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POP-Pincer Osmium-Polyhydrides: Head-to-Head (*Z*)-Dimerization of Terminal Alkynes

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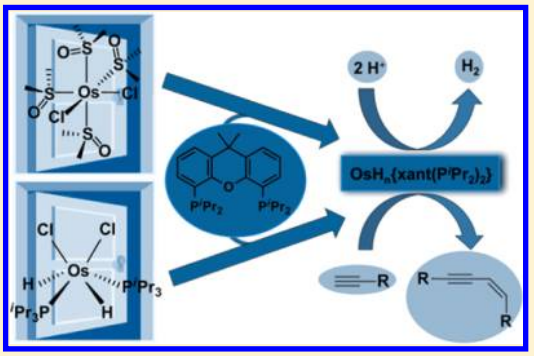
Supporting Information

ABSTRACT: A wide range of osmium-polyhydride complexes stabilized by the POP-pincer ligand xant(P^iPr_2)$_2$ (9,9-dimethyl-4,5-bis(diisopropylphosphino)-xanthene) have been synthesized through *cis*-$OsCl_2\{\kappa$-*S*-$(DMSO)_4\}$ (**1**, DMSO = dimethyl sulfoxide). Treatment of toluene solutions of this adduct with the diphosphine, under reflux, leads to $OsCl_2\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**2**). The reaction of **2** with H_2 in the presence of Et_3N affords $OsH_3Cl\{xant(P^iPr_2)_2\}$ (**3**), which can be also prepared by addition of xant(P^iPr_2)$_2$ to toluene solutions of the unsaturated d^4-trihydride $OsH_3Cl(P^iPr_3)_2$ (**5**). Complex **3** reductively eliminates H_2 in toluene at 90 °C. In the presence of dimethyl sulfoxide, the resulting monohydride is trapped by the *S*-donor molecule to give $OsHCl\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**6**). The reaction of **2** with H_2 is sensible to the Brønsted base. Thus, in contrast to Et_3N, NaH removes both chloride ligands and the hexahydride $OsH_6\{xant(P^iPr_2)_2\}$ (**7**), containing a κ^2-*P*-binding diphosphine, is formed under 3 atm of hydrogen at 50 °C. Complex **7** releases a H_2 molecule to yield the tetrahydride $OsH_4\{xant(P^iPr_2)_2\}$ (**8**), which can be also prepared by reaction of $OsH_6(P^iPr_3)_2$ (**9**) with xant(P^iPr_2)$_2$. Complex **8** reduces H^+ to give, in addition to H_2, the oxidized OsH_4-species $[OsH_4(OTf)\{xant(P^iPr_2)_2\}]^+$ (**10**, OTf = trifluoromethanesulfonate). The redox process occurs in two stages via the OsH_5-cation $[OsH_5\{xant(P^iPr_2)_2\}]^+$ (**11**). The metal oxidation state four can be recovered. The addition of acetonitrile to **10** leads to $[OsH_2(\eta^2\text{-}H_2)(CH_3CN)\{xant(P^iPr_2)_2\}]^{2+}$ (**12**). The deprotonation of **12** yields the osmium(IV) trihydride $[OsH_3(CH_3CN)\{xant(P^iPr_2)_2\}]^+$ (**13**), which is also formed by addition of HOTf to the acetonitrile solutions of **8**. The latter is further an efficient catalyst precursor for the head-to-head (*Z*)-dimerization of phenylacetylene and *tert*-butylacetylene. During the activation process of the tetrahydride, the bis(alkynyl)vinylidene derivatives $Os(C{\equiv}CR)_2(=C{=}CHR)\{xant(P^iPr_2)_2\}$ (R = Ph (**14**), ^{t}Bu (**15**)) are formed.



INTRODUCTION

Pincer ligands develop marked abilities to stabilize less common coordination polyhedra and unusual metal oxidation states due to the disposition of their donor atoms. Consequently, they have a tremendous impact on transition metal chemistry and are viewed as an anchor for the future of the organometallics and homogeneous catalysis.[1] The most commonly encountered linker groups in diphosphine type ligands consist of either a metalated aryl group in anionic systems (PCP)[2] or uncharged pyridines (PNP)[3] or neutral ethers (POP),[4] whereas platinum group metals occupy a prominent place among the metal elements with the notable exception of osmium.[1]

The scarce development of the pincer-osmium chemistry is probably due to the rooted belief that osmium is not useful in catalysis because it is a reductant and prefers to be coordinatively saturated and form redox isomers with greater metal−carbon bond multiplicity.[5] As a consequence of this extended skepticism, not much effort to find starting materials from $OsCl_3{\cdot}H_2O$, similar adducts, or related salts has been done.[6] However, recent findings have proved that osmium can be a promising alternative to the metals classically used in catalysis to promote some organic reactions.[7] In addition, osmium-hydride complexes have been shown to facilitate carbon−carbon and carbon−heteroatom coupling reactions,[8] although it is difficult to rationalize the processes because the products from the reactions of these compounds with unsaturated organic molecules depend on the interactions within the OsH_n units,[9] and further understanding of them is needed.

The chemistry of the osmium-pincer has been mainly focused on a few PCP complexes reported by the groups of Gusev,[10] Jia,[11] and Milstein[12] and PNP compounds described by the groups of Caulton,[13] Gusev,[14] and Jia[15] along with some CCC,[16] CNC,[17] CNN,[18] CNO,[19] and NNN[20] derivatives. In the search for more rigid and robust skeletons than our usual starting fragment *trans*-$Os(P^iPr_3)_2$,[5b,21] three years ago we synthesized the ligands 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene (xant(P^iPr_2)$_2$) and 4,6-bis(diisopropylphosphino)dibenzofuran (dbf(P^iPr_2)$_2$), which were used to prepare the corresponding osmium(III) complexes $OsCl_3(POP)$.[22] Recently, we have

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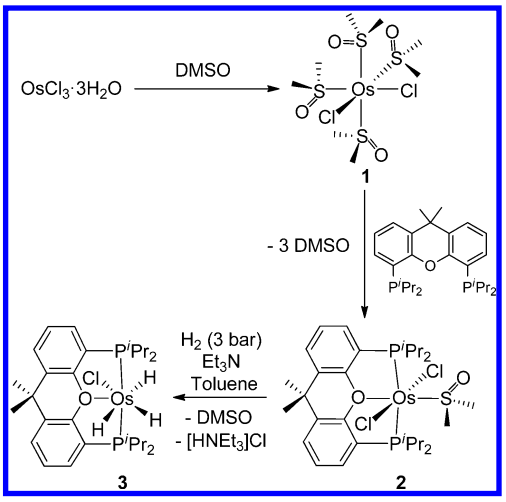
shown an easy and direct access to diamagnetic osmium(II) and osmium(IV) compounds with the dbf(P^iPr_2)$_2$ ligand by using *cis*-$OsCl_2${κ-*S*-$(DMSO)_4$} as starting material. Furthermore, we have proved that osmium is a promising alternative to ruthenium for the direct synthesis of imines from alcohols and amines, with liberation of molecular hydrogen.[23] Now, we have found the entry to diamagnetic xant(P^iPr_2)$_2$ derivatives. In addition, our interest in the interaction within the OsH_n units prompted us to prepare and to study OsH_n{xant(P^iPr_2)$_2$} species and to test the feasibility of the Os{xant(P^iPr_2)$_2$} skeleton in the dimerization of aromatic and aliphatic alkynes.

This paper reveals two entries to diamagnetic osmium complexes with the xant(P^iPr_2)$_2$ ligand, describes the preparation and nature of neutral and cationic OsH_n{xant(P^iPr_2)$_2$} species with n = 1, 3, 4, 5, and 6, and demonstrates the capacity of the tetrahydride OsH_4{xant(P^iPr_2)$_2$} for reducing H^+ and promoting the head-to-head (*Z*)-dimerization of terminal alkynes.

RESULTS AND DISCUSSION

Entries to the Os{xant(P^iPr_2)$_2$} Chemistry. There are relatively few examples in which Os(II)-DMSO species were used as precursors in coordination chemistry, due probably to the high affinity of osmium(II) for *S*-bonding.[24] However, Humphrey and co-workers proved in 1997 that the adduct $OsCl_2(DMSO)_4$ is an useful starting material to prepare $OsCl_2$(chiral bidentate phosphine)$_2$.[25] In the light of this precedent, and because the entry to complexes with the ligand dbf(P^iPr_2)$_2$ from **1** was a success,[23] we decided to start exploring similar entry procedures with xant(P^iPr_2)$_2$. First, we were able to significantly improve the synthetic method of Humphrey to prepare $OsCl_2(DMSO)_4$. Thus, starting from $OsCl_3{\cdot}H_2O$ instead of $[NH_4][OsCl_6]$, we obtain *cis*-$OsCl_2${κ-*S*-$(DMSO)_4$} (**1**) in a selective and direct manner with a 73% yield, which is approximately twice that previously reported. Complex **1** is certainly a good precursor to prepare osmium complexes with the ligand xant(P^iPr_2)$_2$. Treatment of 2-propanol solutions of the diphosphine xant(P^iPr_2)$_2$ with 1.0 equiv of **1**, under reflux for 18 h, leads to $OsCl_2${xant(P^iPr_2)$_2$}(κ-*S*-DMSO) (**2**), which is isolated as an orange solid in 68% yield, according to Scheme 1.

Scheme 1



Complex **2** was characterized by X-ray diffraction analysis. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit.[26] Figure 1 shows a drawing of one of them. As expected for a *mer*-coordination of the pincer, the Os{xant(P^iPr_2)$_2$} skeleton is

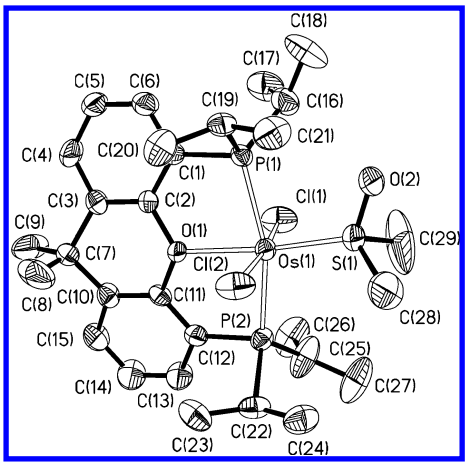


Figure 1. Molecular diagram of **2**. Selected bond lengths (Å) and angles (°): Os(1)−S(1) = 2.1812(18), 2.1727(17), Os(1)−O(1) = 2.247(4), 2.252(4), Os−P(1) = 2.3377(17), 2.3373(17), Os−P(2) = 2.3742(17), 2.3686(18), S(1)−O(2) = 1.483(5), 1.468(5); P(1)−Os(1)−O(1) = 81.28(11), 81.17(12), P(2)−Os(1)−O(1) = 80.80(11), 80.62(12), P(1)−Os(1)−P(2) = 161.43(6), 161.84(6), Cl(1)−Os(1)−Cl(2) = 171.95(8), 175.49(7), O(1)−Os(1)−S(1) = 174.06(1), 173.15(13).

T-shaped with the osmium atom situated in the common vertex and P(1)−Os(1)−O(1), P(2)−Os(1)−O(1), and P(1)−Os(1)−P(2) angles of 81.28(11)° and 81.17(12)°, 80.80(11)° and 80.62(12)°, and 161.43(6)° and 161.84(6)°, respectively. Thus, the coordination geometry around the metal center can be rationalized as a distorted octahedron with *trans* chloride ligands (Cl(1)−Os(1)−Cl(2) = 171.95(8)° and 175.49(7)°) and the oxygen atom of the phosphine *trans* disposed to the dimethyl sulfoxide group (O(1)−Os(1)−S(1) = 174.06(1)° and 173.15(13)°). In agreement with the *S*-bonding of the latter,[27] the IR spectrum contains a ν(S−O) band at 1085 cm^{-1}, which is consistent with S(1)−O(2) distances of 1.483(5) and 1.468(5) Å. The mutually *trans* disposition of the chloride ligands is also evident in the ^1H and the $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2, r.t.), which show two signals for the methyl groups of the phosphine isopropyl substituents (δ_{1H}, 1.36 and 1.31 ppm; δ_{13C}, 21.9 and 21.0 ppm) and one signal for the methyl substituents of the central heterocycle (δ_{1H}, 1.65 ppm; δ_{13C}, 31.9 ppm). According to equivalent P^iPr_2 groups, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 10.3 ppm.

Complex **2** reacts with molecular hydrogen in the presence of a Brønsted base. Thus, the stirring of its toluene solutions in the presence of 2.1 equiv of Et_3N, under 3 atm of hydrogen, at 90 °C, for 60 h leads to the trihydride OsH_3Cl{xant(P^iPr_2)$_2$} (**3**, in Scheme 1), which is isolated as a pale yellow solid in 57% yield. Its formation can be rationalized according to Scheme 2. The dissociation of the dimethyl sulfoxide group from the osmium atom of **2** should afford the five-coordinate species **A**, related to the well-known compound $OsCl_2(PPh_3)_3$.[28] Then, intermediate **A** could coordinate a hydrogen molecule to give **B**. Subsequent heterolytic activation of the coordinated hydrogen molecule[29] should release HCl, which could be trapped by Et_3N, generating **C**. Thus, the addition of a new hydrogen molecule to **C** should lead to **3**.

The sequence of reactions shown in Scheme 1 is a three-step procedure, which allows us to obtain **3** in 28% yield with regard

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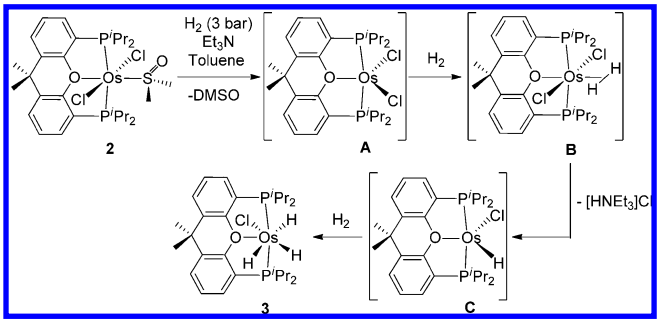
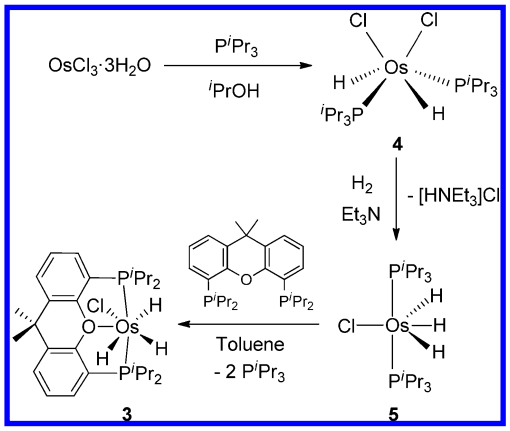
Scheme 2



to $OsCl_3 \cdot H_2O$. In order to increase the obtained amount of trihydride, we designed a new sequence of reactions (Scheme 3).

Scheme 3



This alternative method, which uses the unsaturated six-coordinate d^4-hydride derivatives $OsH_2Cl_2(P^iPr_3)_2$ (**4**) and $OsH_3Cl(P^iPr_3)_2$ (**5**) as intermediate species, leads to **3** in 55% yield with regard to $OsCl_3 \cdot 3H_2O$, although it is also a three-step procedure. Complex **4** is a well-known compound that is obtained in 80% yield by reaction of $OsCl_3 \cdot 3H_2O$ with P^iPr_3 in 2-propanol under reflux.[6d] Its transformation into **5**, by reaction with molecular hydrogen in the presence of Et_3N,[30] has been improved reaching almost quantitative yield (for more details see the Experimental Section). The substitution of P^iPr_3 by xant$(P^iPr_2)_2$ ligand is a relatively rapid process, which is performed in toluene under reflux and affords **3** in an isolated yield of 68% after 4 h.

Complex **3** was also characterized by X-ray diffraction analysis. Figure 2a shows a view of the molecule. The Os{xant$(P^iPr_2)_2$} skeleton is T-shaped with the metal situated in the common vertex, as in **2**. The P(1)−Os−O(1), P(2)−Os−O(1), P(1)−Os−P(2) angles of 82.65(5)°, 82.71(5)°, and 162.90(2)° agree well with the related parameters of **2**. The coordination geometry around the metal center can be rationalized as a distorted pentagonal bipyramid, with the hydride and chloride ligands lying in the perpendicular plane to the P−Os−P direction along with the oxygen atom of the phosphine, which is situated between the chloride and the hydride H(03) (O(1)−Os−Cl(1) = 80.15(6)°, O(1)−Os−H(03) = 85.6(12)°). The DFT optimized structure (Figure 2b) confirms the trihydride character of the OsH_3 unit. The H(01)−H(02) and H(02)−H(03) separations are 1.616 and 1.618 Å, respectively. In accordance with the presence of the hydride ligands, the ^{1}H NMR spectrum in dichloromethane-d_2, at room temperature, shows at −13.17 ppm a triplet with a H−P coupling constant of 11.0 Hz. This is consistent with the operation of two thermally activated site exchange processes within the OsH_3 unit, in agreement with the behavior of other d^4-$OsH_3XY(P^iPr_3)_2$ complexes.[31] Decreasing the temperature of the sample leads to a broadening of the resonance. Between 243 and 233 K, decoalescence occurs and two signals, centered at −12.98 and −13.38 ppm, in a 1:2 intensity ratio are observed. Although at lower temperatures than 233 K the resonance at higher field displays broad, the expected second decoalescence is not reached even at 183 K. According to the trihydride character of the complex, a 400 MHz $T_{1(min)}$ value of 104 ± 3 ms was found for both signals at 233 K. In contrast to the ^{1}H NMR spectrum, the ^{31}P{^{1}H} NMR spectrum is temperature invariant, showing a singlet at 50.6 ppm in agreement with the equivalence of the P^iPr_2 groups.

The position of the chloride ligand determines the nature of the OsH_3 unit. Thus, interestingly, DFT calculations reveal the existence of a *trans*-chloride-oxygen isomer (**3a**), 20.1 kcal·mol^{-1} (ΔG, 1 atm, 298.15 K) less stable than **3**, which is a hydride-dihydrogen species. Figure 3 gives a view of DFT optimized structure of this compound. The coordinated hydrogen molecule lies *trans* to the hydride ligand and is disposed almost parallel to

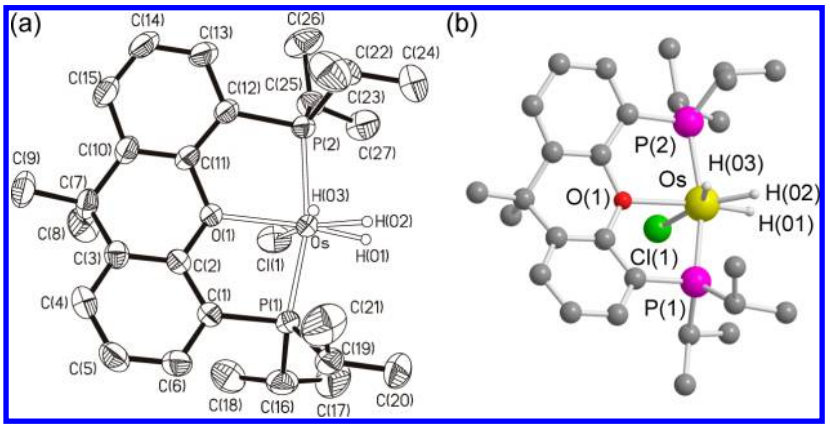


Figure 2. (a) Molecular diagram of **3**. Selected bond lengths (Å) and angles (°): Os−O(1) = 2.224(2), Os−Cl(1) = 2.4840(11), Os−P(1) = 2.2906(12), Os−P(2) = 2.2933(11); P(1)−Os−O(1) = 82.65(5), P(2)−Os−O(1) = 82.71(5), P(1)−Os−P(2) = 162.90(2), O(1)−Os−Cl(1) = 80.15(6). (b) DFT optimized structure of **3**. Selected bond lengths (Å) and angles (°): Os−O(1) = 2.286, Os−Cl(1) = 2.524, Os−P(1) = 2.319, Os−P(2) = 2.319; P(1)−Os−O(1) = 81.9, P(2)−Os−O(1) = 81.9, P(1)−Os−P(2) = 162.9, O(1)−Os−Cl(1) = 76.6.

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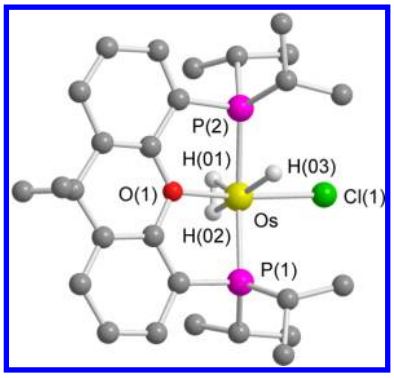
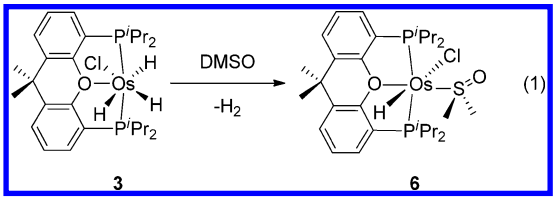


Figure 3. DFT optimized structure of **3a**. Selected bond lengths (Å) and angles (°): Os−O(1) = 2.243, Os−Cl(1) = 2.443, Os−P(1) = 2.307, Os−P(2) = 2.307; P(1)−Os−O(1) = 82.0, P(2)−Os−O(1) = 82.0, P(1)−Os−P(2) = 157.2.

the P−Os−P direction with the hydrogen atoms separated by 0.856 Å.

Complex **3** reductively eliminates a hydrogen molecule in toluene at 90 °C. In the presence of dimethyl sulfoxide, the resulting unsaturated d^6-monohydride species is trapped by the *S*-donor solvent to afford OsHCl{xant(P^iPr_2)$_2$}(κ-*S*-DMSO) (**6**), which is isolated as a white solid in 80% yield, according to eq 1. The *S*-bonding of the dimethyl sulfoxide group is strongly

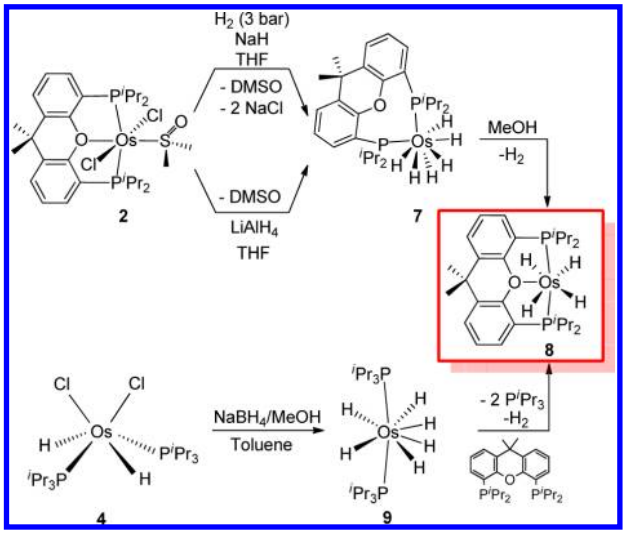


supported by IR, which shows a ν(S−O) band at 1072 cm^{-1} in agreement with **2**. As expected for the presence of a hydride ligand, the ^{1}H NMR spectrum (CD_2Cl_2, r.t.) contains at −18.77 ppm a triplet with a H−P coupling constant of 19.8 Hz, whereas the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 35.4 ppm that is split into a doublet under *off resonance* conditions.

OsH$_6$(xant(P^{i}Pr$_2$)$_2$} and OsH$_4$(xant(P^{i}Pr$_2$)$_2$}. The reaction of **2** with molecular hydrogen is sensible to the Brønsted base used and to the experimental conditions. In contrast to Et_3N in toluene, sodium hydride in tetrahydrofuran removes both chloride ligands and, furthermore, a hydrogen molecule displaces the oxygen atom of the diphosphine, which becomes a κ^2-*P*-binding. Thus, the stirring of the tetrahydrofuran solutions of **2** in the presence of 10 equiv of the superbase, under 3 atm of hydrogen, at 50 °C, for 48 h leads to the hexahydride derivative OsH$_6$(xant(P^iPr_2)$_2$} (**7**), which is isolated as a pale yellow solid in 50% yield according to Scheme 4. A briefer method implies the treatment of tetrahydrofuran solutions of **2** with 20 equiv of $LiAlH_4$, at 80 °C, for 3 h. By this procedure, complex **7** is obtained in 37% yield.

The κ^2-*P*-binding coordination mode of the diphosphine is strongly supported by the ^{1}H NMR spectrum of the compound in dichloromethane-d_2, at room temperature (Figure 4), which shows two double of doublets at 1.13 and 1.07 ppm for the methyl groups of the phosphine isopropyl substituents. In the high field region of the spectrum, the hydride ligands give rise to a singlet at −10.08 ppm, which displays an integrated intensity of 6. According to the classical polyhydride nature of

Scheme 4



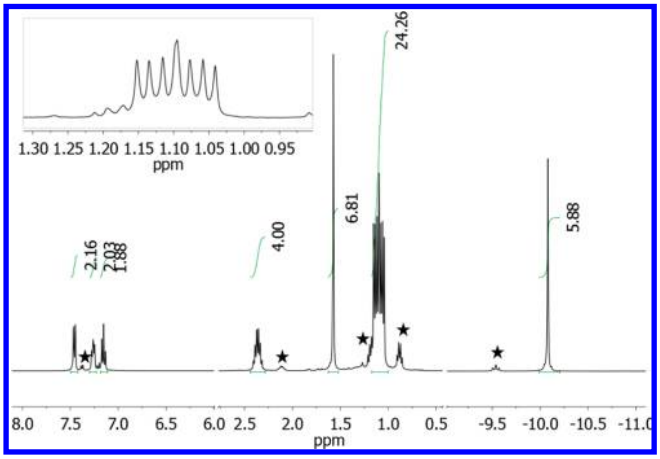


Figure 4. ^{1}H NMR spectrum of **7** (400 MHz, CD_2Cl_2, r.t.) with the integrated intensity of each signal. ★ Resonances corresponding to the complex OsH$_4$(xant(P^iPr_2)$_2$}.

the complex, a 400 MHz $T_{1(min)}$ value of 113 ± 3 ms was found at 228 K for this resonance.

Figure 5 shows the DFT optimized structure of **7**. In agreement with other OsH$_6$-species[6d,32] and related eight-coordinate osmium-polyhydrides,[33] the coordination geometry around the metal center can be rationalized as being derived from a distorted dodecahedron, which is defined by two intersecting BAAB orthogonal (84.11°) trapezoidal planes.[34] One of them contains the atoms H(01), H(03), H(05), and P(1) (maximum deviation 0.183 Å for H(03)) with a H(01)−Os−P(1) angle of 149.8°, whereas the second one contains the atoms P(2), H(06), H(02), and H(04) (maximum deviation 0.180 Å for H(02)) with a P(2)−Os−H(04) angle of 146.4°. The P(1)−Os−P(2) bite angle of the diphosphine of 105.4° is consistent with those reported for other complexes containing κ^2-*P*-bonding xantphos type ligands.[35] As expected for the classical polyhydride character of this species, the separations between the hydride ligands are longer than 1.686 Å (H(04)−H(02) and H(03)−H(01)).

Complex **7** is stable under hydrogen atmosphere at temperatures below 293 K. In methanol, under argon atmosphere, it slowly loses a hydrogen molecule, and the diphosphine coordinates the oxygen atom to the metal center. Thus, the

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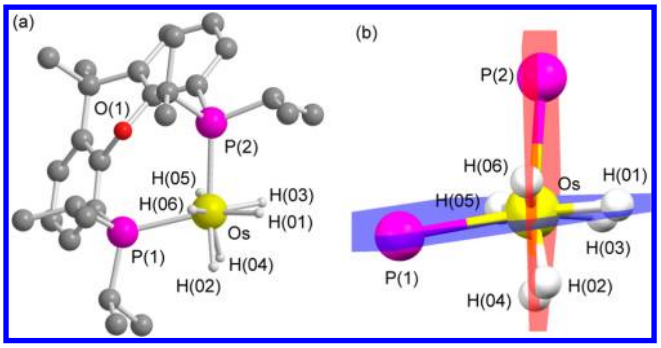


Figure 5. (a) DFT optimized structure of **7**. Selected bond lengths (Å) and angles (°): Os–P(1) = 2.448, Os–P(2) = 2.446; P(1)–Os–P(2) = 105.4. (b) View of the two intersecting BAAB orthogonal trapezoidal planes.

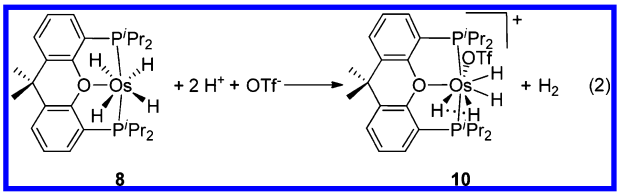
stirring of methanol solutions of **7** at room temperature for six days gives rise to the quantitative precipitation of the tetrahydride derivative $OsH_4\{xant(P^iPr_2)_2\}$ (**8**, in Scheme 4), as a white solid in 30% yield with regard to $OsCl_3{\cdot}3H_2O$. Complex **8** can be prepared through a briefer method by using the dihydride **4**. The latter is initially transformed into the hexahydride $OsH_6(P^iPr_3)_2$ (**9**), which is isolated in 60% yield, after reaction with a toluene suspension of $NaBH_4$ and some drops of methanol.[6d,36] Subsequent treatment of a toluene solution of **9** with 1.1 equiv of the diphosphine affords **8** in a 20% yield with regard to $OsCl_3{\cdot}3H_2O$, after 12 h under reflux.

Complex **8** has been characterized by X-ray diffraction analysis. The structure has four chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 6a shows a drawing of one of them. The $Os\{xant(P^iPr_2)_2\}$ skeleton is T-shaped with the metal situated in the common vertex, as in **2** and **3**. The P(1)–Os(1)–O(1), P(2)–Os(1)–O(1), and P(1)–Os(1)–P(2) angles of 82.00(9), 81.84(9), 82.29(9), and 81.99(9)°, 82.68(9), 82.21(9), 82.57(9), and 81.89(9)°, and 164.53(5), 164.05(5), 164.74(5), and 163.87(5)°, respectively, are consistent with the related parameters of **2** and **3**. Thus, the coordination geometry around the metal center can be rationalized as a distorted pentagonal bipyramid with the hydride ligands lying in the perpendicular plane to the P–Os–P direction along with the oxygen atom of the phosphine, which is situated between H(01) and H(04). The tetrahydride nature of the complex was confirmed by the DFT optimized structure (Figure 6b), which yields H–H separations longer than 1.683 Å (H(02)–H(03)).

The $^{31}P\{^1H\}$ and ^1H NMR spectra of **8** in dichloromethane-d_2 are consistent with the structure shown in Figure 6. In agreement with equivalent P^iPr_2 groups, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 66.3 ppm, which remains invariant between 293 and 193 K. In contrast to the $^{31}P\{^1H\}$ NMR spectrum, the ^1H NMR spectrum is temperature dependent. As expected for two inequivalent hydride positions, two broad resonances centered at −3.14 and at −16.63 ppm are observed in the high field region of the spectrum at 183 K. Between 193 and 203 K, coalescence takes place. According to the classical polyhydride character of the complex, at 213 K, a 400 MHz $T_{1(min)}$ value of 179 ± 3 ms was found for the resulting resonance. The behavior of the hydride resonances with the temperature indicates that in dichloromethane-d_2, the hydride ligands H(01) and H(02) (or H(04) and H(03)) undergo a thermally activated position exchange. A $\Delta G^{\ddagger}_{203}$ value of 8.1 kcal·mol^{-1} was estimated for the process.

Hydrogen Evolution. The H_2 molecule is a promising energy carrier to replace hydrocarbons due to its cleanness. The hydrogen evolution reaction, which implies the reduction of H^+, is the cathodic half reaction in the water splitting process.

The tetrahydride complex **8** is a strong reductor, which is able to promote the reduction of H^+ (eq 2), in spite of the



(2)

high oxidative state of the metal center. Thus, the addition of 4.0 equiv of triflic acid (HOTf) to its dichloromethane-d_2 solutions gives molecular hydrogen and the oxidized OsH_4-species $[OsH_4(OTf)\{xant(P^iPr_2)_2\}]^+$ (**10**). The presence of four hydrogen atoms bonded to the metal center is strongly supported by the ^1H NMR spectrum of the resulting solution, which shows a triplet (J_{H-P} = 4.0 Hz) at −11.62 ppm with an integrated intensity of 4. This resonance exhibits a 400 MHz

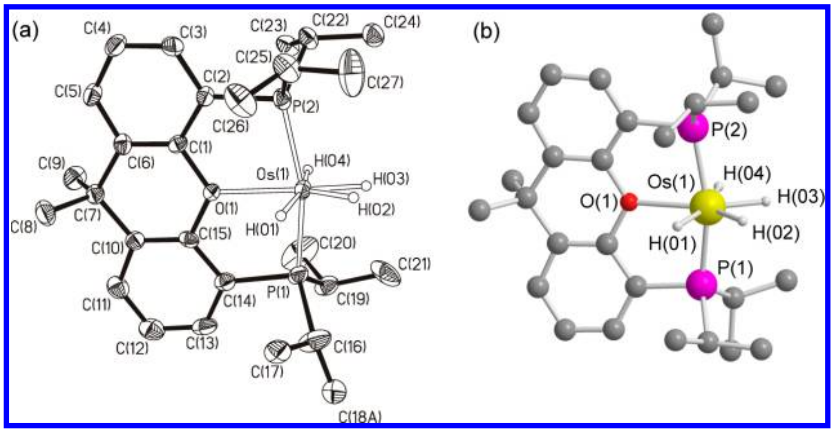


Figure 6. (a) Molecular diagram of **8**. Selected bond lengths (Å) and angles (°): Os(1)–O(1) = 2.222(3), 2.237(3), 2.213(3), and 2.230(4), Os–P(1) = 2.2721(15), 2.2693(14), 2.2693(13), and 2.2692(15), Os–P(2) = 2.2662(15), 2.2719(14), 2.2764(13), and 2.2684(15); P(1)–Os(1)–O(1) = 82.00(9), 81.84(9), 82.29(9), and 81.99(9), P(2)–Os(1)–O(1) = 82.68(9), 82.21(9), 82.57(9), and 81.89(9), P(1)–Os(1)–P(2) = 164.53(5), 164.05(5), 164.74(5), and 163.87(5). (b) DFT optimized structure of **8**. Selected bond lengths (Å) and angles (°): Os(1)–O(1) = 2.285, Os–P(1) = 2.296, Os–P(2) = 2.296; P(1)–Os(1)–O(1) = 82.0, P(2)–Os(1)–O(1) = 82.0, P(1)–Os(1)–P(2) = 163.7.

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$T_{1(min)}$ value of 73 ± 3 ms at 243 K. Between 203 and 193 K, decoalescence occurs and at 183 K two broad signals centered at −9.78 and −13.53 ppm, with a 1:1 intensity ratio, are observed. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 65.9 ppm.

Figure 7 shows the DFT optimized structure of **10**. In agreement with the spectroscopic features, two groups of equivalent

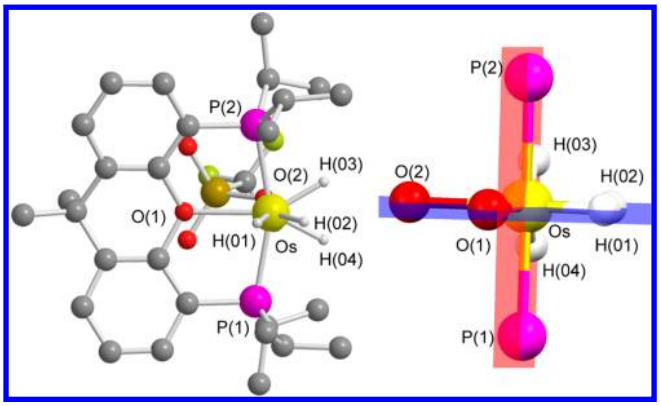

Figure 7. DFT optimized structure of the cation of **10**. Selected bond lengths (Å) and angles (°): Os−O(1) = 2.289, Os−O(2) = 2.166, Os−P(1) = 2.390, Os−P(2) = 2.388; P(1)−Os−O(1) = 80.5, P(2)−Os−O(1) = 80.6, P(1)−Os−P(2) = 160.3.

hydrogen atoms (H(01) and H(02), and H(03) and H(04)) bonded to the metal center are shown. Thus, as expected for an eight-coordinate osmium polyhydride, the ligands around the metal center form a distorted dodecahedron, which is defined by the intersecting P(1), H(04), H(03), and P(2) and O(1), H(01), H(02), and O(2) orthogonal (89.96°) trapezoidal planes. The separation between H(03) and H(04) is 1.545 Å, while H(01) and H(02) form an elongated dihydrogen ligand of 1.25 Å. Some reported osmium skeletons stabilizing dihydride-elongated dihydrogen OsH_4-species are $[Os(\eta^5\text{-}C_5H_5)(PR_3)]^+$ (R = Me,[37] H[38]), $[Os(TACN)(P^iPr_3)]^{2+}$ (TACN = 1,4,7-triazacyclononane), and $[Os(TACD)(P^iPr_3)]^{2+}$ (TACD = 1,4,7-triazacyclodecane).[39] However, $[OsTp(P^iPr_3)]^+$ (Tp = hydridotris(pyrazolyl)borate)[40] and $[Os(BAEA)(P^iPr_3)]^{2+}$ (BAEA = bis(2-aminoethyl)amine)[39] metal fragments favor the formation of bis(dihydrogen) derivatives. In this context, it should be mentioned that OsH_4 species are very sensitive to the L−M−L angles. Small changes in these angles can invert the relative energies of the metal orbitals interacting with those of the dihydrogens.[39,40]

The redox reaction shown in eq 2 occurs in two stages (eqs 3 and 4). Initially, complex **8** adds a proton to afford $[OsH_5\{xant(P^iPr_2)_2\}]^+$ (**11**), which reacts with HOTf to give molecular hydrogen and **10**.

$$\underset{\mathbf{8}}{OsH_4\{xant(P^iPr_2)_2\}} + H^+ \rightarrow \underset{\mathbf{11}}{[OsH_5\{xant(P^iPr_2)_2\}]^+} \quad (3)$$

$$\underset{\mathbf{11}}{[OsH_5\{xant(P^iPr_2)_2\}]^+} + H^+ + OTf^- \rightarrow \underset{\mathbf{10}}{[OsH_4(OTf)\{xant(P^iPr_2)_2\}]^+} + H_2 \quad (4)$$

The most noticeable signal in the ^1H NMR spectrum of **11** is a triplet (J_{H-P} = 5.2 Hz) at −7.71 ppm, which displays an integrated intensity of 5. This resonance does not reach decoalescence even at 183 K and has a short 400 MHz $T_{1(min)}$ value of 20 ± 3 ms at 193 K, which indicates nonclassical interactions in the OsH_5 unit. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 60.7 ppm. DFT calculations reveal that there are three structures differing by 3.0 kcal·mol^{-1} (ΔG, 1 atm, 298.15 K): the hydride-elongated dihydrogen−dihydrogen conformers **11a** and **11b** and the trihydride-elongated dihydrogen **11c**. Figure 8 shows views of their DFT optimized structures. The main difference between **11a** and **11b** is the conformation of the central six-membered ring of the phosphine, which is planar in the first of them and boat in the second one. Conformer **11a** is 2.8 kcal·mol^{-1} more stable than **11b**. In both compounds, the dihydrogen ligand is disposed almost parallel to the P−Os−P direction, with similar H(04)−H(05) bond lengths of 0.873 (**11a**) and 0.870 (**11b**) Å, whereas the elongated dihydrogen ligand H(02)−H(03) lies in the perpendicular plane along with the hydride H(01) and the oxygen atom of the phosphine. The H(01)−H(02) and H(02)−H(03) separations are 1.739 and 1.398 Å (**11a**) and 1.693 and 1.455 Å (**11b**). The disposition of the hydrogen atoms of the OsH_5 unit in **11c** is similar to those of **11a** and **11b** with the H(04)−H(05) bond completely added and the hydrogen atoms H(04) and H(05) separated by 1.762 Å. The separations between H(01) and H(02) and between H(02) and H(03) of 1.886 and 1.473 Å, respectively, are longer than in **11a** and **11b**. These results can be rationalized by means of the fast equilibria shown in Scheme 5.

The metal oxidation state four can be recovered (Scheme 6). The addition of 1.0 equiv of acetonitrile to the dichloromethane-d_2 solutions of **10** produces the replacement of the coordinated trifluoromethanesulfonate anion by the *N*-donor ligand to afford $[OsH_4(CH_3CN)\{xant(P^iPr_2)_2\}]^{2+}$ (**12**), which exhibits a broad resonance at −11.45 ppm, with an integral intensity of 4, in the ^1H NMR spectrum. This resonance has a short 400 MHz $T_{1(min)}$ value of 22 ± 2 ms at 243 K, indicating a significant increase of the nonclassical interactions in the OsH_4 unit with regard to **10**; i.e., the substitution of the trifluoromethanesulfonate anion by the acetonitrile molecule causes the intramolecular reduction of the metal center. Decoalescence occurs between 243 and 233 K and at lower temperatures than the latter two signals at −11.29 and −11.82 ppm, with a 1:1 intensity ratio observed. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 56.7 ppm that is temperature invariant between 293 and 183 K. In accordance with these spectroscopic features, the DFT optimized structure of **12** (Figure 9) supports a dihydride−dihydrogen nature. The dihydrogen ligand is situated in the perpendicular plane to the P−Os−P direction with the hydrogen atoms separated by 0.898 Å, while the hydride ligands lie in the trapezoidal plane containing the phosphorus atoms with the hydrogens separated by 1.475 Å. The addition of 1.0 equiv of Et_3N to the dichloromethane-d_2 solutions of **12** causes its deprotonation and the formation of the osmium(IV) trihydride **13**. The reaction is reversible, and the addition of 1.0 equiv of HOTf to the dichloromethane-d_2 solutions of **13** regenerates **12**.

Complex **13** is the result of the replacement of a hydride ligand of **8** by an acetonitrile molecule. The substitution can be carried out in one-pot synthesis by addition of 4.0 equiv of HOTf to the acetonitrile solutions of **8**. By this procedure, the OTf salt of **13** is isolated as a yellow solid in 63% yield. Figure 10a gives a view of the X-ray structure of the cation of **13**. The distribution of ligands around the metal center is similar to those of **3** and **8** with the acetonitrile molecule occupying the position of the chloride ligand of **3** or the hydride H(04) of **8** and P(1)−Os−O(1), P(2)−Os−O(1), and P(1)−Os−P(2) angles of 82.40(8)°, 82.07(8)°, and 162.29(4)°, respectively.

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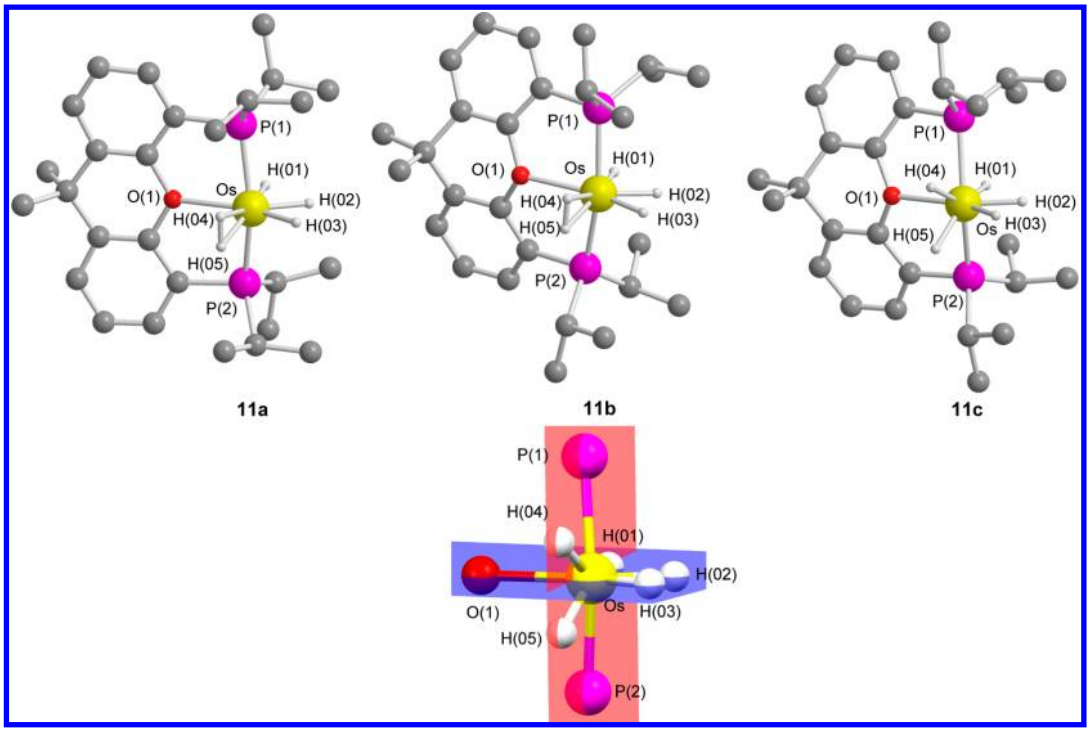
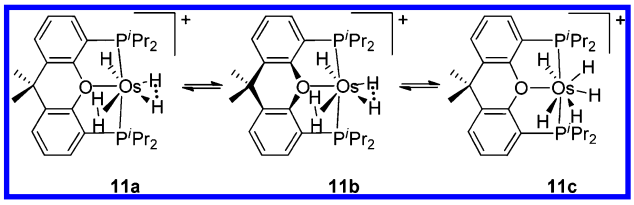
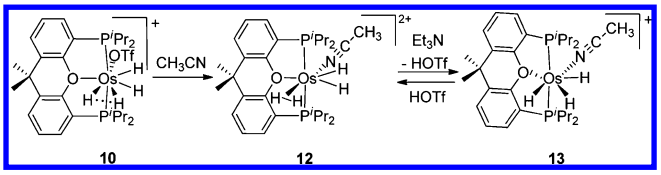


Figure 8. DFT optimized structure of the cations of **11a**, **11b**, and **11c**. Selected bond lengths (Å) and angles (°): Os–O(1) = 2.230 (**11a**), 2.256 (**11b**), and 2.240 (**11c**), Os–P(1) = 2.351 (**11a**), 2.349 (**11b**), and 2.372 (**11c**), Os–P(2) = 2.350 (**11a**), 2.349 (**11b**), and 2.372 (**11c**); P(1)–Os-O(1) = 82.1 (**11a**), 82.8 (**11b**), and 82.6 (**11c**), P(2)–Os–O(1) = 82.2 (**11a**), 82.8 (**11b**), and 82.6 (**11c**), P(1)–Os–P(2) = 159.7 (**11a**), 160.4 (**11b**), and 148.0 (**11c**).

Scheme 5



Scheme 6



The DFT optimized structure (Figure 10b) confirms the trihydride character of the cation and reveals that replacement of the hydride by acetonitrile does not produce any significant change in the nature of the OsH_3 unit. Thus, the H(01)–H(02) and H(02)–H(03) separations of 1.552 and 1.606 Å agree well with those of **3** and **8**.

The position of the acetonitrile molecule also determines the nature of the OsH_3 unit in this case. Similarly to **3**, complex **13** has a hydride–dihydrogen tautomer (**13a**) with the acetonitrile ligand *trans* to the oxygen atom of the phosphine. This species is 10.7 kcal·mol^{-1} (ΔG, 1 atm, 298.15 K) less stable than **13**. Figure 11 shows a view of its DFT optimized structure. The hydrogen molecule is disposed almost parallel to the P–Os–P direction with the hydrogen atoms separated by 0.859 Å. In this context, it should be noted that the difference in stability between **13** and **13a** is significantly smaller than between **3** and **3a**.

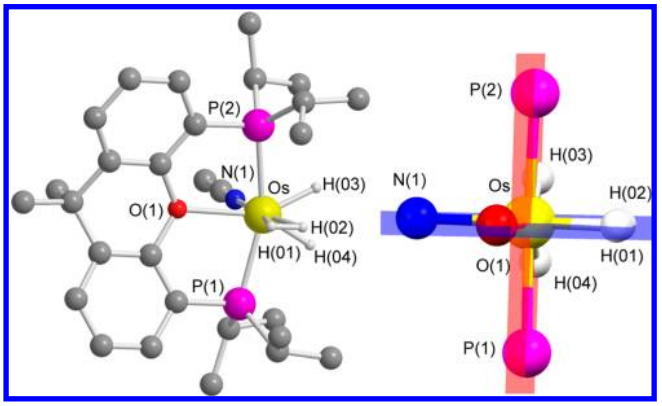


Figure 9. DFT optimized structure of the cation of **12**. Selected bond lengths (Å) and angles (°): Os–N(1) = 2.056, Os–O(1) = 2.298, Os–P(1) = 2.409, Os–P(2) = 2.409; P(1)–Os–O(1) = 80.2, P(2)–Os–O(1) = 80.2, P(1)–Os–P(2) = 159.1.

This appears to be a consequence of the lower donor power of the acetonitrile molecule with regard to the chloride anion and the positive charge of **13a**.[41]

Acetonitrile favors the dihydrogen form with regard to the chloride anion. Hydride site exchange processes in $Os^{IV}H_3$ derivatives implies Os–H stretching, H–H shortening, and subsequent rotation of the resulting dihydrogen ligand.[42] So, lower activation barriers for the hydride site exchanges should be expected in **13** than in **3**. In fact, the ^{1}H NMR spectrum of **13** in dichloromethane-d_2, at room temperature, shows a hydride resonance at −12.58 ppm, which appears as a triplet with a H–P coupling constant of 10.5 Hz. In contrast to **3**, although lowering the sample temperature leads to a broadening of the signal, decoalescence is not reached even at 183 K. It should be also

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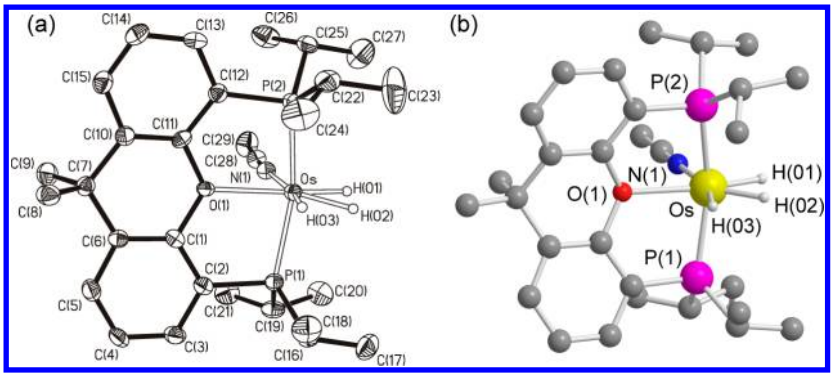


Figure 10. (a) Molecular diagram of the cation of **13**. Selected bond lengths (Å) and angles (°): Os–N(1) = 2.120(4), Os–O(1) = 2.212(3), Os–P(1) = 2.3001(11), Os–P(2) = 2.3072(12); P(1)–Os(1)–O(1) = 82.40(8), P(2)–Os(1)–O(1) = 82.07(8), P(1)–Os(1)–P(2) = 162.29(4). (b) DFT optimized structure of the cation of **13**. Selected bond lengths (Å) and angles (°): Os–N(1) = 2.147, Os–O(1) = 2.280, Os–P(1) = 2.336, Os–P(2) = 2.338; P(1)–Os(1)–O(1) = 82.1, P(2)–Os(1)–O(1) = 82.4, P(1)–Os(1)–P(2) = 159.4.

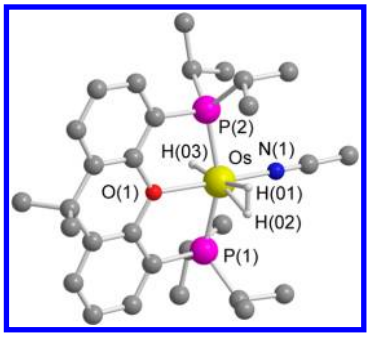
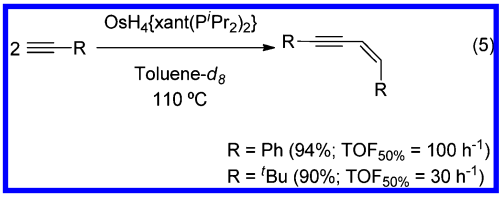


Figure 11. DFT optimized structure of the cation of **13a**. Selected bond lengths (Å) and angles (°): Os–N(1) = 1.964, Os–O(1) = 2.227, Os–P(1) = 2.340, Os–P(2) = 2.340; P(1)–Os–O(1) = 81.8, P(2)–Os–O(1) = 81.8, P(1)–Os–P(2) = 158.2.

mentioned that, in agreement with closer hydride ligands in **13** than in **3**, a shorter 400 MHz $T_{1(min)}$ value of 88 ± 2 ms was found for this resonance at 193 K. The equivalent P^iPr_2 groups display a singlet at 49.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

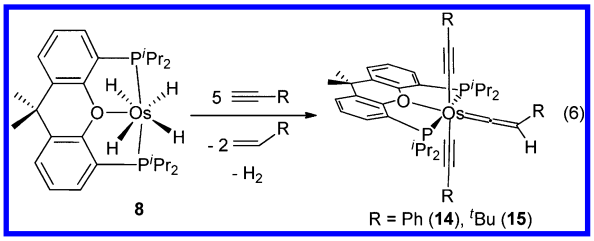
Head-to-Head (*Z*)-Dimerization of Phenylacetylene and *tert*-Butylacetylene Promoted by 8. Transition-metal-catalyzed dimerizations of terminal alkynes are attractive atom-economical C–C bond forming reactions, which afford products containing structural units in natural products and materials.[43] In most cases, mixtures of regio (head-to-head vs head-to-tail) and stereo (*E*/*Z*-head-to-head) isomers have been obtained. From a mechanistic point of view, it has been proposed that the (*Z*)-isomer is generated by intramolecular addition of an alkynyl ligand to the α-carbon atom of a metal-bond vinylidene ligand, while the (*E*)-isomer results from the insertion of a π-bond alkyne into an alkenyl–metal bond.[44]

The regio- and stereoselective head-to-head (*Z*)-dimerization is of special interest, since the resulting (*Z*)-enynes are key units found in a variety of natural occurring anticancer antibiotics.[45] However, it has been hardly achieved.[46] The tetrahydride complex **8** is an efficient catalyst precursor for the regio- and stereoselective head-to-head (*Z*)-dimerization of phenylacetylene and *tert*-butylacetylene. In toluene-d_8 at 110 °C, the enynes (*Z*)-PhC≡CCH=CHPh and (*Z*)-^{t}BuC≡CCH=CH^{t}Bu are formed in 94% and 90% yield with a turnover frequency at 50% conversion ($TOF_{50\%}$) of 100 and 30 h^{-1}, respectively (eq 5). This fact is noticeable, because the osmium catalysts for the alkyne dimerization are extremely rare. The hydride-vinylidene $OsH(\kappa^2\text{-}O_2CCH_3)(=C=CHPh)(P^iPr_3)_2$ catalyzes the dimerization



of phenylacetylene to give a mixture of (*Z*)-PhC≡CCH=CHPh and (*E*)-PhC≡CCH=CHPh in a 5:2 molar ratio.[47] In contrast to the latter and **8**, in the presence of diethylamine, the known complex $OsHCl(CO)(P^iPr_3)_2$[5b] promotes the formation of butatrienes, RCH=C=C=CHR, which are stable under the reaction conditions when R = ^{t}Bu and Cy. For R = Ph, the butatriene polymerizes to –[CH(Ph)C≡CCH(Ph)]$_n$–, while for R = Me_3Si the butatriene isomerizes into the enyne (*Z*)-$Me_3SiC{\equiv}CCH{=}CHSiMe_3$.[48] In addition, it should be noted that the behavior of **8** is also in contrast to those of (PNP)Rh[43a] and (PCP)Ir[43b] pincer-ligated species, which promote the formation of (*E*)-enynes.

Complex **8** is transformed into the bis(alkynyl)vinylidene derivatives $Os(C{\equiv}CR)_2(=C=CHR)\{xant(P^iPr_2)_2\}$ (R = Ph (**14**), ^{t}Bu (**15**)), along with 2 equiv of the corresponding olefin and one hydrogen molecule, under catalytic conditions before the first turnover (eq 6). These species were detected



during the catalysis by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and prepared as analytically pure yellow solids in 79% (**14**) and 87% (**15**) yield at Schlenk scale, by means of the treatment of toluene solutions of **8** with 10 equiv of alkyne at 110 °C, for 2 h. The bis(alkynyl)vinylidene formulation is strongly supported by the ^1H and the $^{13}C\{^1H\}$ NMR spectra of the obtained solids. In the ^1H NMR spectra, the most noticeable signals are the characteristic $C_\beta H$-resonances of the vinylidene ligands which appear at 3.04 ppm (**14**) and at 1.05 ppm (**15**). Furthermore, the spectra reveal a high symmetry in these molecules. Thus, they show two doublets of virtual triplets at 1.61 and 1.51 ppm for **14** and at 1.70 and 1.66 ppm for **15**, corresponding to the

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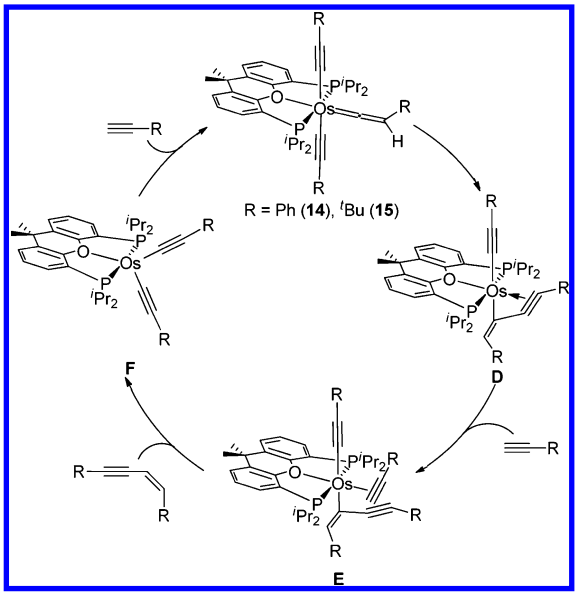
methyl groups of the phosphine isopropyl substituents, and a singlet at 1.28 ppm (**14**) and at 1.30 ppm (**15**), due to the methyl substituent of the central heterocycle of the phosphine, which are consistent with the mutually *trans* disposition of the alkynyl groups and indicate a low activation barrier for the rotation of the vinylidene ligand in agreement with that observed in previous cases.[49] In the $^{13}C\{^1H\}$ NMR spectra, the C_α and C_β resonances of the vinylidene ligands are observed at 300.1 and 106.4 ppm for **14** and at 290.8 and 112.9 ppm for **15**, whereas the C_α and C_β signals of the alkynyl groups appear at 109.5 and 129.3 ppm (**14**) and at 91.6 and 124.0 ppm (**15**). The $^{31}P\{^1H\}$ NMR spectra show singlets at 14.4 (**14**) and at 11.6 ppm (**15**), in agreement with equivalent P^iPr_2 groups.

The formation of **14** and **15** is consistent with a head-to-head (*Z*)-dimerization of the alkynes, which can be rationalized according to Scheme 7. The migratory insertion of the vinylidene ligand into one of the Os-alkynyl bonds could afford the butenynyl intermediates **D**. The displacement of the coordinated carbon−carbon triple bond of the butenynyl ligand by an alkyne molecule should lead to **E**, which could release the (*Z*)-enyne to give **F**. The coordination of a new alkyne molecule to **F** should regenerate **14** or **15**.

Scheme 7



CONCLUDING REMARKS

This work shows two different entries to the chemistry of osmium polyhydrides containing the POP-pincer ligand xant-$(P^iPr_2)_2$, starting from the commercially available $OsCl_3{\cdot}3H_2O$. One route uses the adduct *cis*-$OsCl_2\{\kappa$-*S*-$(DMSO)_4\}$ as intermediate species and allows one to prepare a wide range of $OsH_n\{xant(P^iPr_2)_2\}$ complexes including n = 1, 3, 4, 5, and 6. The other one has been designed to specifically prepare the compounds $OsH_3Cl\{xant(P^iPr_2)_2\}$ and $OsH_4\{xant(P^iPr_2)_2\}$, employs the dihydride $OsH_2Cl_2(P^iPr_3)_2$ as key intermediate, affords similar or better yields, and is more direct. Some of these polyhydrides are hydrogen reservoirs losing molecular hydrogen under mild conditions. An example is the noticeable hexahydride complex $OsH_6\{xant(P^iPr_2)_2\}$, which releases H_2 in methanol at room temperature to afford $OsH_4\{xant(P^iPr_2)_2\}$. This osmium(IV) tetrahydride has a strong reducing power being able to promote the reduction of H^+, in dichloromethane, at room temperature. The process takes place in two stages via a cationic OsH_5-species. The metal oxidation state four can be recovered by treatment of the resulting oxidized OsH_4-species with 1 equiv of acetonitrile and subsequently with 1 equiv of triethylamine. Complex $OsH_4\{xant(P^iPr_2)_2\}$ is also an efficient catalyst precursor for the head-to-head (*Z*)-dimerization of terminal alkynes. Thus, the enynes (*Z*)-RC≡CCH=CHR (R = Ph, ^{t}Bu) are formed in a regio- and stereoselective manner in high yields and good $TOF_{50\%}$ in the presence of this compound. The catalysis takes place through the bis(alkynyl)vinylidene derivatives $Os(C{\equiv}CR)_2(=C{=}CHR)\{xant(P^iPr_2)_2\}$, which are formed during the activation process of the tetrahydride and have been isolated and fully characterized.

In conclusion, we have found two entries to obtain $Os\{xant-(P^iPr_2)_2\}$ complexes, in particular polyhydride derivatives, which are allowing us to discover interesting properties of some compounds of this type as the capacity for reducing H^+ and for promoting the head-to-head (*Z*)-dimerization of terminal alkynes.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. 2-Propanol, methanol, acetonitrile, acetone, and dimethyl sulfoxide (DMSO) were dried and distilled under argon. Other solvents were obtained oxygen- and water-free from an MBraun solvent purification apparatus. NMR spectra were recorded on a Varian Gemini 2000, a Bruker ARX 300 MHz, a Bruker Avance 300 MHz, a Bruker Avance 400 MHz, or a Bruker Avance 500 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$) or external 85% H_3PO_4 ($^{31}P\{^1H\}$), or external $CFCl_3$ (^{19}F). Coupling constants *J* and *N* (*N* = *J*(PH) + *J*(P′H) for ^1H and *N* = *J*(PC) + *J*(P′C) for $^{13}C\{^1H\}$) are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra (HRMS) were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). Phenylacetylene, *tert*-butylacetylene, and triethylamine (Et_3N) were purchased from commercial sources and vacuum distilled. All other reagents were purchased from commercial sources and used as received. 9,9-Dimethyl-4,5-bis(diisopropylphosphino)xanthene $(xant(P^iPr_2)_2)$[22] and $OsH_6(P^iPr_3)_2$[6d,36] were prepared according to the published methods. An improved method for the preparation of *cis*-$OsCl_2\{\kappa$-*S*-$(DMSO)_4\}$ is included.

Synthesis of *cis*-$OsCl_2\{\kappa$-*S*-$(DMSO)_4\}$ (1). A solution of $OsCl_3{\cdot}3H_2O$ (2.00 g, 5.70 mmol) in DMSO (8 mL) was heated under reflux for 15 min. Then, $SnCl_2$ (1.62 g, 8.56 mmol) was added and the mixture was heated until a color change from very dark brown to pale amber was observed. The solvent was removed *in vacuo* and acetone (2 mL) was added to afford a white solid, which was washed with a 1:5 mixture of acetone/diethyl ether (3 × 6 mL). Dichloromethane (40 mL) was added and the suspension was filtered through Celite to remove the tin salts. The filtrate was concentrated to ca. 1 mL, and acetone (2 mL) was added to afford a white precipitate, which was washed with a 1:5 mixture of acetone/diethyl ether (2 × 6 mL) and diethyl ether (2 × 3 mL) and dried *in vacuo*. Yield: 2.40 g (73%). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 3.51 (s, 6H, CH_3), 3.48 (s, 6H, CH_3), 3.35 (s, 6H, CH_3), 2.73 (s, 6H, CH_3).

Synthesis of $OsCl_2\{xant(P^iPr_2)_2\}\{\kappa$-*S*-DMSO) (2). Complex **1** (0.400 g, 0.700 mmol) was added to a solution of $xant(P^iPr_2)_2$ (0.309 g, 0.700 mmol) in 2-propanol (15 mL), and the resulting suspension was heated under reflux for 18 h. Color changed from white to orange with appearance of an orange precipitate when the mixture was cooled to room temperature. After the solvent was removed, the solid was washed with acetone (3 × 2 mL) and diethyl ether (3 × 3 mL) and dried

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in vacuo. Yield: 0.370 g (68%). Anal. Calcd. for $C_{29}H_{46}Cl_2O_2OsP_2S$: C, 44.55; H, 5.93; S: 4.10. Found: C, 44.03; H, 5.65; S: 3.46. HRMS (electrospray, *m*/*z*): calcd. for $C_{27}H_{40}Cl_2OOsP_2$ $[M - DMSO + H]^+$: 705.1600, found: 705.1487. IR (cm^{-1}): ν(O−C) 1184 (s); ν(O═S) 1085 (s). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.58 (dd, J_{H-H} = 7.6, J_{H-H} = 1.4, 2H, CH_{arom}), 7.52 (vtdd, J_{H-H} = 7.6, J_{H-H} = 1.4, *N* = 3.8, 2H, CH_{arom}), 7.32 (t, J_{H-H} = 7.6, 2H, CH_{arom}), 3.77 (s, 6H, $SO(CH_3)_2$), 3.24 (m, 4H, $PCH(CH_3)_2$), 1.65 (s, 6H, CH_3), 1.36 (dvt, J_{H-H} = 7.2, *N* = 15.2, 12H, $PCH(CH_3)_2$), 1.31 (dvt, J_{H-H} = 7.2, *N* = 13.6, 12H, $PCH(CH_3)_2$). $^{13}C\{^1H\}$-APT NMR (100.63 MHz, CD_2Cl_2, 293 K): δ 157.4 (vt, *N* = 12.6, C_{arom}), 132.5 (vt, *N* = 5.6, C_{arom}), 132.3 (s, CH_{arom}), 128.4 (s, CH_{arom}), 125.7 (vt, *N* = 31, C_{ipso}), 125.2 (vt, *N* = 5.2, CH_{arom}), 52.5 (s, $SO(CH_3)_2$), 34.5 (s, $C(CH_3)_2$), 31.9 (s, $C(CH_3)_2$), 27.4 (vt, *N* = 25.7, $PCH(CH_3)_2$), 21.9 and 21.0 (both s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.69 MHz, CD_2Cl_2, 293 K): δ 10.3 (s).

Synthesis of $OsH_3Cl\{xant(P^iPr_2)_2\}$ (3). *Method a:* A Fisher-Porter bottle was charged with a mixture of $OsCl_2\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**2**) (0.200 g, 0.256 mmol) and Et_3N (75 μL, 0.537 mmol) in toluene (25 mL). The bottle was pressurized to 3 atm of H_2, and the mixture was stirred at 90 °C, for 60 h changing the color from orange to pale yellow. After being cooled to room temperature, the mixture was filtered and volatiles were removed *in vacuo*. Addition of pentane to the residue afforded a pale yellow solid, which was washed with pentane (3 × 3 mL) and dried *in vacuo*. Yield: 0.098 g (57%). *Method b:* A solution of $OsH_3Cl(P^iPr_3)_2$ (**5**) (0.600 g, 1.093 mmol) in toluene (7 mL) was added to a solution of $xant(P^iPr_2)_2$ (0.532 g, 1.202 mmol) in toluene (5 mL), and the resulting mixture was heated to reflux for 4 h. After being cooled to room temperature, the solvent was concentrated to ca. 2 mL and pentane was added to afford a yellow precipitate, which was dried to dryness, and washed with methanol (2 × 1 mL). After the solvent was removed, pentane was added to afford a yellow solid, which was washed with pentane (3 × 5 mL) and dried *in vacuo*. Yield: 0.497 g (68%). Anal. Calcd. for $C_{27}H_{43}ClOOsP_2$: C, 48.31; H, 6.46. Found: C, 48.26; H, 6.26. HRMS (electrospray, *m*/*z*): calcd. for $C_{27}H_{43}OOsP_2$ $[M - Cl]^+$: 637.2400, found: 637.2419. IR (cm^{-1}): ν(Os−H) 2106 (w), 1995 (w); ν(C−O) 1182 (m). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.53 (dd, J_{H-H} = 7.4, J_{H-H} = 1.6, 2H, CH_{arom}), 7.51 (m, 2H, CH_{arom}), 7.29 (t, J_{H-H} = 7.4, 2H, CH_{arom}), 2.70 (m, 2H, $PCH(CH_3)_2$), 2.27 (m, 2H, $PCH(CH_3)_2$), 1.84 (s, 3H, CH_3), 1.47 (dvt, J_{H-H} = 7.2, *N* = 14.4, 6H, $PCH(CH_3)_2$), 1.46 (s, 3H, CH_3), 1.36 (dvt, J_{H-H} = 7.4, *N* = 15.8, 6H, $PCH(CH_3)_2$), 1.18 (dvt, J_{H-H} = 7.4, *N* = 16.2, 6H, $PCH(CH_3)_2$), 0.72 (dvt, J_{H-H} = 7.2, *N* = 14.8, 6H, $PCH(CH_3)_2$), −13.17 (t, J_{H-P} = 11.0, 3H, OsH). $^1H\{^{31}P\}$ NMR (400 MHz, CD_2Cl_2, 223 K, high field region): δ −12.98 (br, 2H, OsH), −13.38 (br, 1H, OsH). $^{13}C\{^1H\}$-APT NMR (100.63 MHz, CD_2Cl_2, 293 K): δ 158.2 (vt, *N* = 13.7, C_{arom}), 132.2 (vt, *N* = 5.7, C_{arom}), 131.2 (s, CH_{arom}), 129.6 (vt, *N* = 27, C_{ipso}), 128.0 (s, CH_{arom}), 125.7 (vt, *N* = 4.8, CH_{arom}), 35.6 (s, $C(CH_3)_2$), 34.8 (s, $C(CH_3)_2$), 27.9 (s, $C(CH_3)_2$), 27.8 (vt, *N* = 23.5, $PCH(CH_3)_2$), 26.4 (vt, *N* = 31.8, $PCH(CH_3)_2$), 22.8 (vt, *N* = 4.6, $PCH(CH_3)_2$), 20.7 (vt, *N* = 10.0, $PCH(CH_3)_2$), 20.3 (s, $PCH(CH_3)_2$), 19.4 (vt, *N* = 2.8, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.69 MHz, C_6D_6, 293 K): δ 50.6 (s). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 233 K): 104 ± 3 (−12.98 ppm); 104 ± 3 (−13.38 ppm).

Synthesis of $OsH_3Cl(P^iPr_3)_2$ (5). In a Schlenk flask equipped with a Teflon stopcock, a brown suspension of $OsH_2Cl_2(P^iPr_3)_2$ (**4**) (1 g, 1.712 mmol) in toluene (15 mL) was added Et_3N (1 mL, 7.170 mmol). The Ar atmosphere was displaced with H_2 and stirred for 4 h. During this time, the color of the mixture changed from brown to light brown. It was filtered through Celite, the light brown solution obtained was concentrated to dryness, and a brown solid was obtained. Yield: 0.870 g (92%). NMR spectroscopic data agree with those reported previously for this complex.[30a]

Synthesis of $OsHCl\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (6). A solution of $OsH_3Cl\{xant(P^iPr_2)_2\}$ (**3**) (0.022 g, 0.030 mmol) in toluene-d_8 (0.5 mL) was treated with 0.250 mL of DMSO. The mixture was heated at 90 °C, for 16 h. After being cooled to room temperature, volatiles were removed *in vacuo*, and the resulting white solid was washed with diethyl ether (3 × 3 mL) and dried *in vacuo*. Yield: 0.020 g (80%). Anal. Calcd. for $C_{29}H_{47}ClO_2OsP_2S$: C, 46.60; H, 6.34; S, 4.29. Found: C, 47.00; H, 6.30; S, 4.24. HRMS (electrospray, *m*/*z*): calcd. for $C_{29}H_{47}O_2OsP_2S$ $[M - Cl]^+$: 713.2380, found: 713.2459. IR (cm^{-1}): ν(Os−H) 2119, ν(O−C) 1194 (s); ν(O═S) 1072 (s). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.60 (m, 2H, CH_{arom}), 7.47 (dd, J_{H-H} = 7.7, J_{H-H} = 1.2, CH_{arom}), 7.27 (t, J_{H-H} = 7.7, 2H, CH_{arom}), 3.64 (s, 6H, $SO(CH_3)_2$), 3.11 (m, 2H, $PCH(CH_3)_2$), 2.67 (m, 2H, $PCH(CH_3)_2$), 1.74 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.40 (dvt, J_{H-H} = 6.8, *N* = 20.4, 6H, $PCH(CH_3)_2$), 1.37 (dvt, J_{H-H} = 7.2, *N* = 16, 6H, $PCH(CH_3)_2$), 1.33 (dvt, J_{H-H} = 7.2, *N* = 16, 6H, $PCH(CH_3)_2$), 1.00 (dvt, J_{H-H} = 6.8, *N* = 14, 6H, $PCH(CH_3)_2$), −18.77 (t, J_{P-H} = 19.8, 1H, OsH). $^{13}C\{^1H\}$-APT NMR (100.63 MHz, CD_2Cl_2, 293 K): δ 158.8 (vt, *N* = 12.8, C_{arom}), 132.6 (vt, *N* = 6, C_{arom}), 130.1 (s, CH_{arom}), 127.4 (s, CH_{arom}), 126.5 (vt, *N* = 28.8, C_{ipso}), 125.6 (vt, J_{C-P} = 4.7, CH_{arom}), 57.8 (s, $SO(CH_3)_2$), 34.5 (s, $C(CH_3)_2$) 33.7 (s, $C(CH_3)_2$), 30.4 (vt, *N* = 19.1, $PCH(CH_3)_2$), 28.9 (vt, *N* = 34.8, $PCH(CH_3)_2$), 27.9 (s, $C(CH_3)_2$), 20.1 and 19.8 (both s, $PCH(CH_3)_2$), 19.4 (vt, *N* = 4.4, $PCH(CH_3)_2$), 19.1 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.69 MHz, CD_2Cl_2, 293 K): δ 35.4 (s).

Synthesis of $OsH_6\{xant(P^iPr_2)_2\}$ (7). *Method a:* A Fisher-Porter bottle was charged with $OsCl_2\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**2**) (0.200 g, 0.256 mmol), NaH (0.065 g, 2.700 mmol), and tetrahydrofuran (20 mL). The bottle was pressurized to 3 atm of H_2, and the mixture was stirred at 50 °C, for 48 h. During this time, the color of the mixture changed from orange to pale yellow. After the mixture was cooled to room temperature, it was filtered through Celite, and the resulting yellow solution obtained was dried *in vacuo*. Toluene (10 mL) was added to the residue, and the suspension was filtered through Celite and taken to dryness. Addition of pentane to the residue afforded a pale yellow solid that was washed with pentane and dried *in vacuo*. Yield: 0.080 g (46%). *Method b:* A solution of $OsCl_2\{xant(P^iPr_2)_2\}(\kappa$-*S*-DMSO) (**2**) (0.100 g, 0.128 mmol) in tetrahydrofuran (10 mL) was treated with $LiAlH_4$ (0.124 g, 2.560 mmol). The mixture was heated under reflux for 3 h. After the mixture was cooled to room temperature, it was filtered through Celite, and the resulting yellow solution obtained was dried *in vacuo*. Toluene (10 mL) was added to the residue, and the suspension was filtered and taken to dryness. Addition of pentane to the residue afforded a pale yellow solid that was washed with pentane and dried *in vacuo*. Yield: 0.030 g (37%). HRMS (electrospray, *m*/*z*): calcd. for $C_{27}H_{43}OOsP_2$ $[M - 3H]^+$: 637.2400, found: 637.2509. IR (cm^{-1}): ν(Os−H) 2082, ν(O−C) 1185 (s). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.46 (d, J_{H-H} = 8.0, CH_{arom}), 7.26 (m, 2H, CH_{arom}), 7.15 (t, J_{H-H} = 8.0, 2H, CH_{arom}), 2.36 (m, 4H, $PCH(CH_3)_2$), 1.57 (s, 6H, CH_3), 1.13 (dd, J_{P-H} = 12.0, J_{H-H} = 8.0, 12H, $PCH(CH_3)_2$), 1.07 (dd, J_{P-H} = 16.0, J_{H-H} = 8.0, 12H, $PCH(CH_3)_2$), −10.08 (s, 6H, OsH). $^{13}C\{^1H\}$-APT NMR (100.63 MHz, CD_2Cl_2, 293 K): δ 157.1 (dd, J_{P-H} = 3.0, C_{arom}), 135.8 (dd, J_{P-H} = 1.5, C_{arom}), 129.0 and 125.7 (both s, CH_{arom}), 122.5 (dd, J_{P-H} = 2.0, CH_{arom}), 122.2 (dd, J_{P-H} = 35.2, J_{P-H} = 5.0, C_{ipso}), 36.6 (s, $C(CH_3)_2$), 28.8 (dd, J_{P-H} = 34.2, J_{P-H} = 3.0, $PCH(CH_3)_2$), 27.3 (s, $C(CH_3)_2$), 19.7 (s, $PCH(CH_3)_2$), 18.7 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.69 MHz, CD_2Cl_2, 293 K): δ 4.2 (s). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 228 K): 113 ± 3 (−10.06 ppm).

Synthesis of $OsH_4\{xant(P^iPr_2)_2\}$ (8). *Method a:* A methanol solution of $OsH_6\{xant(P^iPr_2)_2\}$ (**7**) (0.080 g, 0.125 mmol) was stirred at room temperature for 6 days to afford a white precipitate which was isolated by decantation from the mother liquor, washed with cold methanol (2 × 2 mL) and dried *in vacuo*. Yield: 0.070 g (88%). *Method b:* A solution of $OsH_6(P^iPr_3)_2$ (**9**) (0.600 g, 1.162 mmol) in toluene (10 mL) was added to a solution of $xant(P^iPr_2)_2$ (0.566 g, 1.278 mmol) in toluene (5 mL), and the mixture was heated to reflux for 12 h. After being cooled to room temperature, the solvent was concentrated to ca. 2 mL. Addition of methanol led to a white solid which was washed with methanol (2 × 2 mL) and dried under *vacuo*. Yield: 0.290 g (39%). Anal. Calcd. for $C_{27}H_{44}OOsP_2$: C, 50.93; H, 6.96. Found: C, 50.68; H, 6.92. HRMS (electrospray, *m*/*z*): calcd. for $C_{27}H_{43}OOsP_2$ $[M - H]^+$: 637.2400, found: 637.2444. IR (cm^{-1}): ν(Os−H) 2128 (w); ν(C−O) 1188 (m). ^1H NMR (500 MHz, CD_2Cl_2, 293 K): δ 7.47 (m, 2H, CH_{arom}), 7.38 (dd, J_{H-H} = 7.5, J_{H-H} = 2.5, CH_{arom}), 7.20 (t, J_{H-H} = 7.5, 2H, CH_{arom}), 2.12 (m, 4H, $PCH(CH_3)_2$), 1.58 (s, 6H, CH_3), 1.19 (dvt, J_{H-H} = 5.0, *N* = 15.0, 12H, $PCH(CH_3)_2$), 0.89 (dvt, J_{H-H} = 5.0, *N* = 15.0, 12H, $PCH(CH_3)_2$),

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−9.53 (t, J_{P-H} = 12.5, 4H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 183 K, high field region): δ −3.14 (br, 2H, OsH), −16.63 (br, 2H, OsH). $^{13}C\{^1H\}$-APT NMR (125.8 MHz, CD_2Cl_2, 293 K): δ 158.6 (vt, *N* = 13.8, C_{arom}), 131.3 (vt, *N* = 25.2, C_{ipso}), 131.1 (vt, *N* = 5.0, C_{arom}), 130.3 and 127.9 (both s, CH_{arom}), 125.5 (vt, *N* = 5.0, CH_{arom}), 34.3 (s, $C(CH_3)_2$), 33.1 (s, $C(CH_3)_2$), 28.6 (vt, *N* = 28.9, $PCH(CH_3)_2$), 21.3 (vt, *N* = 10.1, $PCH(CH_3)_2$), 19.9 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2, 293 K): δ 66.3 (s). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 213 K): 179 ± 3 (−9.54 ppm).

Formation of $[OsH_2(H\cdots H)(OTf)\{xant(P^iPr_2)_2\}]^+$ (10). A screw-top NMR tube containing a solution of $OsH_4\{xant(P^iPr_2)_2\}$ (**8**) (0.015 g, 0.023 mmol) in 0.5 mL of dichloromethane-d_2 was treated with HOTf (8 μL, 0.092 mmol). The immediate and quantitative conversion of **8** to a new species was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. All our attempts of isolation of the formed species were unsuccessful resulting in complex mixtures of unidentified products. HRMS (electrospray, *m*/*z*): calcd. for $C_{27}H_{43}OOsP_2$ $[M - CF_3SO_3]^+$: 637.2400, found: 637.2494. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.88 (dd, J_{H-H} = 7.6, J_{H-H} = 1.5, 2H, CH_{arom}), 7.69 (m, 2H, CH_{arom}), 7.63 (t, J_{H-H} = 7.6, 2H, CH_{arom}), 3.05 (m, 4H, $PCH(CH_3)_2$), 1.99 (s, 3H, CH_3), 1.51 (dvt, J_{H-H} = 7.5, *N* = 14.8, 6H, $PCH(CH_3)_2$), 1.50 (s, 3H, CH_3), 1.42 (dvt, J_{H-H} = 6.9, *N* = 16.4, 6H, $PCH(CH_3)_2$), 1.38 (dvt, J_{H-H} = 7.5, *N* = 16.4, 6H, $PCH(CH_3)_2$), 0.87 (dvt, J_{H-H} = 6.9, *N* = 18.0, 6H, $PCH(CH_3)_2$), −11.62 (t, J_{P-H} = 4.0, 4H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 183 K, high field region): δ −9.78 (br, 2H, OsH), −13.53 (br, 2H, OsH). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 159.0 (vt, *N* = 12.1, C_{arom}), 134.5 (vt, *N* = 6.8, C_{arom}), 132.7 (s, CH_{arom}), 131.5 (s, CH_{arom}), 129.5 (vt, *N* = 7.5, CH_{arom}), 118.1 (vt, *N* = 20.4, C_{ipso}), 117.5 (q, J_{C-F} = 317.2, CF_3SO_3), 35.2 (s, $C(CH_3)_2$), 30.2 (s, $C(CH_3)_2$), 28.4 (vt, *N* = 29.4, $PCH(CH_3)_2$), 26.9 (s, $C(CH_3)_2$), 24.6 (vt, *N* = 36.2, $PCH(CH_3)_2$), 20.1 (s, $PCH(CH_3)_2$), 20.0 (vt, *N* = 4.5, $PCH(CH_3)_2$), 19.6 and 17.9 (both s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 65.9 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −77.7 (s, CF_3SO_3). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 243 K): 73 ± 3 (−11.69 ppm).

Formation of $[OsH_5\{xant(P^iPr_2)_2\}]^+$ (11). A screw-top NMR tube containing a solution of $OsH_4\{xant(P^iPr_2)_2\}$ (**8**) (0.015 g, 0.023 mmol) in 0.5 mL of dichloromethane-d_2 was treated with HOTf (4 μL, 0.047 mmol). The immediate and quantitative conversion of **8** to a new species was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. All our attempts of isolation of the formed species were unsuccessful, always resulting in complex mixtures of unidentified products. HRMS (electrospray, *m*/*z*): calcd. for $C_{27}H_{43}OOsP_2$ $[M - 2H]^+$: 637.2400, found: 637.2475. ^1H NMR (500 MHz, CD_2Cl_2, 293 K): δ 7.64 (d, J_{H-H} = 8.8, 2H, CH_{arom}), 7.57 (m, 2H, CH_{arom}), 7.47 (t, J_{H-H} = 8.8, 2H, CH_{arom}), 2.56 (m, 4H, $PCH(CH_3)_2$), 1.61 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.27 (dvt, J_{H-H} = 5, *N* = 20, 12H, $PCH(CH_3)_2$), 0.95 (dvt, J_{H-H} = 7.5, *N* = 17.5, 12H, $PCH(CH_3)_2$), −7.71 (t, J_{H-P} = 5.2, 5H, OsH). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 293 K): δ 159.4 (vt, *N* = 10.1, C_{arom}), 133.5 (vt, *N* = 5.0, C_{arom}), 130.7 (s, CH_{arom}), 130.4 (s, CH_{arom}), 128.3 (vt, *N* = 6.3, CH_{arom}), 123.1 (vt, *N* = 40.3, C_{ipso}), 31.1 (s, $C(CH_3)_2$), 30.1 (s, $C(CH_3)_2$), 28.5 (vt, *N* = 34.0, $PCH(CH_3)_2$), 20.8 (vt, *N* = 6.3, $PCH(CH_3)_2$), 19.1 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2, 293 K): δ 60.7 (s). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 195 K): 20 ± 3 (−7.72 ppm).

Formation of $[OsH_2(\eta^2\text{-}H_2)(NCCH_3)\{xant(P^iPr_2)_2\}]^{2+}$ (12). *Method a*: To a screw-top NMR tube charged with a solution of **8** (0.030 g, 0.047 mmol) in dichloromethane-d_2 (0.5 mL) was added HOTf (16.7 μL, 0.188 mmol). After addition of acetonitrile (2.46 μL, 0.047 mmol) the color of the mixture changed from pale yellow to light brown. The immediate and quantitative conversion of **8** to a new species was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. All our attempts of isolation of the formed species were unsuccessful, always resulting in complex mixtures of unidentified products. *Method b*: To a screw-top NMR tube charged with a solution of **13** (0.022 g, 0.026 mmol) in dichloromethane-d_2 (0.5 mL) was added HOTf (2.3 μL, 0.026 mmol). Immediately the color of the mixture changed from yellow to light brown. The immediate and quantitative conversion of **13** to a new species was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.89 (dd, J_{H-H} = 7.5, J_{H-H} = 3, 2H, CH_{arom}), 7.69 (m, 2H, CH_{arom}), 7.64 (t, J_{H-H} = 7.5, 2H, CH_{arom}), 3.02 (m, 2H, $PCH(CH_3)_2$), 2.94 (m, 2H, $PCH(CH_3)_2$), 2.50 (s, 3H, CH_3CN), 1.84 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 1.47 (dvt, J_{H-H} = 6.0, *N* = 18.0, 6H, $PCH(CH_3)_2$), 1.39 (dvt, J_{H-H} = 6.0, *N* = 18.0, 6H, $PCH(CH_3)_2$), 1.32 (dvt, J_{H-H} = 6.0, *N* = 18.0, 6H, $PCH(CH_3)_2$), 0.96 (dvt, J_{H-H} = 6.0, *N* = 18.0, 6H, $PCH(CH_3)_2$), −11.45 (br, 4H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 223 K, high field region): δ −11.29 (br, 2H, OsH), −11.82 (br, 2H, OsH). $^{13}C\{^1H\}$-APT NMR plus HMBC (75.47 MHz, CD_2Cl_2, 233 K): δ 156.8 (vt, *N* = 12.1, C_{arom}), 133.1 (vt, *N* = 7.5, C_{arom}), 132.9 (s, CH_{arom}), 131.5 (s, CH_{arom}), 128.7 (s, CN), 128.6 (vt, *N* = 4.5, CH_{arom}), 116.4 (vt, *N* = 20.4, C_{ipso}), 34.4 (s, $C(CH_3)_2$), 34.2 (s, $C(CH_3)_2$), 29.3 (s, $C(CH_3)_2$), 26.7 (vt, *N* = 30.9, $PCH(CH_3)_2$), 25.0 (vt, *N* = 31.7, $PCH(CH_3)_2$), 19.8, 19.1, 18.1, and 17.6 (all s, $PCH(CH_3)_2$), 4.3 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 56.7 (s). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 243 K): 22 ± 2 (−11.65 ppm).

Synthesis of $[OsH_3(NCCH_3)\{xant(P^iPr_2)_2\}]OTf$ (13). *Method a*: A screw-top NMR tube containing a solution of $OsH_4\{xant(P^iPr_2)_2\}$ (**8**) (0.030 g, 0.047 mmol) in 0.5 mL of dichloromethane-d_2 was treated with HOTf (16.7 μL, 0.188 mmol). After addition of acetonitrile (2.5 μL, 0.047 mmol), the color of the mixture changed from pale yellow to light brown. Addition of Et_3N (6.6 μL, 0.047 mmol) afforded a yellow solution. The immediate and quantitative conversion of **8** to a new species was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. *Method b*: A white suspension of $OsH_4\{xant(P^iPr_2)_2\}$ (**8**) (0.100 g, 0.157 mmol) in acetonitrile (2 mL) was treated with HOTf (55.6 μL, 0.628 mmol). Immediately, a clear solution was obtained. Addition of diethyl ether (3 mL) afforded a yellow precipitate, which was washed with diethyl ether (2 × 2 mL) and dried *in vacuo*. Yield: 0.082 g (63%). Anal. Calcd. for $C_{30}H_{46}F_3NO_4OsP_2S$: C, 43.63; H, 5.61; N, 1.70; S, 3.88. Found: C, 43.51; H, 5.55; N, 1.66; S, 3.80. HRMS (electrospray, *m*/*z*): calcd. for $C_{27}H_{43}OOsP_2$ $[M - CH_3CN]^+$: 637.2400, found: 637.2400. IR (cm^{-1}): ν(C≡N) 2147 (w); ν(Os−H) 1920 (w); ν(O−C) 1097 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.65 (dd, J_{H-H} = 6.8, J_{H-H} = 1.5, 2H, CH_{arom}), 7.53 (m, 2H, CH_{arom}), 7.42 (t, J_{H-H} = 6.8, 2H, CH_{arom}), 2.49 (m, 2H, $PCH(CH_3)_2$), 2.33 (s, 3H, CH_3CN), 1.90 (m, 2H, $PCH(CH_3)_2$), 1.88 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.38 (dvt, J_{H-H} = 7.5, *N* = 16.5, 6H, $PCH(CH_3)_2$), 1.17 (dvt, J_{H-H} = 6, *N* = 18, 6H, $PCH(CH_3)_2$), 1.08 (dvt, J_{H-H} = 7.5, *N* = 16.5, 6H, $PCH(CH_3)_2$), 0.76 (dvt, J_{H-H} = 6.0, *N* = 15.0, 6H, $PCH(CH_3)_2$), −12.58 (t, J_{H-P} = 10.5, 3H, OsH). $^{13}C\{^1H\}$-APT NMR plus HMBC (75.47 MHz, CD_2Cl_2, 293 K): δ 159.7 (vt, *N* = 12.8, C_{arom}), 133.6 (vt, *N* = 6.0, C_{arom}), 131.6 (s, CH_{arom}), 129.9 (s, CH_{arom}), 129.1 (s, CN), 128.1 (q, J_{C-F} = 320.7, CF_3SO_3), 127.8 (vt, *N* = 5.3, CH_{arom}), 126.9 (vt, *N* = 27.9, C_{ipso}), 35.8 (s, $C(CH_3)_2$), 35.6 (s, $C(CH_3)_2$), 29.8 (vt, *N* = 24.9, $PCH(CH_3)_2$), 27.9 (vt, *N* = 34.7, $PCH(CH_3)_2$), 27.6 (s, $C(CH_3)_2$), 21.6 (s, $PCH(CH_3)_2$), 21.1 (vt, *N* = 8.0, $PCH(CH_3)_2$), 20.5 (vt, *N* = 6.0, $PCH(CH_3)_2$), 20.3 (s, $PCH(CH_3)_2$), 4.5 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 49.0 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −78.0 (s, CF_3SO_3). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 193 K): 88 ± 2 (−12.50 ppm).

Synthesis of $Os(C{\equiv}CPh)_2(=C{=}CHPh)\{xant(P^iPr_2)_2\}$ (14). In a Schlenk flask equipped with a Teflon stopcock, a toluene solution of **8** (0.060 g, 0.094 mmol) was treated with phenylacetylene (103 μL, 0.942 mmol) and heated for 2 h at 110 °C. During this time the color of the solution changed from colorless to yellow. After being cooled to room temperature, the solvent was concentrated to ca. 1 mL, and methanol (2 mL) was added resulting in the formation of a yellow solid, which was washed with methanol (3 × 2 mL) and dried *in vacuo*. Yield: 0.070 g (79%). Anal. Calcd. for $C_{51}H_{56}OOsP_2{\cdot}CH_3OH$: C, 64.44; H, 6.24. Found: C, 64.18; H, 6.12. HRMS (electrospray, *m*/*z*): calcd. for $C_{51}H_{57}OOsP_2$ $[M + H]^+$: 939.3498, found: 939.3526. IR (cm^{-1}): ν(C≡C) 2093 (s); ν(=C=C) 1622 (s); ν(O−C) 1177 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.75 (d, J_{H-H} = 8.2, 2H, Ph), 7.37 (t, J_{H-H} = 8.2, 2H, Ph), 7.19 (m, 2H, CH_{arom}−xant(P^iPr_2)$_2$), 7.15 (m, 1H, Ph), 7.08−6.78 (m, 14H, Ph and CH_{arom}−xant(P^iPr_2)$_2$), 3.22 (m, 4H, $PCH(CH_3)_2$), 3.04 (t, J_{P-H} = 3.0, 1H, =C=CH), 1.62 (dvt, J_{H-H} = 6.0, *N* = 15.0, 12H, $PCH(CH_3)_2$), 1.51 (dvt, J_{H-H} = 6.0,

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N = 15.0, 12H, PCH(CH_3)$_2$), 1.28 (s, 6H, CH_3). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.5 MHz, C_6D_6, 293 K): δ 300.1 (t, J_{C-P} = 9.1, Os=C=C), 155.5 (vt, N = 11.3, C_{arom}–xant(P^{i}Pr$_2$)$_2$), 133.7 (s, CH_{arom}–xant(P^{i}Pr$_2$)$_2$), 133.0 (t, J_{C-P} = 2.3, C_{ipso}), 131.9 (vt, N = 5.3, C_{arom}–xant(P^{i}Pr$_2$)$_2$), 130.7 (s, CH_{arom}), 129.3 (t, J_{C-P} = 1.1, C≡C), 129.0 (s, CH_{arom}–xant(P^{i}Pr$_2$)$_2$), 128.3 (s, CH_{arom}), 128.1 (s, CH_{arom}), 127.7 (C_{ipso}–xant(P^{i}Pr$_2$)$_2$, this resonance is masked by the resonance of C_6D_6), 125.2 (s, CH_{arom}), 124.7 (s, CH_{arom}), 124.5 (vt, N = 5.3, CH_{arom}–xant(P^{i}Pr$_2$)$_2$), 122.9 (s, CH_{arom}), 120.3 (s, C_{ipso}), 109.5 (t, J_{C-P} = 12.1, C≡C), 106.4 (t, J_{C-P} = 3.4, Os=C=C), 34.3 (s, C(CH_3)$_2$), 33.1 (s, C(CH_3)$_2$), 27.9 (vt, N = 27.9, PCH(CH_3)$_2$), 21.8 and 20.0 (both s, PCH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 293 K): δ 14.4 (s).

Synthesis of Os(C≡C^{t}Bu)$_2$(=C=CH^{t}Bu){xant(P^{i}Pr$_2$)$_2$} (15). In a Schlenk flask equipped with a Teflon stopcock, a toluene solution of **8** (0.060 g, 0.094 mmol) was treated with *tert*-butylacetylene (116 μL, 0.942 mmol) and heated for 6 h at 110 °C. During this time the color of the mixture changed from colorless to pale brown. After being cooled to room temperature, the solvent was concentrated to ca. 1 mL, and methanol (2 mL) was added resulting in the formation of a yellow precipitate, which was washed with methanol (3 × 2 mL) and dried *in vacuo*. Yield: 0.072 g (87%). Anal. Calcd. for $C_{45}H_{68}OOsP_2$·CH_3OH: C, 60.76; H, 7.98. Found: C, 60.66; H, 7.94. HRMS (electrospray, m/z): calcd. for $C_{45}H_{70}OOsP_2$ $[M + 2H]^+$: 881.4593, found: 881.4804. IR (cm^{-1}): ν(C≡C) 2091 (s); ν(=C=C) 1645 (s); ν(O–C) 1181 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.37 (m, 2H, CH_{arom}), 7.07 (dd, J_{H-H} = 7.5, J_{H-H} = 1.5, 2H, CH_{arom}), 6.90 (t, J_{H-H} = 7.5, 2H, CH_{arom}), 3.44 (m, 4H, PCH(CH_3)$_2$), 1.70 (dvt, J_{H-H} = 7.5, N = 13.5, 12H, PCH(CH_3)$_2$), 1.66 (dvt, J_{H-H} = 7.5, N = 13.5, 12H, PCH(CH_3)$_2$), 1.41 (s, 9H, =C=CC(CH_3)$_3$), 1.30 (s, 6H, CH_3), 1.05 (t, J_{H-P} = 3, 1H, =C=CH), 0.96 (s, 18H, C≡CC(CH_3)$_3$). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.5 MHz, C_6D_6, 293 K): δ 290.8 (t, J_{C-P} = 9.4, Os=C=C), 156.7 (vt, N = 10.6, C_{arom}), 132.6 (s, CH_{arom}), 132.4 (vt, N = 5.3, C_{arom}), 129.8 (vt, N = 32.5, C_{ipso}), 126.9 (s, CH_{arom}), 124.1 (vt, N = 5.3, CH_{arom}), 124.0 (s, C≡C), 112.9 (t, J_{C-P} = 3.8, Os=C=C), 91.6 (t, J_{C-P} = 12.1, C≡C), 34.6 (s, C(CH_3)$_2$), 33.8 (s, =C=CC(CH_3)$_3$), 32.7 (s, C≡CC(CH_3)$_3$), 31.1 (s, C(CH_3)$_2$), 29.2 (s, C≡CC(CH_3)$_3$), 28.4 (vt, N = 26.4, PCH(CH_3)$_2$), 28.0 (s, =C=CC(CH_3)$_3$), 22.6 and 20.6 (both s, PCH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 293 K): δ 11.6 (s).

General Procedure of Dimerization of Terminal Alkynes to (*Z*)–RCH=CHC≡CR (R = Ph or R = ^{t}Bu) Catalyzed by OsH$_4${xant(P^{i}Pr$_2$)$_2$}. A screwtop NMR tube charged with a solution of terminal alkyne (HC≡CR, R = Ph or ^{t}Bu, 0.800 mmol) and OsH$_4${xant(P^{i}Pr$_2$)$_2$} (0.005 g, 0.008 mmol) in toluene-d_8 (0.5 mL) was placed into a thermostatic bath at 110 °C, and the reaction was monitored by ^1H NMR spectroscopy, using dioxane (0.007 mL, 0.080 mmol) as internal standard. After the completion of the reaction (3.75 h for phenylacetylene and 7.80 h for *tert*-butylacetylene), solvent was removed and pentane was added to the crude product. The solution was filtrated through silica gel and analyzed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies (see Supporting Information).

Structural Analysis of Complex 2, 3, 8, and 13. Crystals of **2** were obtained from saturated solutions in diethyl ether. Crystals of **3** and **13** were obtained by slow diffusion of pentane into solutions of the complexes in THF. Crystals of **8** were obtained by slow diffusion of methanol into solutions of the complex in toluene. X-ray data were collected on a Bruker Smart APEX diffractometer equipped with a normal focus, and 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å). Data were collected over the complete sphere, and corrected for absorption by using a multiscan method applied with the SADABS program.[50] The structures were solved by the direct methods. Refinement of complexes was performed by full-matrix least-squares on F^2 with SHELXL97,[51] including isotropic and subsequently anisotropic displacement parameters for nondisordered atoms. Hydride ligands were located in the Fourier difference maps and refined with restrained geometry (Os–H 1.59(5) Å). In **2** 1/2 molecules of disordered diethyl ether were observed in the asymmetric unit. This molecule was refined with restrained geometry. In **8** some isopropyl groups of POP ligands were observed disordered in two positions and refined with isotropic thermal parameters and restrained geometry.

Crystal Data for **2**. $C_{29}H_{46}Cl_2O_2OsP_2S$·1/2($C_4H_{10}O$) M_W 818.82, needle, yellow (0.16 × 0.04 × 0.02), monoclinic, space group $P2_1/n$, a: 18.775(2) Å, b: 13.0623(18) Å, c: 27.771(4) Å, β: 94.263(5)°, V = 6792.1(15) Å^3, Z = 8, Z' = 2, D_{calc}: 1.601 g cm^{-3}, F(000): 3304, T = 100(2) K, μ 4.096 mm^{-1}. 42941 measured reflections (2θ: 3–58°, ω scans 0.3°), 15626 unique (R_{int} = 0.0601); min./max. transm. factors 0.603/0.862. Final agreement factors were R^1 = 0.0443 (10404 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0987, data/restraints/parameters 15626/38/738; GOF = 1.057. Largest peak and hole: 2.056 and −1.015 e/Å^3.

Crystal Data for **3**. $C_{27}H_{43}ClOOsP_2$, M_W 671.20, prism, colorless (0.16 × 0.14 × 0.12), monoclinic, space group $C2/c$, a: 35.13(2) Å, b: 12.148(7) Å, c: 14.516(8) Å, β: 111.788(6)°, V = 5752(6) Å^3, Z = 8, Z' = 1, D_{calc}: 1.550 g cm^{-3}, F(000): 2688, T = 100(2) K, μ 4.655 mm^{-1}. 34295 measured reflections (2θ: 3–58°, ω scans 0.3°), 6929 unique (R_{int} = 0.0334); min./max. transm. factors 0.702/0.862. Final agreement factors were R^1 = 0.0222 (5879 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0569; data/restraints/parameters 6929/0/311; GOF = 1.042. Largest peak and hole: 0.347 and −1.000 e/Å^3.

Crystal Data for **8**. $C_{27}H_{44}OOsP_2$, M_W 636.76, irregular block, colorless (0.24 × 0.08 × 0.06), orthorhombic, space group $Pbca$, a: 22.5833(14) Å, b: 21.4733(14) Å, c: 45.431(3) Å, V = 22031(2) Å^3, Z = 32, Z' = 4, D_{calc}: 1.536 g cm^{-3}, F(000): 10240, T = 100(2) K, μ 4.763 mm^{-1}. 195878 measured reflections (2θ: 3–58°, ω scans 0.3°), 26702 unique (R_{int} = 0.1007); min./max. transm. factors 0.527/0.862. Final agreement factors were R^1 = 0.0377 (17287 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0750; data/restraints/parameters 26702/20/1206; GOF = 1.0202. Largest peak and hole: 2.340 and −1.860 e/Å^3.

Crystal Data for **13**. $C_{29}H_{46}NO_3OsP_2$ × CF_3OS, M_W 825.88, irregular block, colorless (0.30 × 0.04 × 0.03), monoclinic, space group $P2_1/n$, a: 12.7693(8) Å, b: 22.3242(15) Å, c: 12.9072(9) Å, β: 112.1100(10)°, V = 3408.8(4) Å^3, Z = 4, Z' = 1, D_{calc}: 1.609 g cm^{-3}, F(000): 1656, T = 150(2) K, μ 3.946 mm^{-1}. 27839 measured reflections (2θ: 3–58°, ω scans 0.3°), 7993 unique (R_{int} = 0.0410); min./max. transm. factors 0.600/0.862. Final agreement factors were R^1 = 0.0360 (6637 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0778; data/restraints/parameters 7993/3/399; GOF = 1.060. Largest peak and hole: 1.221 and −0.655 e/Å^3.

Computational Details. The theoretical calculations were carried out on the model complexes by optimizing the structure at the m06-DFT[52] levels with the Gaussian 09 program.[53] The basis sets used were LANL2DZ basis and pseudopotentials for Os, and 631G(d,p) for the rest of atoms. The geometries were fully optimized, and subsequent analytical frequency analyses were carried out to confirm the nature of each stationary point.

For the calculations of Gibbs free energies, we used the standard ideal gas-rigid rotor-harmonic oscillator approximation. All the Gibbs energies collected in the text are calculated in a vacuum at 298.15 K and 1 atm.[54]

All discussed relative energies in this paper are referred to as ΔG_{vacuum}, in order to better explain the experimental observations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving the completed ref 53, computational details, tables giving optimized coordinates and energies of all optimized complexes, a CIF giving crystallographic data for compounds **2**, **3**, **8**, and **13**, the ^1H and $^{13}C\{^1H\}$ NMR data for (*Z*)-RCH=CHC≡CR (R = Ph, ^{t}Bu), and the ^1H and $^{31}P\{^1H\}$ NMR spectra for complexes **7**, **10**, **11**, and **12**. 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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