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Vicinal dichlorine elimination at dichloroalkenes promoted by a well-defined iron(0) complex[†]

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Dechlorination reactions at sp² C–Cl bonds by a pentaphosphino zero-valent iron (ZVI) complex are proposed to follow an oxidative addition, β -Cl-elimination pathway en route to iron-chloride, iron-hydride and iron-acetylide products, the distribution being dependent on the nature of alkyne produced.

A current method employed for the remediation of groundwater contaminated with chlorinated solvents^{1,2} is the use of permeable reactive barriers containing bulk iron(0) as the reactive medium.^{3,4} While the potential utility of this method has been recognized, a detailed chemical understanding of the mechanism has lagged behind. This is despite numerous mechanistic studies with various forms of bulk iron. Notably, discrepancies between laboratories exist due to the sensitivity of the results to the iron source and experimental setup. Some speculate that substrates degrade through a hydrogenolysis pathway,^{3,5} while others favor an initial dichlorine elimination pathway which leads to alkyne intermediates en route to the observed products.⁶⁻¹¹

These poorly understood but environmentally interesting reactions inspired the present study focused on improving our *intrinsic* mechanistic understanding of reactions between sp² C-Cl bonds and an iron(0) metal center. While the use of an organometallic complex to study the ZVI system does not directly reflect the coordination environment or bulk properties of iron, it permits for a mechanistic understanding of proposed pathways in a controlled environment that are otherwise difficult to decipher in the heterogeneous system including the observation of intermediates and reactant stoichiometry determination.

A well-defined iron(0) complex we recently reported on, 'SiP₃(dmpm)Fe (1) ('SiP₃ = 'BuSi(CH₂PMe₂)₃, dmpm = Me₂PCH₂Me₂),¹² was tested as a dechlorinating agent of sp² C–Cl bonds here with E/Z-2,3-dichlorohexafluoro-2-butene (DCE-(CF₃)₂) and E/Z-1,2-dichloro-3,3,3-trifluoropropene (DCE-CF₃), which were chosen based on their ¹⁹F NMR properties. Immediate reaction was observed with both substrates upon mixing with 1 in toluene, as indicated by a color change and formation of a precipitate.

In the case of DCE-(CF₃)₂ (Fig. 1) a single iron-containing product was identified by ${}^{31}P{}^{1}H$ NMR and ESI-HRMS based on comparison to the independently synthesized complex, ['SiP₃(dmpm)FeCl][Cl] (2), {}^{12} in 93% yield. Hexafluoro-2-butyne was the only volatile product detected by head-space GC-MS analysis (83% yield).



Fig. 1 The reaction of ${}^{1}SiP_{3}(dmpm)Fe(1)$ with DCE-(CF₃)₂ to give [${}^{1}SiP_{3}(dmpm)FeCI]$ [CI] (2) and hexafluoro-2-butyne.

Reaction with DCE-CF₃ gave three products (Fig. 2), two of which were identified as previously synthesized complexes **2** and ['SiP₃(dmpm)FeH][Cl] (**3**).¹² The third product was believed to be ['SiP₃(dmpm)Fe(C=CCF₃)][Cl] (**4**) based on HRMS and ¹⁹F NMR spectroscopic data. This assignment was confirmed through independent preparation of **4** in 98% yield from 3,3,3trifluoropropyne and **2** in the presence of triethylamine (NEt₃), Fig. 3. The ratio of these three products was dependent on the relative concentrations of reactants as drop-wise addition of **1**



Fig. 2 The reaction of $SiP_3(dmpm)Fe(1)$ with DCE-CF₃ to give ['SiP₃(dmpm)FeC1][Cl] (2), ['SiP₃(dmpm)FeH][Cl] (3), and ['SiP₃(dmpm)-Fe(C=CCF₃)][Cl] (4).



Fig. 3 Method for the independent synthesis of $['SiP_3(dmpm)-Fe(C=CCF_3)][Cl]$ (4).

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(24.0 µmol, 48.0 mM) to DCE-CF₃ (24.0 µmol, 11.2 mM), giving iron-limited reaction conditions, yielded $50 \pm 3\%$ **2**, $29 \pm 1\%$ **3** and $15 \pm 1\%$ **4**, as determined by ³¹P NMR (integrated to an internal standard, tetrabutylammonium hexafluorophosphate, error is standard deviation, n = 3). Under conditions of excess iron achieved by slow addition of DCE-CF₃ to **1**, the amount of **2** decreased to $26 \pm 2\%$ while **3** and **4** increased to $36 \pm 3\%$ and $36 \pm 2\%$, respectively. All three products were unreactive with DCE-CF₃. The only volatile species detected other than unreacted DCE-CF₃ under either set of conditions was trace 3,3,3trifluoropropyne, indicating its role as a reactive intermediate. An insoluble and uncharacterized black solid was observed in both cases. Based on the demonstrated propensity of 3,3,3trifluoropropyne to polymerize¹³ we believe this product to be the corresponding polymer.

The reaction stoichiometry for DCE-(CF₃)₂ and DCE-CF₃ was determined by reacting each substrate with 1 at various ratios ranging from 0:1 to 2:1 (1:substrate) and analyzing the remaining pool of substrate. These results indicate reaction stoichiometries of 1:1 with DCE-(CF₃)₂ and 2:1 with DCE-CF₃ (Fig. 4).



Fig. 4 Fraction of substrate remaining following reaction *versus* the initial ratio of 1 to substrate, DCE-(CF₃)₂ \checkmark and DCE-CF₃ \bullet .

A mechanism for the dechlorination reaction of 1 with DCE- $(CF_3)_2$ and DCE- CF_3 must account for the following key observations: (1) The reaction of 1 with DCE- CF_3 generates three Fecontaining products: 2, 3 and 4; (2) the ratio of those products are dependent on the initial reactant ratio; (3) complete consumption of DCE- CF_3 requires two equivalents of 1 and (4) reaction of 1 and DCE- $(CF_3)_2$ has a 1:1 stoichiometry and gives one iron product, 2.

In the case of DCE-CF₃, two reasonable mechanistic possibilities are either deprotonation of the acidic DCE-CF₃ hydrogen (estimated $pK_a = 22^{14}$) or C–Cl oxidative addition. Direct deprotonation of DCE-CF₃ by **1**, a strong base capable of deprotonating acids whose pK_a is ≤ 25 ,¹² would give **3** and the elimination product, 1-chloro-3,3,3-propyne. The resulting chloro-propyne could then oxidatively add to a second equivalent of **1** to give **4**. Although this route is viable, it does not account for the observation of **2** or 3,3,3-trifluoropropyne.

We therefore suggest a C–Cl activation mechanism, depicted in Scheme 1 with DCE-CF₃, for both substrates. This mechanism is initiated by dissociation of a phosphine arm on either the dmpm or 'SiP₃ ligand. We favor a dissociative substitution based on



Scheme 1 Proposed mechanism for reaction of 1 with DCE-CF₃.

literature precedent for ligand exchange at $L_3Fe^{.15,16}$ Oxidative C–Cl addition leads to an unobserved intermediate that can undergo *syn*- (*Z* isomer) or *anti*- (*E* isomer) β -Cl-elimination, to give **2** and the corresponding elimination products, 3,3,3-trifluoropropyne or hexafluoro-2-butyne. The reaction continues in the case of DCE-CF₃ with deprotonation of 3,3,3-trifluoropropyne by a second equivalent of **1** to give **3** and the corresponding 3,3,3-trifluoropropylide anion. The propylide anion can then substitute for the inner-sphere chloride of **2** to give final products **3** and **4**.

These final steps of the mechanism follow the method for independent preparation of **4** (Fig. 3) from the reaction of **2** with terminal alkynes in the presence of base. We were able to test these proposed steps through independent reactions. Evidence for the abstraction of the acidic proton of 3,3,3-trifluoropropyne (pK_a of 18.5¹⁷) by **1** comes from observation of the characteristic NMR hydride resonance of **3**¹² upon reaction of **1** with 3,3,3-trifluoropropyne. No **4** was formed in this reaction; however, upon addition of **2** to the same reaction mixture, **4** was detected, supporting its formation through this pathway.

The overall stoichiometry of 2:1 for this proposed mechanism agrees with the data obtained from experiments (Fig. 4), with the second equivalent of 1 required because of its fast reaction with 3,3,3-trifluoropropyne. This mechanism agrees with the observation that reaction with DCE-(CF_3)₂ requires only one equivalent of 1 since the non-terminal alkyne produced, hexafluoro-2-butyne, is not subject to deprotonation.

This mechanism also accounts for the difference in the ratios of products in the reaction with DCE-CF₃ depending on the order of reactant addition. The product suite favors 2 when 1 is limited, while conditions where two equivalents of 1 are readily available support the formation of 4 with the concurrent depletion of 2. In addition, the predicted ratio of 1:1 for 3:4 is observed when 1 is readily available. Deviations from this ratio in the iron-limited case may be explained by the expected instability of the 3,3,3-trifluoropropylide anion that may react through other routes before reaction with 2, including polymerization. While the C–Cl activation mechanism better accounts for the observations, it should be noted that a combination of the deprotonation pathway and C–Cl activation pathway could be operating.

This system promotes elimination at both DCE-CF₃ and DCE- $(CF_3)_2$ yet gives a varied product suite, depending on whether an internal or terminal alkyne is produced. It is noteworthy that if similar processes are occuring at bulk iron(0) surfaces, the formation of iron-alkynyl products observed in this study suggests

a possible sink for the C₂-mass that is often unbalanced despite the ability to account for all chloride mass.⁷

Notes and references

- 1 M. J. Moran, J. S. Zogorski and P. J. Squillace, *Environ. Sci. Technol.*, 2007, **41**, 74–81.
- 2 B. L. Rowe, P. L. Toccalino, M. J. Moran, J. S. Zogorski and C. V. Price, *Environ. Health Perspect.*, 2007, 115, 1539–1546.
- 3 R. W. Gillham and S. F. O'Hannesin, Ground Water, 1994, 32, 958–967.
- 4 S. F. O'Hannesin and R. W. Gillham, Ground Water, 1998, 36, 164–170.
- 5 J. Gotpagar, E. Grulke, T. Tsang and D. Bhattacharyya, *Environ. Prog.*, 1997, **16**, 137–143.
- 6 W. A. Arnold and A. L. Roberts, *Environ. Sci. Technol.*, 2000, 34, 1794– 1805.
- 7 R. Orth, T. Dauda and D. E. McKenzie, Pract. Period. Hazard., Toxic, Radioact. Waste Manage., 1998, 2, 123–128.

- 8 A. L. Roberts, L. A. Totten, W. A. Arnold, D. R. Burris and T. J. Campbell, *Environ. Sci. Technol.*, 1996, **30**, 2654–2659.
- 9 T. Campbell, D. Burris, A. Roberts and J. Wells, *Environ. Toxicol. Chem.*, 1997, 16, 625–630.
- 10 C. Su and R. Puls, Environ. Sci. Technol., 1999, 33, 163-168.
- 11 J. Hara, H. Ito, K. Suto, C. Inoue and T. Chida, *Water Res.*, 2005, **39**, 1165–1173.
- 12 K. A. Thoreson, A. D. Follett and K. McNeill, *Inorg. Chem.*, 2010, **49**, 3942–3949.
- 13 A. L. Henne and M. Nager, J. Am. Chem. Soc., 1952, 74, 650-652.
- 14 ACE acidity & basicity calculator, http://aceorganic.pearsoncmg. com/epoch-plugin/public/pka.jap, (accessed October 2009).
- 15 P. M. Burkinshaw, D. T. Dixon and J. A. S. Howell, J. Chem. Soc., Dalton Trans., 1980, 999–1004.
- 16 S. P. Modi and J. D. Atwood, Inorg. Chem., 1983, 22, 26-28.
- 17 A. J. Kresge, P. Pruszynski, P. J. Stang and B. L. Williamson, J. Org. Chem., 1991, 56, 4808–4811.