Elongated σ-Borane versus σ-Borane in Pincer-POP-Osmium Complexes

Miguel A. Esteruelas, *† Israel Fernández, † Cristina García-Yebra, † Jaime Martín, † and Enrique Oñate †

1Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain
2Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad Complutense de Madrid, 28040 Madrid, Spain

Supporting Information Placeholder

ABSTRACT: Square pyramidal metal fragments OsH(X){κ³-P,P,P-[xant(PPr₂)₂]} (X = Cl, H; xant(PPr₂)₂ = 9,9-dimethyl-4,5-bis(diisopropylphosphine)xanthene) coordinate the B-H bond of boranes trans to the ligand X. As a consequence, elongated σ-borane and σ-borane pincer-POP-osmium complexes have been isolated and fully characterized. The interaction between the metal fragment and the coordinated B-H has been analyzed as a function of X, from spectroscopic, X-ray diffraction, and theoretical points of view. The dimeric complex [(OsH···H){κ³-P,P,P-[xant(PPr₂)₂]};(μ-Cl)]_2[BF₄] (3) reacts with catecholborane (HBcat) and pinacolborane (HBpin) to give the elongated σ-borane derivative OsHCl{κ³-H-BR₂}{κ³-P,P,P-[xant(PPr₂)₂]}/(BR₂ = Bcat (4), Bpin (5)), H₂, FBR₂, and BF₃. The elongated σ-borane character of 4 and 5 is supported by X-ray diffraction analysis and DFT-optimized structures of both compounds, which show distances between the coordinated B and H atoms of the borane in the range 1.6-1.7 Å. AIM analysis of 4 reveals a triangular topology for the OsHB unit involving Os-B, Os-H, and B-H bond critical points and a ring critical point. In contrast to 3, the reaction of the tetrahydride complex OsH₂{κ³-P,P,P-[xant(PPr₂)₂]} (6) with HBcat leads to the σ-borane derivative OsH₂{κ³-H-Bcat}{κ³-P,P,P-[xant(PPr₂)₂]} (7), which shows a distance between the atoms of the coordinated B-H bond in the range 1.4-1.5 Å. AIM analysis for the OsHB unit of 7 only displays Os-B and B-H bond critical points therefore lacking a similar topology.

INTRODUCTION

Metal-promoted σ-bond activation reactions are the origin of a great number of processes in the current chemistry. The first step is the coordination of the σ-bond to the metal to form a σ-complex. The metal-bond interaction involves σ-donation from the σ-molecular orbital of the coordinated bond to empty orbitals of the metal and back bonding from the metal to the σ*-molecular orbital of the bond. The balance between donation and back-donation determines the degree of addition of the bond to the metal, which in the majority of cases fits to the separation between the coordinated atoms.1 Dihydrogen compounds form the best-known group of complexes of this type. Depending upon the separation between the coordinated hydrogens, they are classified in Kubas-type complexes (0.8-1.0 Å) and elongated dihydrogens (1.0-1.3 Å). High oxidation states, first-row metals, cationic charges, acidic ligands and tridentate groups enforcing L-M-L angles close to 90° stabilize Kubas-type complexes while low oxidation states, third-row metals, and π-donor ligands favor the formation of elongated dihydrogen compounds.2

The stabilization of σ-E-H bond activation intermediates (B, C, Si, etc) is much more difficult than the stabilization of dihydrogen species.3 As a consequence, very little information is available for σ-E-H complexes. By comparison to the hydrogen molecule, an R-E-H bond (n = 2 or 3) is disymmetric and the substituents at the E atom may tune the acidity of the bond. In addition, in some cases the E atom can possess available empty orbitals, as boron, which alter the balance between donation and back-donation in comparison with the dihydrogen situation. The B-H bond activation is a reaction of great interest in connection with the borylation of organic molecules4 and the dehydrocuping of amineboranes.5 However, scarce examples of complexes containing non-assisted B-H coordination have been reported.6 They include some first-row metals; such as Ti,7 Mn, 8 Ni,9 and Ru.10 These compounds contain small H-M-B angles (32°-38°), whereas the B-H distances are in the range 1.23-1.35 Å. For third-row metals, Heinckey and co-workers have reported the neutron diffraction structure of Ir₄{κ³-P,C,P-[C₆H₃-1,3-(OPBu₂)₂]}{(κ²-H-BH₂)}, which contains a B-H σ-bond coordinated to iridium with a B-H distance of 1.45(5) Å. The pinacolborane (HBpin) counterpart loses molecular hydrogen to afford the square planar derivative Ir₄{κ³-P,C,P-[C₆H₃-1,3-(OPBu₂)₂]}{(κ²-H-Bpin)11} Our group has described the coordination of catecholborane (HBcat) and HBpin to the osmium dihydride OsH₂(CO)(PPr₂)₂ to give OsH₂(CO){κ³-H-BR₂}{κ³-P,P,P-[xant(PPr₂)₂]}.12 There are also a few (C₅Me₅)Rh-complexes bearing hydride and boryl ligands, which show separations between the boron and a hydride in the range 1.60-2.0 Å.13 For these compounds, which could be considered the borane counterparts of the elongated dihydrogen species on the base of this separation, a "residual" B···H interaction has been suggested, although no clear evidence on
their nature has been provided. In contrast to dihydrogen complexes, it remains difficult to assign a correct formulation on the basis of $^{11}$B and $^1$H NMR. Thus, the development of simple methods to assert nature of the interaction of the B-H bond with the metal center, discerning between $\sigma$-borane and elongated $\sigma$-borane, is a need of the field.

Ether-diphosphines (POP) are flexible, which allows them to change their coordination fashion for adapting to the requirement of the participating intermediates in multistep processes. As a consequence of this ability, platinum group metals containing these ligands are playing a main role in homogeneous catalysis. In addition, we have recently shown that osmium polyhydrides bearing 9,9-dimethyl-4,5-bis(diisopropylphosphine) xanthene (xant(PPr$_2$)$_2$) sequentially add $\text{H}^+$ and $\text{H}^+$ or $\text{H}^+$ and $\text{H}^+$ to generate molecular hydrogen in a cyclic manner. During the process the ether-diphosphine changes its coordination mode to stabilize both dihydride and dihydrogen species. Dihydrogens are favored by a $\kappa^3$ dispo- mer coordination with P(1)-Os-P(2), P(1)-Os-O(3), and P(2)-Os-O(3) angles of 161.98(3)$^\circ$ and 161.85(3)$^\circ$, 80.98(6)$^\circ$ and 81.30(6), and 81.27(6) and 80.90(6), respectively. Thus, the coordination polyhedron around the metal center can be rationalized as a distorted octahedron. The perpendicular plane to the P(1)-Os-P(2) direction contains the hydride H(01) ligand and disposed trans to the oxygen atom of the ether-diphosphine (H(01)-Os-O(3) = 165.6(9)$^\circ$ and 166.2(9)$^\circ$) and the coordinated catecholborane molecule situated trans to the chloride ligand with the hydrogen atom H(02) pointing out the B-H-Os bond. The coordination of the B-H bond promotes its elongation. The B-H(02) distances of 1.68(2) and 1.67(2)$^\AA$, 1.601$^\AA$ in the DFT-optimized structure, agree well with the shortest B-H distance in the rhodium complex Rh($\eta^2$-H-BR$_2$)($\kappa^3$-P,O,P-[xant(PPr$_2$)$_2$])(BR$_2$ = Bcat (4), Bpin (5)), which were isolated as white solids in 50-60% yield, together with FBR$_2$ ($\delta_{1H}$ 22.5), BF$_3$ ($\delta_{1H}$ 0.0), and H$_2$ (Scheme 1).

**RESULTS AND DISCUSSION**

**Elongated $\sigma$-Borane**

We have recently shown that the trihdyride derivative OsHCl[$\kappa^3$-P,O,P-[xant(PPr$_2$)$_2$]] (1) adds the proton of HBF$_4$ to afford the compressed dihydrodihydride cation [OsH($\cdot$-$\cdot$-$\cdot$-H)($\kappa^5$-H$_2$)Cl[$\kappa^3$-P,O,P-[xant(PPr$_2$)$_2$]]]$^+$ (2), which is stable under hydrogen atmosphere. Under argon, it dissociates the coordinated hydrogen molecule and the resulting unsaturated dihydride [OsH$_2$Cl($\kappa^2$-P,P-[xant(PPr$_2$)$_2$])]$^+$ (A) rapidly reaches an equilibrium with the dimer [(OsH($\cdot$-$\cdot$-$\cdot$-H)($\kappa^3$-P,O,P-[xant(PPr$_2$)$_2$]))$_2$(μ-Cl)$_2$]$^2^-$.

During the dimerization process, the ether-diphosphine changes its coordination fashion from $\kappa^3$-mer to $\kappa^3$-fac. Now, we have observed that HBcat and HBpin trap the unsaturated dihydride A. In addition, the metal center promotes the heterolytic H-B bond activation of a borane molecule by using a fluoride of the [BF$_4$]$^-$ anion as an external base. Thus, the treatment of dichloromethane solutions of the BF$_3$-salt of 3 with 5.1 mol of HBcat and HBpin, at room temperature, for 10 min leads to the hydride-elongated $\sigma$-borane derivatives OsHCl($\eta^2$-H-BR$_2$)($\kappa^3$-P,O,P-[xant(PPr$_2$)$_2$])(BR$_2$ = Bcat (4), Bpin (5)), which were isolated as white solids in 50-60% yield, together with FBR$_2$ ($\delta_{1H}$ 22.5), BF$_3$ ($\delta_{1H}$ 0.0), and H$_2$ (Scheme 1).

Complex 4 was characterized by X-ray diffraction analysis. The structure has two molecules chemically equivalent but crystallographically independent in the asymmetric unit. Figure 1 shows a view of one of them. The ether-diphosphine is mer coordinated with P(1)-Os-P(2), P(1)-Os-O(3), and P(2)-Os-O(3) angles of 161.98(3)$^\circ$ and 161.85(3)$^\circ$, 80.98(6)$^\circ$ and 81.30(6), and 81.27(6) and 80.90(6), respectively. Thus, the coordination polyhedron around the metal center can be rationalized as a distorted octahedron. The perpendicular plane to the P(1)-Os-P(2) direction contains the hydride H(01) ligand and disposed trans to the oxygen atom of the ether-diphosphine (H(01)-Os-O(3) = 165.6(9)$^\circ$ and 166.2(9)$^\circ$) and the coordinated catecholborane molecule situated trans to the chloride ligand with the hydrogen atom H(02) pointing out the ether. The coordination of the B-H bond promotes its elongation. The B-H(02) distances of 1.68(2) and 1.67(2)$^\AA$, 1.601$^\AA$ in the DFT-optimized structure, agree well with the shortest B-H distance in the rhodium complex Rh($\eta^2$-C$_5$Me$_5$)(Bpin)$_2$(η$^2$-HBpin) (1.53(3) and 1.69(3)$^\AA$) and the coordinated catecholborane character of this species. The B-M-H angles in both compounds are also similar, 53.6(9)$^\circ$ and 53.1(9)$^\circ$ in 4 versus 47.5(8)$^\circ$ and 54.3(10)$^\circ$ in the rhodium derivative. The B-H(02) distance is about 0.5$^\AA$ longer than the B-H(Os) bond lengths in the tetrahydrideboration derivative OsH$_2$($\kappa^2$-H$_2$BH$_3$)(IPr)(PPr$_2$) (1.18(3) and 1.17(3)$^\AA$, IPr = 1,3-bis(2,6-diisopropylphenylimidazolylidene) and about 0.4$^\AA$ longer than the B-H(Os) distances in the dihydrido species Os(Bcat)($\kappa^2$-H$_2$Bcat)(CO)(PPr$_2$) (1.26(3) and 1.27(3)$^\AA$). However, interestingly, the B-H(02) distance is only slightly shorter than the separation between the boron atom and the hydride ligand H(01), 1.70(2) and 1.70(2)$^\AA$; 1.770$^\AA$ in the
DFT-optimized structure. This is consistent with a cis-hydride-elongated σ-borane interaction. “Residual” contacts of this type are common in cis-hydride-elongated dihydrogen species.2c,19 Nevertheless, in this case, it does not appear to involve a true covalent bond (vide infra). It seems to be related to the geometry of the complex and the size of the involved atoms and could be magnified by the different sign of the partial charges on the hydride and on the boron atom of the borane. The interaction between the metal center and the coordinated B-H bond is certainly strong. Thus, the Os-B distance of 1.69(2) and 2.075(3) Å, respectively, 1.623 and 1.68(2) and 1.67(2), P-Os-P = 161.98(3) and 161.85(3), Os(1)-H(01) = 1.582(10) and 1.588(10), Os(1)-H(02) = 1.590(10) and 1.585(10), B(1)-H(01) = 1.70(2) and 1.70(2), B(1)-H(02) = 1.68(2) and 1.67(2), P(1)-Os(1)-P(2) = 161.98(3) and 161.85(3), P(2)-Os(1)-O(3) = 81.27(6) and 80.90(6), P(1)-Os(1)-O(3) = 80.98(6) and 81.30(6), B(1)-Os(1)-H(02) = 53.6(9) and 53.1(9), Os(1)-O(3)-H(01) = 166.5(9) and 166.2(9).

Complex 5 was also characterized by X-ray diffraction analysis. Figure 2 shows a view of the molecule. The coordination polyhedron around the osmium atom resembles that of 4 with a H-Bpin group instead of the H-Bcat ligand and P-Os-P, P-Os-O(2), and H(01)-Os-O(2) angles of 163.05(2)°, 81.577(11)°, and 165.9(10)°, respectively. The strength of the interaction between the B-H bond and the metal center is similar in both compounds. Thus, the B-H(02) and Os-B distances of 1.69(2) and 2.075(3) Å, respectively, 1.623 and 2.071 Â in the DFT-optimized structure, compare well with those of 4.

The 31P{1H}, 1H, and 11B NMR spectra of 4 and 5 are consistent with the structures depicted in Figures 1 and 2. In agreement with the mer-coordination of the ether-diphosphine, the 31P{1H} NMR spectra, in benzene-d6, at room temperature contain a singlet at about 36 ppm. Under the same conditions, the hydride ligand of 4 gives rise to a broad signal at -11.44 ppm in the 1H NMR spectrum, which splits into a triplet (JH,H = 11.0 Hz) in dichloromethane-d2 at 243 K, whereas the hydride ligand of 5 displays a triplet (JH,H = 11.0 Hz) at -12.99 ppm. In contrast to the hydride ligand, the coordinated BH-hydrogen atom gives rise to a broad resonance at -16.59 ppm for 4 and -16.99 ppm for 5, at 243 K and at room temperature. The 11B NMR spectra, in benzene-d6, at room temperature shows a broad signal at 52.0 ppm for 4 and 46.5 ppm for 5.

**Figure 2.** ORTEP diagram of complex 5 with 50 % probability ellipsoids. Hydrogen atoms (except H(01) and H(02)) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os-B(1) = 2.075(3), Os-O(2) = 2.2644(15), Os-P = 2.2989(4), Os-Cl = 2.4603(5), Os-H(01) = 1.577(10), Os-H(02) = 1.586(10), B(1)-H(01) = 1.75(3), B(1)-H(02) = 1.69(2), P-Os-P = 163.05(2), P-Os-O(2) = 81.577(11), H(01)-Os-O(2) = 165.9(10), B(1)-Os-H(02) = 53.1(9).

**Figure 1.** ORTEP diagram of one of the two molecules chemically equivalent but crystallographically independent in the asymmetric unit of the complex 4 with 50 % probability ellipsoids. The solvent molecule and hydrogen atoms (except H(01) and H(02)) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)-B(1) = 2.036(4) and 2.042(4), Os(1)-O(3) = 2.259(2) and 2.251(2), Os(1)-P(2) = 2.3047(8) and 2.3175(8), Os(1)-P(1) = 2.3167(8) and 2.3046(8), Os(1)-Cl(1) = 2.4694(8) and 2.4694(8), Os(1)-H(01) = 1.582(10) and 1.588(10), Os(1)-H(02) = 1.590(10) and 1.585(10), B(1)-H(01) = 1.70(2) and 1.70(2), B(1)-H(02) = 1.68(2) and 1.67(2), P(1)-Os(1)-P(2) = 161.98(3) and 161.85(3), P(2)-Os(1)-O(3) = 81.27(6) and 80.90(6), P(1)-Os(1)-O(3) = 80.98(6) and 81.30(6), B(1)-Os(1)-H(02) = 53.6(9) and 53.1(9), O(3)-Os(1)-H(01) = 166.5(9) and 166.2(9).
the separation between them of 1.81(4) Å, 1.926 Å in the DFT-optimized structure, is about 0.1-0.2 Å longer than in 4, i.e., the boron atom moves away from the hydride the same as approaches the hydrogen atom. This again suggests that in these compounds the proximity between the boron atom and the hydride is a consequence of the geometry of the complexes and the size of the involved atoms.

**Figure 3.** ORTEP diagram of complex 7 with 50 % probability ellipsoids. Hydrogen atoms (except H(01), H(02) and H(03)) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os-B(1) = 2.057(4), Os-O(3) = 2.271(3), Os-P(1) = 2.2832(10), Os-P(2) = 2.2808(10), Os-H(01) = 1.69(5), Os-H(02) = 1.579(14), Os-H(03) = 1.590(14), B(1)-H(01) = 1.49(4), B(1)-H(02) = 1.81(4), P(1)-Os-P(2) = 161.89(4), P(1)-Os-O(3) = 82.06(7), P(2)-Os-O(3) = 81.29(7), H(02)-Os-O(3) = 162.6(17), B(1)-Os-H(01) = 45.5(15).

The 1H, 11B, and 31P{1H} NMR spectra of 7 are consistent with the structure shown in the Figure 3. The 1H NMR spectrum, in toluene-d₈, at 193 K shows the B-H resonance at -1.9 ppm along with the signals corresponding to the inequivalent hydrides at -5.60 and -18.8 ppm. The B-H resonance is temperature invariant between 193 and 298 K. However, the hydride signals are temperature dependent (Figure 4). Thus, they coalesce at 233 K and a hydride signal is observed above this temperature. Figure 4 reveals that the hydride ligands undergo a thermally activated site exchange process, which takes place with an activation barrier of 9 kcal·mol⁻¹. This behavior agrees well with that observed for the iridium complex [IrH₂(κ²-P,P,C,P-[C₆H₃-1,3-(OPBu)₂])][η^2-HBpin] and the osmium-carbonyl derivatives OsH₂(CO)(η²-H-Br₂)(PPr₃)₂ (Br₂ = Bcat, Bpin). The presence of the coordinated H-B bond is also supported by the ¹¹B NMR spectrum at room temperature, which contains a broad resonance centered at 45.5 ppm. A singlet at 56.0 ppm in the ³¹P{¹H} NMR spectrum is another characteristic feature of this complex.

The prompt formation of 7 according to eq 1 is not consistent with the saturated character of 6 neither with a dissociation of the xanthene-ether group prior to the borane coordination. Because transition metal hydride complexes are usually amphoteric, they can experience autoionization. In the case of 7, this should imply the formation of the previously described pentahydride [OsH₅(κ²-P,P-[xant(PPr₃)₂])] (8), containing a P,P-bidentate ether-diphosphine, and the unsaturated osmium (IV) cation [OsH₃(κ²-P,P,O,P-[xant(PPr₃)₂])] (B in eq 2). Thus, the boron atom of the borane could undergo the nucleophilic attack of the pentahydride, which should give rise to the release of a hydride and the formation of OsH₅(Bcat)[κ²-P,P-[xant(PPr₃)₂]] (C), a boryl-pentahydride counterpart of the previously reported hexahydride OsH₆[κ²-

**Figure 4.** High-field region of the ¹H NMR spectrum of 7 between 298 and 193 K.

P,P-[κ²-P,P-[xant(PPr₃)₂]] (eq 3). Then, the generated hydride should be trapped by the cation B to again afford 6 (eq 4), which could further react in the same way until the consumption of the borane, whereas the coordination of the oxygen atom of the xanthene group of C should produce the release of molecular hydrogen and the formation of 7 (eq 5).

The bonding situation in complexes 4 and 7 was analyzed by means of DFT calculations, using the dispersion corrected BP86-D3 functional. The nature of the osmium-boron interactions was investigated using AIM, NBO, and EDA-NOVC methods. Figure 5 shows the Laplacian

**Bonding Situation.** The bonding situation in complexes 4 and 7 was analyzed by means of DFT calculations, using the dispersion corrected BP86-D3 functional. The nature of the osmium-boron interactions was investigated using AIM, NBO, and EDA-NOVC methods. Figure 5 shows the Laplacian...
distributions in the Os–H–B plane for complexes 4 and 7. Both species exhibit a significant Os–B interaction as revealed by the occurrence of a bond critical point (BCP) located between the transition metal and the boron atom, which is associated with a bond path (BP) running between both atoms. Interestingly, whereas a BCP between the osmium and the adjacent hydrogen atom close to the boron is located in complex 4, no such Os–H interaction is found for complex 7 (i.e. absence of a BCP and corresponding BP between both atoms). This finding is consistent with the calculated Wiberg Bond Indices (WBI) for the respective Os–B and Os–H bonds. Thus, whereas similar WBIs were computed for the Os–B bond of both complexes (WBI = 0.68 and 0.65, for compounds 4 and 7, respectively), rather different indices were computed for the Os–H interaction. Indeed, the much lower WBI value of 0.36 computed for 7 (WBI = 0.51 for 4) clearly suggests that the Os–H interaction is much weaker in 7 than in 4. As a consequence, no BCP was located in the corresponding AIM diagram. Therefore, the NBO and AIM methods indicate that although the Os–B bond strength is rather similar in both complexes, their bonding situations are markedly different. While the elongated σ-borane complex 4 is characterized by a three-membered cyclic species possessing one OsBH ring critical point, the σ-borane compound 7 lacks this triangular topology.

Figure 5. Contour line diagrams of ρ(r) for complexes 4 and 7 in the O–Os–B plane. Solid lines indicate areas of charge concentration (V∇ρ(r) < 0) while dashed lines show areas of charge depletion (V∇ρ(r) > 0). The solid lines connecting the atomic nuclei are the bond paths while the small green and red spheres indicate the corresponding bond critical points and ring critical points, respectively. H (○); O (●); Cl (●); Os (●); B(●).

In order to gain more quantitative insight into the bonding situation of complexes 4 and 7, the EDA-NOCV method was applied next. This method combines charge (NOCV) and energy (EDA) partitioning schemes to decompose the deformation density which is associated with the bond formation, Δρ, into different components of the chemical bond. The EDA-NOCV calculations provide pairwise energy contributions for each pair or interacting orbitals to the total bond energy (see further details in the computational details section).

The interaction between the neutral, closed-shell fragments OsHX(POP) and HBcat (X = Cl(4), H(7)) was considered for both complexes 4 and 7. From the data in Table 1, it becomes evident that the above discussed weaker Os–H interaction in the σ-borane complex 7 leads to a significant reduction of the interaction between the HBcat ligand and the transition metal moiety with respect to complex 4 (ΔΔEdisp = 31.9 kcal/mol). The EDA suggests that, despite the lower Pauli repulsion, this reduced interaction in complex 7 is mainly due to less stabilizing electrostatic (ΔΔEelstat = 59.3 kcal/mol) and orbital (ΔΔEorb = 34.7 kcal/mol) attractions.

Table 1. EDA-NOCV results (in kcal/mol) computed at the ZORA-BP86-D3/TZ2P+//BP86-D3/def2-SVP level.

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*Values within parentheses indicate the percentage to the total interaction energy, ΔEint = ΔEPauli + ΔEelstat + ΔEorb + ΔEdisp.

*Values in parentheses are the percentage contributions to the total orbital interactions ΔEorb.
Figure 6. Most important NOCV pairs of orbitals $\Psi_i$, $\Psi_j$ with their eigenvalues $-\nu_i$, $\nu_j$ given in parentheses, and the associated deformation densities $\Delta \rho_k$ and orbital stabilization energies $\Delta E$ for the complexes 4 (a) and 7 (b). The charge flow in the deformation densities takes place in the direction red to blue.

CONCLUDING REMARKS

This study has revealed that the square pyramidal metal fragments OsHX{$\kappa^3-P,O,P-[xant(P\Pi Pr_2)]$} (X = Cl, H) stabilize the coordination of the B-H bond of boranes trans to the X ligand. The strength of the interaction between the metal center and the borane, which involves $\sigma$-donation from the doubly occupied $\sigma$(B-H) orbital to a vacant d atomic orbital of the metal and $d$(Os)$\rightarrow\sigma^*(B-H)$ back-donation, is sensitive to the nature of X, being favored for chloride with regard to hydride. The electron withdrawing ability of the chloride ligand increases the donation from the $\sigma$(B-H) orbital to the osmium atom, whereas its $\pi$-donor power favors the $d$(Os)$\rightarrow\sigma^*(B-H)$ back-donation. As a result, the coordinated B-H bond is significantly longer for complex 4 (X = Cl) than for 7 (X = H). The EDA-NOCV analysis suggests that the computed much lower interaction strength between the metal fragment OsHCl{$\kappa^3-P,O,P-[xant(P\Pi Pr_2)]$} and the borane is mainly due to less stabilizing electrostatic and orbital attractions.

The coordination of the borane to the metal fragment OsHCl{$\kappa^3-P,O,P-[xant(P\Pi Pr_2)]$} affords elongated $\sigma$-borane species, whereas the coordination to the dihydride counterpart OsH$_2${$\kappa^3-P,O,P-[xant(P\Pi Pr_2)]$} gives a $\sigma$-borane compound. NBO-AIM analysis shows marked differences in the bonding situation of both types of derivatives. While elongated $\sigma$-borane complexes are characterized by a three-membered cycle possessing one OsBH ring critical point, the $\sigma$-borane compound lacks this triangular topology.

In conclusion, related elongated $\sigma$-borane and $\sigma$-borane complexes stabilized by OsHX(POP) metal fragments have been isolated, fully characterized, and the interaction between the metal fragments and the coordinated B-H analyzed as a function of X, from spectroscopic, X-ray diffraction, and theoretical points of view.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under argon with rigorous exclusion of air using Schlenk tube or glovebox tech-
niques. 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 and dichloromethane were further stored over P2O5 in the glovebox. Toluene and benzene were stored over sodium in the glovebox. Pinacolborane was purchased from commercial sources and used without further purification. Catecholborane was purchased from commercial sources and distilled in a Kugelroh distillation oven. Complexes OsH₃Cl(κ-P₂O₅-P[xant(P₂Pr₂)]) (1) ([Os(H⁻)⁻(κ-P₂O₅-P[xant(P₂Pr₂)])₂][µ-Cl][BF₄]⁻) (3),17 and OsH₃Cl(κ-P₂O₅-P[xant(P₂Pr₂)]) (4)16 were prepared according to published methods. 1H, 31P(¹H) and 13C(¹H) NMR spectra were recorded on either a Bruker 300 ARX, 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, 313(¹H) Cl or external H₂PO₄(¹H) (1H, 31P(¹H) = 20.3 ppm) and BF₄⁻ (1B). Coupling constants, J and N (N = JₙH + JₚH for ¹H; N = JₚC + JₚH for ³C) are given in hertz. Spectral assignments were achieved by ¹H-¹H COSY, ¹H-³P, ¹H-¹³C APT, ¹H-¹³C and ¹³C-¹³C HMBC experiments. C and H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a Micro-TOF-Q hybrid quadrupole-time-of-flight spectrometer (BrukerDaltonics).

Synthesis of OsH₃Cl(κ-P₂O₅-P[xant(P₂Pr₂)]) (4). To a suspension of [Os(H⁻)⁻(κ-P₂O₅-P[xant(P₂Pr₂)])₂][µ-Cl][BF₄]⁻ (50 mg; 0.033 mmol) in CHCl₃ (3 mL) was added HBF₄·EtOH (18 µL; 0.169 mmol). After 10 min, the colorless solution obtained was taken to dryness. Addition of pentane (1 mL) to the residue allowed the precipitation of a white solid, which was washed twice with pentane (2 mL) and dried under reduced pressure. Yield: 29 mg (50 %). Colorless crystals suitable for X-ray diffraction analysis were obtained by vacuum diffusion of pentane into a tolune solution of the complex. Anal. Calcd. for C₃₃H₅₄BClO₃NaOsP₂: C, 52.52; H, 6.28. Found: C, 52.74; H, 6.32. HRMS (electrospray, m/z): calcld. for C₃₃H₅₄BClO₃NaOsP₂: [M + Na]+: 813.2207, found: 831.2185. ¹H NMR (300.13 MHz, C₆D₆, 298K): δ 7.26 (m, 2H, CH-arom), 7.11 (m, 2H, CH-arom Bcat), 6.89 (m, 4H, CH-arom), 6.82 (m, 2H, CH-arom Bcat), 3.24 (m, 2H, PCH₂ arom), 2.37 (m, 2H, PCH₂ arom) 1.44 (dd, JH-H = 7.9, N = 16.6, 6H, PCH₂ arom), 1.30 (s, 3H, CH₃), 1.21 (m, 18H, PCH₂ arom), 0.93 (s, 3H, CH₃), -1.87 (br, 1H, OsH), -12.23 (br, 2H, OsH). ¹H NMR (400 MHz, C₆D₆, 298K): δ -1.90 (br, 1H, OsH), -5.60 (br, 1H, OsH), -18.83 (br, 1H, OsH). ¹³C(¹H) NMR (121.49 MHz, C₆D₆, 298K): δ 35.6 (s). ¹³B NMR (96.29 MHz, C₆D₆, 298K): δ 45.5 (br).

Reaction of OsH₃Cl(κ-P₂O₅-P[xant(P₂Pr₂)]) with CIBcat. In a nmr tube, a solution of CIBcat (5 mg; 0.032 mmol) in C₆D₆ (0.6 mL) was added to OsH₃Cl(κ-P₂O₅-P[xant(P₂Pr₂)]) (3; 0.041 mg; 0.064 mmol). Immediate quantitative formation of a 1:1 mixture of complexes OsH₃Cl(κ-P₂O₅-P[xant(P₂Pr₂)]) (7) and OsH₃Cl(κ-P₂O₅-P[xant(P₂Pr₂)]) (8) (1) was observed according to NMR measurements.

Crystallographic Details (CIBcat) Coordinates of 4, 5 and 7. Geometry optimizations were performed without symmetry constraints using the Gaussian0929 suite of programs at the BP86/ded2-SVP level of theory using the D3 dispersion correction suggested by Grimme et al.28 This level is denoted BP86/ded2-SVP. Complexes 4, 5 and 7 were characterized by frequency calculations, and have positive definite Hessian matrices thus confirming that the computed structures are minima on the potential energy surface. WBIs have been computed using the NBO method.29

All AIM results described in this work correspond to calculations performed at the BP86-D3/6-31+G(d) (d)WBSTB/6-31G(d) (d) level on the optimized geometry obtained at the BP86-D3/6-31G(d) level. The WBSTB (well-tempered basis sets)30 have been recommended for AIM calculations involving transition metals.31 The topology of the electron density was conducted using the AIMAll program package.32

The interaction between the transition metal fragment and the borane and HBCat in complexes 4 and 7 has been investigated with the EDA-NOCV method,33 which combines the energy decomposition analysis (EDA)34 with the natural orbitals for chemical valence (NOCV)35 methods. Within this approach, the interaction energy can be decomposed into the following physically meaningful terms: 

$\Delta E_{int} = \Delta E_{elec} + \Delta E_{Pauli} + \Delta E_{adiab} + \Delta E_{disp}$

The term $\Delta E_{elec}$ corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the deformed reactants and is usually attractive. The Pauli repulsion $\Delta E_{Pauli}$ produces the destabilizing interactions between occupied orbitals and is
responsible for any steric repulsion. The orbital interaction $\Delta E_{orb}$ accounts for charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals on the other, including HOMO-LUMO interactions) and polarization (empty-occupied orbital mixing on one fragment due to the presence of another fragment). Finally, the $\Delta E_{disp}$ term takes into account the interactions which are due to dispersion forces.

The EDA-NOCV method makes it possible to further partition the total orbital interactions into pairwise contributions of the orbital interactions. Details of the method can be found in the literature.6

The EDA-NOCV calculations were carried out using the BP86-D3/def2-SVP optimized geometries with the program package ADF 2016.01 using the same functional (BP86-D3) in conjunction with a triple-c-$\xi$-quality basis set using uncontracted Slater-type orbitals (STOs) augmented by two sets of polarization function with a frozen-core approximation for the core electrons. An auxiliary set of s, p, d, f, and g STOs were used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.57

Scalar relativistic effects were incorporated by using a multiconfiguration method with the SADLAB program.49 The structures were solved by Patterson or direct methods and refined by full-matrix least squares on $F^2$ with SHELXL2016,46 including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were observed in the least Fourier Maps or calculated, and refined freely or using a restricted riding model. The hydrogen bonded to metal atoms were observed in the last cycles of refinement but refined too close to metals, so a restricted refinement model was used for all of them (d(Or-H) = 1.59(1) Å).

Crystal data for 4: Cu$_2$H$_4$BCl$_2$Os$_2$P$_2$, 2(CH$_2$Cl$_2$), $M_w$ = 958.95, colourless, irregular block (0.238 x 0.188 x 0.082), triclinic, space group P$\overline{1}$, $a$: 11.8674(7) Å, $b$: 16.6502(8) Å, $c$: 20.7567(10) Å, $\alpha$: 104.9624(10)$^\circ$, $\beta$: 96.3580(10)$^\circ$, $\gamma$: 90.1100(10)$^\circ$, $V$: 3936.2(3)$Å^3$, $Z$: 4, $Z': 2$, $D_{calc}$: 1.618 g cm$^{-3}$, F(000): 1920, T = 100(2) K, $\mu$: 3.731 mm$^{-1}$. 39075 measured reflections (2$\theta$: 3.992 mm$^{-1}$, 31075 measured reflections (2$\theta$: 1.31075 mm$^{-1}$). The cif files of 4, 5, and 7 have been deposited with the Cambridge Crystallographic Data Center (Nos. CCDC 1552854, CCDC 1552855, and CCDC 1552856 (7)). X-ray data were collected for the complexes on Bruker Smart APEX DUO (5) or Bruker Smart APEX CCD (4, 7) diffractometers equipped with a normal focus, 2.4 kV sealed tube source (Mo radiation, $\lambda$: 0.71073 Å) operating at 50 kV and 40 mA (4) or 30 mA (5 and 7). Data were collected over the complete sphere. Each frame exposure time was 10 s (5 and 7), or 20 s (4) covering 0.3$^\circ$ in $\omega$. Data were corrected for absorption by using a multiscan method applied with the SADABS program.50

AUTHOR INFORMATION

Corresponding Author
*E-mail for M.A.E.: maester@unizar.es

Notes
The authors declare no competing financial interest.

REFERENCES

Elongated $\sigma$-Borane  $\sigma$-Borane