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Notes

Chelating Monoborane Phosphines: Rational and High-Yield Synthesis of [(COD)Rh{(η^2-BH$_3$)Ph$_2$PCH$_2$PPh$_2$}][PF$_6$] (COD = 1,5-cyclooctadiene)

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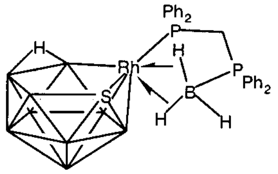
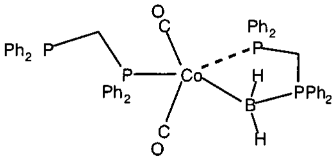
Summary: *The rational and high-yield synthesis of [(COD)Rh{(η^2-BH$_3$)Ph$_2$PCH$_2$PPh$_2$}][PF$_6$] (**1**), which bears a chelating monoborane phosphine, is reported; the solid-state structure shows that the borane coordinates to the metal via two 2e−3c B−H−Rh bonds, which in solution at room temperature are fluxional between all three B−H bonds. Complex **1** is isolated as an air-stable crystalline salt, and its applicability as a catalyst in organic synthesis has been demonstrated in the coupling of boronic acids with enones.*

Introduction

The coordination chemistry of phosphine boranes of the type R$_3$P·BH$_3$ and (R$_3$P)$_2$·B$_2$H$_4$ has recently been explored by Shimoi, as exemplified by the synthesis of complexes such as (CO)$_5$Cr(η^1-R$_3$P·BH$_3$) and (CO)$_4$Cr(η^1:η^1-(R$_3$P)$_2$·B$_2$H$_4$).[1] However, the related compounds in which the borane moiety is complexed with a chelating phosphine have only been mentioned twice in the literature. One of these, recently reported by Barton et al., has a dppm (diphenylphosphinomethane) ligand with an appended BH$_3$ unit that is chelated to a polyhedral rhodathiaborane (**A**).[2] The other contains a formally anionic [PR$_3$·BH$_2$]$^-$ ligand chelated to a cobaltacarbonyl: (CO)$_2$(η^1-dppm)Co(μ-dppm)BH$_2$ (**B**).[3] Both complexes are formed by addition of a monoborane reagent to a suitable metal−phosphine precursor by an undetermined mechanism. It struck us that both of these chelating ligands contain dppm functionalized with monoborane and that such a situation results in the formation of a favored five-membered chelate ring. Consequently we have pursued the synthesis of transition metal coordination complexes with *preformed* Ph$_2$PCH$_2$PPh$_2$·BH$_3$,[4] seeking a high-yield, rational route toward complexes that contain this interesting hybrid[5] ligand. This report outlines the synthesis, structural and preliminary catalytic studies of one such complex: [(COD)Rh{(η^2-BH$_3$)Ph$_2$PCH$_2$PPh$_2$}][PF$_6$] (**1**) (COD = cycloocta-1,5-diene).



(A)



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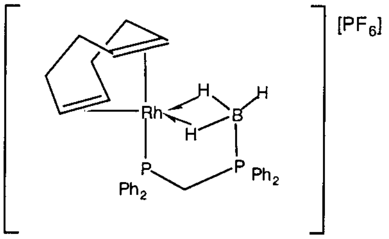

(1)

Results and Discussion

Addition of Ph$_2$PCH$_2$PPh$_2$·BH$_3$ to [(COD)RhCl]$_2$, followed by halide abstraction using TlPF$_6$, affords complex **1**, [(COD)Rh{(η^2-BH$_3$)Ph$_2$PCH$_2$PPh$_2$}][PF$_6$], in excellent yield (85% isolated) as an air-stable microcrystalline solid after workup. Full spectroscopic analysis was performed on this salt, but repeated attempts to produce crystals suitable for X-ray diffraction failed. Anion metathesis replacing [PF$_6$]$^-$ with the bulky [BPh$_4$] anion

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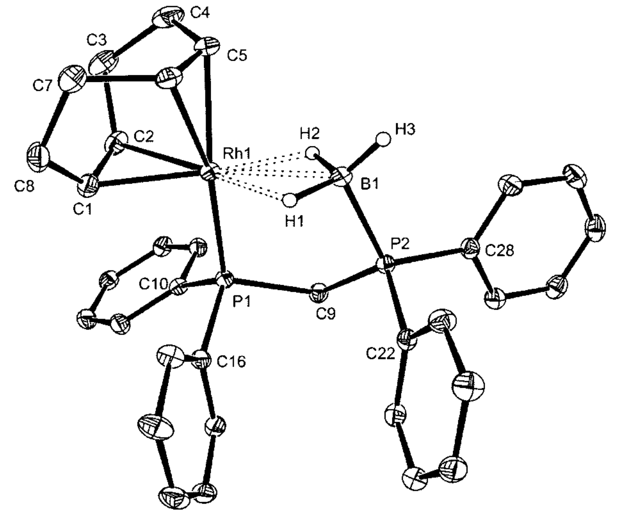

Figure 1. Cation in [(COD)Rh{(η^2-BH$_3$)Ph$_2$PCH$_2$PPh$_2$}][BPh$_4$]·C$_7$H$_8$, **1**. Ellipsoids are shown at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

B(1)−H(1)	1.16(3)	Rh(1)−H(1)	1.82(4)
B(1)−H(2)	1.16(3)	Rh(1)−H(2)	1.91(3)
B(1)−H(3)	1.09(3)	Rh(1)−B(1)	2.313(3)
Rh(1)−C(1)	2.126(3)	Rh(1)−C(2)	2.124(3)
Rh(1)−C(5)	2.249(3)	Rh(1)−C(6)	2.271(3)
Rh(1)−P(1)	2.2743(7)	Rh(1)−B(1)	2.313(3)
P(1)−C(9)	1.849(3)	P(1)−B(1)	1.923(3)
P(1)−B(1)−H(1)	102(3)	P(1)−B(1)−H(2)	102(1)
P(1)−B(1)−H(3)	114(1)	P(2)−C(9)−P(1)	109.74(13)
P(1)−Rh(1)−B(1)	87.26(8)	C(9)−P(1)−Rh(1)	110.93(9)
Rh(1)−B(1)−P(2)	113.07(15)		

afforded suitable crystals for a X-ray study. The solid-state structure of the cation in **1** is presented in Figure 1. This shows that the rhodium is bracketed by a coordinated COD ligand and the chelating phosphine borane. The phosphine ligates to the metal via both the terminal phosphine and BH$_3$ moiety, the latter through *two* B−H−Rh three-center two-electron bonds. This η^2-coordination motif of the borane was initially unexpected, as the formally d^8 Rh(I) metal center requires only one B−H−Rh interaction to attain a 16-electron count. However, similar pentacoordination has been observed previously in Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(COD).[6] All hydrogen atoms on the borane were located and freely refined in the crystal structure. Inspection of the bond lengths and angles surrounding B(1) (Table 1) shows that the two bridging hydrogens [H(1) and H(2)] exhibit similar distances from Rh(1). Notwithstanding that all B−H distances are similar within the bounds of experimental error, there also appears to be a trend suggesting that the B−H bond distances to H(1) and H(2) are slightly longer than found for the terminal hydride, H(3), as expected. The BH$_3$ unit is not tetrahedral, the two bridging hydrogens having compressed P(1)−B(1)−H angles to facilitate efficient bonding with the metal center. The Rh−B distance [2.313(3) Å] is similar to that found in **A** [2.323(2) Å] which also contains a bidentate {PBH$_2$} ligand, this bond length also comparable to those found in {RhL$_2$} fragments *exo* coordinated to polyboranes.[7] The P(1)−Rh(1)−B(1) bite angle at 87.26(8)° is also similar to that in **A** [88.36(6)°]. Comparison of the Rh−C$_{\mathrm{COD}}$ bond lengths demonstrates the differing *trans* influences operating in the chelating ligand in **1**. In particular, the alkene carbon−Rh bonds *trans* to the weakly bound {BH$_2$} fragment are significantly shorter than those *trans* to the phosphine [2.125 Å average for Rh−C(1), Rh−C(2) versus 2.259 Å average for Rh−C(5), Rh−C(6)].

Table 2. Crystallographic Data for Complex 1

empirical formula	C$_{64}$H$_{65}$B$_2$P$_2$Rh
fw	1020.63
temperature (K)	150(2)
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	15.2130(2)
b (Å)	17.1060(3),
c (Å)	21.2800(3)
α (deg)	90
β (deg)	106.2960(9),
γ (deg)	90
U (Å$^{3)}$	5315.29(14)
Z	4
μ (mm^{-1})	0.421
no. of reflns collected	61 419
no. of ind reflns	12 152 [$R_{\mathrm{int}} = 0.0887$]
final R1, wR2 indices [$I > 2\sigma(I)$]	0.0430, 0.0905
R1, wR2 indices (all data)	0.0765, 0.1037
largest diff peak and hole	0.805 and −0.677 e Å^{-3}

The η^2-BH$_3$ binding motif observed in the solid state is not maintained in solution at room temperature, where the NMR spectrum reveals that all of the borane hydrogen atoms are equivalent, with one integral 3H resonance observed at δ −0.25 ppm. This demonstrates that rapid exchange of the three BH bonds in bonding to the Rh center occurs, facilitated through rotation around the P−B bond (as has been observed previously in compound **A**[2]). Cooling to −50 °C resulted in replacement of this single resonance by two peaks in the ^{1}H-{^{11}B} NMR spectrum, at 2.25 ppm (1 H) and −1.48 ppm (2 H), associated with terminal B−H and bridging Rh−H−B bonds, respectively. This low-temperature NMR spectrum is fully consistent with the solid-state structure. Further cooling to −90 °C did not affect the observed spectrum. The remaining observed ^{1}H, ^{31}P, and ^{11}B NMR resonances are entirely consistent with the proposed structure. DFT calculations on complex **1** are in agreement with the observed solid-state and low-temperature solution structures, η^2-coordination of the borane favored over η^1-binding on optimization at the B3PW39/6-31G** level.

We have tested the applicability of complex **1** in C−C bond-forming reactions via 1,4-addition of boronic acids to α,β-unsaturated ketones.[8] Preliminary investigations have shown that **1** is an effective precatalyst (1 mol % catalyst loading) for the addition of phenylboronic acid to cyclohexenone to afford 3-phenylcyclohexanone in 82% isolated yield. We have not investigated the structure of the active catalyst in this reaction, but it is likely that the COD ligand dissociates to afford a species such as [Rh{(η^2-BH$_3$)Ph$_2$PCH$_2$PPh$_2$}(solvent)][PF$_6$] (solvent = dimethoxyethane).[9]

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The η^2-coordination mode of the borane to Rh in **1** is similar to that observed in early transition metal complexes of organohydroborates.[10,11] It is further reminiscent of the way that alkanes are suggested to bind with highly electrophilic late transition metal centers.[12−15] The unexpected η^2-binding mode, air stability, and the preliminary catalytic studies reported here prompt us to suggest that complex **1** and its derivatives should display interesting and accessible chemistry associated with the Rh−H−B linkage in this chelating ligand system, and we are currently actively pursing this.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk line or drybox techniques. CH_2Cl_2 was distilled from CaH_2, and hexane and toluene were distilled from sodium. NMR spectra were measured on Brüker Advance 300 MHz and Varian Mercury 400 MHz FT-NMR spectrometers in CD_2Cl_2 solutions. Residual protio solvent was used as reference (δ, ppm: CD_2Cl_2 5.33) in ^1H NMR. ^{11}B NMR spectra were referenced to $BF_3 \cdot OEt_2$ (external), and ^{31}P NMR spectra were referenced to H_3PO_4 (external). Coupling constants are given in hertz. Elemental analysis was performed in-house in the Department of Chemistry, University of Bath.

Compound 1. $[(COD)RhCl]_2$ (0.105 g, 0.213 mmol) and $Ph_2PCH_2PPh_2 \cdot BH_3$ (0.170 g, 0.426 mmol) were dissolved in CH_2Cl_2 (15 cm^3) and the reaction stirred for 10 min. $TlPF_6$ (0.15 g, 0.43 mmol) was added, and stirring was continued overnight. Filtration away from insoluble TlCl and recrystallization by addition of hexanes afforded pale yellow microcrystals of $[(COD)Rh\{(\eta^2\text{-}BH_3)Ph_2PCH_2PPh_2\}][PF_6]$ (0.273 g, 85% yield). Crystals suitable for an X-ray diffraction study were obtained by methathesis of a CH_2Cl_2 solution of **1** with excess $NaBPh_4$, filtration, and recrystallization from CH_2Cl_2/toluene.

Spectroscopic Data for 1. ^1H (400 MHz) (298 K, CD_2Cl_2): 7.61−7.38 (m, 20 H, Ph), 5.82 (s, 2 H, cod), 3.32 (s, 2 H, cod), 2.17 [virtual t, 2 H, CH_2, J(PH) 8], 2.49 (m, 4 H, cod), 2.30 (m, 4 H, cod), −0.25 [partially collapsed quartet, 3 H, BH_3, J(BH) 82]. $^{31}P\{^1H\}$ (121 MHz) (298 K, CD_2Cl_2): 47.1 [dd, 1 P, J(PP) 61, J(RhP) 145 Hz], 20.3 (br, 1 P), −142.8 [septet, 1 P, PF_6, J(FP) 701], $^{11}B\{^1H\}$ (96 MHz) (298 K, CD_2Cl_2): −24.1 [d br, J(PB) 96]. Selected $^1H\{^{11}B\}$ (400 MHz, 223 K, CD_2Cl_2): 2.25 (1 H, BH), −1.48 (2 H, B−H−Rh). Anal. Calcd for $C_{33}H_{37}BP_3F_6Rh$: C 52.5; H 4.91. Found: C 51.5; H 4.76.

Catalysis. Rhodium complex **1** (1 mol %) and phenylboronic acid (1.5 mmol) were added to a flask containing a magnetic stirring bar. The flask was flushed with nitrogen and then charged with DME (3 mL) and cyclohexanone (1.0 mmol). The mixture was then stirred at 65 °C for 16 h. The product was extracted with ethyl acetate, washed with brine, and dried over $MgSO_4$. Chromatography over silica gel (hexane−ethyl acetate, 10:1) afforded 3-phenylcyclohexenone in 82% yield. The identity of this known compound was confirmed by comparison of its ^1H NMR spectrum with an authentic sample.

DFT Calculations. Calculations on the system were performed using the G98 package.[16] All geometries were optimized using the density functional theory with Becke's three-parameter hybrid exchanged[17] and the Perdue−Wang correlation function (B3PW91).[18] The starting point of the geometry optimizations was derived from the X-ray structure, with the four phenyl groups substituted for methyls. For Rh the Stuttgart-Dresden[19] basis set with corresponding effective core potentials was applied (replacing 28 core electrons for Rh), and the 6-31G** basis set was used for the rest of the atoms.

X-ray Crystallography. The crystal structure data for compound **1** were collected on a Nonius KappaCCD. Structure solution followed by full-matrix least-squares refinement was performed using the SHELX suite of programs throughout.[20]

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Supporting Information Available: Tables giving details of data collection, structure solution and refinement, atomic coordinates, thermal parameters, and bond lengths and angles for $\mathbf{1} \cdot [BPh_4] \cdot C_6H_7$. This material is available free of charge via the Internet at http://pubs.acs.org.

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