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Reactions of an Osmium(IV)-Hydroxo Complex with Amino-Boranes: Formation of Boroxide Derivatives

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Supporting Information

ABSTRACT: The discovery of a reaction which allows preparation of boroxide complexes of platinum group metals and study of their behavior under CO atmosphere is described. The trihydride-osmium(IV)-hydroxo complex $OsH_3(OH)\{\kappa^3\text{-}P,O,P\text{-}[xant(P^iPr_2)_2]\}$ (**1**, $xant(P^iPr_2)_2$ = 4,5-bis-(diisopropylphosphino)xanthene) reacts with the amino-boranes $^iPr(H)NBCy_2$ and $^iPr(H)NBBN$ to give the osmium(IV)-boroxide derivatives $OsH_3(OBR_2)\{\kappa^3\text{-}P,O,P\text{-}[xant(P^iPr_2)_2]\}$ (BR_2 = BCy_2 (**2**), BBN (**3**); BBN = 9-borabicyclo[3.5.1]-nonane) and $^iPrNH_2$ as a consequence of the addition of the O−H bond of the hydroxo ligand of **1** to the B−N bond of the amino-boranes. At room temperature under CO atmosphere, complexes **2** and **3** eliminate H_2 to afford the osmium(II)−boroxide compounds $OsH(OBR_2)(CO)_2\{\kappa^2\text{-}P,P\text{-}[xant(P^iPr_2)_2]\}$ (BR_2 = BCy_2 (**4**), BBN (**5**)) bearing a κ^2-*P,P*-coordinated ether-diphosphine. The subsequent reductive elimination of the borinic acids R_2BOH needs heating and a long duration and leads to the tricarbonyl-osmium(0) derivative $Os(CO)_3\{\kappa^2\text{-}P,P\text{-}[xant(P^iPr_2)_2]\}$ (**6**) with the phosphorus atoms of the diphosphine lying in the equatorial plane of a pentagonal bypyramid of donor atoms around the metal center. In contrast to **2** and **3**, under CO atmosphere, precursor **1** eliminates water to initially give the *trans*-dihydride $OsH_2(CO)\{\kappa^3\text{-}P,O,P\text{-}[xant(P^iPr_2)_2]\}$ (**7**), which subsequently evolves to the *cis*-dihydride-*cis*-dicarbonyl derivative $OsH_2(CO)_2\{\kappa^2\text{-}P,P\text{-}[xant(P^iPr_2)_2]\}$ (**8**) and finally into the tricarbonyl **6**.

INTRODUCTION

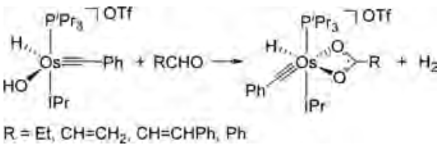
Hydroxide complexes of platinum group metals[1] are a rare and particularly fascinating group of weak hydroxoacids, which have an oxo derivative as a conjugate base, and are at the same time the strong conjugate base of an aquo-complex (Scheme 1). The exciting nature of these species does not correspond to a rich chemistry, which is by contrast underdeveloped, in particular for osmium. In addition to a few dimers,[2] the mononuclear compounds of this element include nitride complexes,[3] half-sandwich species,[4] and hydride-hydroxo derivatives.[5] The latter are particularly challenging because the reductive elimination of water is generally favored from a thermodynamic point of view.[6] Compounds of this class are generally osmium(II)-derivatives and only very recently was isolated a hydride-osmium(IV)-hydroxo complex.[5f] In agreement with the marked ability of pincer ligands to stabilize uncommon species,[7] it contains the POP group 4,5-bis-(diisopropylphosphino)xanthene ($xant(P^iPr_2)_2$).[8]

Scheme 1. Brønsted−Lowry Equilibria for a Metal Hydroxoacid

$$[L_nM(OH_2)]^n \overset{-H^+}{\rightleftharpoons} [L_nM(OH)]^{n-1} \overset{-H^+}{\rightleftharpoons} [L_nM(O)]^{n-2}$$

The previously mentioned duality of the hydroxide complexes is expressed in the respective nucleophilicity and electrophilicity of the oxygen and hydrogen atoms of the hydroxo group in the scarcely performed reactions,[9] as the addition of aldehydes to $[OsH(OH)(CPh)(IPr)(P^iPr_3)]OTf$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene, OTf = CF_3SO_3) which affords the corresponding carboxylate derivatives and molecular hydrogen (Scheme 2).[10]

Scheme 2. Reactions of an Osmium-Hydroxo Complex with Aldehydes



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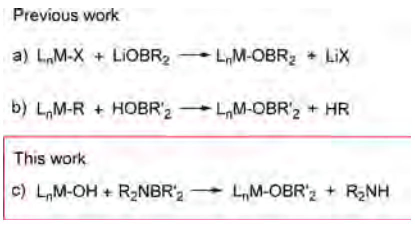
Boroxide groups have been proposed as promising alternative to the alkoxide ligands to better modulate the electronic and steric properties of catalyst precursors of interesting reactions of organic synthesis.[11] The empty p-orbital on the boron allows electron donation from the oxygen lone−lone pairs, which gives rise to a poorer electron donating oxygen group. In addition, although the boroxide ligand bears twice as many carbon substituents as an alkoxide group, the presence of an additional space converts it to be sterically less demanding.[12] Boroxide compounds of metal of s and p blocks[13] and complexes of transition elements of all groups[11,14] have been reported. Nevertheless, one could think that there is a "boroxide wall" around the platinum group metals because the species of these elements are unknown until now. Two main procedures have been employed to generate this type of compound: reactions of a metal halide with a lithium boroxide and protonolysis of metal−carbon, −nitrogen, or −oxygen bonds with a borinic acid[12] (a and b in Scheme 3).

Scheme 3. Synthetic Procedures to Prepare Boroxide Compounds

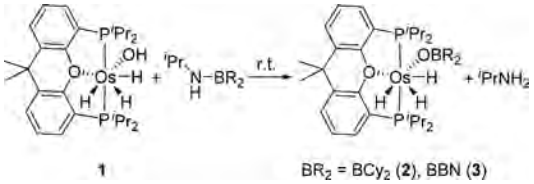


Boron shows higher affinity for oxygen than for nitrogen, which is consistent with the higher dissociation energy of the B−O bonds with regard to the B−N bonds in tricoordinate boron species.[15] This, along with the oxygen nucleophilicity and the hydrogen electrophilicity of the hydroxo ligand in hydroxide complexes, prompted us to try the formation of boroxide species of a platinum group metal by means of the displacement of the amino group of amino-boranes by the conjugate base of a hydroxoacid (c in Scheme 3), in reactions that resemble that shown in Scheme 2. Here, we report a novel procedure which allowed us to isolate the first boroxide complexes of a platinum group metal.

■ RESULTS AND DISCUSSION

Osmium(IV)−Boroxide Derivatives: Formation and Characterization. Metal ions in high oxidation state form strong bonds with oxygen, increasing the electrophilicity of the hydrogen atom of the hydroxo ligand. This fact led us to select the osmium(IV) complex $OsH_3(OH)\{\kappa^3\text{-}P,O,P\text{-}[xant(P^iPr_2)_2]\}$ (**1**) as starting point to achieve our goal. Treatment of toluene solutions of **1** with 1.0 equiv of the amino-boranes $^iPr(H)NBCy_2$ and $^iPr(H)NBBN$ (BBN = 9-borabicyclo[3.3.1]-nonane) at room temperature for 30 min produces the release of isopropylamine and the formation of the desired osmium(IV)-boroxide derivatives $OsH_3(OBR_2)\{\kappa^3\text{-}P,O,P\text{-}[xant(P^iPr_2)_2]\}$ ($BR_2 = BCy_2$ (**2**), BBN (**3**)), which were isolated as pale yellow solids in 50−65% yield (Scheme 4).

Scheme 4. Formation of Boroxide Complexes 2 and 3



The formation of **2** and **3** is strongly supported by the X-ray diffraction structure of **2** (Figure 1a). The Os(POP) skeleton shows the typical T-shape with the osmium atom situated in the common vertex and P1−Os−P2, P1−Os−O2, and P2−Os−O2 angles of 160.90(4)°, 81.75(7)°, and 80.53(7)°, respectively. The coordination geometry around the metal center can be rationalized as a distorted pentagonal bipyramid with the boroxide group and the hydride ligands lying in the perpendicular plane to the P−Os−P direction along with the oxygen atom of the diphosphine, which is situated between the boroxide O1 atom and the hydride H01 (O1−Os−O2 = 81.89(10)°). The osmium−boroxide distance of 2.089(3) Å is long. It compares well with the higher part of the range of the reported osmium(IV)−alkoxide bond lengths (1.90−2.10 Å),[16] whereas the Os−O1−B1 angle of 137.9(3)° significantly deviates from the expected value for sp^2 hybridized oxygen. This angle is about 20° larger than the Os−S−B angle in the borothiolate compounds $OsH(SBR_2)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (113−119°).[17] This is consistent with that observed by Braunschweig and co-workers for the M−chalcogene−B angle, in the borachalcogene complexes $Cp(CO)_2Mn[EB^tBu(IMe)]$ (E = S, Se, Te), which increases by going up in the group, i.e., in the sequence Te < Se < S.[18] However, in contrast to the Braunschweig's compounds, the O1−B bond length of 1.332(6) Å reveals a short chalcogene−boron single bond.[19] The DFT optimized structure (Figure 1b) confirms the trihydride character of the OsH_3 unit, although the calculated separations between H01 and H02 and between H02 and H03 of 1.57 and 1.64 Å, respectively, suggest the presence of weak nonclassical interactions between the hydride ligands.[20]

The ^1H NMR spectra of **2** and **3** in toluene-d_8 also support the presence of weak nonclassical interactions between the hydride ligands. At room temperature, they display only one resonance ($\delta_{1H} \approx -13$), indicating that they are involved in two thermally activated site exchange processes. At temperatures lower than 223 K, three signals are however observed (δ_{1H} −11.60, −11.71, −13.49 (**2**); −11.63, −11.75, −13.61 (**3**)) in agreement with the structures shown in Figure 1. Two of them form an AB spin system with a large *cis* J_{AB} coupling constant of 46.9 Hz for **2** and 98.5 Hz for **3** at 193 K, which slightly decreases as the temperature increases, as expected for quantum−mechanical exchange coupling between the involved hydrides.[21] According to equivalent P^iPr_2 groups, the $^{31}P\{^1H\}$ NMR spectra contain a singlet at 44.2 ppm for **2** and 45.6 ppm for **3**, which is temperature invariant. In the ^{11}B spectra, the boroxide ligands give rise to a broad resonance centered at 48.3 ppm for **2** and at 50.6 ppm for **3**.

Osmium(II)−Boroxide Derivatives: Reactions with CO. Complexes **2** and **3** are not only novel examples of boroxide derivatives but also notable polyhydrides bearing a monodentate monoanionic oxygen-donor ligand.[20] The stability of the H−Os−OBR₂ unit is certainly noticeable. In this context, it should be pointed out that the reductive elimination of molecular hydrogen is kinetically favored with regard to the release of the borinic acid. Thus, the stirring of toluene solutions of both compounds under 1 atm of CO at room temperature for 24 h leads to the respective *cis*-dicarbonyl−hydride−osmium(II)−boroxide derivatives $OsH(OBR_2)(CO)_2\{\kappa^2\text{-}P,P\text{-}[xant(P^iPr_2)_2]\}$ ($BR_2 = BCy_2$ (**4**), BBN

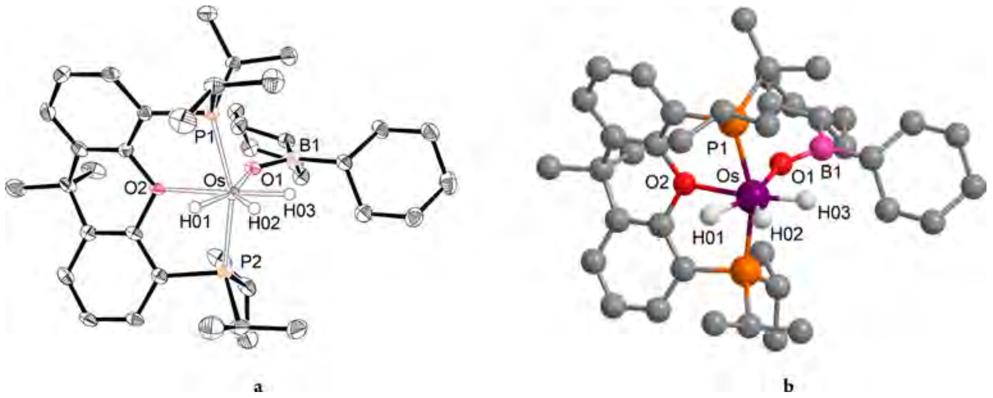
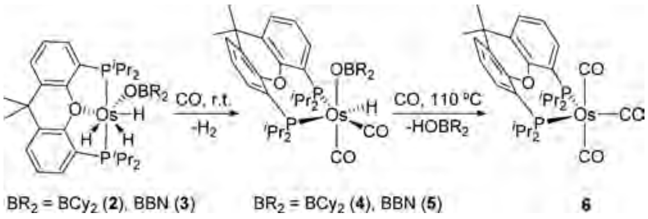


Figure 1. (a) Molecular diagram of complex **2** with 50% probability ellipsoids. Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–O2 = 2.304(3), Os–O1 = 2.089(3), Os–H03 = 1.580(10), Os–H02 = 1.580(10), Os–H01 = 1.580(10), Os–P1 = 2.2893(11), Os–P2 = 2.2891(11), O1–B1 = 1.332(6); P1–Os–P2 = 160.90(4), P1–Os–O2 = 81.75(7), P2–Os–O2 = 80.53(7), O1–Os–O2 = 81.89(10), Os–O1–B1 = 137.9(3). (b) DFT optimized structure of **2**. Selected bond lengths (Å) and angles (deg): Os–O2 = 2.351, Os–O1 = 2.088, Os–H03 = 1.594, Os–H02 = 1.598, Os–H01 = 1.633, Os–P1 = 2.322, Os–P2 = 2.321, O1–B1 = 1.330, H01–H02 = 1.57, H02–H03 = 1.64; P1–Os–P2 = 160.5, P1–Os–O2 = 81.5, P2–Os–O2 = 80.3, O1–Os–O2 = 78.1, Os–O1–B1 = 140.7.

(**5**)), and molecular hydrogen (Scheme 5). The elimination of the borinic acid takes place after the elimination of H_2 on the hydride–osmium(II)–boroxide species and requires heating and time. In toluene under 1 atm of CO, complex **4** loses $HOBCy_2$ to quantitatively afford the tricarbonyl compound $Os(CO)_3$\{κ^2-*P*,*P*-[xant(P^iPr_2)$_2$]\} (**6**) after 4 days at 110 °C. The C-substituents attached to the boron atom influence the elimination rate of the borinic acid. The bicyclic system of **5** favors the reductive elimination with regard to the cyclohexyl groups of **4**. As a consequence, complex **5** cannot be isolated as an analytically pure solid because amounts of the tricarbonyl derivative **6** are formed before the quantitative transformation of **3** into **5** has taken place, even at room temperature.

Scheme 5. Carbonylation of Complexes 2 and 3 in Toluene



Complex **4** was isolated as a white solid in 64% yield and characterized by X-ray diffraction analysis. The structure (Figure 2) proves the reduction of the metal center from +4 to +2, involving the replacement of two hydride ligands by two carbonyl groups. The reduction produces a change in the coordination mode of the diphosphine from κ^3-*P*,*O*,*P* to κ^2-*P*,*P*, in agreement with the flexibility of the ether-diphosphines, which allows them to adapt to the requirements of the particular complex.[8c,i,j,22] The formation of **4** and **5** enlarges into osmium(II), the range of osmium(VI) and osmium(IV) species stabilized by κ^2-*P*,*P*-coordinated ether-diphosphines. The coordination polyhedron around the osmium atom can be rationalized as a distorted octahedron with the boroxide ligand disposed *trans* to a carbonyl group O1–Os–C1 = 174.90(8)°. The perpendicular plane is formed by the other carbonyl group, the hydride ligand, and the phosphorus atoms of the chelate diphosphine (P1–Os–P2 = 108.33(2)°). The coordination of the boroxide ligand does not show any difference with regard to the coordination in **2**. Thus, the Os–O1 and O1–B bond lengths of 2.0857(15) and 1.331(3) Å, respectively, and the Os–O1–B angle of 135.33(16)° are almost identical as those of **2**.

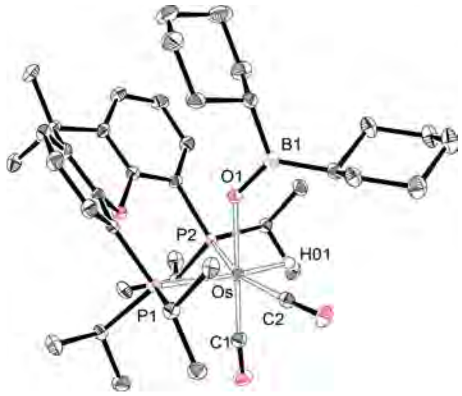


Figure 2. Molecular diagram of complex **4** with 50% probability ellipsoids. Hydrogen atoms (except the hydride) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–O1 = 2.0857(15), Os–H01 = 1.584(10), Os–C2 = 1.886(2), Os–C1 = 1.865(2), Os–P1 = 2.5092(6), Os–P2 = 2.4522(6), O1–B = 1.331(3); O1–Os–C1 = 174.90(8), P1–Os–P2 = 108.33(2), Os–O1–B = 135.33(16).

The IR and $^{13}C\{^1H\}$, ^1H, and $^{31}P\{^1H\}$ NMR spectra of **4** in toluene-d_8 at 203 K are consistent with the structure shown in Figure 2. As expected for a *cis* disposition of the carbonyl groups, the IR contains the characteristic two ν(CO) bands corresponding to a C_{2v} point group at 1998 and 1914 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum, these ligands display double doublets at 186.0 ($^2J_{C-P\ trans}$ = 99.8 Hz, $^2J_{C-P\ cis}$ = 1.0 Hz) and 181.8 ($^2J_{C-P\ cis}$ = 10.5 and 2.1 Hz) ppm. In agreement with the presence of a hydride ligand disposed *trans* to a phosphorus atom and *cis* to other one, the high field region of the ^1H NMR spectrum shows at −6.30 ppm a double doublet with H–P coupling constants of 115.1 and 33.6 Hz, whereas the $^{31}P\{^1H\}$ NMR spectrum contains two doublets at 3.4 and 1.5 ppm with a P–P coupling constant of 26.2 Hz. In accordance with **2**, the ^{11}B NMR spectrum in toluene-d_8 at room temperature shows a broad resonance centered at 50.0 ppm.

Complex **5** exists in solution as a 1:1 mixture of two conformers, which may be related to the disposition of the xanthene linker of the diphosphine with regard to the ligands situated along the boroxide−osmium−carbonyl axis. Their presence is strongly supported by the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra in toluene-d_8 at 203 K. Thus, in agreement with the ^{1}H NMR spectrum of **4**, the ^{1}H NMR spectrum of **5** shows two double doublets at −5.94 ($^{2}J_{P-H\ trans}$ = 99.0 Hz, $^{2}J_{P-H\ cis}$ = 29.94 Hz) and −6.31 ($^{2}J_{P-H\ trans}$ = 107.5 Hz, $^{2}J_{P-H\ cis}$ = 32.5 Hz) ppm, corresponding to the hydride ligand of each conformer, whereas the $^{31}P\{^{1}H\}$ NMR spectrum contains four doublets at 20.7 and 11.4 ($^{2}J_{P-P}$ = 24.5 Hz) ppm and 13.1 and 12.0 ($^{2}J_{P-P}$ = 24.5 Hz) ppm, two for each conformer.

The osmium(0)−tricarbonyl complex **6** was isolated as a yellow solid in 41% yield and characterized by X-ray diffraction analysis. Figure 3 shows a view of the molecule. The coordination polyhedron around the osmium atom can be rationalized as a distorted trigonal bipyramid with two carbonyl groups at the apexes (C1−Os−C3 = 175.12(19)°). The phosphorus atoms of the κ^{2}-coordinated ether-diphosphine and the remaining carbonyl group lie in the equatorial plane, forming P1−Os−P2, P2−Os−C2, and C2−Os−P1 angles of 114.10(4)°, 123.63(17)°, and 122.09(17)°, respectively. The distances between the metal center and the apical carbonyl groups of 1.928(5) (Os−C1) and 1.931(5) (Os−C3) Å are about 0.08 Å longer than the distance between the osmium atom and the equatorial carbonyl group of 1.856(5) (Os−C2) Å. In agreement with the disposition of the carbonyl ligands, the IR in toluene contains three ν(CO) bands at 2003, 1916, and 1900 cm^{-1} with weak, very strong, and strong intensities, respectively. The equivalent phosphorus atoms of the diphosphine display a singlet at 4.5 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum in dichloromethane at room temperature. Complex **6** is notable for two reasons: (i) it enlarges into osmium(0) the range of compounds involving a κ^{2}-*P,P*-coordinated ether-diphosphine and (ii) it is a rare example of $Os(CO)_3P_2$ compound with the phosphorus atoms lying in the equatorial plane of the bipyramid because they always occupy apical positions in the complexes of this class previously reported.[23]

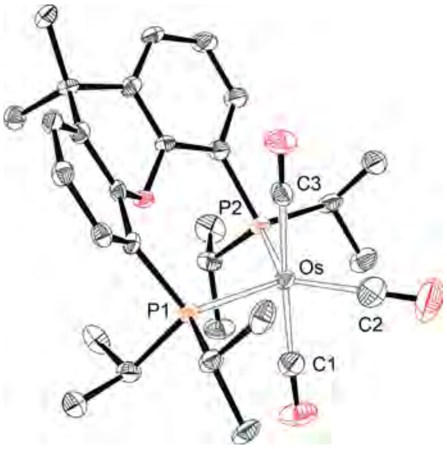
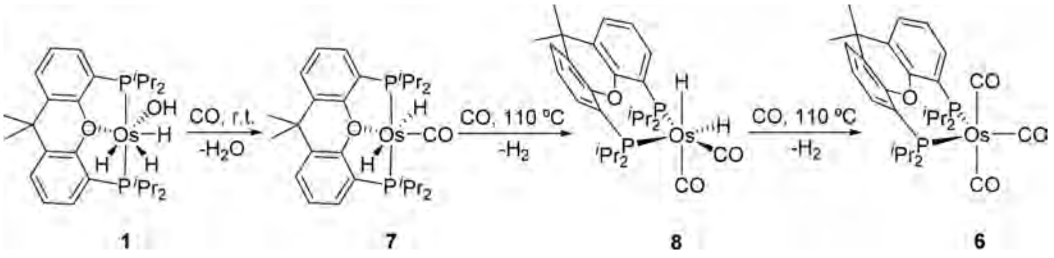


Figure 3. Molecular diagram of complex **6** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os−C3 = 1.931(5), Os−C2 = 1.856(5), Os−C1 = 1.928(5), Os−P1 = 2.3582(11), Os−P2 = 2.3677(11); C1−Os−C3 = 175.12(19), P1−Os−P2 = 114.10(4), P2−Os−C2 = 123.63(17), P1−Os−C2 = 122.09(17).

Reactions of 1 with CO: Reductive Elimination of H_2O. There are marked differences in behavior between the hydroxo precursor **1** and the boroxide derivatives **2** and **3** under 1 atm of CO. In contrast to the latter, complex **1** eliminates the oxygen donor group and a hydride ligand to quantitatively yield the previously described *trans*-dihydride compound $OsH_2(CO)\{\kappa^{3}\text{-}P,O,P\text{-}[xant(P^{i}Pr_2)_2]\}$[8h] (**7**) and water after 24 h in toluene at room temperature (Scheme 6). At 110 °C, complex **7** evolves into the *cis*-dicarbonyl derivative $OsH_2(CO)_2\{\kappa^{2}\text{-}P,P\text{-}[xant(P^{i}Pr_2)_2]\}$ (**8**), as a result of the displacement of the oxygen atom of the diphosphine by a second carbon monoxide molecule and the *trans* to *cis* isomerization of the hydride ligands. Complex **8**, which is a new example of osmium(II) species with a κ^{2}-*P,P*-coordinated ether-diphosphine, is a dihydride counterpart of **4** and **5** bearing a hydride ligand in the position of the boroxide group. Like its analogue, it undergoes reduction into the tricarbonyl derivative **6** under carbon monoxide atmosphere.

The κ^{2}-*P,P*-coordination of the diphosphine in **8** is strongly supported by the ^{1}H NMR spectrum of the complex in toluene-d_8 at room temperature, which shows two double doublets at 0.97 and 0.89 ppm for the methyl groups of the phosphine isopropyl substituents instead of the characteristic doublet of virtual triplets of the κ^{3}-*P,O,P-mer* mode. In addition, in the high field region, the spectrum contains two doublet of doublet of doublets at −7.92 (hydride *cis* to both P atoms) and −10.01 (hydride *trans* to a P atom and *cis* to the other one) ppm with P−P coupling constants of 19.6 and 26.4 and 67.5 and 35.5 Hz, respectively, and a H−H coupling constant of 6.1 Hz. The $^{13}C\{^{1}H\}$ NMR spectrum also supports the structure proposed for **8** in Scheme 6, showing the carbonyl resonances at 188.0 (CO *trans* to a P atom and *cis* to the other one) and 186.0 (CO *cis* to P atoms) ppm as double doublets with C−P coupling constants of 74.1 and 3.4 Hz and 10.0 and 3.6 Hz, respectively. In the $^{31}P\{^{1}H\}$ NMR spectrum, the inequivalent $P^{i}Pr_2$ groups display at 4.2 and 1.9 ppm doublets with a P−P coupling constant of 25.6 Hz.

Scheme 6. Carbonylation of Complex 1 in Toluene



CONCLUDING REMARKS

This study shows a novel reaction in the chemistry of hydroxo-transition-metal complexes, reveals the existence of boroxide derivatives of platinum group metals, demonstrates that the reductive elimination of borinic acids from hydride metal-boroxide compounds is disfavored with regard to the release of molecular hydrogen and to the reductive elimination of water from hydride-metal-hydroxo counterparts, and enlarges the range of metal ions stabilizing compounds with κ^2-*P,P*-coordinated ether-diphosphines.

The oxygen nucleophilicity and hydrogen electrophilicity of hydroxo ligands coordinated to transition metals allow the hydroxo ligand to displace the amino group of $\mathrm{R_2NBR'_2}$ amino-boranes. The reactions afford boroxide derivatives, including compounds of a platinum group metal as osmium. Complexes of this class containing hydride coligands are stable toward the elimination of borinic acids, in contrast to hydride-metal-hydroxo species which show a high tendency to release water. Under carbon monoxide atmosphere, the elimination of molecular hydrogen is observed. The elimination of the borinic acid also occurs but is always a subsequent process and needs heating and a long duration. The ether-diphosphine 4,5-bis(diisopropylphosphino)xanthene stabilizes the resulting species of the above-mentioned processes when the metal center is osmium, adapting its coordination mode to the electronic and steric requirements of each particular complex. As a consequence, the range of compounds bearing the diphosphine κ^2-*P,P*-coordination was enlarged into osmium(II) and osmium(0) derivatives.

In conclusion, a novel reaction in the chemistry of transition-metal-hydroxo complexes has been discovered, which has led us to the preparation of the first boroxide derivatives of a platinum group metal and study of their behavior under a carbon monoxide atmosphere.

EXPERIMENTAL SECTION

All reactions were performed under argon using Schlenk tube or glovebox techniques and dried solvents. Instrumental methods, NMR spectra, X-ray diffraction analysis information and DFT computational details are given in the Supporting Information. Complex $\mathrm{OsH_3(OH)}$-$\{\kappa^3$-*P,O,P*-[xant($\mathrm{P^iPr_2}$)$_2$]$\}$ (**1**) was prepared as published.[5f] Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external $\mathrm{H_3PO_4}$ (^{31}P{^{1}H}) and $\mathrm{BF_3\cdot OEt_2}$ (^{11}B). Coupling constants J and N ($N = J_{\mathrm{PH}} + J_{\mathrm{P'H}}$ for ^{1}H; $N = J_{\mathrm{PC}} + J_{\mathrm{P'C}}$ for ^{13}C) are given in Hertz.

Preparation of ^{i}PrNHBCy$_2$. A 1.6 M solution of ^{n}BuLi in hexane (3.2 mL, 5.12 mmol) was slowly added to a colorless solution of isopropylamine (430 μL, 5.00 mmol) in diethyl ether (10 mL) kept at −78 °C with an acetone/liquid $\mathrm{N_2}$ bath. Upon finishing the addition, formation of a white precipitate (LiNH^{i}Pr) was observed; then, the cold bath was removed, and the mixture was further stirred at room temperature for 1 h. Then, the white suspension thus obtained was again cooled at −78 °C, and a 1.0 M solution of $\mathrm{ClBCy_2}$ in hexane (5.0 mL, 5.00 mmol) was slowly added. Once more, the bath was removed when the addition was finished, and the mixture was further stirred for 2 h at room temperature to ensure reaction completion, after which time was left standing for 1 h to allow deposition of solid LiCl at the bottom of the flask. Then, the solution was filtered with a cannula and a small amount of Celite, and the solvents were subsequently removed under vacuum to afford the amino-borane ^{i}PrNHBCy$_2$ as a colorless viscous oil (950 mg, 81%). ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, 298 K): δ 3.61 (d, br, $J_{\mathrm{HH}} = 11.1$, 1H, N*H*), 3.51 (dsept, 1H, $J_{\mathrm{HH}} = 11.1$, 6.3, 1H, C*H*-^{i}Pr), 1.9−0.9 (m, 22H, Cy), 0.93 (d, $J = 6.3$, 6H, C*H*$_3$-^{i}Pr). ^{13}C{^{1}H} NMR (101 MHz, $\mathrm{C_6D_6}$, 298 K): δ 43.2 (s CH-^{i}Pr), 30.2, 29.5 (2s, 2 × $\mathrm{C^{2,3}}$-Cy), 29.3 (br, $\mathrm{C^1}$ −Cy), 28.6 (s, 2 × $\mathrm{C^{2,3}}$-Cy), 27.7, 27.6 (2s, 2 × C ^{4} −Cy), 26.7 (s, $\mathrm{CH_3}$-^{i}Pr). ^{11}B NMR (160 MHz, $\mathrm{C_6D_6}$) δ 44.7 (s, $\Delta\nu_{1/2}$ ca. 260 Hz, B).

Preparation of ^{i}PrNHBBN. A toluene solution (15 mL) containing $\mathrm{(H\text{-}BBN)_2}$ (610 mg, 2.50 mmol) and excess isopropylamine (470 μL, 5.47 mmol) was stirred for 20 h at 60 °C. Then, the solvent was removed under vacuum to yield the amino-borane ^{i}PrNHBBN as a colorless viscous oil (640 mg, 71%). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 298 K): δ 3.54 (br, 1H, N*H*), 3.39 (dsept, $J = 10.1$, 6.4, 1H, C*H*-^{i}Pr), 2.10−0.95 (m, 14H, BBN), 0.90 (d, $J = 6.4$, 6H, C*H*$_3$-^{i}Pr). ^{13}C{^{1}H} NMR (101 MHz, $\mathrm{C_6D_6}$, 298 K): δ 43.6 (s CH-^{i}Pr), 34.0, 33.6 (2s, 2 × $\mathrm{CH_2}$ -BBN), 27.1 (br, CH-BBN), 26.6 (s, $\mathrm{CH_3}$- ^{i}Pr), 24.1 (s, $\mathrm{CH_2}$ -BBN), 22.3 (br, CH-BBN). ^{11}B NMR (128 MHz, $\mathrm{C_6D_6}$, 298 K): δ 47.9 (s, $\Delta\nu_{1/2}$ ca. 120 Hz, B).

Reaction of 1 with ^{i}PrNHBCy: Preparation of $\mathrm{OsH_3(OBCy_2)}$-$\{\kappa^3$-*P,O,P*-[xant($\mathrm{P^iPr_2}$)$_2$]$\}$ (2). Amino-borane ^{i}PrNHBCy$_2$ (43 mg, 0.184 mmol) was added to a solution of **1** (120 mg, 0.184 mmol) in toluene (5 mL). After 30 min at room temperature, the solution was concentrated, and 2 mL of acetone was added at −50 °C to afford a pale yellow solid, which was washed twice with acetone (1 mL) and dried under reduced pressure. Yield: 95 mg (62%). Anal. Calcd for $\mathrm{C_{39}H_{65}BO_2OsP_2}$: C, 56.51; H, 7.90. Found: C, 56.92; H, 7.91. ^{1}H NMR (300.13 MHz, $\mathrm{C_4D_8O}$, 298 K): δ 7.60 (dd, $^3J_{\mathrm{HH}} = 7.7$, $^4J_{\mathrm{HH}} = 1.2$, 2H, C*H*-arom POP), 7.50 (m, 2H, C*H*-arom POP), 7.27 (dd, $^3J_{\mathrm{HH}} = 7.6$, $^3J_{\mathrm{HH}} = 7.5$, 2H, C*H*-arom POP), 2.51 (m, 2H, $\mathrm{PC}H(\mathrm{CH_3})_2$), 2.26 (m, 2H, $\mathrm{PC}H(\mathrm{CH_3})_2$), 1.89 (s, 3H, $\mathrm{C}H_3$ POP), 1.63−1.52 (10H, $\mathrm{C}H_2$ Cy), 1.48 (s, 3H, $\mathrm{C}H_3$ POP), 1.21−0.94 (10H, $\mathrm{C}H_2$ Cy; 18H, $\mathrm{PCH(C}H_3)_2$), 0.81 (m, 2H, C*H* Cy), 0.73 (dvt, $^3J_{\mathrm{HH}} = 6.9$, $N = 14.2$, 6H, $\mathrm{PCH(C}H_3)_2$), −12.72 (t, $^3J_{\mathrm{HP}} = 11.4$, 3H, Os*H*). ^{1}H NMR (400.13 MHz, $\mathrm{C_7D_8}$, 193 K): δ $\upsilon_{\mathrm{A}} = -11.60$ and $\upsilon_{\mathrm{B}} = -13.49$ (AB system, $^2J_{\mathrm{AB}} = 46.9$, 2H, Os*H*), −11.71 (br, 1H, Os*H*). ^{13}C{^{1}H}-APT NMR (75.47 MHz, $\mathrm{C_4D_8O}$, 298 K): δ 159.8 (vt, $N = 13.3$, *C*-arom POP), 133.5 (vt, $N = 5.6$, *C*-arom POP), 131.0 (s, CH-arom POP), 129.8 (vt, $N = 27.9$, *C*-arom POP), 127.6 (s, CH-arom POP), 125.7 (s, CH-arom POP), 36.1 (br, CH Cy), 35.5 (s, $C(\mathrm{CH_3})_2$ POP), 34.5 (s, $\mathrm{C(CH_3)_2}$ POP), 30.3 and 29.4 (s, $\mathrm{CH_2}$ Cy), 28.6 (vt, $N = 19.2$, $\mathrm{PCH(CH_3)_2}$), 28.4 (s, $\mathrm{CH_2}$ Cy), 26.7 (vt, $N = 33.2$, $\mathrm{PCH(CH_3)_2}$), 26.4 (s, $\mathrm{C(CH_3)_2}$ POP), 21.1 (vt, $N = 10.8$, $\mathrm{PCH(CH_3)_2}$), 20.8 (s, $\mathrm{PCH(CH_3)_2}$), 20.5 (s, $\mathrm{PCH(CH_3)_2}$), 20.0 (vt, $N = 4.5$, $\mathrm{PCH(CH_3)_2}$). ^{31}P{^{1}H} NMR (161.98 MHz, $\mathrm{C_7D_8}$, 298 K): 44.2 (s, POP). ^{11}B NMR (96.30 MHz, $\mathrm{C_6D_6}$, 298 K): δ 48.3 (br). T_1(min) (ms, Os*H*, 400.13 MHz, $\mathrm{C_7D_8}$, 263 K): 74 ± 4 (−12.39 ppm). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a toluene solution of the complex at −30 °C.

Reaction of 1 with ^{i}PrNHBBN: Preparation of $\mathrm{OsH_3(OBBN)}$-$\{\kappa^3$-*P,O,P*-[xant($\mathrm{P^iPr_2}$)$_2$]$\}$ (3). Amino-borane ^{i}PrNHBBN (35 mg, 0.195 mmol) was added to a solution of **1** (120 mg, 0.184 mmol) in toluene (5 mL). After 30 min at room temperature, the solution was concentrated, and 2 mL of acetone was added at −50 °C to afford a pale yellow solid, which was washed twice with acetone (1 mL) and dried under reduced pressure. Yield: 73 mg (51%). Anal. Calcd for $\mathrm{C_{35}H_{57}BO_2OsP_2}$: C, 54.40; H, 7.43. Found: C, 54.76; H, 7.16. ^{1}H NMR (300.13 MHz, $\mathrm{C_4D_8O}$, 298 K): δ 7.59 (dd, $^3J_{\mathrm{HH}} = 7.6$, $^4J_{\mathrm{HH}} = 1.2$, 2H, C*H*-arom POP), 7.51 (m, 2H, C*H*-arom POP), 7.29 (dd, $^3J_{\mathrm{HH}} = 7.6$, $^3J_{\mathrm{HH}} = 7.5$, 2H, C*H*-arom POP), 2.48 (m, 2H, $\mathrm{PC}H(\mathrm{CH_3})_2$), 2.36 (m, 2H, $\mathrm{PC}H(\mathrm{CH_3})_2$), 1.93 (s, 3H, $\mathrm{C}H_3$ POP), 1.87−1.73 (10H, $\mathrm{C}H_2$ BBN), 1.39 (m, 2H, $\mathrm{C}H_2$ BBN), 1.33 (s, 3H, $\mathrm{C}H_3$ POP), 1.22−1.14 (12H, $\mathrm{PCH(C}H_3)_2$), 1.10 (dvt, $^3J_{\mathrm{HH}} = 7.2$, $N = 14.9$, 6H, $\mathrm{PCH(C}H_3)_2$), 0.86 (br, 2H, C*H* BBN), 0.76 (dvt, $^3J_{\mathrm{HH}} = 7.0$, $N = 14.5$, 6H, $\mathrm{PCH(C}H_3)_2$), −12.78 (t, $^3J_{\mathrm{HP}} = 11.8$, 3H, Os*H*). ^{1}H NMR (400.13 MHz, $\mathrm{C_7D_8}$, 193 K): δ $\upsilon_{\mathrm{A}} = -11.63$ and $\upsilon_{\mathrm{B}} = -13.61$ (AB system, $^2J_{\mathrm{AB}} = 98.5$, 2H, Os*H*), −11.75 (br, 1H, Os*H*). ^{13}C{^{1}H}-APT NMR (75.47 MHz, $\mathrm{C_4D_8O}$, 298 K): δ 161.2 (vt, $N = 13.4$, *C*-arom POP), 134.2 (vt, $N = 5.7$, *C*-arom POP), 130.3 (s, CH-arom POP), 129.3 (vt, $N = 28.5$, *C*-arom POP), 126.8 (s, CH-arom POP), 126.0 (vt, $N = 4.8$, CH-arom POP), 35.7 (s, $\mathrm{C(CH_3)_2}$ POP), 35.2 (s, $\mathrm{CH_2}$ BBN), 34.0 (s, $\mathrm{C(CH_3)_2}$ POP), 32.5 (br, CH BBN), 28.1 (vt, $N = 19.3$, $\mathrm{PCH(CH_3)_2}$), 25.5 (s, $\mathrm{CH_2}$ BBN), 24.9 (vt, $N = 32.3$, $\mathrm{PCH(CH_3)_2}$), 23.8 (s, $\mathrm{C(CH_3)_2}$ POP), 20.6 (d, $^2J_{PC} = 6.0$, PCH(CH$_3$)$_2$), 20.4 (d, $^2J_{PC}$ = 6.6, PCH(CH$_3$)$_2$), 20.0 (s, PCH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, C_7D_8, 293 K): 45.6 (s, POP). ^{11}B NMR (96.30 MHz, C_6D_6, 298 K): δ 50.6 (br). T_1(min) (ms, Os*H*, 400.13 MHz, C_7D_8, 233 K): 77 ± 4 (−12.39 ppm).

Reaction of 2 with CO: Preparation of OsH(CO)$_2$(OBCy$_2$){κ^2-*P*,*P*-[xant(P^{i}Pr$_2$)$_2$]} (4). A solution of **2** (85 mg, 0.103 mmol) in toluene (5 mL) was stirred for 24 h under 1 atm of CO. The resulting solution was concentrated, and pentane (1 mL) at 0 °C was added to afford an off-white solid, which was washed twice with pentane (1 mL) and dried under reduced pressure. Yield: 58 mg (64%). Anal. Calcd for $C_{41}H_{63}BO_4OsP_2$: C, 55.77; H, 7.19. Found: C, 55.90; H, 7.30. IR (Toluene, cm^{-1}): ν (CO) 1998 (s), ν (CO) 1914 (s). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.21 (m, 2H, C*H*-arom POP), 6.99−6.88 (4H, C*H*-arom POP), 2.63−2.28 (4H, PC*H*(CH$_3$)$_2$), 1.78−1.58 (6H, C*H*$_2$ Cy), 1.62 (s, 3H, C*H*$_3$ POP), 1.45−0.85 (36H, C*H* Cy, C*H*$_2$ Cy, PCH(C*H*$_3$)$_2$), 1.16 (s, 3H, C*H*$_3$ POP), 0.35 (m, 4H, CH$_2$), −6.51 (m,1H, Os*H*). ^{1}H NMR (400.13 MHz, C_7D_8, 203 K): −6.30 (dd, $^2J_{HH}$ = 33.6, $^2J_{HH}$ = 115.1, 1H, Os*H*). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 298 K): δ 185.7 (d, $^2J_{CP}$ = 98.0, CO), 181.9−181.7 (CO), 156.2 (d, $^2J_{CP}$ = 6.0, *C*-arom POP), 155.4 (d, $^2J_{CP}$ = 6.2, *C*-arom POP), 134.6 (vt, *N* = 3.8, *C*-arom POP), 134.0 (vt, *N* = 3.6, *C*-arom POP), 131.3 (s, CH-arom POP), 131.0 (s, CH-arom POP), 126.1 (s, CH-arom POP), 125.6 (s, CH-arom POP), 123.5 (s, CH-arom POP), 123.4 (s, CH-arom POP), 118.2 (d, $^1J_{CP}$ = 26.9, *C*-arom POP), 113.7 (d, $^1J_{CP}$ = 28.6, *C*-arom POP), 35.9 (s, C(CH$_3$)$_2$ POP), 35.0 (br, CH-Cy), 32.0 (s, C(CH$_3$)$_2$ POP), 30.2 (d, $^1J_{CP}$ = 16.6, PCH(CH$_3$)$_2$), 28.7, 28.7, 28.6, 28.5, 27.8 (all s, CH$_2$−Cy), 27.5 (d, $^1J_{CP}$ = 22.3, PCH(CH$_3$)$_2$), 23.9 (m, PCH(CH$_3$)$_2$), 23.3 (m, PCH(CH$_3$)$_2$), 22.6 (s, C(CH$_3$)$_2$ POP), 20.6 (d, $^2J_{CP}$ = 4.1, PCH(CH$_3$)$_2$), 19.4 (m, PCH(CH$_3$)$_2$), 19.1 (s, PCH(CH$_3$)$_2$), 18.8 (d, $^2J_{CP}$ = 6.3, PCH(CH$_3$)$_2$), 18.6 (br, PCH(CH$_3$)$_2$), 18.1 (d, $^2J_{CP}$ = 2.2, PCH(CH$_3$)$_2$), 18.0 (d, $^2J_{CP}$ = 4.3, PCH(CH$_3$)$_2$), 17.7 (m, PCH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, C_7D_8, 203 K): δ 186.0 (dd, $^2J_{CP}$ = 99.8, $^2J_{CP}$ = 1.0, CO), 181.8 (dd, $^2J_{CP}$ = 10.5, $^2J_{CP}$ = 2.1, CO), ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6, 298 K): δ 3.2 (br, POP). ^{31}P{^{1}H} NMR (161.98 MHz, C_7D_8, 203 K): 3.4 (d, $^2J_{PP}$ = 26.2, POP), 1.5 (d, $^2J_{PP}$ = 26.2, POP). ^{11}B NMR (96.30 MHz, C_6D_6, 298 K): δ 50.0 (br). Crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of the complex in benzene.

Reaction of 3 with CO: Formation of OsH(CO)$_2$(OBBN){κ^2-*P*,*P*-[xant(P^{i}Pr$_2$)$_2$]} (5). Complex **3** (25 mg, 0.035 mmol) in toluene-d_8 (0.5 mL) was placed in a NMR tube equipped with a Teflon screw cap at room temperature under 1 atm of CO. After 24 h, a mixture of **5** and **6** was formed in a 1:1 ratio. Selected spectroscopic data for **5**: ^{1}H NMR (300.13 MHz, C_7D_8, 298 K): −6.69 (dd, $^2J_{HP}$ = 31.7, $^2J_{HP}$ = 110.5, 1H, Os*H*). ^{1}H NMR (400.13 MHz, C_7D_8, 203 K): −5.64 (dd, $^2J_{HP}$ = 29.4, $^2J_{HP}$ = 99.0, 1H, Os*H*), −6.31 (dd, $^2J_{HP}$ = 32.5, $^2J_{HP}$ = 107.5, 1H, Os*H*). ^{13}C{^{1}H} NMR (75.48 MHz, C_7D_8, 298 K): δ 185.4 (dd, $^2J_{CP}$ = 98.0, $^2J_{CP}$ = 3.3, CO), 182.1 (dd, $^2J_{CP}$ = 10.3, $^2J_{CP}$ = 4.5, CO). ^{31}P{^{1}H} NMR (121.49 MHz, C_7D_8, 298 K): δ 10.8 (br, POP). ^{31}P{^{1}H} NMR (161.98 MHz, C_7D_8, 203 K): 20.7 (d, $^2J_{PP}$ = 24.5, POP), 13.1 (d, $^2J_{PP}$ = 24.5, POP), 12.0 (d, $^2J_{PP}$ = 24.5, POP), 11.4 (d, $^2J_{PP}$ = 24.5, POP). ^{11}B NMR (96.29 MHz, C_7D_8, 298 K): δ 51.3 (br).

Preparation of Os(CO)$_3${κ^2-*P*,*P*-[xant(P^{i}Pr$_2$)$_2$]} (6). A solution of **4** (150 mg; 0.170 mmol) in toluene (5 mL) was placed in a Schlenk tube provided equipped with a Teflon screw cap. The solution was stirred at 110 °C under 1 atm of CO for 4 days. After this time, a dark powder and a yellow solution were formed. The yellow solution was filtered, and the solvent was evaporated to obtain a yellow oil. Its treatment with methanol (2 mL) at −50 °C afforded a yellow solid which was dried under reduced pressure. Yield: 50 mg (41%). Anal. Calcd for $C_{30}H_{40}O_4OsP_2$: C, 50.27; H, 5.62. Found: C, 49.93; H, 5.81. IR (Toluene, cm^{-1}): ν (CO) 2003 (w), ν (CO) 1916 (s), ν (CO) 1900 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 7.51 (dd, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.7,2H, C*H*-arom POP), 7.28 (m, 2H, C*H*-arom POP), 7.22 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 7.3, 2H, C*H*-arom POP), 2.50 (m, 4H, PC*H*(CH$_3$)$_2$), 1.57 (s, 6H, C*H*$_3$ POP), 1.11 (dvt, $^3J_{HH}$ = 6.9, *N* = 16.6, 12H, PCH(C*H*$_3$)$_2$), 1.02 (dvt, $^3J_{HH}$ = 6.8, *N* = 15.3, 12H, PCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 298 K): 4.5 (s, POP). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a toluene solution of the complex at −30 °C.

Reaction of 1 with CO: Formation of OsH$_2$CO{κ^3-*P*,*O*,*P*-[xant(P^{i}Pr$_2$)$_2$]} (7). A solution of **1** (0.100 g, 0.153 mmol) in toluene (5 mL) was stirred under 1 atm of CO for 24 h. The resulted solution was concentrated, and pentane (2 mL) at 0 °C was added to afford a yellow solid which was washed with pentane (2 × 2 mL) and dried under reduced pressure. Yield: 50 mg (49%). The solid was characterized as 7 by comparison of its spectroscopic data with those reported in ref 8h.

Reaction of 7 with CO: Formation of OsH$_2$(CO)$_2${κ^2-*P*,*P*-[xant(P^{i}Pr$_2$)$_2$]} (8). A toluene-d_8 solution of 7 (40 mg, 0.06 mmol, in 0.6 mL) was placed in a NMR tube bearing a Teflon screw cap under 1 atm of CO and heated at 110 °C for 8 h. After that, a mixture of **8** and **6** was formed in a 3:1 molar ratio. Spectroscopic data for **8**: ^{1}H NMR (300.13 MHz, C_7D_8, 298 K): δ 7.10 (d, $^3J_{HP}$ = 7.5, 2H, C*H*-arom POP), 6.96 (m, 2H, C*H*-arom POP), 6.93 (m, 2H, C*H*-arom POP), 2.52 (m, 1H, PC*H*(CH$_3$)$_2$), 2.36 (m, 1H, PC*H*(CH$_3$)$_2$), 2.22 (m, 1H, PC*H*(CH$_3$)$_2$), 2.18 (m, 1H, PC*H*(CH$_3$)$_2$), 1.40 (s, 3H, C*H*$_3$ POP), 1.31 (dd, $^3J_{HH}$ = 7.3, $^3J_{HP}$ = 15.0, 3H, PCH(C*H*$_3$)$_2$), 1.28−1.10 (m, 15H, PCH(C*H*$_3$)$_2$), 1.20 (s, 3H, C*H*$_3$ POP), 0.97 (dd, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 12.8, 3H, PCH(C*H*$_3$)$_2$), 0.89 (dd, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 13.8, 3H, PCH(C*H*$_3$)$_2$), −7.92 (ddd, $^2J_{HH}$ = 6.1, $^2J_{HP}$ = 19.6, $^2J_{HP}$ = 26.4, 1H, Os*H*), −10.01 (ddd, $^2J_{HH}$ = 6.1, $^2J_{HP}$ = 35.5, $^2J_{HP}$ = 67.5, 1H, Os*H*). ^{13}C{^{1}H} NMR (75.48 MHz, C_7D_8, 298 K): δ 188.0 (dd, $^2J_{CP}$ = 3.4, $^2J_{CP}$ = 74.1, CO), 186.0 (dd, $^2J_{CP}$ = 3.6, $^2J_{CP}$ = 10.0, CO), 156.0 (d, $^2J_{CP}$ = 6.7, *C*-arom POP), 155.8 (d, $^2J_{CP}$ = 6.9, *C*-arom POP), 134.8 (d, $^3J_{CP}$ = 3.0, *C*-arom POP), 134.4 (d, $^3J_{CP}$ = 3.0, *C*-arom POP), 129.4 (s, CH-arom POP), 125.8 (s, CH-arom POP), 125.8 (s, CH-arom POP), 125.5 (s, CH-arom POP), 123.0 (s, CH-arom POP), 123.0 (s, CH-arom POP), 122.9 (s, CH-arom POP), 122.9 (s, CH-arom POP), 122.4 (d, $^1J_{CP}$ = 26.4, *C*-arom POP), 121.1 (d, $^1J_{CP}$ = 27.9, *C*-arom POP), 36.1 (s, C(CH$_3$)$_2$ POP), 30.6 (s, C(CH$_3$)$_2$ POP), 30.0 (d, $^1J_{CP}$ = 25.2, PCH(CH$_3$)$_2$), 29.1 (d, $^1J_{CP}$ = 21.5, PCH(CH$_3$)$_2$), 26.5 (dd, $^3J_{CP}$ = 2.5, $^1J_{CP}$ = 27.8, PCH(CH$_3$)$_2$), 25.4 (dd, $^3J_{CP}$ = 4.8, $^1J_{CP}$ = 35.4, PCH(CH$_3$)$_2$), 24.6 (s, C(CH$_3$)$_2$ POP), 20.6 (s, PCH(CH$_3$)$_2$), 20.3 (s, PCH(CH$_3$)$_2$), 19.8 (d, $^2J_{CP}$ = 1.7, PCH(CH$_3$)$_2$), 18.8 (d, $^2J_{CP}$ = 5.0, PCH(CH$_3$)$_2$), 18.7 (dd, $^4J_{CP}$ = 1.9, $^2J_{CP}$ = 2.8, PCH(CH$_3$)$_2$), 18.1 (s, PCH(CH$_3$)$_2$), 18.0 (d, $^2J_{CP}$ = 2.3, PCH(CH$_3$)$_2$), 17.6 (d, $^2J_{CP}$ = 3.0, PCH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_7D_8, 298 K): 4.2 (d, $^2J_{PP}$ = 25.6, POP), 1.9 (d, $^2J_{PP}$ = 25.6, POP).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00727.

Instrumental methods; NMR spectra of complexes **2**, **3**, **4**, **5**, **6**, and **8**; IR spectra of complexes **4** and **6**; structural analysis of complexes **2**, **4**, and **6**; and computational details (PDF)

Cartesian coordinates of the optimized structures (XYZ)

Accession Codes

CCDC 1871559−1871561 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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