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Reduction of Benzonitriles via Osmium-Azavinylidene Intermediates Bearing Nucleophilic and Electrophilic Centers

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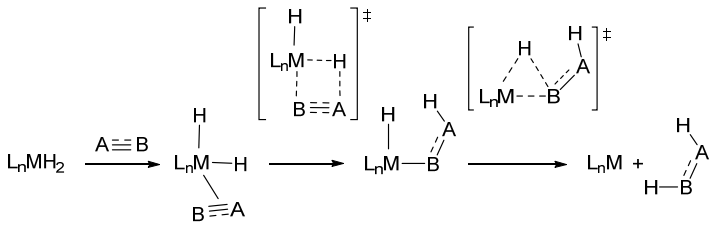
ABSTRACT The reduction of the N-C triple bond of benzonitriles promoted by $OsH_6(P^iPr_3)_2$ (**1**) has been studied. Complex **1** releases a H_2 molecule and coordinates 2,6-dimethylbenzonitrile to afford the tetrahydride $OsH_4\{\kappa^1\text{-}N\text{-}(N{\equiv}CC_6H_3Me_2)\}(P^iPr_3)_2$ (**2**), which is thermally stable towards the insertion of the nitrile into one of the Os-H bonds. In contrast to 2,6-dimethylbenzonitrile, benzonitrile and 2-methylbenzonitrile undergo insertion, via $Os(\eta^2\text{-}N{\equiv}CR)$ intermediates, to give the azavinylidene derivatives $OsH_3(=N=CC_6H_4R)(P^iPr_3)_2$ (R = H (**3**), Me (**4**)). The analysis by means of computational tools (EDA-NOCV) of the bonding situation in these compounds suggests that the donor-acceptor nature of the osmium azavinylidene bond dominates over the mixed electron-sharing/donor-acceptor and pure electron-sharing bonding modes. The N atom is strongly nucleophilic whereas one of the hydrides is electrophilic. In spite of the different nature of these centers, the migration of the latter to the N atom is kinetically prevented. However, the use of water as a proton shuttle allows the hydride migration, as a consequence of a significant decrease of the activation barrier. The resulting phenylaldimine intermediates evolve by means of orthometalation to give $OsH_3\{\kappa^2\text{-}N,C\text{-}(NH=CHC_6H_3R)\}(P^iPr_3)_2$ (R = H (**5**), Me (**6**)). The presence of electrophilic and nucleophilic centers in **3** confers it ability to activate σ-bonds, including H_2 and pinacolborane (HBpin). The reaction with the latter gives $OsH_3\{\kappa^2\text{-}N,C\text{-}[N(Bpin)=CHC_6H_4]\}(P^iPr_3)_2$ (**7**).

INTRODUCTION

Hydrogenations of multiple bonds of organic molecules are thermodynamically favored. However, these processes require the presence of catalysts that significantly decrease the activation energy of the reactions. In the homogeneous processes promoted by transition metal complexes, the formation of a $L_nMH_2(A{=}B)$ dihydride intermediate is usually required. These

species subsequently evolve by means of the sequential transfer of both hydrides from the metal to the A and B atoms involved in the multiple bond. When these atoms have no free electron pairs, the molecule coordinates to the metal center through the multiple bond and both transfers, known as insertion and reductive elimination, are necessarily concerted processes, which occur via four- and three-centers transition states, respectively (Scheme1).[1]

Scheme 1. Hydrogenation of A-B Multiple Bonds Promoted by Dihydride Species



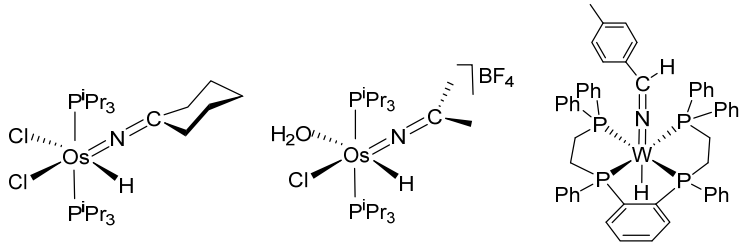
Hydrogenation of nitriles is a significant process because of the wide use of imines and amines for agrochemicals and pharmaceuticals.[2] The presence of a lone pair at the nitrogen atom determines the κ^1-N-coordination of the nitrile,[3] although some complexes showing the coordination of the N-C triple bond have been also isolated and even characterized by X-ray diffraction analysis.[4] The existence of two different coordination modes for these substrates makes possible two different paths for the hydride transfer from the metal to the C_{sp}-atom, which generates an azavinylidene intermediate:[5] a 1,3-hydrogen shift, similar to that proposed for the vinylidenes formation from hydride-metal-alkynyl species,[6] and a direct migration of the hydride to the carbon atom of the coordinated triple bond.[7]

Azavinylidenes are usually viewed as α-nitrogen-counterparts of vinylidenes. However, they compare better with carbynes. Vinylidenes are 2e-donor ligands with a standardized reactivity, which is dominated by the addition of nucleophiles at the α-carbon whereas the electrophiles

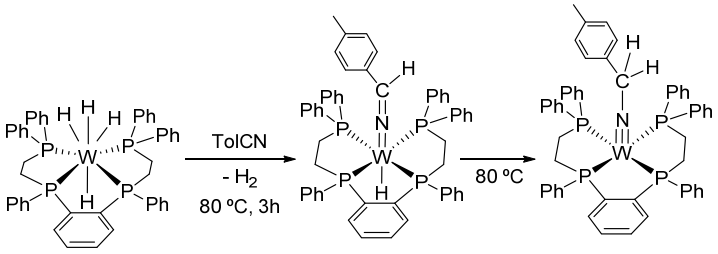
attack at the β-carbon atom.[8] In contrast, both azavinylidenes and carbynes are 3e donors. Their chemical behavior depends on the electronic nature of the metal fragment, although the differences between nitrogen and carbon give rise to significant differences in reactivity. Carbynes coordinated to electron rich metal centers (doublet carbynes) add nucleophiles at the carbyne-carbon atom while carbynes stabilized by electron poorer metal fragments (quartet carbynes) undergo electrophilic attacks at the carbyne-carbon atom.[9] There are also two different behaviors in the azavinylidene chemistry.[10] Some complexes are nucleophilic at the nitrogen atom,[11] while an efficient nucleophilicity transfer from the nitrogen atom to the C_{sp2}-carbon atom appears to take place in others, which add electrophiles at this position.[12]

The nature of the hydride-azavinylidene species, which are the key to the formation of the hydrogenation product imine, has been scarcely studied mainly because they are very rare. An overwhelming evidence of this is the fact that from the 39 azavinylidene derivatives characterized by X-ray diffraction analysis,[13] only three of them belong to this class: the osmium compounds $OsHCl_2(=N=CC_5H_{10})(P^iPr_3)_2$[14] and $[OsHCl(=N=CMe_2)(H_2O)(P^iPr_3)_2]BF_4$[15] and the tungsten derivative $WH(=N=CHTol)(\kappa^4\text{-P4})$ (Tol = *p*-MeC_6H_4, P4 = meso-*o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$)[16] (Chart 1). The reluctance of these hydride-osmium-azavinylidene complexes to undergo reductive elimination of imine has allowed to develop a rich organometallic chemistry, centered in C-N coupling processes.[17] The tungsten derivative has been prepared by insertion of *p*-tolunitrile into one of the hydride ligands of the tetrahydride $WH_4(\kappa^4\text{-P4})$ and, in contrast to the osmium compounds, is highly unstable evolving by means of 1,3-hydrogen shift from the metal center to the C_{sp2} atom of the azavinylidene ligand (Scheme 2);[16] reductive elimination of imine is not observed in this case either.

Chart 1. Hydride-Metal-Azavinylidene Species Previously Characterized by X-Ray Diffraction Analysis



Scheme 2. Formation and Evolution of a Hydride-Tungsten-Azavinylidene Derivative

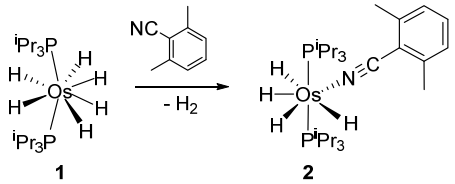


Hexahydride $OsH_6(P^iPr_3)_2$ is a significant polyhydride in the chemistry of the platinum group metals, which has demonstrated a noticeable ability to activate a wide range of σ-bonds.[18] However, its capacity to act as a hydrogenation reagent has not been investigated so far; although due to its high hydride content, one should keep it in mind as a hydrogen reservoir. In the search for understanding the hydrogenation of the triple bond of aromatic nitriles, we have investigated the reactions of the polyhydride with these substrates. In this paper, we report the insertion of benzonitriles in one of the metal-hydride bonds including the characterization of novel polyhydride-metal-azavinylidenes, the mechanism of the insertion, and the analysis of the osmium-azavinylidene bonding situation. In addition, we have studied the imine formation from both experimental and theoretical points of views.

RESULTS AND DISCUSSION

Insertion of Benzonitriles into a M–H bond of $OsH_6(P^iPr_3)_2$ (1). Complex **1** is a saturated compound. However, it easily releases a hydrogen molecule to afford the unsaturated species $OsH_4(P^iPr_3)_2$, which has been previously trapped with diphenylphosphine,[19] pyridines,[20] and boranes.[18g] 2,6-Dimethylbenzonitrile is also able to capture this species. Thus, in toluene, complex **1** reacts with the nitrile to give the saturated tetrahydride-osmium(IV) derivative $OsH_4\{\kappa^1\text{-}N\text{-}(N{\equiv}CC_6H_3Me_2)\}(P^iPr_3)_2$ (**2**), which was isolated as an orange solid in 70% yield (Scheme 3).

Scheme 3. Reaction of 1 with 2,6-Dimethylbenzonitrile



Complex **2** was characterized by X-ray diffraction analysis. The structure (Figure 1) proves the κ^1-N coordination of the nitrile to the metal center. The geometry around the osmium atom is the expected one for a saturated d^4-species; i. e., a distorted pentagonal bipyramid with axial phosphines (P(1)-Os-P(2) = 173.64(7)º). The coordination sphere is completed by the hydrides and the nitrile, which lies between H(01) and H(04). The classical nature of the OsH_4 unit was confirmed by means of the DFT-optimized structure (B3LYP-D3/SDD/6-31G**), which yields a separation between the hydrides longer than 1.70 Å. Despite that, in solution, the hydrides exchange their positions with a low activation energy. Thus, although two hydride resonances should be expected in the ^{1}H NMR spectrum according to Figure 1, only one signal at -9.90 ppm is observed between 298 and 173 K, in toluene-d_8, which displays a 400 MHz $T_{1\,(min)}$ value of

190±3 ms at 203 K. In agreement with equivalent phosphine ligands, the $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet at 44.2 ppm.

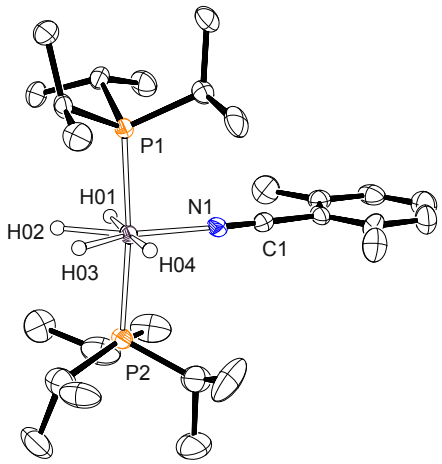
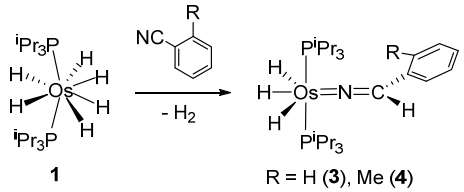


Figure 1. Molecular diagram of complex **2** with 50% probability ellipsoids. Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) for the X-ray and DFT optimized (in square brackets) structures: Os–H(01) = 1.583(13) [1.685], Os–H(02) = 1.584(13) [1.626], Os–H(03) = 1.583(13) [1.626], Os–H(04) =1.586(13) [1.687], Os–P(1) = 2.3193(18) [2.365], Os–P(2) = 2.3164(19) [2.364], Os–N(1) = 2.080(5) [2.081], C(1)–N(1) = 1.136(7) [1.163], H(01)–H(02) = [1.87], H(02)–H(03) = [1.70], H(03)–H(04) = [1.84]. Selected bond angles (deg) for the X-ray and optimized (in square brackets) structures: P(1)–Os–P(2) = 173.64(7) [174.7], H(01)–Os–H(02) = 61(3) [68.8], H(02)–Os–H(03) = 61(3) [63.2], H(03)–Os–H(04) = 57(3) [67.0], H(01)–Os–H(04) = 175(3) [160.6], H(01)–Os–N(1) = 86(2) [79.1], H(04)–Os–N(1) = 94(2) [81.5], Os–N(1)–C(1) = 177.7(5) [178.1].

Complex **2** is thermally stable towards the insertion of the nitrile into one of the Os–H bonds, for at least 3 days, in toluene at 120 ºC. In contrast to 2,6-dimethylbenzonitrile, benzonitrile and 2-methylbenzonitrile undergo insertion. Thus, the treatment of toluene or tetrahydrofuran

solutions of **1** with both nitriles, at 80 ºC, leads to the quantitative formation of the azavinylidene derivatives $OsH_3(=N=CHC_6H_4R)(P^iPr_3)_2$ (R = H (**3**), Me (**4**)), which were isolated as yellow solids (Scheme 4).

Scheme 4. **Insertion of Benzonitriles into an Os–H Bond of 1**



1 R = H (**3**), Me (**4**)

The identity of these novel compounds was confirmed by means of the X-ray analysis of a single crystal of **3**. Figure 2 shows a view of the molecule. The structure with *Cs* symmetry resembles those of complexes $OsH_3X(PR_3)_2$ (PR_3 = P^tBu_2Me, X = Cl; PR_3 = P^iPr_3, X = Cl, Br, I),[21] $OsH_3(OR_f)(P^iPr_3)_2$ (OR_f = OCH_2CF_3, $OCH(CF_3)_2$),[22] $OsH_3(OPh)(P^iPr_3)_2$,[23] $OsH_3Cl(IPr)(P^iPr_3)$ (IPr = 1,3-bis(diisopropylphenyl)imidazolylidene)[24] and $OsH(Bcat)_2Cl(P^iPr_3)_2$ (Bcat = catecholboryl).[25] The phosphines are disposed mutually trans (P(1)-Os-P(2) = 170.62(3)º), whereas the hydrides and azavinylidene lie in the perpendicular plane to the P-Os-P direction. The most noticeable features of this species are the angles in this plane of 116.4(14)º (N(1)-Os-H(01)), 57.0(18)º (H(01)-Os-H(02)), 76.0(19)º (H(02)-Os-H(03)), and 111.0(14)º (H(03)-Os-N(1)), which markedly deviate from 90º. These six-coordinate osmium(IV) species undergo distortion to destabilize one of the t_{2g} set orbitals and to stabilize the other two, resulting to be diamagnetic. Surprisingly, in contrast to **3**, complexes $OsHCl_2(=N=CC_5H_{10})(P^iPr_3)_2$, $OsCl_3(=N=CC_5H_{10})(P^iPr_3)_2$,[14] and $[OsHCl(=N=CMe_2)(H_2O)(P^iPr_3)_2]^+$ [15] display octahedral structures with angles in the perpendicular plane to the P-Os-P direction closer to the ideal value of 90º, despite they are also six-coordinated osmium(IV)-azavinylidene species. The structures of the latter resemble those of the hydride-osmium-carbyne derivatives $OsHCl_2(CR)(P^iPr_3)_2$[26] and

[OsH(CR)(NCCH$_3$)$_2$(P^{i}Pr$_3$)$_2$]$^{2+}$.[27] There are also significant differences between the bond lengths in **3** and those previously reported osmium-azavinylidene compounds. Thus, the osmium-azavinylidene distance of 1.880(3) Å (Os-N(1)) in **3** is between 0.11 and 0.05 Å longer than in the previously reported complexes, while the osmium-phosphorous bonds in **3** (Os-P(1) = 2.3476(8) and Os-P(2) = 2.3366(8)) are between 0.14 and 0.07 Å shorter. These facts suggest noticeable differences in the osmium-azavinylidene bonding situation (*vide infra*).

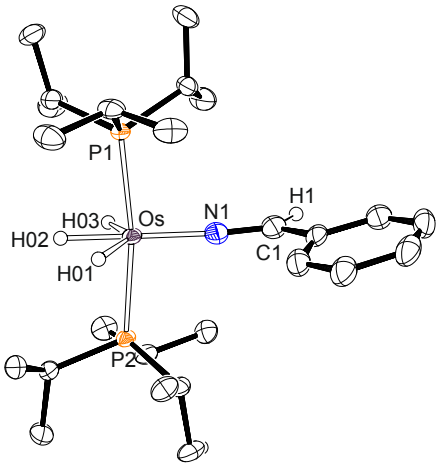


Figure 2. Molecular diagram of complex **3** with 50% probability ellipsoids. Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) for the X-ray and DFT optimized (in square brackets) structures: Os–H(01) = 1.583(10) [1.609], Os–H(02) =1.587(10) [1.676], Os–H(03) = 1.580(10) [1.627], Os–N(1) = 1.880(3) [1.884], Os–P(1) = 2.3476(8) [2.377], Os–P(2) = 2.3366(8) [2.386], N(1)–C(1) = 1.283(5) [1.272]. Selected bond angles (deg) for the X-ray and optimized (in square brackets) structures: P(1)–Os–P(2) = 170.62(3) [174.7], H(01)–Os–H(02) = 57.0(18) [64.1], H(02)–Os–H(03) = 76.0(19) [61.6], N(1)–Os–H(01) = 116.4(14) [123.6], N(1)–Os–H(02) = 172.7(14) [174.8], N(1)–Os–H(03) = 111.0(14) [123.6], Os–N(1)–C(1) = 175.9(3) [169.6].

The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra of **3** and **4** are consistent with the structure shown in Figure 2. In agreement with the presence of three inequivalent hydride ligands in these molecules, the ^{1}H NMR spectra, in benzene-d_6, at room temperature contain three high field resonances between -10.0 and -11.5 ppm. Two of them are broad. This is not surprising since the activation barrier for the rotation of the azavinylidene ligand around the Os-N-C axis in this type of compounds is consistent with a slow process.[14] The signal corresponding to the CH-hydrogen atom of the azavinylidene function is observed at about 5 ppm. In the $^{13}C\{^{1}H\}$ NMR spectra, the resonance due to the C_{sp2}-atom of the azavinylidene moiety appears as a triplet ($^{3}J_{C\text{-}P}$ = 4.1 Hz) at 146.1 ppm for **3** and at 142.0 ppm for **4**. Singlets at about 38 ppm in the $^{31}P\{^{1}H\}$ NMR spectra, corresponding to the equivalent phosphines, are also characteristic features of these complexes.

Mechanism of the Insertion. To gain mechanistic insight about the insertion of the nitriles into one of the Os-H bonds of **1**, we have carried out DFT calculations (B3LYP-D3/SDD/6-31G**) on the reaction with benzonitrile, starting from the tetrahydride $OsH_4(\kappa^1\text{-}N\text{-}N{\equiv}CPh)(P^iPr_3)_2$ (**2t₀**), the benzonitrile counterpart of **2**. The changes in free energy (ΔG) were calculated in toluene at 298.15 K.

The formation of **3** from **2t₀** via a 1,3-hydrogen shift from the metal center to the C_{sp}-atom of the nitrile has an activation energy of 64.4 kcal mol^{-1}, which is not consistent with the experimental observations (see Figure S5). After this finding, we decided to investigate the migration through an $Os(\eta^2\text{-}N{\equiv}CR)$ intermediate (Figure 3).

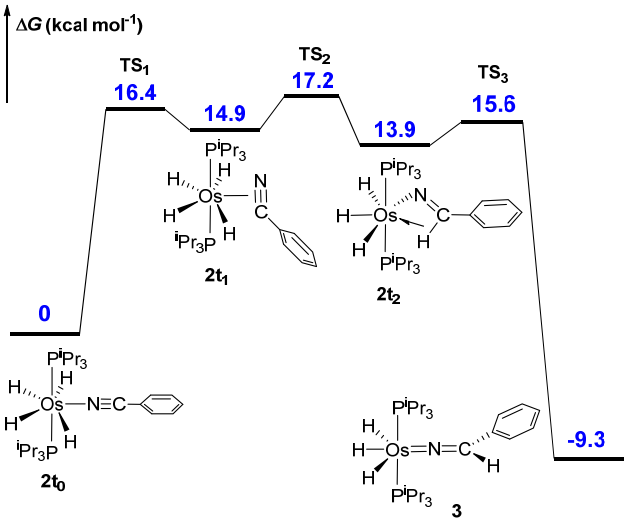
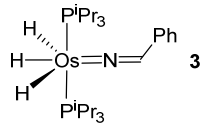
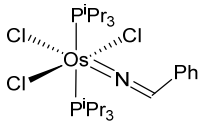
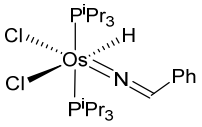


Figure 3. Computed energy profile for the nitrile insertion into one of the Os-H bonds.

First, the isomerization of **2t₀** to afford the η^2-N≡CR derivative $OsH_4(\eta^2\text{-N}\equiv\text{CPh})(P^iPr_3)_2$ (**2t₁**) takes place. This transformation has an activation energy of 16.4 kcal mol^{-1} (**TS₁**) and is endergonic by 14.9 kcal mol^{-1}. The change in the coordination mode gives rise to the elongation of both bonds: C-N, from 1.163 Å in **2t₀** to 1.212 Å in **2t₁**, and Os-N, from 2.080 Å in **2t₀** to 2.236 Å in **2t₁**. The Os-C bond of **2t₁** displays a length of 2.209 Å. The subsequent hydride migration from the metal to the coordinated carbon is the rate determining step for the formation of **3**. It takes place with an activation energy of 17.2 kcal mol^{-1} (**TS₂**); i. e., 0.8 kcal mol^{-1} higher than the previous isomerization. The migration gives rise to the intermediate **2t₂**, which is 1.0 kcal mol^{-1} more stable than **2t₁**. It can be described as a benzylideneamido complex, which saturates the electron deficiency of the metal center with an Os-H-C agostic interaction. The rupture of the latter and the opening of the Os-N-C bond angle from 83.0º to 169.6º finally give the much more stable azavinylidene **3** with a barrier of only 1.7 kcal mol^{-1} (**TS₃**). The computed high exergonicity of the process (-23.2 kcal mol^{-1}) compensates the previous endergonic isomerization step and drives the complete migration reaction forward.

Osmium–Azavinylidene Bonding Situation. The bonding situation in **3** was analyzed and compared with those of the previously reported compounds $OsCl_3(=N=CC_5H_{10})(P^iPr_3)_2$ and $OsHCl_2(=N=CC_5H_{10})(P^iPr_3)_2$[14] by means of the Energy Decomposition Analysis coupled to Natural Orbitals for Chemical Valence method (EDA-NOCV).[28] To this end, we explored the nature of the Os–N bond using two different bonding schemes: the donor-acceptor bonding in their electronic singlet state, with charged fragments ($[OsH_3(P^iPr_3)_2]^+$, $[OsCl_3(P^iPr_3)_2]^+$, $[OsHCl_2(P^iPr_3)_2]^+$ and $[N=CHPh]^-$), and the electron-sharing mixed with donor-acceptor bonding, where the metal fragments ($[OsH_3(P^iPr_3)_2]^\bullet$, $[OsCl_3(P^iPr_3)_2]^\bullet$, and $[OsHCl_2(P^iPr_3)_2]^\bullet$) and the azavinylidene ligand ($[N=CHPh]^\bullet$), were calculated in their doublet state (Table 1). As shown previously, the calculation that gives the smallest orbital term ΔE_{orb} and therefore the smallest change in the electronic structure of the fragments, as a result of the bond formation, indicates the most faithful description of the type of binding.[29] According to the data collected in Table 1,[30] it becomes evident that the donor-acceptor description of the Os–N bond dominates over the mixed electron-sharing/dative bonding in **3**. This situation is markedly different in the related complexes having chloride ligands $OsCl_3(=N=CHPh)(P^iPr_3)_2$ and $OsHCl_2(=N=CHPh)(P^iPr_3)_2$. For them, the mixed electron-sharing/donor-acceptor bonding better describes the Os–N interaction. In this context, it should be mentioned that quantum chemical calculations using density functional theory at the BP86-D3(BJ)/def2-TZVPP level of theory have previously revealed that electrophilic carbyne ligands also engage in a mixture of dative bonding (σ-donation and π-backdonation) and one electron-sharing π-bond. The EDA-NOCV calculations of nucleophilic carbynes using open-shell species in their quartet electronic state gave similar ΔE_{orb} values as neutral fragments in their electronic doublet state.[31]

Table 1. Results of the EDA-NOCV computed at the ZORA-BP86-D3/TZ2P//BP86-D3/def2-SVP Level. Energy values are given in kcal mol^{-1}.

	 **3**					
	Donor-acceptor	**Electron-sharing/Donor-acceptor**	**Donor-acceptor**	**Electron-sharing/Donor-acceptor**	**Donor-acceptor**	**Electron-sharing/Donor-acceptor**
Fragments	$[Os]^+$ $[N=CHPh]^-$	$[Os]^\bullet$ (d) $[N=CHPh]^\bullet$(d)	$[Os]^+$ $[N=CHPh]^-$	$[Os]^\bullet$ (d) $[N=CHPh]^\bullet$(d)	$[Os]^+$ $[N=CHPh]^-$	$[Os]^\bullet$ (d) $[N=CHPh]^\bullet$(d)
ΔE_{int}	-202.2	-112.0	-251.1	-104.4	-258.5	-117.4
ΔE_{Pauli}	244.2	210.0	350.1	285.2	347.1	293.6
ΔE_{elstat}[a]	-277.4 (62.2)	-145.9 (45.3)	-333.8 (55.5)	-188.8 (48.5)	-313.0 (52.4)	-189.5 (46.1)
ΔE_{orb}[a]	-154.7 (34.6)	-161.9 (50.3)	-251.2 (41.8)	-184.5 (47.4)	-268.9 (45.0)	-205.8 (50.1)
ΔE_{disp}[a]	-14.3 (3.2)	-14.3 (4.4)	-16.2 (2.7)	-16.2 (4.1)	-15.7 (2.6)	-15.7 (3.8)
$\Delta E_{orb}(\rho_1)$[b]	-50.9 (32.9)	-81.9 (50.6)	-104.5 (41.6)	-67.5 (36.6)	-127.0 (47.2)	-92.5 (44.9)
$\Delta E_{orb}(\rho_2)$[b]	-27.7 (17.9)	-28.5 (17.6)	-33.1 (13.2)	-36.5 (19.8)	-35.0 (13.5)	-37.6 (18.3)
$\Delta E_{orb}(\rho_3)$[b]	-47.0 (30.4)	-36.9 (22.8)	-75.2 (29.9)	-63.3 (34.4)	-69.5 (7.9)	-57.3 (27.9)
ΔE_{orb}(rest)[b]	-29.1 (18.8)	-14.6 (9.0)	-38.4 (15.3)	-17.0 (9.2)	-37.4 (13.9)	-18.4 (8.9)

[a]The values in parentheses indicate the percentage to the total attractive interaction energy: $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$. [b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

The partitioning of the ΔE_{orb} term by means of the NOCV method indicates that in **3** there are three main orbital interactions between the metal fragment and the azavinylidene ligand, which dominate the total orbital attractions (see Table 1). As depicted in Figure 4, $\Delta E(\rho_1)$ and $\Delta E(\rho_3)$ correspond to the donation of electron density from two nitrogen lone-pairs to the transition metal fragment, π(in plane)-donation and σ-donation, respectively, whereas $\Delta E(\rho_2)$ corresponds to the π-backdonation from the transition metal to the π^*(N=C) molecular orbital. As shown in Figure 4 and Table 1, this π-backdonation orbital interaction is significantly weaker than the in-plane (i.e. σ-bonding and π-donation) interactions, the latter contributing in rather similar extent.

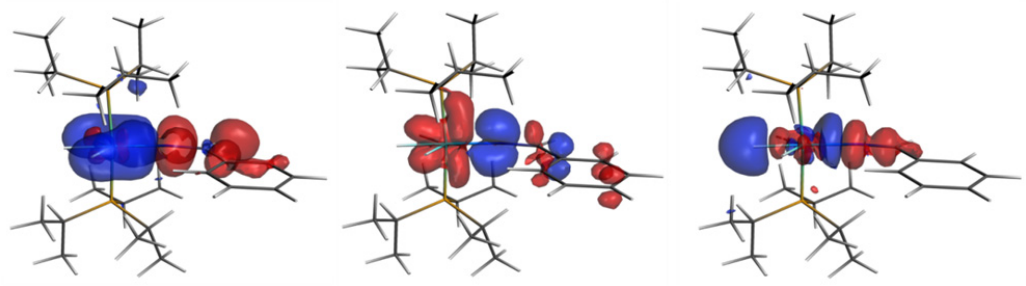
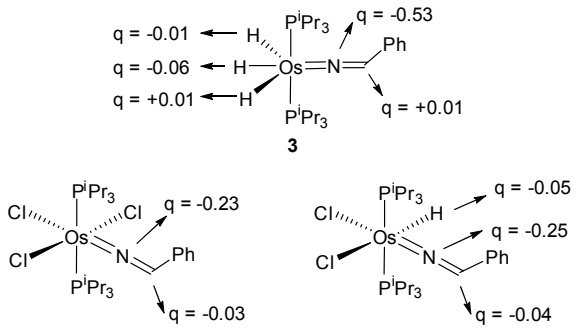


Figure 4. Deformation densities Δρ associated with the strongest pairwise orbital interactions for the Os–N bond in compound **3**. The direction of the charge flow is red→blue.

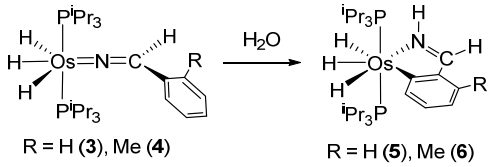
The differences in the osmium-azavinylidene bonding situation are also reflected in the charges on the atoms of the C=N bond and in the hydride ligands (Chart 2). The N atom of the azavinylidene ligand of **3** supports a negative charge which is about twice those on the N atom of the chloride derivatives. On the other hand, while the C atom of the azavinylidene of **3** is slightly positive, those of the chloride counterparts are slightly negative. Interestingly, one of the hydride ligands of the trihydride is slightly positive, whereas the other two and that of the hydride-osmium-dichloride complex are slightly negative.

Chart 2. Computed (BP86-D3/def2-SVP level) NBO Partial Charges



Imine Formation. Azavinylide complexes **3** and **4** are stable in tetrahydrofuran, at 80 ºC, for at least 24 h. Under the same conditions, in toluene, they evolve into the orthometalated phenylmethanimine derivatives $OsH_3\{\kappa^2\text{-}N,C\text{-}(NH{=}CHC_6H_3R)\}(P^iPr_3)_2$ (R = H (**5**), Me (**6**)) in a 25%. The transformation is quantitative in the presence of 1.0 equiv of water, after 2 h in tetrahydrofuran and after 10 min in toluene (Scheme 5). The participation of water in the isomerization process was confirmed by means of the reaction of **3** with D_2O in tetrahydrofuran, which affords selectively and quantitatively $OsH_3\{\kappa^2\text{-}N,C\text{-}(ND{=}CHC_6H_4)\}(P^iPr_3)_2$ (**5-*d***).

Scheme 5. Azavinilydene Isomerization: Formation of Orthometalated Aldimines



R = H (**3**), Me (**4**) R = H (**5**), Me (**6**)

Complexes **5** and **6** were isolated as red solids in 86% and 80% yield, respectively. The isomerization of their precursors was confirmed by means of the X-ray diffraction analysis of the structure of **5**. Figure 5 shows a view of the molecule. The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphines in axial positions (P(1)-Os-P(2) = 165.12(4)º). The hydride ligands and the chelate group (N(1)-Os-C(1) = 74.74(16)º) lie in the perpendicular plane to the P-Os-P axis. The Os-N(1) and Os-C(1) bond lengths of 2.121(4) and 2.123(5) Å are consistent with single bonds, whereas the N(1)-C(7) distance of 1.298(6) Å supports a double bond. All of them compare well with those previously reported for other osmium compounds bearing orthometalated imines.[24,32]

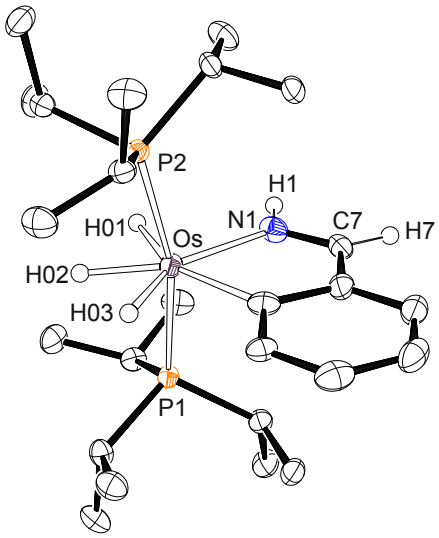


Figure 5. Molecular diagram of complex **5** with 50% probability ellipsoids. Hydrogen atoms (except hydrides and those of the NH=CH unit) are omitted for clarity. Selected bond lengths (Å) for the X-ray and DFT optimized (in square brackets) structures: Os–H(01) = 1.590(10) [1.666], Os–H(02) =1.585(10) [1.627], Os–H(03) = 1.571(10) [1.615], Os–P(1) = 2.3400(10) [2.375], Os–P(2) = 2.3357(10) [2.379], Os–N(1) = 2.121(4) [2.154], Os–C1 = 2.123(5) [2.146], N(1)–C7 = 1.298(6) [1.301]. Selected bond angles (deg) for the X-ray and optimized (in square brackets) structures: P(1)–Os)–P(2) = 165.12(4) [169.0], H(01)–Os–H(02) = 66(2) [64.7], H(02)–Os–H(03) = 64(2) [62.4], and N(1)–Os–C(1) = 74.74(16) [74.6].

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **5** and **6** are consistent with the structure shown in Figure 5. According to the presence of three inequivalent hydride ligands in these molecules, their ^{1}H NMR spectra in toluene-*d*$_{8}$, at 198 K, contain three high field resonances at -7.44, -10.44 and -11.06 ppm for **5** and -7.44, -9.91 and -10.82 ppm for **6**. In the low field region of the spectra, the most noticeable features are the NH- and CH-imine signals, which appear at 9.88 and 8.06 for of **5** and at 9.97 and 8.41 ppm for **6**, respectively. In the ^{13}C{^{1}H} NMR spectra, the signal corresponding to the metalated phenyl carbon atom is observed at 193.4 ppm for **5** and at

194.9 ppm for **6**, whereas the imine-C resonance appears at 171.7 ppm for **5** and at 169.0 ppm for **6**. Both signals display triplets with $^{2}J_{C\text{-}P}$ coupling constants of about 6 Hz and $^{3}J_{C\text{-}P}$ coupling constants of about 3 Hz, respectively. The $^{31}P\{^{1}H\}$ NMR spectra show singlets at about 26 ppm for the equivalent phosphines.

Mechanism of the Isomerization. The formation of **5** and **6** as the result of the isomerization of the respective azavinylidene precursors **3** and **4** involves the electrophilic hydride migration from the metal center to the nucleophilic N atom of the azavinylidene group to afford unsaturated dihydride-osmium-aldimine intermediates, which evolve by oxidative addition of an *ortho*-CH bond of the phenyl substituent of the aldimine. According to the generation of **5-*d***, the hydride migration is promoted by water, which acts as a proton shuttle. In order to confirm this and to understand the intimate details of the process, we carried out DFT calculations (B3LYP-D3/SDD/6-31G**). The changes in free energy (ΔG) were computed in toluene at room temperature. We firstly studied the process without water participation to subsequently compare the results with those obtained in the presence of water.

Figure 6 summarizes the energy profile of the isomerization in the absence of water. The direct migration of the hydride to the nitrogen atom takes place through the expected three-center transition state **TS4** with an activation energy of 31.4 kcal mol^{-1}, which is indeed high. The migration gives rise to the dihydride-osmium-aldimine intermediate **3t1**, which is 13.6 kcal mol^{-1} less stable than the starting azavinylidene complex. Intermediate **3t1** saturates the metal center by means of an agostic interaction between the latter and an *ortho*-CH bond of the phenyl substituent of the imine. The agostic interaction is supported by the computed Os-H, Os-C, and C-H distances of 1.822, 2.355, and 1.169 Å, respectively, which compare well with those reported for Os-H-C agostic interactions characterized by X-ray diffraction analysis.[18c,33] The

rupture of the coordinated C-H bond takes place with an activation energy of 2.5 kcal mol^{-1} (**TS$_5$**) and affords the reaction product.

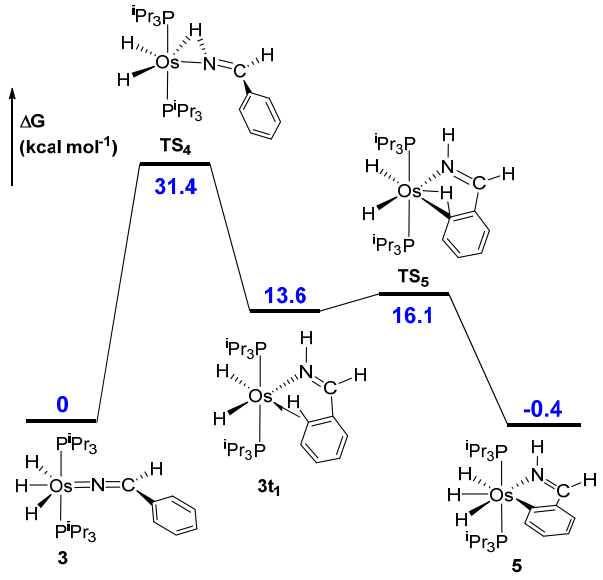


Figure 6. Computed energy profile for the isomerization of **3** into **5**.

The proton shuttle, formed by three water molecules consecutively associated by means of hydrogen bonds, significantly reduces the barrier for the hydride migration to 19.6 kcal mol^{-1} when the central water molecule coordinates to the osmium atom (Figure 7). The coordination has an activation energy of 5.6 kcal mol^{-1} (**TS$_6$**) and affords the intermediate **3t$_2$**, which bears a hydrogen atom of another water molecule in close proximity to the N-atom and the oxygen atom of the third water molecule close to the electrophilic hydride. After the coordination, the hydride migration assisted by the shuttle takes place in two stages. Although a concerted migration in one step also displays a lower barrier than in the absence of water (28.7 vs 31.4 kcal mol^{-1}), this reduction is significantly smaller (2.4 vs 11.8 kcal mol^{-1}). The first stage involves the concerted transfer of a hydrogen atom from the coordinated water molecule to the N-atom, assisted by the closest water molecule to this atom. The process has a very low activation energy of only 0.1

kcal mol^{-1} (**TS$_7$**) and generates the hydroxo-osmium-imine intermediate **3t$_3$**, where the hydroxo ligand is stabilized by means of hydrogen bonds between the latter and the water molecules at the ends of the carrier. Intermediate **3t$_3$** is 3.3 kcal. mol^{-1} more stable than the initial system formed by the azavinylidene complex **3** and three water molecules. The second stage is the regeneration of the coordinated water molecule as a result of the concerted migration of the electrophilic hydride to the hydroxo group via the water molecule close to that hydride, to give the aquo dihydride-osmium-imine intermediate **3t$_4$**. Its activation energy of 22.9 kcal mol^{-1} (**TS$_8$**) is the highest of the entire process. The dissociation of the water molecule from the metal center leads to the dihydride-osmium-imine derivative **3t$_1$**, surrounded by three water molecules, which finally gives **5**. This dissociation occurs with a low barrier of 2.8 kcal mol^{-1} (**TS$_9$**).

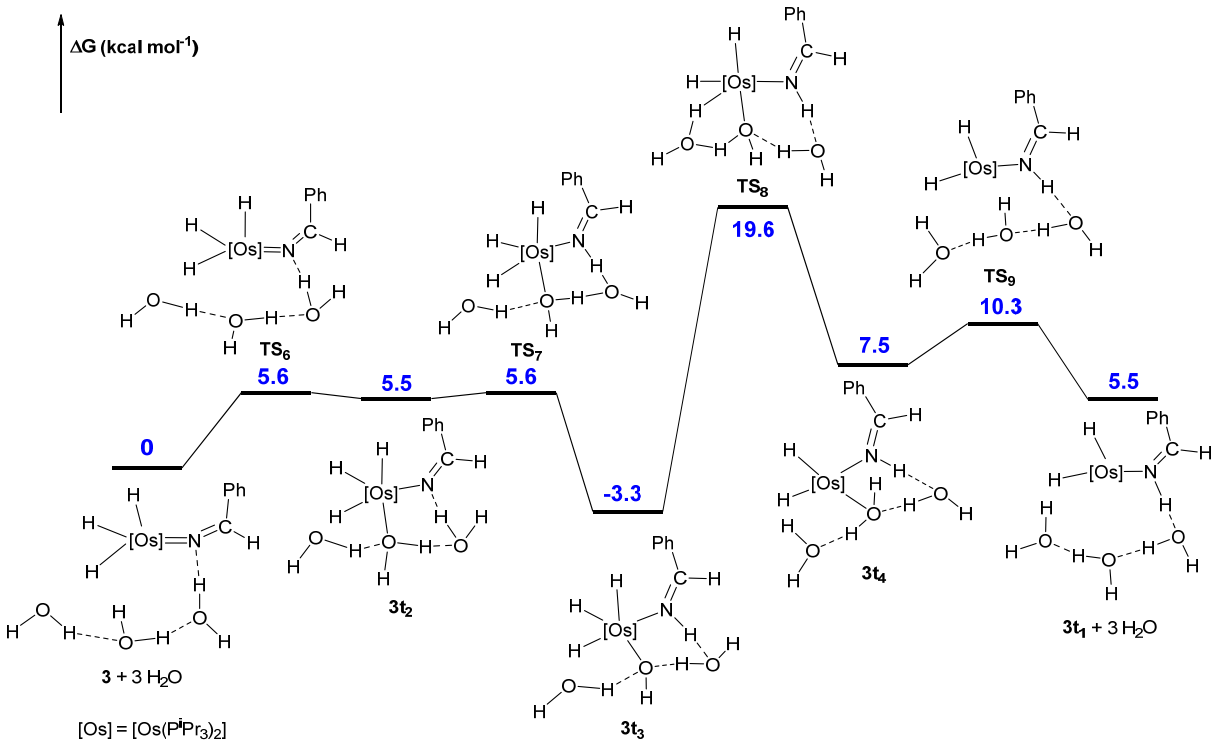


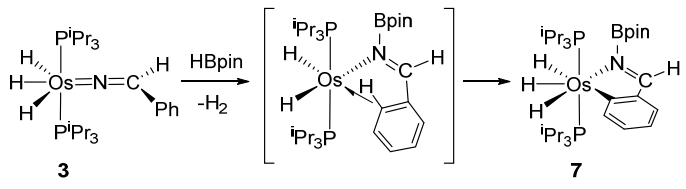
Figure 7. Computed energy profile for the water-assisted hydride migration.

Dual Electrophilic and Nucleophilic Character of the Trihydride-Osmium-Azavinylidene Complexes. Complexes **3** and **4** bear an electrophilic hydride and a nucleophilic N-atom. They are therefore combinations of a Lewis acid and a Lewis base that are kinetically deterred from the imine formation and in this way prevent the evolution of **3** and **4** into the orthometalated aldimine derivatives **5** and **6** (Figure 6).

The presence of both centers in **3** and **4** should grant reactivity of frustrated Lewis pair to these compounds. Since the most noticeable characteristic of a frustrated Lewis pair is their ability to activate σ-bonds,[34,35] we decided to study the reactions of **3** with pinacolborane (HBpin) and molecular hydrogen, in order to confirm such character.

The results prove what expected. The pair formed by the electrophilic hydride and the nitrogen atom of the azavinylidene produces the heterolytic rupture of the sigma H-B bond of the borane in toluene, at 80 ºC. The reaction affords molecular hydrogen and a dihydride-osmium-aldimime species, which undergo the oxidative addition of an *ortho*-CH bond of the phenyl substituent of the imine to give to $OsH_3\{\kappa^2\text{-}N,C\text{-}[N(Bpin)=CHC_6H_4]\}(P^iPr_3)_2$ (**7** in Scheme 6). In agreement with the formation of **7**, complex **3** isomerizes into **5** under 1 atm of H_2.

Scheme 6. **Reaction of 3 with HBpin**



3 **7**

The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra of **7**, in toluene-*d*$_8$, agree well with those of **5** and **6**. Thus, at 183 K, the ^1H NMR spectrum shows the hydride resonances at -6.25, -10.60, and -11.10

ppm whereas the signal due to the imine CH-hydrogen is observed at 9.49 ppm. In the $^{13}C\{^{1}H\}$ NMR spectrum, the resonances corresponding to the metalated and imine C-atoms appear at 204.0 ($^{2}J_{C\text{-}P}$ = 5.6 Hz) and 181.1 ($^{3}J_{C\text{-}P}$ = 3.3 Hz) ppm. The $^{31}P\{^{1}H\}$ NMR spectrum displays a singlet at 26.0 ppm for the equivalent phosphines. A broad signal at 26 ppm, in the $^{11}B\{^{1}H\}$ NMR spectrum, due to the Bpin substituent attached to N-atom is other feature of this species.

CONCLUDING REMARKS

This study shows the reduction of the C-N triple bond of benzonitriles promoted by the hexahydride $OsH_6(P^iPr_3)_2$ and the subsequent orthometalation of the resulting phenyl-aldimines. Furthermore, it analyzes the intimate details of the transfer processes of the two hydride ligands from the metal center to the atoms involved in the triple bond.

The insertion of the substrates into one of the Os-H bond of the polyhydride takes place via an Os(η^2-N≡CR) intermediate in spite that the κ^1-coordination of the nitriles leads to more stable species. The hydride migration to the C-atom of the coordinated triple bond generates novel trihydride-osmium-azavinylidene complexes, which show significant differences in structure and reactivity with the scarce compounds of this class previously reported. The EDA-NOCV analysis has revealed that, in contrast to the previously reported hydride-osmium-azavinylidene and hydride-osmium-carbyne complexes, the donor-acceptor nature of the osmium-azavinylidene bond dominates over the electron-sharing bonding. The N atom of the azavinylidene, strongly nucleophilic, supports a negative charge which is about twice as high as those on the N atoms of the azavinylidenes coordinated to other osmium fragments. Furthermore, one of the three hydrides of the metal fragment is electrophilic, supporting a slightly positive charge.

The migration of the electrophilic hydride to the N atom of the azavinylidene is kinetically prevented in spite of the different nature of both centers. However, water acts as a proton shuttle by significantly decreasing the activation barrier for the migration of the electrophilic hydride. Thus in the presence of water the trihydride-osmium-azavinylidene complexes evolve into dihydride-osmium-phenylaldimines species, which finally undergo orthometalation. The presence of both electrophilic and nucleophilic centers in the trihydride-osmium-azavinylidene compounds confers them reactivity of frustrated Lewis pairs as confirmed by the observed activation of σ-bonds including molecular hydrogen and boranes.

In summary, the insertion of benzonitriles into an Os-H bond of $OsH_6(P^iPr_3)_2$, via Os(η^2-N≡CR) intermediates, leads to trihydride-osmium-azavinylidene complexes bearing an electrophilic hydride and a nucleophilic N atom. These centers, which are kinetically deterred from the imine formation, confer them the ability to heterolytically activate sigma bonds. The use of water as a proton shuttle allows the migration of the electrophilic hydride to the N atom to afford the phenylaldimine, which subsequently undergoes orthometalation.

EXPERIMENTAL SECTION

All manipulations were performed under argon using standard Schlenk-tube or glovebox techniques and dried solvents. All reactions were carried out in Schlenk flasks equipped with a Teflon stopcock. Benzonitrile and *o*-tolunitrile were dried over CaH_2 and distilled prior to use. 2,6-Dimethylbenzonitrile and pinacolborane (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane) were purchased from commercial sources and used without further purification. Complex $OsH_6(P^iPr_3)_2$ (**1**) was prepared according to the published method.[36] Instrumental methods used for characterization, X-ray information, and computational details are given in the Supporting Information. Chemical shifts (in ppm) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$),

external H_3PO_4 ($^{31}P\{^1H\}$), or $BF_3{\cdot}OEt_2$ (^{11}B). Coupling constants, *J*, and *N* ($N = {}^3J_{H\text{-}P} + {}^5J_{H\text{-}P'}$ for ^1H or $^1J_{C\text{-}P} + {}^3J_{C\text{-}P'}$ for ^{13}C) are given in Hertz.

Preparation of $OsH_4\{\kappa^1\text{-}N\text{-}(N{\equiv}CC_6H_4Me_2)\}(P^iPr_3)_2$ (2). 2,6-dimethylbenzonitrile (52.4 mg, 0.4 mmol) was added to a solution of **1** (200 mg, 0.4 mmol) in 3 mL of toluene and it was heated at 120 ºC for 3 days. After cooling at room temperature, the solvent was removed under reduced pressure to afford a dark orange oil. The oil was dissolved in pentane and concentrated to dryness several times (4 x 2 mL) until it afforded an orange solid that was washed at -78 ºC with further portions of pentane (2 x 2 mL) and dried in vacuo. Dark orange single crystals suitable for X-ray diffraction analysis were grown from a solution of **2** in pentane at -30 ºC. Yield: 182 mg (70%). Anal. Calcd for $C_{27}H_{55}NOsP_2$: C, 50.21; H, 8.58; N, 2.17. Found: C, 50.62; H, 8.42; N, 1.89. IR (ATR, cm^{-1}): *ν*(CN) 2360, *ν*(Os–H) 1740. ^1H NMR (300.13 MHz, THF-d_8, 298 K): δ 7.28 (m, 1H, CH_{Ar}), 7.11 (m, 2H, CH_{Ar}), 2.43 (s, 6H, $C_{Ar}CH_3$), 1.92 (m, 6H, CH ^{i}Pr), 1.21 (dvt, $^3J_{H\text{-}H}$ = 7.0, *N* =12.4, 36H, CH_3 ^{i}Pr$_3$), -9.90 (t, $^3J_{H\text{-}P}$ = 13.4, 4H, OsH_4). $^{31}P\{^1H\}$ NMR (121.4 MHz, THF-d_8, 298 K): δ 44.2 (s). $^{13}C\{^1H\}$ APT NMR (75.48 MHz, THF-d_8, 298 K): δ 140.2 (s, $C_q^{2,6}$ Ar), 129.8 (s, C^4H_{Ar}), 126.3 (s, $C^{3,5}H_{Ar}$), 122.9 (s, C_q^1 Ar), 113.0 (s, CN), 25.9 (vt, *N* = 23.8, CH ^{i}Pr), 18.7 (s, CH_3 ^{i}Pr and $C_{Ar}CH_3$). $T_{1\,(min)}$ (OsH_4, 400 MHz, C_7D_8, 203 K): 190 ± 3 ms.

Preparation of $OsH_3(=N{=}CHPh)(P^iPr_3)_2$ (3). Benzonitrile (41.2 μL, 0.4 mmol) was added to a solution of **1** (200 mg, 0.4 mmol) in 3 mL of toluene. The resulting solution was heated at 80 ºC for 15 min.[37] The reaction crude was concentrated to dryness under reduced pressure giving a dark yellow oil. The addition of pentane (2 mL) at -78 ºC afforded a yellow solid which was washed with further portions of pentane (2 x 2 mL) and dried in vacuo. Yield: 200 mg (81%). Orange single crystals suitable for X-ray diffraction analysis were grown from a solution of **1** in pentane at -30 ºC. Anal. Calcd for $C_{25}H_{51}NOsP_2$: C, 48.60; H, 8.32; N, 2.27. Found: C, 48.93; H,

8.64; N, 2.30. IR (ATR, cm^{-1}): ν(Os–H) 2113, 2097, 1977. ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.52 (m, 2H, *o*-CH Ph), 7.26 (m, 2H, *m*-CH Ph), 6.96 (m, 1H, *p*-CH Ph), 4.70 (br, 1H, NCH), 1.95 (m, 6H, CH ^{i}Pr), 1.18 (m, 36H, CH_3 ^{i}Pr), -10.56 (br, 1H, OsH), -11.10 (br, 1H, OsH), -11.41 (br t, $^{3}J_{H\text{-}P}$ = 13.1, 1H, OsH). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 37.9 (s). $^{13}C\{^{1}H\}$ APT NMR (75.48 MHz, C_6D_6, 298 K): δ 146.1 (t, $^{3}J_{C\text{-}P}$ = 4.1, NCH), 130.7 (s, C_q Ph), 128.0 (s, *m*-CH Ph), 126.7 (s, *p*-CH Ph), 125.0 (s, *o*-CH Ph), 26.8 (vt, *N* = 25.2, CH ^{i}Pr), 20.4, 20.3 (both s, CH_3 ^{i}Pr).

Preparation of $OsH_3(=N=CHC_6H_4Me)(P^iPr_3)_2$ (4). The same procedure described for **3** was followed starting from *o*-tolunitrile (23.7 μL, 0.2 mmol) and **1** (100 mg, 0.2 mmol). A yellow solid was obtained. Yield: 42 mg (33%).[38] Anal. Calcd for $C_{26}H_{53}NOsP_2$: C, 49.42; H, 8.45; N, 2.22. Found: C, 49.78; H, 8.03; N, 2.32. ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.19 (m, 1H, CH_{Ar}), 7.34 (m, 1H, CH_{Ar}), 6.98-6.99 (m, 2H, CH_{Ar}), 4.89 (br, 1H, NCH), 2.26 (s, 3H, $C_{Ar}CH_3$), 1.97 (m, 6H, CH ^{i}Pr), 1.19 (m, 36H, CH_3 ^{i}Pr), -10.33 (br, 1H, OsH), -11.05 (br, 1H, OsH), -11.20 (br t, $^{3}J_{H\text{-}P}$ = 13.0, 1H, OsH). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 37.7 (s). $^{13}C\{^{1}H\}$ APT NMR (75.48 MHz, C_6D_6, 298 K): δ 142.0 (t, $^{3}J_{C\text{-}P}$ = 4.1, NCH), 132.4 (s, C_q Ar), 130.3 (s, CH_{Ar}), 127.9 (s, C_q Ar), 126.1, 125.5, 125.4 (all s, CH_{Ar}), 26.9 (vt, *N* = 25.2, CH ^{i}Pr), 20.4 (s, CH_3 ^{i}Pr), 18.4 (s, $C_{Ar}CH_3$).

Preparation of $OsH_3\{\kappa^2\text{-}C,N\text{-}(NH=CHC_6H_4)\}(P^iPr_3)_2$ (5). Water (1.4 μL, 0.08 mmol) was added to a solution of **3** (50 mg, 0.08 mmol) in 2 mL of tetrahydrofuran and was heated at 80 ºC for 2 h. After cooling at room temperature, the solvent was removed under reduced pressure to afford a red oil. The addition of pentane (2 mL) at -78 ºC afforded a red solid that was dried in vacuo. Yield: 43 mg (86%). Red single crystals suitable for X-ray diffraction analysis were grown from a solution of **5** in pentane at -30 ºC. Anal. Calcd for $C_{25}H_{51}NOsP_2$: C, 48.60; H,

8.32; N, 2.27. Found: C, 48.84; H, 8.63; N, 2.16. IR (ATR, cm^{-1}): *ν*(N–H) 3345, *ν*(Os–H) 2163, 2124, 1941. ^{1}H NMR (300.13 MHz, C_7D_8, 298 K): δ 9.88 (br, 1H, NH), 8.73 (m, 1H, CH_{Ar}), 8.06 (dt, $^{3}J_{H-H}$ = 10.1, $^{4}J_{H-P}$ = 2.2, 1H, CH_{imine}), 7.53 (m, 1H, CH_{Ar}), 6.90 (m, 1H, CH_{Ar}), 6.87 (m, 1H, CH_{Ar}), 6.96-6,87 (m, 2H, CH_{Ar}), 1.73 (m, 6H, CH ^{i}Pr), 0.95 (m, 36H, CH_3 ^{i}Pr), -9,75 (br, 3H, OsH_3). ^{1}H NMR (400.13 MHz, C_7D_8, 193 K): δ 9.58 (br, 1H, NH), 8.97 (m, 1H, CH_{Ar}), 7.97 (br d, $^{3}J_{H-H}$ = 10.1, 1H, CH_{imine}), 7.72 (m, 1H, CH_{Ar}), 7.10 (m, 2H, CH_{Ar}), 1.65 (m, 6H, CH ^{i}Pr), 0.98 (m, 36H, CH_3 $^{i}Pr_3$), -7.44, -10.44, -11.06 (all br, 1H each, OsH_3). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, C_7D_8, 298 K): δ 26.0 (s). $^{13}C\{^{1}H\}$ APT NMR (75.48 MHz, C_7D_8, 298 K): δ 193.4 (t, $^{2}J_{C-P}$ = 5.8, Os–C_{Ar}), 171.7 (t, $^{3}J_{C-P}$ = 2.3, CH_{imine}), 146.5 (s, CH_{Ar}), 144.4 (s, C_q Ar), 128.9, 127.9, 118.1 (all s, CH_{Ar}), 27.3 (vt, *N* = 25.2, CH ^{i}Pr), 19.7, 19.6 (both s, CH_3 ^{i}Pr). $T_{1(min)}$ (ms, OsH, 400 MHz, C_7D_8, 223 K): 88 ± 5 (−7.48 ppm), 130 ± 5 (−10.01 ppm), 105 ± 5 (−10.89 ppm).

Formation of $OsH_3\{\kappa^2$-*C*,*N*-(ND=CHC_6H_4)}($P^{i}Pr_3$)$_2$ (5-*d*). Two NMR tubes were charged with **3** (31 mg, 0.05 mmol) and 0.5 mL of THF (tube A) or 0.5 mL of THF-d_8 (tube B), respectively. D_2O (0.9 μL, 0.05 mmol) was added to both NMR tubes and then they were heated at 80 ºC for 2 h. Spectroscopic data for tube A: ^{2}H NMR (46.07 MHz, THF, 298 K): δ 11.45 (br, 1H, ND). Tube B: the ^{1}H NMR (300.13 MHz, THF-d_8, 298 K) data were identical to those reported for **5** with the exception of signal at δ 8.63 (imine CH), which appears as a s instead of a d, and the intensity of the signal at δ 11.45 (0.1H, NH).

Preparation of $OsH_3\{(\kappa^2$-*C*,*N*-(NH=CHC_6H_3Me)}($P^{i}Pr_3$)$_2$ (6). The same procedure described for **5** was followed starting from **4** (50 mg, 0.08 mmol). A red solid was obtained. Yield: 40 mg (80%). Anal. Calcd for $C_{26}H_{53}NOsP_2$: C, 49.42; H, 8.45; N, 2.22. Found: C, 49.73; H, 7.98; N, 2.29. IR (ATR, cm^{-1}): *ν* (N–H) 3345, *ν* (Os–H) 2163, 2123, 1941. ^{1}H NMR (300.13 MHz, C_6D_6,

298 K): δ 9.97 (br, 1H, NH), 8.71 (m, 1H, CH_{Ar}), 8.41 ($^3J_{H-H}$ = 10.5, 1H, CH_{imine}), 6.92 (m, 1H, CH_{Ar}), 6.72 (m, 1H, CH_{Ar}), 2.48 (s, 3H, $C_{Ar}CH_3$), 1.80 (m, 6H, CH ^{i}Pr), 1.00 (m, 36H, CH_3 ^{i}Pr$_3$), -9,34 (br, 3H, OsH_3). ^{1}H NMR (400.13 MHz, C_7D_8, 193 K): δ 9.75 (br, 1H, NH), 8.92 (m, 1H, CH_{Ar}), 8.17 (m, 1H, CH_{imine}), 7.10 (m, 1H, CH_{Ar}), 6.86 (m, 1H, CH_{Ar}), 2.68 (s, 3H, $C_{Ar}CH_3$), 1.73 (m, 6H, CH ^{i}Pr), 1.05 (m, 36H, CH_3 ^{i}Pr$_3$), -7.44, -9.91, -10.82 (all br, 1H each, OsH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_7, 298 K): δ 26.3 (s). $^{13}C\{^1H\}$ APT NMR (75.48 MHz, C_6D_6, 298 K): δ 194.9 (t, $^2J_{C-P}$ = 5.6, Os–C_{Ar}), 169.0 (t, $^3J_{C-P}$ = 2.6, CH_{imine}), 145.0 (s, CH_{Ar}), 143.2 (s, C_q Ar), 137.4 (s, $C_{Ar}CH_3$), 128.7 (CH_{Ar}), 119.8 (s, CH_{Ar}), 27.4 (vt, N = 25.2, CH ^{i}Pr), 20.3 (s, $C_{Ar}CH_3$), 19.8, 19.8 (both, s, CH_3 ^{i}Pr).

Preparation of $OsH_3\{\kappa^2$-N,C-[N(Bpin)=CHPh]$\}(P^iPr_3)_2$ (7) Pinacolborane (4.5 μL, 0.045 mmol) was added to a solution of **3** (20 mg, 0.03 mmol) in 0.5 mL of toluene-d_8 and it was heated at 80 ºC for 18 h. After this time, the NMR spectra showed quantitative formation of **7**; however, all attempts to isolate this compound as a solid were unsuccessful due to partial hydrolysis of the B-N bond. ^{1}H NMR (400.13 MHz, C_7D_8, 298 K): δ 9.32 (s, 1H, CH_{imine}), 8.79 (m, 1H, CH_{arom}), 7.73 (m, 1H, CH_{arom}), 6.92 (m, 1H, CH_{arom}), 6.85 (m, 1H, CH_{arom}), 1.95 (m, 6H, CH ^{i}Pr), 1.21 (s, 12H, CH_3 Bpin), 1.06 (m, 36H, CH_3 ^{i}Pr$_3$), -8.82 (br, 2H, OsH), -10.92 (br, 1H, OsH). ^{1}H NMR (400.13 MHz, C_7D_8, 183 K): δ 9.49 (s, 1H, CH_{imine}), 8.93 (m, 1H, CH_{arom}), 7.72 (m, 1H, CH_{arom}), 7.10 (m, 1H, CH_{arom}), 6.92 (m, 1H, CH_{arom}), 1.76 (m, 6H, CH ^{i}Pr), 1.06 (s, 12H, CH_3 Bpin), 0.99 (m, 36H, CH_3 ^{i}Pr$_3$), -6.25 (br, 1H, OsH), -10.60 (br, 1H, OsH), -11.10 (br, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_7D_8, 298 K): δ 26.0 (s). ^{11}B NMR (128.38 MHz, C_7D_8, 298 K): δ 26 (br). $^{13}C\{^1H\}$ APT NMR (75.48 MHz, C_7D_8, 298 K): δ 204.0 (t, $^2J_{C-P}$ = 5.6, Os–C_{Ar}), 181.1 (t, $^3J_{C-P}$ = 3.3, CH_{imine}), 147.3 (s, C_q Ar), 146.1, 131.9, 128.4, 118.1 (all s, CH_{Ar}), 83.3 (s, C_q Bpin), 27.5 (vt, N = 24.2, CH ^{i}Pr), 24.5 (s, CH_3 Bpin), 20.1, 19.9 (both s, CH_3 ^{i}Pr).

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

General information, crystallographic data, computational details, NMR and IR spectra (PDF)

Cartesian coordinates of calculated structures (XYZ)

Accession Codes

CCDC 1907065-1907067 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_ request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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SYNOPSIS

The insertion of benzonitriles into an Os-H bond of $OsH_6(P^iPr_3)_2$, via $Os(\eta^2\text{-}N{\equiv}CR)$ intermediates, leads to trihydride-osmium-azavinylidene complexes bearing an electrophilic hydride and a nucleophilic N atom. These centers, which are kinetically deterred from the imine formation, confer them the ability to heterolytically activate sigma bonds. The use of water as a proton shuttle allows the migration of the electrophilic hydride to the N atom to afford phenylaldimines, which subsequently undergoes orthometalation.

TOC graphic