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Isolation of the reactive intermediate in palladium-catalysed coupling of secondary phosphine–boranes with aryl halides

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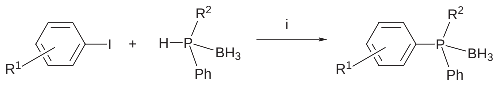
$Ph_2PH·BH_3$ is converted into its K salt with $KOSiMe_3$ in THF, and the anion reacts with (dppp)Pd(Ph)I to produce the complexed secondary phosphine–borane which decomposes to $PPh_3·BH_3$ at −10 °C; the C_6F_5 analogue has been crystallographically characterised.

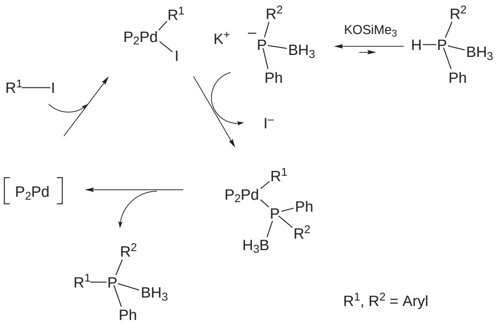
The ability of palladium complexes to effect catalysed σ-bond couplings has been extended significantly in recent years with some emphasis on the formation of C–heteroatom bonds.[1] Formation of C–P bonds has been achieved by the Pd-catalysed reaction of secondary phosphine oxides $R_2P(H)O$ with aryl triflates;[2] if the phosphine rather than the phosphine oxide is desired then either Ni or Pd catalysis with R_2PH as the nucleophile may be effective.[3] Less success has been achieved with secondary phosphine boranes, although the coupling reaction with ArI has been demonstrated.[4]

Following Imamoto's work,[4] satisfactory conditions were established for the catalytic synthesis of triarylphosphine–boranes, *e.g.* $Ar_3P·BH_3$ **1a–d** from ArI, but less cleanly from aryl triflates (Scheme 1). An important observation was that the reaction took place at ambient temperature or below (0 °C). Monitoring by ^{31}P NMR demonstrated that after completion of the reaction, only (dppf)Pd(Ar)I **2** was present when an excess of ArI was used.[5] Initial attempts at defining intermediates in the catalytic reaction were unsuccessful. When complex **2** (Ar = Ph) was generated *in situ* from either the corresponding (dppf)PdC_8H_8 complex[6] or (dppf)Pd(CH_2=$CHCO_2Me$)[7] rapid reaction with $K^+Ph_2P·BH_3^-$ (optimally generated from the secondary phosphine–borane and $KOSiMe_3$; quantitative by NMR spectroscopy) was observed at −70 °C in THF (Scheme 2). The product $Ph_3P·BH_3$ could be characterised in the solution above −30 °C, but intermediates were too ill-defined to characterise. Hence our attention shifted to the corresponding dppp complexes, known[5,8] to react more slowly than their dppf analogues in the reductive elimination step as a consequence of the smaller chelate bite angle.

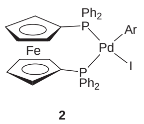


	R^1	R^2
1a	H	Ph
b	*p*-MeO	Ph
c	*o*-F	Ph
d	H	*o*-An

Scheme 1 *Reagents and conditions*: i, dppf$PdCl_2$ (5 mol%), K_2CO_3 (2 equiv.), MeCN, (for **1a**) room temp., 24 h, 92%; (for **1b**) room temp., 18 h, 89%; (for **1c**) 50 °C, 48 h, 74%; (for **1d**) 30 °C, 24 h, 90%.



Scheme 2



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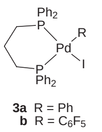

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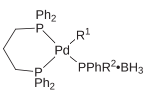
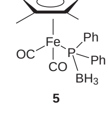
b R = C_6F_5



4a R^1 = Ph, R^2 = Ph
b R^1 = C_6F_5, R^2 = Ph



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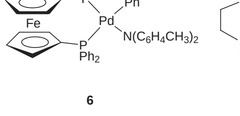

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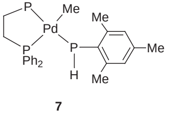

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Addition of $KOSiMe_3$ to an equimolar mixture of complex **3a** and $Ph_2PH·BH_3$ in THF at −70 °C led to an immediate and quantitative change to a single new species whose distinctive ^{31}P NMR spectrum is shown in Fig. 1, revealing the *trans*-relationship of (P1–Pd–P3–B). This is consistent with the structure **4a**, whose spectrum persisted up to 0 °C. At that temperature it decomposed (half-life *ca*. 30 min.) giving rise only to $Ph_3P·BH_3$ and an unidentified Pd product; when reaction was carried out in the presence of an excess of PhI, species **3a** was regenerated. The same type of transformation was shown to occur with other secondary phosphine–boranes and other PdArI complexes, as indicated. With more electron-withdrawing aryl groups in Ar–Pd, the elimination step was slower.

The linkage between the stoichiometric and catalytic reactions was strengthened by experiments where the breakdown of adduct **4a**, which led quantitatively to the formation of $Ph_3P·BH_3$ **1a**, was followed by ^{31}P NMR (Fig. 2). An identical reaction was carried out with a four-fold excess of both the

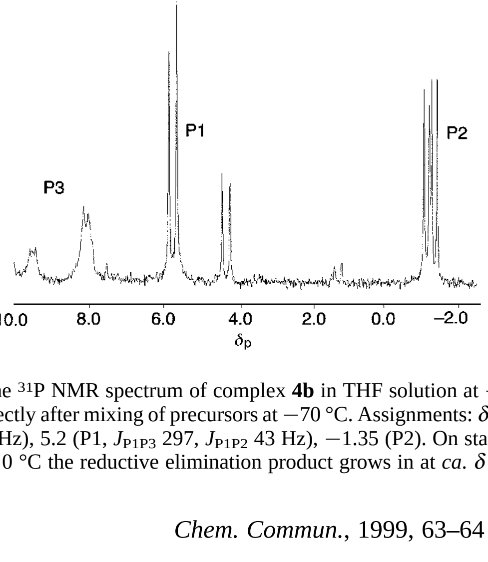

Fig. 1 The ^{31}P NMR spectrum of complex **4b** in THF solution at −50 °C, taken directly after mixing of precursors at −70 °C. Assignments: δ 9.0 (P3, J_{P2P3} 31 Hz), 5.2 (P1, J_{P1P3} 297, J_{P1P2} 43 Hz), −1.35 (P2). On standing at or above 0 °C the reductive elimination product grows in at *ca*. δ 1.

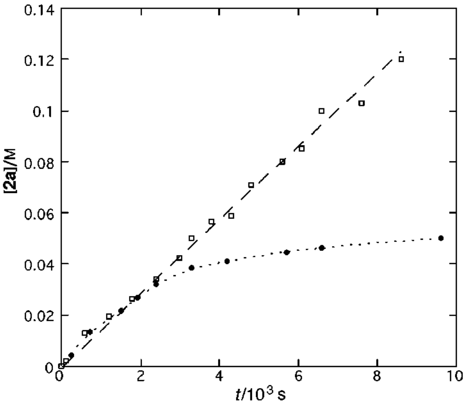

Fig. 2 (●) Stoichiometric formation of borane **1a** from breakdown of complex **4a**, 0.0532 M in THF at 0 °C, reaction followed by loss of **4a** in the ^{31}P NMR spectrum, dotted line is smoothed curve. (☐) Catalytic turnover of a mixture of PhI and $KPh_2P\cdot BH_3$ (both 0.213 M) in THF at 0 °C in the presence of complex **3a** (0.0532 M), followed by the appearance of borane **1a**. The dashed line is the predicted rate of turnover based on the rate-constant 2.9×10^{-4} s^{-1} derived for the stoichiometric process above.

anion and PhI, and catalytic turnover was followed by the appearance of **2a**. Within experimental error, the rate of catalytic turnover is defined by the rate of the reductive elimination step. This provides firm support for the mechanism suggested in Scheme 2. A correlation between reductive elimination and catalytic turnover has been observed for the C–C bond forming step in the breakdown of (dppf)Pd(Ph)Me.[5]

In the extreme case of **3b**, the intermediate complex **4b** was formed cleanly at −70 °C but was stable in solution at ambient temperature for a significant period of time (half-life *ca.* 96 h) and could be isolated by filtration through silica and precipitation. The isolated material gives rise to phosphine–borane **2e** on redissolution and prolonged standing, accompanied by some decomposition to the phosphine oxide. In characterisation of complex **4b**, we observed an unusual [M − 1] cation peak in the electrospray mass spectrum† which will be the subject of further investigation; such behaviour has previously been observed in the mass spectra of amine–boranes.[9] Recrystallisation (CH_2Cl_2, Et_2O) gave blocks suitable for X-ray analysis.‡ The structure is shown in Fig. 3 and demonstrates a slightly distorted square planar arrangement with the Pd–P bond of the phosphine borane only slightly longer than Pd–P bonds in the chelate (0.237 *vs.* 0.233 nm). The only previous example of a simple η^1-coordinated phosphine–borane structure is that of complex **5**, which is a stable isolable material.[10]

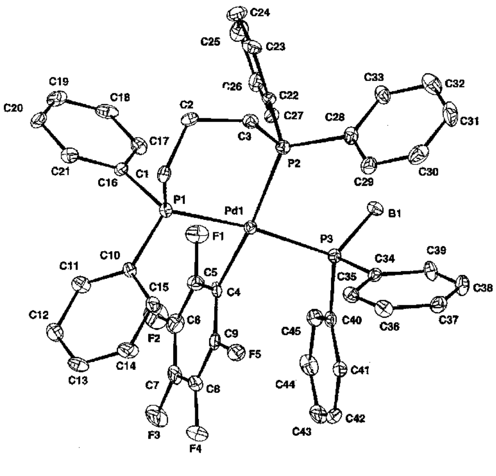

Fig. 3 The X-ray crystal structure of complex **4b**. Selected bond lengths and angles: Pd(1)–P(1) 2.337(2), Pd(1)–P(2) 2.334(2), Pd(1)–P(3) 2.375(2), Pd(1)–C(4) 2.053(6), P(3)–B(1) 1.925(6); C(4)–Pd(1)–P(2) 170.4(2), C(4)–Pd(1)–P(1) 87.6(2), P(2)–Pd(1)–P(1) 90.84(6), C(4)–Pd(1)–P(3) 88.0(2), P(2)–Pd(1)–P(3) 94.35(6), P(1)–Pd(1)–P(3) 173.09(6) B(1)–P(3)–Pd(1) 119.4(2).

These experiments indicate that the catalytic cycle for phosphinylation of aryl iodides with secondary phosphine–boranes is very simple, and the true reactive intermediate is amenable to characterisation. Unlike the corresponding intermediate **6** observed in catalytic amination,[11] it reacts rapidly below ambient temperature and very likely does not involve prior chelate dissociation. Studies of the reductive elimination of neutral Pd phosphido complex **7** and analogous (dppe)Pd η^1-Ar η^1-(PPh_2) complexes have been carried out by Glueck and co-workers,[12] who generated these intermediates by deprotonation of cationic phosphine complexes.

Future work will be directed towards stereochemical control of the P–Pd addition step with a view to applications in the asymmetric synthesis of arylphosphines.

We thank CNRS for granting leave of absence to A-C. G., EPSRC and NATO for support and Johnson-Matthey for loans of Pd salts. We greatly appreciate an open exchange of information with Professor David Glueck (Dartmouth).

Notes and references

† *Selected data* for **4b**: δ_P(CD_2Cl_2, 202 MHz) 14.3 (P3, $J_{1,3}$ 296), 1.95 (P1, $J_{1,2}$ 49.5, $J_{1,3}$ 296) −1.2 (P2, $J_{2,1}$ 49.5, $J_{2,3}$ 34); δ_B(CD_2Cl_2, 80 MHz) −33.2 (br s); δ_F(CD_2Cl_2, 235 MHz) −164.3 (m), −163.4 (m), −114.8 (m); δ_H(CD_2Cl_2, 500MHz) 1.90 (m, CH_2) , 2.35 (m, CH_2P) , 2.55 (m, CH_2P) , 6.95, 7.04, 7.2, 7.24, 7.3, 7.4 (H_{ar}); δ_C(CD_2Cl_2, 125 MHz) 18.1 (CH_2), 23.6 (CH_2P), 27.3 (CH_2P), 126.9 (Ar), 127.4 (Ar), 127.8 (Ar), 129.3 (Ar), 130.2 (Ar), 130.9 (Ar), 132.3 (Ar), 132.9 (Ar), 133.8 (Ar), 138.5 (Ar); *m/z* (ES, +30 V) 883.02 ([M − 1]$^+$, 100%), 717.06 ([M − C_6F_5]$^+$, 70%), 703.03 ([M − C_6F_5 − BH_3]$^+$, 68%).

‡ *Crystal data* for $C_{45}H_{39}BF_5P_3Pd\cdot 0.5CH_2Cl_2$ M_r = 927.35, monoclinic, space group $P2_1/c$, a = 11.481(2), b = 27.923(6), c = 14.005(3) Å, β = 107.15(3)°, U = 4290(2) Å^3, Z = 4, D_c = 1.436 g cm^{-3}, μ = 0.660 mm^{-1}, F(000) 1884, T = 150(2) K, Crystal size 0.18 × 0.14 × 0.10 mm, 6219 independent reflections, 15833 collected. Refinement method: full-matrix least-squares on F^2, Goodness-of-fit on F^2 = 0.877, Final R indices [$I > 2\sigma(I)$] R_1 = 0.0424, ωR_2 = 0.0951. CCDC 182/1086.

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