

Room-temperature hydrodebromination of 4,4'-dibromobiphenyl catalyzed by 1,1'-bis(diphenylphosphino) ferrocene complexes of palladium

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Abstract

Hydrodebromination of 4,4'-dibromobiphenyl to 4-bromobiphenyl and biphenyl was studied by using a variety of metal complexes of Ru(II), Ni(II), Pd(II), Pt(II) and Cu(I) under different ligand environments. Palladium complexes are most effective in giving biphenyl whereas other complexes give 4-bromobiphenyl. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) is the best phosphine ligand whereas NaBH₄ and *N,N,N',N'*-tetramethylethylenediamine are the best reductant and base, respectively. The use of catalytic PdCl₂(CH₃CN)₂ and PdCl₂(dppf) gives 4-bromobiphenyl (86%) and biphenyl (100%) respectively. PdCl₂(dppf) is effective even at a low concentration of 3.5 mol.% and at room temperature (r.t.) with a short reaction time (10 min) and performs better than Pd on charcoal (5%). It also leads to a complete breakdown of 4-monobromobiphenyl and decabromobiphenyl giving 100% of biphenyl in 4 min and 40 h, respectively. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Bromobiphenyls; Biphenyl; Debromination; Reduction; Ferrocenyl phosphine

1. Introduction

Polychlorinated biphenyls (PCBs) are serious environmental contaminants [1,2] with documented adverse health effects on humans [3] and animals [4]. Their polybromo congeners (PBBs) are also toxic [5–15] with reportedly higher potency [16]. They share some similar pyrolysis products with dioxin and dibenzofuran whose toxicological data have been established [17]. Exposure to PBBs, which are very persistent in the animal body and environment [5], has

showed toxic effects in every animal species tested. It is therefore not surprising that research on degradation of PBBs is progressing at a blistering pace [18–24]. Although a biodegradation approach [25–27] is popular, it has serious difficulties especially with biphenyls which are highly halogenated. Chemical treatments are hampered by the thermal and chemical stability of these PBBs. Catalytic hydroreduction of polyhalogenated aromatics has met with varying degrees of success. Some representative catalysts include supported palladium catalysts [28], palladium on carbon [29–33] and palladium complexes [34–38] whereas the reductants used

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include PMHS (polymethylhydrosiloxane) [39], aluminium powders [40], NaBH_4 [41–43], KOH [44], H_2 [29–32] and MgH_2 [37]. Recent work on metallocenyl diphosphine [e.g., $(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{M}$ ($\text{M} = \text{Fe}$ (1,1'-bis(diphenylphosphino)ferrocene (dppf)) and Ru (1,1'-bis(diphenylphosphino)ruthenocene (dppr))] complexes of palladium by us [45,46,66] and other researchers [47–50] proved that these are suitable catalysts in reduction, hydrogenation, Grignard and other cross-couplings. Low-valent complexes such as $\text{Pd}(\text{dipp})_2$ [$\text{dipp} = 1,3$ -bis(diisopropylphosphino)propane] have also been reported to be effective in promoting dehalogenation of organic halides [38]. These data prompted us to examine the catalytic value of these metal complexes, especially metallocenyl diphosphine complexes of Pd, in hydrodebromi-

nation. In this paper, by using 4,4'-dibromobiphenyl as a model, we report the effect of different metal catalysts and the influence of supporting ligands, reductants, bases, catalyst concentration, solvent, reaction atmosphere and sequence of additions of reactants on the catalytic efficiency.

2. Results and discussion

Debromination of 4,4'-dibromobiphenyl by NaBH_4 was examined at r.t. under the influence of a variety of Ru(II), Cu(I), Ni(II), Pd(II) and Pt(II) catalysts. Some representative data are given in Table 1. The effect of phosphine as a co-catalyst in some Pd-catalyzed reactions was studied.

Table 1

Effects of different metal catalysts on the debromination of 4,4'-dibromobiphenyl at r.t. ($\text{C}_{12}\text{H}_8\text{Br}_2:\text{NaBH}_4:\text{catalyst}:\text{TMEDA} = 1:6.9:n:6.9$)

Entry	Catalyst (<i>n</i>) ^a	Reaction time	Conversion of 4,4'-DBB ^b %	Yield of 4-BB ^b %	Yield of biphenyl%	Br% ^c
1	No catalyst (0)	1 day	38	38	0	19
2	$\text{RuCl}_2(\text{dppr})(\text{PPh}_3)$ (0.05)	1 day	11	11	0	6
3	$\text{RuCl}_2(\text{CO})(\text{dppr})$ (0.05)	1 day	14	14	0	7
4	$\text{Cu}(\text{PPh}_3)_2(\text{BH}_4)$ (0.05)	1 day	39	39	0	20
5	$\text{NiCl}_2(\text{dppp})$ (0.05)	1 day	39	10	29	34
6	$\text{NiCl}_2(\text{dppf})$ (0.05)	1 day	39	13	26	33
7	$\text{PtCl}_2(\text{dppf})$ (0.05)	1 day	13	13	0	7
8	$\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.05)	1 day	86	86	0	43
9	$\text{PdCl}_2(\text{PPh}_3)_2$ (0.05)	1 day	63	54	9	36
10	$\text{PdCl}_2(\text{PPh}_3)_2 + 2\text{PPh}_3$ (0.05:0.10)	1 day	62	54	8	35
11	$\text{PdCl}_2(\text{dppf})$ (0.05)	10 min	100	0	100	100
12	$\text{PdCl}_2(\text{dppf}) + \text{dppf}$ (0.05:0.05)	1 day	100	0	100	100
		10 min	16	16	0	8
13	$\text{PdCl}_2(\text{dppr})$ (0.05)	1 day	100	27	73	87
14	$\text{Pd}(\text{OAc})_2 + 4\text{PPh}_3$ (0.05:0.20)	1 day	81	61	20	51
15	$\text{Pd}(\text{OAc})_2 + 2\text{dppf}$ (0.05:0.10)	1 day	100	0	100	100
		10 min	6	6	0	3
16	$\text{Pd}(\text{OAc})_2 + 2\text{dppr}$ (0.05:0.10)	1 day	100	31	69	85
17	$\text{Pd}/\text{C}^{\text{d}}$ (0.05)	10 min	95	33	62	78
18	$\text{PdCl}_2(\text{P-P})^{\text{d}}$ (0.05)	10 min	0	0	0	0
	(P-P = 2PPh_3 , dppf, dppr)					

Conditions: substrate = 4,4'-dibromobiphenyl (0.060 g, 0.19 mmol); catalyst (as shown in table); base = TMEDA (0.2 ml, 1.3 mmol); reductant = NaBH_4 (0.05 g, 1.3 mmol). Order of reagent addition: substrate → catalyst → THF → base → reductant.

^a*n* = Mole ratio w.r.t. substrate (4,4'-dibromobiphenyl).

^b4,4'-DBB = 4,4'-dibromobiphenyl, 4-BB = 4-bromobiphenyl.

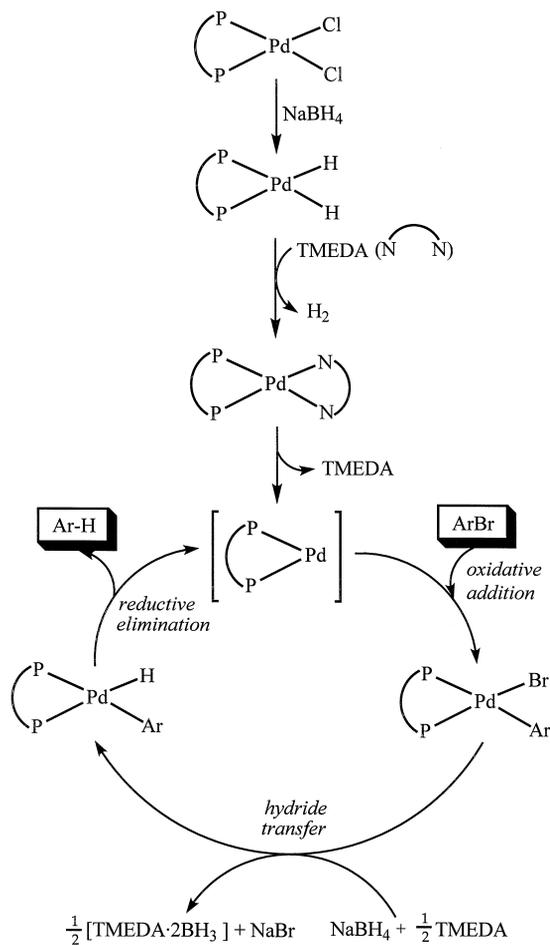
^cBr% = debromination efficiency which is expressed in terms of the summation of the % yields of the (partially) debrominated products, proportionated by the degree of bromination, viz. $(\text{Yield of 4-BB}) \times 1/2 + (\text{Yield of biphenyl}) \times 2/2$.

^d H_2 gas as reductant.

Palladium shows the highest level of activity among the four metals examined. Among the Pd(II) complexes, PdCl₂(dppf) is most efficient at r.t. At a 5 mol.% catalyst level, 4,4'-dibromobiphenyl converts cleanly (with 100% efficiency) to biphenyl after 10 min (Entry 11). No other brominated aromatics are detected at the end of the reaction. Such efficiency is matched only by Pd(OAc)₂ with added dppf after 1 day (Entry 15). PdCl₂(dppf) is even more potent than a commercial hydrogenation catalyst-Pd/C-which gives biphenyl (62%) and 4-bromobiphenyl (33%) after 10 min (Entry 17). Besides Pd, Ni is the only metal which is capable of giving biphenyl (Entries 5 and 6).

Selective yield of 4-bromobiphenyl over biphenyl is best obtained when PdCl₂(CH₃CN)₂ is used (Entry 8). This selective hydrodebromination would have significant implication in organic synthesis of monobrominated biphenyls and other aromatics. Other Pd systems which show a satisfactory debromination efficiency are Pd(OAc)₂/PPh₃ (Entry 14) and PdCl₂(PPh₃)₂ with (Entry 10) or without (Entry 9) added PPh₃.

The proposed catalytic mechanism (Scheme 1) involves a sequence of oxidative addition, hydride transfer and reductive elimination.¹ The catalyst used is strictly a pre-catalyst as reduction to a low-valent complex is a prerequisite for oxidative addition to occur. Although PdCl₂(PPh₃)₂ is routinely used in similar catalytic reactions, its activity is significantly lower than that of a metallocenyl phosphine (dppf) complex (comparing Entries 9 and 11). Some possible reasons are: (a) the chelating effect in dppf lends greater stability to the unsaturated 14-electron intermediate, [Pd(dppf)], formed from the reduction of the pre-catalyst and at the



Scheme 1.

reductive elimination step; (b) better σ -donor ability of dppf enables the metal centre to be more electron-rich thus favouring oxidative addition; (c) larger chelate angle subtended by a metallocenyl phosphine promotes reductive elimination through a steric influence; (d) large chelate ring in dppf encourages phosphine dissociation (through ring-opening) which has been shown to be a key prerequisite for the reductive elimination step. However, the use of a bigger metallocenyl phosphine ring such as dppr in PdCl₂(dppr) would erode some of the benefits due to the larger ring strain and easier dissociation of dppr. Dppf thus represents a good compromise between chelate stability and phosphine dissociation. The lower debromination effi-

¹ Addition of free phosphines facilitates the reduction of Pd(OAc)₂ to the active Pd(0) catalyst. In other situations, e.g., PdCl₂(dppf), addition of excess phosphine is undesirable since it competes for the vacant site and interferes with the oxidative addition step.

ciency of $\text{PdCl}_2(\text{dppr})$ (Entry 13) is thus not surprising.

The relative ease of oxidative addition for $\text{M}(\text{PR}_3)_4$ ($\text{R} = \text{Ph}$ [51], Et [52]) has been reported to be $\text{M} = \text{Ni} > \text{Pd} > \text{Pt}$. This is consistent with the poor activity of the present $\text{Pt}(\text{II})$ complexes (Entry 7). Although $\text{Ni}(0)$ complexes undergo oxidative addition easily, the greater resistance for $\text{Ni}(\text{II})$ towards reductive elimination accounts for the unsatisfactory yields in Entries 5 and 6. Similarly, the difficulty for $\text{Ru}(\text{II})$ and $\text{Cu}(\text{I})$ to undergo reductive elimination explains the poor performance of their complexes.

Although H_2 is a conventional reagent used in reductions catalyzed by Pd/C , replacement of NaBH_4 by H_2 (Entry 18) gives no observable products. This supports the proposed mechanism as $\text{Pd}(\text{II})$ complexes are not easily reduced to $\text{Pd}(0)$ species by H_2 gas and H_2 is not a ready source of H^- for the hydride transfer reaction.

Reduction of $\text{Pd}(\text{OAc})_2$ to a $\text{Pd}(0)$ phosphine complex in the presence of free phosphine has been documented [53]. The good efficiency observed when dppf is present in this system (Entry 15) is consistent with this proposal. The active catalyst thus generated would be similar to that from $\text{PdCl}_2(\text{dppf})$ except that a longer induction period is necessary for the active catalyst to be formed.

These results suggest that $\text{PdCl}_2(\text{dppf})$ is the catalyst-of-choice in our system. This complex offers an added advantage in its high activity at low concentration level. At 3.5 mol.% level, the biphenyl yield is kept at 100%. This decreases to 63% when the catalyst level is at 2.1%.

Although dppf functions well as a supporting ligand, its presence in excess is detrimental to catalytic action. The biphenyl yield drops remarkably from 100% to 0% and to 0% and debromination efficiency slides sharply from 100% to 8% and to 4% as the dppf :substrate mole ratio increases from 0 to 0.05 and to 0.10 respectively. The level of retardation increases as the concentration of phosphine increases. This

effect is attributed to the blockage of the vacant sites which inhibits the oxidative addition process.

The effects of LiH , HCO_2H , N_2H_4 , LiAlH_4 and NaBH_4 as reducing agents are examined. The first three show negligible effect and LiAlH_4 gives 20% yield of 4-bromobiphenyl. Only NaBH_4 , which is a ready source of H^- , is capable of achieving 100% debromination. The debromination effect increases from 56% to 100% when the NaBH_4 :substrate ratio is increased from 1.7 to 6.9.

The catalytic efficiency is dependent on the reaction atmosphere. Whilst complete debromination is achieved under argon atmosphere, only 39% debromination (or 11% yield of biphenyl) is achieved when the reaction is carried out in air. The air sensitivity of the intermediate $\text{Pd}(0)$ species is the most probable problem. Three reaction solvents were examined—THF, EtOH and EtOH/ CH_3CN (1:3). Complete debromination was achieved only when THF was used. The good solvation property of THF and its stabilizing effect towards the metal are likely advantages.

The debromination efficiency invariably increases when a base is added to the reaction mixture (Table 2). The effectiveness of eight bases on the debromination of 4,4'-dibromobiphenyl is compared. Tetramethylethylenediamine (TMEDA), a bidentate amine with mild coordinating ability, is the only one which can achieve a 100% debromination (i.e., a 100% yield of biphenyl) (Entry 5) [compared to 32% debromination (or 7% yield of biphenyl) (Entry 1) when a base is not added]. The effect of TMEDA is suggested to be threefold: (a) weak coordination to the electronically and coordinatively unsaturated intermediate in form of $[\text{Pd}(\text{dppf})(\text{tmeda})]$ thereby stabilizing the catalyst and minimizing catalyst decomposition. The weak donor ability of TMEDA ensures its cleavage upon entry of the substrate; (b) capture of BH_3 from BH_4^- provides an extra drive for hydride transfer to the Pd centre. The resultant $\text{TMEDA} \cdot 2(\text{BH}_3)$ adduct, which was verified

Table 2

Effects of different bases on the debromination of 4,4'-dibromobiphenyl at r.t. ($C_{12}H_8Br_2:NaBH_4:PdCl_2(dppf):base = 1:6.9:0.035:6.9$)

Entry	Base	Reaction time (min)	Conversion of 4,4'-DBB ^a %	Yield of 4-BB ^a %	Yield of biphenyl	Br% ^b
1	No base	10	56	49	7	32
2	EtNH ₂	10	67	58	9	38
3	Et ₃ N	10	92	57	35	63
4	EDA ^c	10	55	49	6	31
5	TMEDA ^c	10	100	0	100	100
6	DETA ^c	10	95	52	43	69
7	NDA ^c	10	100	31	69	84
8	TMNDA ^c	10	86	63	23	54
9	NaHCO ₃	10	65	56	9	37

Conditions: substrate = 4,4'-dibromobiphenyl (0.060 g, 0.19 mmol); catalyst = PdCl₂(dppf) (0.005 g, 0.0067 mmol); base (1.3 mmol) (as shown in table); reductant = NaBH₄ (0.05 g, 1.3 mmol). Order of reagent addition: substrate → catalyst → THF → base → reductant.^a 4,4'-DBB = 4,4'-dibromobiphenyl, 4-BB = 4-bromobiphenyl.^b Br% = debromination efficiency which is expressed in terms of the summation of the % yields of the (partially) debrominated products, proportionated by the degree of bromination, viz. (Yield of 4-BB) × 1/2 + (Yield of biphenyl) × 2/2.^c EDA = ethylenediamine; TMEDA = *N,N,N',N'*-tetramethylethylenediamine; DETA = diethylenetriamine; NDA = 1,8-naphthalenediamine; TMNDA = *N,N,N',N'*-tetramethyl-1,8-naphthalenediamine.

by GC/MS, could also serve as an additional hydride source [54]; (c) alternative debromination pathway through the elimination of HBr. Although such elimination is not a pre-condition according to the proposed mechanism, intermolecular elimination of HBr from the hydride intermediate and the oxidative addition product could also benefit the debromination. The promotional effect of TMEDA increases as its concentration increases. The maximum efficiency (100%) is reached when the base to substrate ratio reaches 1.4. This is consistent with the proposed roles played by TMEDA in the debromination mechanism.

Interestingly, subtle changes in the order of reagent additions can cause a significant effect on the rate of the debromination. When the substrate is added first, which is most reasonable, there are six possibilities (A–F) in the order of addition of the other reagents, viz. A: s → c → b → r; B: s → c → r → b; C: s → b → r → c; D: s → b → c → r; E: s → r → b → c; F: s → r → c → b [s = substrate (4,4'-dibromobiphenyl); b = base (TMEDA); c = catalyst (PdCl₂(dppf)); r = reductant (NaBH₄)]. Since the effects of A–C are similar to those of D–F respectively, we chose to examine the addition orders A–C in detail. Total destruction of 4,4'-

dibromobiphenyl and 100% yield of biphenyl under the order A, B and C are accomplished in 10, 35 and 25 min, respectively. Order A is thus the recommended sequence of addition whereby the reducing agent is added last. This shows the key role of the reducing agent and that the active catalyst, [Pd(dppf)], thus formed receives the best protection (by the solvent, base and substrate) in A. The relatively poor performance in B illustrates the supportive role played by the base and that it should be present in excess at the onset of the catalytic cycle.

When the debromination experiments are extended to 4-monobromobiphenyl, 4,4'-dibromobiphenyl and decabromobiphenyl as substrates, complete degradation of the substrate is achieved and the yields of biphenyl reach 100% after 4 min, 10 min and 40 h of reaction time. This is consistent with the proposed mechanism in which debromination occurs in sequence and the highly brominated derivatives break down to the lower bromo derivatives before biphenyl is obtained. The present results suggest clearly that highly brominated biphenyls can be degraded at r.t. as effectively as the lower brominated ones, albeit with a longer reaction time. This provides clear indication that other polybromoaromatics can undergo hydrodebromina-

tion at ambient conditions. This has important implications towards our target in devising an efficient and effective chemical means to detoxify and remove PBBs and PCBs from our environment.

3. Experimental

All reactions were carried out under an atmosphere of argon unless otherwise stated. All solvents were degassed before use. Approximately 20 ml of THF was used as solvent. 4-bromobiphenyl, 4,4'-dibromobiphenyl or decabromobiphenyl was used as the substrate. The catalysts tested were $\text{RuCl}_2(\text{dppr})(\text{PPh}_3)$ [55], $\text{RuCl}_2(\text{CO})(\text{dppr})$ [55], $\text{RuCl}_2(\text{CH}_3\text{CN})_2(\text{dppr})$ [55], $\text{Cu}(\text{PPh}_3)_2(\text{BH}_4)$ [56], $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ [57], $\text{NiCl}_2(\text{dppp})$ [58], $\text{NiCl}_2(\text{dppf})$ [59], $\text{PtCl}_2(\text{dppf})$ [60,61], $\text{PtCl}_2(\text{dppr})$ [62], $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ [63], $\text{Pd}(\text{OAc})_2$ supported by PPh_3 , dppf [64] or dppr [62], $\text{PdCl}_2(\text{PPh}_3)_2$ [65], $\text{PdCl}_2(\text{dppf})$ [47], $\text{PdCl}_2(\text{dppr})$ [62] and Pd/C (5% Pd). Five reductants were examined, viz. NaBH_4 , LiH , HCOOH , N_2H_4 and LiAlH_4 . The bases tested were NaHCO_3 , EtNH_2 , Et_3N , EDA (ethylenediamine), TMEDA (*N,N,N',N'*-tetramethylethylenediamine), DETA (diethylenetriamine), TMNDA (*N,N,N',N'*-tetramethyl-1,8-naphthalenediamine) and NDA (1,8-naphthalenediamine). The sequence of addition of the reagents was: substrate, catalyst, THF, base, and, lastly, reductant. The reaction was terminated by filtering the resultant suspension into a volumetric flask (50 ml). An internal standard, naphthalene (3.500 g/250 ml), was added and made up to the mark. The yields of the products were determined by GC (HP 5890 Series II) analysis. The column used was HP I cross-linked methyl silicon gum (25 m \times 0.32 mm \times 0.52 μm film thickness) whereas the chromatograms were plotted by HP 3396 Series II Integrator. Analysis was carried out by injecting 2.0 μm of a sample into the GC column. An initial temperature of 100°C was maintained for 3 min, after which it was increased at a rate of 5°C/min

before attaining a maximum temperature of 280°C after 39 min and this temperature was maintained for the last 5 min. 1.0 ml of naphthalene as an internal standard was added to the reaction mixture for GC analysis after the experiment was terminated.

The debromination efficiency (Br%) is expressed in terms of the summation of the % yields of the (partially) debrominated products, proportionated by the degree of bromination.

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