Highly efficient catalytic hydrodehalogenation of polychlorinated biphenyls (PCBs)†

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The hydrodehalogenation of polychlorinated phenyls and biphenyls (PCBs), catalysed by palladium *N*-heterocyclic carbene complexes, proceeds with excellent yields, at very low catalyst loadings and at room temperature, using isopropanol as the hydrogen source and NaOH as the base.

Polychlorinated biphenyls (PCBs) belong to the list of persistent organic pollutants (POPs) included in the Stockholm Convention.[1] These substances were heavily used from the 1930s to the 1970s by industry, mainly as insulation in electrical transformers. During this period, there was often no effective control on waste disposal so these substances have spread throughout the environment, at such an extent that almost all living creatures, including humans, have been exposed to them. Awareness of the presence of PCBs in the environment and their toxicity to humans and wildlife grew in the 1960s and 1970s, leading to a ban in 1979 on their sale and production.[2] The destruction of PCBs is often performed by incineration, which raises environmental concerns and prompted researchers to develop greener remediation methodologies. Amongst those, hydrodehalogenation has been shown to be a viable alternative by means of biodegradation strategies[3] and transition metal catalysed processes.[4] Among the various transition metals, palladium is the most commonly used, both for heterogeneous and homogeneous reactions.

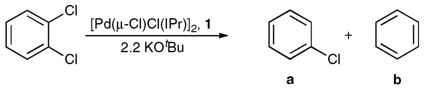
The dimeric species of type [Pd(μ-Cl)Cl(NHC)]$_2$ are efficient systems for cross coupling reactions.[5] [Pd(μ-Cl)Cl(IPr)]$_2$, **1**, (IPr = *N*,*N*′-bis-(2,6-(diisopropyl)phenyl)imidazol-2-ylidene) was recently shown to be an excellent precatalyst for the Suzuki–Miyaura coupling involving challenging aryl chlorides at low catalyst loading and under mild and economical reaction conditions.[5b] Since it has been suggested that the Suzuki–Miyaura reaction and the catalytic hydrodehalogenation are intertwined, sharing the oxidative addition step and leading in both instances to the (IPr)–Pd(0) species after one turnover,[6] we believed that in the absence of boronic acid, our system might effectively perform the hydrodehalogenation reactions of polychlorinated phenyls and biphenyls (PCBs). Herein we disclose the hydrodehalogenation of PCBs efficiently promoted by a well-defined palladium complex bearing a *N*-heterocyclic carbene (NHC).

1,2-Dichlorobenzene was chosen as a model substrate for the initial assessment of [Pd(μ-Cl)Cl(IPr)]$_2$, **1**, in hydrodehalogenation, with isopropanol as hydrogen source and solvent, and KO^{t}Bu as base (Table 1). This preliminary investigation showed that the reaction proceeds at room temperature, and that within 10 minutes, quantitative dehalogenation occurred, using 2 mol% Pd (Table 1, entry 1). Attempts to decrease the catalyst loading were then undertaken and it was found that, at room temperature, 1 mol% Pd was at least needed for the reaction to reach completion, but required 24 h (Table 1, entries 2–4). The use of higher temperatures was then envisioned and permitted to decrease the catalyst loading to 0.04 mol% Pd at 60 °C (Table 1, entries 5–7) and 0.008 mol% Pd at 80 °C (Table 1, entries 8 and 9). The use of even lower catalyst loadings was also attempted, but led to poorer conversion.

Investigation of the catalyst sensitivity was then undertaken. While the reaction could not be conducted under air (Table 1, entry 10), the presence of water (5% in ^{i}PrOH) did not significantly alter catalytic activity (at rt, with 0.2 mol% Pd 43% of benzene formed).

The use of EtOH and MeOH, as solvents and hydrogen sources, was also attempted. For these experiments, sealed tubes were used; in both cases, the reaction did not take place (Table 1, entries 11 and 12). In order to further assess the

Table 1 Hydrodehalogenation of 1,2-dichlorobenzene[a]



Entry	Cat. loading/ mol% (Pd)	Solvent	T/°C	Time	Conv.[b] (%) a	b
1	2	^{i}PrOH	rt	10 min	—	100
2	1	^{i}PrOH	rt	24 h	—	100
3	0.5	^{i}PrOH	rt	24 h	—	95
4	0.2	^{i}PrOH	rt	24 h	37	63
5	0.1	^{i}PrOH	60	24 h	—	100
6	0.04	^{i}PrOH	60	24 h	—	100
7	0.02	^{i}PrOH	60	24 h	15	85
8	**0.008**	**^{i}PrOH**	**80**	**24 h**	**—**	**100**[c]
9	0.004	^{i}PrOH	80	24 h	23	76
10	0.2	^{i}PrOH	rt	24 h	—	[d]
11	0.004	EtOH	80	24 h	8	—
12	0.004	MeOH	80	24 h	1	—

[a] Reaction conditions: 1,2-dichlorobenzene (1 mmol), KO^{t}Bu (2.2 mmol), solvent (2 mL). [b] Conversion to C_6H_6 and/or C_6H_5Cl, based on 1,2-dichlorobenzene, determined by GC, minimum average of two runs. [c] TON per Cl = 25 000. [d] Reaction performed under air.

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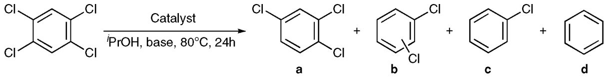
Table 2 Hydrodehalogenation of 1,2,4,5-tetrachlorobenzene[a]



Entry	Catalyst	Cat. loading/ mol% (Pd)	Base	Conv.[b] (%) a	b[c]	c	d
1	[Pd(μ-Cl)Cl(IPr)]$_2$ **1**	0.04	KO^{t}Bu	—	—	—	100[d]
2	[Pd(μ-Cl)Cl(IPr)]$_2$ **1**	0.02	KO^{t}Bu	—	1	4	95
3	[Pd(μ-Cl)Cl(SIPr)]$_2$ **2**	0.02	KO^{t}Bu	—	—	26	64
4	[Pd(μ-Cl)Cl(IMes)]$_2$ **3**	0.02	KO^{t}Bu	—	16	73	11
5	[Pd(μ-Cl)Cl(SIMes)]$_2$ **4**	0.02	KO^{t}Bu	—	62	34	4
6	[Pd(η^3-cinnamyl)Cl(IPr)] **5**	0.02	KO^{t}Bu	—	—	55	45
7	[Pd(η^3-allyl)Cl(IPr)] **6**	0.02	KO^{t}Bu	—	9	51	40
8	[Pd(μ-Cl)Cl(IPr)]$_2$ **1**	0.04	NaOMe	4	14	48	23
9	[Pd(μ-Cl)Cl(IPr)]$_2$ **1**	0.04	NaOH	—	—	—	100[d]

[a] Reaction conditions: 1,2,4,5-tetrachlorobenzene (0.5 mmol), ^{i}PrOH (2 mL), base (2.2 mmol), 24 h. [b] Conversion to hydrodehalogenation products, based on 1,2,4,5-tetrachlorobenzene, determined by GC, minimum average of two runs. [c] Ratio of dichlorobenzene isomers: *ortho–meta–para* = 1 : 0.1 : 0.3. [d] TON per Cl = 10 000.

generality of the reaction, hydrodehalogenation of 1,2,4,5-tetrachlorobenzene, a more challenging polychlorinated phenyl derivative, was studied (Table 2).

The reaction proceeded smoothly towards the formation of benzene, when using KO^{t}Bu (10% excess with respect to Cl) as the base, and 0.04 mol% Pd of catalyst **1**, in isopropanol. (Table 2, entry 1). The catalyst loading was further decreased, and a satisfactory 95% conversion was obtained (Table 2, entry 2). These reaction conditions were used to compare catalytic efficiency of congeners of complex **1**, the dimers [Pd(μ-Cl)Cl(SIPr)]$_2$, **2**, [Pd(μ-Cl)Cl(IMes)]$_2$, **3** and [Pd(μ-Cl)Cl(SIMes)]$_2$, **4** (Fig. 1). The nature of the NHC ligand leads to drastic changes in catalyst performance, with conversions to benzene ranging from 4 to 95%, the IPr-bearing system being the most efficient (Table 2, entries 2–5). Interestingly, the monomeric complexes bearing an IPr ligand [Pd(η^3-cinnamyl)Cl(IPr)], **5**, and [Pd(η^3-allyl)Cl(IPr)], **6** (Fig. 1), performed poorly compared to [Pd(μ-Cl)Cl(IPr)]$_2$, **1** (Table 2, entries 2, 6 and 7).[7] A drawback of the system depicted so far is the cost of the base used (KO^{t}Bu). Screening of alkoxide bases showed that while unsatisfactory results were obtained with NaOMe (complete formation of benzene was achieved only when using 150% excess with respect to Cl), complete dehalogenation was achieved with the inexpensive NaOH (Table 2, entries 8 and 9).

Finally, the best system found ([Pd(μ-Cl)Cl(IPr)]$_2$, **1**–NaOH–^{i}PrOH) was applied to the dehalogenation of a range of polychlorinated biphenyls (Table 3).

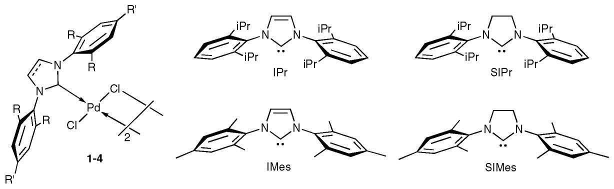
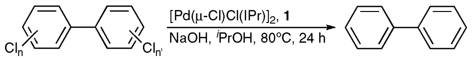
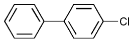
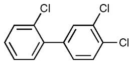
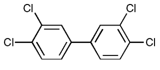
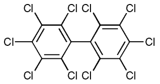


Fig. 1 Well-defined systems studied.

Table 3 Hydrodehalogenation of polychlorinated biphenyls[a]



Entry	Substrate	Cat loading (mol% Pd)	Conv.[b] (%)	Yield[c] (%)	TON (per Cl)
1		0.04	>99	92	2 500
2		0.04	>99	91	7 500
3		0.04	>99	95	10 000
4		1	>99	84	1 000

[a] Reaction conditions: substrate (0.04–1 mmol), ^{i}PrOH (2–3 mL), NaOH (10% excess with respect to Cl), 24 h. [b] Conversion to biphenyl, based on chlorinated substrate, determined by GC. [c] Isolated yield, minimum average of two reactions.

Application of the methodology to mono- and poly-chlorinated biphenyl derivatives was successful, as all reactions proceeded quantitatively. For mono-, tri- and tetra-chlorobiphenyl substrates, very low catalyst loadings were used (0.04 mol% Pd) to achieve complete conversion to biphenyl (Table 3, entries 1–3). Remarkably, our system was able to fully hydrodehalogenate decachlorobiphenyl (Table 3, entry 4).

In conclusion, the commercially available[8] [Pd(μ-Cl)Cl(IPr)]$_2$, **1**, was shown to hydrodehalogenate polychlorinated phenyls and PCBs under very mild reaction conditions, using inexpensive reagents. While strong bases, strong reducing agents and harsh reaction conditions are generally used for such transformations, NaOH as base and isopropanol as reducing agent were found sufficient in the present system. The methodology developed offers a very powerful, low-cost and safe technology for the destruction of PCBs, whose proliferation in the environment continues to be a serious health issue. It also offers a system capable of promoting the room temperature dechlorination of chloroarenes at low Pd loading, a reaction of significant interest in organic synthesis.[9]

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