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# Birch reduction of aryldialkylphosphine–boranes

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ABSTRACT

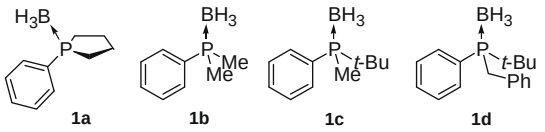
Aryldialkylphosphine–boranes undergo facile Birch-type reduction to afford cyclohexadienyldialkylphosphine–boranes in high yields. Judicious choice of the metal and the reaction conditions allows for complete elimination of the undesired P–Ph bond cleavage.



Apart from the established methods for the modification of organophosphorus compounds via transformations at phosphorus or through elaboration of their carbon chains,[1] structural modifications of *P*-aryl groups in organophosphorus compounds are markedly less developed and are effected mainly within the outer sphere of the aryl substituent.[2–6] The classical and synthetically useful method for arene modification leading to 1,4-cyclohexadienyl systems through a two-electron reduction by alkali metals, the Birch reduction, is only scarcely represented in organophosphorus chemistry. Examples include exploratory Birch reductions of some electron-rich tertiary triarylphosphines[7–9] and a more recent related dearomatisation of *N*-benzyl diarylphosphinamides through anionic cyclisation in the presence of a lithium base.[10,11] An efficient conversion of a common *P*-phenyl or *P*-aryl substituent into a non-aromatic 1,4-cyclohexadienyl group possessing an isolated double bond functionality bonded to a phosphorus atom could open new possibilities for the synthesis of many other structurally diverse phosphorus compounds. Typically, however, treatment of *P*-phenyl (or *P*-aryl) substituted organophosphorus compounds with alkali metals results in cleavage of the *P*-phenyl (or *P*-aryl) bond,[12–14] hence modification of the reaction conditions is required to shift the reaction towards the formation of the Birch-type products. Herein, we present our results on Birch reductions of dialkylphenylphosphine–boranes which are expected to furnish valuable electron-rich, protected trialkylphosphine- boranes.[15]

Four model dialkylphenylphosphine–boranes **1a–d** were selected for the test experiments (Fig. 1). They represent symmetrically and non-symmetrically substituted cyclic and acyclic systems and include one example possessing a cleavable benzyl substituent.

Preliminary experiments with **1a** performed under classical Birch conditions (2 equiv Na/MeOH, $NH_{3\ liq.}$) revealed that the reductions were not selective and the secondary phosphine–borane **2a**, a product of P–Ph bond cleavage, and the expected Birch reduction product **3a** were both detected in the reaction mixture along with some unreacted starting material (Scheme 1).




1a 1b 1c 1d

**Figure 1.** Model phosphine–boranes **1a–d**.

An increased amount of alkali metal and methanol in the reaction mixture shifted the reaction completely towards formation of the secondary phosphine–borane **2a** and the presence of the Birch reduction product **3a** was not detected (Scheme 1). Although the viability of the desired Birch reduction was in principle confirmed, it became apparent that more favourable reaction conditions were needed to secure the formation of the Birch–type product with higher selectivity. Thus, we screened the reactivity of the model phosphine–boranes **1a–d** with different alkali metals under modified Birch reduction conditions. The results are presented in Table 1.

Under standard conditions (−70 °C, 5 min) lithium was the least selective among the alkali metals tested and showed the greatest tendency to cause P–Ph bond cleavage (Table 1, entries 1 and 7). The reason may lie in its high redox potential (−3.04 V) which forces cleavage of the P–Ph bond. The tendency to favour P–Ph bond cleavage as compared to Birch reduction decreased on changing the metal from lithium to potassium (Table 1, entries 3, 6, 9 and 14) and to sodium (Table 1, entries 2, 5, 8 and 11), with the latter showing the highest selectivity towards the formation of 3-(1,4-cyclohexadienyl)-substituted phosphine–boranes.

The reduction of benzyl-*t*-butyl-phenylphosphine–borane (**1d**) was different from the three other boranes as even with sodium as the reducing agent, secondary phosphine–borane **4d** was obtained as the main product as a result of benzyl group cleavage (Table 1, entry 11). Shortening the reaction time had little or no influence on the product ratio (Table 1, entry 15). It appeared, however, that the proton source added to the reaction mixture could markedly influence both the product ratio and the reaction yields

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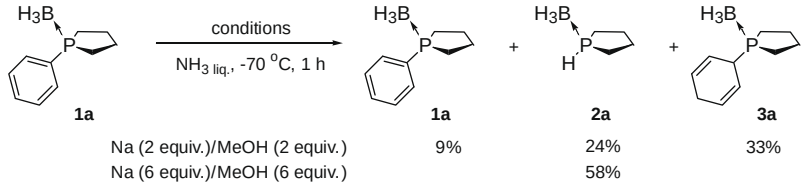
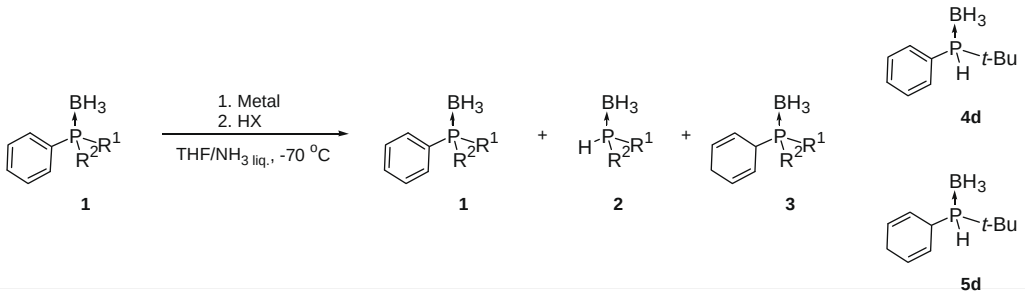



**Scheme 1.** Classical Birch reduction of **1a**.

**Table 1**
Alkali metal screening on the Birch reduction of aryldialkylphosphine–boranes **1a–d**

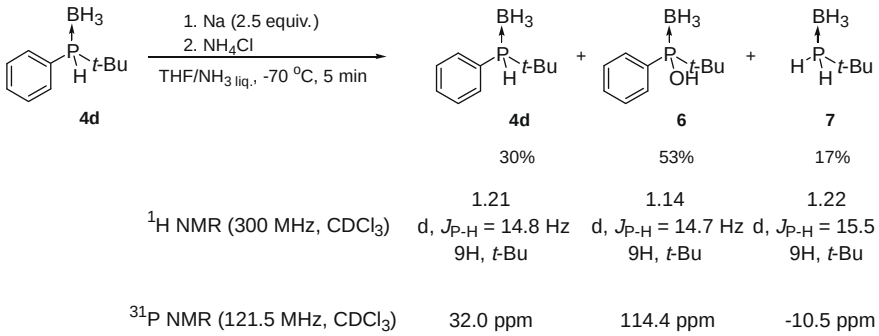



| Entry | Phosphine | Metal (equiv) | Time, HX | Yield % | | |
|---|---|---|---|---|---|---|
| | | | | **1** | **2** | **3** |
| 1 | **1a** | Li (2.5) | 5 min, $NH_4Cl$ | 21 | 37 | 19 |
| 2 | **1a** | **Na (2.5)** | **5 min**, **$NH_4Cl$** | – | – | **84** |
| 3 | **1a** | K (2.5) | 5 min, $NH_4Cl$ | – | 28 | 36 |
| 4 | **1b** | Li (2.5) | 5 min, $NH_4Cl$ | 23 | n.d. | 42 |
| 5 | **1b** | **Na (2.5)** | **5 min**, **$NH_4Cl$** | – | **n.d.** | **83** |
| 6 | **1b** | K (2.5) | 5 min, $NH_4Cl$ | 15 | n.d. | 68 |
| 7 | **1c** | Li (2.5) | 5 min, $NH_4Cl$ | 67 | traces | 15 |
| 8 | **1c** | Na (2.5) | 5 min, $NH_4Cl$ | 9 | 9 | 60 |
| 9 | **1c** | **K (2.5)** | **5 min**, **$NH_4Cl$** | – | – | **100** |
| 10 | **1d** | Li (2.5) | 5 min, $NH_4Cl$ | – | (**4d**) 62 | 8 |
| 11 | **1d** | Na (2.5) | 5 min, $NH_4Cl$ | 39 | (**4d**) 22 | 19 |
| 12 | **1d** | Na (2.5) | 5 min, AcOH (3.0 equiv) | 16 | (**4d**) 30 | 39 |
| 13 | **1d** | Na (2.5) | 5 min, TsOH (3.0 equiv) | 4 | (**4d**) 40 | 53 |
| 14 | **1d** | K (2.5) | 5 min, $NH_4Cl$ | – | (**4d**) 81 | 15 |
| 15 | **1d** | K (2.5) | 1 min, $NH_4Cl$ | 30 | (**4d**) 55 | 10 |
| 16 | **1d** | Mg (1.2) | 20 min, $NH_4Cl$ | 60 | – | 25 |
| 17 | **1d** | **Mg (4.0)** | **20 min**, **$NH_4Cl$** | – | – | **63 (5d) 15** |

n.d. = not determined.

by favouring the formation of the Birch-type product (Table 1, entries 12 and 13).

Evaluation of the results revealed that in the series studied, the selectivity towards the formation of the Birch-type products increased in the order Li < K < Na which is the reverse correlation of the metal redox potentials (Li −3.04 V, K −2.92 V, Na −2.71 V). A simple extrapolation of this correlation led to the assumption that magnesium (Mg −2.35 V) might be an even better reducing agent than sodium for the desired Birch reduction of arylphosphine–boranes. Indeed, treatment of **1d** with a solution of magnesium in liquid ammonia, prepared by electrolysis of metallic magnesium in the presence of ammonium tetrafluoroborate as a charge carrier, led to the formation of the desired Birch reduction product **3d** as the main product accompanied, somewhat unexpectedly, by *t*-butyl-3-(1,4-cyclohexa-dienyl)phosphine–borane **5d** (Table 1, entry 17). It appears that the latter compound is formed from the Birch




**Scheme 2.** Attempted Birch reduction of **4d**.

reduction product **3d** by a consecutive P–benzyl bond cleavage rather than by the reverse order of events. An attempted Birch reduction of *t*-butylphenylphosphine–borane **4d** under the same reaction conditions afforded only phosphinous acid–borane **6** and primary phosphine–borane **7** without any detectable traces of **5d**, along with some unreacted starting material (Scheme 2). This suggests that with **4d** as the starting material, deprotonation was the main reaction occurring under the applied conditions.

In conclusion, the presented results demonstrate that by judicious choice of the metal and the reaction conditions the Birch-type reduction of a *P*-phenyl ring in dialkylphenylphosphine–boranes can be accomplished with high selectivity and in high yields. Conditions have also been developed under which the reduction can be accomplished without cleaving the benzyl substituent present in the substrate.

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## Supplementary data

Supplementary data (full experimental details and analytical data of new compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.10.008.

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