Letter

Complete debromination of polybrominated benzenes at room temperature catalyzed by palladium metallocenyl diphosphine complexes

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Abstract

Pd-catalyzed reductive debromination of highly brominated benzenes is studied as a model for degradation of polybrominated biphenyls (PBBs). A complete conversion of hexabromobenzene to benzene at room temperature has been achieved. Both $PdCl_2[(C_5H_4PPh_2)_2M]$ (M = Fe, Ru) show excellent catalytic activities in the presence of $NaBH_4$ as a reducing agent and $Me_2NC_2H_4NMe_2$ as a base. © 1997 Elsevier Science B.V.

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Polybrominated biphenyls (PBBs) are serious environmental contaminants [1–3] with documented cyto- and genotoxicity [4,5] and long-term health effects [6]. Recent studies estimated their half-life in the body to be about 11 years and their possible association with breast cancer [7]. A person infested with 46 ppb of PBB is estimated to take over 60 years for this level to fall below the current detection level of 1 ppb [8]. It is therefore not surprising that research on degradation of PBBs and the congeneric PCBs

is progressing at a blistering pace [9–15]. Although a biodegradation approach [16–18] is generally favoured, it has met with serious difficulties especially with highly halogenated halobiphenyls. Chemical treatments are hampered by the thermal and chemical stability of PBBs. Catalytic hydrodehalogenation of polyhalogenated aromatics has met with varying degrees of success. Some representative catalysts include supported palladium catalysts [19], palladium on carbon [20–24] and palladium complexes [25–29], whereas the reductants used include PMHS [30], aluminium powder [31], $NaBH_4$ [32–34], KOH [35], H_2 [20–24] and MgH_2 [28]. The use of ferrocenyl phosphine complexes as catalysts in reduction, hydrogenation, Grignard and other cross-couplings has been reported by us [36,37] and other groups [38–41]. These results prompted us to examine

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the catalytic value of these complexes in this direction. Although Pd complexes are known to catalyse the reduction of haloaromatics by hydrogen, thermal conditions are applied and the catalysts used are almost invariably based on the PPh_3 ligand system. In this letter, using hexabromobenzene and other highly brominated benzenes as models, we demonstrate a catalytic reductive debromination mechanism whereby a complete degradation with high degrees of debromination can be achieved at ambient conditions. The effects of catalysts, reductants, and the supporting bases are examined. The value of metallocenyl phosphine as a supporting ligand is emphasized.

Hexabromobenzene, 1,2,4,5-tetrabromobenzene, 1,3,5-tribromobenzene, 1,2,4-tribromobenzene, 1,2-dibromobenzene, 1,4-dibromobenzene, 1,3-dibromobenzene and monobromobenzene are used as substrates. The catalysts tested are $Pd(OAc)_2$ supported by PPh_3, dppf or dppr; $PdCl_2(PPh_3)_2$, $PdCl_2(dppf)$ and $PdCl_2(dppr)$. The use of $Pd(OAc)_2$ as a pre-catalyst to the active Pd^0 species is established [42,43]. Three common reductants are examined, viz., $NaBH_4$, LiH and HCOOH. The bases tested are $NaHCO_3$, NaOH, Et_3N, TMMDA, TMEDA, TMNDA and NEDA. The rates and yields of debromination depend critically on the choice of catalyst, reducing agent and base [1]. Irrespective of the catalyst used, $NaBH_4$ is at least 50 times more active (in terms of product yields) than the others and is the reductant of choice. Negligible activity is observed when the catalyst is absent. Catalysts with bidentate metallocenyl diphosphines viz. $PdCl_2(dppf)$ [38–41] and $PdCl_2(dppr)$ [44–46] are active even at room temperature and generally the best performers. Introduction of a base improves both

reaction rates and yields with TMMDA and TMEDA showing the most significant enhancement. For example, the debromination efficiency (expressed in terms of the summation of the % yields of the (partially) debrominated products, proportionated by the degree of bromination) increases from 51 to 95% (after 24 h) when TMEDA is added to a mixture catalyzed by $PdCl_2(dppr)$.

Debromination of hexabromobenzene, a model for other highly brominated aromatics, is monitored under different catalysts (5% mole ratio) over a period of 7 h at room temperature (Fig. 1). Complete degradation of the substrate is observed in all cases, but only $PdCl_2(dppf)$ and $PdCl_2(dppr)$ give monobromobenzene and benzene as the predominant products. Other catalysts generally yield dibromobenzenes as the major products and 1,2,4-tribromobenzene as a minor product (Table 1). The only other catalytic mixture which gives a good debromination profile is $Pd(OAc)_2$ when supported by dppr. A satisfactory efficiency of 81 and 88% for $PdCl_2(dppf)$ and $PdCl_2(dppr)$ is achieved within 1 h. In the former, this steadily rises to a remarkable 100% efficiency after 7 h. Without any residual brominated products, this represents a complete conversion of hexabromobenzene to benzene, thus demonstrating a remarkably efficient reductive debromination at room temperature. Similar complete conversions of 1,2,4,5-tetrabromobenzene, 1,3,5-tribromobenzene, 1,2,4-tribromobenzene, 1,2-dibromobenzene, 1,4-dibromobenzene, 1,3-dibromobenzene and monobromobenzene to benzene (in 2, 7, 1.5, 2, 1, 6 and 2 h respectively) have also been achieved.

Another merit of $PdCl_2(dppf)$ as a catalyst is its high activity even at very low concentrations. The debromination efficiency at room temperature maintains a satisfactory level of 97 and 94% even when the catalyst concentration (defined as [cat]/[sub] ratio) is reduced to 2.5 and 1.25% respectively. To examine the ceiling of the catalytic efficiency, we have carried out the debromination reactions of hexabromoben-

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[1] In a typical reaction, to a THF solution (20 ml) of substrate (0.22 mmol) was added a base (3.30 mmol), reducing agent (2.64 mmol) and catalyst (0.011 mmol) and the mixture stirred at room temperature. The resultant suspension was filtered into a volumetric flask, an internal standard (biphenyl) was added. The yields of the products were determined by GC.
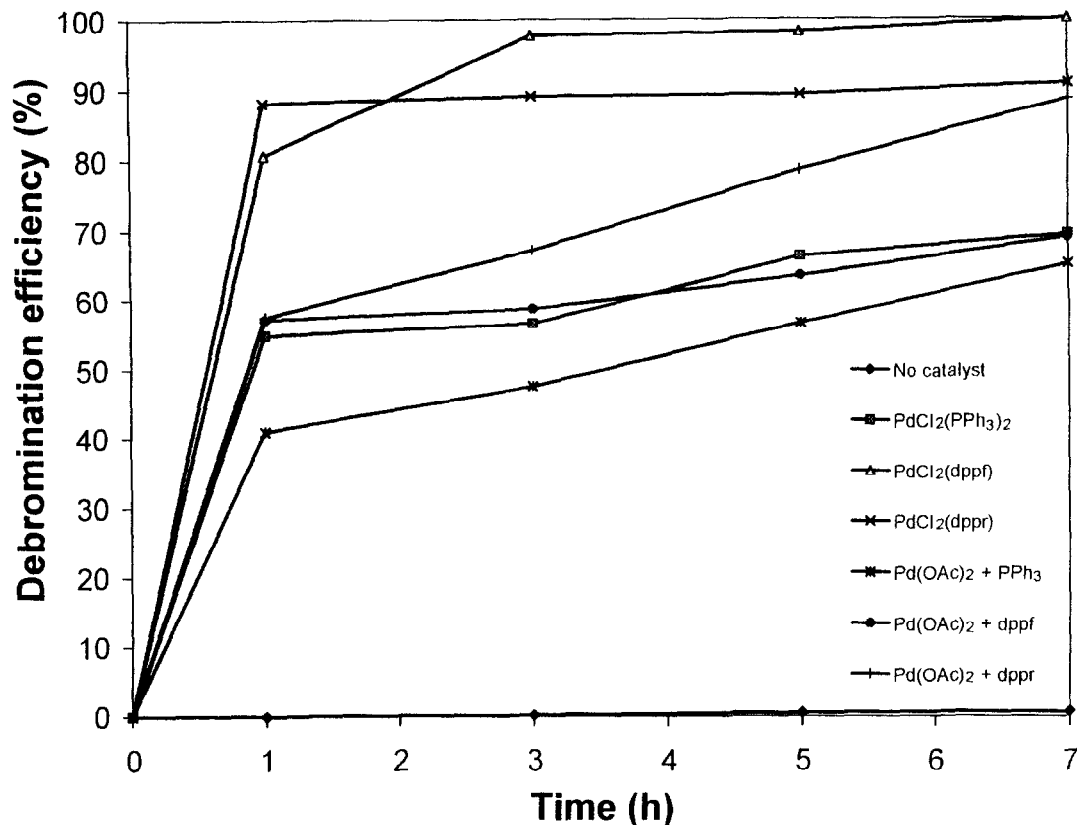
Fig. 1. Pd-catalyzed debromination of C_6Br_6 at room temperature over a period of 7 h.

Table 1
Different catalyst effects on the debromination of hexabromobenzene after 7 h of reaction at room temperature (C_6Br_6:NaBH$_4$:TMEDA:catalyst = 1:12:15:n)

Catalyst mole ratio w.r.t. substrate (n)	Yield of PBB[a] (%)	Yield of 1,2,4-TRBB[a] (%)	Yield of 1,2-DB[a] (%)	Yield of (1,3 + 1,4)[b]-DB[a] (%)	Yield of BB[a] (%)	Yield of benzene (%)	Conversion of HBB[a] (%)	Debromination efficiency (%)
No catalyst (0)	4	0	0	0	0	0	4	1
PdCl$_2$(PPh$_3$)$_2$ (0.05)	0	17	15	47	8	13	100	69
PdCl$_2$(dppf) (0.05)	0	0	0	0	0	100	100	100
PdCl$_2$(dppr) (0.05)	0	0	0	0	55	45	100	91
Pd(OAc)$_2$ + PPh$_3$ (0.05:0.20)	0	19	19	53	9	0	100	65
Pd(OAc)$_2$ + dppf (0.05:0.10)	0	0	42	45	14	0	100	69
Pd(OAc)$_2$ + dppr (0.05:0.10)	0	0	0	0	69	32	100	89

[a] BB, bromobenzene; DB, dibromobenzene; TRBB, tribromobenzene; TEBB, tetrabromobenzene; PBB, pentabromobenzene; HBB, hexabromobenzene.
[b] 1,3- and 1,4-DB cannot be differentiated by GC under the conditions used.
[c] The debromination efficiency (%) is expressed in terms of the summation of the % yields of the (partially) debrominated products, proportionated by the degree of bromination, viz. (yield of PBB) × 1/6 + (yield of 1,2,3,4-TEBB) × 2/6 + (yield of 1,2,3,5-TEBB) × 2/6 + (yield of 1,2,4,5-TEBB) × 2/6 + (yield of 1,2,3-TRBB) × 3/6 + (yield of 1,2,4-TRBB) × 3/6 + (yield of 1,3,5-TRBB) × 3/6 + (yield of 1,2-DB) × 4/6 + (yield of (1,3 + 1,4)-DB) × 4/6 + (yield of BB) × 5/6 + (yield of benzene) × 6/6.
[d] The yields of 1,2,3,4-, 1,2,3,5- and 1,2,4,5-TEBB and 1,2,3- and 1,3,5-TRBB are 0% for all catalysts used.

Table 2
Debromination of hexabromobenzene at very low catalyst level after 55 h (C_6Br_6:$NaBH_4$:TMEDA:$PdCl_2$(dppf) = 1:12:15:n)

n	Temperature	Yield of PBB[a] (%)	Yield of 1,2,3,4-TEBB[a] (%)	Yield of 1,2,4,5-TEBB[a] (%)	Yield of 1,2,4-TRBB[a] (%)	Yield of (1,3 + 1,4)[b]-DB[a] (%)	Yield of BB[a] (%)	Yield of benzene (%)	Conversion of HBB[a] (%)	Debromination efefficiency (%)
1:250	r.t.	51	7	42	0	0	0	0	100	24
1:500	r.t.	43	6	51	0	0	0	0	100	26
1:500	reflux	0	0	0	40	10	30	20	100	71

[a] BB, bromobenzene; DB, dibromobenzene; TRBB, tribromobenzene; TEBB, tetrabromobenzene; PBB, pentabromobenzene; HBB, hexabromobenzene.

[b] 1,3- and 1,4-DB cannot be differentiated by GC under the conditions used.

[c] The definition of the debromination efficiency (%), see Table 1.

[d] The yields of 1,2,3,5-TEBB, 1,2,3- and 1,3,5-TRBB and 1,2-DB are negligible in all cases.
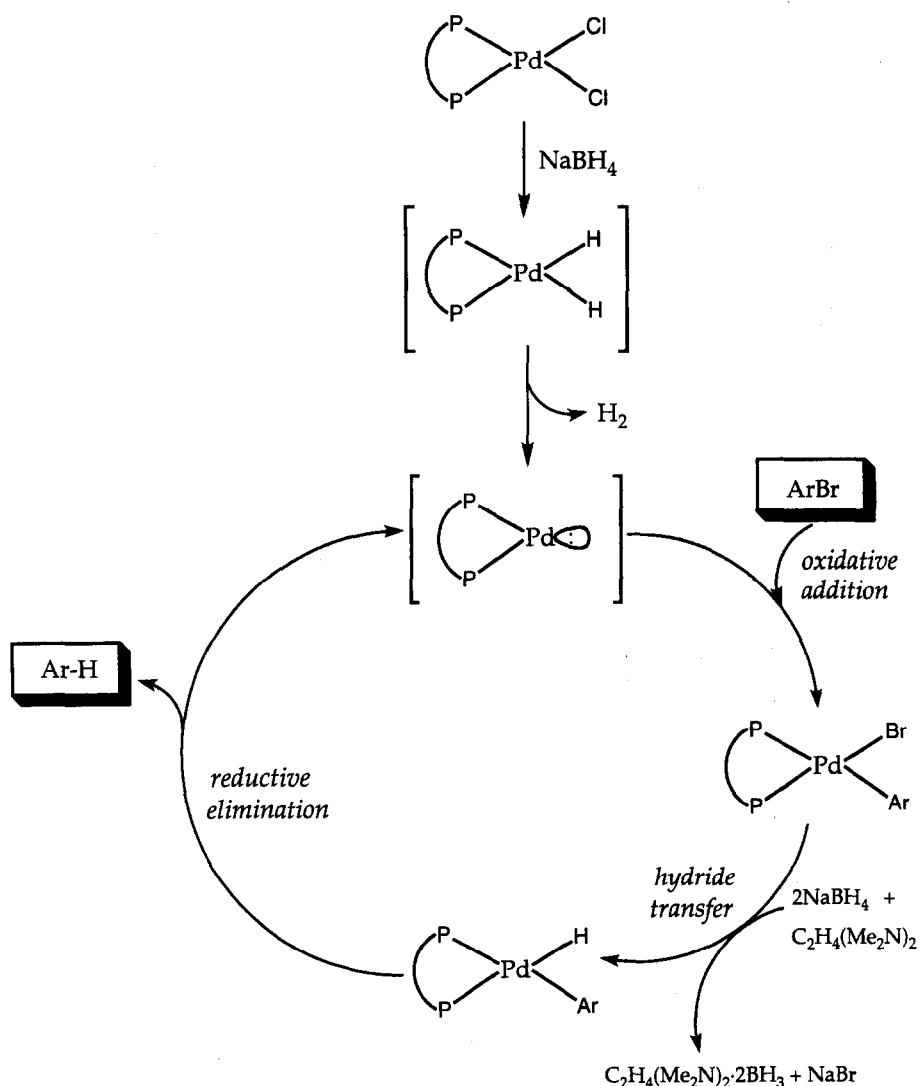
Scheme 1. Proposed mechanism for the reductive debromination of ArBr by $NaBH_4$ catalyzed by $PdCl_2$(P–P) (Ar, aryl; P–P, diphosphine).

zene at a substrate/catalyst ratio as high as 250 or 500 (Table 2). Even at such low catalyst levels, degradation of hexabromobenzene occurs rapidly and completes within minutes. A longer reaction time only helps the formation of the lower bromobenzenes. At room temperature, 1,2,4,5-tetrabromobenzene is the principal product whereas at refluxing conditions, benzene and other lower brominated benzenes are formed. In all cases, however, the debromination efficiency invariably decreases when free dppf is added to the mixture; the level of retardation increases as the concentration of free dppf increases.

A mechanistic cycle based on oxidative addition, hydride transfer (transmetallation) and reductive elimination can be proposed (Scheme 1). A similar mechanism has been proposed by Milstein et al. [47] in an elegant work on aryl chlorides. Evidence of a rate-determining oxidative addition step is aslo available [48]. There are four possible reasons for the catalytic enhancement of the metallocenyl phosphines: (a) a large bite size and chelate angle promote the reductive elimination; (b) a better σ-donating effect (compared to PPh_3) favours the oxidative addition; (c) the large chelate ring encourages phosphine dissociation (through ring-opening), which has been shown to be a key prerequisite for reductive elimination to occur [49,50]; (d) stabilization of an unsaturated 14-electron intermediate, formed during reduction of the pre-catalyst or at the reductive elimination step, by the bulky phosphines. The effect of the base is less clear. Our results suggest a two-fold effect [2]: (1) weak coordination to the electronically unsaturated intermediate and hence stabilization of the catalyst; (2) capturing of BH_3 from BH_4^- thus providing an extra drive for hydride transfer to the Pd centre. The resultant

TMEDA $\cdot$ 2(BH_3) (verified by GC/MS) could also serve as an additional hydride source. The reducing ability of amine-BH_3 adduct has been demonstrated [51]. The phosphine inhibitive effect is consistent with the blockage of the vacant site on [Pd(dppf)] in suppression of the dissociation step mentioned above in (c).

The ferrocenyl system catalyzes bromobenzenes to undergo complete hydrodebromination at room temperature. The efficiency is superior to that shown by $Pd(PPh_3)_4$ which achieves similar results but under refluxing conditions (67°C (100%)) [28] and 110°C (75%)) [26]. Pd/C catalysts have been shown to be similarly (or more) active [20–24] but the use of H_2 gas, which needs special equipment for safety reasons, is not ideal and, like many other heterogeneous systems, the chemo- and regio-selectivities are low. The use of other metal systems has been reported. The more active systems include Ni(II) [52] and Ti(IV) [53] complexes but they are disadvantaged by the use of high levels of catalyst (10–20 mol% Ni(II)) or high temperatures (75°C for the Ti(IV) system).

The present results suggest a facile mechanism for reductive debromination of aromatics under ambient conditions. This could offer a catalytic methodology for the degradation and detoxification of PBBs and PCBs in environmental cleansing. Current efforts are directed at these targets.

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[2] We currently do not discount the possibility of intra- or inter-molecular acid (HBr) elimination promoted by TMEDA although there is no evidence to suggest this. Absence of biphenyl as a by-product also does not support this proposal.

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