

## Structures of $\text{XH}_4^+$ and $\text{XH}_6^+$ ( $\text{X} = \text{B}, \text{Al}$ and $\text{Ga}$ ) Cations\*

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**Abstract** Structures and energies of  $\text{XH}_4^+$  and  $\text{XH}_6^+$  ( $\text{X} = \text{B}, \text{Al}$  and  $\text{Ga}$ ) have been calculated at the density functional theory (DFT) B3LYP/6-311++G(3df,2pd) level. Calculations indicate that although the structure with a three center two electron (3c-2e) bond is the global minimum for  $\text{BH}_4^+$ , the global minima of  $\text{AlH}_4^+$  and  $\text{GaH}_4^+$  are not those with one 3c-2e bond, but those with two 3c-2e bonds. For calibration, both structures of  $\text{AlH}_4^+$  were also calculated at the *ab initio* CCSD(T)/cc-pVTZ level and results in agreement with the DFT results were found. Similar calculations also indicate that although the  $\text{C}_{2v}$  symmetrical structure with two 3c-2e bonds is the global minimum for  $\text{BH}_6^+$ , the global minima of  $\text{AlH}_6^+$  and  $\text{GaH}_6^+$  are not the  $\text{C}_{2v}$  symmetrical structures with two 3c-2e bonds but the  $\text{C}_2$  symmetrical structures with three 3c-2e bonds.

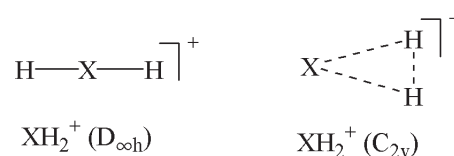
**Keywords** Density functional calculations, Boronium ion, Three center two electron bond

### Introduction

Recently we reported [1] the *ab initio* calculated structures of singlet  $\text{XH}_2^+$  ( $\text{X} = \text{B}, \text{Al}$  and  $\text{Ga}$ ). The linear  $\text{D}_{\infty\text{h}}$  symmetrical structure was preferred for singlet  $\text{BH}_2^+$ . However, the global minima of  $\text{AlH}_2^+$  and  $\text{GaH}_2^+$  are not of linear  $\text{D}_{\infty\text{h}}$  symmetry but  $\text{C}_{2v}$  symmetrical with 3c-2e bonds [2] (Scheme 1). The  $\text{D}_{\infty\text{h}}$  symmetrical structures of  $\text{AlH}_2^+$  and  $\text{GaH}_2^+$  were found to be significantly less stable than the

corresponding  $\text{C}_{2v}$  symmetrical structures by 13.1 and 21.5 kcal mol<sup>-1</sup>, respectively.

In continuation of our study we have now extended our investigations to  $\text{XH}_4^+$  and  $\text{XH}_6^+$  ( $\text{X} = \text{B}, \text{Al}$  and  $\text{Ga}$ ) by density functional theory (DFT) calculations. Studies show that although the structure with a three center two electron (3c-2e) bond is the global minimum for  $\text{BH}_4^+$ , the global minima of  $\text{AlH}_4^+$  and  $\text{GaH}_4^+$  are not those with one 3c-2e bond but



$\text{X} = \text{B}$ ;  $\text{D}_{\infty\text{h}}$  is more stable than  $\text{C}_{2v}$   
 $\text{X} = \text{Al}, \text{Ga}$ ;  $\text{C}_{2v}$  is more stable than  $\text{D}_{\infty\text{h}}$

**Scheme 1**  $\text{D}_{\infty\text{h}}$  and  $\text{C}_{2v}$  symmetrical structures of  $\text{XH}_2^+$

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70<sup>th</sup> birthday with friendship and admiration

**Table 1** Total energies (-au), ZPE (kcal mol<sup>-1</sup>) [a] and relative energy (kcal mol<sup>-1</sup>) [b]

	B3LYP/ 6-311++G(3df,2pd)	ZPE	rel. energy
BH <sub>4</sub> <sup>+</sup> <b>1a</b>	26.85282	21.3	0.0
BH <sub>4</sub> <sup>+</sup> <b>1b</b>	26.72413	14.4	73.8
AlH <sub>4</sub> <sup>+</sup> <b>2a</b>	244.52035	16.0	8.9
AlH <sub>4</sub> <sup>+</sup> <b>2b</b>	244.53083	13.6	0.0
GaH <sub>4</sub> <sup>+</sup> <b>3a</b>	1926.93681	15.8	22.9
GaH <sub>4</sub> <sup>+</sup> <b>3b</b>	1926.96961	13.6	13.6
BH <sub>6</sub> <sup>+</sup> <b>4a</b>	28.07020	33.3	0.00
AlH <sub>6</sub> <sup>+</sup> <b>5a</b>	245.71310	25.1	4.6
AlH <sub>6</sub> <sup>+</sup> <b>5b</b>	245.71335	20.7	0.0
GaH <sub>6</sub> <sup>+</sup> <b>6a</b>	1928.12572	24.3	20.3
GaH <sub>6</sub> <sup>+</sup> <b>6b</b>	1927.82481	20.1	0.0

[a] zero point vibrational energies (ZPE) at B3LYP/6-311++G(3df,2pd)/B3LYP/6-311++G(3df,2pd) scaled by a factor of 0.96; [b] relative energy based on B3LYP/6-311++G(3df,2pd)/B3LYP/6-311++G(3df,2pd) + ZPE

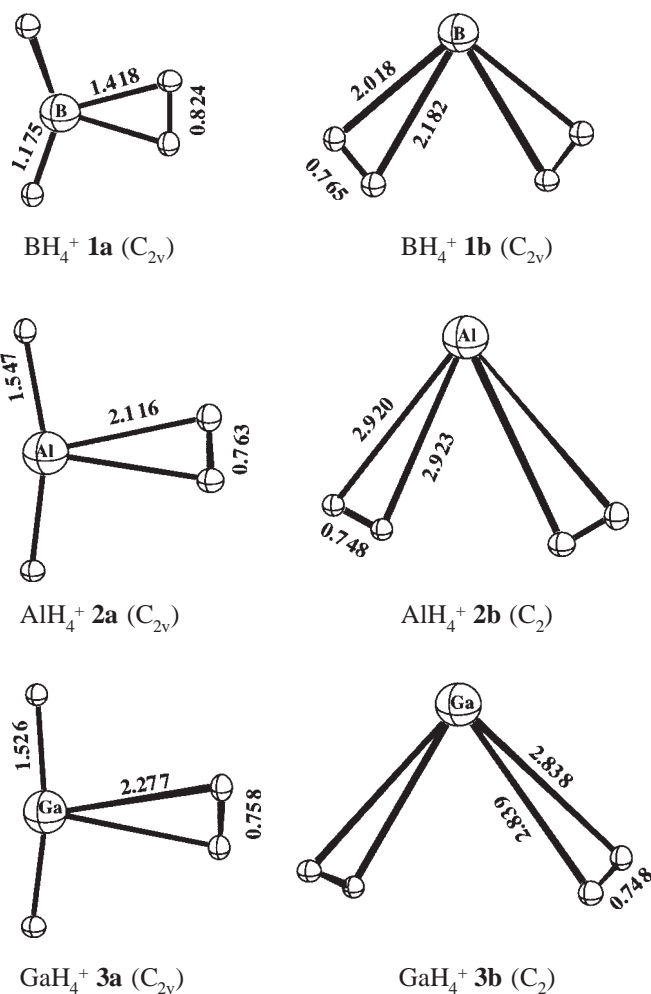
rather those with two 3c-2e bonds. Similar results were also found for the XH<sub>6</sub><sup>+</sup> (X = B, Al and Ga) cations, which can be derived by reacting XH<sub>4</sub><sup>+</sup> and H<sub>2</sub>.

## Results and discussion

Calculations were carried out with the Gaussian 98 program.[3] The geometry optimizations and frequency calculations were performed at the DFT [4] B3LYP [5]/6-311++G(3df,2pd) [6] level. Frequency calculations were used to characterize the optimized structures as minima (number of imaginary frequencies (NIMAG) = 0) and to evaluate zero point vibrational energies (ZPE), which were scaled by a factor of 0.96. Final energies were calculated at the B3LYP/6-311++G(3df,2pd)/B3LYP/6-311++G(3df,2pd) + ZPE level. B3LYP/6-311++G(3df,2pd) geometrical parameters and final energies will be discussed throughout, unless stated otherwise. For calibration, geometry optimizations and energy calculations of AlH<sub>4</sub><sup>+</sup> were also carried out with the *ab initio* coupled cluster method [6] at the CCSD(T)/cc-pVTZ [7] level. Calculated energies are given in Table 1.

XH<sub>4</sub><sup>+</sup> (X = B, Al and Ga)

**BH<sub>4</sub><sup>+</sup>**: Two C<sub>2v</sub> symmetrical structures, **1a** and **1b** (Figure 1) were found to be minima on the potential energy surface (PES)

**Figure 1** B3LYP/6-311++G(3df,2pd) optimized structures of **1-3**

of singlet BH<sub>4</sub><sup>+</sup> at the B3LYP/6-311++G(3df,2pd) level, as indicated by frequency calculations at the same level. Structure **1a** is, however, 73.8 kcal mol<sup>-1</sup> more stable than **1b** (Table 1). Structure **1a** contains a 3c-2e bond whereas structure **1b** is characterized by two 3c-2e bonds and a formal lone pair on the boron atom. The each 3c-2e interaction in **1b** involving boron and a H<sub>2</sub> molecule can also be considered to involve three center three electron (3c-3e) bonding as there are six total valence electrons including the boron lone pair. However, such 3c-3e bonding involving two hydrogen atoms and boron is highly unlikely.[8] Previously Rasul and Olah [9] and DePuy *et al.* [10] calculated structure **1a** and found similar results. The planar C<sub>2v</sub> symmetrical structure with a 3c-2e bond is also preferred for CH<sub>4</sub><sup>2+</sup>, as shown by Wong and Radom.[11] The tetracoordinate boronium ion BH<sub>4</sub><sup>+</sup> can be prepared readily[10] in the gas phase.

**AlH<sub>4</sub><sup>+</sup>**: C<sub>2v</sub> structure **2a** with a 3c-2e bond and C<sub>2</sub> structure **2b** with two 3c-2e bonds were also found to be minima on the PES of singlet AlH<sub>4</sub><sup>+</sup> (Figure 1). However, unlike BH<sub>4</sub><sup>+</sup> the structure **2a** is 8.9 kcal mol<sup>-1</sup> less stable than **2b** (Table

**Table 2**  $\Delta H_0$  of deprotonation and dehydrogenation (kcal·mol<sup>-1</sup>) [a]

reaction		$\Delta H_0$
BH <sub>4</sub> <sup>+</sup> <b>1a</b>	→ BH <sub>3</sub> + H <sup>+</sup>	138.4
BH <sub>4</sub> <sup>+</sup> <b>1a</b>	→ BH <sub>2</sub> <sup>+</sup> + H <sub>2</sub>	16.5
AlH <sub>4</sub> <sup>+</sup> <b>2b</b>	→ AlH <sub>3</sub> + H <sup>+</sup>	185.0
AlH <sub>4</sub> <sup>+</sup> <b>2b</b>	→ AlH <sub>2</sub> <sup>+</sup> + H <sub>2</sub>	0.8
GaH <sub>4</sub> <sup>+</sup> <b>3b</b>	→ GaH <sub>3</sub> + H <sup>+</sup>	202.8
GaH <sub>4</sub> <sup>+</sup> <b>3b</b>	→ GaH <sub>2</sub> <sup>+</sup> + H <sub>2</sub>	1.2
BH <sub>6</sub> <sup>+</sup> <b>4a</b>	→ BH <sub>5</sub> + H <sup>+</sup>	156.0
BH <sub>6</sub> <sup>+</sup> <b>4a</b>	→ BH <sub>4</sub> <sup>+</sup> <b>1a</b> + H <sub>2</sub>	17.5
AlH <sub>6</sub> <sup>+</sup> <b>5b</b>	→ AlH <sub>5</sub> + H <sup>+</sup>	186.9
AlH <sub>6</sub> <sup>+</sup> <b>5b</b>	→ AlH <sub>4</sub> <sup>+</sup> <b>2b</b> + H <sub>2</sub>	0.6
GaH <sub>6</sub> <sup>+</sup> <b>6b</b>	→ GaH <sub>5</sub> + H <sup>+</sup>	205.0
GaH <sub>6</sub> <sup>+</sup> <b>6b</b>	→ GaH <sub>4</sub> <sup>+</sup> <b>3b</b> + H <sub>2</sub>	0.7

[a] B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df,2pd) + ZPE

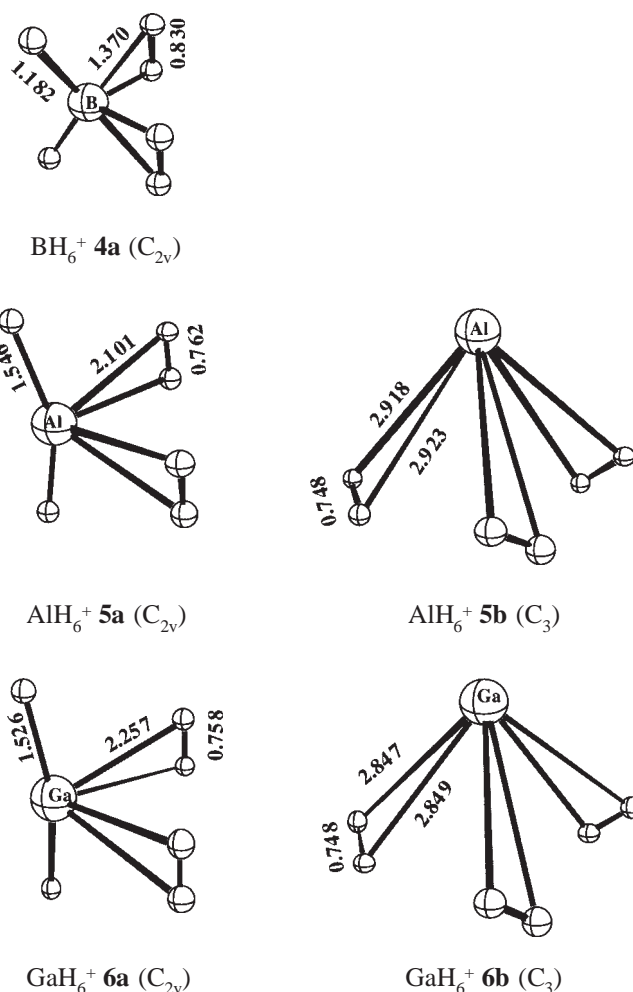
1). AlH<sub>4</sub><sup>+</sup> is isoelectronic with SiH<sub>4</sub><sup>2+</sup>. Similar to **2b**, the C<sub>2v</sub> structure with two 3c-2e bonds was also calculated to be the global minimum for the singlet SiH<sub>4</sub><sup>2+</sup>. [12] For calibration, structures **2a** and **2b** were also calculated at the *ab initio* CCSD(T)/cc-pVTZ level (total energies are -244.05288 and -244.06242 au, respectively). Zero point vibrational energies (ZPE) of **2a** and **2b** are 16.0 and 13.5 kcal mol<sup>-1</sup> calculated at the MP2/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) level and scaled by a factor of 0.93. Thus, at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level, structure **2a** is also 8.5 kcal mol<sup>-1</sup> less stable than **2b**.

**GaH<sub>4</sub><sup>+</sup>**; Similar to AlH<sub>4</sub><sup>+</sup>, C<sub>2v</sub> structure **3a** with a 3c-2e bond and C<sub>2</sub> structure **3b** with two 3c-2e bonds (Figure 1) were found to be minima on the PES of GaH<sub>4</sub><sup>+</sup>. Structure **3a** is 22.9 kcal mol<sup>-1</sup> less stable than **3b** (Table 1).

XH<sub>6</sub><sup>+</sup> (X = B, Al and Ga)

**BH<sub>6</sub><sup>+</sup>**: The C<sub>2v</sub> symmetrical **4a** was found to be the only stable minimum for the singlet hexacoordinated boronium ion BH<sub>6</sub><sup>+</sup> at the B3LYP/6-311++G(3df,2pd) level. Structure **4a**, isoelectronic as well as isostructural [13] with CH<sub>6</sub><sup>2+</sup>, was previously calculated [9,10] using *ab initio* methods and similar results as reported here were found. Structure **4a** contains two 3c-2e bonds and two 2c-2e bonds (Figure 2). The BH<sub>6</sub><sup>+</sup> ion was generated in the gas phase by DePuy *et al.* [10] Attempts to find a third 3c-2e bonded stable minimum of BH<sub>6</sub><sup>+</sup> (similar to **5b** of AlH<sub>6</sub><sup>+</sup> as discussed next) failed because of rearrangement to form the more stable **4a**.

**AlH<sub>6</sub><sup>+</sup>**: The C<sub>2v</sub> symmetrical structure **5a** and C<sub>3</sub> symmetrical **5b** were found to be the stable minima for singlet AlH<sub>6</sub><sup>+</sup> (Figure 2). Previously Olah and Rasul [14] reported the struc-

**Figure 2** B3LYP/6-311++G(3df,2pd) optimized structures of **4 - 6**

ture **5a** calculated by *ab initio* methods. Structure **5a** contains two 3c-2e bonds and two 2c-2e bonds. Structure **5b** is characterized by three 3c-2e bonds and a formal lone pair on the aluminum atom. Energetically, however, structure **5a** is 4.6 kcal mol<sup>-1</sup> less stable than the structure **5b**.

**GaH<sub>6</sub><sup>+</sup>**; Similar to AlH<sub>6</sub><sup>+</sup>, C<sub>2v</sub> symmetrical **6a** and C<sub>3</sub> symmetrical **6b** (Figure 2) were found to be minima on the PES of GaH<sub>6</sub><sup>+</sup>. The structure **6a** with two 3c-2e bonds was found to be 20.3 kcal mol<sup>-1</sup> less stable than **6b** with three 3c-2e bonds (Table 1).

In the higher analogs of XH<sub>4</sub><sup>+</sup> (X = B, Al and Ga), structures with two 3c-2e bonds are increasingly more favorable than the structures with one 3c-2e bond. Similarly, in the higher analogs of XH<sub>6</sub><sup>+</sup> (X = B, Al and Ga) structures with three 3c-2e bonds are increasingly more favorable than the structures with two 3c-2e bonds. A similar trend was found in the series XH<sub>2</sub><sup>+</sup> (X = B, Al and Ga) [2], XH<sub>3</sub><sup>+</sup> (X = B, Al and Ga) [15] and XH<sub>3</sub><sup>+</sup> (X = C, Si, Ge, Sn and Pb). [16] Structures **1-3b** can be considered as donor-acceptor complexes of two H<sub>2</sub> and X<sup>+</sup> (X = B, Al and Ga). Similarly, structures **5-6b**

can be considered as donor-acceptor complexes of three  $H_2$  and  $X^+$  ( $X = Al$  and  $Ga$ ). The nature of the interaction between donor and acceptor of the complexes depends on the relative electron transfer ability of the  $\sigma_{H-H}$  to the empty p orbital at  $X$ . Therefore, the stability of the bent structures depends on the size as well as the electronegativity of the  $X$ . Localization of lone pair of electrons thus readily takes place at the heavier atoms (inert pair effect).[17]

The relative stabilities of  $XH_4^+$  and  $XH_6^+$  ( $X = B, Al$  and  $Ga$ ) towards deprotonation were calculated (Table 2). Deprotonation of  $BH_4^+$  **1a** is disfavored by 138.4 kcal mol<sup>-1</sup>. On the other hand, deprotonation of **2b** and **3b** are disfavored by 185.0 and 202.8 kcal mol<sup>-1</sup>, respectively. Deprotonation of  $XH_6^+$  ( $X = B, Al$  and  $Ga$ ) were also found to be highly unfavorable by 156 - 205 kcal mol<sup>-1</sup>.

Relative stabilities of the most stable isomers of  $XH_4^+$  and  $XH_6^+$  ( $X = B, Al$  and  $Ga$ ) towards dissociation into  $XH_2^+$  and  $H_2$  and  $XH_4^+$  and  $H_2$ , respectively, were also calculated and listed in Table 2. The dissociation of boron complex **1a** is disfavored by 16.5 kcal mol<sup>-1</sup>. On the other hand, dissociation of aluminum and gallium complexes **2b** and **3b** are disfavored by only 0.8 and 1.0 kcal mol<sup>-1</sup>, respectively. The dissociation of hexacoordinated complexes **4a**, **5b** and **6b** are disfavored by 17.5, 0.6 and 0.7 kcal mol<sup>-1</sup> respectively. Thus, thermodynamically tetra- and hexacoordinated aluminum and gallium complexes **3-4b** and **5-6b** are unstable towards dehydrogenation.

## Conclusions

The structures of  $XH_4^+$  and  $XH_6^+$  ( $X = B, Al$  and  $Ga$ ) have been calculated by using DFT theory. The present DFT study at the B3LYP/6-311++G(3df,2pd) level indicates that although the structure **1a** with a 3c-2e bond is the global minimum for  $BH_4^+$ , the global minima of  $AlH_4^+$  and  $GaH_4^+$  are not **2a** and **3a** with 3c-2e bonds, but **2b** and **3b**, respectively, with two 3c-2e bonds and a localized lone pair. Similar studies also indicate that the global minimum structure of the singlet  $AlH_6^+$  and  $GaH_6^+$  are  $C_3$  symmetrical **5b** and **6b** with three 3c-2e bonds.

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**Supplementary material available** Cartesian coordinates of the B3LYP/6-311++G(3df,2pd) optimized structures of **1-6** in XYZ format.

## References

- Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Phys. Chem.*; in press
- Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley & Sons: New York, 1987.
- Gaussian 98 (Revision A.5), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, R. E.; 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1998.
- Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.
- Becke's Three Parameter Hybrid Method Using the LYP Correlation Functional: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.
- Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- Akiba, K. *Chemistry of Hypervalent Compounds*; Wiley-VCH: New York, 1999.
- Rasul, G.; Olah, G. A. *Inorg. Chem.* **1997**, *36*, 1278.
- (a) DePuy, C. H.; Gareyev, R.; Hankin, J.; Davico, G. E. *J. Am. Chem. Soc.* **1997**, *119*, 427. (b) DePuy, C. H.; Gareyev, R.; Hankin, J.; Davico, G. E.; Krempp, M.; Damrauer, R. *J. Am. Chem. Soc.* **1998**, *120*, 5086.
- Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 1155.
- Rasul, G.; Olah, G. A. *Inorg. Chem.* **1999**, *38*, 4132.
- (a) Lammertsma, K.; Olah, G. A.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 6851. (b) Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Schleyer, P. v. R.; Simonetta, M. *J. Am. Chem. Soc.* **1983**, *105*, 5258.
- Olah, G. A.; Rasul, G. *Inorg. Chem.* **1998**, *37*, 2047.
- Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Mol. Struct. (THEOCHEM)* **1998**, *455*, 101.
- Kapp, J.; Schreiner, P. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 12154.
- Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley & Sons: New York, 1988; p 208.