Osmium-Promoted Transformation of Alkyl Nitriles to Secondary Aliphatic Amines: Scope and Mechanism

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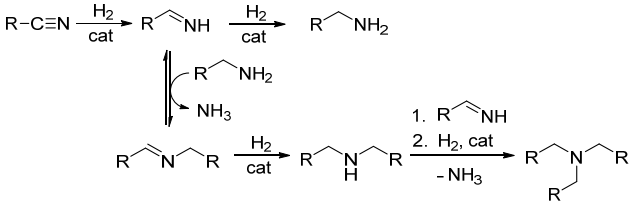
ABSTRACT: The transformation of alkyl nitriles to symmetrical and asymmetrical secondary aliphatic amines promoted by the hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) is described and the mechanisms of the reactions involved are established. Complex **1** catalyzes the above mentioned transformations of aryl-, pyridyl- and alkoxy-functionalized alkyl nitriles of linear or branched chain. The formation of the secondary amines involves primary imines, primary amines, and secondary imines as organic intermediates. The reactions take place under mild conditions (toluene, 100 ºC, and 4 bar of H_2). Stoichiometric reactions of **1** with pivalonitrile and 2-methoxyacetonitrile have allowed us to isolate the trihydride-azavinylide derivatives $OsH_3\{=N=CHR\}(P^iPr_3)_2$ (R = ^{t}Bu (**3**), CH_2OMe (**4**)). Their formation involves the insertion of the N-C triple bond of the substrates into an Os-H bond of the unsaturated tetrahydride $OsH_4(P^iPr_3)_2$ (**A**), which is generated by reductive elimination of H_2 from the hexahydride precursor. The reaction of these trihydride-azavinylidene species with H_2 is the key step for the reduction of the N-C triple bond of the nitriles. In the absence of H_2, the attack of **A** to the azavinylidene ligand produces the rupture of its $C(sp^2)$-$C(sp^3)$ bond. As a consequence of this attack and the presence of primary imines and amines in the reaction media, the binuclear complexes $(P^iPr_3)_2H_4Os(\mu\text{-CN})OsH_3\{\kappa^1\text{-}N\text{-}(NH{=}CHCH_2OMe)\}(P^iPr_3)_2$ (**5**) and $(P^iPr_3)_2H_4Os(\mu\text{-CN})OsH_3\{\kappa^1\text{-}N\text{-}(NH_2CH_2CH_2OMe)\}(P^iPr_3)_2$ (**6**) have been isolated and characterized by X-ray diffraction analysis, for 2-methoxyacetonitrile. DFT calculations reveal noticeable similarities between the hydrogenations of nitriles to primary imines and of primary imines to primary amines.

INTRODUCTION

Aliphatic amines are one of the most relevant organic molecules. The alkyl groups appended to the nitrogen atom control the physical properties of the compounds, which are important for regulating key biological interactions. Thus, aliphatic amines are common among pharmaceutical agents, small-molecules biological probes, and preclinical candidates.[1] Traditional procedures for their production involve N-alkylation of amines and carbonyl reductive amination.[2] The reaction between simple amines and alkyl halides enables the construction of higher order amines. However, despite the great efforts carried out, there is not a general procedure that guarantees high selectivity.[3] Carbonyl reductive amination is the most widely employed alternative to the N-alkylation, but its use generates too many environmental problems.[3,4] As a consequence of these issues, new strategies based on transition-metal catalysis are being developed, including hydroamination, hydroaminoalkylation, $C(sp^3)$-H functionalization, or visible light photoredox catalysis.[5]

Reduction of alkyl nitriles with molecular hydrogen catalyzed by transition metal complexes is other of these new strategies, which represents a "*green*" synthesis of aliphatic amines.[6] As a consequence, a limited number of homogeneous catalysts of Mn,[7] Re,[8] Fe,[9] Ru,[10] Co,[11] Rh,[12] Ir,[13] and Pd[14] have been developed for this reaction. However, it is a scarcely employed procedure due to its several serious drawbacks: somewhat harsh conditions, such as high pressure and elevated temperature,[7-10,11a,c] are generally required as well as the need of additives,[8,9b,11a,b,12] including strong bases.[7,11c] Moreover, the hydrogenation often leads to mixtures of primary, secondary, and tertiary amines, which are generated through hydrogenation-condensation sequences,[8,10a,13] in addition to imine intermediates (Scheme 1).[15]

Scheme 1. Hydrogenation-Condensation Sequences for Nitriles



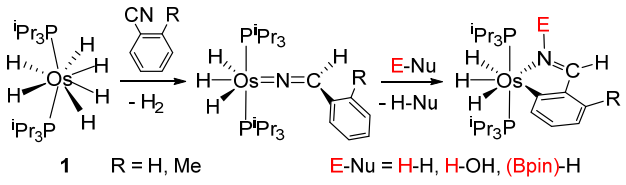
Osmium catalysts have not been employed up to now, for the hydrogenation of nitriles to amines. The use of Os in homogeneous catalysis has been traditionally associated to Sharpless dihydroxylation and reactions akin to that.[16] Nevertheless, it has been also useful in some other processes of organic synthesis,[17] including the reduction of unsaturated C-C and C-O bonds.[18] Most recently, it has been revealed as a particularly promising alternative for reactions related to the hydrogen economy.[18d,19] It is remarkable the catalytic behavior of the hydroxo derivative $[Os(OH)(\eta^6\text{-}p\text{-cymene})IPr][CF_3SO_3]$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene), which has shown to be efficient in the hydrogen transfer from 2-propanol to aldehydes,[20] the α-alkylation of aryl nitriles and methyl ketones,[21] and the hydration of nitriles to amides.[22] Other complexes with good performance are its polyhydrides,

which have shown their ability to dehydrogenate amine boranes[23] and liquid organic hydrogen carriers such as alcohols,[24] cyclic amines,[24c,25] and formic acid.[26]

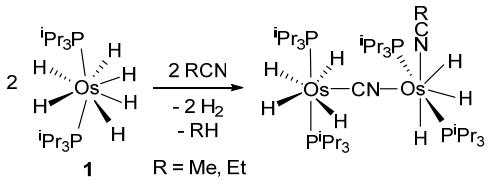
The d^2-hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) occupies a particularly privileged position among the polyhydrides of platinum group metals;[27] its easy synthesis in high yield,[28] its ability to activate σ-bonds of a wide range of molecules[29] including β-lactams[30] and nucleosides,[31] and its use as starting point in the preparation of novel Os(II)-[32] and Os(IV)-phosphorescent[33] emitters turns it into one of the corner stones of the modern stoichiometric chemistry of this element. We now show that is also an efficient and stable catalyst for the selective preparation of symmetrical and asymmetrical secondary amines by means of the hydrogenation of alkyl nitriles, under mild conditions, within reach of the most modest organic chemistry laboratory, without specific equipment for catalysis.

We reported one year ago that complex **1** inserts benzonitriles to afford trihydride-osmium-azavinylidene species. These compounds heterolytically activate σ-bonds, including molecular hydrogen, to give phenylaldimines derivatives, which undergo a strong stabilization by orthometalation (Scheme 2).[34] Previously, we had observed that, in contrast to aromatic nitriles, acetonitrile and propionitrile experience a C(sp)-C(sp^3) bond activation reaction, to release methane and ethane, respectively, and yield the binuclear species $(P^iPr_3)_2H_4Os(\mu\text{-CN})OsH_3(RCN)(P^iPr_3)_2$ (R = Me, Et) bearing a CN bridge (Scheme 3).[35] In the search for understanding the difference in behavior between both classes of nitriles, we deepened into the reactions of the hexahydride with alkyl nitriles, discovering that under hydrogen atmosphere the C-C rupture is inhibited and secondary amines resulting from reactions of reduction-condensation-reduction are selectively formed. This paper reports the first osmium catalyst for the hydrogenation of alkyl nitriles to aliphatic amines, the isolation and full characterization of key intermediates of the reactions, and the mechanism of the reduction.

Scheme 2. Reactions of $OsH_6(P^iPr_3)_2$ with Benzonitriles



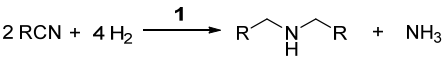
Scheme 3. Reactions of $OsH_6(P^iPr_3)_2$ with Acetonitrile and Propionitrile



RESULTS AND DICUSSION

Reaction Conditions and Scope. We initially tested two very different nitriles such as 2-methoxyacetonitrile and 2-phenylacetonitrile, in order to optimize the necessary amount of catalyst to selectively obtain the secondary amines in high yield, in a general manner. The tests were performed with 0.72 M toluene-d_8 solutions of nitrile, contained in a Fisher-Porter bottle, at 100 ºC, and 4 bar of hydrogen (Table 1). Under these conditions, 2-methoxyacetonitrile is selectively transformed to bis(2-methoxyethyl)amine in 50% yield, after 24 h, in the presence of 2 mol% of complex **1** as catalyst (entry 1). The yield of the reaction increases up to 72% after 14 h (entry 2) and to 99% after 24 h (entry 3) with 5 mol% of catalyst. In the presence of the same amount of complex **1**, diphenethylamine was only obtained in 59% yield after 24 h (entry 4), so the amount of catalyst was incremented until 10 mol%. Under the new conditions, the transformation of 2-phenylacetonitrile into the secondary amine was almost quantitative (entry 5). In view of these results, we decided to work with 10 mol% of catalyst.

Table 1. Optimization for the Catalytic Hydrogenation of Nitriles to Symmetrical Secondary Amines[a]



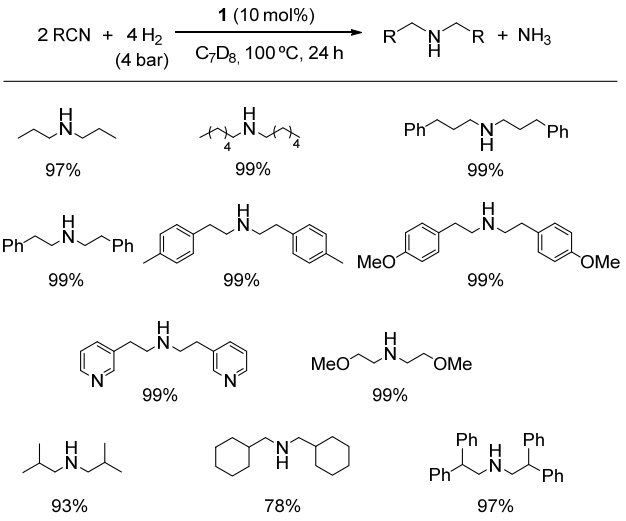
entry	nitrile	**1** (mol%)	H_2 (bar)	time (h)	yield (%)[b]
1	MeO CN	2	4	24	50
2	MeO CN	5	4	14	72
3	MeO CN	5	4	24	99
4	Ph CN	5	4	24	59
5	Ph CN	10	4	24	99

[a]All reactions were carried out in 0.5 mL of C_7D_8 at 100 ºC with 0.36 mmol of nitrile (0.72 M). [b]Yields were determined by ^{1}H NMR spectroscopy using mesitylene as internal standard.

Scheme 4 shows the generated amines under the selected conditions. Complex **1** catalyzes the hydrogenation of alkyl nitriles including substrates of linear chain such as propionitrile and hexanenitrile, aryl-functionalized chain such as 3-phenylpropanenitrile and 2-phenylacetonitriles, and pyridyl- and alkoxy-functionalized chain such as 2-(pyridin-3-yl)acetonitrile and 2-methoxyacetonitrile. In all the cases the corresponding secondary amines were quantitatively formed after 24 h. Although the formation of the amine is sensitive to the steric hindrance of the substituent of the nitrile, complex **1** is also efficient for the transformation of branched chain nitriles such as isobutyronitrile, cyclohexanecarbonitrile, and 2,2-diphenylacetonitrile. With these nitriles, secondary amines were obtained in 78-97% yield after 24 h. Complex **1** also promotes the reduction of pivalonitrile. However, in this case, the reaction displays 65% of secondary imine (2,2-dimethyl-*N*-neopentylpropan-1-imine), 20% of primary imine (2,2-dimethylpropan-1-imine), and 15% of primary amine (2,2-dimethylpropan-1-amine), after 24 h (Figure S34). The composition of the mixture indicates that the steric hindrance of the secondary imine prevents its reduction to the corresponding amine. The only metal species detected by NMR spectros-

copy at the end of the reactions was, in all cases, the hexahydride complex **1**.

Scheme 4. Hydrogenation of Nitriles to Symmetrical Secondary Amines Catalyzed by 1[a]

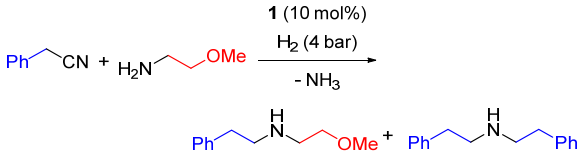


[a]Reaction conditions: nitrile (0.36 mmol), **1** (0.036 mmol; 10 mol%) in 0.5 mL of C_7D_8, 4 bar of H_2, at 100 ºC for 24 h. Yields were determined by ^{1}H NMR spectroscopy using mesitylene as internal standard.

The direct selective formation of secondary aliphatic amines by hydrogenation of nitriles is comparatively less frequent than the formation of primary amines. Sato, Kayaki, and Ikariya have reported that the cationic half-sandwich C,N chelating Rh-complex [Cp*Rh(NCMe){κ^2-*C*,*N*-(NH_2CPh_2-2-C_6H_4)}]SbF_6 also yields secondary amines, in the presence of $AgSbF_6$, under 10 bar of hydrogen,[12b] whereas Berke and coworkers have observed that a Re(I)-nitrosyl compound efficiently catalyzes the hydrogenation of nitriles to secondary amines, but 50 bar of hydrogen and the presence of Et_3SiH as an additional additive, are necessary in this case.[8] High hydrogen pressures (30-60 bar) and the presence of additives ($NaEt_3BH$, NaOEt, or KO^{t}Bu) are typical experimental conditions for catalysts of 3d metals (Mn, Fe, Co),[7,9,11a,c] although Fout and coworkers have observed that a Co(III) complex bearing a C,C,C-pincer ligand is able to exceptionally work under 4 bar of hydrogen, in the presence of $NaEt_3BH$ and KO^{t}Bu.[11b] Furthermore, they lead to primary amines since the hydrogenation of the imine is faster than the amine-imine condensation. Catalysts of platinum group metals need lower pressures. Prechtl and coworkers have reported a Ru(II) catalyst stabilized by a P,N,P-pincer ligand, which acts under 4 bar of hydrogen but the reaction stops in the secondary imines.[10a] Complex $RhH(P^iPr_3)_3$ reduces aromatic and aliphatic nitriles to primary amines under ambient conditions.[12a]

The ability of **1** to hydrogenate imines at slower rate than that of the imine-amine condensation should allow us to generate asymmetrical secondary amines by introducing an external primary amine in the reaction medium. This catalysis, which has been scarcely explored,[10c] is a promising alternative to the hydroamination of alkenes and alkynes that avoids the regioselectivity problems of these additions and the use of a second catalyst for the reduction of the secondary imines resulting from the N-H addition to a C-C triple bond.[36] According to this, once examined the ability of **1** to promote the selective formation of symmetrical secondary aliphatic amines, we decided to study its capacity to generate asymmetrical secondary aliphatic amines. Firstly, we studied the hydrogenation of 2-phenylacetonitrile in the presence of 2-methoxyethan-1-amine, under our standard conditions, in order to optimize the necessary amount of external amine, to selectively obtain the asymmetrical secondary amines in high yields (Table 2). When the reaction was performed using a nitrile:amine 1.0:1.0 molar ratio, the symmetrical secondary amine was the major reaction product, 82% (entry 1). However, the selectivity was reversed when nitrile:amine 1.0:2.5 and 1.0:5.0 molar ratios were used. Under these conditions, 2-methoxy-*N*-phenethylethan-1-amine was quantitatively formed (entries 2 and 3). In view of these results, we decided to perform the hydrogenations in the presence of 2.5 equiv of external amine.

Table 2. Optimization for the Catalytic Hydrogenation of Nitriles to Asymmetrical Secondary Amines[a]

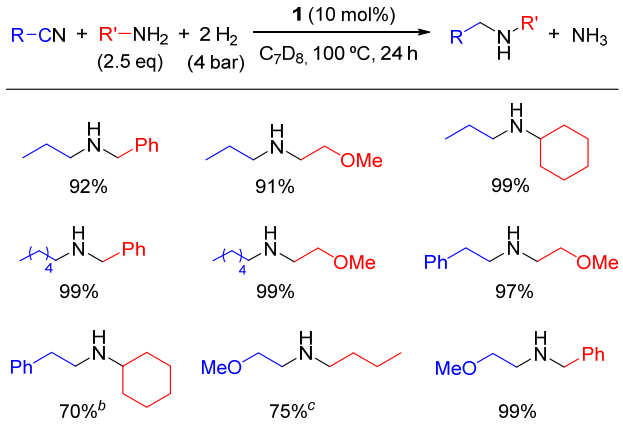


entry	equiv of amine	% asymmetrical amine	% symmetrical amine
1	1.0	17	82
2	2.5	97	0
3	5.0	99	0

[a]Reaction conditions: nitrile (0.36 mmol), catalyst (0.036 mmol; 10 mol%) in 0.5 mL of C_7D_8, 4 bar of H_2, at 100 ºC for 24 h. Yields were determined by ^{1}H NMR spectroscopy using mesitylene as internal standard.

Scheme 5 shows the generated asymmetrical secondary amines, which involve the hydrogenation of aliphatic nitriles of linear unfunctionalized and aryl- and alkoxy-functionalized chain in the presence of primary alkylamines of linear phenyl- and alkoxy-functionalized chain, and branched chain amines. These classes of amines include butan-1-amine, phenylmethanamine, 2-methoxyethan-1-amine, and cyclohexanamine, respectively. All secondary amines were formed in high yields, 70-99%, after 24 h of reaction.

Scheme 5. Hydrogenation of Nitriles to Asymmetrical Secondary Amines Catalyzed by 1.[a]

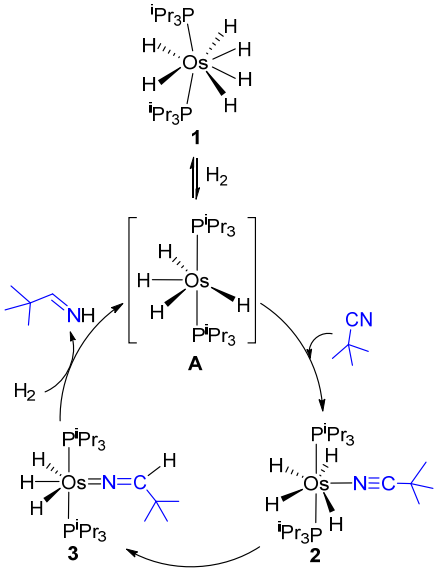


[a]Reaction conditions: nitrile (0.36 mmol), amine (0.90 mmol), **1** (0.036 mmol; 10 mol%) in 0.5 mL of C_7D_8, 4 bar of H_2, at 100ºC during 24 h. Yields were determined by ^{1}H NMR spectroscopy using mesitylene as internal standard. [b,c]29% (*b*) and 24% (*c*) of symmetrical secondary amine is also formed.

Reactions of 1 with Pivalonitrile and 2-Methoxyacetonitrile under Argon Atmosphere. Having demonstrated the ability of **1** to promote the formation of symmetrical and asymmetrical secondary aliphatic amines by means of the hydrogenation of alkyl nitriles, we decided to study the reactions of the catalyst with the title mentioned nitriles, under argon atmosphere, to gain mechanistic insight about the catalysis and to understand why the rupture of the C(sp)-C(sp^3) bond of the nitriles, now, does not take place. Pivalonitrile was selected because its hydrogenation and subsequent condensation to secondary imine were the most difficult and, at first glance, seems to be the most appropriate to isolate catalytic intermediates. On the other hand, the presence of an alkoxy substituent at 2-methoxyacetonitrile should favor the rupture of its C(sp)-C(sp^3) bond.

The warming of toluene solutions of **1**, at 130 ºC, in the presence of 1.0 equiv of pivalonitrile initially gives rise to the release of a hydrogen molecule from the starting compound, to afford the unsaturated tetrahydride intermediate $OsH_4(P^iPr_3)_2$ (**A**), which is trapped by the nitrile. The resulting saturated tetrahydride $OsH_4\{\kappa^1$-*N*-(N≡C^{t}Bu)$\}(P^iPr_3)_2$ (**2**) is unstable and evolves to the trihydride-azavinylidene derivative $OsH_3(=N=CH^tBu)(P^iPr_3)_2$ (**3**). According to this, a 35:65 mixture of **2** and **3** is formed after 3 h. Under molecular hydrogen (1 bar, 100 ºC, 10 min), the mixture of **2** and **3** regenerates **1** and gives 2,2-dimethylpropan-1-imine (Figures S69 and S70), to close a stoichiometric cycle for the hydrogenation of the nitrile (Scheme 6). Any evidence for the formation of binuclear compounds related to those shown in Scheme 3 was not found. The cycle shown in Scheme 6 is strong evidence in favor of the participation of trihydride-azavinylidene derivatives, related to **3**, as key intermediates in the hydrogenations shown in Schemes 4 and 5.

Scheme 6. Stoichiometric Cycle for the Hydrogenation of Pivalonitrile in the Presence of 1



Spectroscopic features of **2** are: a triplet ($^2J_{H-P}$ = 13.2 Hz) at -9.98 pmm due to the hydride ligands, in the ^{1}H NMR spectrum, which are involved in a thermally activated position exchange process, in agreement with that previously observed for the related compound $OsH_4\{\kappa^1$-*N*-[N≡C(2,6-$C_6H_3Me_2$)]$\}(P^iPr_3)_2$[34] and a singlet at 43.1 ppm in the ^{31}P{^{1}H} NMR spectrum. In contrast to **2**, the hydride ligands of **3** give rise to three resonances at -9.86, -11.57, and -13.56 ppm in the ^{1}H NMR spectrum, whereas the ^{31}P{^{1}H} NMR spectrum displays a singlet at 37.3 ppm. Crystals suitable for the X-ray diffraction analysis of **3** were obtained from the mixture. The structure (Figure 1), which confirms the trihydride-azavinylidene nature of the molecule, displays C_S symmetry with *trans*-phosphines (P(1)-Os-P(2) = 173.31(3)º), as expected for a six-coordinate d^4 OsH_3XL_2 species.[34,37]

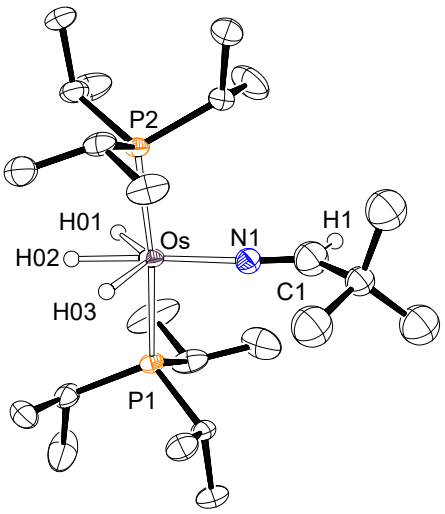


Figure 1. Molecular structure of complex **3** (ellipsoids are drawn at the 50% probability level). Hydrogen atoms of the phosphine ligands and *tert*-butyl group are omitted for clarity. Selected bond distances (Å) and angles (deg): Os-P(1) = 2.3362(7), Os-P(2) = 2.3359(7), Os-N(1) = 1.922(3); P(1)-Os-P(2) = 173.31(3).

The reaction of **1** with 2-methoxyacetonitrile shows significant differences with regard to that with pivalonitrile, which are consistent with a faster hydrogenation of the nitrile and a higher tendency to undergo the C(sp)-C(sp^3) bond rupture. It was performed in closed NMR tubes and was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy at 50 and 80 ºC (Figures S69-S72). The warming of toluene-d_8 solutions of **1**, at 80 ºC, in the presence of 1.0 equiv of 2-methoxyacetonitrile affords three Os-compounds, the trihydride-azavinylidene derivative $OsH_3(=N=CHCH_2OMe)(P^iPr_3)_2$ (**4**) and the binuclear complexes $(P^iPr_3)_2H_4Os(\mu\text{-}CN)OsH_3\{\kappa^1\text{-}N\text{-}(NH=CHCH_2OMe)\}(P^iPr_3)_2$ (**5**) and $(P^iPr_3)_2H_4Os(\mu\text{-}CN)OsH_3\{\kappa^1\text{-}N\text{-}(NH_2CH_2CH_2OMe)\}(P^iPr_3)_2$ (**6**), bearing an imine and an amine ligand, respectively, generated from the hydrogenation of the nitrile. Figure 2 shows the course of the transformation as a function of the time.

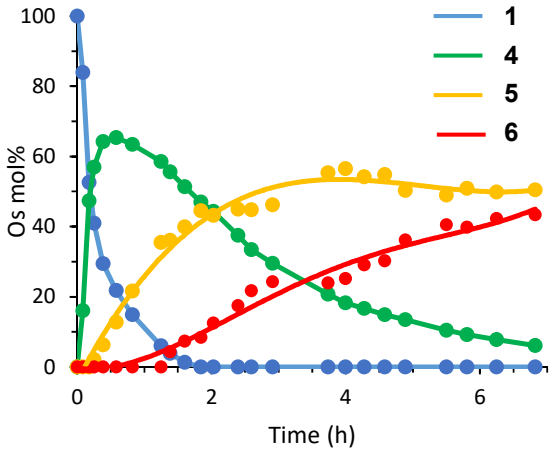


Figure 2. Profile for the progress of the reaction of **1** with 2-methoxyacetonitrile (1:1 molar ratio; both 0.1 M) in toluene-d_8 at 80 ºC.

The trihydride-azavinylidene derivative **4** is the first metal-complex formed and the major product at the beginning of the reaction. At 50ºC, it reaches 88% of the total osmium after 25 h, and can be isolated from the mixture as a yellow oil. Its ^{1}H and ^{31}P{^{1}H} NMR spectra agree well with those of the pivalonitrile counterpart **3**. Thus, the ^{1}H NMR spectrum displays three hydride resonances at -11.23, -11.57, and -11.66 ppm, whereas the ^{31}P{^{1}H} shows a singlet at 38.2 ppm. According to Scheme 6, complex **4** is the source of the imine ligand of **5**, since it should react with the molecular hydrogen released in the formation of the tetrahydride intermediate **A**, responsible of its formation (route a in Scheme 7). The unsaturated tetrahydride **A** should also promote the hydrogenation of a part of the generated imine to afford the amine ligand of **6** (route b in Scheme 7). The profile of the curves shown in Figure 2 suggests that binuclear skeleton of **5** and **6** is the consequence of the attack of **A** to the C(sp^2)-atom of the azavinylidene ligand of **4** (route c in Scheme 7), which could give the binuclear intermediate **B**, releasing dimethyl ether. A subsequent C-to-Os 1,2-hydrogen shift should afford **C**, which could yield **5** and **6** by coordination of the imine and amine generated in the hydrogenation processes (routes a and b). The higher steric hindrance of the *tert*-butyl group with regard to -CH_2OMe, which prevents the approach of **A** to the C(sp^2)-atom of the azavinylidene, could explain why **3** does not give binuclear species. The formation of **5** and **6** is inhibited under hydrogen atmosphere. This inhibition may be due to the decrease of the concentration of the tetrahydride **A** and/or the increase of the rate of hydrogenation of **4**. The fact that **1** is the only spectroscopically detected species in the hydrogenation reactions and the high yield of the obtained products in the catalysis rule out the mediation of the binuclear species in the catalytic cycles, since the construction of the binuclear skeleton involves the loss of 0.5 equiv of substrate per equiv of catalyst.

Crystals suitable for X-ray diffraction analysis of **5** and **6** were obtained from the reaction crude. The respective structures (Figures 3 and 4) prove the binuclear character of these complexes and confirm the presence of the linear Os(1)-N(1)-C(1)-Os(2) bridge, which displays Os(1)-N(1)-C(1) and N(1)-C(1)-Os(2) angles of 171.2(6)º and 179.6(9)º for **5** and 178.2(5)º and 178.9(6)º for **6** and a N(1)-C(1) bond length of 1.171(12) Å for **5** and 1.165(7) Å for **6** in agreement with the previously reported acetonitrile derivative $(P^iPr_3)_2H_4Os(\mu\text{-}CN)OsH_3\{\kappa^1\text{-}N\text{-}(N\equiv CMe)\}(P^iPr_3)_2$.[35] The coordination polyhedra around the osmium atoms can be rationalized as distorted pentagonal bipyramids with axial phosphines (P(1)-Os(1)-P(2) = 170.86(8)º and P(3)-Os(2)-P(4) = 170.40(9)º for **5** and P(1)-Os(1)-P(2) = 163.94(6)º and P(3)-Os(2)-P(4) = 168.32(6)º for **6**). The equatorial planes form an angle of 77(2)º for **5** and 67(1)º for **6**. According to the presence of OsH_4P_2 and OsH_3P_2 moieties, the ^{1}H NMR spectra, in toluene-d_8, at room temperature contain two hydride resonances in a 4:3 intensity ratio at -10.37 and -11.78 ppm for **5** and at -10.56 and -12.98 ppm for **6**, whereas the ^{31}P{^{1}H} NMR spectra contain two signals around 44 and 24 ppm, in approximately a 1:1 intensity ratio.

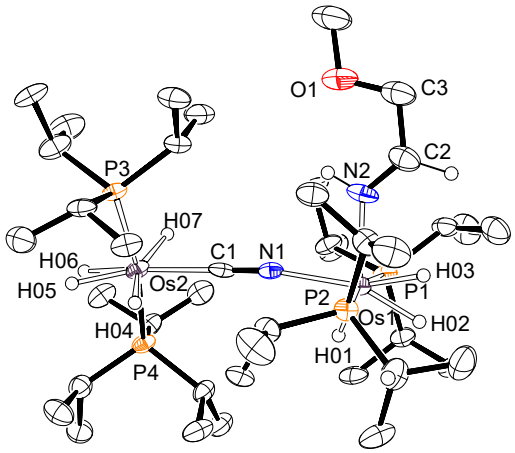
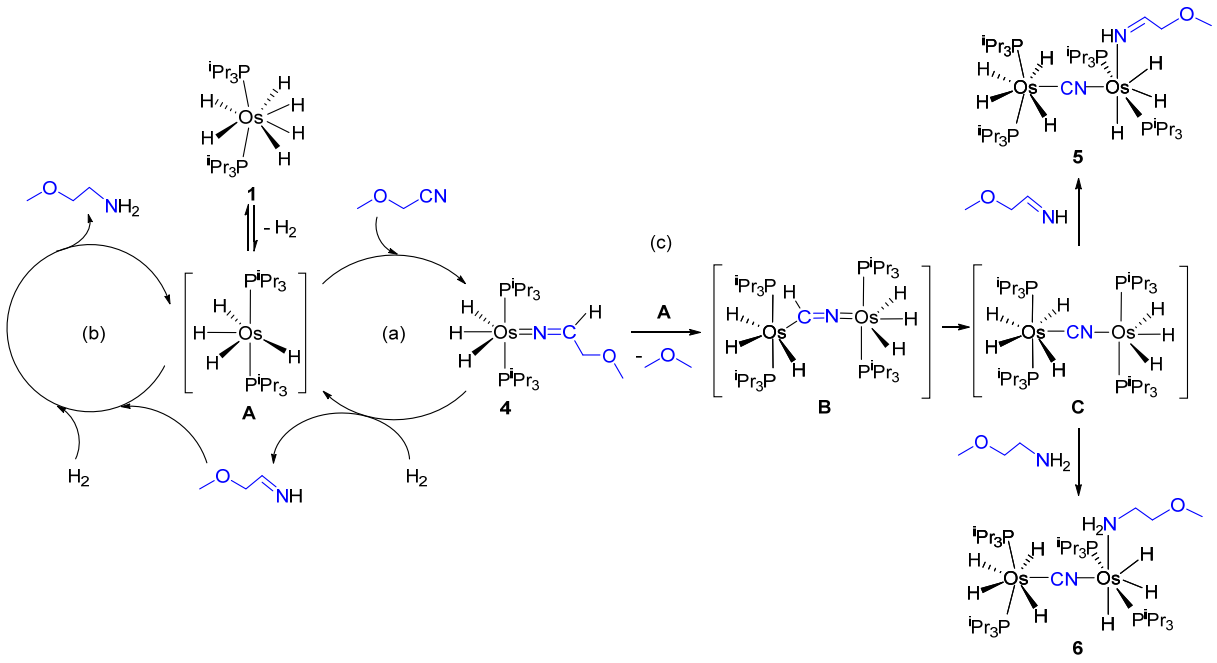


Figure 3. Molecular structure of complex **5** (ellipsoids are drawn at the 50% probability level). Hydrogen atoms except hydrides and those attached to nitrogen and C_α atoms of the imine ligand are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)–N(1) = 2.142(8), Os(1)–N(2) = 2.150(8), Os(2)–C(1) = 2.051(10), N(1)–C(1) = 1.171(12), N(2)–C(2) = 1.275(14); Os(1)–N(1)–C(1) = 171.2(6), N(1)–C(1)–Os(2) = 179.6(9), P(1)–Os(1)–P(2) = 170.86(8), P(3)–Os(2)–P(4) = 170.40(9).

Scheme 7. Stoichiometric Reactions of 1 with 2-Methoxyacetonitrile under Argon



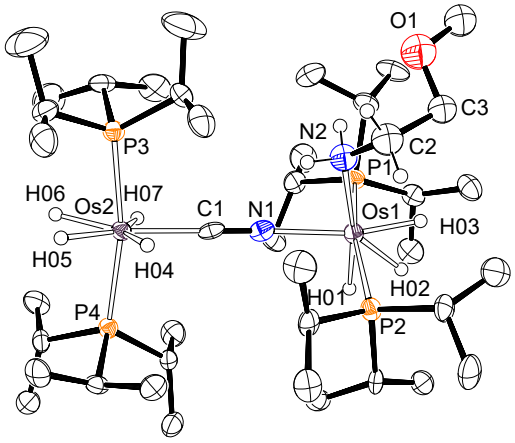


Figure 4. Molecular structure of complex **6** (ellipsoids are drawn at the 50% probability level). Hydrogen atoms except hydrides and those attached to nitrogen and C_α atoms of the amine are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)–N(1) = 2.136(6), Os(1)–N(2) = 2.226(8), Os(2)–C(1) = 2.057(7), N(1)–C(1) = 1.165(7), N(2)–C(2) = 1.480(13); Os(1)–N(1)–C(1) = 178.2(5), N(1)–C(1)–Os(2) = 178.9(6), P(1)–Os(1)–P(2) = 163.94(6), P(3)–Os(2)–P(4) = 168.32(6).

DFT Study of the Hydrogenation Mechanism. The products of the reactions of **1** with both pivalonitrile and 2-methoxyacetonitrile, complexes **3** and **4**, are an overwhelming experimental evidence supporting that the trihydride-azavinylidene derivatives $OsH_3(=N=CHR)(P^iPr_3)_2$ act as key intermediates in the hydrogenation of the alkyl nitriles to the corresponding primary imines (Schemes 6 and 7a). Nevertheless there are two points that still need to be clarified: the formation of these intermediates and their reaction with molecular hydrogen. To gain insight into them, we carried out DFT calculations (B3LYP-D3/SDD/6-31G**) using propionitrile as substrate model. The changes in free energy (ΔG) were calculated in toluene at 298.15 K and 1 atm.

Two coordination modes have been observed for nitrile ligands κ^1-N[38] and η^2-C≡N.[39] As a consequence, two different paths for the azavinylidenes formation are in principle possible: 1,3-hydrogen shift, similar to that proposed for the isomerization of hydride-metal-alkynyl species into vinylidene complexes,[40] and 1,2-hydrogen migration from the metal to the carbon atom of the coordinated triple bond.[41] Previous DFT calculations on the formation of the phenylazavinylidene derivative $OsH_3(=N=CHPh)(P^iPr_3)_2$ revealed a much higher activation energy for the 1,3-hydrogen shift than for the 1,2-hydrogen migration (64.4 *versus* 17.2 kcal mol^{-1}) even though the intermediate $OsH_4(\eta^2$-N≡CPh)$(P^iPr_3)_2$ is 14.9 kcal mol^{-1} less stable than the species $OsH_4(\kappa^1$-N≡CPh)$(P^iPr_3)_2$.[34] The replacement of the phenyl substituent of the nitrile by an ethyl group modifies the situation. Although the relative stability of the κ^1-N and η^2-C≡N forms does not significantly change, the activation energy for the 1,3-hydrogen shift dramatically decreases with regard to that reported for the aromatic nitrile. As a consequence, the 1,3-hydrogen shift (Figure 5) is now slightly favored with regard to the 1,2-hydrogen migration (15.8 *versus* 16.9 kcal mol^{-1}). Both hydrogen shifts lead to intermediate $\mathbf{t_1}$, which is between 14.8 and 15.3 kcal mol^{-1} less stable than the saturated tetrahydride $\mathbf{t_0}$, the ethyl counterpart of **2**. It can be described as a propylideneamido compound, which saturates the electron deficiency of the metal center with an Os-H-C agostic interaction. The breakage of this interaction and the opening of the Os-N-C bond angle afford the azavinylidene $\mathbf{t_2}$, the ethyl counterpart of complexes **3** and **4**, with a barrier of 2.5 kcal mol^{-1}. Trihydride-azavinylidene $\mathbf{t_2}$ is 8.1 kcal mol^{-1} more stable than $\mathbf{t_0}$.

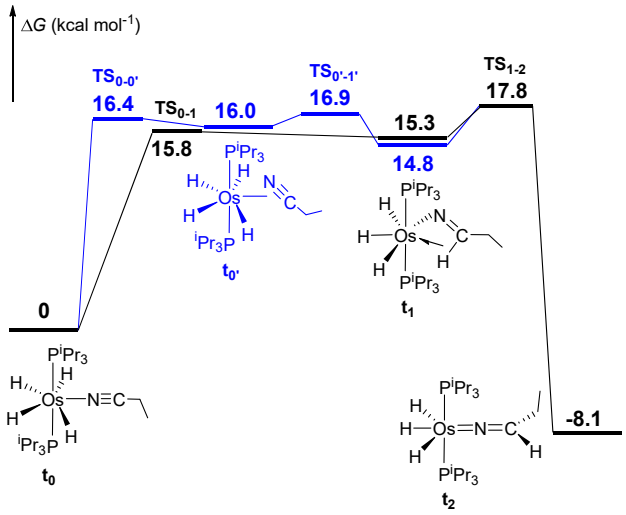


Figure 5. Computed energy profile for the formation of the model azavinylidene $OsH_3(=N=CHEt)(P^iPr_3)_2$ (**t₂**) via 1,3-hydrogen shift (—) or via 1,2-hydrogen migration on a η^2-CN intermediate (—).

The reaction of the azavinylidene intermediate **t₂** with hydrogen is the stage of highest barrier in the nitrile-to-imine hydrogenation process. Its course is a function of the asymmetry of the azavinylidene ligand since two approaches of the hydrogen molecule to the Os-N bond are possible in the azavinylidene plane: entry by the ethyl substituent side or by the C-H-hydrogen atom side. The latter is slightly favored (Figure 6, 27.8 *versus* 28.3 kcal mol^{-1})[42] and involves an outer sphere step, which affords the tetrahydride **t₃ₐ** with a coordinated primary *cis*-imine. In contrast to the entry by the C-H-hydrogen side, the approach of the hydrogen molecule by the ethyl group side generates a Kubas-type dihydrogen intermediate **t₄** ($d_{H\text{-}H}$ = 0.842 Å), which is 13.4 kcal mol^{-1} less stable than **t₂**. The subsequent migration of one of the atoms of the dihydrogen ligand to the nitrogen atom leads to **t₃b**, related to **t₃ₐ** but bearing a *trans*-imine. The dissociation of the imine from **t₃** regenerates the tetrahydride **A**, closing the cycle for the hydrogenation of the nitrile to the primary imine.

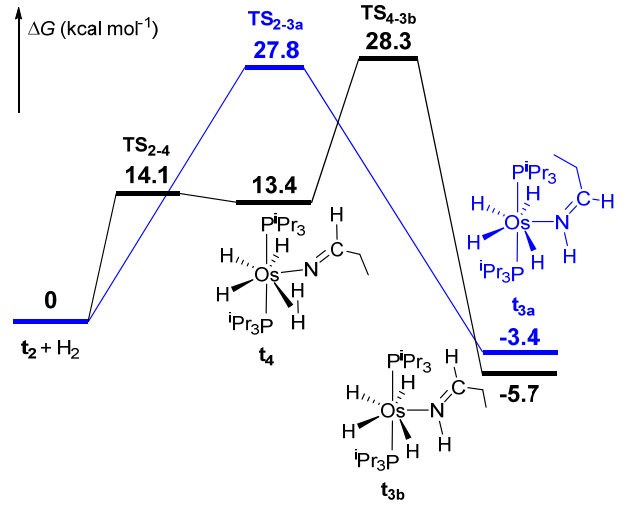


Figure 6. Computed energy profile for the reaction of the model azavinylidene **t₂** with H_2: outer sphere (—) and inner sphere via a dihydrogen intermediate (—).

Once clarified the hydrogenation of the nitrile to the primary imine, we calculated the imine-to-amine hydrogenation. Because the nitrile-to-imine and imine-to-amine hydrogenations should be similar processes, we assumed that the key intermediates of the imine-to-amine hydrogenation are $OsH_3(=NHR)(P^iPr_3)_2$, amido-counterparts of the azavinylidene derivatives. Accordingly, we divided the process in two stages: imine insertion (Figure 7) and reaction of the amido intermediate with molecular hydrogen (Figure 8).

The migration of one of the hydride ligands of both **t₃ₐ** (*cis*-imine) and **t₃b** (*trans*-imine) to the C(sp^2)-atom of the coordinated imine initially affords **t₅**, which is 14.9 and 17.5 kcal mol^{-1} less stable than **t₃ₐ** and **t₃b**, respectively. However, the Os-to-C migration depends upon the stereochemistry of the imine. While the insertion of the *cis*-imine takes place through an 1,2-hydrogen shift via an η^2-imine intermediate **t₆**, the insertion of the *trans*-imine occurs in one step by an 1,3-hydrogen shift. The first path is slightly favored with regard to the second one (19.3 *versus* 19.7 kcal mol^{-1}). Like **t₁**, intermediate **t₅** saturates the electron deficiency of the metal center with an Os-H-C agostic interaction. The rupture of the Os-H interaction affords the *n*-propylamido derivative **t₇**, with a barrier of 3.8 kcal mol^{-1}. Intermediate **t₇** is 1.4 kcal mol^{-1} less stable than **t₃b** and 1.2 kcal mol^{-1} more stable than **t₃ₐ**.

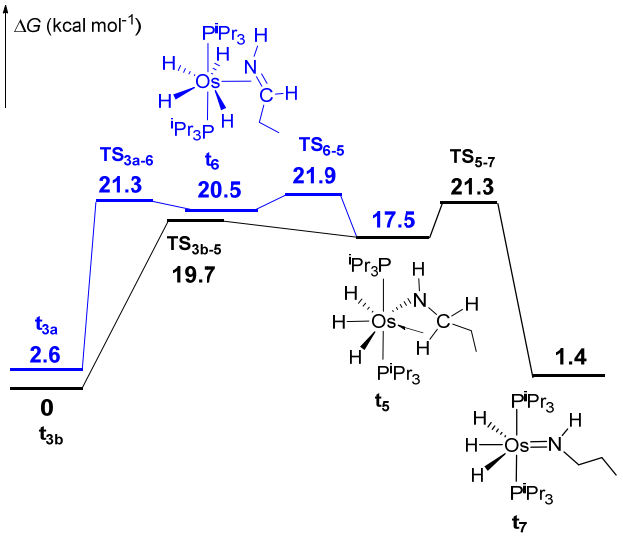


Figure 7. Computed energy profile for the insertion of the imine ligand into one of the Os-H bonds of **t₃ₐ** (*cis*-imine) and **t₃b** (*trans*-imine).

The main difference between the amido **t₇** and the azavinylidene **t₂** is the disposition of the N-donor ligand. In contrast to the azavinylidene group, the *n*-propylamido ligand lies in the same plane as the P-Os-P direction; as a consequence, the hydrogen molecule has only one way of approaching to the Os-N bond. This approach initially leads to the Kubas-type dihydrogen species **t₈** ($d_{H\text{-}H}$ = 0.861 Å), which is only 10.4 kcal mol^{-1} less stable than **t₇**. This dihydrogen compound is the propylamido counterpart of **t₄**. Like the latter, it undergoes an Os-to-N migration of one of the atoms of the coordinate hydrogen molecule, to directly afford the tetrahydride-amine derivative **t₉** with a barrier of 18.2 kcal mol^{-1}, with regard to **t₇**; *i. e.*, around 10 kcal mol^{-1} lower than that shown in Figure 6

for the transformation of $\mathbf{t_2}$ into $\mathbf{t_3}$. The dissociation of the amine from $\mathbf{t_9}$ regenerates the tetrahydride **A**.

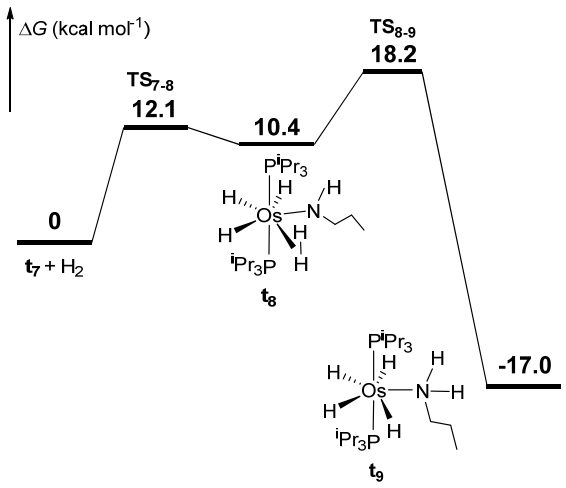


Figure 8. Computed energy profile for the reaction of the *n*-propylamido intermediate $OsH_3(=NH^nPr)(P^iPr_3)_2$ ($\mathbf{t_7}$) with H_2.

CONCLUDING REMARKS

This study has revealed that the previously reported C-C rupture of alkyl nitriles, which is promoted by the d^2-hexahydride complex $OsH_6(P^iPr_3)_2$ under argon atmosphere, is inhibited under molecular hydrogen. In toluene, at 100 ºC, this polyhydride catalyzes the hydrogenation of the nitriles, under 4 bar of hydrogen, to give symmetrical secondary aliphatic amines. The scope of substrates includes aryl-, pyridyl- and alkoxy-functionalized alkyl nitriles of linear or branched chain. The secondary amines are the result of the formation of primary-imines and -amines, which condense to afford secondary imines, under the reaction conditions. The subsequent hydrogenation of these imines finally yields the secondary amines. The condensation is faster than the imine hydrogenation; as a consequence, the introduction of an external primary alkylamine in the reaction medium allows the generation of asymmetrical secondary aliphatic amines. The procedure works with primary alkylamines of linear, phenyl- and alkoxy-functionalized chain, and branched chain amines.

Trihydride-azavinylidene derivatives $OsH_3(=N=CHR)(P^iPr_3)_2$ are the common key intermediates of both processes: the hydrogenation of alkyl nitriles to primary imines and the C-C rupture of the nitriles. Their formation involves the insertion of the N-C triple bond of the substrates into an Os-H bond of the unsaturated tetrahydride $OsH_4(P^iPr_3)_2$, which is generated by reductive elimination of hydrogen from the hexahydride precursor. Once formed the trihydride-azavinylidene intermediates, the hydrogenation of the nitriles involves the reaction between molecular hydrogen and the azavinylidene ligand to yield the imines and regenerate the unsaturated tetrahydride catalyst. In the absence of molecular hydrogen, the attack of the tetrahydride to the $C(sp^2)$-atom of the azavinylidene produces the C-C rupture.

In summary, we have discovered the first osmium catalyst for the efficient formation of symmetrical and asymmetrical secondary aliphatic amines, starting from nitriles, under mild conditions. In addition, we have elucidated the mechanism of the involved reactions and have rationalized the C-C rupture of alkyl nitriles promoted by the hexahydride $OsH_6(P^iPr_3)_2$.

EXPERIMENTAL SECTION

Complex $OsH_6(P^iPr_3)_2$ (**1**) was prepared according to the published method.[28] General information and 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, $^{13}C\{^1H\}$) and external H_3PO_4 ($^{31}P\{^1H\}$). 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.

Catalytic Hydrogenation of Nitriles to Symmetrical Secondary Amines. The respective nitrile (0.36 mmol) and mesitylene as internal standard (50 µL, 0.36 mmol) were added to an NMR tube containing a solution of **1** (18.6 mg, 0.036 mmol) in 0.5 mL of C_7D_8. The mixture was checked by ^1H NMR and transferred via cannula to a Fisher-Porter bottle (70 mL). The Ar atmosphere was replaced by H_2 and the system was pressurized to 4 bar. The mixture was magnetically stirred and heated at 100 ºC, in an oil bath, for 24 h. Then it was cooled down to room temperature, depressurized, and checked by ^1H NMR. Yields were calculated based on the integration of characteristic peaks of the formed amines against the internal standard. The results are the average of at least two duplicate runs. After the crude was checked by ^1H NMR, 10 mL of pentane were added over the reaction mixture. While stirring, several drops of concentrated HCl (aq) were added to the mixture until a white solid appeared. The solid was dissolved in MeOH and filtered through neutral alumina; the solvent was removed under vacuum giving the corresponding amine hydrochlorides, which were characterized by ^1H and ^{13}C NMR and HR-MS spectroscopy (See Supporting Information).

Catalytic Hydrogenation of Nitriles to Asymmetrical Secondary Amines. The same procedure described for the hydrogenation of the nitriles to symmetrical secondary amines was followed except that 0.9 mmol of external amine were also added to the reaction mixture.

Reaction of 1 with Pivalonitrile: Formation of $OsH_4\{\kappa^1$-*N*-$(N\equiv C^tBu)\}(P^iPr_3)_2$ (2) and $OsH_3\{=N=CH(^tBu)\}(P^iPr_3)_2$ (3). Pivalonitrile (22 µL, 0.2 mmol) was added to a solution of **1** (100 mg, 0.2 mmol) in 2 mL of toluene. The resulting solution was heated at 130 ºC for 3 h. The reaction crude was concentrated to dryness under reduced pressure giving an orange oil. The addition of pentane (2 mL) at -78 ºC afforded an orange solid which was washed with further portions of pentane (2 x 2 mL) and dried in vacuo. The resulting orange solid is a 35:65 mixture of isomers **2** and **3**. Anal. Calcd for $C_{23}H_{55}NOsP_2$: C, 46.21; H, 9.27; N, 2.34. Found: C, 46.40; H, 9.43; N, 2.49. IR (ATR, cm^{-1}): ν(C-N) and ν(Os–H) 2090 (w), 1978 (m), 1790 (m). Some orange crystals of **3**, suitable for X-ray diffraction analysis, were grown from a solution of the orange solid in pentane at -30 ºC. Spectroscopic data for **2**: ^1H NMR (300.13 MHz, C_7D_8, 298 K): δ 2.03 (m, 6H, CH ^{i}Pr), 1.32 (m, 36H, CH_3 ^{i}Pr), 0.89 (s, 9H, $CH_3{}^t$Bu), -9.98 (t, ${}^3J_{H\text{-}P}$ = 13.2, 4H, OsH_4). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_7D_8, 298 K): δ 43.1 (s).$^{13}C\{^1H\}$ APT NMR (75.48 MHz, C_7D_8, 298 K): δ 129.9 (CN, inferred from the HMBC (^1H, ^{13}C) spectrum), 29.3 (C_q ^{t}Bu, inferred from the HMBC (^1H, ^{13}C) spectrum, 27.1 (CH_3, ^{t}Bu), 26.8 (vt, *N* = 24.8, CH, ^{i}Pr), 20.1. (CH_3, ^{i}Pr). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 2.05 (m, 6H, CH ^{i}Pr), 1.44 (s, 9H, ^{t}Bu), 1.38-1.30 (m, 36H, CH_3 ^{i}Pr), -10.24 (t, ${}^3J_{H\text{-}P}$ = 13.2, 4H, OsH_4). Spectroscopic data for **3**. ^1H NMR (300.13 MHz, C_7D_8, 298 K): δ 3.24 (m, 1H, N=CH), 2.04 (m, 6H, CH ^{i}Pr), 1.22 (m, 36H, CH_3 ^{i}Pr), 1.08 (s, 9H, $CH_3{}^t$Bu), -9.86 (t, ${}^3J_{H\text{-}P}$ = 9.5, 1H, OsH), -11.57 (br, 1H, OsH), -13.56 (br t, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_7D_8, 298 K): δ 37.3 (s). $^{13}C\{^1H\}$ APT NMR (75.48 MHz, C_7D_8, 298 K): δ 155.9 (N=CH, inferred from the HMBC (^1H, ^{13}C) spectrum), 29.3 (C_q ^{t}Bu inferred from the HMBC (^1H, ^{13}C) spectrum, 28.5 (CH_3, ^{t}Bu), 26.9 (vt, *N* = 24.1, CH, ^{i}Pr), 20.4. (CH_3, ^{i}Pr). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 3.17 (m, 1H, N=CH), 2.21 (m, 6H, CH ^{i}Pr), 1.38-1.30 (m, 36H, CH_3 ^{i}Pr), 1.12 (s, 9H, $CH_3{}^t$Bu), -10.00 (br, 1H, OsH), -11.85 (s, 1H, OsH), -13.59 (td, ${}^3J_{H\text{-}P}$ = 14.5, ${}^4J_{H\text{-}H}$ = 6.1, 1H, OsH).

Reaction of 1 with 2-Methoxyacetonitrile: Formation of $OsH_3(=N=CHCH_2OMe)(P^iPr_3)_2$ (4), $(P^iPr_3)_2H_4Os(\mu$-CN)$OsH_3\{\kappa^1$-

***N*-(NH=CHCH$_2$OMe)}(P^{i}Pr$_3$)$_2$ (5), and (P^{i}Pr$_3$)$_2$H$_4$Os(*μ*-CN)OsH$_3${*κ*^{1}-*N*-(NH$_2$CH$_2$CH$_2$OMe)}(P^{i}Pr$_3$)$_2$ (6)**. Two NMR tubes were charged with 2-methoxyacetonitrile (4 μL, 0.05 mmol), **1** (25 mg, 0.05 mmol), and 0.5 mL of toluene-d_8. One of them was heated at 50 ºC and the other one at 80 ºC. The monitoring of these reactions by ^{1}H and ^{31}P{^{1}H} NMR (Figures S71–S74) showed the formation of complexes **4**, **5**, and **6**.

Isolation of OsH$_3$(=N=CHCH$_2$OMe)(P^{i}Pr$_3$)$_2$ (4). *Method a*: 2-Methoxyacetonitrile (15 μL, 0.2 mmol) was added to a solution of **1** (100 mg, 0.2 mmol) in 2 mL of toluene. The resulting solution was heated at 50 ºC for 25 h, and then it was concentrated to dryness under reduced pressure giving a yellow oil that was washed with further portions of pentane (2 x 2 mL) and vacuum-dried. Yield: 20 mg (17 %). *Method b*: 2-Methoxyacetonitrile (150 μL, 2.0 mmol) was added to a solution of **1** (100 mg, 0.2 mmol) in 2 mL of toluene. The resulting solution was heated at 80 ºC for 30 min, and then it was concentrated to dryness under reduced pressure giving a yellow oil that was washed with further portions of pentane (2 x 2 mL) and vacuum-dried. Yield: 23 mg (19 %). HR-MS (electrospray): *m/z* calcd for $C_{21}H_{51}NOOsP_2$ $[M]^+$ 587.3056; found 587.3152. ^{1}H NMR (300.13 MHz, C_7D_8, 298 K): δ 4.39 (m, 2H, OCH_2), 3.90 (br, 1H, N=CH), 3.21 (s, 3H, OCH_3), 1.98 (m, 6H, CH ^{i}Pr), 1.20 (dvt, $^3J_{H-H}$ = 6.8, *N* =13.1, 36H, CH_3 ^{i}Pr), -11.23 (br, 1H, OsH), -11.57 (br, 1H, OsH), -11.66 (br t, $^3J_{H-P}$ = 12.7, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, C_7D_8, 298 K): δ 38.2 (s). ^{13}C{^{1}H} APT NMR (75.48 MHz, C_7D_8, 298 K): δ 145.2 (t, $^3J_{C-P}$ = 3.8, N=CH), 69.0 (s, OCH_2), 57.7 (s, OCH_3), 26.3 (vt, *N* = 25.0, CH ^{i}Pr), 20.1 (s, CH_3 ^{i}Pr).

Identification of (P^{i}Pr$_3$)$_2$H$_4$Os(*μ*-CN)OsH$_3${*κ*^{1}-*N*-(NH=CHCH$_2$OMe)}(P^{i}Pr$_3$)$_2$ (5). Methoxyacetonitrile (15 μL, 0.2 mmol) was added to a solution of **1** (100 mg, 0.2 mmol) in 3 mL of toluene-d_8. The resulting solution was heated at 50 ºC for 44 h. After this time, the ^{1}H and ^{31}P{^{1}H} NMR of the reaction crude showed a mixture of **4** and **5** in a 5.7:1.0 molar ratio. Selected spectroscopic data for **5**: ^{1}H NMR (300.13 MHz, C_7D_8, 298 K): δ 10.62 (d, $^3J_{H-H}$ = 22.3, 1H, N*H*=CH), 7.84 (br d, $^3J_{H-H}$ = 22.3, 1H, NH=C*H*), 2.08 (m, 12H, CH ^{i}Pr), 1.43 (dvt, $^3J_{H-H}$ = 5.2, *N* =12.1, 36H, CH_3 ^{i}Pr), -10.37 (t, $^3J_{H-P}$ = 14.7, 4H, OsH_4), -11.78 (t, $^3J_{H-P}$ = 12.8, 3H, OsH_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_7D_8, 298 K): δ 44.3 (s, $POsH_4$), 24.5 (s, $POsH_3$). A small amount of colorless single crystals of **5** suitable for X-ray diffraction analysis were grown from a solution of the mixture in pentane at -30 ºC.

Isolation of (P^{i}Pr$_3$)$_2$H$_4$Os(μ-CN)OsH$_3${*κ*^{1}-*N*-(NH$_2$CH$_2$CH$_2$OMe)}(P^{i}Pr$_3$)$_2$ (6). 2-Methoxyacetonitrile (15 μL, 0.2 mmol) was added to a solution of $OsH_6(P^iPr_3)_2$ (100 mg, 0.2 mmol) in 3 mL of toluene. The resulting solution was heated at 80 ºC for 24h. The reaction crude was concentrated to dryness under reduced pressure giving a dark orange oil. The addition of pentane (2 mL) at -78 ºC afforded a white solid that was washed with further portions of pentane (2 x 2 mL) and dried in vacuo. Yield: 43 mg (38%). Colorless single crystals suitable for X-ray diffraction analysis were grown from a solution of **6** in pentane at -30 ºC. Anal. Calcd for $C_{40}H_{100}N_2OOs_2P_4$: C, 42.53; H, 8.92; N, 2.48. Found: C, 42.99; H, 9.28; N, 2.55. IR (ATR, cm^{-1}): ν(NH) 3348 (w), ν(Os–H) and ν(CN) 2078 (s), 1826 (s). ^{1}H NMR (300.13 MHz, C_7D_8, 298 K): δ 3.20 (br, 2H, OCH_2), 2.88 (s, 3H, OCH_3), 2.72 (br, 2H, NCH_2), 1.99-1.81 (m, 12H, CH ^{i}Pr), 1.24 (dvt, $^3J_{H-H}$ = 6.8, *N* =12.5, 36H, CH_3 ^{i}Pr), 1.04 (m, 36H, CH_3 ^{i}Pr), -10.56 (t, $^3J_{H-P}$ = 14.7, 4H, OsH_4), -12.98 (t, $^3J_{H-P}$ = 13.7, 3H, OsH_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_7D_8, 298 K): δ 44.4 (s, $POsH_4$), 24.8 (s, $POsH_3$). ^{13}C{^{1}H} APT NMR (75.48 MHz, C_7D_8, 298 K): δ 73.8 (s, OCH_2), 58.1 (s, OCH_3), 51.6 (s, NCH_2), 28.8 (vt, *N* = 23.2, CH ^{i}Pr), 25.8 (vt, *N* = 23.0, CH ^{i}Pr), 20.7, 20.1 (both s, CH_3 ^{i}Pr). The *μ*-CN signal is not observed.

Structural Analysis of Complexes 3, 5, and 6. X-ray data were collected for the complexes 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 covering 0.3º in ω. The hydrogen atoms were observed in the last Fourier Maps or calculated, and refined freely or using a restricted riding model. The hydrides were located but refined with fixed Os-H distances (1.59 Å). The azavinylidene ligand of complex **3** was observed disordered and was refined with two moieties, complementary occupancy factors, and isotropic displacement parameters. The hydrides (also disordered) were refined with a fixed distance Os-H using the expected geometry as template. The crystal of **6** is the result of the co-crystallization 0.75/0.25 of amine (**6**)/imine (**5**) complexes. The disordered ligands were refined with complementary occupancy factors. The mayor component (**6**) was refined freely with anisotropic thermal parameters. The minor component was refined with restricted geometry, and isotropic displacement parameters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General information, crystallographic data, computational details, NMR and IR spectra and energies of computed structures (PDF)

Cartesian coordinates of calculated structures (XYZ)

Accession Codes
CCDC 1993553-1993555 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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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENT

Financial support from the MINECO of Spain (Projects CTQ2017-82935-P (AEI/FEDER, UE) and RED2018-102387-T), Gobierno de Aragón (Group E06_20R and project LMP148_18), FEDER, and the European Social Fund is acknowledged. The BIFI Institute and CESGA Supercomputing Center are acknowledged for technical support and the use of computational resources.

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Table of Contents graphic