Repercussion of a 1,3-Hydrogen Shift in a Hydride-Osmium-Allenylidene Complex

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ABSTRACT: An unusual 1,3-hydrogen shift from the metal center to the Cβ atom of the C3-chain of the allenylidene ligand in a hydride-osmium(II)-allenylidene complex is the beginning of several interesting transformations in the cumulene. The hydride-osmium(II)-allenylidene complex was prepared in two steps, starting from the tetrahydride dimer \([(OsH−H)\{κ^3-P,O,P-\{xant\{P^3Pr_2\}_2\}\}]_2(μ-Cl)_2[BF_4]_2\) (1). Complex 1 reacts with 1,1-diphenyl-2-propyn-1-ol to give the hydride-osmium(II)-allenylidene \([OsHCl(≡CH≡CPh)_2\{κ^3-P,O,P-\{xant\{P^3Pr_2\}_2\}\}]_2[BF_4]_2\) (2), which yields \(OsHCl(≡C=≡CPh)_2\{κ^3-P,O,P-\{xant\{P^3Pr_2\}_2\}\}]_2[BF_4]_2\) (3) by selective abstraction of the Cα−H hydrogen atom of the allenylidene ligand with K′BuO. Complex 3 is metastable. According to results of DFT calculations, the migration of the hydride ligand to the Cα atom of the cumulene has an activation energy too high to occur in a concerted manner. However, the migration can be catalyzed by water, alcohols, and aldehydes. The resulting allenylidene-osmium(0) intermediate is unstable and evolves into a 7:3 mixture of the hydride-osmium(II)-indenylidene \([OsHCl(≡CH≡CPh)_2\{κ^3-P,O,P-\{xant\{P^3Pr_2\}_2\}\}]_2[BF_4]_2\) (4) and the osmanaphthalene \([OsCl(C_9H_6Ph)\{κ^3-P,O,P-\{xant\{P^3Pr_2\}_2\}\}]_2\) (5). Protonation of 4 with HBF_4 leads to the elongated dihydrogen complex \([OsCl(η^2-H_2)\{≡C=≡CPh\}_2\{κ^3-P,O,P-\{xant\{P^3Pr_2\}_2\}\}]_2[BF_4]_2\) (6), while the protonation of 5 regenerates 2. In contrast to 4, complex 6 evolves to a half-sandwich indenyl derivative, \([Os(η^2-IndPh)H\{κ^3-P.O,P-\{xant\{P^3Pr_2\}_2\}\}]_2[BF_4]_2\) (7). Phenylacetylene also provokes the 1,3-hydrogen shift in 3. However, it does not participate in the migration. In contrast to water, alcohols, and aldehydes, it stabilizes the resulting allenylidene to afford \([Os(≡CH≡CPh)_2(η^2-HC≡CPh)\{κ^3-P,O,P-\{xant\{P^3Pr_2\}_2\}\}]_2[BF_4]_2\) (8).

INTRODUCTION

Transition metal unsaturated carbene complexes, particularly vinylidene and allenylidene derivatives, are modern and powerful tools in organic and organometallic synthesis. Their use is allowing the development of previously inaccessible or difficult transformations, which simplifies the building of a diverse range of types of carbon–carbon and carbon–heteroatom bonds. Other tools of paramount relevance are the transition metal hydride complexes. They are classical inorganic compounds, which are increasingly used in homogeneous catalysis. The reason for this fact is because they are ideal for setting unsaturated organic molecules at metal fragments, can generate radicals with Markovnikov selectivity by H-transfer, and have demonstrated a marked ability to functionalize C−H bonds as consequence of their capacity to activate σ-bonds. Thus, complexes bearing both classes of ligands have an enormous potentiality, being the stabilization and control over their chemical properties a challenge of first magnitude.

The main problem for the development of the stoichiometric chemistry of these bifunctional compounds, which enables to understand the catalytic performance, is their low stability, since they are thermodynamically unstable with regard to the 1,2-insertion products (eq 1). As a consequence, only a scarce number of hydride-vinylidene complexes of 8 group metals have been isolated and fully characterized so far, mainly osmium derivatives, whereas the known hydride-allenylidene compounds are reduced to the cations \([OsH\{≡C=C=CPh\}_2\}{(CH_3CN)_2\{P^3Pr_2\}_2}\] and \([OsH\{≡C=C=CPh\}_2\}(η^2-HC≡CPh)\{P^3Pr_2\}_2]\) and the neutral iridium(III) complexes IrHCl\{≡C=C=CPhR\}(P^3Pr_2)\) (R = Ph, ‘Bu), although only some reactivity of the first of them has been investigated.

Transition metal allenylidene complexes can be grouped into electrophiles and nucleophiles, according to the reactivity of the unsaturated Cα-chain. While electrophiles have attracted
great attention, nucloephiles have been scarcely studied. The nucleophilic allenylidenes are characterized by addition of electrophiles to C\(\beta\). With alcohols, the great majority of them are inert. However, the allenylidene ligand of cation [OsH(\(\eta^1\)-C=C=CPh\(\eta^1\))(CH\(_3\)CN)\(_2\)(PP\(\text{Pr}_3\))\(_2\)]\(^+\) displays super-nucleophilic behavior, which allows the reduction of the C\(\alpha\)-C\(\beta\) double bond of the unsaturated chain (Scheme 1). The 1,3-addition of the O–H alcohol bond to the metal center and the C\(\beta\) atom affords an alkoxide-hydride-carbyne intermediate, which leads to dihydride-carbyne species by \(\beta\)-hydrogen elimination of the alcoholate. The subsequent migration of one of the hydrides to the carbene C\(\alpha\) atom gives the reduction product hydride-alkenylcarbene.\(^{11 a,d}\)

The hydride ligand of [OsH(\(\eta^1\)-C=C=CPh\(\eta^1\))(CH\(_3\)CN)\(_2\)(PP\(\text{Pr}_3\))\(_2\)]\(^+\) is certainly efficient for fixing unsaturated organic molecules beside the allenylidene ligand. It reacts with terminal alkynes to a\(^1\) dihydrogen-carbyne intermediate, which leads to dihydride-carbyne species by elimination of the alcoholate. The subsequent migration of this hydride atom a\(^1\) lignand gives the reduction product hydride-alkenylcarbene.\(^{11 a,d}\)

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According to such ability, xant(PP\(\text{Pr}_3\))\(_2\) is adapted to the requirements of the reactions in which its complexes participate, enabling the necessary geometrical transformations on the metal coordination sphere through changes in its coordination mode.\(^{14}\) As proof-of-concept validation, besides species bearing the diphosphine \(\kappa^3\)-P,O,P-mer coordinated,\(^{15}\) complexes with the ligand in fashions \(\kappa^3\)-P,O,P-fac,\(^{16}\) \(\kappa^2\)-P,P-cis,\(^{17}\) and \(\kappa^2\)-P,P-trans\(^{4b,18}\) have been also isolated. This is allowing to perform reactions\(^ {17}\) to isolate compounds\(^{20}\) initially forbidden, and as result, interesting catalysts for a wide range of processes are being discovered.\(^{18 a,c,19,21}\) The proved flexibility and great coordinative versatility of xant(PP\(\text{Pr}_3\))\(_2\) inspired us to use it to address the preparation of a neutral hydride-osmium(II)-allenylidine complex. Its stabilization would permit to study its behavior toward alcohols, water, and terminal alkynes and to in this way answer the question above.

This paper reports the preparation of a neutral hydride-osmium(II)-allenylidine complex structurally related to the cation [OsH(\(\eta^1\)-C=C=CPh\(\eta^1\))(CH\(_3\)CN)\(_2\)(PP\(\text{Pr}_3\))\(_2\)]\(^+\) and, in order to address the question raised, analyzes its behavior toward alcohols, water, aldehydes, and phenylacetylene, which promote an unusual 1,3-hydrogen shift from the metal center to the C\(\beta\) atom of the cumulene.

### RESULTS AND DISCUSSION

**Preparation of the Neutral Hydride-Osmium(II)-Allenylidine Complex.** Scheme 3 summarizes the strategy employed to obtain the target compound. We selected the tetrahydride dimer ([OsH(\(\cdot \cdot \cdot \)-H)]\(\kappa^3\)-P,O,P-[xant(PP\(\text{Pr}_3\))\(_2\)])\(_2\)[\(\mu\)-Cl\] \(_2\)[BF\(_4\)] \(_2\) \(_2\) (1) as the starting point, despite the \(\kappa^2\)-P,O,P-fac coordination of the ether-diphosphine, because it reacts with weak Lewis bases to give mononuclear six-coordinate elongated dihydrogen derivatives, displaying a tridentate ligand \(\kappa^3\)-P,O,P-mer coordinated. For instance, acetonitrile yields [OsCl(\(\eta^2\)-H\(_2\))(CH\(_3\)CN)\(_2\)][\(\kappa^3\)-P,O,P-[xant(PP\(\text{Pr}_3\))\(_2\)]][BF\(_4\)]. The fac-disposition of the diphosphine in 1 stabilizes the dimeric structure with regard to the mer-coordination due to a decrease of the steric hindrance experienced by the isopropyl substituents of the unsaturated fragments. However, the coordination mer is favored over fac for mononuclear saturated metal centers. Acetonitrile breaks the chloride bridges of the dimer, saturating the osmium center. At a time, the compressed dihydrogirdes are approached to form an elongated dihydrogen, whereas the ether-diphosphine changes its disposition from fac to mer, as a consequence of the disappearance of the steric hindrance.\(^ {16}\) In this context, it should be mentioned that unsaturated osmium-dihydride complexes, which afford dihydrogen species by coordination of electron poor Lewis bases, react with propargyl alcohols to give hydride-osmium-alkenylcarbene derivatives. The \(\kappa\)-C≡C coordination of the alkynol at the vacancy promotes its tautomerization to hydroxyvinylidenec, which undergoes dehydration and addition of the acidic atom of the generated dihydrogen.\(^{14}\) According to this, 1,1-diphenyl-2-propyn-1-ol reacts with the tetrahydride dimer, in fluorobenzene at 80 °C, to form the expected hydride-osmium-alkenylcarbene [OsHClI(\(\equiv\equiv\)CCH\(_2\)(C\(_6\)H\(_5\))\(_2\)][\(\kappa^2\)-P,O,P-[xant(PP\(\text{Pr}_3\))\(_2\)][BF\(_4\)] \(_2\) (2), through intermediates A and B. Complex 2 was isolated as a red solid in 76% yield. Despite the expected acidity of the hydride ligand of 2, the treatment of its tetrahydrofuran solutions with 1.1 equiv of K\(\text{BuO}\) produces the selective abstraction of the C\(\beta\)-H hydrogen atom of the alkenylcarbene ligand. The deprotona-
formation of the alkenylcarbyne ligand and the mer-disposition of the diphosphine, which coordinates with P(1)−Os−P(2), P(1)−Os−O(1), and P(2)−Os−O(1) angles of 155.95(2)°, 79.32(4)°, and 79.57(4)°, respectively. Thus, the coordination polyhedron around the osmium atom can be rationalized as a distorted octahedron with the carbyne group disposed trans to the oxygen atom of the diphosphine (C(1)−Os−O(1) = 173.09(8)°) and the hydride ligand situated trans to the chloride anion (H(01)−Os−Cl(1) = 158.8(9)°). The most conspicuous feature of the structure is the very short Os−C(1) bond length of 1.731(2) Å, which is fully consistent with an Os−C(1) triple bond formation. The alkenylcarbyne proposal is supported by the bond lengths and angles within the carbon donor ligand. Carbons C(1) and C(2) are separated by 1.423(3) Å, whereas the C(2)−C(3) distance is 1.360(3) Å. The angles around C(2) and C(3) lie in the range 112−127°. In agreement with the presence of a hydride ligand, the 1H NMR spectrum, in dichloromethane-d2, at room temperature shows a triplet (JH−H = 16.4 Hz) at −5.59 ppm. In the low field region of the spectrum, the most noticeable signal is a singlet at 5.55 ppm corresponding to the C(sp2)−H hydrogen atom of the alkynyl group. In the 13C{1H} NMR spectrum, C(1)−C(3) resonances are observed at 166.9 and 130.8 ppm as singlets. The 31P{1H} NMR spectrum contains a singlet at 52.9 ppm, as expected for equivalent PPr2 groups.

Complex 3 has been also characterized by X-ray diffraction analysis. The coordination around the osmium atom resembles that of 2, with the allenyldiene ligand in the position of the alkenylcarbyne group; i.e., a distorted octahedral arrangement with P(1)−Os−P(2), C(1)−Os−O(1), and H(01)−Os−Cl(1) angles of 160.88(6)°, 177.8(2)°, and 164(2)°, respectively. The diphénylallenylidene ligand is bonded to the metal center in a nearly linear fashion (Os−C(1)−C(2) = 175.1(6)° and C(1)−C(2)−C(3) distances of 1.858(6), 1.261(8), and 1.351(8) Å, respectively, compare well with those reported for the previously structurally characterized osmium-allenylidene complexes. In agreement with them, C(1)−C(2) and C(2)−C(3) are about 0.05 Å shorter and longer, respectively, than the bond length expected for a carbon−carbon double bond (about 1.30 Å), which suggests a notable contribution of the canonical form [M]=[C≡C−C≡C−CPh3] to the structure of the C2-chain. In accordance with the presence of hydride and allenyldiene ligands, the IR spectrum of the molecule contains the corresponding characteristic ν(Os−H) and ν(C≡C−C) bands at 2090 and 1863 cm−1. In the 1H NMR spectrum, in dichloromethane-d2, at room

Figure 1. Molecular diagram of the cation of complex 2 (ellipsoids shown at 50% probability). All hydrogen atoms (except C(sp2)−H and the halide) are omitted for clarity. Selected bond distances (Å) and angles (deg): Os−P(1) = 2.3487(6), Os−P(2) = 2.3601(6), Os−O(1) = 1.731(2), Cl(1)−Os−Cl(1) = 158.8(9), Os−C(1)−C(2) = 1.731(2), C(1)−C(2) = 1.423(3), C(2)−C(3) = 1.360(3); P(1)−Os−P(2) = 155.95(2), C(1)−Os−O(1) = 173.09(8), Cl(1)−C(2)−C(3) = 127.8(2), C(2)−C(3)−C(4) = 124.0(2), C(2)−C(3)−C(10) = 119.3(2), P(1)−Os−O(1) = 79.32(4), P(2)−Os−O(1) = 79.57(4), H(01)−Os−Cl(1) = 158.8(9).
of the hydride ligand and the C(sp²) atom of the carbocycle. Figure 3 shows its structure which proves the C(1)−Cl(1) = 2.4846(16), Os−P(1) = 2.3252(9), Os−P(2) = 2.2952(9), Os−O(1) = 2.2772(2), Os−Cl(1) = 2.5254(8), Os−H(01) = 1.573(10), Os−C(1) = 1.9013(3), C(1)−C(2) = 1.457(5), C(2)−C(3) = 1.360(5), C(3)−C(4) = 1.495(5), C(4)−C(5) = 1.414(4), C(5)−C(1) = 1.492(5), P(1)−Os−P(2) = 148.66(3), C(1)−Os−O(1) = 175.26(11), P(1)−Os−O(1) = 77.63(6), H(01)−Os−Cl(1) = 172.7(12).

The coordination polyhedron around the osmium atom is the expected octahedron with the ether-diphosphine κ₃-P,O,P-mer coordination (P(1)−Os−P(2) = 148.66(3)°, P(1)−Os−O(1) = 77.63(6)°, and P(2)−Os−O(1) = 77.53(6)°), the carbonyl disposed trans to the ether group (C(1)−Os−O(1) = 175.26(11)°), and the hydride ligand disposed trans to the chloride anion (H(01)−Os−Cl(1) = 172.7(12)°). The Os−C(1) bond length of 1.9013 Å confirms the Os−C double bond. The presence of the hydride ligand in the molecule is also supported by the ¹H NMR spectrum, in dichloromethane-d₆, at 223 K, which contains a triplet (J_H-P = 21.9 Hz) at −18.54 ppm. In the ³¹P[¹H] NMR spectrum, the resonance corresponding to C(1) appears at 232.4 ppm. The ³¹P[¹H] NMR spectrum displays a singlet at 53.3 ppm for the equivalent PP₂ groups.

Complex 5 is also certainly noticeable, since is a new member of the scarcely represented family of metalanaphthalene derivatives within the class of metalaraomatic compounds.

Isomerization of 3 Promoted by Water, Alcohols, and Aldehydes. Treatment of 3 with 1−2 equiv of water, methanol, 2-propanol, or benzaldehyde, in fluoro benzene, at 80 °C, for 16 h gives rise to its quantitative isomerization into a 7:3 mixture of the derivatives hydride-indenylidene OsHCl(κ²-P,Pr₂)₂(P(ant)(PPr₂)₂) (4) and osmanaphthalene OsCl(C₉H₆Ph){κ³-P,Pr₂,P-[ant(PPr₂)₂]} (5) (Scheme 4), which were separated by using their different solubility in methanol and isolated as red and green crystals, respectively.

Complex 4 is a notable example of stable hydride-indenylidene, which does not evolve to the half-sandwich indenyl species. Figure 3 shows its structure which proves the cyclization of the cumulene of 3 and the mutual disposition cis of the hydride ligand and the C(sp³) atom of the carbocycle. The coordination polyhedron around the osmium atom is the expected octahedron for a six-coordinate octahedron with the ether-diphosphine κ³-P,O,P-mer coordinated (P(1)−Os−P(2) = 148.66(3)°, P(1)−Os−O(1) = 77.63(6)°, and P(2)−Os−O(1) = 77.53(6)°), the carbonyl disposed trans to the ether group (C(1)−Os−O(1) = 175.26(11)°), and the hydride ligand disposed trans to the chloride anion (H(01)−Os−Cl(1) = 172.7(12)°). The Os−C(1) bond length of 1.9013 Å confirms the Os−C double bond. The presence of the hydride ligand in the molecule is also supported by the ¹H NMR spectrum, in dichloromethane-d₆, at 223 K, which contains a triplet (J_H-P = 21.9 Hz) at −18.54 ppm. In the ³¹P[¹H] NMR spectrum, the resonance corresponding to C(1) appears at 232.4 ppm. The ³¹P[¹H] NMR spectrum displays a singlet at 53.3 ppm for the equivalent PP₂ groups.
Thus, the Os–C(1) distance of 1.8616(18) Å is about 0.19 Å shorter than the Os–C(5) bond length of 2.046(15) Å, whereas bonds C(2)–C(3), C(4)–C(5), C(6)–C(7), and C(8)–C(9) are shorter than bonds C(3)–C(4), C(5)–C(6), C(7)–C(8), and C(9)–C(4) (1.35–1.40 Å versus 1.39–1.46 Å). With regard to the chloride anion, the ether linker of the diphosphine appears to have a stabilizing effect on the Os–C multiple bonds when it is situated trans to them. In this context, it should be noted that such disposition is observed in the four complexes, 2–5, which could be related to the greater π-donor ability of oxygen with regard to chlorine and the π-acceptor capacity of the C-donor ligands. The existence of a markedly dominant resonance form can explain the low NICS(0) and NICS(1) values computed, 2.4 and −2.6 ppm, respectively, which are however in agreement with those found in other metalaaromatic complexes of this class.26 The $^{13}$C($^1$H) NMR spectrum of the green crystals, in dichloromethane-$d_2$ at room temperature, also supports the dominant contribution of the resonance form a to the structure of the metalabicycle. In agreement with an almost double character of the Os–C(1) bond, the resonance corresponding to C(1) appears at 248.1 ppm, while the signal due to C(5) is observed at higher field, 168.9 ppm, as expected for an Os–C(sp$^3$) almost single bond. The $^{31}$P($^1$H) NMR spectrum shows a singlet at 33.4 ppm, in accordance with the equivalence of the PPr$_2$ groups disposed mutually trans.

Isomerization reactions from 3 into 4 and 5 are water-, alcohol-, and aldehyde-catalyzed competitive processes. The molar ratio between the isomeric products is independent of the catalyst. In order to understand this fact, we carried out the isomerization in the presence of D$_2$O and methanol-$d_4$. In both cases, we obtained the 7:3 mixture of the monodeuterated isomers 4-$d_1$ and 5-$d_1$ with the deuterium atom bonded to the C(2) atom of the compounds (Scheme 5); i.e., the C$_\beta$ atom of the cumulene of 3.

The position of the deuterium atom, analogous in each compound, points out that the first step is common for both isomerization reactions and involves a catalyst-mediated 1,3-hydrogen shift from the metal center to the C$_\beta$ atom of the cumulene of 3. To gain insight about this unusual migration and the subsequent cyclization processes, we carried out DFT calculations at the dispersion-corrected SMD(2-methoxyethanol)-B3LYP-D3//SDD(f)/6-31-G** level (Figures S35–S37; see computational details in the Supporting Information). The changes in free energy ($\Delta G$) were calculated at 298.15 K and 1 atm. Figure 5 shows the computed energy profile, whereas Scheme 6 gathers all the intermediates involved in the reaction.

The direct migration of the hydride to the C$_\beta$ atom of the allenylidene ligand, through a four-center transition state, is energetically prohibited since it must be overcome a barrier of 71.4 kcal mol$^{-1}$ (Figure S35). The migration in two consecutive 1,2-hydrogen shifts, via an allenyl intermediate (Figure S36) is also energetically forbidden. Although the activation energy for the formation of the allenyl species is reduced to 28.1 kcal mol$^{-1}$, the transition state for the second migration lies 51.5 kcal mol$^{-1}$ over 3. However, the proton shuttle formed by two water molecules consecutively associated by means of hydrogen bonds, significantly reduces
the barrier for the 1,3-hydrogen shift to 18.3 kcal mol\(^{-1}\). The hydride ligand interacts with the oxygen atom of one of the water molecules to place a hydrogen atom of another close to the C\(\beta\) atom of cumulene. This allows a cyclic transition state of eight-members (TS\(_{C \rightarrow C}\); Figure S38), much less tensioned than that for the direct migration, which affords the five-coordinate osmium(0) intermediate C. In spite of its saturated character, the latter oxidatively adds the ortho-CH bond of a phenyl substituent of the alkenylcarbyne ligand in one step through the transition state TS\(_{C \rightarrow D}\), which lies 23.3 kcal mol\(^{-1}\) over C. The approach of the C–H bond to the metal center causes the dissociation of the oxygen atom of the ether-diphosphine, before the C–H cleavage. The oxidative addition generates the osmanaphthylene D, which is 7.3 kcal mol\(^{-1}\) less stable than 3. The existence of this class of compounds has been experimentally demonstrated by Jia, Lin, and co-workers.\(^{27}\) Osmanaphthylene D bears both fragments of the C–H bond activation disposed cis to the Os–C triple bond of the metalacycle. In agreement with the Jia and Lin calculations, the 1,2-carbon-migration leads to the hydride-osmium-indenylidene derivative 4, whereas the 1,2-hydride-migration gives the osmanaphthalene 5. The barriers are similar, 26.0 kcal mol\(^{-1}\) for the former and 26.9 kcal mol\(^{-1}\) for the second. As expected for the composition of the isomerization mixture, complex 4 is slightly more stable than 5, 2.8 kcal mol\(^{-1}\). In spite of this small difference, they do not interconvert after isolation, as corresponds to the very high barrier for the isomerization on both sides. The intramolecular insertion reactions initially afford the respective five-coordinate species E and F, which subsequently coordinate the oxygen atom of the ether-diphosphine to yield the isomerization products.

The different behavior of 3 and the cation [OsH(\(\equiv C\equiv C\equiv\text{CPh}_3\))\((\text{CH}_2\text{CN})_2(\text{PPr}_3)_2\)]\(^+\) toward alcohols is evident. On the basis of experimental observations and DFT results, this fact can be rationalized on both the differences in coordination ability between an acetonitrile ligand and the oxygen atom of the diphosphine and the difference in charge between the complexes. The greater coordination capacity of the ether group of the diphosphine with regard to the acetonitril ligand prevents the coordination of the alcoholate, resulting from the protonation of the C\(\beta\) atom of the cumulene. In this context, it should be mentioned that deuterium labeling experiments and theoretical calculations on the hydrogenation of the cation indicate that the \(\beta\)-hydrogen elimination in the coordinated alkoxide group is the key for the reduction, because the formation of a dihydride-carbyne species, with a cis disposition of the carbyne to both hydrides (trans between them), is essential to the 1,2-hydrogen shift from the metal center to the C\(\beta\) atom of the carbyne (Scheme 1).\(^{114}\) In addition, the neutral character of 3 with respect to the cationic nature of [OsH(\(\equiv C\equiv C\equiv\text{CPh}_3\))\((\text{CH}_2\text{CN})_2(\text{PPr}_3)_2\)]\(^+\) increments the basicity of the metal center in the former, which increases the activation energy for the hydride migration from the metal center to the C-donor ligand\(^{28}\) and, at a time, favors the oxidative addition of the phenyl C–H bond in C.

**Protonation of 4 and 5.** Indenylidene complexes display a marked tendency to evolve to indenyl derivatives by 1,2-shift of an 1-\(\text{e}^-\) donor ligand, including chloride, from the metal center to the carbenic carbon atom.\(^{27,28}\) In addition, it has been argued that one of the difficulties in the synthesis of metalanaphthalene compounds could be due to its lower stability relative to the indenyl derivatives. So, the stability of 4 and 5 first surprised us and then encouraged us to promote their transformation to indenyl species, in particular that of 4. In this context, we noted that the carbenic carbon atom of alkylidene-osmium(II) complexes has amphiphilic character, reacting with both nucleophiles and electrophiles, including \(\text{H}^+\).\(^{30}\) Thus, we decided to study the protonation of both 4 and 5.

Addition of 1.0 equiv of HBF\(_4\) to a dichloromethane solution of 4 at 223 K immediate and quantitatively affords the

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**Scheme 6. Mechanism of the Water-Catalyzed Isomerization of Complex 3**
elongated dihydrogen derivative [OsCl(η²-H₂)(─Cᵤ₃IndPh)(κ²-P₂O₃P₂-x[PnPr₃]₂)]BF₄ (6). In agreement with the presence of a coordinated hydrogen molecule in the complex, its ¹H NMR spectrum shows a broad resonance at ~6.04 ppm, which exhibits a 300 MHz T₁(min) value of 31 ± 3 ms, at 217 K, whereas the H—D coupling constant in the partially deuterated species is 20 Hz. These values allow us to calculate H—H separations of 1.00 and 1.08 Å, respectively. ¹H NMR spectrum shows a broad resonance at 7.21 ppm, corresponding to the equivalent P₁ and characteristic features of this species. At room temperature, the acidic hydrogen atom of the dihydrogen ligand migrates to the carbenic carbon atom of the indenylidene, to generate an indenyl ligand. The migration is quantitative after 1 h and causes the formal oxidation of the metal center from Os²⁺ to Os⁴⁺. The generated indenyl ligand displaces the acidic hydrogen atom of the dihydrogen ligand, to form an indenyl ligand. The migration is quantitative after 1 h and causes the formal oxidation of the metal center from Os²⁺ to Os⁴⁺. The generated indenyl ligand displaces the acidic hydrogen atom of the dihydrogen ligand, to form an indenyl ligand. The migration is quantitative after 1 h and causes the formal oxidation of the metal center from Os²⁺ to Os⁴⁺.
this, the addition of DBF$_4$ to the dichloromethane-$d_1$ solution of 5 selectively leads to 2-$d_1$ containing a deuterium atom at one of the ortho-carbon atoms of a phenyl substituent of the alkenylcarbene ligand (Scheme 8).

**Scheme 8. Protonation of Complex 5 Using DBF$_4$**

![Scheme 8](https://placeHolder.com)

**Reaction of 3 with Phenylacetylene.** Treatment of toluene solutions of hydride-osmium(II)-allenylidene complex with 4 equiv of the alkyne, for 2 days, at room temperature, leads to the α-alkyne-osmium(0)-alkenylcarbene [Os≡CC(Cd)$_2$][η$_2$-HC≡CPh)(κ$^3$-P$_1$O$_2$P$_2$-xant(PP$_2$)$_2$)]Cl (8). The salt was isolated as a brown solid in 58% yield. The reaction implies a 1,3-hydrogen shift from the metal to the C$_p$ atom of the allenylidene ligand, which produces the Os$^{2+}$-to-Os$^{0}$ reduction of the central ion, the displacement of the chloride anion by the alkyne, and a change in the coordination of the ether-diphosphine from $κ^3$-$P_1P$-$O$-$mer$ to $κ^3$-$P_1P$-$O$-$fac$ (Scheme 9).

**Scheme 9. Reaction of Complex 3 with Phenylacetylene**

![Scheme 9](https://placeHolder.com)

Figure 7 shows a view of the structure of the cation, which proves the three previously mentioned transformations on the metal coordination sphere. The coordination polyhedron around the osmium atom can be rationalized as a distorted trigonal bipyramid with the oxygen atom of the diphosphine and the alkenylcarbene ligand at the apexes (O(1)−Os−C(1) = 165.8(3)°), whereas the PPr$_2$ groups and the C(16)−C(17) triple bond of the alkyne lie in the equatorial plane. The P(1)−Os−P(2) angle of 109.51(9)° compares well with that of 7, as expected, since the same coordination mode for the ether-diphosphine is observed in both complexes. The alkylene coordinates to the osmium atom with Os−C(16) and Os−C(17) distances of 2.065(10) and 2.098(9) Å, respectively. The coordination produces a slight elongation of the triple bond, according to the usual Chatt−Dewar−Ducanson bonding model. Thus, the C(16)−C(17) bond length of 1.280(13) Å is intermediate between triple and double bond. The osmium-carbene bond length Os−C(1) of 1.708(10) Å and the C(1)−C(2) and C(2)−C(3A) distances of 1.441(13) and 1.313(16) Å, respectively, are similar to those of 2. The $^1$H, $^{13}$C($^1$H), and $^{31}$P($^1$H) NMR spectra, in dichloromethane-$d_2$, at 253 K, are consistent with the structure shown in Figure 7. In the $^1$H, the most noticeable signals are a doublet ($^{15}$J$_{H−P}$ = 9.6 Hz) at 8.57 ppm, corresponding to the C(sp$^2$)−H hydrogen atom of the coordinated alkyne, and a singlet at 5.68 ppm due to the carbyne. The $^{13}$C{($^1$H)} shows the resonance due to the C$_p$ atom of the cumulene carbon atom at 265.0 ppm, whereas the signals assigned to the coordinated atoms of the alkyne are observed at 133.9 and 117.7 ppm. The $^{31}$P{($^1$H)} contains an AB spin system centered at 41.6 ppm and de$^{15}$J = 53.0 Hz and $^{15}$J$_{A−B}$ = 16.9 Hz, in agreement with inequivalent PPr$_2$ groups.

The formation of 8 appears to be consistent with the isomerization of 3 to 4 and 5, at least on an initial examination. Moreover, one could think that 8 is the result of trapping the intermediate C of Scheme 6 by means of the coordination of phenylacetylene. However, it should be noted that, although the C(sp$^2$)−H hydrogen atom of the alkyne is also fairly acidic, phenylacetylene has not an equivalent to the oxygen of the catalysts promoting the isomerization (water, alcohols, and aldehydes) to interact with the hydride ligand of 3 and to approach the acidic proton to the C$_p$ atom of the cumulene. In view of this inconsistency, we decided to carry out the reaction of 3 with PhC≡CD. Under the same conditions as that employed to form 8, 8-$d_1$ was quantitative and selectively obtained (Scheme 10).

The position of the deuterium atom at the coordinated alkyne of 8-$d_1$ indicates that the 1,3-hydrogen shift in this case occurs by a different manner to those previously discussed. A feasible alternative could involve the reductive elimination of HCl as consequence of the acidicification of the metal center, due to the initial replacement of the oxygen atom of the ether-diphosphine by the alkyne. Once the reduction has taken place, the recoordination of the ether linker, now $κ^3$-$P_1P$-$O$-$fac$ with the oxygen atom trans to the cumulene, and the subsequent
dene ligands, which have a common characteristic: the strong nucleophilic character of the central carbon atom of the C–C chain. Nevertheless, they show different behavior due to different abilities of the coligands. The poor coordinating capacity of the acetonitrile ligand of the cation allows the reduction of the Cα–Cβ double bond, while the association of the hydride ligand of 3 with the oxygen atom of the alcohol permits to lower the activation barrier for the 1,3-hydrogen shift from the metal to the Cβ atom of the cumulene; i.e., the coligands of allenylidene complexes are not innocent; they can have a direct participation in the reactions of the C–C chain.

In summary, a new reactivity pattern for hydride-allenylidene complexes has been observed, which is of interest in connection with the isomerization phenyllallenylidene-to-indenylidene and the transformation hydride, indenylidene-to-indenyl. Furthermore, it can help to systematize the preparation of metalanaphthalene derivatives.

### EXPERIMENTAL SECTION

**General Information.** All reactions were carried out with exclusion of air using Schlenk-tube techniques or in a drybox. Instrumental methods and X-ray details are given in the Supporting Information. In the NMR spectra (Figures S1–S34) the chemical shifts (in ppm) are referenced to residual solvent peaks (1H, 13C{1H}) or external 85% H₃PO₄ (13C{1H}). Coupling constants J and N (N = Jₚ-H + Jr-H for 1H and N = Jₚ-C + Jr-C for 13C{1H}) are given in hertz. [Os(HCl)(≡CCH-)C₆H₄(=CH₂)]PF₆ (2). Complex 2 (500 mg, 0.33 mmol) in fluorobenzene (4 mL) was treated with 1,1-diphenyl-2-propyn-1-ol (550 mg, 2.64 mmol), in the presence of 4 Å molecular sieves (2 g). After 2 h, at 80 °C, the resulting suspension was separated from the molecular sieves by decantation with a canule. Then, the liquid phase was removed and the dark red solid was washed with diethyl ether (3 × 3 mL) and pentane (6 × 3 mL) and dried under vacuum. Yield: 475 mg (76%).

**Preparation of [OsHCl(≡CCH-)C₆H₄(=CH₂)](x²-P,OP-P-xant-(PP₃)₂)BF₄ (3).** Complex 2 (500 mg, 0.33 mmol) in fluorobenzene (4 mL) was treated with 1,1-diphenyl-2-propyn-1-ol (550 mg, 2.64 mmol), in the presence of 4 Å molecular sieves (2 g). After 2 h, at 80 °C, the resulting suspension was separated from the molecular sieves by decantation with a canule. Then, the liquid phase was removed and the dark red solid was washed with diethyl ether (3 × 3 mL) and pentane (6 × 3 mL) and dried under vacuum. Yield: 475 mg (76%).

**CONCLUDING REMARKS**

This study has revealed the existence of a 1,3-hydrogen shift in the elusive hydride-metal-allenylidene complexes, which is responsible for the isomerization of the cumulene to indenylidene and the transformation of the hydride-allenylidene unit into the metalaromatic bicycle meta-indanaphthalene. The hydrogen shift, which has an activation energy too high to occur in a concerted manner, is catalyzed by water, alcohols, and aldehydes. Phenyllacetylene also provokes the 1,3-hydrogen shift; however, it does not participate in the migration. In contrast to water, alcohols, and aldehydes, it provokes the 1,3-hydrogen shift; however, it does not participate in the migration. In contrast to water, alcohols, and aldehydes, it stabilizes the resulting alkenylcarbyne, preventing its evolution into indenylidene or metalanaphthalene.

This study has also illustrated a new behavior of transition metal allenylidene complexes toward alcohols. Until now, these compounds had shown three different conduct. Those with electrophilic nature form α,β-unsaturated alkoxycarbenic derivatives, as a result of the 1,2-addition of the O–H bond of the alcohol to the Cα–Cβ double bond of the allenylidene. Nucleophilic allenylidene are inert, and the cation [OsH(≡ C≡C≡CPh₂)(CH₂CN)₂(PPr₃)₂]^+ undergoes reduction of the Cα–Cβ double bond as a consequence of a hydrogen transfer reaction from the alcohol to the complex.
acetonitrile (5 mL) afforded a green solid, that was washed further with acetonitrile (3 x 3 mL) and dried under a vacuum. Yield: 390 mg (86%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated dichloromethane solution at -4 °C. Anal. Calc’d for C₄₂H₅₁ClOO₅P₂: C, 58.69; H, 5.98. Found: C, 59.02; H, 6.04. HRMS (electrospray, m/z) calc’d for C₄₂H₅₁ClOO₅P₂ [M + H]⁺: 861.2797, found 861.2742. IR (cm⁻¹) ν(O=H) 2900 (w); ν(O=O=C=C) 1863 (m); ν(C=C) 1395 (s). ¹H NMR (400.13 MHz, CDCl₃, 298 K) δ 7.70 (d, J_H-H = 7.4, 2H, CH-arom, POP), 7.50 (m, 2H, CH-arom, POP), 7.30 (t, J_H-H = 7.6, 2H, CH-arom, POP), 7.22 (t, J_H-H = 7.8, 4H, CH-C, Ph), 2.99 (m, 2H, PCH(C(CH₃)₂)), 2.56 (m, 2H, PCH(C(CH₃)₂)), 1.80 (s, 3H, C(CH₃)₂), 1.51 (d, J_H-H = 7.2, N = 14.8, 6H, CH₃), 1.51 (s, 3H, CH₃), 1.44 (d, J_H-H = 7.5, N = 15.8, 6H, PCH(C(CH₃)₂)), 1.20 (d, J_H-H = 7.2, N = 16.1, 6H, PCH(CH₂)), 0.89 (d, J_H-H = 7.1, N = 14.9, 6H, PCH(CH₂)), -0.82 (s, J_H-H = 17.4, H, O=P). ³¹P{¹H} NMR (100.64 MHz, CDCl₃, 298 K) δ 256.1 (t, J_P-P = 4.1, Os=C=O=C, 242.5 (t, J_P-P = 10.4, Os=C=Os), 157.0 (vt, N = 12.4, C-arom), 154.8 (t, J_P-P = 2.4, Os=C=O=C, 132.2 (vt, N = 5.4, C-arom), 131.6 (s, CH-arom, POP), 129.1 (s, CH-C, Ph), 129.0 (s, C-arom, POP), 128.9 (s, CH-arom, POP), 126.3 (s, C-CH₃), 126.3 (s, p-CH₃), 125.9 (vt, N = 5.0, CH-arom, POP), 120.4 (s, C-iso, Ph), 35.6 (s, C(CH₃)₂), 34.7 (s, C(CH₃)₂), 29.5 (s, C(CH₃)₂), 29.3 (vt, N = 23.4, PCH(CH₃)), 28.7 (vt, N = 30.9, PCH(CH₃)), 22.2 (s, PCH(CH₂)), 20.0 (s, PCH(C(CH₃)₂)), 19.9 (vt, N = 5.6, PCH(CH₂)), 19.3 (vt, N = 2.8, PCH(CH₂)). ¹³C{¹H} NMR (121.49 MHz, CDCl₃, 298 K) δ 27.6 (s).

Preparation of Os[Cl(C₄₃H₅₁ClOO₅P₂)-CH(C₂H₅)]₂ (4d-C₄₃H₅₁ClOO₅P₂). Two screw-top NMR tubes were charged with 3 (50 mg, 0.058 mmol) then, 0.4 mL of dichloromethane-d₂ was added to one of them and 0.4 mL of dichloromethane to the other. Subsequently, the solutions were treated with 2 μL of D₂O or methanol-d₄ (1 : 2 equiv). After 16 h, at 80 °C, ³¹P{¹H} NMR spectra showed quantitative formation of 4d₁ and 5d₁ in a 7.3:1 molar ratio. HRMS (TIFS-electrospray-TOF, m/z) calc’d for C₄₂H₅₁ClOO₅P₂ [M – Cl]: 826.3087, found 826.3073 and C₃8H₃O₅P₂ [M – Cl]: 269.4 (4d₂) and 256.6 (5d₂). ²H NMR (61.42 MHz, CD₂Cl₂, 298 K) δ 7.60 (br, 4d₁), 7.36 (br, 5d₁).

Preparation of [Os(C₂H₅ClO₂P₂)₃(O)P-xant(PP₃)]BF₄ (6). A solution of 4 (50 mg, 0.058 mmol) in dichloromethane-d₂ (0.5 mL), contained in a screw top NMR tube, was cooled at 195 K and treated with HBF₄·OEt₂ (8.8 μL, 0.064 mmol). Immediately it was introduced into a precooled NMR probe at 223 K and its spectra were recorded at this temperature. Quantitative and immediate formation of 6 was observed.

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Preparation of [OsH(CH\(\text{P}P\text{R}_{2})\text{Cl}]$\text{BF}_4$ (7). A solution of 4 (200 mg, 0.23 mmol) in dichloromethane (5 mL) was treated with HBF\(_4\)·OEt\(_2\) (35 µL, 0.26 mmol) and stirred at room temperature for 2 h. After that time, a brown precipitate was formed, which was filtered off, washed with ether (3×3 mL) and dried under vacuum. Brown solid; yield: 65 mg (58%).

HRMS (electrospray, $m/z$) calcld. for C\(_{50}\)H\(_{65}\)O\(_4\)N\(_2\)P\(_4\)S: [M − $\text{Cl}$]: 927.3494, found 927.3464. IR (cm\(^{-1}\)) ν(C=C) 1541 (m), ν(C=C) 1541 (m). $\delta_{\text{H}}\text{NMR}$ (59.93 MHz, CD\(_2\)Cl\(_2\), 243 K) δ 8.57 (d, $\delta_{\text{P}}$ = 3.6, 1H, HCl), 8.22–7.10 (m, 19H, CH-arom), 6.38 (d, $\delta_{\text{H},\text{H}}$ = 6.8, 2H, CH-arom), 5.81 (s, 1H, Os=O−C−C), 3.42 (m, 1H, PCH(\(\text{CH}_3\))\(_2\)), 2.99 (m, 1H, PCH(\(\text{CH}_3\))\(_2\)), 2.57 (m, 1H, PCH(\(\text{CH}_3\))\(_2\)), 2.35 (m, 1H, PCH(\(\text{CH}_3\))\(_2\)), 1.76 (s, 3H, C\((\text{CH}_3)\)\(_3\)), 1.46–1.26 (m, 9H, PCH(\(\text{CH}_3\))\(_2\)), 1.21–1.00 (m, 9H, PCH(\(\text{CH}_3\))\(_2\)), 1.06 (s, 3H, C\((\text{CH}_3)\)\(_3\)), 0.96 (dd, $\delta_{\text{H},\text{H}}$ = 14.5, $\delta_{\text{H},\text{H}}$ = 6.7, 3H, PCH(\(\text{CH}_3\))\(_2\)), 0.71 (dd, $\delta_{\text{H},\text{H}}$ = 18.3, $\delta_{\text{H},\text{H}}$ = 6.9, 3H, PCH(\(\text{CH}_3\))\(_2\)).

Preparation of Os\(_{\text{Cl}(\text{CH}_2)\text{P}(\text{CH}_3)\text{P}(\text{CH}_3)$\(_2\)}(\(\text{BF}_4$). A mixture of 8 (50 mg, 0.052 mmol) and NaBF\(_4\) (0.034 mg, 0.031 mmol) in 7 mL of acetone was stirred for 3 h. After this time, the solvent was removed under a vacuum and 8 mL of dichloromethane were added. The suspension was filtered through Celite and the resulting solution was concentrated until dry. The residue was washed with diethyl ether ($5 \times 8$ mL) and vacuum-dried. Crystals of 8·BF\(_4\) suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a solution of 8 in dichloromethane. Yield: 46 mg (88%).

IR (cm\(^{-1}\)) ν(C=C) 1541 (m), ν(C=C) 1541 (m). $\delta_{\text{H}}\text{NMR}$ (59.93 MHz, CD\(_2\)Cl\(_2\), 243 K) δ 8.57 (d, $\delta_{\text{P}}$ = 3.6, 1H, HCl), 8.22–7.10 (m, 19H, CH-arom), 6.38 (d, $\delta_{\text{H},\text{H}}$ = 6.8, 2H, CH-arom), 5.81 (s, 1H, Os=O−C−C), 3.42 (m, 1H, PCH(\(\text{CH}_3\))\(_2\)), 2.99 (m, 1H, PCH(\(\text{CH}_3\))\(_2\)), 2.57 (m, 1H, PCH(\(\text{CH}_3\))\(_2\)), 2.35 (m, 1H, PCH(\(\text{CH}_3\))\(_2\)), 1.76 (s, 3H, C\((\text{CH}_3)\)\(_3\)), 1.46–1.26 (m, 9H, PCH(\(\text{CH}_3\))\(_2\)), 1.21–1.00 (m, 9H, PCH(\(\text{CH}_3\))\(_2\)), 1.06 (s, 3H, C\((\text{CH}_3)\)\(_3\)), 0.96 (dd, $\delta_{\text{H},\text{H}}$ = 14.5, $\delta_{\text{H},\text{H}}$ = 6.7, 3H, PCH(\(\text{CH}_3\))\(_2\)), 0.71 (dd, $\delta_{\text{H},\text{H}}$ = 18.3, $\delta_{\text{H},\text{H}}$ = 6.9, 3H, PCH(\(\text{CH}_3\))\(_2\)).
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**Notes**

The authors declare no competing financial interest.

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