Catalytic dechlorination of polychlorinated biphenyls (PCBs) using amine functionalised titanocenes†

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Received 31st March 2009, Accepted 8th June 2009
First published as an Advance Article on the web 29th June 2009
DOI: 10.1039/b906311k

Novel ring-functionalised titanocene dichloride compounds have been prepared and tested for catalytic activity for the dechlorination of polychlorinated biphenyls (PCBs) under Schwartz conditions; they represent the first examples of metal complexes that are active under these conditions without the need for toxic additives, such as pyridine.

PCBs are a class of chlorinated organic compound which were manufactured in large quantities until their production was banned by international treaty, due to concerns over their threat to human health. PCBs are extremely persistant and remain as a contaminant in soil and waterways around the globe. A wide variety of destruction methods have been proposed but, to the best of our knowledge, no commercial solution has been developed to de-contaminate land which contains PCBs.

In 1995, Schwartz and co-workers reported the first catalytic molecular based dechlorination of chlorinated hydrocarbons. Their method used titanocene dichloride (Cp_2TiCl_2; Cp = η-C_5H_5) as a pre-catalyst together with $NaBH_4$ and pyridine in glyme solvents at 125 °C under a N_2 atmosphere.[1, 2] The method has many advantages over other methods. For example, it is reductive and so precludes the formation of oxidised dioxin-like side-products which are even more toxic than PCBs. Wright *et al.* have shown that the methodology is also applicable to use on contaminated soil.[3] Work within this research group has shown that iron-arene systems also behave in a similar way to the Schwartz system with a catalyst that can be synthesised on the bench, not requiring exclusion of air and moisture.[4]

The major disadvantage of the Schwartz reaction is its use of the toxic base, pyridine.[5] Therefore we have targeted and tested a series of amine functionalised titanocene dichlorides which mimicks the chemical environment and geometry of the active site proposed by Schwartz *et al.* Two of these were shown to be active when a non-toxic base was used as an additive and ^{11}B NMR studies were carried out on samples of the reaction mixture to probe the species present.

A mechanism of the PCB dechlorination using titanocne pre-catalysts was proposed by Schwartz *et al.* and a simplified version is shown in Fig. 1. The essential pyridine base was proposed by Schwartz to have two roles: complexing with the titanocene (III) hydride to form (**2**); and complexing with the BH_3 to form a pyridine·BH_3 adduct. The use of other bases in the Schwartz reaction have been reported in the literature, although they do not perform as well.[3]

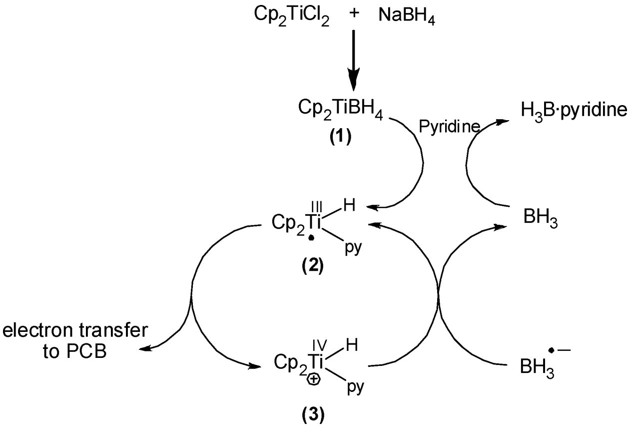

Fig. 1 Simplified form of the Schwartz reaction mechanism proposed by Schwartz *et al.*[2]

Modification of the catalyst

Novel titanium-based catalysts were devised which contain a cyclopentadienlyl ring with a teathered amine base which is capable of intramolecularly coordinating to the titanium centre, as shown in compound (**2**) in Fig. 1. These compounds were all synthesised using known literature methods and are shown in Fig. 2.[6–9] These compounds were targeted since they represented varying degrees of association between the nitrogen and titanium atoms: Compound (**4**) contains a permanent bond between titanium and nitrogen; Compound (**5**) has no permanent bond, although it is proposed that an association between the two atoms is probable and that the coordination site of the titanium centre can be considered partially blocked, as is the case in

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† Electronic supplementary information (ESI) available: **Sup 1**: ^{11}B NMR data for diglyme solutions of various catalysts with one equivalent of BH_3·THF and Schwartz reactions of Cp_2TiCl_2 with different bases. Samples run at room temperature and data corrected relative to a PPN[BH_4] in $CHCl_3$ insert; **Sup 2**: ^{11}B NMR data obtained from aliquots of various Schwartz reactions. Samples run in diglyme at room temperature and data corrected relative to a PPN[BH_4] in $CHCl_3$ insert. **Sup 3**: Crystal data and refinement details for (**4**). **Sup 4**: Bond lengths (Å) for (**4**). **Sup 5**: Bond angles (°) for (**4**). CCDC reference number 725827. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906311k

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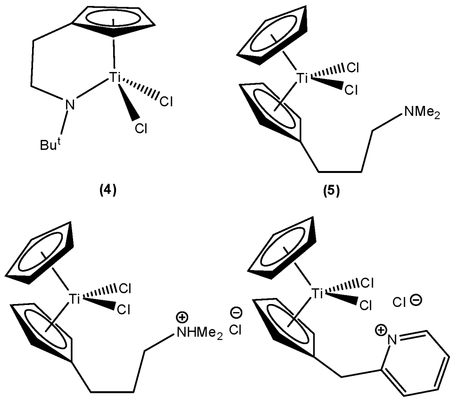
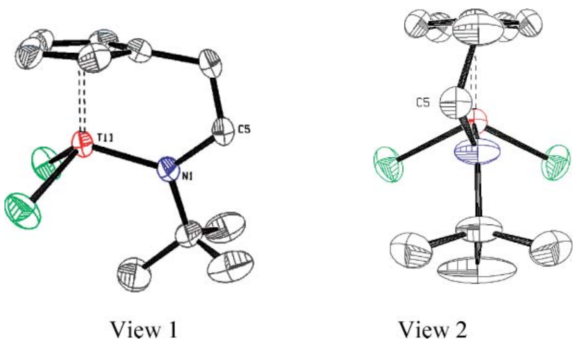


Fig. 2 Target compounds. These have a range of different coordination modes including permanently coordinated (**4**), associated (**5**), not associated/coordinated (**6**) and (**7**).

similar compounds;[10,11] Compounds (**6**) and (**7**) have a greater air/moisture stability since they are hydrochloride salts. This extra stability can be attributed to the quaternary nitrogen centre providing protection against hydrolysis.[12]

During the course of this work bright red crystals of compound (**4**) suitable for X-ray structural determination§ were obtained by slow cooling in toluene to −80°C. Two views of the molecular structure are shown in Fig. 3.



View 1 View 2

Fig. 3 Crystal structure of (**4**). Thermal ellipsoids are drawn at 50% and H atoms have been omitted for clarity. A full list of bond lengths and bond angles is given in the ESI.†

Compound (**4**) has monomeric titanium centres which have distorted tetrahedral geometry. The cyclopentadienyl ring-functionalised ligand is η^5:η^1 bonded with the C5 rings disordered over two positions about the mirror plane shown in Fig. 3. Comparison with the N^{i}Pr analogue of this compound shows that there is negligible difference in the Ti-Cl, Ti-N and Ti-Cp distances in the two compounds.[9] The increase in steric bulk between N^{i}Pr and N^{t}Bu does affect other aspects of the structure: There is a decrease in the Ti-N-C5 angle from 129.2° to 122.4°; The Cl-Ti-Cl angle increases from 103.4° to 105.3°; and the N-Ti-Cp angle increases from 104.4° to 106.5°. This can be rationalised by visualising the extra methyl group on the ^{t}Bu analogue causing further crowding of the titanium centre and so pushing the chlorine atoms further apart, thus increasing the angle.

Catalytic testing

All the compounds synthesised 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 of either pyridine or dimethyloctylamine (DMO) 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. Separate tests using DMO with Cp_2TiCl_2 have shown that this base is inactive under these reaction conditions over 24 hours.

The results of catalytic testing are given in Table 1. Almost all of the catalysts tested initially turned a vivid purple colour, characteristic of formation of the borohydride (**1**), the only exception being $Cp^{NBu}TiCl_2$ (**4**) which had a red and green initial stage with pyridine and DMO respectively. All mixtures changed colour over time to dark brown and the reaction with $Cp^{NBu}TiCl_2$ was accompanied by a green shade with both bases. A light coloured precipitate was observed within the first one or two hours in all tests. Successful tests with pyridine were accompanied by substantial amounts of dark precipitate, but this was not the case in all the tests with DMO.

All the base appended catalysts tested were active in the Schwartz reaction when pyridine was used. However, (**4**) and (**5**) showed only trace activity when DMO was used as the co-base. (**4**) is electron deficient compared to the other compounds tested and this results in reduced biphenyl detected compared to (**5**) when tested with pyridine after 4 hours which demonstrates reduced initial activity of the catalyst. Schwartz proposed that pyridine was such a successful additive due to it facilitating outer sphere electon transfer to the PCB. It is tentatively proposed that the lack of activity when using (**4**) and (**5**) is due to the fact that in these compounds the aminoalkyl chain is not facilitating electron transfer to the PCB molecule. Instead it would seem that the activity achieved with these compounds is due to coordination of the co-base. In the case of pyridine, the activity is lower than that observed with Cp_2TiCl_2 due to the sterically more demanding nature of the aminoalkyl appended catalysts. Likewise DMO gives very little activity, since it is inactive even with Cp_2TiCl_2 so using more bulky catalysts reduces this activity even further.

The difference in activity between (**5**) and (**6**) at first seems strange since they both contain the same aminoalkyl chain. However, it has previously been observed that protonating these species can drastically change their chemical reactivity and it is proposed that this is also the case in the Schwartz reaction.[13,14]

As with the hydrochloride salt of the amine appended catalyst (**6**), compound (**7**) is able to catalytically dechlorinate PCBs either when pyridine or DMO is used as the co-base (yields of biphenyl of 34% and 27% after 24 hours respectively). These

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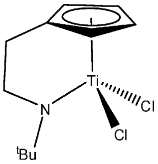
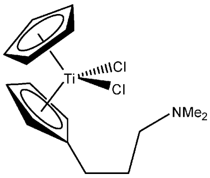
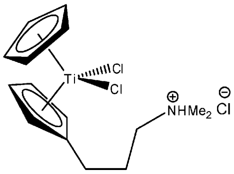
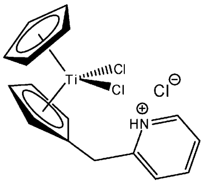
§ Crystal data for (**4**): monoclinic, space group $P2_1/m$, $a = 7.3084(15)$ Å, $b = 10.576(2)$ Å, $c = 8.5363(17)$ Å, $\beta = 102.70(3)°$, $V = 643.7(2)$ Å^3, 2695 measured reflections, 1534 independent ($R_{int} = 0.018$). 89 parameters, $R_1 = 0.0393$, $wR_2 = 0.0975$. The data were collected at 150 K on a Enraf-Nonius Kappa CCD diffractometer with graphite-monochromated MoK$_\alpha$ radiation. Intensity data were processed using the DENZO-SMN package.[17] The structure was solved using SIR92.[18] Subsequent full-matrix least-squares refinement was carried out using the SHELXL-97 program suite.[19]

Table 1 Results of catalytic testing of amine appended catalysts (**4**), (**5**) and (**6**) and pyridine appended catalyst (**7**). * = 40% # = 49% yield biphenyl after 48 hours respectively

	Biphenyl yield (%) at given time (hours)/base used			
	Pyridine		Dimethyloctylamine	
Catalyst	4	24	4	24
Cp_2TiCl_2	20	60	0	Trace
 (**4**)	0	33	0	Trace
 (**5**)	20	29	0	Trace
 (**6**)	36	43	0	18*
 (**7**)	15	34	0	27#

two compounds represent the only two known catalysts which are able to function in the Schwartz reaction without added pyridine under these reaction conditions. It is interesting to note that the pyridine appended catalyst has a lower conversion to biphenyl than Cp_2TiCl_2, despite having a pyridyl unit readily placed to coordinate (yields of biphenyl of 34% and 56% after 24 hours respectively). This may be either due to the extreme moisture sensitivity of the pyridine appended reaction mixture or due to the fact that the pyridyl arm blocks coordination of free pyridine to the titanium centre and so hinders formation of the active catalyst containing free pyridine. It is probable that the observed difference in activity is due to a combination of these reasons. The pendant pyridine may block coordination of free pyridine to the titanium centre and this competition would explain the lower yield of biphenyl after 4 and 24 hours. The extreme moisture sensitivity of the active catalyst would explain the fact that the same yield of biphenyl as that achieved when using Cp_2TiCl_2 is not reached even on increased reaction time.

When compound (**7**) is used as the catalyst, there is a much smaller contrast between the catalyst's performance when using pyridine and when using DMO as the co-base than there is when compound (**6**) is used as the catalyst. This suggests that there is in fact very little coordination of the co-base, and the observed activity is mostly due to the pendant pyridine coordinating to the titanium centre to form the active species. If this is true then it would imply that the coordinated pyridine pendant is facilitating electron transfer to the PCB molecule as was intended.

^{11}B NMR analysis

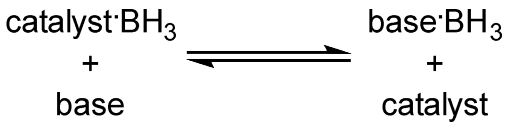
To probe the species present in these Schwartz reactions, ^{11}B NMR spectra were taken of aliquots from the reaction mixtures. ^{11}B NMR data were collected from the Schwartz reactions of all catalysts which yielded positive results and are given in **Sup 2**.† **Sup 1**† gives some standard results; Data for the BH_3 adducts of catalysts (**4**), (**5**), (**6**) and (**7**) were obtained by adding a stoichiometric amount of $BH_3 \cdot THF$ to the catalyst in diglyme. Pyridine·BH_3 and DMO·BH_3 were obtained by analysis of the reaction mixture of Cp_2TiCl_2 when using pyridine and DMO respectively. Aliquots were taken from the reaction mixture at the start of the reaction (before heating), at 1 hour and at 24 hours.

The data in **Sup 1**† show that the BH_3 adducts of each of the catalysts all have very similar chemical shifts. It is likely that (**5**) and (**6**) have different chemical shifts, despite their similar structure, because of the slightly different amounts of highly coordinating THF added to the mixtures. $BH_3\cdot THF$ will be in equilibrium with catalyst·BH_3 and the values can be considered a weighted average of the two. Since ^{11}B NMR can be very broad, it is difficult to ascertain the significance of any difference in coupling constants between (**4**), (**5**), (**6**) and (**7**). The pyridine·BH_3 and DMO·BH_3 adducts have very similar chemical shifts to each other. Their coupling constants are also similar to each other, but are significantly lower than the catalyst·BH_3 adducts.

Comparison of the data from the Schwartz reaction in Table 1 with the NMRs in **Sup 2**† enables some conclusions to be drawn about the species present in each of the Schwartz reactions, as well as some speculation as to the other species that might be present.

The ^{11}B chemical shift of the aliquot from the initial stages of the Schwartz reaction using (**4**) with pyridine (–5.85 ppm) suggests that the species formed is not the BH_3 adduct of pyridine but rather (**4**)·BH_3 (–6.43 ppm). The difference between the values of the aliquot and the control experiment suggest that there is exchange solution between (**4**)·BH_3 and pyridine·BH_3, with the position of equilibrium equilibrium lying predominantly in favour of (**4**)·BH_3. As such, the chemical shift can be considered a weighted average of the two species, suggesting approximately 88% of the BH_3 adducts present are (**4**)·BH_3. The disappearance of all boron signals after 24 hours suggests that any boron present has precipitated out of solution. It is proposed that complexed boron chains have formed which are not soluble and are not observed in the solution ^{11}B NMR spectrum. Such behaviour has been observed in similar compounds.[16]

The ^{11}B chemical shift from the initial aliquot of the Schwartz reaction of (**5**) with pyridine (–5.82 ppm) suggests that the adduct (**5**)·BH_3 (–6.27 ppm) is the main species present in the initial stages of the reaction. As with the data from (**4**), the slight difference between the values from the aliquot and the control experiment suggests an equilibrium between (**5**)·BH_3 and pyridine·BH_3, with the position of equilibrium suggesting that (**5**)·BH_3 is making up just under 90% of the adducts present. This generic equilibrium is shown in Fig. 4.



$$\begin{matrix}\text{catalyst}\cdot BH_3 \\ + \\ \text{base}\end{matrix} \rightleftharpoons \begin{matrix}\text{base}\cdot BH_3 \\ + \\ \text{catalyst}\end{matrix}$$

Fig. 4 Proposed exchange between BH_3 adducts in the Schwartz reaction. The resulting chemical shift is weighted and so the position of equilibrium approximately correlates with the proportion of each species present in solution.

Schwartz reactions using (**6**) with pyridine and DMO give ^{11}B chemical shifts which suggest that the equilibrium exchange between (**6**)·BH_3 and base·BH_3 contains different proportions of species in the two reactions. In the initial stages of the reaction with pyridine as the added base, the ^{11}B chemical shift of the aliquot (–5.89 ppm) suggests that (**6**)·BH_3 (–7.17 ppm) is the major component of the system, making up approximately 76% of the adducts present. In the 1 hour aliquot the ^{11}B chemical shift has changed to –3.34 ppm suggesting that pyridine·BH_3 makes a more significant proportion of the mixture (–1.94 ppm), with (**6**)·BH_3 making up only 27% of the adducts present. The aliquot after 24 hours gave resonances at –9.25 ppm and 20.93 ppm suggesting that, as in the Schwartz reaction with (**4**) and (**5**), catalyst oligomers have formed BH_3 adducts. The ^{11}B chemical shifts from aliquots of the Schwartz reaction of (**6**) with DMO (–3.15 ppm) suggest that from the very start of the reaction the equilibrium of (**6**)·BH_3 and DMO·BH_3 has a higher proportion of DMO·BH_3, with (**6**)·BH_3 making up approximately 27% of the adducts present. Furthermore the observed chemical shift does not change significantly over 24 hours and this would seem to suggest that the proportion of the two adducts remains essentially unchanged. DMO is more basic than pyridine and it is tentatively proposed that the differing proportions of base·BH_3 formation suggested by the ^{11}B NMR data are due to the DMO competing more effectively with the catalyst appended nitrogen centre than the pyridine does. It is proposed that by forming the DMO·BH_3 species more readily the appended amine spends more time able to coordinate to the titanium centre and this may facilitate electron transfer to the PCB.

The data for the Schwartz reactions using compound (**7**) with pyridine and DMO suggest that, as was also the case with (**6**), in the initial stages of the reaction the catalyst is behaving differently with each of the two co-bases. The ^{11}B chemical shifts imply that there is exchange between (**7**)·BH_3 and base·BH_3 in the solution. The initial aliquot from the Schwartz reaction of (**7**) with DMO gives a resonance whose chemical shift (–3.27 ppm) implies that a significant proportion of DMO·BH_3 (–1.66 ppm) is present in addition to (**7**)·BH_3 (–5.97 ppm). Approximately 37% of the adducts present are (**7**)·BH_3. The ^{11}B chemical shift remains approximately constant over the course of 24 hours, suggesting that the proportion of species present is the same. The aliquots from the Schwartz reaction of (**7**) with pyridine, both initially and after 1 hour, suggest that the major species present (–5.66 ppm) is (**7**)·BH_3 (–5.97 ppm), suggesting that approximately 92% of the species present are due to (**7**)·BH_3. This suggests very little exchange with pyridine·BH_3 and so the appended pyridine spends very little time able to coordinate to the titanium centre. This would suggest that the catalytic activity shown by (**7**) with pyridine as base is due to coordination of the added base rather than intramolecular coordination of the appended pyridine. The fact that only broad resonances are observed in this reaction after 24 hours suggests the possible formation of oligomers as was also proposed with the other catalysts. In contrast, the ^{11}B chemical shift for (**7**) with DMO suggests a larger proportion of DMO·BH_3 and so it can be concluded that the appended pyridine spends a larger proportion of time free to coordinate to the titanium centre. This would suggest that the observed catalytic activity is due to intramolecular coordination of pyridine and so the proposed electron transfer can be facilitated this way, as was intended. For the aminoalkyl appended species, it is proposed that the difference in activity with pyridine and DMO as the added base is due to the fact that the more basic DMO competes more effectively with the appended base to coordinate to BH_3 than pyridine does.

This section has confirmed for the first time that the hydrochloride salts of both amine and pyridine appended titanocene dichloride catalysts are able to function with a non-aromatic amine added as co-base; without added pyridine. The pK_a values of (**6**) and (**7**) would almost certainly have (**7**) as the most acidic, so one would expect this to be deprotonated more rapidly in the Schwartz reaction than (**6**). However, this does not seem to affect the catalytic performance of this species in dechlorination of PCBs.

The fact that such high yields of biphenyl are achieved when using DMO as co-base, compared to when using the standard Cp_2TiCl_2 catalyst, implies that the proposed electron transfer to the PCB molecule is mediated by the pendant base, rather than by coordination of the co-base. This supposition is corroborated by the ^{11}B NMR data from aliquots of the relevant reactions. The ^{11}B chemical shifts suggest varying degrees of exchange between the BH_3 adducts of the co-base and the catalyst. When a greater proportion of base·BH_3 is observed this suggests the appended base is more free to coordinate to the titanium centre and this is the case with both the hydrochloride salt catalysts. It is proposed that by spending more time coordinated to the titanium centre, these species are more likely to facilitate the proposed electron transfer to the PCB by this intramolecular coordination. Of compounds (**6**) and (**7**) it seems that the latter, with the appended pyridine, represents the catalyst of choice and DMO the co-base of choice. Despite the slightly reduced biphenyl yields compared to those obtained using pyridine as the co-base, all evidence suggests that the catalyst is functioning with minimal coordination of the DMO and the yield of biphenyl achieved is in fact almost within experimental error of the reaction using added pyridine.

Experimental

In a typical dechlorination reaction a prepared mix of Aroclor 1242, pyridine or dimethyloctylamine and diglyme was added under N_2 and the reaction was heated to 125°C and stirred. The Aroclor 1242, base and solvent were dried/degassed as appropriate using standard techniques. 1 ml aliquots for GC analysis were taken at 4 hours and 24 hours. 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 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 minutes before ramping at 10 °C/minute up to 200 °C. This temperature was then held for a further 4 minutes. Peak integrations were analysed by Thermo Electron Corporations Chrom-Card data system Ver. 2.3. The results quoted are averages of multiple runs. Aliquots for ^{11}B NMR analysis were injected straight into an NMR tube modified with a Young's tap and under a flush of nitrogen. The tube contained an insert of $[PPN][BH_4]$ in $CHCl_3$. NMR spectra were then run as soon as possible. ^{11}B chemical shifts were referenced relative to $BF_3 \cdot OEt_2$ ($\delta = 0$) and then corrected relative to the shift of a $[PPN][BH_4]$ in $CHCl_3$ insert ($\delta = -36.0$).

Conclusions

Despite an aromatic base being required when using Cp_2TiCl_2 as the catalyst, it was found that titanocenes appended with a non-aromatic amine, (**6**), could give significant yields of biphenyl even when using the non-aromatic amine DMO as the co-base. It can be concluded from this observation that the readiness of the added base to coordinate and how readily the appended species dissociates are the important factors. By using an amine appended catalyst, the close proximity of the appended amine to the titanium centre promotes coordination and so formation of the proposed active species.

The catalytic performance was improved on changing the appended non-aromatic amine for pyridine, (**7**). Analysis of ^{11}B NMR data from aliquots of all the Schwartz reactions indicated that the pendant amine was more readily displaced from the titanium centre when it was non-aromatic, particularly when pyridine was used as the co-base. When DMO was used as the co-base, the appended pyridine seemed to stay coordinated to the titanium even in the later stages of the reaction and so it can be proposed that this system is behaving as was originally desired; the appended pyridine is coordinating to the titanium to form the proposed active species and to facilitate electron transfer to the PCB molecule with the DMO trapping out BH_3 and not coordinating to the titanium centre to any significant degree.

Although appending pyridine to the catalyst does not remove it from the system in itself, it represents a significant step towards being able to safely remove any traces of pyridine from the system following reation. Unpublished results from this group have shown that the reaction can be effected by using a catalyst immobilised on a solid support. Once compound (**7**) has been successfully immobilised in the same way, it will offer a method for removing all traces of pyridine from the vessel following reaction.

Acknowledgements

The authors thank the EPSRC for a studentship (AEDF).

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