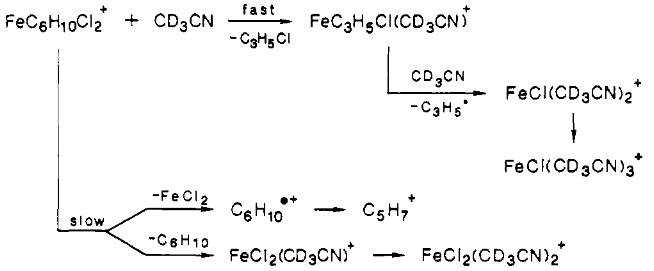
structure is not consistent with the observed allyl chloride loss, which may arise from structure **4**. Thus we conclude that $FeC_6H_{10}Cl_2^+$ ion is actually a mixture of two complexes **3** and **4**. In order to test this hypothesis, ligand exchange was attempted: $FeC_6H_{10}Cl_2^+$ was submitted to reaction with acetonitrile or trideuterated acetonitrile in the second collision cell, at a variable reaction time. The following reaction sequences were observed.



$FeC_3H_5Cl(CD_3CN)^+$ ion, deriving from rapid replacement of allyl chloride by acetonitrile in structure **4**, leads successively to $FeCl(CD_3CN)_2^+$ and $FeCl(CD_3CN)_3^+$ ions. After a short time (ca. 0.2 ms) the sum of the relative intensities of these three ions remained constant and equal to approximately 40% of the total ion current. Therefore the *m/z* 208 ion mixture reacted with acetonitrile should contain ca. 40% of structure **4**. The remaining slower reactions of *m/z* 208, involving either $C_6H_{10}^{•+}$ formation or replacement of neutral C_6H_{10} with acetonitrile, are in good agreement with structure **3**. **4** → **3** isomerization reactions will now be attempted.

The reactivity of methallyl chloride with iron complexes was also investigated: with $Fe(CO)_n^+$ it is the same as that of allyl chloride. With $FeC_3H_5Cl^+$ no significant ligand exchange was observed, as expected from structure **1**; the major reaction was chloride abstraction.

$$FeC_3H_5Cl^+ + C_4H_7Cl \rightarrow C_4H_7^+\ (m/z\ 55) + C_3H_5FeCl_2$$
$$C_4H_7Cl \searrow C_8H_{13}^+\ (m/z\ 109)$$

Ion $FeC_6H_{10}Cl_2^+$ gave the expected rapid but incomplete substitution of one allyl chloride ligand by methallyl chloride, followed however by complex reactions.

The coupling reaction occurring within the $FeC_6H_{10}Cl_2^+$ complex and leading after fragmentation to hexadiene radical cation is analogous to the transition-metal-promoted coupling of allylic halides in solution (Corey reaction).[15] Interestingly, occurrence of this solution-like reaction requires the presence of several ligands on the starting iron complex ion. Further investigation is in progress to determine the scope of this reaction concerning the nature of the metal ion and ligands as well as of the organic halide.

Acknowledgment. We are indebted to the Ministère de l'Education Nationale (Ecole Normale Supérieure and Grant "Action Recherche Universitaire Entreprise") and to the Centre National de la Recherche Scientifique for their financial support of this work. We thank Dr. Nicole Morin for helpful technical assistance and Daniel Jaouen for writing the software for the instrument. The efficient technical assistance of the Nermag staff is gratefully acknowledged.

Registry No. 1, 119909-88-5; **3**, 119909-89-6; **4**, 119909-90-9; Fe^+, 14067-02-8; $FeCO^+$, 35038-14-3; $Fe(CO)_2^+$, 35038-15-4; $Fe(CO)_3^+$, 35038-16-5; $Fe(CO)_4^+$, 35038-17-6; $Fe(CO)_5^+$, 59699-78-4; allyl chloride, 107-05-1.

Supplementary Material Available: Experimental spectra for all the processes mentioned in the text (primary reaction or CAD) (34 pages). Ordering information is given on any current masthead page.

---

[15] Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: 1982.

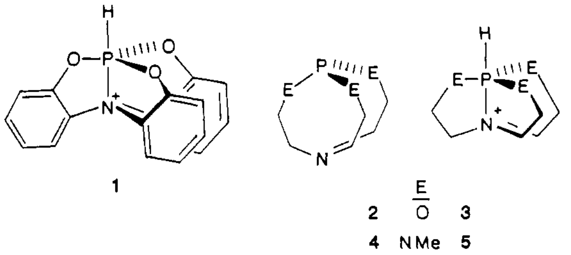
The Unusually Robust P-H Bond in the Novel Cation $HP(NMeCH_2CH_2)_3N^+$

C. Lensink, S. K. Xi, L. M. Daniels, and J. G. Verkade*

Gilman Hall, Department of Chemistry
Iowa State University, Ames, Iowa 50010

Received December 22, 1988

It was reported recently on the basis of NMR solution data that the phosphatrane cation **1** is unstable and was therefore not isolated.[1] In earlier publications from our laboratories, we observed, on the other hand, that the unstable prophosphatrane **2** readily protonates to form the stable cation **3**.[2-4] Here we show that in contrast to **2**, compound **4** is stable and is capable of deprotonating a variety of weak acids, including water, to form the unusually stable cation **5**.



1

E
2 O **3**
4 NMe **5**

Cation **5** is prepared as the chloride by adding a solution of $(HMeNCH_2CH_2)_3N$[5] (1.67 g, 11.4 mmol) in CH_2Cl_2 (20 mL), over a period of 5 min to a stirred solution of $ClP(NMe_2)_2$ (1.76 g, 11.4 mmol) and Et_3N (1.5 g, 15 mmol) in CH_2Cl_2 (30 mL). Stirring at room temperature for 1 h followed by removal of the solvent and Et_3N afforded **5** as the chloride in quantitative yield. The salt was recrystallized from hexane/chloroform at −20 °C to give an 82% yield of the product as a colorless crystalline solid.[6] Treatment of **5** (Cl^-) with $AgBF_4$ in CH_2Cl_2 gave the BF_4^- salt in quantitative yield. The ^{31}P NMR chemical shift of −10.6 ppm for **5** is indicative of five-coordinate phosphorus,[2,7] as is its one-bond H-P coupling constant of 491 Hz (**3**, 794 Hz;[2] **1**, 849 Hz[1]). The existence of an N_{ax}–P bond in **5** in solution is suggested by the observation of substantial $PN_{ax}CH_2$ coupling (4.7 Hz) and the observation of two-bond $PN_{ax}C$ coupling (6.1 Hz). These couplings are absent in prophosphatranes **2**[3] and **4**.[5] The structure of **5** was confirmed for the BF_4^- salt by X-ray crystallographic means (Figure 1).[8] Although the H-P hydrogen in **5**(BF_4^-) could not be located, the sum of the NPN angles in the equatorial plane (358.9 (4)°), the nearly right-angle relationship of the N_{ax}–P bond with the N_{eq}–P linkages (average 86.3 (4)°), the detection of the ^1H–^{31}P coupling in solution, and the directionality of the N_{ax} lone

---

[1] Mueller, E.; Burgi, H.-B. *Helv. Chem. Acta* **1987**, *70*, 1063.

[2] Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 6607.

[3] van Aken, D.; Castelyns, A. M. C. F.; Verkade, J. G.; Buck, H. M. *J. R. Neth. Chem. Soc.* **1979**, *98*, 12.

[4] Clardy, J. C.; Milbrath, D. S.; Springer, J. P.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 623.

[5] Lensink, C.; Schmidt, H.; Xi, S. K.; Verkade, J. G. *Zeitschr. Anorg. Allg. Chemie*, accepted for publication.

[6] NMR data: ^{31}P ($CDCl_3$) δ −10.6; ^1H ($CDCl_3$) δ 2.61 (9 H, d, CH_3, $^3J_{PH}$ = 17.4 Hz), δ 3.03 (6 H, dt, $N_{ax}CH_2$, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 6.2 Hz), δ 3.58 (6 H, dt, $N_{eq}CH_2$, $^3J_{PH}$ = 4.7 Hz, $^3J_{HH}$ = 6.2 Hz), δ 5.20 (1 H, d, $^1J_{PH}$ = 491 Hz); ^{13}C ($CDCl_3$), δ 34.4 (d, CH_3, $^2J_{PC}$ = 17.1 Hz), δ 41.3 (d, $N_{ax}CH_2$, $^2J_{PC}$ = 6.1 Hz), δ 47.3 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 7.3 Hz).

[7] Carpenter, L. E.; de Ruiter, B.; van Aken, D.; Buck, H. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 4918.

[8] Crystal data: space group $Cmc2_1$, a = 8.7251 (5) Å; b = 12.3824 (7) Å, c = 13.1330 (7) Å, V = 1418.9 (2) Å^3, Z = 4, d_{calcd} = 1.423 g/cm^3, μ (MoKα) = 2.24 cm^{-1}; 897 unique reflections for $2 < \theta < 25°$, 760 observed ($F_o^2 > 3\sigma(F_o^2)$). The choice of the acentric space group was suggested by intensity statistics and was confirmed by successful refinement of the structure. The structure was solved by direct methods. Since the phosphatrane cage resides on a crystallographic mirror plane, a slight disorder arises from the possible orientations of atoms C(3), C(6), and C(7). The occupancies of the two orientations of the BF_4^- ion refined to 56.1 (5)% for the major orientation. Refinement of 113 parameters converged with agreement factors of the following: $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ = 0.0887 and $R_2 = \mathrm{sqrt}[\Sigma w(F_o - F_c)^2/\Sigma w(F_o^2)]$ = 0.1189. The refinement was carried out with the SHELX-76 package.

0002-7863/89/1511-3478$01.50/0

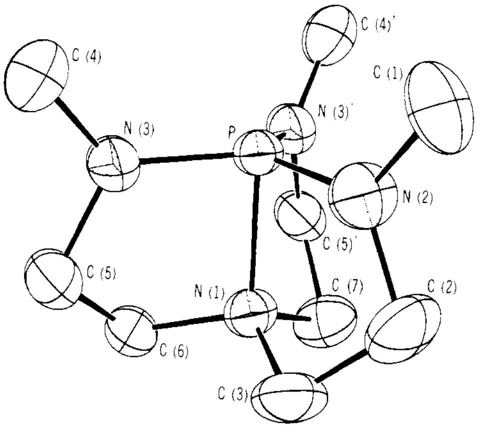
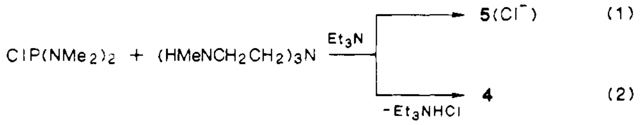


Figure 1. ORTEP drawing and atomic numbering scheme for $5(BF_4^-)$. Pertinent bond distances are P–N(1), 1.967 (8); P–N(2), 1.62 (1); and P–N(3), 1.661 (7) Å; important bond angles are N(1)PN(2), 85.9 (4); N(1)PN(3), 86.5 (2); N(2)PN(3), 120.7 (3); and N(3)PN(3)′, 117.5 (4)°.

pair toward the phosphorus is consistent with the H–P proton occupying the vacant axial position. The $P-N_{ax}$ bond distance in **5** (1.967 Å) is comparable to that in **3** (1.986 Å).[4] The considerably shorter $P-N_{eq}$ distances compared with the $P-N_{ax}$ distance in $5(BF_4^-)$ may reflect a combination of the diminished σ bond order in the axial three-center four-electron system[9] and the lack of $N_{ax}-P$ π bonding.

The first indication of the remarkable stability of **5** became evident in reaction 1. The presence of triethylamine was intended to remove HCl, thereby leading to the synthesis of the prophosphatrane **4** in reaction 2.[10] Instead, $5(Cl^-)$ was isolated.



$$ClP(NMe_2)_2 + (HMeNCH_2CH_2)_3N \xrightarrow{Et_3N} \begin{cases} \longrightarrow 5(Cl^-) & (1) \\ \xrightarrow[-Et_3NHCl]{} 4 & (2) \end{cases}$$

Furthermore, efforts to remove the proton in $5(Cl^-)$ with DBU in DMSO, *n*-BuLi in THF, CaH_2 in CH_2Cl_2, or KOH in refluxing toluene led only to the recovery of $5(Cl^-)$. Slowly heating $5(Cl^-)$ with a large excess of anhydrous NaOH to 200 °C under vacuum over a period of several hours also gave no indication of reaction. Above 200 °C a sudden sublimation of **4** from the reaction mixture is observed. Extraction of the crude reaction mixture with benzene afforded a 53% yield of **4**.[11,12]

These results strongly imply that **4** is a powerful base. This was confirmed by monitoring with ^1H and ^{31}P NMR spectroscopy a CD_3CN solution of **4** to which excess weak acid was added. Indeed, **4** deprotonates PhOH ($pK_a = 10$), $(CN)_2CH_2$ ($pK_a = 11$),[13] protonated "Proton Sponge" (1,8-(bisdimethylamino)-naphthalene·HI, $pK_a = 12.3$),[14] $(EtOOC)_2CH_2$ ($pK_a = 13$),[13] and H_2O ($pK_a = 15.7$)[15] to give **5** as the only phosphorus-containing product. With 1 equiv of H_2O, an equilibrium mixture of **4** and **5** is observed in a ratio of ca. 4:1. It is noteworthy that the only product detected in the reaction with H_2O is **5** since $P(NR_2)_3$ systems are well known to be hydrolytically unstable, giving rise to P–N bond cleavage. The lack of reaction of **4** with *t*-BuOH ($pK_a = 16.5$)[16] indicates that the pK_a of **5** is approximately 16. Thus **5** is a weaker acid by at least ca. seven orders of magnitude compared with typical R_3PH^+ species (pK_a = 8–9[17]). The diverse chemistry of this versatile system is currently under further investigation.

Acknowledgment. J. G. Verkade thanks the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank the W. R. Grace Company for a generous research sample of tren. The X-ray structure determination of $5(BF_4^-)$ was carried out at the Iowa State Molecular Structure Laboratory. We thank Yingzhong Su for experimental assistance.

Supplementary Material Available: Tables of crystal data, positional and anisotropic thermal parameters, and bond lengths and bond angles (5 pages); tables of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

---

(9) Carpenter, L. E.; Verkade, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 7084.

(10) The reaction of $P(NMe_2)_3$ with $(HMeNCH_2CH_2)_3N$ to form **4** is exceedingly slow.

(11) Charring frequently occurs leading to low yields of **4** in this unreliable reaction.

(12) NMR data: ^{31}P (C_6D_6) δ 120.8; ^1H (CD_3CN) δ 2.60 (9 H, d, CH_3, $^3J_{PH}$ = 11.0 Hz), δ 2.76 (12 H, br, CH_2); ^{13}C (C_6D_6) δ 37.2 (CH_3, $^2J_{PC}$ = 41.0 Hz), δ 49.4 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 6.7 Hz), δ 51.3 (s, $N_{ax}CH_2$).

(13) Pearson, L. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439.

(14) Alder, R. W.; Bowmann, P. S.; Steele, W. R. S.; Winterman, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 723.

(15) Harned, H. S.; Robinson, R. A. *Trans. Faraday Soc.* **1940**, *36*, 2747.

(16) Reeve, W.; Erikson, C. A.; Aluotto, P. F. *Can. J. Chem.* **1979**, *57*, 2747.

(17) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.

Definitive Characterization of the $C_3H_7^+$ Potential Energy Surface

Wolfram Koch*[†] and Bowen Liu

IBM Almaden Research Center
650 Harry Road, San Jose, California 95120-6099

Paul von Ragué Schleyer

Institut für Organische Chemie der Friedrich-Alexander
Universität Erlangen-Nürnberg
Henkestrasse 42, D-8520 Erlangen
Federal Republic of Germany

Received December 15, 1988

Because of its fundamental nature and small size, the $C_3H_7^+$ cation has been investigated extensively,[1] both experimentally[2-5] and computationally.[1,6-8] General features only have been established, not the detailed nature either of the two stable isomers (the 2-propyl cation and protonated cyclopropane) or of the related transition structures. The first minimum to be established by frequency analysis was published only very recently,[8] and this did not benefit from optimization at electron-correlated levels. The super acid study of Saunders et al.[2] led to three important conclusions, based on the results of multiple labeling and of kinetic analysis of ^2H and ^{13}C scrambling. Both protonated cyclopropane

---

[†] Present address: IBM Wissenschaftliches Zentrum, Tiergartenstrasse 15, D-6900 Heidelberg, F.R.G.

(1) Reviews: (a) Coxon, J. M.; Battiste, M. A. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; J. Wiley and Sons: New York, 1987; Chapter 6. (b) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985; pp 331.

(2) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53. Also see ref 1b.

(3) Lias, S. G.; Liebman, J. L.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (See Table 3.3, p 703.)

(4) Chon, S.-L.; Franklin, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 6347. Also see: Viviani, D.; Levy, J. B. *Int. J. Chem. Kinet.* **1979**, *11*, 1021.

(5) Schulz, J. C.; Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3917.

(6) For a description of the theoretical model, see: Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley Interscience: New York, 1986.

(7) Reviews: (a) Hehre, W. J. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1972; Chapter 7, pp 277. (b) Radom, L.; Poppinger, D.; Haddon, R. C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1976; Vol. V, Chapter 38, pp 2303.

(8) Dewar, M. J. S.; Healy, E. A.; Ruiz, J. M. *J. Chem. Soc., Chem. Commun.* **1987**, 943. No minima were identified in the highest level earlier study (Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649); also see: *The Carnegie-Mellon Quantum Chemistry Archive*; 3rd ed.; Whiteside, R. A., Frisch, M. F., Pople, J. A., Eds.; Carnegie-Mellon University: Pittsburgh, PA, 1983.

0002-7863/89/1511-3479$01.50/0