁻¹ to the transannular stretch in various organic silatranes.^{49c} Two experiments have been carried out on the polycrystalline parent **I** (R = H). A Raman spectrum and its associated force field calculation missed the transannular stretch due to its low Raman intensity.^{49e} An IR and Raman study observed an intense IR transition (with low Raman intensity) at 313 cm⁻¹ but did not assign this or any other band to the transannular stretch.^{49g}

Table 5 compares the theoretical MP2/6-31G(d) spectrum with the experimental data.^{49g} After reordering the three computed bands near 610 cm⁻¹, there is a clear match in the intensity patterns for all bands shown. The calculated 267-cm⁻¹ mode corresponds to the strong IR absorption observed at 313 cm⁻¹. A vibrational decomposition analysis shows that the Si–N stretch coordinate is 62% of this mode. A large IR intensity is to be expected, as the dipole moment of silatranes is known to undergo a large change with the Si–N distance, which is responsible for the shortening of the Si–N distance in the solid state.^{47a} Bearing in mind that the experiment is carried out on a solid sample, where the Si–N bond should be slightly stronger,^{49g} there is good agreement between the computed Si–N stretching frequency and experiment.

Comparisons of Bonding Characteristics. Because of the reasonable match between the experimental and computed MP2/

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Table 5. Vibrational Frequencies of Silatrane (I)^a

mode	experiment ^b		sym ^c	MP2/6-31G(d)		
	IR	Raman		ω^d	IR ^e	Raman ^f
1			a	80.0	0.205	0.013
2	184 w	249 w	e	176.4	0.116	1.181
3	250 s	249 w	e	260.5	0.402	0.522
4	313 s	316 w	a	266.6	1.375	0.611
5			a	321.4	0.017	0.269
6	345 w	347 m	e	365.2	0.178	1.840
7	465 vw	468 m	e	449.7	0.019	0.671
8	491 vw	492 m	a	495.7	0.060	2.825
9	589 s	596 vs	a	620.0	0.153	14.527
10		625 sh	e	610.5	0.073	1.642
11	629 vs	634 s	a	603.0	2.179	1.068
12	755 vs	755 sh	e	777.4	3.452	6.440
13		764 s	a	785.4	0.006	2.571

^a Only modes up to 800 cm⁻¹ are given. Silatrane is a C₃ molecule with 44 vibrational modes, 22 of a, and 22 of e symmetry. ^b Reference 49g, with their characterization of intensities. ^c Symmetry of the mode. ^d Frequency in cm⁻¹. ^e IR intensity in D/amu Å². ^f Raman intensity in Å⁴/amu.

Table 6. Atrane Bonding Characteristics^a

	R ^b	ω^c	k ^d	boi ^e	μ^f
Silatrane (I)					
R = H	2.302	267 (62)	0.83	0.225	6.68
R = CH ₃	2.384	226 (61)	0.72	0.179	
R = F	2.269	250 (63)	0.91	0.254	
Phosphatrane (II)					
R = H	2.110	354 (67)	1.34	0.367	5.82 ^g
5-Carbaphosphatrane (III)					
R = H	1.907	626 (37)	2.89	0.731	4.61
R = CH ₃	1.922	580 (26)	2.77	0.709	
R = OH	1.915	564 (21)	3.39	0.732	
R = F	1.903	603 (25)	3.04	0.754	
R = Cl	1.905	627 (40)	2.98	0.732	

^a This table contains computational results obtained at the MP2/6-31G(d) level. ^b Transannular distance, in Å. ^c Transannular vibrational frequency, in cm⁻¹. For carbaphosphatrane, the normal modes are more mixed than in the other atranes, so the frequency shown is the one with the greatest contribution of P–C stretch. Values in parentheses, percent. ^d Transannular force constant, in mdyn/Å. ^e Mayer's bond order index for the transannular bond. ^f Dipole moment, in D. ^g This ion's dipole moment is computed with respect to its center of mass.

6-31G(d) frequencies in silatrane, the force constant matrix can be assumed to be fairly accurate at this level of theory. Accordingly, MP2/6-31G(d) force fields were obtained for the isoelectronic atrane series I–III (R = H) and for a number of substituted compounds. Their stretching force constants are given in Table 6, along with bond orders. The parent R = H force constants for silatrane I, phosphatrane II, and 5-carbaphosphatrane III are 0.83, 1.34, and 2.89 mdyn/Å respectively, in the ratio 0.62:1:2.16. The bond order formula does not correspond to an experimental, which the force constant is in principle, but the bond orders are remarkably similar in their ratios, namely, 0.61:1:1.99. The force constant values indicate that the transannular bond in 5-carbaphosphatrane is more than 3 times stronger than in silatrane.⁵⁰

Supporting evidence for increased carbaphosphatrane transannular bonding is as follows. Silatrane shows matching variations in its bond lengths, force constants, and bond orders

(50) All three atranes actually have very similar first-order wave functions: of the 64 valence electrons, the weakly occupied MP2/6-311G(2d,d) natural orbitals contain a total of 0.99, 1.00, and 1.02 e⁻ for silatrane, phosphatrane, and 5-carbaphosphatrane, and the occupancy of the highest of the principal natural orbitals is 1.950, 1.947, and 1.946 e⁻, respectively. Thus, it is simply the smaller force constant in silatrane that makes accurate computation of its true length more difficult, not a lack of single reference character.

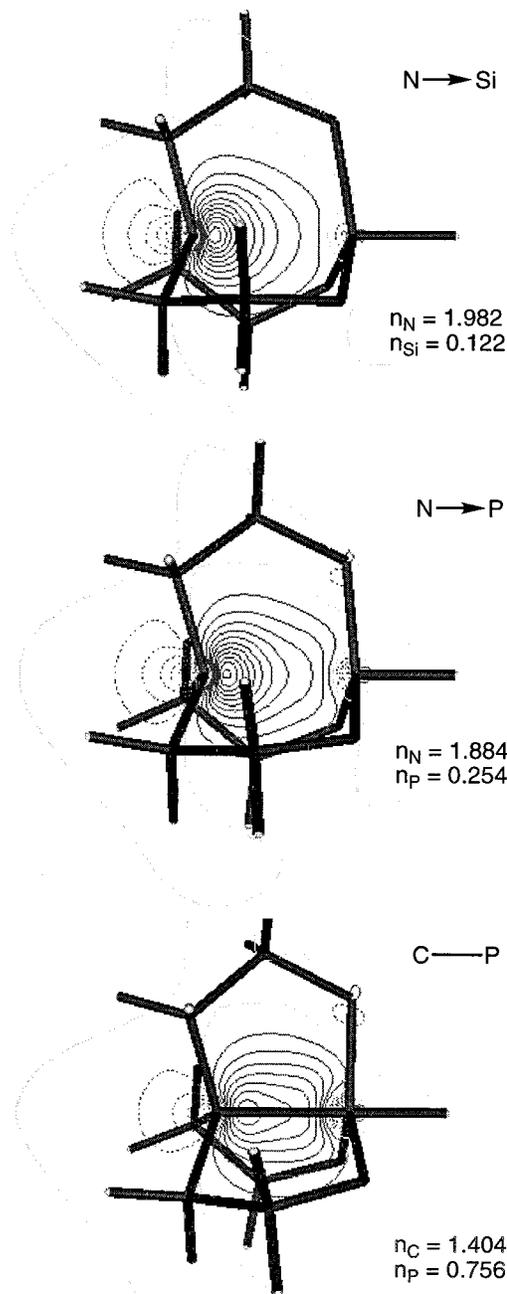


Figure 4. Transannular RHF/6-31G(d) localized orbital at the MP2/6-31G(d) structures. Each contour represents 0.05 b^{-3/2}. Numerical values are the Mulliken population analysis of each pair, which sum to more than 2 because of small negative populations on the other atoms.

upon substitution, but 5-carbaphosphatrane's larger force constants mean its bond is not sensitive to substitution. The dipole moments given in Table 6 decrease from silatrane to 5-carbaphosphatrane, indicating less ionic character in the transannular bonds. This is born out in Figure 4, which shows the localized RHF/6-31G(d) orbitals, at MP2/6-31G(d) geometries. The contour lines indicate 5-carbaphosphatrane possesses much more covalent character, as does the partitioning of these electrons pairs by population analysis. A comparison of the sum of the van der Waals radii, the computed transannular distances, and the sum of the covalent radii, respectively, confirms the same point.⁵¹ For the parents, these three values are as follows:

(51) Emsley, J. *The Elements*; Clarendon Press: Oxford, U.K., 1991.

silatrane, 3.54, 2.33, and 1.87; phosphatrane, 3.44, 2.12, and 1.80; and 5-carbaphosphatrane, 3.75, 1.90, and 1.87. In 5-carbaphosphatrane, the transannular distance is not much larger than the P–C covalent radii sum, while the weaker silatrane bond is longer than this sum.

The frequency attributed to the 5-carbaphosphatrane stretch in Table 6 is around 600 cm^{-1} , considerably lower than the 888-cm^{-1} observed band attributed above to the PC stretch. The alkyl side group in the small model **III** is less rigid than the benzene side groups present in **IV**, which must be a large factor in this difference.

Conclusion

5-Carbaphosphatranes, a new class of main group atranes, were synthesized. X-ray crystallographic analysis revealed a nearly ideal trigonal bipyramidal structure of 1-hydro-5-carbaphosphatrane that positions the most electronegative oxygens at equatorial sites. The structural parameters of **1** are quite similar to usual phosphatranes. The coupling constants for the transannular bonds of 5-carbaphosphatranes are extraordinarily

large for those of apical bonds of phosphoranes but quite similar to those of phosphatranes. Such similarities between 5-carbaphosphatranes and phosphatranes are due to the isoelectronic structure of both compounds. Theoretical calculations indicated that the transannular bond in 5-carbaphosphatrane is twice as strong as that of phosphatrane and more than 3 times stronger than that of silatrane, reflecting the difference between a substantially covalent C–P bond and the more ionic N→P or N→Si dative bonds.

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Supporting Information Available: X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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