Inorg. Chem. **2005**, *44*, 6500–6502

Inorganic Chemistry
Communication

Solvent-Dependent Crystallization of 1-Hydro-6-carbaphosphatrane and Its Tautomer

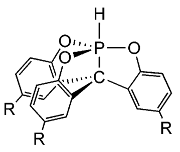
Shin-ya Nakafuji,[†] Junji Kobayashi,[†] Takayuki Kawashima,*[,†] and Michael W. Schmidt[‡]

Department of Chemistry, Graduate School of Science, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and 201 Spedding Hall, Iowa State University,
Ames, Iowa 50011

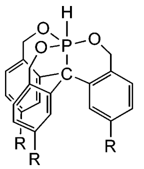
Received May 2, 2005

1-Hydro-6-carbaphosphatrane **2** was obtained as a mixture with its tautomer, **3**. Tautomers **2** and **3** were isolated by the recrystallization from different solvents, respectively, and each structure was determined by X-ray crystallographic analysis. Variable-temperature NMR experiments revealed that pentacoordinate **2** and tricoordinate **3** are under the equilibrium, showing that **3** is more stable. The theoretical calculations found a weaker transannular PC bond in **2** than in 1-hydro-5-carbaphosphatrane, **1**, which can be considered to be the reason 1-hydro-6-carbaphosphatrane **2** is less stable than its tautomer **3**.

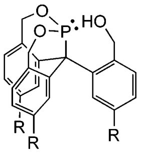
Pentacoordinate phosphorus compounds exhibit dynamic behavior, i.e., nondissociative intramolecular positional isomerization,[1] and in a particular case, dissociative tautomerization.[2] These motions usually lead a pentacoordinate phosphorane to the most stable stereoisomer according to the apicophilicity rule.[3] Recently, several examples of phosphoranes in the "anti-apicophilic" arrangement, breaking the apicophilicity rule, have been reported, whose syntheses were achieved by using multidentate ligands.[4] From such a viewpoint, we have reported the synthesis, structure, and bonding properties of 5-carbaphosphatrane, **1**,[5] with three five-membered rings, which has a perfectly "anti-apicophilic" arrangement, and have shown that a possible tricoordinate tautomer is not observed spectroscopically. Interest in the effect of the ring rigidity on the relative stability between stereoisomers or between tautomers prompted us to develop a novel tetradentate ligand with three six-membered rings, which is more flexible than the three five-membered rings reported previously.[5]



1 (R=*t*-Bu)
7 (R=H)



2 (R=*t*-Bu)
8 (R=H)



3 (R=*t*-Bu)
9 (R=H)

If the tautomers (e.g., keto−enol tautomers) exist in an interconverted mixture, the thermodynamically more stable tautomer can usually be isolated. The thermodynamically less stable tautomer can sometimes be isolated by kinetic control but often only by oneway conversion into another tautomer, such as substitution.[6,7] Among tautomerization involving a phosphorus atom, that between a pentacoordinate phosphorane and a tricoordinate phosphine has been extensively investigated.[8] However, Holmes et al. recently reported a unique tautomerism between a tricoordinate phosphine and

---

[*] To whom correspondence should be addressed. E-mail: takayuki@chem.s.u-tokyo.ac.jp.

[†] The University of Tokyo.

[‡] Iowa State University.

(1) Holmes, R. R. *Pentacoordinated Phosphorus − Structure and Spectroscopy*; ACS Monograph 175, 176; American Chemical Society: Washington, DC. 1980; Vol. I, II.

(2) Burgada, R.; Setton, R. *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley Publishers: New York, 1994; Vol. 3, Chapter 3, and references therein.

(3) (a) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613. (b) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5849. (c) Trippett, S. *Phosphorus Sulfur* **1976**, *1*, 89. (d) Wang, P.; Zhang, Y.; Glaser, R.; Reed, A. E.; Schleyer, P. v. R.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 55. (e) Thatcher, G. R. J.; Campbell, A. S. *J. Org. Chem.* **1993**, *58*, 2272.

(4) For examples of other phosphoranes with an apical P−C bond, see: (a) Antipin, M. Yu.; Chernega, A. N.; Struchkov, Yu. T.; Kozlov, E. S.; Boldeskul, I. E. *Zh. Strukt. Khim.* **1987**, *28*, 105. (b) Francke, R.; Sheldrick, W. S.; Röschenthaler, G.-V. *Chem. Ber.* **1989**, *122*, 301. (c) Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552. (d) Kojima, S.; Kajiyama, K.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **1996**, *118*, 12866. (e) Vollbrecht, S.; Vollbrecht, A.; Jeske, J.; Jones, P. G.; Schmutzler, R.; du Mont, W.-W. *Chem. Ber.* **1997**, *130*, 819. (f) Kojima, S.; Sugino, M.; Matsukawa, S.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **2002**, *124*, 7674. (g) Kommana, P.; Kumar, N. S.; Vittal, J. J.; Jayasree, E. G.; Jemmis, E. D.; Swamy, K. C. K. *Org. Lett.* **2004**, *6*, 145.

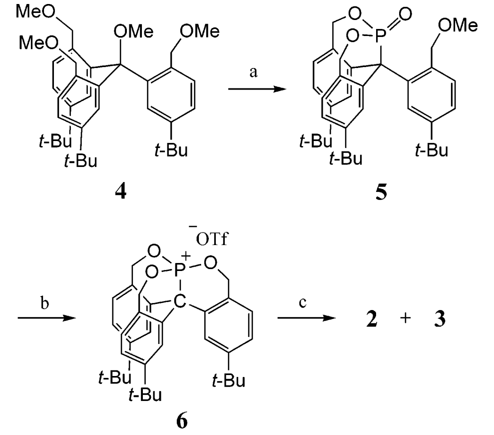
(5) (a) Kobayashi, J.; Goto, K.; Kawashima, T. *J. Am. Chem. Soc.* **2001**, *123*, 3387. (b) Kobayashi, J.; Goto, K.; Kawashima, T.; Schmidt, M. W.; Nagase, S. *J. Am. Chem. Soc.* **2002**, *124*, 3703.

(6) (a) Hart, H. *Chem. Rev.* **1979**, *79*, 515. (b) Capon, B.; Guo, B.-Z.; Kwok, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135. (c) Watanabe, S.; Goto, K.; Kawashima, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 3195.

(7) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 442.

10.1021/ic050679d CCC: $30.25

Scheme 1. Syntheses of **2** and **3**[a]



[a] Conditions: (a) 1) LiNaph, 2) PCl_3, reflux, 3) aq. H_2O_2, 45%; (b) MeOTf, room temperature, 79%; (c) LiAl(O−*t*-Bu)$_3$H, room temperature, 63%.

a hexacoordinate phosphate and isolation of each tautomeric form by changing a substituent on the phosphorus atom.[9] To the best of our knowledge, there is still no example where both tautomers have been isolated and their structures decisively determined. Herein, we report the syntheses, isolation, structures, and dynamic behavior of 1-hydro-6-carbaphosphatrane **2** with three six-membered rings and its tautomer, **3**.

Methyl ether **4** was lithiated with 2 equiv of lithium naphthalenide (LiNaph), and subsequent treatment with phosphorus trichloride under refluxing condition gave a bicyclic phosphonite as a result of two intramolecular cyclization reactions with loss of chloromethane,[5,10] which is oxidized to a bicyclic phosphonate, **5**, by aqueous H_2O_2. A phosphonium salt, **6**, was obtained by the reaction of **5** with 5 equiv of methyl triflate. Treatment of **6** with 1 equiv of lithium tri(*t*-butoxy)aluminum hydride gave 1-hydro-6-carbaphosphatrane **2** and its tautomer, phosphonite **3** as a mixture.

^{31}P NMR spectra of **2** and **3** showed the signals at δ_P −58 and 123, respectively. The signal of **2** was observed at a higher-field region than that of **1** (δ_P 2.7),[5] attributable to the strong electron-donating ability of benzyloxy groups to the phosphorus center. The $^1J_{PH}$ and $^1J_{PC}$ values of **2** are 882 and 121 Hz, respectively. These values are extraordinarily large for the coupling constants of apical bonds in usual phosphoranes and are comparable to those of **1** and other "anti-apicophilic" phosphoranes. In ^{1}H NMR spectra, the P−H proton signal was observed at δ 6.06 in $CDCl_3$, showing solvents effects (δ 7.13 in C_6D_6, δ 5.97 in THF-d_8).

Table 1. Thermodynamic Parameters for Eq 1 at 298 K

	solvent	K_{eq}	$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)	$\Delta S°$ (J/(mol K))
exp	benzene	1.3	−0.2	3.4	50
	$CHCl_3$	2.4	−0.5	2.8	46
	THF	4.5	−0.8	2.5	46
calcd		12	−1.5	0.9	34

Variable-temperature NMR in various solvents was measured in order to investigate the dynamic equilibrium between **2** and **3**. The K_{eq} value for eq 1 is determined over a temperature range of 307−342 K, and thermodynamic parameters are estimated from a van't Hoff plot. They were also obtained by theoretical calculations on the model compounds **8** and **9** (without *t*-Bu groups) at the B3LYP/6-31G(d) level (Table 1).[11] While **2** is enthalpicly favorable, **3** is more stable due to entropy effects. Taking into consideration that an analogous trivalent species was not observed in the case of **1**, ring expansion from five-membered ring to six-membered rings destabilizes the "anti-apicophilic" phosphorane form. In addition, the ratio of **2** and **3** depends on the polarities of solvents. The tautomer **3**, which has a larger dipole moment than **2** as predicted by theoretical calculations, is preferred to **2** in a more polar solvent. Hydrogen bonding between **3** and THF may

$$\mathbf{2}(\mathbf{8}) \overset{K_{eq}}{\rightleftharpoons} \mathbf{3}(\mathbf{9}) \tag{1}$$

contribute to its stability in THF.

Single crystals of **2** and **3** were obtained by the slow evaporation of saturated solutions of a mixture of **2** and **3** in ether or benzene, respectively. It is interesting to point out that the ratios of **2**/**3** are 0.4:1 and 0.64:1 in ether and in benzene, respectively, and **3** is the favored tautomer in both solvents. The reason solvent-dependent crystallization occurred in this system remains unclear.

The structures of **2** and **3** were definitively determined by X-ray crystallographic analysis (Figure 1).[12,13] To the best of our knowledge, this is the first example of isolation and structural determination of both tri- and pentavalent tautomers. **2** has a slightly distorted trigonal bipyramidal geometry around the phosphorus, and the apical positions are occupied with hydrogen and carbon atoms, while three

---

(8) (a) Hellwinkel, D. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 3, Chapter 5B, pp 185−339. (b) Sanchez, M.; Wolf, R.: Burgada, R.; Mathis, F. *Bull. Soc. Chim. Fr.* **1968**, 773. (c) Burgada, R. *Bull. Soc. Chim. Fr.* **1975**, 407. (d) Savignac, Ph.; Richard, S. B.; Leroux, Y.; Burgada, R. *J. Organomet. Chem.* **1975**, *93*, 331.

(9) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 7035.

(10) Yoshifuji, M.; Nakazawa, M.; Sato, T.; Toyota, K. *Tetrahedron* **2000**, *56*, 43.

(11) The theoretical calculations were performed using the Gaussian98 program package. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Crystal data for **2**: monoclinic, $P2_1/n$, colorless, a = 15.220(1) Å, b = 11.916(3) Å, c = 17.379(4) Å, β = 103.8927(9)°, V = 3059.6(12) Å^3, 120 K, Z = 4, R1 = 0.060, wR2 = 0.164, GOF =1.048.

(13) Crystal data for **3**: monoclinic, $P2_1/c$, colorless, a = 11.740(16) Å, b = 10.492(14) Å, c = 23.80(3) Å, β = 90.617(7)°, V = 2932(7) Å^3, 120 K, Z = 4, R1 = 0.088, wR2 = 0.212, GOF =1.128.

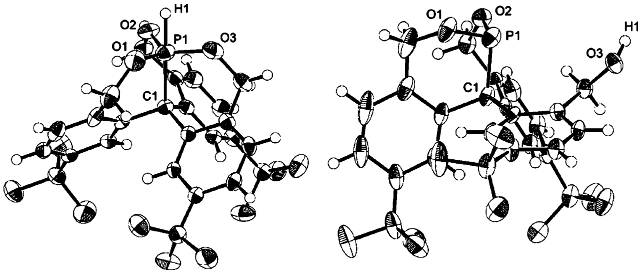


Figure 1. ORTEP drawings of **2** (left) and **3** (right) with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) and angles (deg) of **2**: P1−C1, 1.934(3); P1−H1, 1.38 (3); P1−O1, 1.595(3); P1−O2, 1.622(3); P1−O3, 1.615(2); O1−P1−O2, 119.15(13); O1−P1−O3, 119.47(13); O2−P1−O3, 117.99(13); C1−P1−O1, 96.13(12); C1−P1−O2, 96.38(11); C1−P1−O3, 95.93(12); H1−P1−C1, 179.6(13).

Table 2. AIM Analyses of 6-Carbaphosphatrane and 5-Carbaphosphatrane

	P−C	P−O	P−H	P−C	P−O	P−H
	8			**7**		
ρ(r)	0.1447	0.1598	0.1899	0.1575	0.1592	0.1905
$\nabla^2\rho$(r)	−0.3188	0.7513	−0.1622	−0.3737	0.6736	−0.1699

Table 3. Bonding Characteristics of Carbaphosphatranes[a]

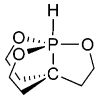
	10	11	12	13
R^b	1.907	1.937	1.906	1.939
k^c	2.89	2.68	2.72	2.20
m^d	4.61	3.11	3.10	4.63

[a] This table contains computational results obtained at the MP2/6-31G(d) level. [b] Transannular distance, in Å. [c] Transannular force constant, in mdyn/Å. [d] Dipole moment, in D.

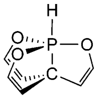
oxygen atoms are located at the equatorial positions, indicating that **2** is a 10-P-5 phosphorane in the perfectly "anti-apicophilic" arrangement. Unlike the C_{3v} structure of **1**, **2** has a propellerlike C_3 structure due to three six-membered rings. While the P−H and P−O bond lengths of **2** are typical lengths, as was the case for **1**, the P−C bond length is slightly longer than typical values for the apical P−C bond of a phosphorane.[4c]

To clarify the bonding properties of perfectly "anti-apicophilic" phosphoranes, especially about a transannular P−C bond, an Atoms in Molecules (AIM) analysis[14] was carried out for the model compounds **8** and **7** without *t*-Bu groups at the B3LYP/6-31G(d)//HF/6-31G(d) level. The results are summarized in Table 2. The electron densities and Laplacian values for the P−H and P−O bonds of **8** are similar to those of **7**, except for the larger Laplacian values of P−O bond in **8**, indicating a stronger ionic character. On the other hand, the electron densities and Laplacian values for the P−C bond of **8** are decreased. These results suggest that the P−C bond of **8** is weaker than that of **7**.

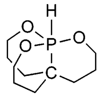
To pursue the question of the P−C bond strengths, further theoretical investigations were performed[15] for the four model compounds, **10**−**13**, containing saturated or unsaturated five- or six-membered rings optimized at the MP2/6-31G(d) level. While the six-membered rings in **12** took chair conformations, those of **13** with olefin moieties exhibited boat conformations, quite similar to the crystal structure of **2**. Since the olefin models seem useful, MP2/6-31G(d) force fields were obtained for **10**−**13**. The results are summarized in Table 3. **10** and **12** with the saturated rings have similar stretching force constants, 2.89 and 2.72 mdyn/Å, respectively. In the cases of **11** and **13**, the force constants decreased to 2.68 and 2.20 mdyn/Å, respectively, indicating that the P−C bonds are weakened by the introduction of unsaturated bonds and **13** has the weakest P−C bond. These phenomena are probably caused by the strain due to the planarity of the olefin, and surprisingly, the weakening of the P−C bond is larger for six-membered rings than for five-membered rings. Therefore, we can speculate that the decrease in stability of the pentavalent 1-hydro-6-carbaphosphatrane species **2** (relative to **3**) is caused by ring strain in six-membered unsaturated rings.



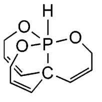
10



11



12



13

In summary, we have isolated 1-hydro-6-carbaphosphatrane **2** and its tautomer, **3**, by solvent-dependent crystallization and demonstrated their dynamic behavior in solution. X-ray crystallographic analysis showed that **2** has the perfectly "anti-apicophilic" arrangement and **2** showed the spectroscopic properties characteristic for the perfectly "anti-apicophilic" phosphoranes. Only a small energy difference between **2** and its tautomer **3** exists, as revealed by variable-temperature NMR experiments. Theoretical calculations (AIM bonding analysis, stretching force constants) suggest that the observation of tautomer **3** is due to a weaker P−C bond in **2** than in **1**.

Acknowledgment. This work was partly supported by Grants-in-Aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry (T.K.) and for Scientific Research No. 15015001 (T.K.) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Details of experimental procedure and X-ray crystallographic file (CIF) for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050679D

---

(14) Bader, R. F. W. *Atoms in Molecules: a quantum theory*; Clarendon Press: Oxford, 1994.

(15) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.