

XH₅²⁺ Dications and XH₆³⁺ Trications (X = N, P, and As)¹

Golam Rasul,* G. K. Surya Prakash, and George A. Olah*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry University of Southern California, University Park Los Angeles, California 90089-1661

Received August 26, 1997

Revised Manuscript Received November 7, 1997

There is continued theoretical² and experimental³ interest in higher coordinate⁴ multicharged main group compounds. We recently reported on the calculated structures and energies of parent hexa-, hepta-, and octacoordinate boronium⁵ and alonium⁶ ions as well as pentacoordinate ammonium dication (NH₅²⁺)⁷ and sulfonium trication (SH₅³⁺).⁸ Schmidbaur and his associates have prepared a wide variety of dipositively charged gold complexes of main group elements including carbon⁹ {[C₆H₅]₃-PAu]₆C²⁺, nitrogen¹⁰ {[C₆H₅]₃PAu]₅N²⁺, phosphorus¹¹ {[C₆H₅]₃PAu]₅P²⁺, sulfur¹² {[C₆H₅]₃PAu]₄S²⁺, and oxygen¹³ {[C₆H₅]₃PAu]₄O²⁺ and determined their X-ray structures. These represent isolobal analogues of CH₆²⁺, NH₅²⁺, PH₅²⁺, SH₄²⁺, and OH₄²⁺, respectively.

Zeller and Schmidbaur¹⁴ have succeeded to prepare and identified in solution the hexacoordinate tripositively charged octahedral {[C₆H₅]₃PAu]₆P³⁺ complex. This is the isolobal analogue of PH₆³⁺. However, no single crystal of the complex could be obtained to allow structural study.¹⁴

In contrast to the pentacoordinate nitrogen and phosphorus complexes no similar arsenic complex could be so far observed. Schmidbaur et al. have prepared¹⁵ only the four-coordinate square pyramidal {[C₆H₅]₃PAu]₄As⁺ complex of arsenic and determined its X-ray structure.

In continuation of our study of higher coordinate onium superelectrophiles¹⁶ we have now extended our investigations to the structures and energetics of XH₅²⁺ and XH₆³⁺ (X = N, P, and As) by ab initio calculations.

Calculations were carried out with Gaussian 94.¹⁷ The geometry optimizations and frequency calculations were performed at the MP2/6-31G** level.^{18a} From calculated frequen-

(1) Chemistry in Superacids. 34. Part 33: Olah, G. A.; Burrichter, A.; Rasul, G.; Hachoumy, M.; Prakash, G. K. S. *J. Am. Chem. Soc.*, in press.

(2) (a) Olah, G. A.; Rasul, G. *Acc. Chem. Res.* **1997**, *30*, 245. (b) Haberlen, O. D.; Schmidbaur, H.; Rosch, N. *J. Am. Chem. Soc.* **1994**, *116*, 8241. Gorling, A.; Rosch, N.; Ellis, D. E.; Schmidbaur, H. *Inorg. Chem.* **1991**, *30*, 3986. Schreiner, P. R.; Schaefer, H. F.; Schleyer, P. v. R. *Advances in Gas Phase Ion Chemistry*; JAI Press Inc.: Greenwich, CT, 1996; p 125. Schreiner, P. R.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1995**, *103*, 5565.

(3) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, *24*, 391.

(4) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; John Wiley & Sons: New York, 1987. Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985.

(5) Rasul, G. A.; Olah, G. A. *Inorg. Chem.* **1997**, *36*, 1278.

(6) Olah, G. A.; Rasul, G. A. *Inorg. Chem.*, in press.

(7) Olah, G. A.; Burrichter, A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 4594.

(8) Olah, G. A.; Rasul, G.; Prakash, G. K. S. *Chem. Eur. J.* **1997**, *3*, 1039.

(9) Scherbaum, F.; Grohmann, A.; Huber B.; Krüger, C.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1544.

(10) Grohmann, A.; Riede, J.; Schmidbaur, H. *Nature* **1990**, *345*, 140.

(11) Schmidbaur, H.; Beruda, H.; Zeller, E. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *87*, 245.

(12) Zeller, E.; Beruda, H.; Schmidbaur, H. *Inorg. Chem.* **1993**, *32*, 3203.

(13) Schmidbaur, H.; Hofreiter, S.; Paul, M. *Nature* **1995**, *377*, 503.

(14) Zeller, E.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1993**, 69.

(15) Zeller, E.; Beruda, H.; Kolb, A.; Bissinger, P.; Schmidbaur, H. *Nature* **1991**, *352*, 141.

(16) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.

Table 1. Total Energies (–au) and ZPE^a (kcal/mol)

	MP2/6-31G**// MP2/6-31G**	QCISD(T)/6-311G**// QCISD(T)/6-311G**	G2
1	56.574 97 (29.3)	56.619 56	56.623 69
2	56.124 23 (26.2)	56.168 08	56.176 59
3	342.809 23 (24.8)	342.881 76	342.891 25
4	342.775 52 (23.4)		342.861 53
5	341.577 72 (13.9)	341.634 23	341.646 25
6	342.454 19 (25.3)	342.537 70	342.544 88
7	2 234.083 66 (22.8)	2 236.299 42	2 236.310 42
8	2 234.037 47 (21.5)		2 236.267 68
9	2 232.863 53 (13.0)	2 235.069 78	2 235.086 44
10	2 233.763 01 (23.4)	2 235.989 62	2 235.997 03
NH ₃ ²⁺	55.173 60 (17.0)		55.229 50
NH ₄ ⁺	56.733 68 (29.7)		56.781 40
PH ₄ ⁺	342.893 61 (21.7)		342.975 73
AsH ₄ ⁺	2 234.141 88 (20.2)		2 236.366 44
H ₃ ⁺	1.324 28 (12.6)		1.324 45
H ₂	1.157 66 (6.6)		1.166 36

^a Zero-point vibrational energies (ZPE) at MP2/6-31G**/MP2/6-31G** scaled by a factor of 0.93.

cies, the optimized structures were characterized as minima (NIMAG = 0) or transition structure (NIMAG = 1). For the MP2/6-31G**-optimized structures further geometry optimizations were carried out at the QCISD(T)/6-311G** level. For improved energy, the Gaussian-2 (G2) energies^{18b} were computed. Calculated energies are given in Table 1. MP2/6-31G** geometrical parameters and G2-calculated energies will be discussed throughout, unless stated otherwise.

NH₅²⁺: Olah et al. previously reported⁷ structures, energies, and dissociation barriers of NH₅²⁺. We have calculated the NH₅²⁺ only to compare it with the PH₅²⁺ and AsH₅²⁺. The calculated C_{4v} symmetric stable minimum **1** for NH₅²⁺ is shown in Figure 1. In **1**, one hydrogen atom is bonded to the nitrogen atom by sharing two valence electrons and the remaining four hydrogen atoms are bonded to the nitrogen atom by sharing only six valence electrons.

NH₆³⁺: At the MP2/6-31G** level the D_{3h} symmetric form **2** is found to be the only stable minimum for parent NH₆³⁺. The N–H bond distance of the trication is 1.210 Å. This is slightly longer than those of the dication **1**. There may be some bonding interaction between two adjacent hydrogens (H_a and H_b) which are separated by 1.390 Å. Using G2 theory the dissociation of **2** into NH₅²⁺ and H⁺ was calculated to be exothermic by 280.6 kcal/mol (Scheme 1). Thus **2** is highly unstable thermodynamically. On the other hand, dissociation of **2** into NH₃²⁺ and H₃⁺ was also found to be exothermic by 236.8 kcal/mol.

PH₅²⁺: Unlike the C_{4v} symmetrical **1**, the C_s symmetrical structure **3** is the only stable minimum on the potential energy surface of PH₅²⁺. The C_{4v} symmetrical structure of PH₅²⁺ is not a minimum at the MP2/6-31G** level and contains two imaginary frequencies (i.e., NIMAG = 2) in its calculated vibrational frequencies at the same MP2/6-31G** level. Structure **3** contains a three-center–two-electron (3c–2e) bond and resembles a complex between PH₃²⁺ and H₂. The structure **3** is similar to the C_s symmetry structure of parent CH₅⁺.^{2a}

(17) Gaussian 94 (Revision A.1): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(18) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986. (b) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

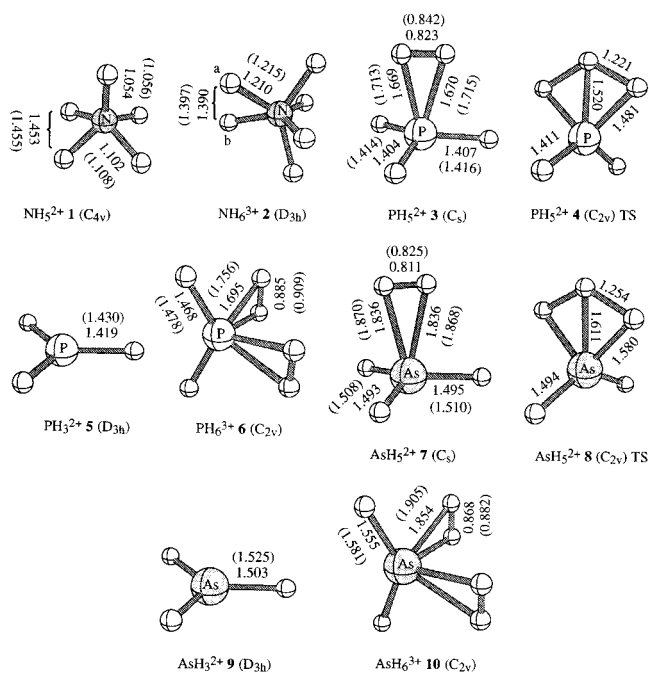


Figure 1. MP2/6-31G** structures of 1–10 (QCISD(T)/6-311G**).

Scheme 1^a

	ΔH (kcal/mol) ^a
NH_5^{2+} (1) \rightarrow NH_4^+ + H^+	-99.0
NH_5^{2+} (1) \rightarrow NH_3^{2+} + H_2	+143.0
NH_6^{3+} (2) \rightarrow NH_5^{2+} (1) + H^+	-280.6
NH_6^{3+} (2) \rightarrow NH_3^{2+} + H_3^+	-236.8
PH_5^{2+} (3) \rightarrow PH_4^+ + H^+	-53.0
PH_5^{2+} (3) \rightarrow PH_3^{2+} (5) + H_2	+49.4
PH_6^{3+} (6) \rightarrow PH_5^{2+} (3) + H^+	-217.4
PH_6^{3+} (6) \rightarrow PH_3^{2+} (5) + H_3^+	-267.2
AsH_5^{2+} (7) \rightarrow AsH_4^+ + H^+	-35.2
AsH_5^{2+} (7) \rightarrow AsH_3^{2+} (9) + H_2	+36.2
AsH_6^{3+} (10) \rightarrow AsH_5^{2+} (7) + H^+	-196.7
AsH_6^{3+} (10) \rightarrow AsH_3^{2+} (9) + H_3^+	-259.7

^a With the G2 method.

Structure 3 can also be viewed as a proton inserted into one of the σ P–H bonds of PH_4^+ to form a 3c–2e bond between phosphorus and hydrogen. The phosphorus in PH_4^+ , however, does not undergo formal expansion of the valence octet involving d orbitals of phosphorus upon protonation since no minima of PH_5^{2+} other than 3 could be located on its potential energy surface.

The electron-deficient P–H distances of 3c–2e interaction of 1.670 and 1.669 Å are expectedly about 0.3 Å longer than those of P–H bonds of 2c–2e at the MP2/6-31G** level. The H–H distance in the 3c–2e interaction of 0.823 Å is only 0.089 Å longer than that found in the hydrogen itself at the same MP2/6-31G** level of theory. The both P–H and H–H bonds of 3 become slightly longer upon optimizations with the higher QCISD(T)/6-311G** levels of theory.

The transition structure 4 (Figure 1), for intramolecular hydrogen transfer in 3, was located. 4 lies 18.7 kcal/mol higher than 3. Thus, hydrogen scrambling in 3 through transition state 4 has a substantial kinetic barrier. At G2 the dissociation of 3 into PH_4^+ and H^+ is calculated to be exothermic by 53.0 kcal/mol (Scheme 1). In contrast, dissociation of 1 into NH_4^+ and H^+ is more exothermic by 99.0 kcal/mol.

We also calculated the reaction of PH_3^{2+} 5 with H_2 , which is calculated to be exothermic by 49.4 kcal/mol. The optimized structure of PH_3^{2+} 5 is given in Figure 1.

PH_6^{3+} : The C_{2v} symmetric structure 6 is the only minimum that was located on the potential energy surface of PH_6^{3+} . 6 is characterized with two 3c–2e bonds and two 2c–2e bonds and resembles a complex between PH_2^{3+} and two hydrogen molecules (Figure 2). The P–H and H–H distances of 3c–2e interaction are 1.695 and 0.885 Å. The dissociation of 6 into 3 and H^+ is 217.4 kcal/mol exothermic, whereas into PH_3^{2+} 5 and H_3^+ is even more exothermic by 267.2 kcal/mol (Scheme 1).

AsH_5^{2+} : Similar to 3, the C_s symmetrical 7 with a 3c–2e bond is the only stable minimum on the potential energy surface of AsH_5^{2+} . Similar to PH_5^{2+} , the C_{4v} symmetrical structure of AsH_5^{2+} is also not a minimum at the MP2/6-31G** level and contains two imaginary frequencies in its calculated vibrational frequencies. Even the arsenic atom in AsH_4^+ does not undergo formal expansion of the valence octet involving d orbitals of arsenic upon protonation since no minima of AsH_5^{2+} other than 7 could be located on its potential energy surface. Intramolecular hydrogen scrambling in 7 through the transition structure 8 (Figure 1) has also a high kinetic barrier of 26.8 kcal/mol. Dissociation of 7 into AsH_4^+ and H^+ is exothermic by only 35.2 kcal/mol (Scheme 1).

Calculations also shows that the reaction of 9 with H_2 will be exothermic by 36.2 kcal/mol. The optimized structure of 9 is given in Figure 1.

AsH_6^{3+} : The MP2/6-31G** optimization shows that the C_{2v} symmetrical structure 10 with two 3c–2e bonds and two 2c–2e bonds is the only minimum on the potential energy surface of AsH_6^{3+} . The calculated geometries are given in Figure 1. We have also calculated (with G2) the exothermicities of the dissociation of 10 into 7 and H^+ and into 9 and H_3^+ and found them to be 196.7 and 259.7 kcal/mol, respectively (Scheme 1).

In the series NH_5^{2+} , PH_5^{2+} , and AsH_5^{2+} , the calculated ΔH of protodissociations of the dications indicate an increase in the stabilities of the dications toward protodissociation with the increase in the size of the central atoms. Similarly, in the series NH_6^{3+} , PH_6^{3+} , and AsH_6^{3+} , the stabilities of the trications toward protodissociation also increase with the increase in the size of the central atoms.

The important implication of this work is to understand the nature of bonding of highly electron-deficient higher coordinate main group ions (superelectrophiles).¹⁶ Although such main group di- or trications may not be observed as long-lived species in superacid media, computational characterization gives additional support for their transient existence and involvement in superacid-catalyzed processes. Hydrogen–deuterium exchange studies in superacids will be reported separately.

In conclusion, the present ab initio study indicates that the C_s symmetrical structures 3 and 7 are the stationary points on the potential energy surfaces of PH_5^{2+} and AsH_5^{2+} , respectively. The optimized structure shows that both 3 and 7 contain a 3c–2e bond. The D_{3h} symmetrical 2, C_{2v} symmetrical 6, and C_{2v} symmetrical structure 10, on the other hand, were located as stable minima on the potential energy surfaces of NH_6^{3+} , PH_6^{3+} , and AsH_6^{3+} , respectively. 6 and 10 were characterized with two 3c–2e bonds and two 2c–2e bonds.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

JA9729948