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Exchange reactions of chloriranium and chlorirenium ions: a G2 investigation

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Abstract

Ab initio molecular orbital calculations at the G2 level have been used to study exchange reactions between cationic three-membered chlorine heterocycles and unsaturated hydrocarbons. The reactions are predicted to proceed with little or no overall barrier. The relationship of the theoretical findings to relevant experimental observations is discussed. The electronic characteristics of the exchange transition structures are compared with those for the analogous sulfur and phosphorus systems. The structures can be understood qualitatively in terms of a principal interaction resembling the triple-ion configuration found for S_N2 transition structures and a secondary back-bonding interaction. (Int J Mass Spectrom 185/186/187 (1999) 263–270) © 1999 Elsevier Science B.V.

Keywords: G2 theory; Three-membered heterocyclic ions; π interactions; Exchange; Back bonding

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1. Introduction

A large body of data supports the existence of chloriranium ions (e.g. **1**). Their intermediacy in the chlorination of alkenes was suggested in 1937 by Roberts and Kimball [1] to account for the stereospecificity of this reaction. Early stereochemical investigations of the chlorination reaction [2] were elaborated by several workers using classical techniques [3–6], and in many cases the stereochemical outcome was found to be consistent with the intermediacy of substituted chloriranium ions. Fahey et al. used NMR spectroscopy to analyse the reaction products from alkene chlorination [7,8], and concluded that the stereochemical outcome is best accounted for by the intermediacy of bridged ions in the case of 1,2-dialkylalkenes, whereas a phenyl substituent favors the open-chain 2-chloro-substituted carbocation [7,8]. An unambiguous proof for the existence of chloriranium ions in the condensed phase comes from NMR spectra of chloriranium ions in superacid media [9,10]. The NMR results were found to be consistent with the bridged isomer in the unsubstituted case and the open-chain isomer in the case of tetramethyl substitution [10]. In the gas phase, thermochemical measurements [11] and ion/molecule reactions [12,13] suggest that the loss of $Cl^{\cdot}$ from 1,2-dichloroethylene radical cation and of $Br^{\cdot}$ from 1-bromo-2-chloroethylene radical cation lead to **1**.

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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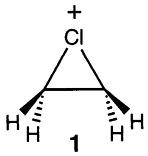

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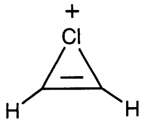
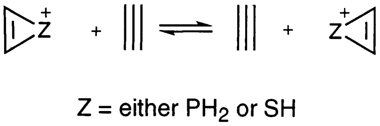


2

A number of theoretical investigations of the $C_2H_4Cl^+$ surface predict that **1** is the second lowest energy isomer and that **1** is separated from the global minimum (the 1-chloroethyl cation) by a significant barrier [12,14,15]. The open-chain isomer of **1**, the 2-chloroethyl cation, lies high in energy and when electron correlation is included, it collapses to the bridged structure [15]. These theoretical findings thus support the existence of **1** in the gas phase. The structures of substituted chloriranium ions have also been addressed theoretically. Early lower level calculations [16] predicted that the open-chain β-chloroethyl cation isomers of the methylchloriranium ion, the 1,1-dimethylchloriranium and the 1,1,2,2-tetramethylchloriranium ions are preferred, whereas the bridged structure is preferred for 1,2-dimethylchloriranium ion. However, our preliminary investigations indicate that some of these results may change upon the inclusion of electron correlation [17]. For example, calculations at the MP2(full)/6-31G(d) level predict that the 1,1,2,2-tetramethylchloriranium ion has a stable bridged structure, with attempts to locate the open-chain isomer also leading to the bridged form.

Theory predicts that the $C_2H_2Cl^+$ and $C_2H_4Cl^+$ surfaces are quite similar when electron correlation is taken into account [18,19]. Again, the bridged chlorirenium ion structure (**2**) lies second lowest on the surface and is separated by a significant barrier from the global minimum (the 1-chlorovinyl cation). The open-chain β-chlorovinyl cation isomer of **2** was found to be a saddle point [19]. No conclusive experimental evidence for the existence of **2** has yet been reported.

We have recently applied high level ab initio techniques in the investigation of a novel exchange reaction between unsaturated hydrocarbons and the heterocyclic sulfur and phosphorus ions analogous to **1** and **2** [e.g. (1)] [20,21]:



(1)

The reactions were predicted to be very low energy processes for all the systems investigated. Such exchange reactions had been observed previously in the condensed phase for certain three-membered phosphorus heterocycles [22] and had been referred to as π-ligand exchange because of their resemblance to π-ligand exchange in organometallic chemistry. Exchange has yet to be observed in the sulfur systems, but has been shown to be feasible in certain chlorine systems. Thus, Heck et al. [23] have reported that the chloriranium ion does indeed undergo exchange with tetramethylethylene and ethyl vinyl ether in a Fourier transform ion cyclotron resonance (FTICR) cell but there is a preferred addition–elimination reaction. In fact, *only* this reaction was observed when the C═C double bond is provided by perdeuteroethylene, propene, or methyl vinyl ether [23].

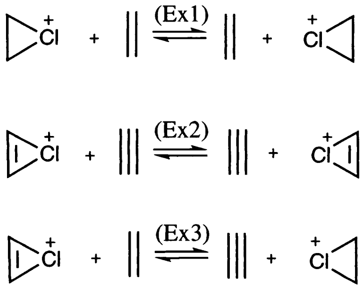
In the present article, we have employed high level ab initio molecular orbital calculations to investigate whether the exchange reactions of **1** and **2** are also low energy processes. This may provide an understanding of the observed reactivity of **1** towards alkenes and give an indication of the feasibility of other possible exchange reactions of **1** and **2** in the gas phase. In addition, comparisons between the present results and the results for the corresponding phosphorus and sulfur systems enable us to discuss electronic aspects of the exchange reactions in more detail.

2. Computational methods

Ab initio molecular orbital calculations [24] were carried out using a modified form of G2 theory [25] with the GAUSSIAN 94 [26] and MOLPRO 96 [27] systems of programs. G2 theory effectively corresponds to a QCISD(T)/6-311 + G(3df,2p) single-point energy calculation on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies (ZPVEs) and a so-called higher level correction. G2 theory was developed by Curtiss et al. [25] with the aim of obtaining atomization energies of molecules, ions, and free radicals to an accuracy of 10 kJ mol^{-1}. This reliability has been shown to extend to other thermochemical properties such as ionization energies, electron affinities, bond energies, proton affinities, acidities, and reaction barriers [25,28]. In the present work, we have used a slightly modified version of G2 theory to make possible direct comparison with our previous results for the analogous sulfur and phosphorus systems [20,21]. The modification is to use ZPVEs calculated from MP2(full)/6-31G(d) harmonic vibrational frequencies scaled by 0.9646 [29] rather than from scaled HF/6-31G(d) frequencies. The method is formally referred to as G2(ZPE═MP2) [30], but we use the G2 label here for the sake of brevity. The transition structures for the reactions reported in this work have been confirmed in each case by the calculation of vibrational frequencies (one imaginary frequency) and an intrinsic reaction coordinate analysis. Calculated G2 total energies are presented in Table 1. Relative energies within the text correspond to G2 values at 0 K.

3. Results and discussion

In the present article we have investigated the possible exchange reactions between ethylene or acetylene and the chloriranium or chlorirenium ion. A schematic representation of these exchange reactions (Ex1–Ex3) is displayed in Scheme 1.



Scheme 1.

In the following sections, the characterized pathways for the exchange reactions in Scheme 1 are discussed and compared with available experimental results, and with theoretical results for the corresponding sulfur and phosphorus cases [20,21]. Figs. 1 and 2 depict MP2(full)/6-31G(d) optimized structures for all species investigated, including optimized values of selected geometric parameters. Barriers and reaction energies for the reactions in Scheme 1, calculated at the G2 level at 0 K, are given in Table 2. Schematic energy profiles are displayed in Figs. 3, 4, and 5.

Table 1
G2(ZPE═MP2) Total energies (Hartrees, 0 K)[a]

Molecule[b]	Energy
3	−78.41652
4	−77.18868
5	−537.83438
6	−536.56731
7	−616.26063
8	−613.76808
9	−615.03230
TS-Ex1	−616.24457
Ts-Ex2	−613.76063

[a] Referred to for simplicity as G2 within the text.

[b] See Figs. 1 and 2.

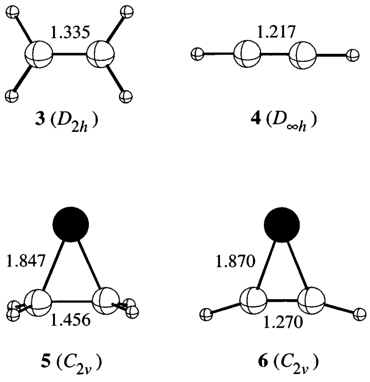


Fig. 1. Selected MP2(full)/6-31G(d) geometrical parameters of reactant molecules involved in the Ex1–Ex3 exchange reactions. Bond lengths in Å.

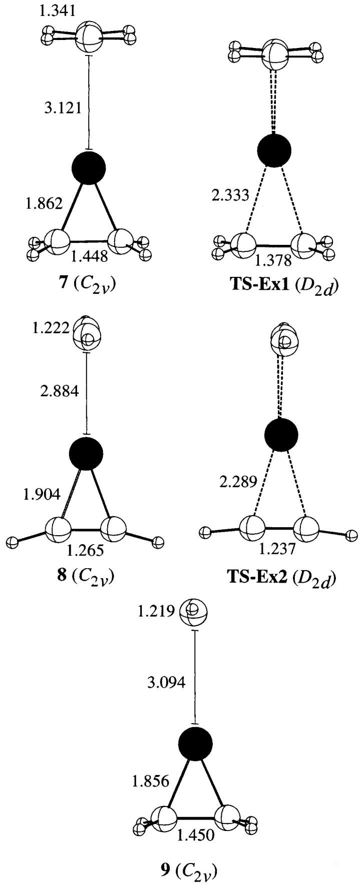
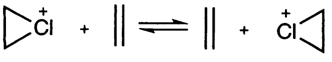
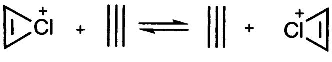
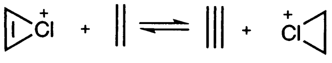


Fig. 2. Selected MP2(full)/6-31G(d) geometrical parameters of complexes and transition structures involved in the Ex1–Ex3 reactions. Bond lengths in Å.

Table 2
Calculated barriers and reaction energies for exchange[a]

Reaction	Barrier	Reaction energy
	16.6	0.0
	−12.2	0.0
	[b]	−103.0

[a] G2 values in kJ mol^{-1} at 0 K.
[b] Reaction proceeds without a barrier.

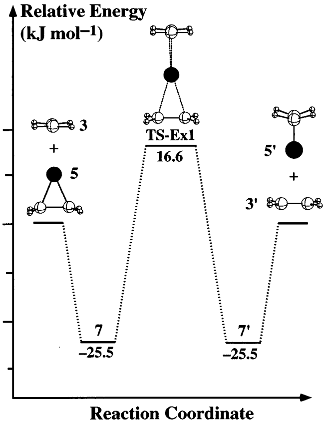


Fig. 3. Schematic energy profile for the Ex1 reaction.

3.1. Exchange reactions

In the identity reaction Ex1, the chloriranium ion **5** reacts with ethylene to form the initial C_{2v} complex **7**, bound relative to the reactants by 25.5 kJ mol^{-1} (Fig. 3). The product and reactant complexes are connected by the D_{2d} transition structure **TS-Ex1** at 16.6 kJ mol^{-1}.

The Ex2 reaction proceeds in a manner very similar to Ex1. Again, a C_{2v} complex **8** is formed initially, this time however between the chlorirenium ion **6** and acetylene (Fig. 4). The complex is bound by 31.7 kJ mol^{-1} relative to the separated reactant

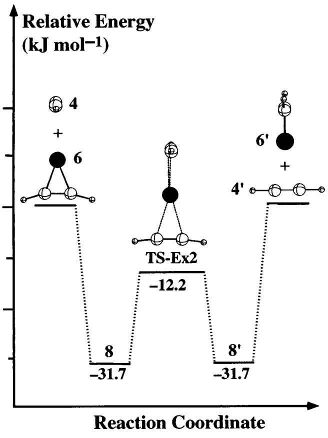


Fig. 4. Schematic energy profile for the Ex2 reaction.

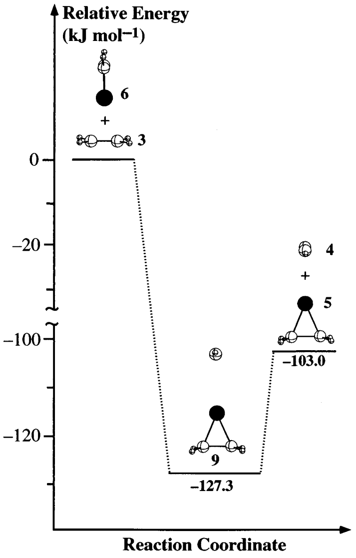


Fig. 5. Schematic energy profile for the Ex3 reaction.

molecules. The D_{2d} transition structure **TS-Ex2** at -12.2 kJ mol^{-1} connects the reactant complex **8** with the product complex **8′**. It can be seen that there is no *overall* barrier (relative to the reactants) for this reaction.

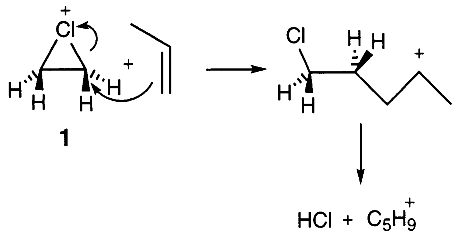
In the Ex3 exchange reaction, the chlorirenium ion **6** reacts with ethylene to form, directly without a barrier, a C_{2v} complex **9** between the chloriranium ion **5** and acetylene (Fig. 5). The suggestion that complex **9** is formed without a barrier is supported by the fact that all attempts to find a second complex between the chlorirenium ion and ethylene yielded complex **9**. This complex is bound by 24.3 kJ mol^{-1} relative to the chloriranium ion and acetylene and the exothermicity for the reaction is predicted to be significant (103.0 kJ mol^{-1}).

The pathway for exchange that we have identified is characterized by motions in two orthogonal planes, the first defined by the chlorine atom and the carbon atoms of the original ring and the second by the chlorine atom and the carbon atoms of the incoming hydrocarbon. In the first plane, the C–Cl bonds of the reactant ion are broken and this is concerted with the formation of the Cl–C bonds of the product ion in the second plane.

The Ex1 exchange reaction is predicted to proceed with a barrier of 16.6 kJ mol^{-1} whereas Ex2 has a lower barrier (-12.2 kJ mol^{-1}). This is consistent with the greater amount of strain released when the C–Cl bonds of the unsaturated chlorirenium ion are stretched. The large exothermicity for reaction Ex3 undoubtedly contributes to the disappearance of any barrier in this case.

3.2. Experiment versus theory

The prediction by the present calculations that the exchange reactions Ex1–Ex3 have low barriers could be taken to indicate that these reactions should be observable in gas-phase experiments. Relevant experiments have in fact been carried out by Heck et al. for the reaction of **1** with a series of alkenes (including C_2D_4) in an FTICR cell [23]. Exchange is indeed observed for reactions with tetramethylethylene and ethyl vinyl ether but there is a preferred addition–elimination reaction. In fact *only* this reaction [e.g. (2)] is observed when the C═C double bond is provided by perdeuteroethylene, propene or methyl vinyl ether [23].



(2)

The observation of exchange between the chloriranium ion and tetramethylethylene but not in the case of reactions with perdeuteroethylene and propene may be rationalized in terms of the thermodynamic driving force induced by the higher Cl$^+$ affinity [31] of the former. A 176 kJ mol^{-1} difference between the Cl$^+$ affinity of ethylene and tetramethylethylene has been predicted at the HF/3-21G level [16], and we find this difference to be 135.2 kJ mol^{-1} at MP2(full)/6-31G(d) + ZPVE [17]. A similar argument can be used

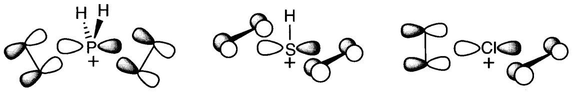


Fig. 6. The principal electronic interaction in exchange transition structures occurs between the empty *p* orbital on the heteroatom and two filled π orbitals.

to rationalize the reactions of **1** with methyl vinyl ether and ethyl vinyl ether. Exchange is only observed for the latter, which is consistent with the 15.2 kJ mol^{-1} greater Cl$^+$ affinity of ethyl vinyl ether, predicted at MP2(full)/6-31G(d) + ZPVE [17].

Exchange reactions similar to Ex2 and Ex3 have been observed experimentally in the condensed phase for certain phosphorus systems [22]. Since the barriers for the Ex2 and Ex3 reactions for the chlorine systems are either smaller than those found for the corresponding phosphorus systems (Ex2) or absent (Ex3), the Ex2 and Ex3 exchange reactions are likely to be feasible in the gas phase. The addition–elimination reaction is a complicating aspect. However, it might be expected that this reaction would be more difficult in the case of the chlorirenium ion and substituted chlorirenium ions (than for the corresponding chloriranium ions) because it would involve initial S$_N$1 or S$_N$2 attacks on vinyl centers, reactions that are known to have quite high energy demands [32,33].

3.3. Exchange in ionic three-membered phosphorus, sulfur, and chlorine heterocycles: electronic considerations

We find that the electronic characteristics of the transition structures for exchange in three-membered phosphorus, sulfur, and chlorine heterocyclic ions are similar. In qualitative terms, the principal interaction can be thought of as that occurring between the empty *p* orbital on the heteroatom and the filled π orbitals of the two hydrocarbons in question. This is illustrated in Fig. 6 for the transition structure in the chlorine Ex1 exchange reaction and for the analogous phosphorus and sulfur transition structures. This interaction resembles closely the triple-ion configuration ($X^- \cdots CH_3^+ \cdots X^-$) found in S$_N$2 transition structures [34].

The qualitative electronic description of the exchange transition structures can be elaborated to include a secondary back-bonding interaction between the lone pair(s) on the heteroatom and the π* orbitals of the two hydrocarbons involved (Fig. 7). This interaction can be used to rationalize the orientation of the incoming hydrocarbon in the phosphorus, sulfur, and chlorine exchange transition structures, as follows.

In the case of the phosphorus systems, a back-bonding interaction between the sp^2-type lone pair on the PH$_2^+$ moiety and the π* orbitals of the two hydrocarbons in question explains why the two C–P bonds closest to the lone pair are shortest. In addition, for maximum overlap between the lone pair and the π* orbitals, the five heavy atoms are required to be in the same plane (Fig. 7), which is indeed the case [20].

The transition structures for exchange in the sulfur systems have the SH$^+$ moiety perpendicular to the plane defined by the four carbon atoms and symmetrically placed with respect to these atoms [21]. This orientation is determined by the interaction between the *p* type lone pair on the SH$^+$ moiety and the π* orbitals of the two unsaturated hydrocarbons involved in the reaction (Fig. 7).

Finally, the exchange transition structures for the chlorine systems have the unsaturated hydrocarbons oriented in two perpendicular planes (Fig. 2), as opposed to the situation for the phosphorus and sulfur systems where the hydrocarbons are in the one plane. This orientation can again be rationalized in terms of a back-bonding interaction (Fig. 7). In this case, two *p* type lone pairs on chlorine are available for interaction with the π* orbitals of the hydrocarbons. Maximum delocalization of electron density will occur when each of the hydrocarbons interacts with a

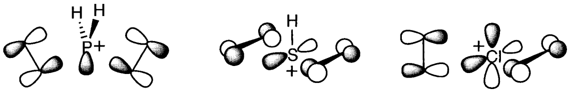


Fig. 7. A secondary back-bonding interaction in exchange transition structures occurs between the (filled) lone pair(s) on the heteroatom and two π* orbitals.

single lone pair. This requires a perpendicular orientation of the hydrocarbons, as illustrated in Fig. 7.

4. Concluding remarks

The present investigation has provided a fascinating insight into the reactivity of chlorirenium and chloriranium ions towards unsaturated hydrocarbons. We predict that the exchange reactions should proceed with either very low barriers (Ex1 and Ex2) or no barrier at all (Ex3) and therefore they should be observable in the gas phase. Previous experimental work has found that addition–elimination is preferred over exchange in the reaction between the chloriranium ion and a set of unsaturated hydrocarbons. The experimental results suggest that only alkenes with a Cl^+ affinity much larger than that of ethylene can introduce a thermodynamic driving force sufficiently large to obtain even small amounts of exchange product. Addition–elimination is considered less likely to compete with exchange in the case of the Ex2 and Ex3 reactions and in reactions of substituted chlorirenium ions. The exchange reactions are therefore more likely to be experimentally observable in these cases.

The theoretical results provide a detailed picture of the electronic characteristics of the chlorine exchange transition structures and their relationship with the corresponding phosphorus and sulfur exchange transition structures. The predicted structures can be understood in terms of two interactions: a primary interaction between an empty p orbital on the heteroatom and the π orbitals of the two hydrocarbons, and a secondary back-bonding interaction between the lone pair(s) on the heteroatom and the π^* orbitals of the hydrocarbons.

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References

[1] I. Roberts, G.E. Kimball, J. Am. Chem. Soc. 59 (1937) 947.
[2] C.F. Freudenberg, Stereochemie, Frantz Deuticke, Vienna, 1933, p. 520.
[3] H.J. Lucas, C.W. Gould, J. Am. Chem. Soc. 63 (1941) 2541.
[4] S.J. Christol, F.R. Steinmitz, P.S. Ramey, J. Am. Chem. Soc. 78 (1956) 4939.
[5] S.J. Christol, R.S. Bly, J. Am. Chem. Soc. 82 (1960) 142.
[6] P.B.D. de la Mare, N.V. Klassen, R. Koenigsberger, J. Chem. Soc. (1961) 5285.
[7] R.C. Fahey, C. Schubert, J. Am. Chem. Soc. 87 (1965) 5172.
[8] R.C. Fahey, J. Am. Chem. Soc. 88 (1966) 4681.
[9] G.A. Olah, Halonium Ions, Wiley, New York, 1975.
[10] G.A. Olah, J. Am. Chem. Soc. 96 (1974) 3565.
[11] D.W. Berman, V. Anicich, J.L. Beauchamp, J. Am. Chem. Soc. 101 (1979) 1239.
[12] C.F. Rodriquez, G. Javahery, A.C. Hopkinson, D.K. Bohme, Eur. Mass Spectrom. 1 (1995) 437.
[13] R.A.J. O'Hair, M.A. Freitas, T.D. Williams, J. Org. Chem. 61 (1996) 2374.
[14] H. Lischka, H.-J. Köhler, J. Am. Chem. Soc. 100 (1977) 5297.
[15] C.F. Rodriquez, D.K. Bohme, A.C. Hopkinson, J. Am. Chem. Soc. 115 (1993) 3263.
[16] S. Yamabe, T. Tsuji, K. Hirao, Chem. Phys. Lett. 146 (1988) 236.
[17] T.I. Sølling, L. Radom, Unpublished results.
[18] T.P. Hamilton, H.F. Schaefer, J. Am. Chem. Soc. 113 (1991) 7147.
[19] C.F. Rodiquez, D.K. Bohme, A.C. Hopkinson, J. Org. Chem. 58 (1993) 3344.
[20] T.I. Sølling, M.A. McDonald, S.B. Wild, L. Radom, J. Am. Chem. Soc. 120 (1998) 7063.
[21] T.I. Sølling, S.B. Wild, L. Radom, Chem. Eur. J., in press.
[22] D.C.R. Hockless, M.A. McDonald, M. Pabel, S.B. Wild, J. Organomet. Chem. 529 (1997) 189.
[23] A.J.R. Heck, L.J. de Koning, N.M.M. Nibbering, Org. Mass Spectrom. 28 (1993) 235.
[24] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.
[25] L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople, J. Chem. Phys. 94 (1991) 7221.
[26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94 (Rev. E.2), Gaussian Inc., Pittsburgh, PA, 1995.
[27] MOLPRO 96 is a package of ab initio programs written by H.J. Werner and P.J. Knowles with contributions from J. Almlof, R.D. Amos, M.J.O. Deegan, S.T. Elbert, C. Hempel, W. Meyer, K. Peterson, R. Pitzer, A.J. Stone, P.R. Taylor, and R. Lindh.
[28] For recent reviews, see (a) L.A. Curtiss, K. Raghavachari, Quantum Mechanical Electronic Structure Calculations with

Chemical Accuracy, S.R. Langhoff (Ed.), Kluwer Academic, Dordrecht, 1995; (b) K. Raghavachari, L.A. Curtiss, Modern Electronic Structure Theory, D.R. Yarkony (Ed.), World Scientific, Singapore, 1995.
[29] J.A. Pople, A.P. Scott, M.W. Wong, L. Radom, Isr. J. Chem. 33 (1993) 345.
[30] L.A. Curtiss, K. Raghavachari, J.A. Pople, J. Chem. Phys. 103 (1995) 4192.
[31] The term Cl^+ affinity denotes the reaction energy for the formation of a chloriranium ion from a Cl^+ ion and an alkene, as suggested in [23].
[32] M.N. Glukhovtsev, A. Pross, L. Radom, J. Am. Chem. Soc. 116 (1994) 5961.
[33] P.J. Stang, Acc. Chem. Res. 11 (1978) 107.
[34] M.N. Glukhovtsev, A. Pross, L. Radom, J. Am. Chem. Soc. 117 (1995) 2024.