

Iron-Promoted C–C Bond Formation in the Gas Phase

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Abstract: An unusual iron transfer and carbon–carbon coupling take place in gas-phase ionized mixtures containing ferrocene and dichloromethane. Ferrous chloride and the protonated benzenium ion are eventually formed by a thermal and efficient reaction, through stable intermediates that undergo a remarkable reorganization. The mechanism of the concerted iron extrusion, carbon–chlorine bond activation and carbon–carbon bond formation is elucidated by electronic structure calculations that show the crucial role of iron.

Always in the spotlight of scientific research, iron is unique in nature as a vital element in the Earth's biosphere and a major component in the Earth's metallic core. Among the low-valent iron species, ferrocene ($\eta^5\text{-C}_5\text{H}_5\text{Fe(II)}$) holds a special position as the archetypal organometallic compound and the prototype of metallocenes,^[1] its charged fragment ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) can be seen as a Fe(I)-ligated cation.^[2] The great potential of ferrocene to address highly relevant issues, such as biosensor design, cancer drugs, dye-sensitized solar cells,^[3] is mainly due to its excellent redox properties; as an example, the cytotoxic properties of ferrocenium salts can be exclusively traced to the oxidized charged form ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$).^[4] In many cases these properties are combined with Lewis acids properties.

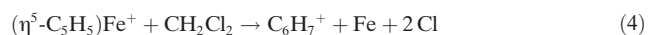
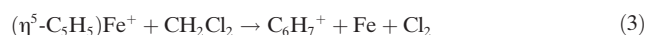
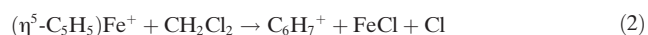
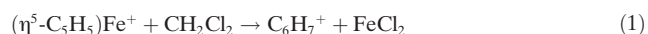
To unravel the intrinsic features of the ligated metal, both ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) and ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) cations have been extensively investigated in the gas phase. In particular, ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) has been shown to react rapidly with several inorganic and organic nucleophiles (L), whereas ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) was found to be unreactive.^[5] The reactions of ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) with L invariably give the ligated [$(\eta^5\text{-C}_5\text{H}_5\text{Fe-L})^+$] ions. Nucleophiles L having halogen atoms, such as substituted pyridines PyX and methyl halides CH_3X (X = F, Cl, Br), give HX loss and products containing the ($\text{C}_5\text{H}_4\text{Fe}$) kernel.^[5b] According to the widely suggested mechanism, the ligated ions show the nucleophile coordinated with the metal rather than with the carbon ring of the reactant.

Conversely, C–C bond formation has been observed in solution in alkyl halides reactions catalyzed by iron,^[6] and in

the gas phase in hydrocarbons reactions mediated by bare Fe^+ and Fe_n^+ cations.^[7]

As a whole, the nature of the products obtained in the reactions of ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) indicates that, irrespective of the coordination site of the added nucleophile, the coordination of the iron with the carbon ring is always preserved. A rare interesting example of extrusion of iron is given by the reaction in matrix of ferrocene and ozone, that gives hematite Fe_2O_3 by atomic layer deposition upon red or infrared irradiation.^[8] Although the process is promising for solar energy conversion devices, so far no evidence for thermal reactions has been found. Here we report the formation of ferrous chloride and protonated benzenium ion by an effective thermal reaction observed in ionized mixtures containing ferrocene and dichloromethane, where the iron atom proves to play a crucial role in the formation of the new C–C bond. Due to the good reducing power and flocculating ability, ferrous chloride is largely used in the treatment of waste water and remediation of industrial waste ores containing Cr(VI).^[9]

The iron-containing cations formed by ionization of ferrocene in the gas phase are ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$), ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$), Fe^+ . Under certain conditions, like in the high-pressure source of a mass spectrometer, ligated ions [$(\eta^5\text{-C}_5\text{H}_5\text{Fe-L})^+$] are observed following the introduction of a nucleophile L. For instance, ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) ($\text{L} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$) is formed just by addition of ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) to ferrocene. Following the introduction of CH_2Cl_2 , further to [$(\eta^5\text{-C}_5\text{H}_5\text{Fe-CH}_2\text{Cl}_2)^+$], one observes an abundant ion formally corresponding to C_6H_7^+ (m/z 79). Such a reactivity has been investigated by ion-molecule reactions (IMR) of selected iron-containing cations with the nucleophile CH_2Cl_2 . To this end, ferrocene has been gently ionized by electrospray of a CH_3CN solution, and the nucleophile CH_2Cl_2 has been separately admitted into the reaction cell of an ion-trap mass spectrometer. Under these conditions, the ligated ions [$(\eta^5\text{-C}_5\text{H}_5\text{Fe-H}_2\text{O})^+$] and [$(\eta^5\text{-C}_5\text{H}_5\text{Fe-CH}_3\text{CN})^+$] are observed. All the ions containing the C_5H_5 moiety have been then isolated and reacted with the nucleophile CH_2Cl_2 . The experiments prove that all ions are unreactive, with the exception of ($\eta^5\text{-C}_5\text{H}_5\text{Fe}^+$) that gives C_6H_7^+ by reaction with CH_2Cl_2 . The possible reactions of formation are the following [Eqs. (1)–(4)]:



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Experiments and electronic structure calculations have been performed to assign one of the above processes to the reaction observed, to elucidate the mechanism and assess the relevance of the process by measuring the rate constant and efficiency.

As anticipated, under high-pressure conditions, the intermediate $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2\text{Cl}_2]^+$ is detected by ionization of a mixture of ferrocene and CH_2Cl_2 . The structural analysis of the intermediate has been performed by recording collision-activated dissociation (CAD) spectra of the mass- and energy-selected isotopomers $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2^{35}\text{Cl}_2]^+$ (m/z 205) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2^{35}\text{Cl}^{37}\text{Cl}]^+$ (m/z 207) (Figure 1 A).

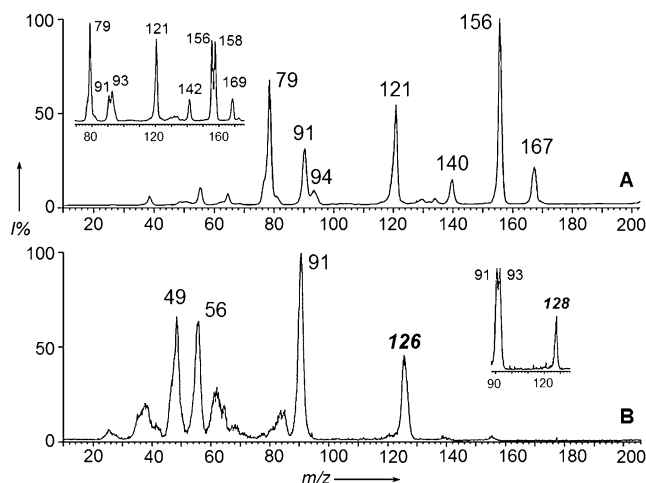


Figure 1. A) CAD spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2^{35}\text{Cl}_2]^+$ ions (m/z 205), with a partial spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2^{35}\text{Cl}^{37}\text{Cl}]^+$ ions (m/z 207) in the inset. B) N_r R spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2^{35}\text{Cl}_2]^+$ showing the peak at m/z 126, from the reionization of FeCl_2 , displaced to m/z 128 in the N_r R spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2^{35}\text{Cl}^{37}\text{Cl}]^+$ in the inset.

Most salient results are 1) the C_6H_7^+ ion (m/z 79) indicates that C–C bond formation does occur through the intermediate $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2\text{Cl}_2]^+$, 2) the FeCl^+ ion (m/z 91 or 91–93) indicates that iron transfer to chlorine does occur through the probed intermediate, 3) the minor peak formally corresponding to $\text{Fe-CH}_2\text{Cl}_2^+$ (m/z 140 or 142) confirms the occurrence of the iron transfer from $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ to CH_2Cl_2 .

Other peaks, albeit abundant, correspond to fragments containing the $\text{C}_5\text{H}_5\text{Fe}$ kernel, that is, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe-Cl}^+$ (m/z 156) and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ (m/z 121), or its dissociation products like in $(\text{C}_2\text{H}_3)\text{Fe-CH}_2\text{Cl}_2^+$ (m/z 167), whereas minor peaks (m/z 38, 49, 56, 65, 94) are relevant to consecutive dissociations of the $\text{C}_5\text{H}_5\text{Fe}$, C_5H_5 , and CH_2Cl_2 moieties.

To assess the nature of the neutral species formed from the carbon coupling reaction leading to C_6H_7^+ [Eqs. (1)–(4)], N_r R (neutral fragments reionization) experiments have been performed. The technique allows the analysis of the neutral species associated with the charged fragments detected in the CAD spectrum of the intermediate.^[10] To this end, all charged fragments are separated from all neutral species, and the latter are then reionized. The N_r R spectra of mass-selected $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2^{35}\text{Cl}_2]^+$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2^{35}\text{Cl}^{37}\text{Cl}]^+$ ions show intense peaks corresponding to the $\text{Fe}^{35}\text{Cl}_2^+$ and

$\text{Fe}^{35}\text{Cl}^{37}\text{Cl}^+$ ions at m/z 126 and 128, respectively (Figure 1 B). These ions, absent in the CAD spectra, can only be formed by reionization of FeCl_2 specifically produced from the dissociation of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2\text{Cl}_2]^+$ intermediate, as the neutral counterpart of the C_6H_7^+ ion. On this basis, one can assign reaction (1) to the process leading to the C_6H_7^+ ion.^[11]

The kinetic study of the reaction (1) shows that it is fast and efficient. Due to the background water, the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-H}_2\text{O}]^+$ adduct is formed together with C_6H_7^+ (Figure 2). This

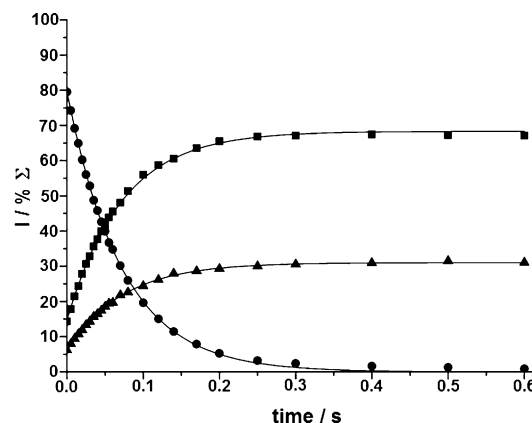


Figure 2. Kinetic plot and best-fit lines of the reaction of thermal $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ ions with CH_2Cl_2 . Pressure of $\text{CH}_2\text{Cl}_2 = 4.9 \times 10^{-7}$ Torr, $\bullet$ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ ($R^2 = 0.9996$), $\blacksquare$ C_6H_7^+ ($R^2 = 0.9990$), and $\blacktriangle$ $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-H}_2\text{O}]^+$ ($R^2 = 0.9991$).

may cause some precursor ion loss, and hence an accurate calibration procedure has been performed to subtract the background contribution (see the Supporting Information). Apart from this, the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ with CH_2Cl_2 yields only one product, namely C_6H_7^+ . Figure 2 shows the time profile relevant to the formation of C_6H_7^+ , that occurs with the rate constant $k_1 = 7.1 \times 10^{-10}$ ($\pm 30\%$) $\text{cm}^3 \text{s}^{-1} \text{molecule}^{-1}$ and the efficiency $k/k_{\text{coll}} = 63\%$ (k_{coll} = collision rate).

Electronic structure calculations identify a potential energy surface for the reaction (1), which is consistent with the experimental evidence. Figure 3 reports the structures of the minima and saddle points identified on the energy profile of Figure 4.

As shown, the first adduct **1** $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\cdots\text{Cl-CH}_2\text{Cl}]^+$ is formed with no barrier by interaction of a chlorine atom of CH_2Cl_2 with the iron atom of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$. The ion **1** shows a long Fe–Cl bond and the positive charge predominantly located on the CH_2Cl_2 moiety ($0.72 e^-$); it isomerizes to the ion **2** by overcoming a barrier of 25.8 ($\Delta G^\circ = 27.3$) kcal mol^{-1} (**TS**₁), which allows the activation of the first C–Cl bond and insertion of the iron atom. In ion **2**, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-(Cl)}\cdots\text{CH}_2\text{Cl}]^+$, the chlorine atom interacting with Fe is in fact no longer bound to the CH_2Cl group, whereas a new Fe–C bond is formed and the iron atom thus appears three-coordinate. Both ions **1** and **2** are very stable with respect to the reactants; their presence within the ionic populations probed in the experiments is proved by the abundant CAD fragment at m/z 156 (or 158), corresponding to the loss of the

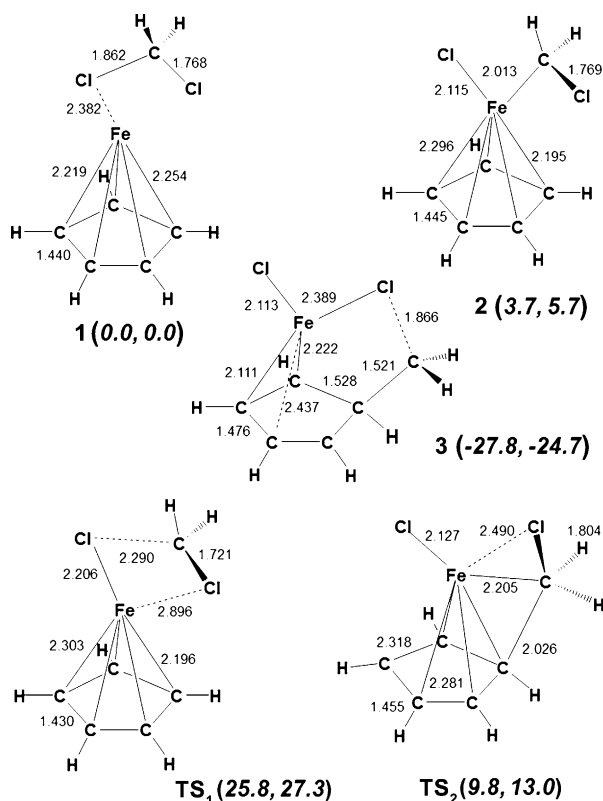


Figure 3. Geometries of the minima and saddle points located on the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2\text{Cl}_2]^+$ potential energy surface, optimized at the BPW91 level of theory. Bond lengths in angstroms and angles in degrees. Energy values relative to **1** (ΔH° , ΔG°) in kcal mol^{-1} , computed at the CCSD(T) level of theory.

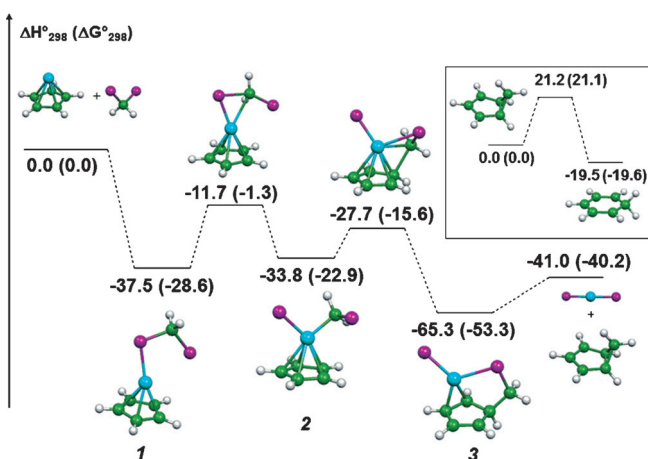


Figure 4. Schematic energy diagram of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe-CH}_2\text{Cl}_2]^+$ potential energy surface. ΔH° (ΔG°) values (kcal mol^{-1}) computed at CCSD(T) level of theory. The inset shows the likely rearrangement of protonated fulvene to the benzenium ion.

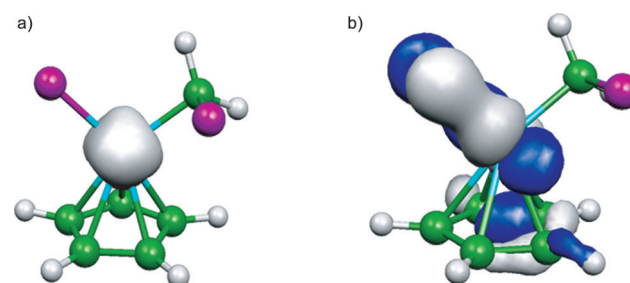
CH_2Cl radical. A further barrier of only 6.1 ($\Delta G^\circ = 7.3$) kcal mol^{-1} (**TS**₂) separates **2** from the adduct **3**, which eventually displays a weak residual interaction between the iron atom and the $\eta^5\text{-C}_5\text{H}_5$ group. In this step, the CH_2 group is carried from the iron to the carbon ring, the new C–C bond is formed

and the Fe– CH_2 interaction is replaced by an elongated Fe–Cl bond.

The ion **3** is prone to the dissociation into FeCl_2 and $(\eta^5\text{-C}_5\text{H}_5)\text{CH}_2^+$, the bicyclic form of protonated fulvene. Given the exothermicity of the whole process, $(\eta^5\text{-C}_5\text{H}_5)\text{CH}_2^+$ is likely to isomerize to the more stable benzenium ion C_6H_7^+ .^[12] The CAD spectrum of the ion at m/z 79 obtained from reaction (1) is in fact indistinguishable from that of authentic benzenium ions obtained by protonation of benzene (Figures 1S and 2S).^[13]

Clearly, the formation of the C–C bond and the rearrangement leading to FeCl_2 require a stepwise sequence that is expected to be entropically demanding. Nonetheless, it occurs below the reactants energy and the whole process to the benzenium ion C_6H_7^+ proves to be fast and exoergic ($\Delta G^\circ = -59.8$ kcal mol^{-1}). The computed exothermicity, $\Delta H^\circ = -60.5$ kcal mol^{-1} , is also in very good agreement with the experimentally derived value, $\Delta H^\circ = -61.8$ kcal mol^{-1} .^[14]

The evidence from experiment and theory points to the occurrence of an iron-mediated C–C bond formation. The nature of the bonding and the multiplicity of L– Fe^+ cationic complexes strictly depend on the ligand, for instance $(\text{C}_6\text{H}_6)\text{Fe}^+$ has three unpaired electrons, $(\text{C}_5\text{H}_5\text{N})\text{Fe}^+$ is σ bound and has five unpaired electrons, whereas $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ has four unpaired electrons in its ground state.^[2,15] $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ can be seen as a covalently bound $(\eta^5\text{-C}_5\text{H}_5)\text{-Fe(I)}^+$ ion, or as coming from the electron transfer from Fe(I)^+ to $(\eta^5\text{-C}_5\text{H}_5)$ and back donation from the π electrons of $(\eta^5\text{-C}_5\text{H}_5)^-$ to the 4s, 4p or 3d orbitals of Fe(II)^{++} .^[2] Accordingly, the Lewis acid properties of this iron-containing ion and the spd hybridization allow three-coordination of Fe without change of multiplicity (Scheme 1). While in ion **1** the



Scheme 1. a) Spin density plot and b) doubly occupied frontier molecular orbital (MO) of the intermediate **2**.

interaction with the nucleophile is predominantly electrostatic, in ion **2** the three-coordinate iron proves to be the carrier of the CH_2 group from the halomethane to the $(\eta^5\text{-C}_5\text{H}_5)$ group. The reaction does not occur with CH_4 or other halomethanes, showing that the chlorine atom plays its part too. Notably, cyclometalated transition-metal complexes, like $[\text{Pt}(\text{bipy-H})]^+$, give PtCl_2 loss when reacting with CH_2Cl_2 .^[16]

In conclusion, we have reported an unprecedented reaction between CH_2Cl_2 and the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ ion, that exclusively gives FeCl_2 and C_6H_7^+ . Both products have been detected by independent experiments, and the reaction has been found to be fast and effective. The iron atom plays a key

role in the carbon–carbon coupling, also facilitated by the chlorine atom that contributes effectively to the observed remarkable reorganization.

Experimental Section

The experiments were performed using a modified LTQ XL linear ion trap mass spectrometer (Thermo Fisher Scientific) fitted with an electrospray ionization (ESI) source, and a modified ZABSpec oa-TOF instrument (VG Micromass) of EBE-TOF configuration described elsewhere.^[17] The potential energy surface of the species of interest was investigated by locating the lowest stationary points at the BPW91/6-311 + G** level of theory,^[18] and the energy of the main stationary points was computed at the higher level of calculation CCSD(T)/6-311 + G**.^[19] Experimental details and computational methods are described in the Supporting Information.

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Keywords: carbon–carbon coupling · gas-phase chemistry · ion–molecule reactions · iron · reaction mechanisms

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- [1] a) T. J. Kealy, P. L. Pauson, *Nature* **1951**, *168*, 1039; b) S. A. Miller, J. A. Tebbboth, J. F. Tremaine, *J. Chem. Soc.* **1952**, 632.
- [2] M. Sodupe, C. W. Bauschlicher, *Chem. Phys. Lett.* **1993**, *207*, 19.
- [3] a) K. Heinze, H. Lang, *Organometallics* **2013**, *32*, 5623; b) R. Sun, L. Wang, H. Yu, Z. u. Abidin, Y. Chen, J. Huang, R. Tong, *Organometallics* **2014**, *33*, 4560; c) S. Takahashi, J.-i. Anzai, *Materials* **2013**, *6*, 5742; d) S. S. Braga, A. M. S. Silva, *Organometallics* **2013**, *32*, 5626; e) T. Daeneke, T. H. Kwon, A. B. Holmes, N. W. Duffy, U. Bach, L. Spiccia, *Nat. Chem.* **2011**, *3*, 211.
- [4] P. Köpf-Maier, H. Köpf, E. W. Neuse, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 456; *Angew. Chem.* **1984**, *96*, 446.
- [5] a) R. R. Corderman, J. L. Beauchamp, *Inorg. Chem.* **1978**, *17*, 68; b) V. I. Baranov, G. Javahery, D. K. Böhme, *Chem. Phys. Lett.* **1995**, *239*, 339; c) V. I. Baranov, D. K. Böhme, *Int. J. Mass Spectrom. Ion Proc.* **1995**, *149/150*, 543; d) R. Bakhtiar, D. B. Jacobson, *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 938; e) R. K. Milburn, V. I. Baranov, A. C. Hopkinson, D. K. Böhme, *J. Phys. Chem. A* **1998**, *102*, 9803; f) V. I. Baranov, D. K. Böhme, *Int. J. Mass Spectrom.* **2001**, *210/211*, 303; g) V. I. Baranov, D. K. Böhme, *Int. J. Mass Spectrom.* **2001**, *204*, 209; h) G. Innorta, S. Torroni, F. Basili, A. Di Fabio, *J. Organomet. Chem.* **2002**, *650*, 69.
- [6] E. Nakamura, N. Yoshikai, *J. Org. Chem.* **2010**, *75*, 6061.
- [7] a) K. Eller, H. Schwarz, *Chem. Rev.* **1991**, *91*, 1121; b) L. Capron, H. Mestdag, C. Rolando, *Coord. Chem. Rev.* **1998**, *178–180*, 269; c) D. K. Böhme, H. Schwarz, *Angew. Chem. Int. Ed.* **2005**, *44*, 2336; *Angew. Chem.* **2005**, *117*, 2388; d) M. Schlangen, H. Schwarz, *Catal. Lett.* **2012**, *142*, 1265.
- [8] R. W. Kugel, L. F. Pinelo, B. S. Ault, *J. Phys. Chem. A* **2015**, *119*, 2371.
- [9] a) L. E. Eary, D. Rai, *Environ. Sci. Technol.* **1988**, *22*, 972; b) H. Strasser, H. Brunner, F. Schinner, *J. Ind. Microbiol.* **1995**, *14*, 281; c) W. Fu-qiang, L. Jian-jun, Z. Yi-min, *Desalin. Water Treat.* **2013**, *51*, 5727; d) S. C. Jagupilla, M. Wazne, D. H. Moon, *Chemosphere* **2015**, *136*, 95.
- [10] a) C. A. Schalley, G. Hornung, D. Schröder, H. Schwarz, *Chem. Soc. Rev.* **1998**, *27*, 91; b) F. Cacace, G. de Petris, M. Rosi, A. Troiani, *Angew. Chem. Int. Ed.* **2001**, *40*, 1938; *Angew. Chem.* **2001**, *113*, 1992; c) G. de Petris, G. Angelini, O. Ursini, M. Rosi, A. Troiani, *Angew. Chem. Int. Ed.* **2012**, *51*, 1455; *Angew. Chem.* **2012**, *124*, 1484; d) G. de Petris, A. Troiani, M. Rosi, G. Angelini, O. Ursini, *ChemPlusChem* **2013**, *78*, 1065.
- [11] The FeCl⁺ ion at *m/z* 91 in the N₂R spectrum does not account for reaction (2), as it can largely be formed by dissociation of the reionized FeCl₂⁺ ion. More important, the reaction (2) is computed to be endothermic by 46.7 kcal mol^{−1} (Figure 4S). Likewise, the reactions (3) and (4) can be excluded because no signal at *m/z* 70 (Cl₂⁺) is detected, and the unresolved peaks in the low-mass range *m/z* 35–40 come from consecutive dissociations of higher-mass fragments. In addition, Δ*H*^o (3) = 65.6 kcal mol^{−1} and Δ*H*^o (4) = 107.7 kcal mol^{−1}, whereas Δ*H*^o (1) = −60.5 kcal mol^{−1}.
- [12] G. Bouchoux, M. Yanez, O. Mo, *Int. J. Mass Spectrom.* **1999**, *185/187*, 241. The bicyclic (η⁵-C₅H₅)CH₂⁺ isomer can rearrange to α-protonated fulvene, methylene-protonated fulvene, and the most stable benzenium ion, by overcoming barriers of 32.7, 35.1 and 21.2 kcal mol^{−1}, respectively. Taking into account the energy partitioning between the products of the reaction (1), only the last process is expected.
- [13] a) M. T. Bowers, D. D. Elleman, R. M. O'Malley, K. R. Jennings, *J. Phys. Chem.* **1970**, *74*, 2583; b) S. G. Lias, P. Ausloos, *J. Chem. Phys.* **1985**, *82*, 3613. Authentic benzenium ions C₆H₇⁺ are prepared by proton transfer from CH₅⁺ to benzene and deactivation by collisions with methane (Figure 1S–2S); strictly, the result indicates that if a fraction of protonated fulvene survives, this is comparable to the small fraction of non-benzenium ions possibly formed by protonation of benzene.
- [14] a) Y. Huang, B. S. Freiser, *J. Am. Chem. Soc.* **1990**, *112*, 5085; b) NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Gaithersburg MD, 20899, <http://webbook.nist.gov> (Eds. P. J. Linstrom, W. G. Mallard), **2005**; c) E. Goos, A. Burcat, B. Ruscic, Active Thermochemical Tables (ATcT) available at: <http://burcat.technion.ac.il/dir>, **2015**.
- [15] M. Diefenbach, C. Trage, H. Schwarz, *Helv. Chim. Acta* **2003**, *86*, 1008.
- [16] B. Butschke, H. Schwarz, *Int. J. Mass Spectrom.* **2011**, *306*, 108.
- [17] a) G. de Petris, A. Cartoni, A. Troiani, V. Barone, P. Cimino, G. Angelini, O. Ursini, *Chem. Eur. J.* **2010**, *16*, 6234; b) F. Bernardi, F. Cacace, G. de Petris, F. Pepi, I. Rossi, A. Troiani, *Chem. Eur. J.* **2000**, *6*, 537; c) G. de Petris, M. Rosi, A. Troiani, *J. Phys. Chem. A* **2007**, *111*, 6526.
- [18] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244.
- [19] a) R. J. Bartlett, *Annu. Rev. Phys. Chem.* **1981**, *32*, 359; b) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479; c) J. Olsen, P. Jorgensen, H. Koch, A. Balkova, R. J. Bartlett, *J. Chem. Phys.* **1996**, *104*, 8007.

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