

On the Versatile and Unusual Coordination Behavior of Ambiphilic Ligands σ -R₂P(Ph)BR'₂

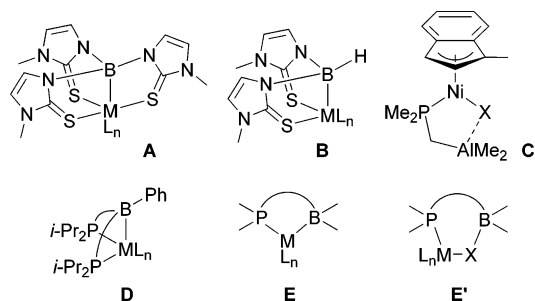
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Transition metal complexes featuring Lewis acid moieties directly linked to the metal center or at the near periphery have attracted increasing interest over the past decade. In particular, the structural characterization of metallaboratranes **A** and **B** have allowed for a better understanding of the propensity of group 13 Lewis acids to behave as σ -acceptor ligands.^{1–3} Ligands featuring pendant borane and alane moieties have also been investigated as promising candidates for organometallic catalysis, notably via intramolecular activation of M–X bonds.^{4,5} Accordingly, Zargarian recently induced spectacular rate enhancement in PhSiH₃ dehydrogenative oligomerization with the bifunctional Me₂PCH₂AlMe₂ cocatalyst, which was proposed to form bridged Ni^{II} complexes **C**.⁶

In this context, we have previously described the coordination of a preformed tridentate PBP ligand, leading to **D**-type complexes featuring Rh^I → B interactions.⁷ Here we report the synthesis and structural characterization of **E**-type complexes, providing thereby the first evidence for M → B interactions that are supported by a single donor buttress. The structural versatility of such ambiphilic monophosphine–borane ligands is also substantiated by the preparation of a related **E'**-type complex featuring a rare example of P → M–X → B coordination.⁸



Scheme 1

center with the metal fragment, whose nature was deduced from an X-ray diffraction study (Figure 1).⁹ Complex **2a** adopts a six-membered ring structure, the bidentate PB ligand bridging the Pd–Cl bond via P → Pd and Cl → B interactions. The latter contact is clearly supported by the short CIB distance (2.16 Å) and by noticeable pyramidalization of the boron environment ($\Sigma B_{\alpha} = 349.1^{\circ}$). Complex **2a** affords a rare example of M–Cl → B interaction.¹¹

In addition, the phosphine–borane **1a** readily displaced the labile dimethyl sulfide ligand from (Me₂S)AuCl in dichloromethane at room temperature, as deduced from the mass, ³¹P, and ¹H NMR data of the resulting complex **3a** (45% isolated yield). The ¹¹B NMR chemical shift remains almost identical upon coordination ($\delta^{11}\text{B}$ 80 ppm for **3a** versus 76 ppm in **1a**), suggesting a weak, if any, interaction of the boron center with the metal fragment. The coordination mode of **3a** was unambiguously established by an X-ray diffraction study (Figure 1).^{9,12} As a result of the nearly linear PAuCl arrangement (170.18°), the CIB distance (4.08 Å) is much higher than that observed in **2a**, ruling out the presence of a Cl → B interaction. The gold atom deviates from the mean plane of the ligand (torsion angle AuPCC of 30°), but the AuB distance remains rather short (2.90 Å).¹³ This value is much smaller than the sum of the van der Waals radii (~3.7 Å) and suggests the presence of a gold–boron interaction, despite the marginally pyramidalized environment around boron ($\Sigma B_{\alpha} = 358.6^{\circ}$).¹⁴

To confirm this unusual bonding situation, the related complex **3b** featuring a highly electrophilic borafluorene moiety¹⁵ was prepared from the corresponding phosphine–borane **1b**. In marked contrast with that observed for **3a**, the presence of a gold–boron interaction in solution was indicated by the ¹¹B NMR resonance signal (**3b**, 55 ppm), which is shifted to high-field by about 10 ppm compared to that of free PhBFlu (64.5 ppm)^{16a} and very similar to that recently reported for a borafluorene/ π -complex (57 ppm).^{16b} In the solid-state structure of **3b**,^{9,12} the torsion AuPCC angle was found to be only 13°, resulting in a significantly shortened boron–gold distance (2.66 Å) and in a slightly pyramidalized environment around boron ($\Sigma B_{\alpha} = 355.8^{\circ}$).

The monophosphine–borane ligand **1a** was readily prepared in 77% yield by coupling the related (*o*-bromophenyl)phosphine with chlorodicyclohexylborane.^{9,10} The propensity of **1a** to act as an ambiphilic bidentate ligand via P → M–Cl → B or P → M → B interactions was then investigated. With this in mind, PdCl(allyl) and AuCl were chosen as representative metal fragments of various electronic and geometric properties (*d*⁸/*d*¹⁰ configuration and bent/linear P → M–Cl skeleton).

The dimeric precursor [Pd(μ -Cl)(allyl)]₂ was readily cleaved with **1a** (Scheme 1). The corresponding complex **2a** was isolated as a yellow powder in 56% yield and fully characterized by multinuclear NMR and mass spectrometry. The ¹¹B NMR resonance signal for **2a** (47 ppm) is shielded by 29 ppm compared to that of the free ligand **1a**. This supports a rather strong interaction of the boron

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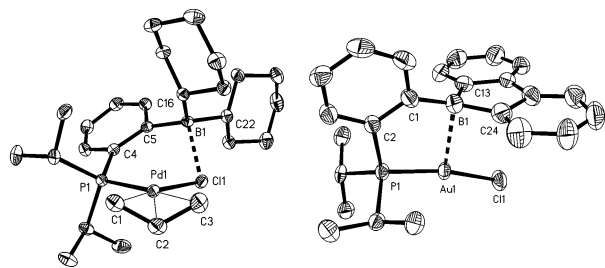


Figure 1. Thermal ellipsoid diagram (50% probability) of **2a** (left) and **3b** (right). Selected bond lengths (Å) and angles (deg): (**2a**) P1–Pd1 2.296(5), Pd1–C11 2.352(1), C11–B1 2.165(2), Pd1–C1 2.136(2), Pd1–C3 2.205(2), C5–B1–C16 113.14(17), C5–B1–C22 118.37(17), C16–B1–C22 117.58(17); (**3b**) P1–Au1 2.242(2), Au1–C11 2.302(2), Au1–B1 2.663(8), P1–Au1–C11 170.18(6), C1–B1–C13 125.6(6), C1–B1–C24 127.8(7), C13–B1–C24 102.4(6).

Table 1. Experimental and Theoretical (*) Data for Complexes **3a,b**: Selected Bond Length (Å), Boron Pyramidalization and Torsion Angle (deg), and Total Atomic and Fragment Charges Derived from NPA Analyses

complex	geometric data			NPA charges			
	AuB	ΣB_{α}	AuPCC	P	Au	Cl	BR' ₂
3a	2.90	358.6	30.0				
3b	2.66	355.8	13.1				
3a*	2.99	358.5	21.1	1.00	0.31	−0.58	0.29
3b*	2.63	353.8	5.7	1.02	0.41	−0.57	0.14

To gain further insight into the unusual AuB interactions encountered in complexes **3a,b**, DFT calculations were carried out at the BP86/[LanL2DZ(Au),6-31G*(C,P,B,Cl,H)] level of theory.⁹ The optimized geometries well reproduced those obtained experimentally (Table 1). Noteworthy, the shortening of the AuB distance from **3a** to **3b** is accompanied by a significant decrease of the total natural charge for the BR'₂ fragment (from 0.29 to 0.14), as derived from Natural Population Analyses (NPA).¹⁷ The noticeable influence of the boron electrophilicity supports some transfer of electron density from the metal to the σ -acceptor ligand. This is further substantiated by the increase predicted for the charge of the gold atom from (*i*-Pr₂PPh)AuCl (0.25) to **3a** (0.31) and **3b** (0.41). The contribution of such donor (Au) \rightarrow acceptor (B) interactions in complexes **3a,b** was also evidenced by second-order perturbation theory analyses (NBO calculations).⁹ So far, M \rightarrow B interactions have only been characterized in 16e or 18e complexes using tri- or tetra-dentate ligands.¹⁷ Complexes **3** provide evidence for such interactions that occur in 14e complexes and that are supported by a single donor buttress.

In conclusion, monophosphine–boranes were shown to behave as bidentate ambiphilic ligands via P \rightarrow M–X \rightarrow B or P \rightarrow M \rightarrow B interactions. Further investigations are currently in progress (i) to evaluate the scope of such unusual bonding situations with regards to the metal and co-ligands involved, (ii) to precise the relative stability of the various coordination modes for a given complex, and (iii) to determine the influence of the boron coordination on the geometry and reactivity of the resulting complexes.^{18,19}

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Supporting Information Available: Experimental and computational details; spectroscopic and X-ray crystallographic data for **1–3** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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