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# The Quest for Tetracoordinated Halonium Ions: A Theoretical Investigation

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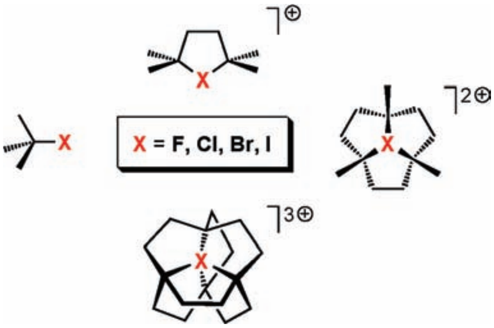
## ABSTRACT



**Di-, tri-, and tetravalent halonium ions have been investigated by theoretical means with respect to their geometries and their electronic structure using DFT as well as MP2 calculations. Even tricationic species where halides (F, Cl, Br, and I) are surrounded by an appropriate tetracationic hydrocarbon cage are calculated to be stable species. All halides show bonding interactions with all four cationic carbon centers.**

The quest for unusual binding situations[1] has fascinated chemists from the very beginning when scientists started to understand the way in which a chemical bond is formed.[2] Not only were highly strained molecular entities investigated[1] but also so-called hypervalent bonding situations in which a main group element contains formally more than eight electrons in its valence shell.[3] Another unusual type of bond formation, this time not in contrast to the octet rule, is further binding of remaining lone pairs of the main group VI and VII elements to carbocations. Oxonium ions **2** ($R_3O^+$) are widely known as intermediates of various transformations in organic chemistry;[4] that have also been isolated[5] and have been used as Meerwein's salt in synthesis.[6] However, their halogen counterparts, the halonium ions **5** ($R_2Hal^+$),[7] are less famous. Nevertheless, they play an important role in organic reactions such as halogenation and Friedel−Crafts alkylations.[8] Dialkylhalonium ions were even isolated as stable $SbXF_5^-$ salts.[9]

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(1) Selected examples: (a) de Meijere, A.; Khlebnikov, A. F.; Kozhushkov, S. I.; Miyazawa, K.; Frank, D.; Schreiner, P. R.; Rinderspacher, B. C.; Yufit, D. S.; Howard, J. A. K. *Angew. Chem.* **2004**, *116*, 6715−6719; *Angew. Chem., Int. Ed.* **2004**, *43*, 6553−6557. (b) Ajami, D.; Oeckler, O.; Simon, A.; Herges, R. *Nature* **2003**, *426*, 819–821. (c) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239–5240. (d) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem.* **1978**, *90*, 551−552; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520−521. (e) Werz, D. B.; Düfert, A. *Org. Lett.* **2008**, *10*, 5231–5234.

(2) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1939.

(3) (a) Musher, J. I. *Angew. Chem.* **1969**, *81*, 68−83; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54−68. (b) Gleiter, R.; Hoffmann, R. *Tetrahedron* **1968**, *24*, 5899–5911. (c) Ramsden, C. A. *Chem. Soc. Rev.* **1994**, *23*, 111–118.

(4) Olah, G. A.; Laali, K. K., Wang, Q.; Prakash, G. K. S. *Onium Ions*; J. Wiley and Sons: New York, 1998.

(5) (a) Francl, M. M.; Hansell, G.; Patel, B. P.; Swindell, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 3535–3539. (b) Etzkorn, M.; Aniszfeld, R.; Li, T.; Buchholz, H.; Rasul, G.; Prakash, G. K. S.; Olah, G. A. *Eur. J. Org. Chem.* **2008**, 4555–4558. (c) Mascal, M.; Hafezi, N.; Meher, N. K.; Fettinger, J. C. *J. Am. Chem. Soc.* **2008**, *130*, 13532–13533. (d) Haley, M. M. *Angew. Chem.* **2009**, *121*, 1572−1574; *Angew. Chem., Int. Ed.* **2009**, *48*, 1544−1545.

(6) Meerwein, H. *Org. Synth.* **1966**, *46*, 113–115.

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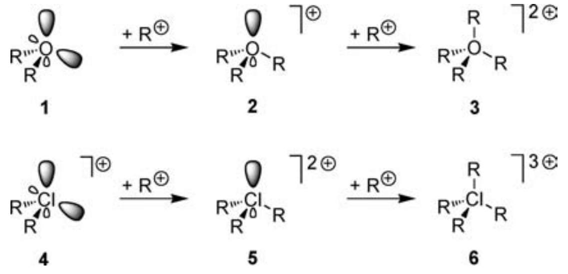
Recently, we elucidated in a theoretical study the possibility to utilize the remaining lone pair of a trivalent oxonium ion **2** for further binding to a carbocation to afford a tetracoordinated oxonium dication **3** (Scheme 1).[10]

**Scheme 1.** Repetitive Binding of Carbocations to Ether **1** Leading to a Trivalent Oxonium Ion **2** and Tetravalent Oxonium Dication **3** and Comparison with the Halogen Counterparts **4**−**6**



Appropriately designed hydrocarbon cages led to the conclusion that a tetracoordination of oxygen should be accessible. From this result arose the question whether halogen lone pairs could also accommodate a carbocation as binding partner led via the experimentally well-known disubstituted monocationic to tri- and tetracoordinated di- and tricationic halonium ions (Figure 1).

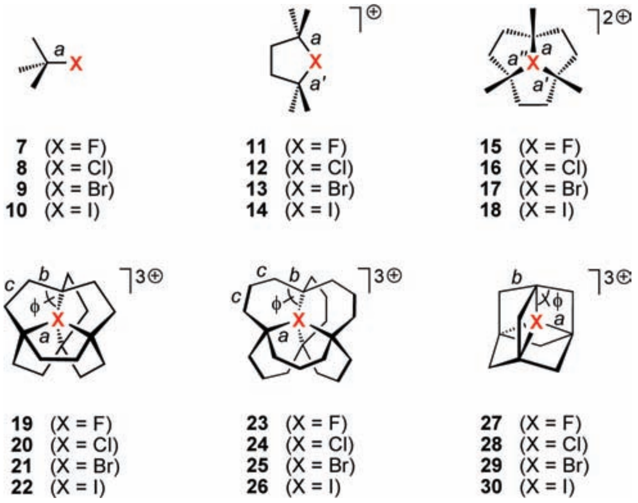


**Figure 1.** Parent *t*-butyl halides **7**−**10**, divalent halonium ions **11**−**14**, trivalent halonium dications **15**−**18**, and tetravalent caged halonium trications **19**−**30** with ethano, propano, and methano bridges. Definition of the most relevant geometrical parameters (used in Table 1).

This idea inspired us to sytematically elucidate the different kinds of halonium ions starting with *t*-butyl halides **7**−**10** as parent compounds; the formal attachment of one or two carbocationic centers affords the corresponding divalent cyclic halonium ions **11**−**14** and their trivalent counterparts **15**−**18**, respectively. Of course, the most intriguing question is whether a tetracoordination might also be in reach. Therefore, we extended the above-mentioned series of compounds **7**−**18** to three types of hexacyclic trications with a caged halogen atom (Figure 1) varying in the cage size. The medium-sized cages **19**−**22** use ethano bridges, the larger cages **23**−**26** propano bridges and even halogens caged in an adamantane-like structure **27**−**30** (methano bridges) were investigated. All these cages can also be seen as a halide anion that is coordinated by a tetradentate tetracation.

For all compounds **7**−**30** the geometrical parameters were optimized (without any symmetry restriction ($C_1$) and for compounds **19**−**26** also in point group $T$ and for **27**−**30** in $T_d$) using density functional theory (DFT)[11] by applying the three-parameter hybrid functional by Becke (B3)[12] and the correlation functional by Lee, Yang, and Parr (LYP).[13] As basis set we used 6-311G(d) as suggested by Pople et al.,[14,15] implemented in Gaussian 03.[16] All minima were characterized by frequency calculations (NImag = 0), and all energies are corrected by zero-point vibrational energies.

A comparison in the series of divalent halonium ions **11**−**14** reveals interesting differences. The fluoronium ion **11** shows two highly different distances *a*/*a*′ (152 pm vs 194 pm) whereas all the heavier analogues **12**−**14** reveal the same distance *a*/*a*′. By comparing the length *a*/*a*′ in the halonium ions with the parent *t*-butyl halides it is seen that heavier halogens only augment this distance by a small percentage (9% for **12**, 7% for **13**, and only 5% for **14**).

An elucidation of the trivalent species **15**−**18** reveals some astounding differences. The fluorine containing congener **15** shows three highly different distances *a*/*a*′/*a*″ from the center to the cationic carbons (152.0 pm vs 203.5 pm vs 250.7 pm), whereas the heavier analogues **16**−**18** show two distances *a*/*a*′ of almost similar length and one distance *a*″ that exceeds the other two by about 90 pm. A complete list of the most important geometrical parameters including bond lengths and angles of compounds **7**−**18** is provided in the Supporting Information.

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(7) (a) Olah, G. A.; Rasul, G.; Hachoumy, M.; Burrichter, A.; Prakash, G. K. S. *J. Am. Chem. Soc.* **2000**, *122*, 2737–2741. (b) Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 2448–2456. (c) Boldyrev, A. I.; Simons, J. *J. Chem. Phys.* **1992**, *97*, 4272–4281. (d) Damrauer, R.; Leavell, M. D.; Hadad, C. M. *J. Org. Chem.* **1998**, *63*, 9476–9485. (e) Teberekidis, V. I.; Sigalas, M. P. *Tetrahedron* **2003**, *59*, 4749–4756.

(8) Olah, G. A. *Halonium Ions*; Wiley-Interscience: New York, 1975.

(9) (a) Olah, G. A.; DeMember, J. R.; Mo, Y. K.; Svoboda, J. J.; Schilling, P.; Olah, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 884–892. (b) Olah, G. A.; DeMember, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 2113–2115.

(10) Schneider, T. F.; Werz, D. B. *Org. Lett.* **2010**, *12*, 772–775.

(11) (a) Kohn, W.; Sham, L. J. *Phys. Rev. A: At., Mol., Opt. Phys.* **1965**, *140*, 1133–1138. (b) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989.

(12) (a) Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155–2160. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

(13) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Chem. Phys.* **1994**, *98*, 11623–11627.

(14) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

(15) SDB-cc-pVTZ (with ECP) for I: (a) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408–3420. (b) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431–1441.

(16) Frisch, M. J.; et al. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford CT, 2004 (see Supporting Information for the complete citation).

**Table 1.** Most Important Geometrical Parameters $a$, $b$, $c$ and $\varphi$ (as defined in Figure 1) of **19−28** (Calculated at the B3LYP/6-311G(d) Level of Theory), Wiberg Bond Indices (WBI),[17] Complexation Energies $\Delta H_f$, Natural (NPA) Charges and Chemical Shifts $\delta$ (Calculated at the B3LYP/6-311++G(2df, 2pd) Level of Theory)

| | **19** | **20** | **21** | **22** | **23** | **24** | **25** | **26** | **27** | **28** |
|---|---|---|---|---|---|---|---|---|---|---|
| $a^a$ [pm] | 183.6 | 186.1 | 190.8 | 199.0 | 219.7 | 226.5 | 228.1 | 230.2 | 150.7 | 161.0 |
| $b^a$ [pm] | 151.4 | 157.3 | 159.7 | 162.9 | 148.4 | 150.1 | 151.2 | 152.8 | 170.4 | 179.9 |
| $c^a$ [pm] | 157.4 | 158.6 | 160.0 | 162.9 | 154.8 | 156.2 | 156.7 | 157.5 | - | - |
| $\varphi^a$ [deg] | 93.7 | 95.2 | 94.8 | 94.0 | 96.1 | 96.7 | 97.4 | 98.5 | 79.0 | 78.3 |
| WBI (X−C)$^b$ | 0.25 | 0.69 | 0.80 | 0.89 | 0.17 | 0.38 | 0.48 | 0.64 | 0.35 | 0.89 |
| NPA Charge (X)$^b$ [e] | −0.339 | +0.982 | +1.499 | +2.517 | −0.489 | +0.152 | +0.539 | +1.308 | −0.230 | +1.527 |
| NPA Charge (C)$^b$ [e] | +0.526 | +0.148 | −0.012 | −0.234 | +0.523 | +0.370 | +0.281 | +0.102 | +0.493 | −0.108 |
| $\Delta H_f$ [kJ/mol] $^c$ | 1987 | 1322 | 1155 | 906 | 1857 | 1465 | 1392 | 1269 | 1369 | 489 |
| $\delta$ (C) [ppm] $^d$ | 281.9 | 179.4 | 143.6 | 85.6 | 314.8 | 271.1 | 245.9 | 191.3 | 273.0 | 80.2 |
| $\delta$ ($\underline{C}H_2$) [ppm] $^d$ | 52.7 | 56.7 | 57.5 | 57.4 | 50.7 | 46.3 | 44.7 | 41.5 | 86.9 | 117.9 |
| $\delta$ ($C\underline{H}_2$) [ppm] $^d$ | 4.23 | 4.18 | 4.18 | 4.33 | 3.76 | 3.59 | 3.49 | 3.24 | 7.31 | 7.98 |

[a] Values calculated in point group $T$ (**19−26**) or $T_d$ (**27, 28**) respectively. In all cases the total energy obtained in point group $T$ or $T_d$ was lower than in point group $C_1$. [b] Calculated by a natural bond orbital (NBO) analysis using the B3LYP/6-311G(d) density. [c] Values of $\Delta H_f$ are based on the energies of a tetracation and a halide anion, and are not corrected for basis set superposition effects (BSSE). [d] Relative to Tetramethylsilane.

Interestingly, when the hydrocarbon cages are used to generate the tricationic species **19−22** an optimization in point group $T$ reveals the lowest energy conformer; all distances $a$ are equal and tetravalent halogens revealing the typical tetrahedral angle of about 109° at the caged halogen are observed. Because of the limited size of the cage the distances $a$ increase only slightly for the different halonium ions **19−22** (Table 1). In Figure 2 we summarize the development of the mean values of distance $a$ in the various species **7−22**.

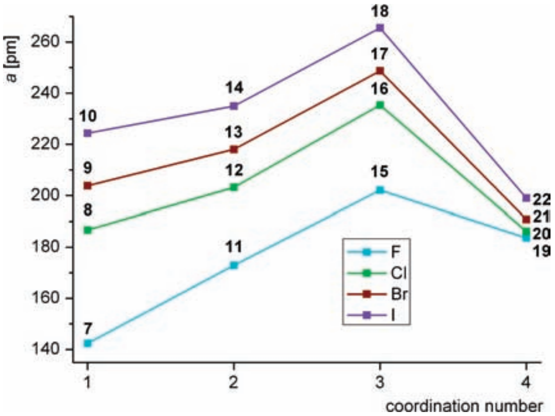

**Figure 2.** Mean value of distances $a/a'/a''$ in compounds **7−22** depending on the coordination number of the halogen as calculated on the level of B3LYP/6-311G(d).

The larger size of chlorine, bromine and iodine is more strongly mirrored in the increase of distance $b$ and illustrates the strain associated with the hosting of these heavier elements (up to 163 pm in **22**). Another parameter that describes the strain of the cage is the angle $\varphi$: Values higher than 90° show an attractive interaction between the halogen and the former trivalent carbon. Whereas in the larger cage series **23−26** higher values of $\varphi$ (96−99°) are observed indicating enough space for the heavier halogens, the cage compounds with ethano bridges **19−22** show angles only in the range of 94−95° (Table 1). For the adamantane-like structures (point group $T_d$) our calculations have shown that only fluorine ($a$ = 149.2 pm, $\varphi$ = 79°) and chlorine ($a$ = 160.9 pm, $\varphi$ = 78°) are able to be accommodated inside the cage. The larger halogens burst their hosts; no stable structures were found on their potential energy surface. In Figure 3, we have depicted the optimized structures of four species (**13**, **15**, **22**, and **28**).

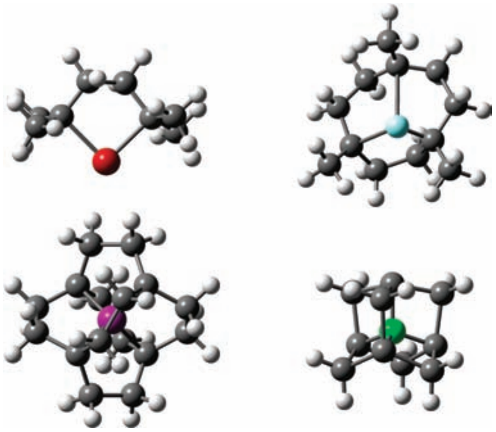

**Figure 3.** Optimized structures of monocation **13** (top left), dication **15** (top right), and trications **22** (bottom left) and **28** (bottom right) as calculated on the level of B3LYP/6-311G(d).

Whereas in all cases the distances $a$ are longer than in the analogous caged chalcogenium dications,[10] the angles $\varphi$ are smaller. This fact illustrates a better binding of the carboca-

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(17) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083–1096.

tions to the lone pairs of the more nucleophilic chalcogens in comparison with the lone pairs of the halogens.

We also performed a natural bond orbital analysis that reveals that the Wiberg bond indices (WBI)[17] are only 0.25 for the fluorine containing congener **19**. In general, these bond indices are much smaller for the caged halogens compared with analogous caged chalcogens.[10] The differences of the WBIs between the smaller and the larger cage compounds reveal a forced binding of the cations to the halogen. In addition, the natural population analysis afforded natural charges, presented in Table 1, for the halogen (X) and the carbocationic centers (C). The most electronegative element, fluorine, always carries a negative charge (**19**, **23**, and **27**), whereas the other guests are able to accommodate more positive charge with increasing size.

The trications might also be regarded as halide anions complexed by a tetradentate tetracation. In order to get an impression of the energy associated with such a conceivable complexation process we also calculated the potential energies of the separated ions on one hand and the potential energy of the corresponding trications on the other (see Supporting Information). Their difference can be considered as complexation energy and is denoted as $\Delta H_f$ in Table 1. For all cage compounds the $\Delta H_f$ value decreases with increasing size of the heteroelement. This behavior reflects the decreasing ionic character of the X−C bonds when going from fluorine-containing to iodine-containing compounds. For **28** this value is rather low due to the highly strained adamantane-like structure with the hosted chloride inside.

All the cage compounds **19**−**28** were also investigated by means of the MP2 level of theory (MP2/6-311G(d))[18] to take electron correlation effects into account which often play a crucial role in weak interactions.[19] Respective values in analogy to Table 1 are given in the Supporting Information. In general the distances are slightly shorter than the corresponding ones obtained by density functional theory.

In order to test the flexibility of the caged halogen in the medium-sized cages **19**−**22** we performed relaxed energy scans of the trications by varying one of the distances *a* ($C_1$). These results are illustrated in Figure 4. It is noteworthy that the potential energy surface of the fluorine-containing species **19** is rather flat revealing a high flexibility of the hosted fluoride. It is unequivocally shown, by tighter potential wells in the series from **19** (F) to **22** (I), that the heavier the halogen, the greater the stability of the tetracoordination. The bending of the curves in the case of **21** and **22** at distances of about 250 pm mirrors the fact that their trivalent halonium ions are considerably stabilized. In the case of **22**, even a local minimum for such a trivalent iodonium ion is found.

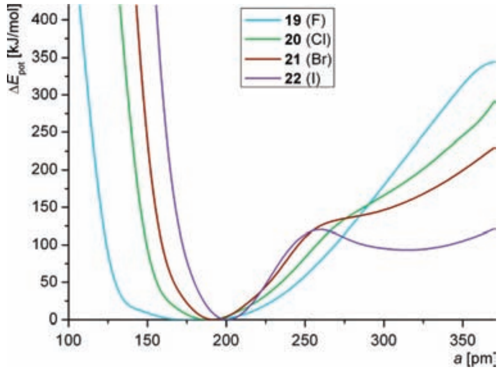

**Figure 4.** Potential energy of the trications **19**−**22** depending on the distance *a* between the caged halogen and one carbocationic center according to B3LYP/6-311G(d).

For all caged tetracoordinated halogens **19**−**28** we also computed the NMR chemical shifts ($\delta$) of the most relevant carbon and hydrogen atoms (Table 1). With the exception of the adamantane-like structures **27** and **28** the $^{1}$H NMR chemical shifts do not reveal any significant differences within the series. However, the $^{13}$C NMR shifts of the cationic centers unambigiously demonstrate the higher ionic character when the cage size is increased (downfield-shifted chemical shifts). The most extreme values are observed in the fluorine-containing compound **23** with the large cage (315 pm) and on the other hand in the highly strained adamantane cage **28** (80 ppm).

Computational studies postulating charged species must always include realistic anions. Therefore, DFT calculations with $PF_6^-$ as well as tetraphenylborates as counterions (see Supporting Information) were performed.[20] However, the geometrical parameters for the tetracoordinated species were only slightly different; in all cases the tetracoordination of the caged halogens stays intact.

In conclusion, we present a systematic investigation of di-, tri, and tetravalent halonium ions by means of B3LYP as well as MP2 calculations. Whereas trivalent halonium ions commonly exhibit two different X−C bond lengths (even three in the case of F), our computations have also revealed that tetracoordinated species are local minima on the potential energy surface. Such tetracoordinated halonium trications exhibiting four equal X−C bond distances were designed by using simple hydrocarbon cages with four carbocationic centers. With appropriate large noncoordinating anions as counterions (e.g., tetraphenylborates) these remarkable compounds should be in reach and are waiting to be synthesized.

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**Supporting Information Available:** Gaussian Archive Entries and optimized structures for all calculated species. Full ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622. (b) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem. Symp.* **1977**, *12*, 149–163.

(19) (a) Bleiholder, C.; Werz, D. B.; Köppel, H.; Gleiter, R. *J. Am. Chem. Soc.* **2006**, *128*, 2666–2674. (b) Bleiholder, C.; Gleiter, R.; Werz, D. B.; Köppel, H. *Inorg. Chem.* **2007**, *46*, 2246–2260.

(20) For an overview: Krossing, I.; Raabe, I. *Angew. Chem.* **2004**, *116*, 2116−2142; *Angew. Chem., Int. Ed.* **2004**, *43*, 2066−2090.