Novel catalysts for dechlorination of polychlorinated biphenyls (PCBs) and other chlorinated aromatics†

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Diiron complexes of fluorene and fluorene* (1,2,3,4,5,6,7,8,9-nonamethylfluorene) have been found to be catalysts for the dechlorination of chlorinated aromatics, such as PCBs.

About a third of all persistent and toxic pollutants are chloro-organic compounds,[1] and collectively they represent a major global environmental hazard. The worst examples are the toxic polychlorinated biphenyls (PCBs). A total of 750,000 tonnes of PCBs (as 60–70 congener mixtures) were produced between 1929 and 1976 when they were banned by international treaty. Since then levels have been monitored in many locations around the globe and PCBs have been shown to be still ubiquitous and persistent. Their chemical inertness, which was once one of their industrial advantages due to their resistance to attack by acids and bases, now makes them such significant and persistent environmental pollutants. Methods now exist for their destruction in bulk quantities, usually by very high temperature incineration. However, significant quantities of PCBs still reside in contaminated effluent, soils or sediments and to date there is no cost effective chemical method for their destruction.

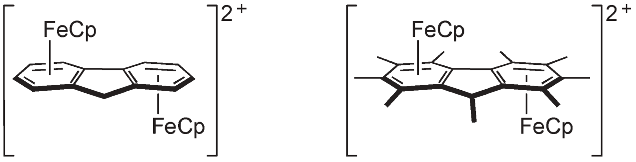
Although Kagan's reagent (SmI_2) is relatively efficient at dechlorinating PCBs giving only mono or dichlorinated biphenyl, it requires 1.7 equivalents of SmI_2 per equivalent of PCB and is only most effective when used with hexamethylphosphoramide (HMPA), which is highly toxic.[2] $PdCl_2(dppf)$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) uses very mild conditions, but very little dechlorination of PCBs is observed even after 4 days reflux.[3]

In 1995 Liu and Schwartz reported the first catalytic molecular-based dechlorination of chlorinated aromatic hydrocarbons. They reported that titanocene dichloride (Cp_2TiCl_2; Cp = η-C_5H_5) could be used as a catalyst for the dechlorination of PCBs producing biphenyl as the only organic product and at the relatively low temperature of 125 °C.[4] They also showed that this system would be catalytically active towards chlorinated benzenes.[5] Using a reductive process rather than an oxidative process, such as when using Fenton's reagent,[6] had the advantage that no harmful side products could be produced by incomplete reaction. Knowles and co-workers demonstrated that this approach could in principle be applied to contaminated soils, although there were major catalyst compatibility issues to be overcome.[7] There is a clear need to discover new catalytic systems so that they can be developed into efficient systems for treating low level PCB contaminated waste.

Given that the reaction proceeds *via* reduction of the metal we have been screening a range of electron rich metal complexes in order to try and discover new active catalytic systems. For example, 19- and 20-electron iron η-arene species have been shown previously to be powerful reducing agents but we found them to be inactive catalysts for PCB dechlorination, since the ligand is reduced by $NaBH_4$.[8] However, in the course of these investigations we investigated the activity of two novel electron-rich di-iron fluorene complexes, $[(FeCp)_2FluH]^{2+}[PF_6]_2$; (**1**)[9] and $[(FeCp)_2Flu^*H]^{2+}[PF_6]_2$; (**2**)[10] (Flu = η^6-$C_{13}H_{10}$; Flu* = η^6-$C_{13}Me_9H$), Fig. 1. Electrochemical studies on both **1** and **2** show they both exhibit two well resolved 1-electron reduction steps (ΔE = 300 and 350 mV for **1** and **2** respectively) which demonstrate substantial electronic communication between the two iron centres mediated through the fluorene ligands. Here we report the use of **1** and **2** as catalysts for the dechlorination of both PCBs and other chlorinated aromatics. As far as we are aware this is only the second example of a catalytic transition metal based dechlorination system. The only previous report using iron catalysts was the high temperature dechlorination using colloidal iron particles.[11]

The crystal structure of $\mathbf{2}[BF_4]_2$ is shown in Fig. 2.‡ Crystals were grown by slow diffusion of diethyl ether into a saturated solution of $\mathbf{2}[BF_4]_2$ in nitromethane. The crystal structure is similar to the Flu″H analogue with the principal difference being that the methyl substituent on the capping carbon (C_1) causes the ligand to twist at an angle of 15.5 degrees. When viewed as a space filling model it becomes apparent that this change in geometry is necessary to accommodate the methyl substituent.

Both **1** and **2** were tested as catalysts for the dechlorination of Aroclor 1242, an industrial mixture of PCBs.§ The conditions chosen were similar to those used by Schwartz and co-workers. 0.75 mmol of catalyst was combined with 19.2 mmol $NaBH_4$, 20 mmol pyridine and 1.24 g of Aroclor 1242 (equivalent to 15 mmol of Cl). 27.5 cm^3 of diglyme was used as solvent and the reaction mixture heated to 125 °C overnight. Since many Fe arene



$\mathbf{1}[PF_6]_2$ $\mathbf{2}[PF_6]_2$

Fig. 1 Structures of **1** and **2**.

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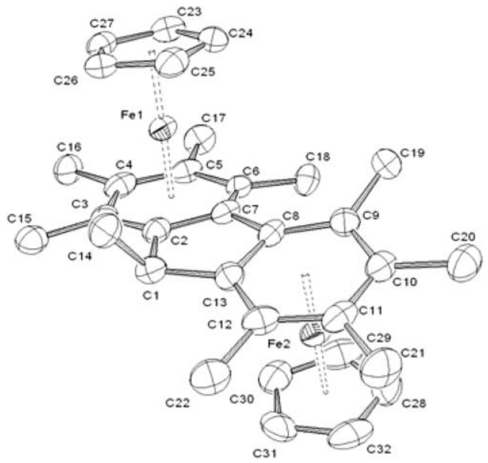

Fig. 2 Crystal structure of [(FeCp)$_2$Flu*H](BF$_4$)$_2$; **2**. Thermal ellipsoids drawn at 50% probability, H atoms and BF$_4^-$ counterions omitted for clarity.

complexes are slightly light sensitive, tests were run both in light and in darkness.

For both **1** and **2** after 24 hours no PCB could be detected in the reaction mixture by GC chromatography. Biphenyl was the only observed organic product. Initially the reaction mixture was orange, and over 24 hours it alternated between orange and dark brown, the final mixture being dark brown in colour. It is proposed that this indicates the alternation between the Fe(II) and Fe(I) states. A proposed reaction mechanism is shown in Fig. 3. NaBH$_4$ readily reduces one iron centre to Fe(I). This extra electron can then be transferred to the PCB molecule in an analogous fashion to the mechanism proposed by Schwartz for Ti(III). The resulting PCB radical anion may then lose Cl$^-$ before abstracting H$^\cdot$ from BH$_4^-$. The resulting BH$_3^{\cdot -}$ is then scavenged by complexation with the pyridine, as was demonstrated using ^{11}B NMR by Schwartz for the Cp$_2$TiCl$_2$ case.[4]

Quantitative analysis of PCB destruction indicated slight differences in the catalytic performance between **1** and **2**. The methylated analogue, **2**, was more active, giving an average yield of 49.0% biphenyl compared to 39.1% for the non-methylated analogue, **1**. The yield dropped slightly in both cases when the reactions were performed under normal laboratory lighting to 45.6% and 35.0% respectively. Schwartz has proposed that the Cp$_2$TiCl$_2$ catalysed dechlorination of PCBs proceeds *via* a radical process. We attribute the the non-quantitative conversion of all the PCB congeners to biphenyl as due to coupling of the dechlorinated hydrocarbons during the reaction. For comparison, tests using Cp$_2$TiCl$_2$ under the same conditions gave an average biphenyl yield of 55.7%. However, for both **1**, **2** and Cp$_2$TiCl$_2$ no PCBs could be detected in the reaction mixture by GC chromatography.

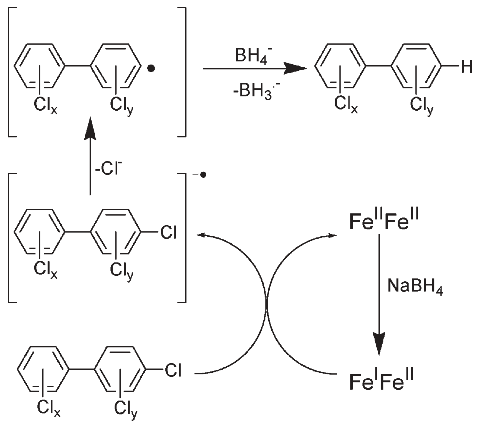

Fig. 3 Proposed catalytic cycle for dechlorination of PCBs.

The lifetime of **2** as a PCB dechlorination catalyst was investigated by doubling the quantities of pyridine, reducing agent and Aroclor 1242 present in the reaction mixture. The same quantity of catalyst was able to continue dechlorination for 48 hours. At this point the catalyst was no longer active and only monochlorinated biphenyls and biphenyl could be detected. Under the same reaction conditions Cp$_2$TiCl$_2$ remained active for much longer. Cp$_2$TiCl$_2$ was able to dechlorinate 6 times the amount of Aroclor 1242 used in a standard test (when NaBH$_4$ and pyridine were also increased proportionally) and was still functioning after 336 hours, at which point the test was stopped. Calculating a turnover number for these catalysts is difficult, since the number of cycles completed until the catalyst ceases working depends on the degree of chlorination of remaining molecules. However, it can be estimated that **2** is able to complete approximately 100 dechlorination cycles per molecule whereas after 336 hours Cp$_2$TiCl$_2$ had completed around 300 dechlorination cycles.

1,2,4,5-Tetrachlorobenzene is often used as simple mimic for the complex PCB congener mixtures. Chlorinated benzenes have similar reduction potentials to PCBs and so should be dechlorinated under similar conditions. We found that only **2** was effective at dechlorinating 1,2,4,5-tetrachlorobenzene. The reason for **1** being unreactive is as yet unclear. The dechlorination pathway could be followed qualitatively using GC chromatography. The dechlorination was shown to proceed stepwise and *via* 1,4-dichlorobenzene and 1,2-dichlorobenzene. 1,3-dichlorobenzene was only detected in trace amounts. This can be rationalised by considering the localisation of the negative charge during the reduction.[12] The colour changes for the reaction were the same as on PCBs above. The identical behaviour of **2** towards these two substrates would suggest potential applications in dechlorinating other chlorinated aromatics. Similarly **1** could also be used, however, it is less reducing than the methylated analogue, so one would not expect it to have such wide applicability. It should be possible, due to the stepwise nature of the dechlorination to partially dechlorinate other polychlorinated substrates by quenching the reaction after a predetermined time.

In conclusion, [(FeCp)$_2$FluH][PF$_6$]$_2$; **1** and [(FeCp)$_2$Flu*H][PF$_6$]$_2$; **2** are rare examples of molecular organotransition metal compounds that are able to catalytically reductively dechlorinate commercial PCB mixtures. **2** is also able to catalytically dechlorinate tetrachlorobenzene. The redox activity and the mixed valance nature of these complexes seem to be important contributing factors to their activity.

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Notes and references

‡ Crystal data for **2**[BF$_4$]$_2$: monoclinic, space group $P2_1/n$, $a = 9.5417(3)$ Å, $b = 26.6042(10)$ Å, $c = 12.3888(4)$ Å, $\beta =$ °, $V = 2994.81(18)$ Å^3, 23181 measured reflections, 6378 independent (R_{int} 0.063). 477 parameters, $R =$

0.0785, wR = 0.0713. The data were collected at 150 K on a Enraf-Nonius Kappa CCD diffractometer with graphite-monochromated MoK_α radiation. Intensity data were processed using the DENZO-SMN package.[13a] Structure was solved using SIR92.[13b] Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[13c]

§ In a typical dechlorination reaction a prepared mix of Aroclor 1242 (or 1,2,4,5-tetrachlorobenzene), pyridine and diglyme was added under N_2 and the reaction was heated to 125 °C and stirred. The chlorinated aromatic, base and solvent were dried/degassed as appropriate using standard techniques. 1 ml aliquots were taken at 4 h and 24 h for Aroclor 1242 and 1, 2, 4 and 24 h for 1,2,4,5-tetrachlorobenzene. These aliquots were quenched immediately in 1.5 ml water and then stored in test tubes at −80 °C until analysis. Samples were thawed before diluting with 100 ml of a 0.0025 mol dm^{-3} of 1,2,4-trichlorobenzene in $CHCl_3$. 1 μL of the organic layer was then injected into a Finnigan TraceGC ultra with FID using a 25 m non-polar SGE BPX-05 column. The column was held at 60 °C for 4 min before ramping at 10 °C min^{-1} up to 200 °C. This temperature was then held for a further 4 min. Peak integrations were analysed by Thermo Electron Corporations Chrom-Card data system Ver. 2.3. The results quoted are averages of multiple runs.

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