Preparation of phenolic compounds by decarboxylation of hydroxybenzoic acids or desulfonation of hydroxybenzenesulfonic acid, catalysed by electron rich palladium complexes†

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Phenolic compounds can be prepared by catalytic decarboxylation of 4-hydroxybenzoic acid or desulfonation of 4-hydorxybenzene sulfonic acid. Palladium complexes are shown to be highly active in the decarboxylation reaction, but complexes of platinum or ruthenium also show some activity in this reaction. Highly electron donating diphosphines such as BDTBPMB or monophosphines such as P^tBu_3 were found to be more effective than the less donating dppe or PPh_3. The addition of D_2O led to deuteration of the aromatic ring mainly in the position *ortho* to the hydroxyl group. Phenol can also be generated by SO_3 extrusion from 4-hydroxybenzenesulfonic acid catalysed by highly electron rich palladium complexes.

Introduction

The generation of C–C bonds is one of the most important steps in the synthesis of new organic molecules. For this transformation, new reactions are being developed everyday, giving organic chemists new tools for the synthesis of interesting molecules. However, very often the reactions need certain functional groups to lead the reaction down a specific pathway. This then improves the selectivity of the route. For example, the generation of C–C bonds by C–H activation is a highly desirable route due to the low levels of waste produced. One example is the Murai reaction,[1] which involves the ethylation of aromatic rings. This ethylation is often *ortho*-directed by a carbonyl group, which coordinates to the catalyst.

Often these directing groups must be removed to generate the desired molecules. However, the breaking of a C–C bond is also unusual and only a few routes have been described for this removal. One route to C–C bond breaking is decarboxylation. Some methods have been developed for this attractive reaction, making it more accessible. The most common catalytic system formed by copper salts with quinoline usually gives high conversion, but requires high temperatures (~200 °C).[2] The use of stoichiometric mercury salts significantly decreases the requirement for high temperatures.[3] Although the mercury system was proven to be highly robust, allowing the reaction to be carried out in the presence of oxygen and light, the toxicity of the mercury compounds has limited the use of this route.

Palladium chemistry seems to be an attractive alternative to improve the available methods. Recently, some procedures based on palladium catalysts have been described for decarboxylation,[4] or for decarboxylative cross coupling.[5,6] These methods yield high conversions and selectivities, but usually require a high loading of palladium and a long reaction time. This low activity of palladium complexes may be due to its low nucleophilicity. In this paper, we explore whether phosphine complexes of palladium may be more active in this reaction so that a decreased loading of palladium could be used to obtain high conversions.

Experimental

The metal complexes $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone), $[Pd(OAc)_2]$, $[Ru(acac)_3]$ (acacH = 2,4-pentanedione), CuI, $Cu(OAc)_2$ were purchased from Sigma-Aldrich and used as received. $[PdCl_2]$ was purchased from Lancaster and used as received. $[Rh(CO)_2(acac)]$ was purchased form Alfa Aesar and used as received. $[Ir(acac)(CO)_2]_2$ (Lancaster), $[Pd(MeCN)_4][BF_4]$ (Aldrich) and $[Pt(MeCN)_2Cl_2]$ (Aldrich) were stored under argon in a glove box. $[Pd(MeCN)_2Cl_2]$ was prepared according to literature.[7]

1,2-Bis(di*tert*butylphosphinomethyl)benzene (BDTBPMB, Lucite International), and tri*tert*butylphosphine (Aldrich) were stored and handled in a glove box. Bis(diphenylphosphino)-methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), 1,1′-bis(diphenylphosphino)ferrocene (dppf), triphenylphosphine, tribenzylphophine and tricyclohexylphosphine (Aldrich) were used as received. Chlorodiphenylphosphine (Aldrich) was stored under argon. 2,6-Bis((diphenylphosphino)methyl)pyridine,[8] and Xantphos[9] were prepared according to the literature. Triethylamine (Avocado) and 4-hydroxybenzenesulfonic acid (Aldrich) were degassed by the bubbling of argon, and stored under argon. 4-Hydroxybenzoic acid, sodium fluoride, sodium chloride, sodium bromide, sodium iodide, phenol, benzoic acid and silver triflate (Aldrich) were used as received.

Diethyl ether, toluene and tetrahydrofuran were dried on alumina columns, degassed by the bubbling of argon and stored under

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† Dedicated to Professor Douglas Lloyd in his 60th anniversary of teaching.

argon. Dry *o*-dichlorobenzene (Aldrich) was used as received. D_2O (Aldrich) was degassed by the bubbling of argon, and stored under argon.

Decarboxylation of 4-hydroxybenzoic acid. 4-Hydroxybenzoic acid (2 g, 14.5 mmol) and $Pd(OAc)_2$ (16 mg, 0.07 mmol) were placed in a degassed autoclave. BDTBPMB (60 mg, 0.15 mmol) was dissolved in toluene (10 mL) in a degassed Schlenk flask. The solution was transferred to the autoclave *via* cannula. The autoclave was heated at 140 °C for 5 h. The autoclave was then cooled and vented. The solution was analysed by GCFID and GCMS.

Gas chromatographic analyses were carried out on a Hewlett-Packard 5890 series gas chromatograph equipped with a flame ionisation detector for quantitative analyses and a Hewlett-Packard 5890 series mass selective detector for qualitative analyses. A SupelcoMDN-35 35% phenyl/65% methyl-polysiloxane column, 30 m long and 250 mm diameter was employed. The flow rate of helium was 2.0 cm^3 min^{-1} at 50 °C for 4 min then the temperature was raised at 20 °C min^{-1} to 130 °C, held for 2 min, then raised at 20 °C min^{-1} to 220 °C and held for 23.5 min.

Results and discussion

Decarboxylation

Treating 4-hydroxybenzoic acid with palladium(II) acetate (0.5 mol%) and BDTBPMB[10] at 140 °C produces phenol (72%) (Fig. 1). To develop a better knowledge of the activity of the phosphine-palladium complexes in this reaction, two blank assays were carried out (Table 1, entries 1 and 2). In the first of these, 4-hydroxybenzoic acid was heated in the absence of a catalyst.

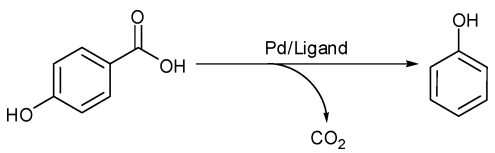

Fig. 1 Decarboxylation of 4-hydroxybenzoic acid.

Table 1 Preliminary results in the decarboxylation of 4-hydroxybenzoic acid[a]

Entry	Ligand	Yield (%)
1[b]	—	0
2	—	17
3	BDTBPMB (1 mol%)	72
4	BDTBPMB (2 mol%)	70
5	BDTBPMB (4 mol%)	74
6	dppm (1 mol%)	9
7	dppe (1 mol%)	65
8	dppp (1 mol%)	41
9	dppb (1 mol%)	10
10	dppf (1 mol%)	23
11	Xantphos (1 mol%)	28
12	2,6-Bis(Diphenylphosphinomethyl)pyridine (1 mol%)	14
13	PPh_3 (2 mol%)	20
14	PBz_3 (2 mol%)	60
15	PCy_3 (2 mol%)	67
16	P^tBu_3 (2 mol%)	78

[a] Conditions: 4-hydroxybenzoic acid (2 g, 14.5 mmol), palladium acetate (16 mg, 0.07 mmol), ligand (as described), toluene (10 mL), 140 °C, 5 h. [b] No palladium acetate was added.

No conversion was found (Table 1, entry 1). Low conversion was obtained in the reaction catalysed only by palladium acetate (Table 1, entry 2). Increasing the concentration of BDTBPMB did not make a significant difference in the conversion or stability of the catalyst (Table 1, entries 4 and 5). The reaction appears to be very specific. No conversion was observed when using benzoic, 3-hydroxybenzoic or 4-methoxybenzoic acids.

Assuming that a palladium complex of the diphosphine BDTBPMB is involved, a mechanism can be proposed (Fig. 2). The first step of this mechanism is the formation of the palladium complex **1** from palladium acetate and BDTBPMB. The reaction of this with 4-hydroxybenzoic acid could generate the hydride complex **2**, which can generate the aryl species **3** by decarboxylation. This species could then give the final product (the phenol) by reductive elimination, while regenerating the catalyst **1**. In this mechanism, we have proposed a Pd(0)/Pd(II) cycle as has been proven for ethene carbonylation using the same system.[10g] We note, however that the Pd(0) precursor, $[Pd_2(dba)_3]$ gives lower conversions than do Pd(II) precursors under the same conditions. It is known that $[Pd_2(dba)_3]$ forms [Pd(BDTBPMB)(dba)] on reaction with BDTPBMB, but that this protonates on an O atom of the dba ligand.[10j] Entry into the catalytic cycle from this complex can be inhibited so this might account for the low conversion using $[Pd_2(dba)_3]$. Without more detailed studies of the actual mechanism, the assignment of the oxidation states and structures of the various intermediates must be considered as tentative.

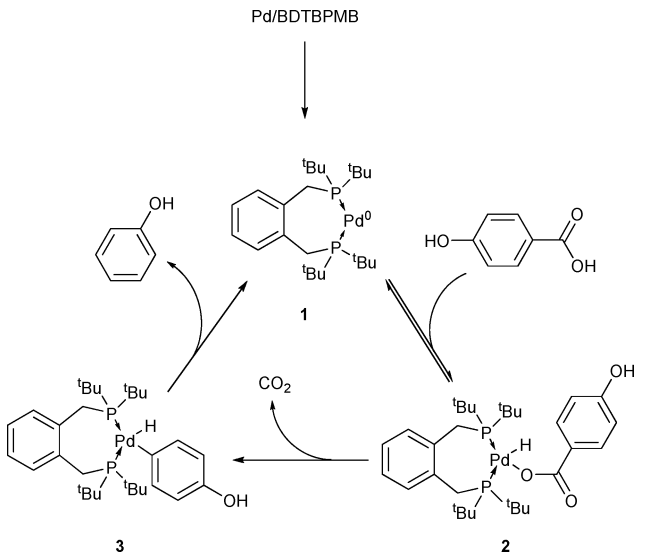

Fig. 2 Hypothetical mechanism of the decarboxylation reaction.

For a better understanding of the decarboxylation reaction, different phosphines were tested. Using diphosphines with a small bite angle, such as dppm, the conversion was much reduced (9%, Table 1, entry 6) compared with that obtained when using BDTBPMB. A significant increase in conversion (65%) was obtained when the bite angle of the phosphine (dppe) was increased (Table 1, entry 7) but the conversion decreased again when using dppp (41%), which has a bigger bite angle than dppe (Table 1, entry 8). This effect was more evident when dppb was used. Only low conversion (10%) was obtained under these conditions (Table 1, entry 9). Diphosphines with a bigger bite angle such as

dppf, Xantphos and 2,6-bis(diphenylphosphinomethyl)pyridine gave low conversions (Table 1, entries 10 to 12). In the case of monophosphines, the commonly-used triphenylphosphine gave only low conversion (Table 1, entry 13). When the reaction was carried out using PBz_3 or PCy_3, which are significantly more electron donating than PPh_3, moderate conversions were obtained (Table 1, entries 14 and 15). These conversions are much higher than those obtained using PPh_3. Therefore, it can be concluded that highly electron donating ligands facilitate the reaction. This was supported by the use of P^tBu_3, a highly electron donating phosphine, which gave high conversion (78%, Table 1, entry 16).

Having determined the general scope of the decarboxylation of 4-hydroxybenzoic acid catalysed by phosphine complexes of palladium, the effect of reaction parameters and additives was studied using the BDTBPMB/Pd system. Reducing the reaction temperature to 120 °C led to a substantial decrease in yield (Table 2, entry 1). No conversion was found at 100 °C (Table 2, entry 2). The use of microwave heating has often proven to be more efficient, lowering the reaction time and leading to high conversion at lower temperatures due to more efficient heating of the reaction mixture.[11] However, in this particular case, no conversion was obtained when the reaction was carried out under microwave heating at 100 °C over 30 min (Table 2, entry 3). Decarboxylation in diethyl ether give slightly lower yield (Table 2, entry 4) than when the reaction was carried in toluene (Table 1, entry 3). A low yield was obtained when 1,2-dichlorobenzene or tetrahydrofuran were used as solvents (Table 2, entries 5 and 6).

The addition of halides may play an important role in organometallic catalysis[12] This effect may be due to the coordination of the halide atom at some point in the catalytic cycle, therefore modifying the electron density of the catalyst by either σ or π-donation. When the reaction was carried out in the presence of NaI or NaBr, no appreciable differences (Table 2, entries 7 and 8) were obtained with respect to the results obtained under normal conditions (Table 1, entry 3). However, NaCl lowered the conversion significantly (Table 2, entry 9). This result is even more evident when NaF was used (Table 2, entry 10).

Other palladium precursors have been tested under the normal decarboxylation conditions. Using $[Pd(MeCN)_2Cl_2]$ as the precursor to the palladium-BDTBPMB complex, the reaction yielded moderate conversion (Table 2, entry 11), significantly lower than that obtained when the reaction was carried out under normal conditions using $[Pd(OAc)_2]$ as the precursor (Table 1, entry 3). This decrease in conversion can probably be attributed to the inhibiting effect of the two chloride atoms present in $[Pd(MeCN)_2Cl_2]$. (Table 2, entry 9). Therefore, it was thought that the addition of a chloride scavenger, such as a silver compound, may increase the conversion of the decarboxylation reaction when using $[Pd(MeCN)_2Cl_2]$. However, when silver triflate was added, only traces of product were obtained in the reaction (Table 2, entry 12). More success was obtained when the chlorides were removed by using $[Pd(MeCN)_4][BF_4]_2$ (Table 2, entry 13). The use of a palladium(0) precursor, $[Pd_2(dba)_3]$, gave only low conversion (Table 2, entry 14).

According to the proposed mechanism, the addition of base to the medium can generate three acid–base equilibria: the formation of benzoates and/or phenolates and, depending on the acidity of complexes **2** and **3**, the removal of the hydrido ligand attached to palladium by deprotonation of these complexes. It is plausible to think that these deprotonations can inhibit the catalytic cycle by removing active palladium species from the cycle.

To test this hypothesis, an experiment under normal conditions in the presence of Et_3N (200 mol% with respect to 4-hydroxybenzoic) was carried out. Unexpectedly, a similar conversion was obtained in this case (Table 2, entry 15). This result can be explained considering that BDTBPMB is a highly electron donating phosphine, and so its palladium complexes are highly

Table 2 Catalysed decarboxylation of 4-hydroxybenzoic acid[a]

Entry	Metal compound	Solvent	*T* (°C)	Additive	Yield (%)
1	$[Pd(OAc)_2]$	Toluene	120	—	17
2	$[Pd(OAc)_2]$	Toluene	100	—	0
3[b]	$[Pd(OAc)_2]$	Toluene	100	—	0
4	$[Pd(OAc)_2]$	Et_2O	140	—	62
5	$[Pd(OAc)_2]$	*o*-$C_6H_4Cl_2$	140	—	36
6	$[Pd(OAc)_2]$	THF	140	—	20
7	$[Pd(OAc)_2]$	Toluene	140	NaI (5 mol%)	70
8	$[Pd(OAc)_2]$	Toluene	140	NaBr (5mol%)	70
9	$[Pd(OAc)_2]$	Toluene	140	NaCl (5 mol%)	40
10	$[Pd(OAc)_2]$	Toluene	140	NaF (5 mol%)	8
11	$[Pd(MeCN)_2Cl_2]$	Toluene	140	—	45
12	$[Pd(MeCN)_2Cl_2]$	Toluene	140	AgOTf (2 mol%)	2
13	$[Pd(MeCN)_4][BF_4]_2$	Toluene	140	—	85
14	$[Pd_2(dba)_3]$	Toluene	140	—	21
15	$[Pd(OAc)_2]$	Toluene	140	Et_3N (200 mol%)	75
16	$[Rh(acac)(CO)_2]$	Toluene	140	—	55
17	$[Pt(MeCN)_2Cl_2]$	Toluene	140	—	27
18	$[Ru(acac)_3]$	Toluene	140	—	22
19	$Cu(OAc)_2$	Toluene	140	—	Traces
20	CuI	Toluene	140	—	0
21	$[Ir(acac)(CO)_2]$	Toluene	140	—	Traces

[a] Conditions: 4-hydroxybenzoic acid (2 g, 14.5 mmol), metal precatalyst (0.07 mmol), BDTBPMB (60 mg, 0.15 mmol), solvent (10 mL), 5 h. [b] The reaction was heated by microwave over 30 min.

basic. This favours protonation of the palladium centre, but the presence of additional base may deprotonate the metal centre and inhibit the catalysis.

In order to extend this study, a series of experiments with other metal catalysts in the presence of BDTBPMB was carried out. When the reaction was carried out using a rhodium catalyst ([Rh(acac)(CO)$_2$]), a moderate conversion was obtained (Table 2, entry 16). [Pt(MeCN)$_2$Cl$_2$] and [Ru(acac)$_3$] gave low conversions (Table 2, entries 17 and 18). Only traces of phenol were obtained when the reaction was catalysed by copper salts or the iridium complex, [Ir(acac)(CO)$_2$] (Table 2, entries 19, 20 and 21).

Considering the equilibrium that takes place in the presence of deuterated water (D_2O), d^2-phenol might be expected to form as a result of decarboxylation (Fig. 3). However, when the reaction was carried out under normal conditions with 2 mL of D_2O, compounds containing three or four atoms of deuterium were formed along with the expected d^1- and d^2-phenol (Table 3, entry 1). The deuteration was more appreciable when the volume of D_2O was increased to 10 mL. Under these conditions, d^4-phenol was the main product with some d^5-phenol and d^6-phenol also being formed (Table 3, entry 2).

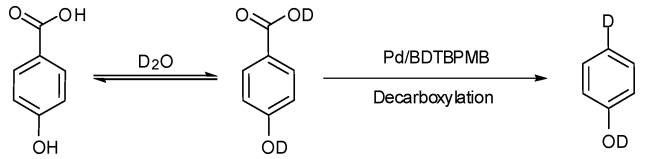

Fig. 3 Decarboxylation of 4-hydroxybenzoic acid in the presence of D_2O.

This increased D incorporation may perhaps be explained by catalytic C–H activation. It should be noted that the Pd/BDTBPMB system has been proven to be active in C–H activation in the position *ortho* to a carbonyl group on an aromatic ring[10l] and that Pd/BDTBPMB can promote C–H activation (β-H abstraction in alkene isomerisation).[10f] Therefore, it is plausible to propose C–H activation of the aromatic ring, followed by

Table 3 Deuteration of phenol formed during the decarboxylation of 4-hydroxybenzoic acid catalysed by [Pd(OAc)$_2$]/BDTBPMB in the presence of D_2O[a]

Entry	D_2O (mL)	Yield (%)	d^0	d^1	d^2	d^3	d^4	d^5	d^6
1	2	57	4	20	41	32	3	0	0
2	10	24	0	1	10	37	46	5	1
3[b]	10	0	22	47	28	3	0	0	0
4[c]	10	—	24	49	22	5	0	0	0
5[d]	10	—	6	22	35	28	9	0	0

[a] Conditions: 4-hydroxybenzoic acid (2 g, 14.5 mmol), [Pd(OAc)$_2$] (16 mg, 0.07 mmol), BDTBPMB (60 mg, 0.15 mmol), toluene (10 mL), 140 °C, 5 h. [b] Blank assay: labelling pattern for recovered 4-hydroxybenzoic acid (2 g, 14.5 mmol), toluene (10 mL), D_2O (10 mL), 140 °C, 5 h. [c] Blank assay: phenol (1.4 g, 14.5 mmol), toluene (10 mL), D_2O (10 mL), 140 °C, 5 h. [d] Blank assay: phenol (1.4 g, 14.5 mmol), benzoic acid (1.8 g, 14.5 mmol), toluene (10 mL), D_2O (10 mL), 140 °C, 5 h.

H/D exchange of the Pd–H with D_2O and reductive elimination, generating a C–D bond in the position *ortho* to the -COOH group. (Fig. 4, route A). Another possible explanation for this observation may be that H/D exchange occurs in the *ortho* and *para* positions of phenol. This reaction may be catalysed by the palladium complex (Fig. 4, route B) or may simply be non-catalysed due to the partial acidity present in those positions. An NMR study of the crude reaction showed that the deuteration was mainly found in the *ortho* position with respect to the hydroxyl group.

To test the possible involvement of a non-catalysed route, a blank assay was carried out (Table 3, entry 3). In the absence of a catalyst, a small amount of deuteration in the aromatic ring of the recovered 4-hydroxybenzoic acid was obtained (3% d^3-4-hydroxybenzoic acid), but this is insufficient to explain the results in the presence of Pd/BDTBPMB. A very similar labelling pattern for the recovered phenol to that obtained for recovered 4-hydroxybenzoic acid in the blank experiment was obtained when phenol was used in a blank reaction (Table 3, entry 4), but significantly more D incoporaton occurred when phenol was

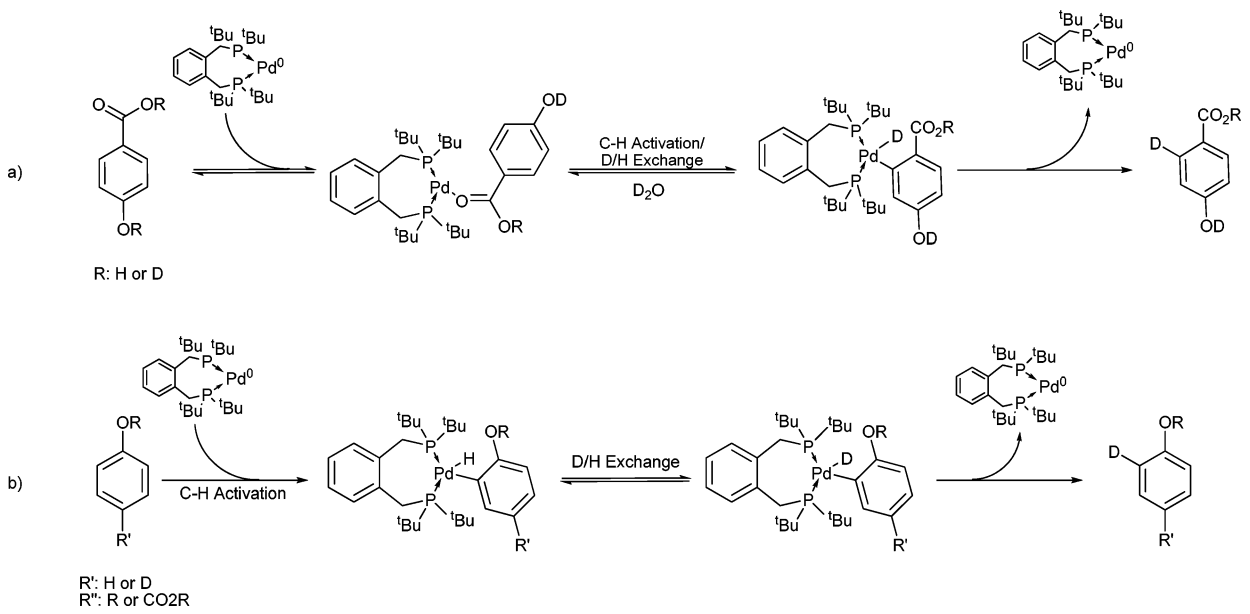

Fig. 4 Hypothetical mechanism for deuterium incorporation.

reacted in the presence of benzoic acid, so as to simulate the acidity of the catalytic solutions. In this case (Table 3, entry 5), 28% of the recovered phenol was d^3 and 9% was d^4, showing that acid conditions can affect the incorporation of D into phenol. However, this incoproration is still much less than in the presence of the Pd/BDTBPMB, which gives 37% d^3, 46% d^4 and small amounts of d^5 and d^6 phenol.

Although an increase in D_2O increased the amount of deuteration in the product, it also significantly lowered the yield of the decarboxylation (Table 3, entries 1 and 2). This can be explained by the instability of the catalyst in the presence of water.[13]

Desulfonation

Desulfonation of aromatic sulfonic acids is a difficult process, which usually requires sulfuric acid under harsh conditions,[14] or stoichiometric reductive agents such as RANEY® Nickel[15] to give good conversion. Hence, the possibility of palladium-catalysed desulfonation is considered to be a highly attractive route.

Comparing benzoic acid and benzenesulfonic acid, some similarities can be found. Both compounds possess an acidic proton, and the distance between the *ipso* carbon and this proton is two bonds. Thus, it is possible that the results obtained in the decarboxylation can be extrapolated to desulfonation by synthesising phenol from 4-hydroxybenzenesulfonic acid (Fig. 5).

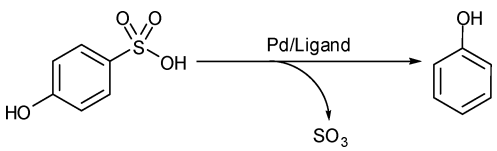

Fig. 5 Generation of phenol by extrusion of SO_3.

For the initial study, a blank assay was carried out. The substrate showed certain thermal instability, and the reaction without any catalyst gave moderate conversion (Table 4, entry 1). The optimum conditions obtained from decarboxylation were examined. After 5 hours, high conversion was obtained (Table 4, entry 2). The use of P^tBu_3 in place of BDTBPMB increased the conversion (Table 4, entry 3). However, PBz_3 did not provide significant activity (Table 4, entry 4). High conversion was obtained when $[Pd(OAc)_2]$ was replaced by $[Pd(MeCN)_4][BF_4]_2$ (Table 4, entry 5) for a reaction using BDTBPMB as the ligand.

In conclusion, systems formed from highly electron rich palladium complexes have been proven to be active in the decarboxylation of 4-hydroxybenzoic acid. Although the reaction required high temperatures (~140 °C), this temperature is significantly lower than that required in other catalytic systems such as the Cu/quinoline system.[2] Different phosphines and conditions were tested, and it can be concluded that highly electron donating phosphines such as BDTBPMB or P^tBu_3 are ideal for this reaction. $[Pd(MeCN)_4][BF_4]_2$ has also been proven to be an interesting alternative as the palladium precursor.

Different metal catalysts were tested for the decarboxylation, and it was found that palladium complexes are significantly more active that the other metals which were tested.

The addition of D_2O to the medium resulted in deuteration of the aromatic ring. This deuteration has been proven to be mainly in the position *ortho* to the hydroxyl group.

Palladium catalysts have been proven to be active in the desulfonation reaction by significantly lowering the reaction temperature and giving high conversion in this reaction.

Table 4 Elimination of SO_3 from 4-hydroxybenzenesulfonic acid[a]

Entry	Palladium species	Ligand	Yield (%)
1	—	—	44
2	$[Pd(OAc)_2]$	BDTBPMB (1 mol%)	70
3	$[Pd(OAc)_2]$	P^tBu_3 (2 mol%)	83
4	$[Pd(OAc)_2]$	PBz_3 (2 mol%)	44
5	$[Pd(MeCN)_4][BF_4]_2$	BDTBPMB (1 mol%)	93

[a] Conditions: 4-hydroxybenzenesulfonic acid (2.9 mL, 14.5 mmol), palladium precatalyst (0.7 mmol), ligand (as described), toluene (10 mL), 140 °C, 5 h.

Acknowledgements

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