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C–Cl/Si–H Exchange catalysed by P,N-chelated Pt(II) complexes†

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Alkyl chlorides R–Cl are dehalogenated by $HSiMe_2Ph$ in the presence of catalytic amounts of the complex [(κ²-*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$]PtMeCl to give R–H and $ClSiMe_2Ph$.

Many methods for the hydrodechlorination of organic compounds employ heterogeneous catalysts; frequently however, they are non-selective, and severe reaction conditions are often necessary. Only a few homogeneous catalysts are known, for example the hydrodechlorination of aryl chlorides by methanol or sodium formate in the presence of Pd(0) complexes,[1] or by hydrogen in the presence of Rh(III) complexes.[2] In these reactions, hydrogen, methanol or formate is the hydrogen source, and chlorides are the chlorine sink. Alkyl halides can be reduced by organotin hydrides; chlorides usually require heating or catalysis by a free radical source.[3] The hydridostannane has a twofold role as the hydrogen source and to bind the halide. Since these reactions proceed by a free radical mechanism, organosilicon hydrides cannot be used in the same way, although these compounds are more readily available than organotin hydrides.

In this communication we report preliminary results on a Pt complex catalysed dechlorination reaction with hydridosilanes. We have recently found that the use of hemilabile P,N chelating ligands such as $Ph_2PCH_2CH_2NMe_2$ greatly enhances the reactivity of Pt(II) complexes towards bonds, which are difficult to activate.[4] For example, the reaction of (P⋂N)$PtMe_2$ (P⋂N = (κ²-*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$) with $ClSiMe_2Ph$ quantitatively gave the disilane $Ph_2Me_4Si_2$ (together with chlorinated Pt complexes), while reaction with CCl_4, $CHCl_3$, CH_2Cl_2 or CH_3Cl resulted in the oxidative addition of the C–Cl bond followed by several elimination and rearrangement reactions.[5]

In the course of these studies we found that $HSiMe_2Ph$ reacts with chlorinated hydrocarbons in the presence of catalytic amounts of (P⋂N)PtMeCl (**1**). When **1** was reacted with a 10-fold excess of $HSiMe_2Ph$ (**2**) in $CDCl_3$ solution at 60 °C in a Teflon vessel, the appearance of $ClSiMe_2Ph$ (**3**) and the concomitant consumption of $HSiMe_2Ph$ was observed by $^{29}Si\{^1H\}$ NMR spectroscopy.[6] $CHDCl_2$ and CH_2DCl were clearly identified as the other products by the typical triplets in the $^{13}C\{^1H\}$ NMR spectrum, which are due to $^1J_{CD}$ coupling, and also by $^2H\{^1H\}$ NMR spectroscopy. The conversion of the hydridosilane to the chlorosilane was about 37% after 6 h and 100% after 15 h. When further $HSiMe_2Ph$ was periodically added, the $CDCl_3$ was eventually completely consumed.

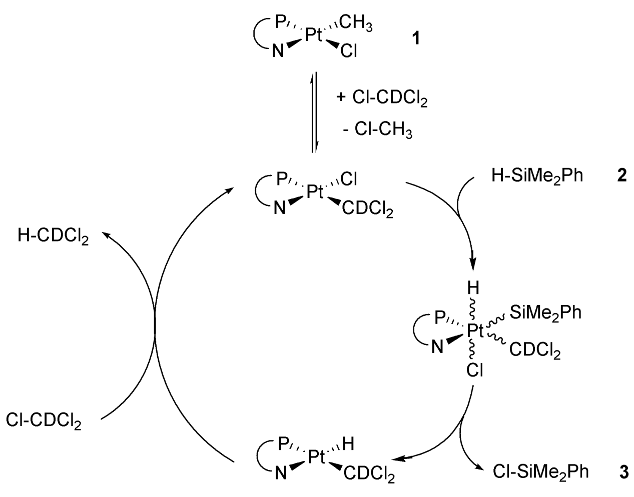
The same results were obtained when $CHCl_3$ and $HSiMe_2Ph$ were reacted in a 1 : 1 ratio in benzene at 60 °C instead of using $CDCl_3$ or $CHCl_3$ as the solvent (eqn. (1)). When **1**, $CHCl_3$ and $HSiMe_2Ph$ (**2**) were employed in a 1/10/10 molar ratio (0.4 mmol of **2** and $CHCl_3$ in 0.7 ml benzene; Teflon vessel), conversion was complete after 12 h. With 1 mol% of **1** conversion was about 62% after 40 h at 60 °C.

$$CHCl_3 + HSiMe_2Ph \xrightarrow{\mathbf{1}\,(cat.)} ClSiMe_2Ph + CH_2Cl_2/CH_3Cl \quad (1)$$

Complex **1** is nearly quantitatively retained during the reaction. Only after long reaction times were traces of a new complex with a $^1J_{PPt}$ coupling constant similar to that of **1** detected. The $^1J_{PPt}$ coupling of the new complex was typical for Pt(II) complexes with a *trans* Cl–Pt–P arrangement. As the same complex was observed in the reaction with all other alkyl chlorides (see below), the new complex could be (P⋂N)Pt($SiMe_2Ph$)Cl (**4**). We did not succeed to in separating **4** from the reaction mixture due to the small amounts formed.

The best results were observed when the reactions were carried out in Teflon NMR tubes. When the reactions were performed in glass NMR tubes, traces of $(PhMe_2Si)_2O$ were formed as a by-product, and the reaction rate decreased. However resolution of the NMR spectra is lower when a Teflon liner is used. Therefore, in some reactions described in this article, it was not possible to quantify the degree of conversion exactly by integrating the ^1H NMR signals.

A possible reaction sequence is shown in Scheme 1 with $CDCl_3$ as the chlorinated hydrocarbon. Complex **1** does not react with either $HSiMe_2Ph$ or $CDCl_3$ alone under the same conditions to form a new detectable complex. On the other hand, the formation of the catalytic species must be the result of an initial reaction of **1** with either $HSiMe_2Ph$ or $CDCl_3$. The initial step being the reaction of the silane with **1** to give **4** is not possible, as methane would have to be irreversibly eliminated. This would result in the consumption of complex **1** during the course of the reaction; however, this is not observed. Alternatively, **1** could reversibly react with $CDCl_3$ by CH_3Cl elimination to form (P⋂N)Pt($CDCl_2$)Cl. The experimental data suggest that only the isomer in which the chlorine ligand is *cis* to the phosphorus atom is able to carry on the catalytic cycle. Since complex **1** does not react with hydridosilanes, the structurally and electronically related *trans* isomer can hardly be expected to do so. Theoretical investigations (see ESI†) showed that the *cis* isomer is energetically less stable than the *trans* isomer. However, both isomers are likely to be in equilibrium with each other and complex **1**. Oxidative addition of the hydridosilane **2** to the intermediate (P⋂N)Pt($CDCl_2$)Cl and reductive elimination of $ClSiMe_2Ph$ (**3**) would give



Scheme 1

† Electronic supplementary information (ESI) available: quantum chemical calculations. See http://www.rsc.org/suppdata/cc/b2/b205405a/

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(P⋂N)Pt($CDCl_2$)H. $CDCl_3$ is added then, and reductive elimination of $HCDCl_2$ completes the catalytic cycle. This mechanism would be similar to that proposed for the catalytic hydrodechlorination of aryl chlorides with methanol or sodium formate in the presence of Pd(0) complexes,[1] where $L_2Pd(Cl)Ar$ is a key intermediate (which is analogous to (P⋂N)PtCl($CDCl_2$)) which then undergoes ligand exchange with the reducing agent (OMe^- or $HCOO^-$) to give $L_2Pd(H)Ar$ as the other intermediate (which is analogous to (P⋂N)Pt($CDCl_2$)H).

While (P⋂N)$PtCl_2$ is not catalytically active, analogous results were obtained with (P⋂N)$PtMe_2$ as the catalyst, but the reaction was much slower and resulted in side-products due to Me/SiR_3 exchange. This indicates that the dimethyl complex must first be converted to **1**. Complex **1** is spectroscopically observed in the reaction mixture. The conversion of (P⋂N)$PtMe_2$ to **1** by alkyl chlorides was described earlier.[5]

The occurrence of CH_2DCl in the reaction of $CDCl_3$ shows that the cycle does not stop with the dehalogenation of chloroform. To test the influence of the alkyl chloride on the reaction rates, CCl_4 and CH_2Cl_2 were similarly reacted. When **1**, CCl_4 and $HSiMe_2Ph$ were reacted in a 1/50/50 molar ratio in benzene in a Teflon NMR tube at 60 °C, conversion was complete after 4.5 h, *i.e.* the reaction is distinctly faster than with $CHCl_3$. $CHCl_3$ was detected by ^{1}H NMR spectroscopy as the dechlorination product.[7] **1** was again the only observable phosphorus-containing complex in the reaction mixture. Reaction of $HSiMe_2Ph$ with CH_2Cl_2 under the same conditions was consequently much slower. Although the catalyst concentration was raised to a molar ratio of 1/10/10 (**1**, CH_2Cl_2 and $HSiMe_2Ph$, respectively), only 12% conversion was observed after 24 h. CH_3Cl was not detected by NMR because of its volatility at reaction temperature. The dechlorination of dissolved CH_3Cl was even slower with only 5% conversion after 24 h. We could not detect methane for the same reasons. Thus, the observed order of reactivity is $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$ when **1** is used as the catalyst.

Since the postulated intermediates are not amenable to spectroscopic investigation, quantum chemical calculations were carried out with the program package Gaussian98. The system was simplified by replacing the chelating ligand $Ph_2PCH_2CH_2NMe_2$ by NH_3 and PH_3 groups and the hydridosilane $HSiMe_2Ph$ by SiH_4. The activation step was calculated as well as the two exchange reactions interconverting (P⋂N)Pt(CH_xCl_{3-x})Cl and (P⋂N)Pt(CH_xCl_{3-x})H in Scheme 1 (see ESI†). At present only the total energy difference between products and reactants has been calculated, *i.e.* no information about the activation energies is currently available. The calculations were performed for $x = 0, 1, 2, 3$, which correspond to CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl. For all calculated energies the exothermicity is $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$, except in the activation step where $CHCl_3 < CCl_4$. Although the chosen model is a crude approximation it shows the same trend as found for the order of reactivity in the experimental results.

The clear sequence of reactivity allows the selective dechlorination of hydrocarbons under given experimental conditions. For example, the dehalogenation of CCl_4 can be stopped at the stage of $CHCl_3$. We have previously observed in other reactions that the reactivity of Pt(II) complexes with hemilabile P,N ligands can be varied by modification of the chelating ligand (variation of the ring size and rigidity of the metal chelate, variation of the substituents at the nitrogen atom). Preliminary qualitative tests showed that the activity of the complexes [(κ^2-*P*,*N*)-$Ph_2P(CH_2)_nNR_2$]PtMeCl to catalyse the reaction discussed in this paper is $Ph_2PCH_2CH_2N^iPr_2 \approx Ph_2PCH_2CH_2CH_2NMe_2 > Ph_2PCH_2CH_2NEt_2 > Ph_2PCH_2CH_2NMe_2$.

The reactions described in this communication were not observed when the corresponding bis(diphenylphosphino)-ethane (dppe)-substituted complexes were employed, *i.e.* the hemilabile nature of the P⋂N ligands and/or the different *trans* influence of the P and N donor centers is responsible for the observed reactivity enhancements.

In most dehalogenation reactions, a metal chloride is the chlorine sink, and the liberated lattice energy drives the reaction energetically forward. In the catalytic dechlorination described in this paper, a strong Si–Cl bond is instead formed. A related reaction is the hydrodefluorination of C_6F_6 by $HSi(OEt)_3$ catalyzed by $(Me_3P)_3RhC_6F_5$ reported earlier.[8]

In the Pt complexes reported in this communication, the deliberate combination of a particular P,N-chelating ligand (to tailor the reactivity of the catalyst) and a particular hydridosilane (to tailor the strength of the resulting Si–Cl bond) may allow the development of tailor-made dehalogenation catalysts for specific halogen compounds and may also be interesting in preparative chemistry to obtain hydrocarbons from the corresponding halogen compounds under mild conditions.

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Notes and references

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6 To a solution of 26.2 mg (0.052 mmol) of **1** in 0.7 ml of $CDCl_3$ in a flame-dried and argon-saturated NMR tube was added 81 μl (0.52 mol) of $HSiMe_2Ph$ (**2**). The sample was then kept at 60 °C in the closed NMR tube, and NMR spectra were taken at regular intervals. NMR spectra after 6 h (60 °C): ^{29}Si{^{1}H} NMR: $\delta = -16.87$ (s, **2**), 20.14 (s, **3**), −1.12 (s, traces). ^{13}C{^{1}H} NMR: $\delta = -6.84$ (s, **2**), 0.97 (s, **3**), 30.65 (t, $^1J_{CD} = 42.4$ Hz, CH_2DCl), 53.83 (t, $^1J_{CD} = 54.0$ Hz, $CHDCl_2$). ^{2}H{^{1}H} NMR: $\delta = 5.53$ ($^2J_{HD} = 1.1$ Hz, $CHDCl_2$), 3.25 ($^2J_{HD} = 2.1$ Hz, CH_2DCl). ^{1}H NMR: $\delta = 0.43$ (d, $^3J_{HH} = 3.8$ Hz, $SiMe_2$, **2**), 0.75 (s, $SiMe_2$, **3**), 0.63 (d, $^3J_{PH} = 2.8$ Hz, $^2J_{PtH} = 73.7$ Hz), 2.3–2.7 (m, CH_2CH_2, **1**), 2.87 (s, $^3J_{PtH} = 11.5$ Hz, NMe_2, **1**), 5.28 (s, $CHDCl_2$), 4.54 (sept, $^3J_{HH} = 3.7$ Hz, HSi, **2**), 7.4–7.8 (m, PPh). ^{31}P{^{1}H} NMR: $\delta = 26.89$ (s, $^1J_{PtP} = 4712$ Hz, **1**), 29.10 (s, $^1J_{PtP} = 4684$ Hz, traces).
7 Spectra at 33% conversion (60 °C, C_6D_6): ^{29}Si{^{1}H} NMR: $\delta = -16.93$ (s, **2**), 19.94 (s, **3**), traces of −1.12 (s). ^{1}H NMR: $\delta = 0.33$ (d, $^3J_{HH} = 3.7$ Hz, $SiMe_2$, **2**), 0.56 (s, $SiMe_2$, **3**), 1.27 (d, $^1J_{PH} = 3.4$ Hz, $^2J_{PtH} = 74.7$ Hz), 1.8–2.1 (m, CH_2CH_2, **1**), 2.65 (s, $^3J_{PtH} = 11.5$ Hz, NMe_2, **1**), 4.54 (s, CH_2Cl_2), 4.69 (sept, $^3J_{HH} = 3.8$ Hz, HSi, **2**), 6.47 (s, $CHCl_3$), 7.1–7.7 (m, H_{ar}). ^{31}P{^{1}H} NMR: $\delta = 26.56$ (s, $^1J_{PtP} = 4684$ Hz).
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