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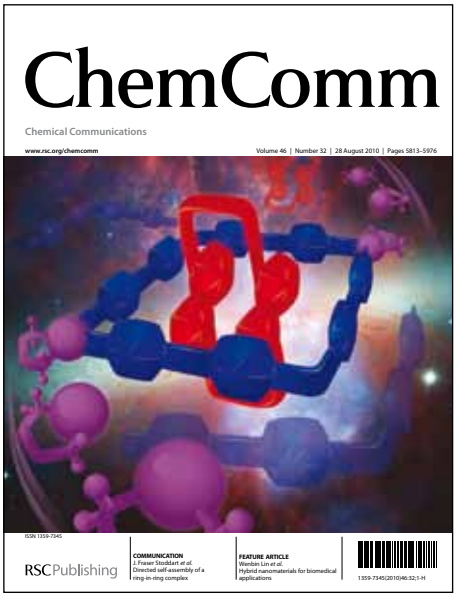

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Communication

A Simple Route to Azaborinylphosphines: Isoelectronic B-N Analogues of Arylphosphine Ligands

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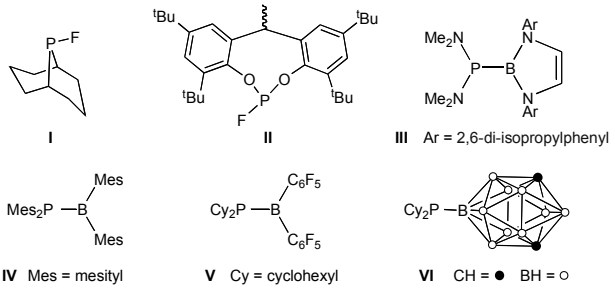
Azaborinylphosphines are readily prepared by the reaction of silylphosphines with a chloroborane under mild conditions; they are shown to contain P–B bonds that are sufficiently robust to allow these ligands to be used in homogeneous catalysis.

Phosphorus(III) ligands have been a cornerstone of much coordination chemistry and homogeneous catalysis for half a century.[1] The strength of P-C, P-N and P-O bonds makes ligands based on these bonds robust and amenable to design, in terms of stereoelectronic properties, to an unsurpassed level of finesse. As a result, a cornucopia of applications in catalysis has emerged based on P-donor complexes.

Ligands containing P–F and P–B bonds have been underdeveloped despite the fundamental interest arising from the extremes of electron density that these bonds might be predicted to confer on the P atom. Recently, fluorophosphines (e.g. fluorophobane **I**)[2] and fluorophosphites (e.g. **II**),[3] which contain inert P-F bonds, have not only been reported but have been shown to have potentially commercial applications in hydroformylation[4] or hydrocyanation[5] catalysis.

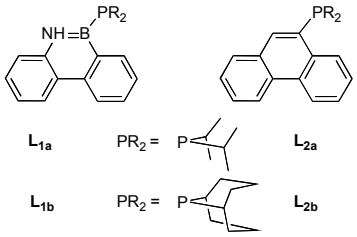
The low electronegativity of boron (B: 2.0; P: 2.2; C: 2.5) combined with the electron deficiency of BX_3 compounds makes the coordination chemistry of borylphosphines (phosphinoboranes) fascinating to explore. The reactive P–B bond can be stabilised by: (i) having π-donating NR_2 substituents on the B as in (**III**);[6] (ii) having very bulky aryl substituents on the B as in (**IV**);[7] (iii) enhancing the P–B π-bonding by having electron–accepting groups on B and electron-donating groups on P as in (**V**);[8,9] (iv) incorporating the B into a carborane as in (**VI**);[10] The proposition that the coordination chemistry of borylphosphines should be academically interesting has been validated by the report of the remarkably strong σ-donor capacity of (**VI**)[10] and the Pt(0) complex of (**V**) which is the first example of side-on, alkene-like coordination of phosphinoborane.[9] None of the previously reported phosphinoboranes have been shown to be ligands that support homogeneous catalysis.

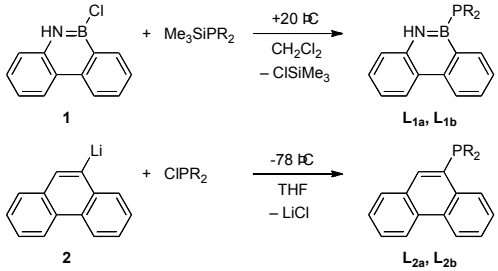
We are interested in the preparation of phosphorus ligands in which a BN formally replaces an isoelectronic CC group in an aromatic ring to produce azaborinyl analogues of aryl phosphines and compare their properties. It was predicted that the azaborinylphosphines would be stabilised by the aromaticity of the BN-containing ring and therefore may be



potentially useful as ligands. Here we describe a simple, high-yielding route to azaborinylphosphines, compare their structural and electronic properties with the parent arylphosphines, and show that these azaborinylphosphines form stable complexes with Rh which are catalysts for hydrogenation.

The first targets were phosphines $\mathbf{L_{1a}}$ and $\mathbf{L_{1b}}$ derived from the BN analogue of phenanthrene and these were to be compared with the all-carbon analogues $\mathbf{L_{2a}}$ and $\mathbf{L_{2b}}$. The readily prepared[6,7] chloroborane **1** was the proposed precursor to $\mathbf{L_{1a}}$ and $\mathbf{L_{1b}}$. However, **1** did not react with the secondary phosphines HP^iPr_2 or HPPhob in the presence of amine (NEt_3 and NEt^iPr_2) bases and treatment of **1** with $LiPR_2$ led to the formation of secondary phosphine R_2PH (~70%, by ^{31}P NMR spectroscopy) and a mixture of several B-containing products (according to ^{11}B NMR spectroscopy). It was reasoned that a non-basic source of PR_2 was required and so we turned our attention to silylphosphines. The chloroborane **1** reacts with $Me_3SiP^iPr_2$ or $Me_3SiPPhob$‡ rapidly and quantitatively under mild conditions to give the desired azaborinylphosphines $\mathbf{L_{1a}}$ and $\mathbf{L_{1b}}$ (Scheme 1). The facility of these reactions was a surprise since it had been reported[11] that formation of $[Et_2P–BZ_2]_n$ from the reaction of Et_2PSiMe_3 with $ClBZ_2$ (Z = F, Cl, Br, O^nBu or ^nPr) required several hours at high temperatures (120–180 °C) and in the case of Z = NMe_2, the route was unsuccessful.

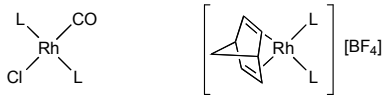




Scheme 1. Synthesis of the azaborinylphosphines and their carbon analogues

The phenanthryl analogues $\mathbf{L_{2a}}$ and $\mathbf{L_{2b}}$ are new compounds‡ that have been prepared from the lithio reagent according to Scheme 1 which is a modification of the method reported for the preparation of the 9-diphenylphosphinophenanthrene.[12] The broad ^{31}P NMR signals for the azaborinylphosphines are at -49.1 ppm for $\mathbf{L_{1a}}$ and -64.5 ppm for $\mathbf{L_{1b}}$ which are both ~ 40 ppm to high field of the phenanthrene analogues $\mathbf{L_{2a}}$ (-7.2 ppm) and $\mathbf{L_{2b}}$ (-23.8 ppm) but close in chemical shift to the silylphosphine precursors $^{i}Pr_2PSiMe_3$ (-44.0 ppm) and $PhobPSiMe_3$ (-67.4 ppm). The similarity of the δ_P values for the analogous P–B and P–Si compounds is an NMR manifestation of the B-Si diagonal relationship.

In order to compare the donor properties of ligands $\mathbf{L_{1a}}$ and $\mathbf{L_{1b}}$ with $\mathbf{L_{2a}}$ and $\mathbf{L_{2b}}$, the corresponding *trans*-[RhCl(CO)L_2] complexes **3a**,**b** and **4a**,**b** were prepared and their crystal structures determined (Figs. 1 and 2). Complexes **3a** and **3b** are the first examples of rhodium complexes of phosphinoboranes.[13] The structures of azaborinylphosphine complex **3a** and its phenanthrylphosphine analogue **4a** are isomorphous and all the Rh-ligand bonds are essentially the same lengths (Fig. 1). The conformations of the ligands in complexes **3b** and **4b** featuring the PhobP group are quite different from their $^{i}Pr_2P$ analogues **3a** and **3b**. The 90˚ torsion angles, Rh–P–B–N in **3b** and Rh–P–C–C in **4b**, contrast with the *ca*. 140˚ for these angles in the analogues **3a** and **4a**. One plausible explanation for this difference is that the phobane ligands are prevented from adopting a 140˚ conformation because of unfavourable clashing of the 10-X–H (X = N or C) with axial protons within the phosphabicycle that would result; the rigidity of the phobane makes these clashes unavoidable whereas the greater rotational freedom of the isopropyl groups of the $^{i}Pr_2P$ group allows the 140˚ conformer to be adopted.[14] Another striking structural difference is that the PhobP complexes **3b** and **4b** exhibit extensive π-stacking between the aromatic units whereas the $^{i}Pr_2P$ analogues **3a** and **4a** do not; this is illustrated in the crystal packing structures for **3b** and **4b** shown in Fig. 3.



3a, **3b** L = $\mathbf{L_{1a}}$, $\mathbf{L_{1b}}$ **5a**, **5b**
4a, **4b** L = $\mathbf{L_{2a}}$, $\mathbf{L_{2b}}$ **6a**, **6b**

Table 1. IR[a], ^{31}P NMR[b] and catalytic[c] data for the Rh complexes.

Complex	ν(CO) / cm^{-1}	δ_P / ppm	J_{RhP} / Hz	Rel. TOF
3a	1951	0.8	~120[d]	-
3b	1946	-17.6	~120[d]	-
4a	1966	33.8	121	-
4b	1951	15.3	118	-
5a	-	-20.6	129	15
5b	-	-30.7	130	≥30
6a	-	19.3	146	1
6b	-	-2.0	152	12

[a] Measured in CH_2Cl_2. [b] Measured in CD_2Cl_2. [c] Cyclohexene hydrogenation carried out in CD_2Cl_2 with ~10 mg cyclohexene, 5 mol% catalyst and 2 bar H_2. Conversions were monitored by ^{1}H NMR spectroscopy. [d] Estimated from weak NMR signals. [e] Relative TOF were estimated from rates of product formation at low conversion. The value of TOF for **6a** was *ca.* 8 h^{-1}

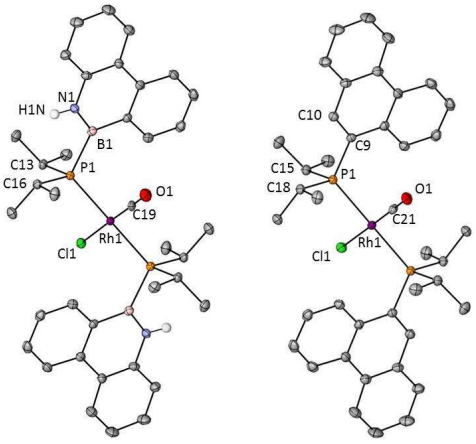


Fig. 1. Thermal ellipsoid (50% probability) plot of **3a** (left) and **4a** (right), omitting all C-H hydrogen atoms. Selected bond lengths [Å] and angles [°] for **3a**: Rh1-P1 2.3407(6), C19-O1 1.171(6), N1-B1 1.406(3), P1-B1 1.957(3), Rh1-P1-B1-N1 143.64. For **4a**: Rh1-P1 2.3369(6), C21-O1 1.147(7), P1-C9 1.843(2), Rh1-P1-C9-C10 142.61.

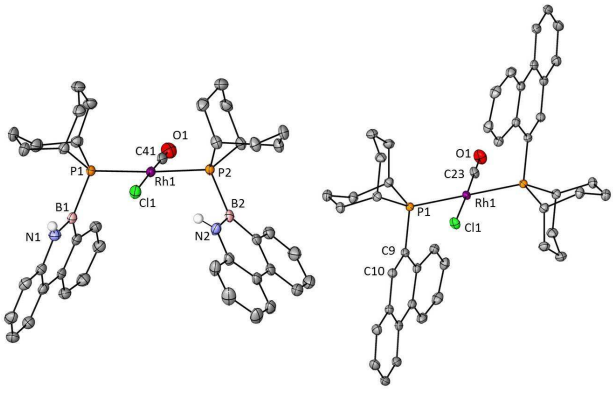


Fig. 2. Thermal ellipsoid (50% probability) plot of **3b** (left) and **4b** (right), omitting all C-H hydrogens. Selected bond lengths [Å] and angles [°] for **3b**: P1-Rh1 2.3296(5), P2-Rh1 2.3304(5), C41-O1 1.078(3), B1-P1 1.941(2), B2-P2 1.962(3), B1-N1 1.404(3), B2-N2 1.408(4), Rh1-P1-B1-N1 96.50, Rh1-P2-B2-N2 -71.78. For **4b**: Rh1-P1 2.3313(3), O1-C23 1.155(4), P1-C9 1.8281(11), Rh1-P1-C9-C10 98.72.

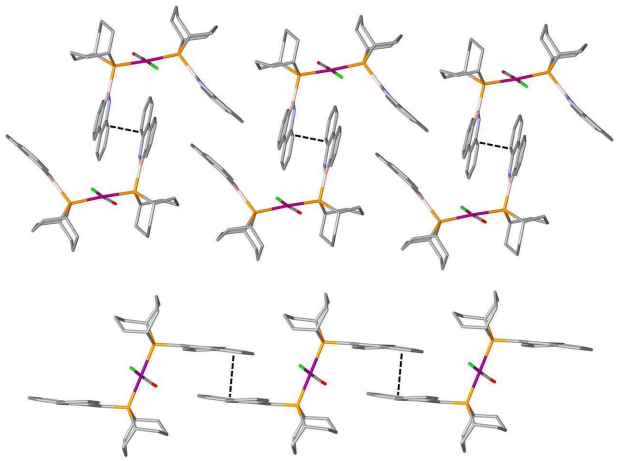


Fig. 3. Crystal packing structures of **3b** (top) and **4b** (bottom).

The ν(CO) values for **3a,b** and **4a,b** show that the B-N ligands $\mathbf{L_{1a}}$ and $\mathbf{L_{1b}}$ are more electron-donating than their C-C counterparts $\mathbf{L_{2a}}$ and $\mathbf{L_{2b}}$ (Table 1), as was expected from the prediction that the boryl substituent would make the P-donor electron-rich.[10] It was hoped that the borylphosphines $\mathbf{L_{1a}}$ and $\mathbf{L_{1b}}$ would be members of a new class of ligands for catalysis. Therefore $[Rh(nbd)_2][BF_4]$ was reacted with 2 equivalents of $\mathbf{L_{1a}}$ and $\mathbf{L_{1b}}$ to generate single products, assigned the structures **5a** and **5b** on the basis of their ^{31}P NMR spectra (see Table 1 for the data) which were tested for the catalytic hydrogenation of cyclohexene. The catalytic results obtained for **5a** and **5b** and the phenanthryl analogues **6a** and **6b** are collected in Table 1. In all cases 100% conversion of the cyclohexene was observed. It is clear from Table 1 that (a) the borylphosphine complexes **5a** and **5b** are more efficient catalysts than their phenanthrene phosphine counterparts **6a** and **6b**; (b) the bicyclic phosphine complexes **5b** and **6b** are more efficient catalysts than their acyclic counterparts **5a** and **6a**.

Addition of water (*ca.* 0.1% by volume) to CH_2Cl_2 solutions of the borylphosphines $\mathbf{L_{1a}}$ or $\mathbf{L_{1b}}$ led to 100% hydrolysis to R_2PH and 10-hydroxy-9,10-azabora-phenanthrene in less than 5 min. In similar aqueous media, the Rh-coordinated $\mathbf{L_{1b}}$ in **5b** was significantly more resistant to hydrolysis than the free ligand with 75% of the complex remaining after 5 min. Nevertheless it was possible that the favourable catalytic results given in Table 1 for the borylphosphine complexes were the result of hydrolysis by adventitious water giving a highly active catalyst. To refute this proposition, the hydrogenation was carried out using a sample of **5b** which had been deliberately hydrolysed prior to the catalysis. Using this degraded catalyst, after 5 min, only *ca.* 5% cyclohexene conversion was observed, compared to the 100% conversion when pure **5b** was used as the catalyst.

In conclusion, it has been shown that the reaction of silyl phosphines $^{i}Pr_2PSiMe_3$ and $PhobPSiMe_3$ with 9-aza-10-bora-10-chlorophenanthrene afforded the corresponding azaborinyl phosphines under very mild conditions. The generality of this P–Si → P–B conversion for the synthesis of BN analogues of arylphosphines is currently under investigation. Moreover azaborinyl phosphines have proved to be competent ligands for rhodium-catalysed hydrogenation and indeed produce more active catalysts than their arylphosphine analogues.

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Notes and references

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† Electronic Supplementary Information (ESI) available: syntheses, experimental details and crystallographic data. CCDC 973285-973291. For ESI and crystallographic data in CIF format see DOI: 10.1039/b000000x/

‡ The crystal structures of $PhobPSiMe_3$, $\mathbf{L_a}$ and $\mathbf{L_{2b}}$ (as a mixture with its oxide) are described in the ESI.

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