Boryl-Dihydrideborate Osmium Complexes: Preparation, Structure and Dynamic Behavior in Solution

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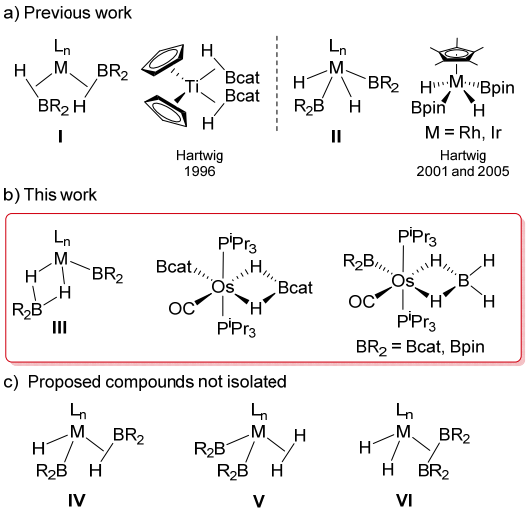
Supporting Information Placeholder

ABSTRACT: The metal fragment $Os(CO)(P^iPr_3)_2$ stabilizes boryl-dihydrideborate species, which can be viewed as snapshots of states of B–H oxidative addition of a R_2BH molecule and frustrated B–H bond activation of a second one. Complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**2**) shows tendency to dissociate the olefin. The resulting dihydride $OsH_2(CO)(P^iPr_3)_2$ (**3**) rapidly coordinates catecholborane (HBcat) and pinacolborane (HBpin) to give the corresponding σ-borane derivatives $OsH_2(\eta^2\text{-}HBR_2)(CO)(P^iPr_3)_2$ (BR_2 = Bcat (**4**), Bpin (**5**)). Complex **4** reacts with a second molecule of HBcat to release H_2 and to afford the octahedral boryl-dihydrideborate derivative $Os(Bcat)(\kappa^2\text{-}H_2Bcat)(CO)(P^iPr_3)_2$ (**6**), which undergoes a thermally activated Bcat site exchange process in solution. Borane displaces catecholborane from the dihydrideborate of **6** to generate the boryl-tetrahydrideborate $Os(Bcat)(\kappa^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**7**). This compound and the Bpin counterpart $Os(Bpin)(\kappa^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**8**) have been also prepared by reaction of the corresponding $Os(BR_2)Cl(CO)(P^iPr_3)_2$ with $Na[BH_4]$.

INTRODUCTION

The activation of B–H bonds is a reaction of great interest in connection with relevant catalytic processes including the hydroboration of unsaturated organic molecules,[1] the dehydrogenative borylation of hydrocarbons,[2] and the dehydrocoupling of Lewis adducts, mainly ammonia-borane.[3] It is well stablished that the first step for the cleavage of the B–H bond is its coordination to an unsaturated transition metal to form $M(\eta^2\text{-}H\text{–}BR_2)$ σ-complexes, from which a limited number have been isolated and characterized.[4] This intermediates can evolve by oxidative addition,[5] heterolytic cleavage,[6] or σ-bond metathesis[7] depending upon the nature of the metal center and the co-ligands of the complex.

The simultaneous or sequential activation of the B–H bond of two R_2BH molecules shows high complexity. This is in a part due to the number and variety of possible reactions between the B–H units and the ligands of the precusors.[8] On the other hand, it has been proposed[9] that the release of labile and inert groups from the metal coordination sphere allows the formation of six different types of compounds (Scheme 1): di(σ-borane) (**I**), dihydride-diboryl (**II**), boryl-dihydrideborate (**III**), hydride-boryl-σ-borane (**IV**), diboryl-dihydrogen (**V**), and dihydride-diborane (**VI**); although only di(σ-borane)[10] and dihydride-diboryl[9,11] species have been previously isolated and characterized. In this paper, we report the first compounds of the type boryl-dihydrideborate. They are formed via a σ-borane intermediate.

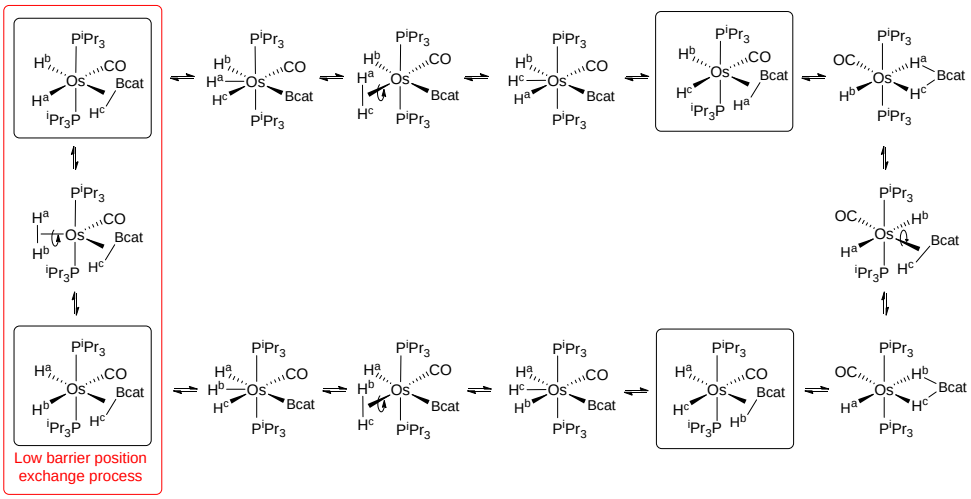


Scheme 1. Possible Compounds with two R_2BH units in the Metal Coordination Sphere

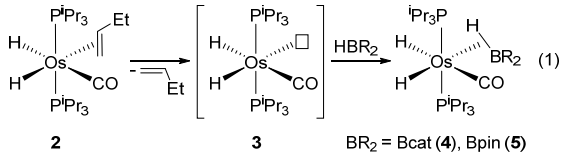
RESULTS AND DISCUSSION

The five-coordinate complex $OsHCl(CO)(P^iPr_3)_2$[12] (**1**) reacts with ^{n}BuLi to afford the dihydride-1-butene derivative $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**2**), as a

Scheme 2. Exchange Processes in 4



consequence of the substitution of the chloride ligand by a butyl group and a subsequent β-hydrogen elimination reaction at the alkyl unit.[13] This compound shows tendency to dissociate the olefin, at room temperature, and the resulting unsaturated dihydride $OsH_2(CO)(P^iPr_3)_2$ (**3**) has been shown to promote the release of 1 equiv of molecular hydrogen from ammonia-borane and the formation of polyaminoborane via a Shimoi type intermediate.[14] In accordance with this precedent, we have now discovered that the addition of 1.0 equiv of catecholborane (HBcat) and pinacolborane (HBpin) to pentane solutions of **2** gives rise to the coordination of the BH bond of the boranes to **3** to form the σ-borane derivatives $OsH_2(\eta^2\text{-}HBR_2)(CO)(P^iPr_3)_2$ (BR_2 = Bcat (**4**), Bpin (**5**)), which are isolated as yellow (**4**) and white (**5**) solids in high yield (70% (**4**), 75% (**5**)), according to eq 1. These compounds are diagonal counterparts of the trihydride-silyl derivatives $OsH_3(SiR_3)(CO)(P^iPr_3)_2$ (SiR_3 = $SiHPh_2$, $SiPh_3$, $Si(OMe)_2Ph$),[15] which were obtained from the hydride-tetrahydrideborate complex $OsH(\kappa^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$[16] by replacement of the BH_3 moiety by the corresponding $HSiR_3$ silane and a subsequent oxidative addition of the Si–H bond.



Complex **5** has been previously generated *in situ* from the borylthiolate-dihydrogen complex $OsH(SBpin)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ by means of a borylthiol-pinacolborane exchange, and characterized by NMR spectroscopy.[17] The ^1H, ^{11}B, and $^{31}P\{^1H\}$ NMR spectra of **4**, in toluene-d_8, are consistent with those of **5**. The hydrogen atoms bonded to the metal center undergo two thermally activated site exchange processes, involving the hydride positions and those with the B–H site. Figure 1 shows the $^1H\{^{11}B\}$ NMR spectrum, in the high field region, as a function of the temperature. In agreement with **5** and the dihydride-iridium complex $IrH_2(^t\text{BuPOCOP})(\eta^2\text{-H–Bpin})$ (^{t}BuPOCOP = $\kappa^3\text{-}C_6H_3\text{-}1,3\text{-}[OP(^t\text{Bu})_2]_2$),[18] the hydride-hydride site exchange needs an activation energy significantly lower than the hydride-BH site exchange. Thus, the $^1H\{^{11}B\}$ NMR spectrum, at 183 K, shows two high field resonances at −8.5 and −10.1 ppm, in a 1:2 intensity ratio, corresponding to the BH-hydrogen atom and the hydride ligands, respectively. As expected for the classical nature of the hydride ligands, a 300 MHz $T_{1(min)}$ value of 167 ms was found at 213 K for the highest field signal, in spite of the presence of the boron atom.[19] At about 253 K, the coalescence between the hydride and BH resonances occurs and, at temperatures higher than 253 K, only one resonance centered at −9.7 ppm is observed. The presence of a coordinated HBcat group in **4** is also supported by the ^{11}B NMR spectrum, which shows a broad signal at 38 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 39 ppm, in accordance with equivalent phosphines.

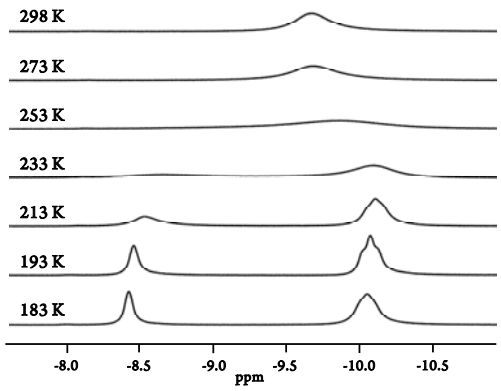
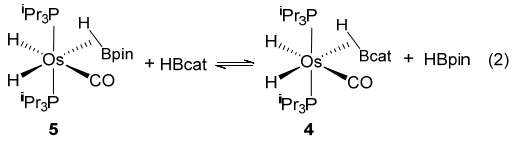


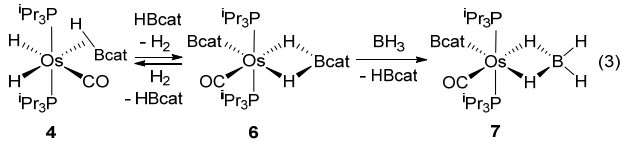
Figure 1. High field region of the $^1H\{^{11}B\}$ NMR spectrum (300 MHz, toluene-d_8) of **4** as a function of temperature.

The exchange processes can be rationalized according to Scheme 2. The hydride-hydride site exchange could take place via dihydrogen species, whereas the hydride-BH site exchange should proceed through trihydride-boryl intermediates related to the trihydride-silyl counterparts, previously mentioned, hydride-boryl-dihydrogen derivatives, and hydride-dihydrideborate species.[20]

The M(η^2-H–BR_2) interaction involves σ-donation from the σ-orbital of the coordinated B–H bond to empty orbitals of the metal and back-bonding from the metal into the boron p_z-orbital which competes with oxygen π-donation from the boron substituents, for **4** and **5**. The decrease of the oxygen π-donation, strengthens the metal back-bonding and therefore increase the stability of the σ-complex. In contrast to pinacolborane, the catecholate oxygens have the possibility of delocalizing electron density into the aromatic system. As a result the catecholborane complex **4** is more stable than the pinacolborane derivative **5**. Thus, at 243 K, the addition of 1.2 equiv of HBcat to pentane solutions of **5** leads after 7 days to the equilibrium shown in eq 2 with an equilibrium constant *K* of 16, determined by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S1).



Complex **4**, in contrast to **5**, reacts with a second molecule of HBcat, at room temperature. Treatment of pentane solutions of **4** with 1.2 equiv of the boron hydride for 3 h affords molecular hydrogen and the novel boryl-dihydrideborate complex Os(Bcat)(κ^2-H_2Bcat)(CO)(P^iPr_3)$_2$ (**6**), which was isolated as a white solid in almost quantitative yield. The reaction is reversible, at room temperature and under 1.2 atm of H_2, the benzene-d_6 solutions of **6** regenerate **4** and HBcat (eq 3).



Complex **6** was characterized by X-ray diffraction analysis. The structure (Figure 2) proves the boryl-dihydrideborate nature of the compound. The coordination geometry around the osmium atom can be described as a distorted octahedron, with *trans* phosphines (P1–Os–P2 = 173.239(19)°). The perpendicular plane is formed by the chelate dihydrideborate ligand, which acts with a H01–Os–H02 bite angle of 68.4(11)° and the boryl and carbonyl groups. The separation between the metal center and the borate boron atom of 2.244(3) Å is in keeping with other crystallographically characterized osmium-hydrideborate complexes.[21] According to an sp^3-hybridization at the borate boron atom, the angles around B1 are between 104.5(16)° and 113.4(10)°. The osmium-boryl bond length of 2.076(3) Å (Os–B2) compares well with those reported for other osmium-boryl derivatives.[22] The O4–B2–Os and O5–B2–Os angles of 129.07(19)° and 123.43(18)°, respectively, support the sp^2-hybridization at B2.

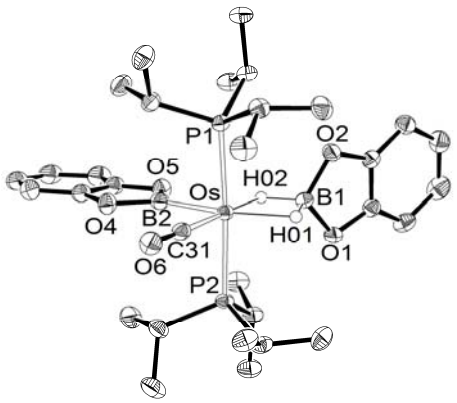
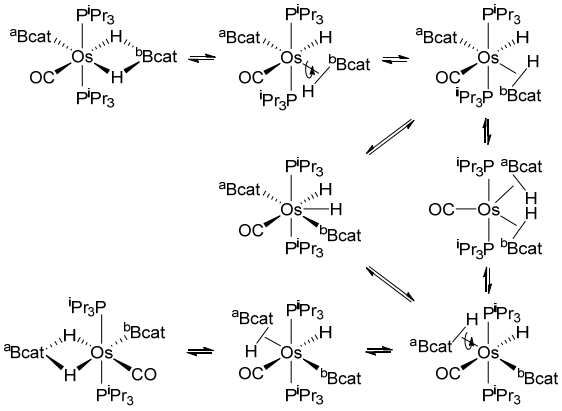


Figure 2. Molecular diagram of **6** with 50% probability ellipsoids. The labels of the carbon atoms of the phosphine and Bcat groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–B2 2.076(3), Os–H01 1.84(2), Os–H02 1.72(3), B1–H01 1.26(2), B1–H02 1.27(2); P1–Os–P2 173.239(19), H01–Os–H02 68.4(11), H01–B1–H02 104.5(16), H01–B1–O1 113.1(10), H01–B1–O2 112.1(9), H02–B1–O1 106.8(10), H02–B1–O2 113.4(10), O4–B2–Os 129.07(19), O5–B2–Os 123.43(18).

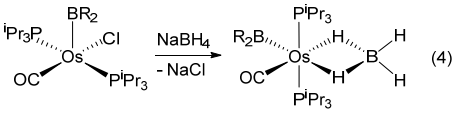
The Bcat groups of **6** exchange their position, in solution, at room temperature. Thus, the ^{11}B NMR spectrum in toluene-d_8 shows only a broad resonance centered at 38 ppm whereas, in the ^1H NMR spectrum, the inequivalent OsHB-hydrogen atoms display only one resonance at −6.9 ppm. At 183 K, both resonances split into two signals, which appear at 47 (OsBcat) and 29 (Os(κ^2-H_2Bcat)) and −6.2 and −7.5 ppm, respectively. The fluxional process could takes place via hydride-boryl-σ-borane intermediates in equilibrium with di(σ-borane) and dihydride-diboryl species, according to Scheme 3. In agreement with equivalent phosphines, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 23.7 ppm.

Scheme 3. Bcat Position Exchange in 6



Borane displaces catecholborane from the dihydrideborate of **6**, in agreement with the niobium complex Nb(η^5-C_5Me_5)(κ^2-H_2Bcat′) (cat′ = $O_2C_6H_3$-4-^{t}Bu)[23] and as expected for the transitory formation of a more stable M(η^2-H–BH_2) intermediate. Thus, the addition of 1.0 equiv of BH_3·THF to pentane solutions of **6** gives rise to the instantaneous and quantitative generation of the boryl-tetrahydrideborate derivative Os(Bcat)(κ^2-H_2BH_2)(CO)(P^iPr_3)$_2$ (**7**), which was isolated as a white solid in 99% yield (eq 3). This compound can be also prepared in isolated

yield of 63%, by means of the replacement of the chloride ligand of the five-coordinate boryl complex $Os(Bcat)Cl(CO)(P^iPr_3)_2$[8c] with a tetrahydrideborate anion (eq 4). Similarly, treatment of tetrahydrofuran solutions of $Os(Bpin)Cl(CO)(P^iPr_3)_2$[22j] with 2.0 equiv of $Na[BH_4]$, for 50 minutes, at room temperature affords the pinacolboryl counterpart $Os(Bpin)(\kappa^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**8**) along with about 23% of the hydride $OsH(\kappa^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$.[16] After recrystallization in pentane at 243 K, complex **8** was obtained as pure yellow crystals in 18% yield.



BR_2 = Bcat, Bpin BR_2 = Bcat (**7**), Bpin (**8**)

Complex **7** was also characterized by X-ray diffraction analysis. The structure has two molecules chemically equivalent but crystallographically independent in the asymmetric unit. Figure 3 shows a view of one of them. The coordination polyhedron around the osmium atom is as that of **6** with the tetrahydrideborate ligand occupying the position of the dihydridecatecholborate group and P1–Os–P2 and H2a–Os–H2b angles of 176.45(5)° and 171.57(5)° and 64(2)° and 67.1(10)°, respectively. The osmium-boryl bond lengths, Os–B1, of 2.067(6) and 2.045(6) Å are almost statistically identical to that **6**, whereas the separations between the metal center and the tetrahydrideborate boron atom B2 of 2.313(7) and 2.304(9) Å are between 0.04 and 0.02 Å longer than the separation between the metal center and the dihydridecatecholborate boron atom of **6**. The angles around B1 and B2 support the respective sp^2- and sp^3- hybridizations at these atoms (see Supporting Information) and therefore the boryl and borate nature of the corresponding ligands.

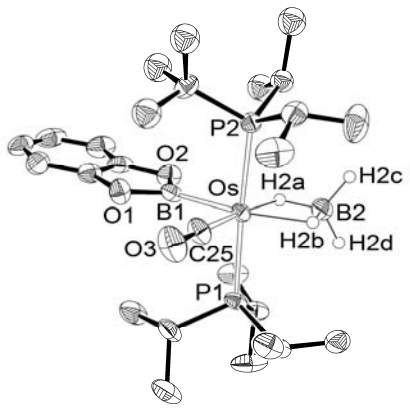


Figure 3. Molecular diagram of **7** with 50% probability ellipsoids. The labels of the carbon atoms of the phosphine and Bcat ligands are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–B1 2.067(6), 2.045(6); Os–H2a 1.75(6), 1.86(8); Os–H2b 1.83(6), 1.59(8); B2–H2a 1.20(4), 1.301(10); B2–H2b 1.27(4), 1.296(10); B2–H2c 1.10(5), 1.05(6); B2–H2d 1.12(5), 1.04(6); P1–Os–P2 176.45(5), 171.57(5); H2a–Os–H2b 64(2), 67.1(10).

The ^{11}B, ^1H, and $^{31}P\{^1H\}$ NMR spectra of **7** and **8**, in toluene-d_8, at room temperature are consistent with the structure shown in Figure 3. In agreement with the presence of boryl and borate ligands, the ^{11}B spectra contain two broad resonances at 43 (Bcat) and 8 (BH_4) ppm for **7** and at 37 (Bpin) and 7 (BH_4) ppm for **8**. In the ^1H NMR spectra, the inequivalent OsHB-hydrogen atoms displays resonances, in the high field region, at −4.6 and −6.6 ppm for **7** and at −4.7 and −6.7 ppm for **8** whereas the inequivalent terminal BH_2-hydrogen atoms give rise in the low field region to a broad signal centered at about 6.4 ppm for **7** and at about 6.1 ppm for **8**. The $^{31}P\{^1H\}$ NMR spectra show singlets at 27.9 (**7**) and 26.6 (**8**) ppm, as expected for equivalent phosphines.

CONCLUDING REMARKS

In conclusion, the metal fragment $Os(CO)(P^iPr_3)_2$[14,24] stabilizes boryl-dihydrideborate species, in contrast to $Ti(\eta^5\text{-}C_5H_5)_2$ and $M(\eta^5\text{-}C_5Me_5)$ (M = Rh, Ir). Because complexes boryl-dihydrideborate in reality are snapshots of states of B–H oxidative addition of a R_2BH molecule and frustrated B–H bond activation of a second one, the compounds here reported suggest that the nucleophilicity of the osmium unit $Os(CO)(P^iPr_3)_2$ is intermediate between those of the $Ti(\eta^5\text{-}C_5H_5)_2$ and $Rh(\eta^5\text{-}C_5Me_5)$ metal fragments.

EXPERIMENTAL SECTION

General Information. All manipulations were performed with rigorous exclusion of air at an argon/vacuum manifold using standard Schlenk-tube techniques or in a dry-box (MB-UNILAB). Solvents were dried by the usual procedures and distilled under argon prior to use or obtained oxygen- and water-free from an MBraun solvent purification apparatus. Pentane was stored over P_2O_5 in the dry-box. Pinacolborane (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was purchased from commercial sources and used without further purification. Catecholborane (HBcat = 1,3,2-benzodioxaborolane) was purchased from commercial sources and distilled in a Kugelrohr distillation oven. The starting materials $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**1**),[13] $Os(Bcat)Cl(CO)(P^iPr_3)_2$,[8c] $Os(Bpin)Cl(CO)(P^iPr_3)_2$,[22j] were prepared according with the published methods. NMR spectra were recorded on a Varian Gemini 2000, a Bruker ARX 300, a Bruker Avance 300 MHz or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$), external H_3PO_4 ($^{31}P\{^1H\}$), or $BF_3{\cdot}OEt_2$ (^{11}B). Coupling constants, J, and N ($N = J_{H\text{-}P} + J_{H\text{-}P'}$ or $J_{C\text{-}P} + J_{C\text{-}P'}$) are given in hertz. Infrared spectra were recorded on a Perkin-Elmer spectrum One Spectrometer (ATR). C and H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of $OsH_2(\eta^2\text{-}H\text{–}Bcat)(CO)(P^iPr_3)_2$ (4). Catecholborane (18.5 μL, 0.174 mmol) was added to a colorless solution of **1** (100 mg, 0.174 mmol) in 3 mL of pentane. The suspension was stirred at room temperature for 5 minutes. After that, the suspension was filtered through Celite. The filtrate was concentrated to dryness to give a yellow solid. Yield 80 mg (70 %). Anal. Calcd for $C_{25}H_{49}BO_3OsP_2$: C, 45.45; H, 7.48. Found: C, 45.48; H, 7.69. IR (ATR, cm^{-1}): ν(CO) 1938 (s). $^1H\{^{11}B\}$ NMR (300 MHz, C_7D_8, 298 K): δ 6.88 (m, 2H, Bcat), 6.72 (m, 2H, Bcat), 2.26 (m, 6H, PC*H*CH_3), 1.21 (dvt, N = 14.0, $J_{H\text{–}H}$ = 7.0, 18H, PCHC*H*$_3$), 1.16 (dvt, N = 13.8, $J_{H\text{–}H}$ = 7.0, 18H, PCHC*H*$_3$), − 9.7 (br, 3H, BH and OsH). $^1H\{^{11}B\}$ NMR (300 MHz, C_7D_8, 193 K): δ −8.5 (br, 1H, BH), −10.1 (br, 2H, OsH). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_7D_8, 298 K): δ 38.7 (s). ^{11}B NMR (96.29 MHz, C_7D_8, 298 K): δ 38 (br).

Preparation of $OsH_2(\eta^2\text{-}H\text{–}Bpin)(CO)(P^iPr_3)_2$ (5). Pinacolborane (25.3 μL, 0.174 mmol) was added to a solution of **1** (100 mg, 0.174 mmol) in 3 mL of pentane. The suspension was stirred at room temperature for 5 minutes. After that, the suspension was filtered through Celite. The filtrate was concentrated to dryness to give a white

solid. Yield 87 mg (75 %). Anal. Calcd for $C_{25}H_{57}BO_3OsP_2$: C, 44.90; H, 8.59. Found: C, 44.84; H, 8.55. IR (ATR, cm^{-1}): ν(CO) 1943 (s). $^1H\{^{11}B\}$ NMR (400 MHz, C_7D_8, 298 K): δ 2.30 (m, 6H, PC*H*CH_3), 1.23 (dvt, N = 14, J_{H-H} = 7.2, 18H, PCHC*H*$_3$), 1.21 (dvt, N = 14.2, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.1 (s, 12H, Bpin), −9.8 (br, 1H, BH), −10.5 (br, 2H, OsH). $^1H\{^{11}B\}$ NMR (400 MHz, C_7D_8, 283 K): δ −9.5 (br, 1H, BH), −9.8 (br, 1H, OsH), −11.2 (dt, 1H, J_{H-P} = 20.1, J_{H-H} = 5.2, OsH). $^{31}P\{^1H\}$ NMR (162 MHz, C_7D_8, 298 K): δ 38.0 (s). ^{11}B NMR (128 MHz, C_7D_8, 298 K): δ 34 (br). NMR spectroscopic data are identical to those previously reported by us.[17]

Reaction of 5 with 1.2 equiv of Catecholborane. Catecholborane (18.5 μL, 0.174 mmol) was added to a colorless solution of **5** (100 mg, 0.150 mmol) in 2 mL of pentane. After 7 days at 243 K, the $^{31}P\{^1H\}$ and ^{11}B NMR spectra of this solution, showed the presence of **4** and **5** in a molar ratio of 1:0.17 (Figures S1 and S2).

Preparation of Os(Bcat)(κ²-H_2Bcat)(CO)(P^iPr_3)$_2$ (6). Catecholborane (18.5 μL, 0.174 mmol) was added to a solution of **4** (100 mg, 0.151 mmol) in 1 mL of pentane. Immediately, the solution changed from yellow to colorless. The solution was stirred at room temperature for 3 h. During this time a white solid was formed. This solid was separated by decantation and dried in vacuo. Yield: 114 mg (97%). Anal. Calcd for $C_{31}H_{52}B_2O_5OsP_2$: C, 47.82; H, 6.73. Found: C, 47.70; H, 6.95. IR (ATR, cm^{-1}): ν(CO) 1960 (s). $^1H\{^{11}B\}$ NMR (300 MHz, C_7D_8, 298 K): δ 6.98 (m, 4H, Bcat), 6.78 (m, 4H, Bcat), 2.67 (m, 6H, PC*H*CH_3), 1.11 (dvt, *N* = 13.4, J_{H-H} = 6.8, 36H, PCHC*H*$_3$), −7.0 (br, 2H, BH). $^1H\{^{11}B\}$ NMR (300 MHz, C_7D_8, 183 K): δ −6.2 (br, 1H, BH), −7.5 (br, 1H, BH). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_7D_8, 298 K): δ 23.7 (br). ^{11}B NMR (96.29 MHz, C_7D_8, 298 K): δ 38 (br). ^{11}B NMR (96.29 MHz, C_7D_8, 183 K): δ 47 (br, OsBcat), 29 (br, Os(κ²-H_2Bcat)).

Reaction of 6 with H_2. A Young NMR tube containing a solution of **6** (15 mg, 0.019 mmol) in 0.5 mL of C_6D_6 was placed under hydrogen atmosphere (1.2 atm). Immediately, the solution changed from light yellow to colorless. The NMR spectra showed the complete conversion of **6** to **4** along with the formation of HBcat.

Preparation of Os(Bcat)(κ²-H_2BH_2)(CO)(P^iPr_3)$_2$ (7). *Method A.* BH_3·THF (15.3 μL, 1.0 M, 0.015 mmol) was added to a NMR tube containing a solution of **6** (12 mg, 0.015 mmol) in 0.5 mL of C_7D_8. Immediately, the solution changed from light yellow to colorless. The NMR spectra showed the complete conversion of **6** to **7** along with the formation of HBcat.

Method B. $NaBH_4$ (62 mg, 1.639 mmol) was added to a solution of Os(Bcat)Cl(CO)(P^iPr_3)$_2$ (200 mg, 0.289 mmol) in 5 mL of THF. The suspension was stirred at room temperature for 20 minutes. During this time the suspension changed from light yellow to colorless. The solvent was removed in vacuum. Pentane (5 mL) was added, and the resulting suspension was filtered through Celite. The filtrate was concentrated to dryness to give a white solid. Yield 122 mg (63%).

Method C. BH_3·THF (151 μL, 1.0 M, 0.151 mmol) was added to a yellow solution of **4** (100 mg, 0.151 mmol) in 2 mL of pentane. The resulting colorless solution was stirred at room temperature for 5 minutes. After that, the solvent was removed in vacuum to give a white solid. Yield 101 mg (99 %). Anal. Calcd for $C_{25}H_{50}B_2O_3OsP_2$: C, 44.65; H, 7.49. Found: C, 44.75; H, 7.55. IR (ATR, cm^{-1}): ν(BH) 2480, 2443 (w), ν(CO) 1924 (s). $^1H\{^{11}B\}$ NMR (300 MHz, C_7D_8, 298 K): δ 7.21 (m, 2H, Bcat), 6.84 (m, 2H, Bcat), 6.44 (br, 2H, BH), 2.56 (m, 6H, PC*H*CH_3), 1.20 (dvt, *N* = 14.0, J_{H-H} = 7.1, 18H, PCHC*H*$_3$), 1.00 (dvt, *N* = 13.0, J_{H-H} = 6.8, 18H, PCHC*H*$_3$), −4.6 (br, 1H, BH), −6.6 (br, 1H, BH). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 27.9 (s). ^{11}B NMR (96.29 MHz, C_6D_6, 298 K): δ 43 (br, Bcat), 8 (br, BH_4).

Preparation of Os(Bpin)(κ²-H_2BH_2)(CO)(P^iPr_3)$_2$ (8). $NaBH_4$ (97 mg, 2.564 mmol) was added to a solution of Os(Bpin)Cl(CO)(P^iPr_3)$_2$ (200 mg, 0.285 mmol) in 5 mL of THF. The suspension was stirred at room temperature for 50 minutes. During this time the suspension changed from yellow to light yellow. The solvent was removed in vacuo. Pentane (5 mL) was added, and the resulting suspension was filtered through Celite. The filtrate was concentrated to dryness to give a 1:0.3 mixture of complexes **8** and OsH(κ²-H_2BH_2)(CO)(P^iPr_3)$_2$[16] as a light yellow solid (123 mg). This mixture was recrystallized in 3 mL of pentane at −30 °C to give **8** as yellow crystals. Yield 35 mg (18%). Anal. Calcd for $C_{25}H_{58}B_2O_3OsP_2$: C, 44.12; H, 8.59. Found: C, 44.10; H, 8.63. IR (ATR, cm^{-1}): ν(BH) 2474, 2455 (w), ν(CO) 1909 (s). $^1H\{^{11}B\}$ NMR (300 MHz, C_7D_8, 298 K): δ 6.13 (br, 2H, BH), 2.70 (m, 6H, PC*H*CH_3), 1.37 (dvt, *N* = 13.9, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.20 (dvt, *N* = 13.4, J_{H-H} = 6.1, 18H, PCHC*H*$_3$), 1.22 (s, 12H, Bpin), −4.7 (br, 1H, BH), −6.7 (br, 1H, BH). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 26.6 (s). ^{11}B NMR (96.29 MHz, C_6D_6, 298 K): δ 37 (br, Bpin), 7 (br, BH_4).

Structural Analysis of 6 anf 7. X-ray data were collected on a Bruker Smart APEX DUO diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 (**6**) or 40 (**7**) mA. Data were collected over the complete sphere. Each frame exposure time was 10s (**6**) or 30s (**7**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[25] The structures were solved by the direct methods. Refinement of both complexes was performed by full-matrix least-squares on I^2 with SHELXL97,[26] including isotropic and subsequently anisotropic displacement parameters (for non-hydrogen non disordered atoms). The hydrogen atoms attached to boron and osmium atoms were found in the last cycles of difference of Fourier and refined freely in **6**. However, they did not refine properly in **7**, so a restricted model was used to force the same geometry around the boron atom in the two independent molecules. The other hydrogen atoms were calculated and refined riding to bonded atoms. In addition two triisopropylphosphines were observed disordered and were refined with two moieties and complementary occupancy factors and isotropic displacement parameters.

Crystal data for **6**: $C_{31}H_{52}B_2O_5OsP_2$, M_W 778.49, irregular block, colourless (0.40 x 0.15 x 0.12), monoclinic, space group $P2_1/c$, *a*: 12.8512(15) Å, *b*: 16.8240(19) Å, *c*: 16.3209(18) Å, β: 101.268(2) °, *V* = 3460.7(7) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.494 g cm^{-3}, F(000): 1576, *T* = 100(2) K, μ 3.812 mm^{-1}. 26959 measured reflections (2θ: 3-58°, ω scans 0.3°), 8956 unique (R_{int} = 0.0279); min./max. transm. factors 0.619/0.862. Final agreement factors were R^1 = 0.0216 (7865 observed reflections, I > 2σ(I)) and wR^2 = 0.0552; data/restraints/parameters 8956/0/388; GoF = 1.003. Largest peak and hole: 1.724 and −0.971 e/Å^3.

Crystal data for **7**: $C_{25}H_{50}B_2O_3OsP_2$, M_W 672.41, irregular block, colourless (0.15 x 0.12 x 0.09), monoclinic, space group $P2_1/c$, *a*: 26.620(4) Å, *b*: 9.7721(14) Å, *c*: 24.328(3) Å, β: 108.669(2)°, *V* = 5995.6(15) Å^3, *Z* = 8, *Z'* = 2, D_{calc}: 1.490 g cm^{-3}, F(000): 2720, *T* = 100(2) K, μ 4.383 mm^{-1}. 62803 measured reflections (2θ: 3-51°, ω scans 0.3°), 15525 unique (R_{int} = 0.0415); min./max. transm. factors 0.692/0.862. Final agreement factors were R^1 = 0.0399 (12285 observed reflections, I > 2σ(I)) and wR^2 = 0.0890; data/restraints/parameters 15525/28/616; GoF = 1.106. Largest peak and hole: 2.482 and −2.123 e/Å^3.

ASSOCIATED CONTENT

Supporting Information

$^{31}P\{^1H\}$ and ^{11}B NMR spectra of the reaction of **5** with 1.2 equiv of HBcat and CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **6** and

7. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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