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Ligand Design

Single Oxygen-Atom Insertion into P–B Bonds: On- and Off-Metal Transformation of a Borylphosphine into a Borylphosphinite

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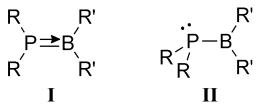
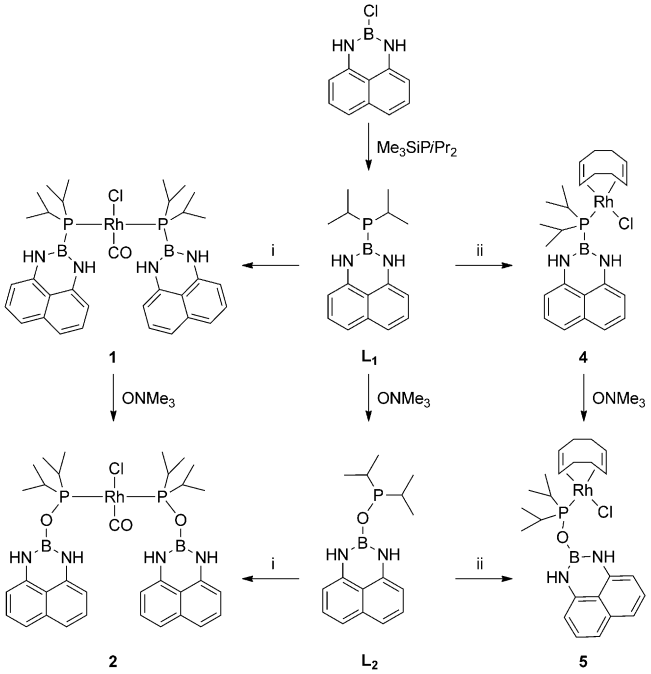
Abstract: An oxygen atom is selectively inserted into the P–B bond of a borylphosphine ($\mathbf{L_1}$) by reaction with Me_3NO to afford the corresponding borylphosphinite ($\mathbf{L_2}$). This transformation can also be effected when $\mathbf{L_1}$ is coordinated to rhodium. The ν(CO) values for *trans*-[RhCl(CO)(L)$_2$] reveal very different electronic properties for coordinated $\mathbf{L_1}$ and $\mathbf{L_2}$ which translate into the strikingly different performances of the complexes [RhCl(L)(cod)] (L = $\mathbf{L_1}$ or $\mathbf{L_2}$, cod = 1,5-cyclooctadiene) in hydrosilylation and hydroboration catalysis.

The varied chemistry of phosphinoboranes can be rationalised by reference to the P–B bonding, which can be described by the Lewis structures **I** (phosphinoborane) and **II** (borylphosphine) shown below. The P–B bond order and its reactivity depend on the stereoelectronic effects of the P- and B-substituents.[1] Phosphinoboranes have been shown to heterolytically cleave H_2,[2] dehydrogenate amine-boranes[3] and react with compounds containing C≡N, C=O and C=C functionalities.[4] Furthermore, they have the capacity to ligate as κ^1-P[1a] or η^2-P=B[5] and we have shown that they can be ligands for efficient homogeneous alkene hydrogenation catalysis.[6]



Here we report the insertion of an oxygen atom (from O_2 or *N*-oxides) into a P–B bond to convert a borylphosphine into a borylphosphinite, which have contrasting σ-donor/π-acceptor ligand properties and show very different performance in catalysis. The insertion of an oxygen atom into single bonds is rare[7] outside the realm of monoxygenases.[8] Peroxides will insert O atoms into the C–C bond of ketones to give esters (the Bayer–Villiger reaction[9]) and amine-oxides[10] have been used for oxygen insertion into Si–Si,[11] C–B,[12] B–B[13] and B–Ru[14] bonds. The insertion of S and Se atoms into P–B bonds of 1-phospha-2-bora-acenaphthene has been previously reported[15] but, in other cases, elemental chalcogens have been shown to react with compounds containing P–B bonds to give P^V products.[16]

The borylphosphine $\mathbf{L_1}$ was prepared in quantitative yield from the chlorosilane elimination reaction[6,17] shown in Scheme 1; $\mathbf{L_1}$ has been fully characterised (see the Supporting Information for the data), including its ^{31}P NMR spectrum, which shows a signal at −48.4 ppm that is broad ($w_{1/2}$ = 67 Hz) due to unresolved coupling to quadrupolar ^{11}B. Treatment of $\mathbf{L_1}$ with one equivalent of Me_3NO (TMAO) led to complete conversion to a product assigned structure $\mathbf{L_2}$ on the basis of the following NMR data. The ^{31}P NMR signal for $\mathbf{L_2}$ is a sharp singlet (consistent with the loss of $^1J_{PB}$ coupling) at 134.8 ppm, a chemical shift that is similar to that of the phosphinite *i*Pr$_2$POPh (149 ppm).[18] The ^{11}B NMR chemical shift of $\mathbf{L_2}$ is 22.2 ppm (compared with 32.0 for $\mathbf{L_1}$).



Scheme 1. Synthesis of ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ and complexes **1**, **2**, **4** and **5** via off-metal and on-metal routes. Reagents: i) [RhCl(CO)$_2$]$_2$; ii) [RhCl(cod)]$_2$.

Solid TMAO is a convenient reagent for the conversion of $\mathbf{L_1}$ to $\mathbf{L_2}$ because it is easy to control the stoichiometry and the volatile NMe_3 by-product is readily removed, although the

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same transformation was observed in the reaction of $\mathbf{L_1}$ with O_2.

Thus, when a CH_2Cl_2 solution of $\mathbf{L_1}$ was stirred under 2 atm of O_2 for 2 days, unexpectedly the main species present (ca. 80% according to ^{31}P NMR spectroscopy) was unreacted $\mathbf{L_1}$ and, of the several products detected, $\mathbf{L_2}$ was prominent (see the Supporting Information for the ^{31}P NMR spectrum of the reaction mixture).

The complexes *trans*-[RhCl(CO)(L)$_2$] (**1**, L = $\mathbf{L_1}$) and (**2**, L = $\mathbf{L_2}$) were prepared (see Scheme 1) in order to compare the donor characteristics of the two ligands (see Table 1). IR spectroscopy

Table 1. IR[a] and ^{31}P NMR[b] data for the complexes *trans*-[RhCl(CO)(L)$_2$].

Complex	Ligand	ν(CO) [cm^{-1}]	δ_P [ppm]	$^1J_{PRh}$ [Hz]
1	$\mathbf{L_1}$	1956	−4.9	≈110 (br)
2	$\mathbf{L_2}$	1977	145.1	125
3	$\mathbf{L_3}$	1984	161.8	134
[RhCl(CO)(*i*Pr$_2$PPh)$_2$][19]	*i*Pr$_2$PPh	1965	42.6	124.4

[a] Measured in CH_2Cl_2. [b] Measured in CD_2Cl_2 (for **1** and **2**) or $CDCl_3$ (for **3** and *trans*-[RhCl(CO)(*i*Pr$_2$PPh)$_2$]).

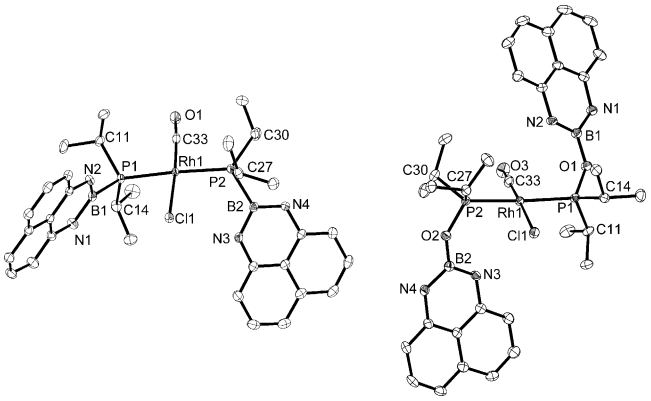


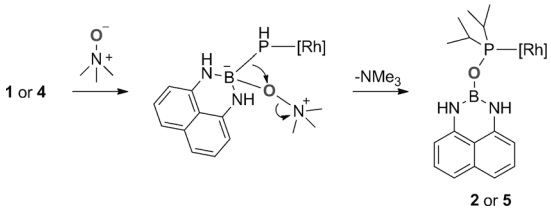
Figure 1. Thermal ellipsoid (50% probability) plot of **1** (left) and **2** (right), omitting all hydrogen atoms. Selected bond lengths [Å] and angles [°] for complex **1**: Rh1–C33 1.7967(15), Rh1–P1 2.3333(4), Rh1–P2 2.3574(4), Rh1–Cl1 2.3888(3), P1–B1 1.9585(16), P2–B2 1.9533(16), P1–C11 1.8584(14), P1–C14 1.8526(15), P2–C27 1.8634(15), P2–C30 1.8562(15), N1–B1 1.415(2), N2–B1 1.406(2), N3–B2 1.410(2), N4–B2 1.4129(19), O1–C33 1.1548(18), B1-P1-P2-B2 96.2. Complex **2**: Rh1–C33 1.813(2), Rh1–P1 2.3176(6), Rh1–P2 2.3278(6), Rh1–Cl1 2.3670(6), P1–O1 1.6254(17), P2–O2 1.6183(16), P1–C11 1.827(2), P1–C14 1.837(2), P2–C27 1.838(2), P2–C30 1.827(2), C33–O3 1.152(3), O1–B1 1.385(3), O2–B2 1.379(3), B1–N1 1.416(3), N2–B1 1.411(3), N3–B2 1.415(3), N4–B2 1.417(3), O1-P1-P2-O2 143.8.

revealed a difference of 21 cm^{-1} between the ν(CO) stretching frequencies for **1** (1956 cm^{-1}) and **2** (1977 cm^{-1}), consistent with $\mathbf{L_1}$ being a much more electron-donating ligand than $\mathbf{L_2}$. Comparison of these values to those for the analogues *trans*-[RhCl(CO)(L)$_2$] for L = *i*Pr$_2$PPh (1965 cm^{-1})[19] and L = *i*Pr$_2$POPh ($\mathbf{L_3}$) (**3**, 1984 cm^{-1}; see the Supporting Information for experimental details) shows that, as previously demonstrated,[17] the naphthalene-derived boryl fragment is more electron donating than phenyl. The ^{31}P NMR spectra of **1** and **2** were markedly different: the signal for **1** is a doublet at −4.9 ppm ($^1J_{PRh}$ ≈110 Hz), which is broad due to the unresolved $^1J_{PB}$ coupling, whereas the signal for **2** is a sharp doublet at 145.1 ppm ($^1J_{PRh}$ = 125 Hz).

Complexes **1** and **2** have been characterised crystallographically and as is clear from Figure 1, the conformations adopted in the solid state are quite different (B1-P1-P2-B2 and O1-P1-P2-O2 torsion angles of 96.2° and 143.8° in **1** and **2** respectively). The B–O bond lengths in **2** (1.385(3) and 1.379(3) Å) are typical of single bonds with little evidence of B–O π-overlap (cf. the B=O determined in an oxoborane was 1.304(2) Å[20]).

It is of interest to compare the product of oxidation of secondary phosphines R_2PH with that of the boryl phosphine $\mathbf{L_1}$. Oxidation of secondary phosphines gives P^V secondary phosphine oxides $R_2P(=O)H$ as the major species in prototopic equilibrium with their P^{III} hydroxyphosphine R_2POH tautomers. In the oxidation of $\mathbf{L_1}$ by TMAO, no P^V products were detected. The results of oxidation of coordinated $\mathbf{L_1}$ described below show that a mechanism in which the phosphorus lone pair is not involved in the oxygenation of $\mathbf{L_1}$ to give $\mathbf{L_2}$ is feasible.

Addition of two equivalents of TMAO to a solution of complex **1** in CH_2Cl_2 gave **2** cleanly and in less than 5 min according to ^{31}P NMR spectroscopy. The chemoselectivity of this oxidation for the P–B bond was a surprise considering the complex has a low-valent Rh^I centre as well as a coordinated CO, which might be expected to react with TMAO to generate coordinative unsaturation by release of CO_2.[21] The facility with which **1** is converted to **2** shows that the P lone pair need not be involved in the oxygenation of the P–B bonds of $\mathbf{L_1}$ and leads to the mechanism suggested in Scheme 2, in which



Scheme 2. Suggested mechanism for the on-metal oxygen insertion into **1** and **4**.

a Lewis acid-base adduct is the intermediate; this mechanism is reminiscent of that suggested by Yamashita et al.[14] for the oxygenation of a B–Ru bond with morpholine-*N*-oxide (NMO).

The consequences of the different ligating properties of borylphosphine $\mathbf{L_1}$ and borylphosphinite $\mathbf{L_2}$, in catalysis have been investigated by comparing the performance of complexes of the type [RhCl(L)(cod)][22] (cod = 1,5-cyclooctadiene) in hydrosilylation and hydroboration catalysis (see below). The reaction of $\mathbf{L_1}$ or $\mathbf{L_2}$ with [RhCl(cod)]$_2$ produced [RhCl(L)(cod)] (**4**, L = $\mathbf{L_1}$; **5**, L = $\mathbf{L_2}$). Complex **5** was also prepared quantitatively by the addition of TMAO to **4** (see Scheme 1 and the Supporting Information for the characterising data). Crystals of **4** and **5** suitable for X-ray diffraction were grown from CH_2Cl_2/pentane and CH_2Cl_2/hexane respectively and their crystal structures are

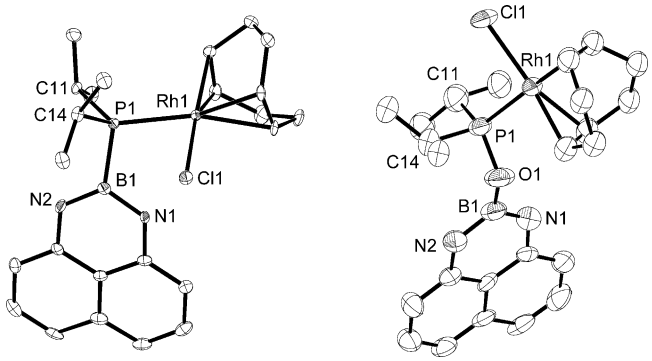


Figure 2. Thermal ellipsoid (50% probability) plot of **4** (left) and **5** (right), omitting all hydrogen atoms. For **5**, only one orientation of the disordered *i*Pr groups attached to P are shown for clarity. Selected bond lengths [Å] for complex **4**: Rh1–P1 2.3498(9), Rh1–Cl1 2.3775(9), P1–B1 1.962(4), P1–C11 1.874(3), P1–C14 1.873(3), N1–B1 1.404(5), N2–B1 1.407(5). Complex **5**: Rh1–P1 2.261(3), Rh1–Cl1 2.397(2), P1–O1 1.624(7), P1–C11 1.841(11), P1–C14 1.865(11), O1–B1 1.373(14), N1–B1 1.413(10), N2–B1 1.417(10).

shown in Figure 2. The ^{31}P NMR signal for **4** is a singlet at −16.2 ppm with the expected ^{103}Rh coupling subsumed by the broadness of the signal ($w_{1/2}$ = 285 Hz), whereas a sharp doublet at 152.3 ppm ($^{1}J_{PRh}$ = 174 Hz) was observed for **5** (Figure 3).

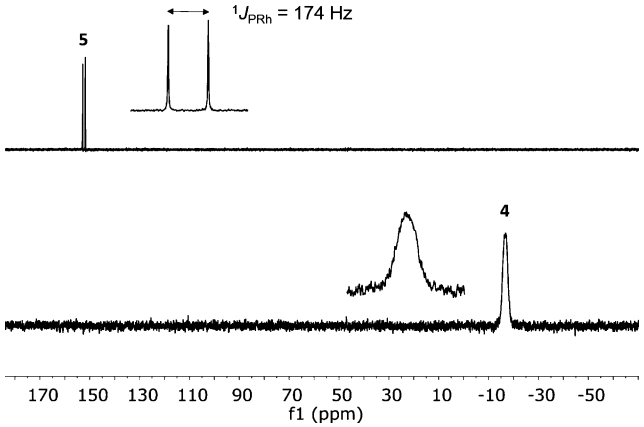
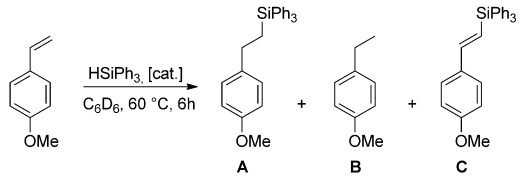


Figure 3. ^{31}P{^{1}H} spectra of **4** (bottom) and **5** (top) in CD_2Cl_2.

The catalytic activities of complexes **4** and **5** were measured for the hydrosilylation and hydroboration of 4-methoxystyrene. For the hydrosilylation reactions (Scheme 3), solutions of 4-methoxystyrene (1 eq), Ph_3SiH (1.05 eq) and the catalyst (2 mol%) in C_6D_6 were heated at 60 °C for 6 h and the conversions monitored by ^{1}H NMR spectroscopy; the results are given in Table 2.



Scheme 3. Hydrosilylation of 4-methoxystyrene with Ph_3SiH.

Table 2. Hydrosilylation of 4-methoxystyrene with Ph_3SiH.

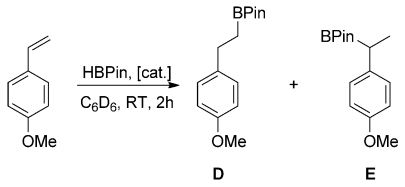
Pre-catalyst[a]	Conversion [%]	A	B	C
4	8	4	1	3
5	96	53	20	23
6	6	5	<1	1

[a] Conditions: 60 °C, C_6D_6, 6 h, alkene/silane ratio: 1:1.05, 2 mol% pre-catalyst. Conversion to products monitored by ^{1}H NMR spectroscopy.

The conversion obtained with the L_2 complex **5** was 96% compared with only 8% with the L_1 analogue **4**. This large difference in activity prompted us to screen the analogous complex [RhCl(*i*Pr$_2$POPh)(cod)] (**6**) featuring the ligand *i*Pr$_2$POPh (L_3) (see the Supporting Information for details). Complex **6** was tested under the same catalysis conditions and just 6% conversion was observed which shows that the boryloxy ligand L_2 has considerable advantages in terms of catalyst activity over both L_1 and L_3 for this reaction.

The Rh-catalysed hydrosilylation of olefins is often accompanied by numerous by-products of isomerisation, oligomerisation, polymerisation, dehydrogenative silylation and hydrogenation of the alkene.[23] In our case, three major products were obtained: the expected hydrosilylated product **A**, the hydrogenated species **B** and the dehydrogenative silylation product **C**. In each case, the hydrosilylated product **A** was the major product with a selectivity of over 50% with the productive catalyst **5**.

The hydroboration of *p*-methoxystyrene with pinacol borane (HBPin, see Scheme 4) is catalysed by complexes **4**–**6** (Table 3). Complex **5** is very active and highly selective for the linear product **D** in contrast to the less active and unselective catalyst **4**. The POC catalyst **6** showed similarly high activity to the POB catalyst **5** but interestingly the selectivity is switched to the branched product **E**. It is known that the hydroboration of styrene derivatives can be steered to Markovnikov and anti-



Scheme 4. Hydroboration of 4-methoxystyrene with pinacolborane (HBPin).

Table 3. Hydroboration of 4-methoxystyrene with pinacolborane.

Pre-catalyst[a]	Conversion [%]	D	E	Other[b]
4	53	20	17	16
5	>99	80	4	15
6	>99	6	77	16

[a] Conditions: RT, C_6D_6, 2 h, alkene/borane ratio: 1:1.1, 2 mol% pre-catalyst. Conversion to products monitored by ^{1}H NMR spectroscopy. [b] Several unidentified by-products (see ^{1}H NMR spectra in the Supporting Information).

Markovnikov selectivities by modifications of the catalyst;[24] the very different results obtained with L_1, L_2 and L_3 for this reaction reflect their fundamentally different ligating properties.

It has been shown that a single oxygen atom insertion into the P–B bond of L_1 occurs upon reaction with TMAO to give L_2, which is a new type of ligand that we have called a borylphosphinite to stress the relationship to phosphinites, the well-known hydrocarbyl analogues. The P–B oxygenation can be performed on free or bound ligand L_1. This O insertion transforms the ligand from an electron-rich to an electron-poor donor in one step; a similar process with conventional P–C ligands is inconceivable. The large difference detected in the ligand binding properties of L_1 and L_2 is reflected in the catalytic activity and selectivity of their complexes **4** and **5** in the catalytic hydrosilylation and hydroboration of *p*-methoxystyrene. The clean insertion of O into a B–P bond is a new reaction with the potential to be general.

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Keywords: oxygen insertion · phosphinoboranes · hydrosilylation · hydroboration · phosphane ligands

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