Ambiphilic Ligands

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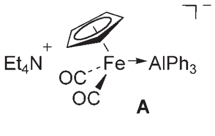
Rhodium(I) Complexes of a PBP Ambiphilic Ligand: Evidence for a Metal→Borane Interaction**

*Sébastien Bontemps, Heinz Gornitzka, Ghenwa Bouhadir, Karinne Miqueu, and Didier Bourissou**

Transition-metal complexes of Group 13 elements,[1] and especially of boron,[2] have attracted considerable interest over the last decade. A wide variety of coordination modes have been characterized structurally and investigated theoretically.[3] In particular, the possibility for Lewis acids ER_3 (E = B, Al…) to behave as σ-acceptor ligands has been demonstrated, although examples of such $M \rightarrow ER_3$ interactions remain very rare. Indeed, despite the structural characterization of the transition metal→alane complex $Et_4N^+[CpFe(CO)_2(AlPh_3)]^-$ (**A**) as early as 1979,[4] it was not until 1999 that Hill reported the first solid-state structure of a borane complex.[5a] The synthesis of the ruthenaboratrane **B** clearly represents a major breakthrough, the borane moiety being generated in the coordination sphere of the metal by B–H activation of a tris(azolyl)borate. Following the same strategy, a few related metallaboratranes (Os, Pt, Rh, Ir, Co) have recently been prepared.[5b–h] Notably, the contribution of M→B interactions[6] has also been pointed out in the bonding description of the tantalocene–borataalkene η²-complexes **C**[7,8] and the boryl-bridged complexes **D**–**F** (cat = 1,2-$O_2C_6H_4$).[9]



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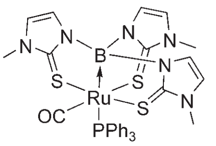

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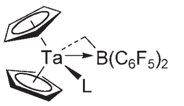

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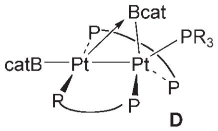

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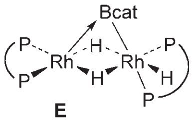

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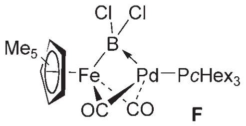
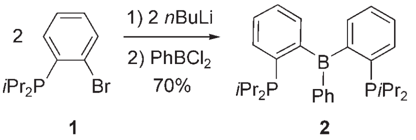


F

Besides the fundamental aspects associated with the bonding description of such transition metal→borane interactions, new insights might also be expected for their use in organometallic catalysis. Indeed, ligands featuring pendant borane moieties can be reasonably assumed to interact with the coordination sphere of transition metals not only by activating an M–X bond[10,11] or anchoring a substrate,[12] but also by coordinating as σ-acceptor ligands. With this in mind, we have recently initiated a research program aimed at exploring the use of so-called ambiphilic ligands. Here we report the synthesis of a diphosphanylborane derivative and its tridentate coordination to Rh^I fragments. The presence of a Rh→B interaction has been demonstrated by both structural analyses and DFT calculations.

To disfavor an intramolecular phosphane→borane interaction, a phenyl ring was chosen as a rigid two-carbon linker for the target PBP ambiphilic ligand.[13] Starting from readily available (*o*-bromophenyl)phosphane **1**,[14] the desired ligand **2** was obtained in 70% yield by bromine–lithium exchange followed by electrophilic trapping with dichlorophenylborane (Scheme 1). The monomeric structure of **2** was suggested by mass spectrometry and confirmed by multinuclear NMR



Scheme 1. Synthesis of the diphosphanylborane **2**.

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[*] S. Bontemps, Dr. H. Gornitzka, Dr. G. Bouhadir, Dr. D. Bourissou
Laboratoire Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069)
Université Paul Sabatier
118, route de Narbonne, 31062 Toulouse Cedex 09 (France)
Fax: (+33) 5-6155-8204
E-mail: dbouriss@chimie.ups-tlse.fr
Dr. K. Miqueu
Laboratoire de Chimie Théorique et Physico-Chimie Moléculaire (UMR 5624)
Avenue de l'Université, BP 1155, 64013 Pau Cedex (France)

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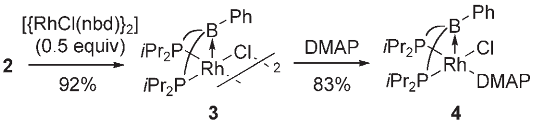
spectroscopy. Indeed, the ^{31}P NMR chemical shift for **2** (δ = 11 ppm) is very similar to that of **1** (δ = 9 ppm), and a broad signal is observed at δ = 43 ppm in the ^{11}B NMR spectrum, as expected for a triaryl borane.

The presence of an occupied, nonbonding d_{z^2} orbital makes square-planar d^8-ML$_4$ fragments ideal candidates for the study of metal→borane interactions.[15] The propensity of **2** for tridentate coordination through P→M and M→B interactions was thus investigated by treating it with half an equivalent of [{Rh(μ-Cl)(nbd)}$_2$] (nbd = 2,5-norbornadiene) in dichloromethane (Scheme 2). The yellow precipitate that spontaneously formed at room temperature was collected by filtration and analyzed spectroscopically. The ^{31}P NMR spectrum at room temperature in solution is only poorly resolved, with several broad signals being observed, probably due to conformational restrictions. At −60 °C, however, one of the conformers becomes largely predominant. It exhibits two magnetically differentiated phosphorus atoms (δ = 74.7 and 64.2 ppm ($J_{P,P}$ = 24.3 Hz)) coupled to rhodium ($^1J_{P,Rh}$ = 151.9 and 160.0 Hz, respectively), thereby unambiguously establishing the coordination of both phosphorus atoms to the rhodium center. Moreover, the mass spectrum is consistent with a dimeric structure of general formula [{RhCl(**2**)}$_2$]. All these features were confirmed by an X-ray diffraction study (Figure 1 a).[16] Complex **3** adopts a centrosymmetric and planar[17] chloro-bridged structure in the solid state. The rhodium center is surrounded by two phosphorus and two chlorine atoms organized in a perfectly planar arrangement (ΣRh$_\alpha$ = 359.8°). The bite angle of the diphosphane skeleton (P-Rh-P = 98.5°) is at the lower limit of those observed for related POP diphosphanes featuring donor diphenylether backbones (102–123°).[18] The two phenyl linkers adopt slightly different conformations (Rh-P-C$_{ipso}$-C$_{ortho}$ torsion angles of 17.8° and 24.1°), in agreement with the inequivalence of the two phosphorus atoms in the ^{31}P NMR spectrum in solution at −60 °C and in the solid state at room temperature (δ = 76.9 ($^1J_{P,Rh}$ = 166.6 Hz) and 66.5 ppm ($^1J_{P,Rh}$ = 162.8 Hz)). Interestingly, due to the folding of this rather rigid ligand, the boron atom comes close to the metal center, almost perpendicularly to the square coordination plane (P-Rh-B = 81.1° and 80.3°). The Rh–B distance (2.306 Å) is noticeably longer than the metal–boron distances observed in metallaboratranes (2.09–2.21 Å). Although these values cannot be rigorously compared to each other as the position *trans* to the borane is occupied by a donor ligand in metallaboratranes but not in complex **3**, the presence of a Rh→B interaction in **3** is further supported by the pyramidalization of the boron environment (ΣB$_\alpha$ = 338.8°) and by the significant high-field shift of the ^{11}B NMR resonance signal ($\Delta\delta$ = −23 ppm compared to that of the free ligand **2**).



Scheme 2. Synthesis of the rhodium(I) complexes **3** and **4**.

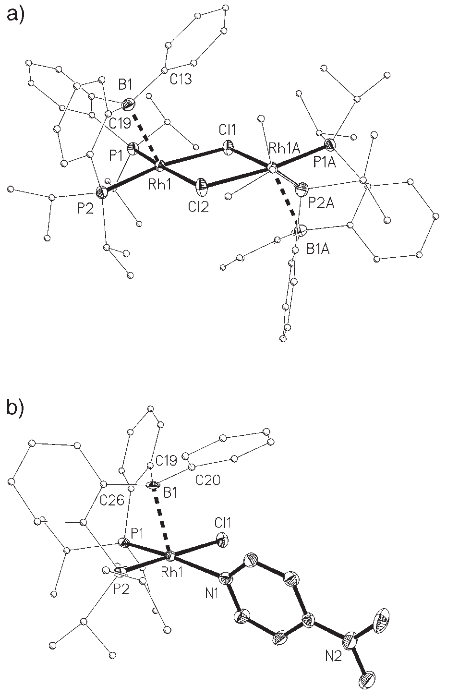


Figure 1. Molecular views of **3** (a) and **4** (b) in the solid state. Hydrogen atoms have been omitted for clarity. The thermal ellipsoids are shown at 50% probability for (a) and 50% probability for (b). Selected bond lengths [Å] and angles [°]: **3**: Rh1–P1 2.2507(13), Rh1–P2 2.2710(13), Rh1–B1 2.306(3), Rh1–Cl2 2.4381(13), Rh1–Cl1 2.4492(13); P1-Rh1-P2 98.52(4), C13-B1-C19 116.3(3), C13-B1-C12 113.3(3), C19-B1-C12 109.2(3), P1-Rh1-B1 81.18(10), P2-Rh1-B1 80.41(10), B1-Rh1-Cl2 103.81(9), B1-Rh1-Cl1 106.09(10); **4**: Rh1–P2 2.2560(12), Rh1–P1 2.2856(12), Rh1–B1 2.295(5), Rh1–N1 2.153(4); P2-Rh1-P1 97.59(4), C20-B1-C19 117.6(4), C20-B1-C26 114.1(4), C19-B1-C26 108.5(4), N1-Rh1-B1 110.75(16), P2-Rh1-B1 83.55(13), P1-Rh1-B1 80.06(13), N1-Rh1-Cl1 83.63(10).

As a first evaluation of the strength of the Rh→B interaction, complex **3** was then treated with *N*,*N*-dimethylaminopyridine (DMAP) in dichloromethane (Scheme 2). Although the ^{1}H and ^{13}C NMR spectra revealed the presence of a coordinated DMAP in the ensuing complex **4**, no significant modification was observed by ^{11}B and ^{31}P NMR spectroscopy. An X-ray diffraction analysis (Figure 1 b)[16] revealed that cleavage of the chloro bridge had taken place due to the coordination of the Lewis basic pyridine to the metal center rather than to the boron atom. It is noteworthy that the Rh→B interaction is not significantly affected, as clearly indicated by the similarity in the geometric parameters of both complexes. Indeed, the rhodium center in the monomeric complex **4** also adopts an overall square-pyramidal geometry (P-Rh-P bite angle of 97.6°), the Rh–B distance (2.295 Å) is only marginally shorter than in **3**, and the boron environment is still significantly pyramidalized (340.3°).

To gain further insight into the nature of the Rh–B interaction, ab initio calculations[19] were performed for the mononuclear complex **4*** featuring model diphosphanylborane and DMAP ligands (methyl groups at phosphorus, hydrogen atoms at nitrogen). The key features of complex **4** (Rh–B and Rh–P bond lengths and boron pyramidalization) could be very well reproduced, especially at the BP86/[CEP-

31G(Rh),6-31G*(C,P,B,N,Cl,P,H)] level of theory (Table 1). Notably, the two-center, two-electron bonding interaction between the metal center and borane moiety is apparent from the frontier molecular orbitals of **4*** (major contribution from the d_{z^2}(Rh) orbital to the HOMO (Figure 2a) with little distortion due to its interaction with a vacant boron orbital, and antibonding combination of the d_{z^2}(Rh) and 2p(B) orbitals in the LUMO (Figure 2b)). This qualitative description was further confirmed by a natural bond orbital (NBO) analysis, second-order perturbation theory being particularly suitable for the description of donor–acceptor interactions. A natural localized molecular orbital (NLMO) was found to account for the Rh–B bonding interaction (Figure 2c) with about 79.3% contribution from the rhodium lone-pair (d_{z^2}) and major "delocalization tails" (17.1%) from a vacant boron orbital. In agreement with the pyramidalization of the boron environment, this transfer of electron density from the metal to the σ-acceptor ligand is accompanied by some hybridization of the formerly vacant 2p(B) orbital (the corresponding natural atomic orbital (NAO) decomposition of the NLMO features 12.7% of s character).[19] Although the precise value for this donor–acceptor interaction is meaningless (in the range 30–58 kcal mol^{-1}, depending on the level of calculations), its magnitude is remarkable and in good agreement with the observation of the cleavage of the chloro bridge and retention of the Rh→B interaction in the reaction of complex **3** with DMAP.

Table 1: Selected bond lengths [Å] and angles [°] for complexes **4** and **4***.

	Rh–P	Rh–B	P-Rh-P	P-Rh-B	ΣRh_α	ΣB_α
X-ray	2.286(1)	2.295(5)	97.59(4)	80.1(1)	360.2	340.2
	2.256(1)			83.6(1)		
B3LYP/	2.296	2.458	97.52	78.13	359.3	344.6
LanL2DZ(Rh)[a]	2.265			81.38		
BP86/	2.282	2.392	97.39	78.61	359.2	342.8
LanL2DZ(Rh)[a]	2.249			82.04		
BP86/CEP-	2.281	2.384	97.38	78.51	359.2	339.2
31G(Rh)[a]	2.251			81.97		
BP86/SDD(Rh)[a]	2.274	2.381	97.41	78.63	359.2	342.2
	2.241			82.10		

[a] The 6-31G* basis set was used for C,P,B,Cl,N,P,H.

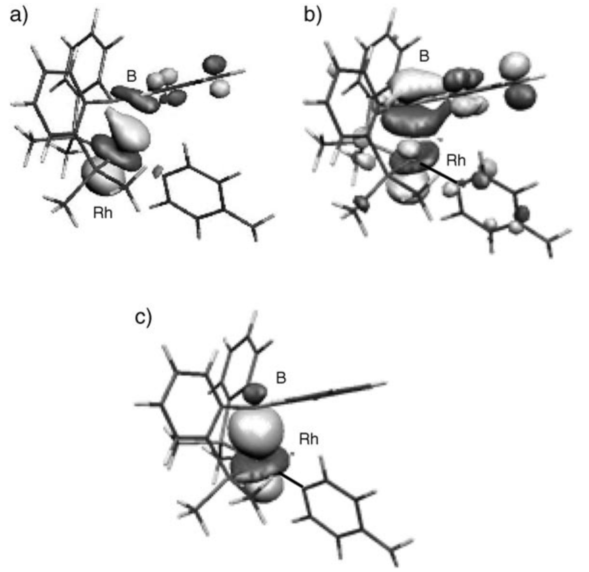


Figure 2. Molekel plots (cutoff: 0.04) of the HOMO (a), LUMO (b), and NLMO (c) accounting for the Rh–B interaction in the model complex **4*** at the BP86/[CEP-31G(Rh),6-31G*(C,P,B,N,Cl,P,H)] level of theory.

In conclusion, evidence for Rh→B interactions has been provided by both structural analyses and DFT calculations for the 16-electron square-pyramidal Rh^{I} complexes **3** and **4** derived from the ambiphilic PBP ligand **2**. This highlights that these very rare transition metal→borane interactions 1) are readily accessible by coordination of preformed borane-containing ligands, 2) exist even in complexes not featuring donor ligands in the position *trans* to the Lewis acid, and 3) are resistant to the action of a Lewis base such as DMAP. The influence of such M→B interactions on the reactivity of the resulting complexes is currently under investigation, as are variations of the metal fragment and of the stereoelectronic properties of the ambiphilic ligand.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon, using standard Schlenk techniques. Unless otherwise stated, the NMR spectra were recorded at 293 K.

2: *n*BuLi (2.5 M in hexane, 5.2 mL, 12.9 mmol) and dichlorophenylborane (0.84 mL, 6.5 mmol) were successively added at −40 °C and −78 °C, respectively, to a solution of **1** in toluene (20 mL). After warming to room temperature, the volatiles were removed under vacuum, the residue was dissolved in diethyl ether (20 mL), and the salts were removed by filtration. Diphosphanylborane **2** (2.04 g, 69%) was obtained as a white solid upon removal of the solvent. M.p. 95–97 °C; ^{11}B NMR (128.4 MHz, C_6D_6): $\delta = 43.1$ ppm; ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): $\delta = 11.0$ ppm; MS (EI, 70 eV): *m*/*z*: 474 $[M]^+$.

3: A solution of **2** (1.00 g, 2.1 mmol) in CH_2Cl_2 (6 mL) was added at −78 °C to a solution of $[\{Rh(\mu\text{-}Cl)(nbd)\}_2]$ (486 mg, 1.1 mmol) in CH_2Cl_2 (10 mL). After warming the mixture to room temperature and stirring for 1 h, complex **3** (921 mg, 72%) was collected by filtration. Crystals suitable for X-ray crystallography were obtained from a saturated toluene solution at −4 °C. M.p. 205 °C; ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = 20.0$ ppm; ^{31}P{^{1}H} NMR (161.8 MHz, solid state): $\delta = 76.9$ (d, $^1J_{P,Rh} = 166.6$ Hz), 66.5 ppm (d, $^1J_{P,Rh} = 162.8$ Hz); ^{103}Rh NMR (15.8 MHz, $CDCl_3$, 213 K) $\delta = -7365$ ppm; MS (DCI/NH_3): *m*/*z*: 1242 $[M+NH_4]^+$; C,H analysis (%) calcd. for $C_{30}H_{41}BClP_2Rh$: C 58.80, H 6.74; found: C 58.99, H 7.11.

4: A solution of DMAP (40 mg, 0.33 mmol) in CH_2Cl_2 (2 mL) was added at −78 °C to a solution of **3** (200 mg, 0.16 mmol) in CH_2Cl_2 (10 mL). After warming to room temperature, complex **4** (203 mg, 83%) was collected by filtration. Crystals suitable for X-ray crystallography were obtained from a saturated THF/pentane solution at −20 °C. M.p. 137 °C; ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = 19.4$ ppm; ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): $\delta = 66.8$ (dd, $^1J_{P,Rh} = 169.8$, $^2J_{P,P} = 31.0$ Hz), 65.3 ppm (dd, $^1J_{P,Rh} = 144.5$, $^2J_{P,P} = 31.0$ Hz); ^{103}Rh NMR (15.8 MHz, $CDCl_3$): $\delta = -7552$ ppm.

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[16] Crystal data for **3**: $C_{35.25}H_{46.5}BClP_2Rh$, $M = 681.33$, tetragonal, space group $P4_22_12$, $a = b = 20.711(11)$, $c = 15.503(9)$ Å, $V = 6650(7)$ Å^3, $Z = 8$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.713\ \mathrm{mm}^{-1}$, crystal size $0.2 \times 0.3 \times 0.3\ \mathrm{mm}^3$, 39070 reflections collected (6801 independent, $R_{int} = 0.1009$), 453 parameters, $R1(I>2\sigma(I)) = 0.0312$, $wR2(\text{all data}) = 0.0711$, largest diff. peak and hole: 0.750 and -0.337 e Å^{-3}. **4**: $C_{41}H_{59}BClN_2OP_2Rh$, $M = 807.01$, triclinic, space group $P\bar{1}$, $a = 10.0198(8)$, $b = 10.2336(8)$, $c = 21.9239(18)$ Å, $\alpha = 100.279(2)$, $\beta = 91.578(2)$, $\gamma = 115.263(1)°$, $V = 1986.8(3)$ Å^3, $Z = 2$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.612\ \mathrm{mm}^{-1}$, crystal size $0.1 \times 0.3 \times 0.4\ \mathrm{mm}^3$, 8716 reflections collected (5588 independent, $R_{int} = 0.0822$), 452 parameters, $R1(I>2\sigma(I)) = 0.0434$, $wR2(\text{all data}) = 0.0966$, largest diff. peak and hole: 1.018 and -0.578 e Å^{-3}. Data for all structures were collected at 133(2) K for an oil-coated, shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97),[20] and refined using the least-squares method on F^2.[21] CCDC-286287 (**3**) and -286288 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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