Dihydroboration of Alkyl Nitriles Catalyzed by an Osmium-Polyhydride: Scope, Kinetics, and Mechanism

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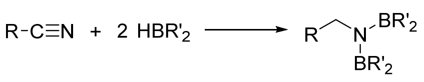
ABSTRACT: Complex $OsH_6(P^iPr_3)_2$ is an efficient catalyst precursor for the addition of pinacolborane and catecholborane to the C-N triple bond of alkyl nitriles. In this way, a variety of *N*,*N*-diborylamines have been isolated and fully characterized, including thirteen derivatives not described so far. The range of nitriles used is wide and comprises substrates having unfunctionalized linear and branched chains, and functionalized chains with methoxide, trifluoromethyl, aryl, pyridyl, benzoyl, or cyanide groups. Kinetic studies demonstrate that the overall process consists of two consecutive irreversible reactions: the catalytic metal-promoted monohydroboration of the nitrile to afford the borylimine and the metal-free stoichiometric hydroboration of the latter to give the diborylamine. The mechanism of the hydroboration has been established by combining the kinetic analysis of the catalysis, stoichiometric reactions, and DFT calculations. The rate determining step of the catalysis is the insertion of the C-N triple bond of the nitrile into the Os-B bond of an osmium-σ-borane intermediate and is regio-directed by the nucleophilicity of the nitrogen atom and the electrophilicity of the carbon atom of the nitrile.

INTRODUCTION

Borylamines are excellent tools to build C–C bonds and useful synthetic surrogates which easily undergo transformations into a wide array of functional groups.[1] The most economical and eco-friendly route for their preparation is without a shred of doubt the direct borylation of C–N multiple bonds, since it employs mild reaction conditions, offers excellent functional group tolerance, and leads to high purity products.[2]

Dihydroboration of nitriles results in the formation of *N*,*N*-diborylamines (eq 1).[3] Reactions are typically performed using catalysts, mainly based on transition metal complexes; although over the last years, they have been extended to some main-groups metals[4] and f-block elements.[5] It is usually assumed that the addition of both borane molecules to the C–N triple bond takes place with the participation of a catalyst. Transition metal catalysts include complexes of 3d and 4d elements, while efficient compounds of 5d metals are unknown. The former are based on Mn, Co, and Ni. Baik, Trovitch, and coworkers have reported a β-diketiminate-manganese-hydride catalyst. For this particular case, experimental and computational results suggest that the dihydroboration of nitriles involves insertion of the C–N triple bond of the nitrile into the Mn–H bond, followed by σ-bond metathesis between amide intermediates and the incoming pinacolborane (HBpin).[6] This research group has also discovered a cobalt(II) catalyst.

Computational evaluation of the reaction coordinate points out that the B–H addition and nitrile insertion steps could take place on an antiferromagnetically coupled triplet spin manifold.[1f] Fout and coworkers have extended the use of a cobalt(I) catalyst for the anti-Markovnikov hydroboration of terminal alkenes to the dihydroboration of nitriles,[7] whereas Hayrapetyan, Khalimon, and coworkers have employed the commercially available Co(acac)/dpephos system for this reaction.[1g] Nakajima, Shimada, and coworkers have observed that simple nickel salts, Ni(acac)$_2$ and its derivatives, are efficient for hydroboration of nitriles with catecholborane (HBcat).[8] Catalysts of 4d metals are centered on Mo and Ru. Nikonov's group has reported that imido-molybdenum(IV)-hydride complexes also catalyze the dihydroboration of a variety of nitriles with HBcat. Mechanistic studies suggest that the catalysis proceeds through a series of agostic borane-amido and borylimino intermediates. No evidence for the B–H oxidative addition to the Mo(IV) center to afford boryl species was found.[1b,9] Ruthenium compounds have been employed by the groups of Szymczak,[10] Gunanathan,[11] and Tobita.[1e] In addition, Nakazawa and coworkers have developed an iron-indium cooperative system efficient for both dihydroboration of nitriles and dihydro(boration-silylation) of acetonitrile.[12] We here describe the features of the first osmium catalyst, which is also the first one of a 5d metal, and demonstrate that only the addition of the first borane molecule to the nitrile is a catalytic metal-promoted process, while the second addition is a metal-free stoichiometric reaction.



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Osmium complexes have been comparatively much less employed than derivatives of ~~the~~ other platinum group metals in catalysis,[13] with the notable exception of the Sharpless dihydroxylation and reactions akin to that.[14] However, some of them are reaching significant relevance as useful tools in organic synthesis[15] and particularly for acceptorless dehydrogenative processes.[13d,16] The success of osmium-polyhydride compounds in the dehydrogenation of amine boranes[17] and liquid organic hydrogen carriers such as alcohols,[18] cyclic amines,[18c,19] and formic acid[20] is remarkable.

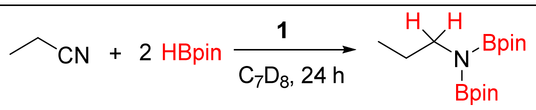
Complex $OsH_6(P^iPr_3)_2$ (**1**) occupies a particularly privileged position within the chemistry of platinum groups metals because of its ability to carry out stoichiometric transformations, especially σ-bond activation reactions.[21] On the other hand, the catalytic properties of this polyhydride have been unexplored until recently, except for its use in promoting the classical Tishchenko dimerization of aldehydes.[22] We have recently shown that complex **1** 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 4 bar of hydrogen.[23] We have now discovered that this hexahydride is an efficient catalyst precursor for the dihydroboration of a wide variety of alkyl nitriles with both HBpin and HBcat. This paper shows the scope of the catalysis, its kinetic analysis, and the mechanism of the metal-promoted B–H addition to the C–N triple bond.

RESULTS AND DISCUSSION

Reaction Conditions and Scope. We initially studied the dihydroboration reactions with HBpin and started by optimizing the temperature and the catalyst loading to obtain the diborylamines in high yield, in a general way. For that purpose, we selected propionitrile as model substrate and performed the reactions in NMR tubes, under an argon atmosphere, with 0.34 M and 0.68 M solutions of nitrile and borane, respectively, in toluene-d_8 as solvent. The amount of diborylamine formed was quantified by ^{1}H NMR spectroscopy using mesitylene (0.34 M) as an internal standard (Table 1). Under the above-mentioned conditions, the reaction does not work in the absence of **1**, at 50 ºC. However, the diborylamine is formed in 32% yield, after

24 h, in the presence of 2 mol% of the hexahydride compound, at the same temperature. An increment of the amount of catalyst precursor to 5 mol% increases the yield to 87%, which further rises up to 92% with a slight increase of the temperature to 60°C. In view of these results, we decided to carry out the dihydroboration of nitriles using 5 mol % of the hexahydride complex, at 60 °C.

Table 1. Optimization for the Catalytic Dihydroboration of Alkyl Nitriles[a]

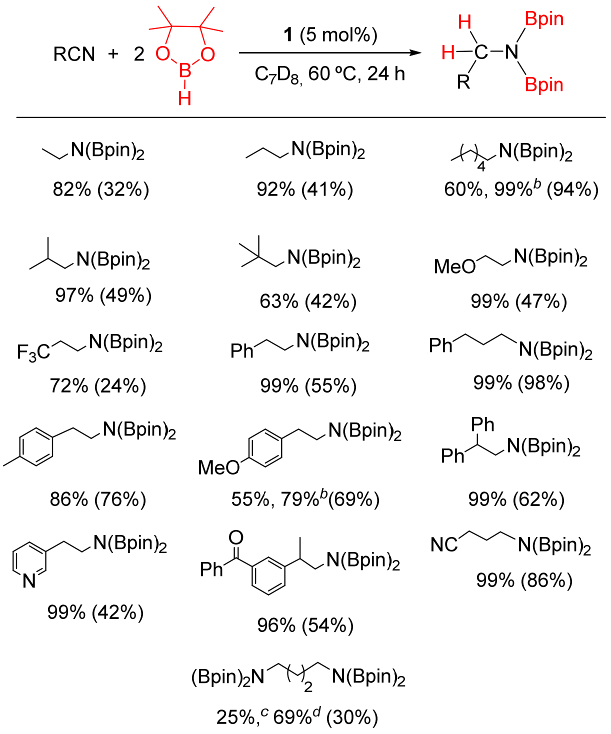


Entry	**1** (mol %)	*T* (°C)	Yield (%)[b]
1	0	50	0
2	2	50	32
3	5	50	87
4	5	60	92

[a] Reaction conditions: propionitrile (12.3 μL, 0.17 mmol), HBpin (50 μL, 0.34 mmol), mesitylene (24 μL, 0.17 mmol), in 0.5 mL of C_7D_8, for 24 h. [b] Yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

Scheme 1 shows the diborylamines generated under the selected conditions. Complex **1** displays good tolerance to functional groups. Accordingly, it promotes the dihydroboration of a noticeable variety of alkyl nitriles, including unfunctionalized substrates of linear and branched chains, among others, the challenging trisubstituted pivalonitrile, and functionalized alkyl nitriles with methoxide, trifluoromethyl, aryl, pyridyl, benzoyl, or cyanide groups. The corresponding sixteen diborylamines were formed, in all cases, in excellent yields after 24 or 48 h (checked by ^{1}H-NMR) and were isolated in moderate to good yields. These results therefore confirm the wide scope and functional group tolerance of the transformation. In this context, it is noteworthy the preparation of the unpublished products *N*,*N*-di(pinacolboryl)- hexylamine, 3,3,3-trifluoropropylamine, 3-phenylpropylamine, 4-methylphenethylamine, 2-(pyridin-3-yl)ethylamine, 2-(3-benzoylphenyl)-propyl)amine, 4-(di(pinacolboryl)amino)butanenitrile, and *N*,*N*,*N'*,*N'*-tetra(pinacolboryl)-1,4-diamine. Particularly remarkable is the sequential tetrahydroboration of succinonitrile, which allows the quantitative formation of the dihydroboration amino-nitrile product and its isolation in 86% yield.

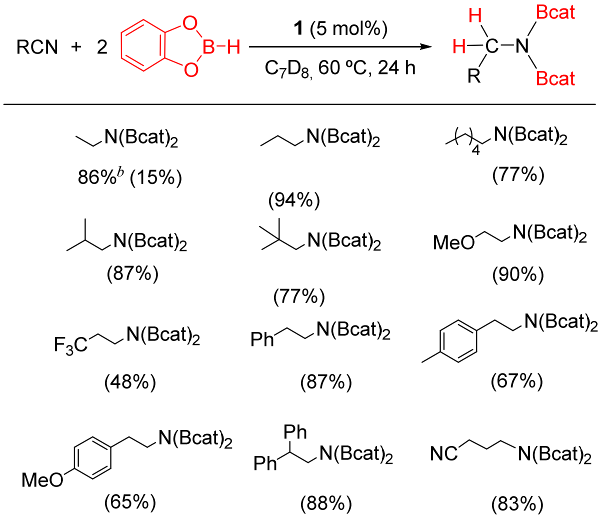
Scheme 1. Dihydroboration of Nitriles with Pinacolborane[a]



[a]Reaction conditions: nitrile (0.17 mmol), HBpin (0.34 mmol), mesitylene (0.17 mmol), **1** (8.5×10^{-3} mmol, 5 mol%), in 0.5 mL of C_7D_8, at 60 ºC for 24 h. Yields were determined by ^1H NMR spectroscopy using mesitylene as internal standard. Isolated yields are given between brackets. [b]Yield after 48 h. [c]HBpin (0.68 mmol). [d]HBpin (0.68 mmol) for 48 h.

Having demonstrated the ability of **1** to promote the dihydroboration of alkyl nitriles with HBpin, we next decided to explore the dihydroboration with HBcat. The reactions were performed under our standard optimized conditions except for the temperature, which was lowered to 50 ºC in order to prevent partial decomposition of the borane. Similar to the process involving HBpin, two molecules of HBcat were efficiently added to the C–N triple bond of the same alkyl nitriles, in the presence of the hexahydride complex. In the absence of the catalyst precursor, the addition did not take place in this case either. A noticeable difference between the $RCH_2N(Bpin)_2$ and $RCH_2N(Bcat)_2$ amines is the insolubility of the latter in the reaction medium, which facilitates their isolation. As a consequence, twelve $RCH_2N(Bcat)_2$ amines were isolated in good yields, after 24 h; some of them not described so far (Scheme 2).

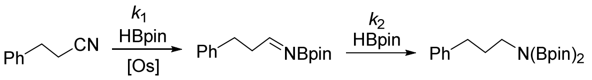
Scheme 2. Dihydroboration of Nitriles with Catecholborane[a]



[a]Reaction conditions: nitrile (0.23 mmol), HBcat (0.46 mmol), mesitylene (0.23 mmol), **1** (1.15 x 10^{-2} mmol, 5 mol%), in 0.5 mL of C_7D_8, at 50 ºC for 24 h. Isolated yields are given between brackets. [b]Yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

Kinetic Analysis. In order to gain insight into the intimate details of the dihydroboration, the kinetics of the addition of HBpin to 3-phenylpropanenitrile in toluene-d_8 was studied, under pseudo-first order conditions. The transformation was followed by ^{1}H NMR spectroscopy in the 344–369 K temperature range, for concentrations of catalyst precursor and borane between 4.6 x

10^{-3} and 7.6 x 10^{-3} M and 1.52 and 3.03 M, respectively, and the initial concentration of nitrile of 7.6 x 10^{-2} M. The spectra revealed that the dihydroboration is a process consisting of two consecutive irreversible reactions (eq 2), namely the monohydroboration of the nitrile to afford the borylimine (k_1) and the hydroboration of the latter to give the diborylamine (k_2). Figure 1 shows the course of one of the reactions.



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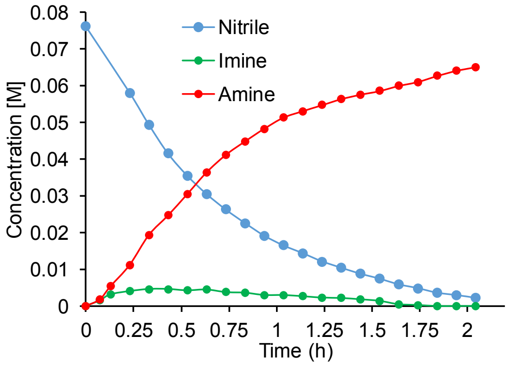


Figure 1. Composition of the reaction mixture as a function of time for the dihydroboration of $PhCH_2CH_2CN$ (7.6 x 10^{-2} M) with HBpin (2.62 M) catalyzed by **1** (7.6 x 10^{-3} M) at 353 K.

The change in nitrile, borylimine, and diborylamine concentrations over the time accordingly fits to eqs 3-5:[24]

$$[\mathrm{RCN}] = [\mathrm{RCN}]_0 e^{-k_1^{\mathrm{obs}} t} \tag{3}$$

$$[\mathrm{RCHNBpin}] = \frac{k_1^{\mathrm{obs}}[\mathrm{RCN}]_0}{k_2^{\mathrm{obs}} - k_1^{obs}}\left(e^{-k_1^{\mathrm{obs}} t} - e^{-k_2^{\mathrm{obs}} t}\right) \tag{4}$$

$$[\mathrm{RCH_2N(Bpin)_2}] = [\mathrm{RCN}]_0 + \frac{[\mathrm{RCN}]_0}{k_1^{\mathrm{obs}} - k_2^{\mathrm{obs}}}\left(k_2^{\mathrm{obs}} e^{-k_1^{\mathrm{obs}} t} - k_1^{\mathrm{obs}} e^{-k_2^{\mathrm{obs}} t}\right) \tag{5}$$

where

$$k_1^{\mathrm{obs}} = k_{1a}^{\mathrm{obs}}[\mathrm{Os}]^a \tag{6}$$

and

$$k_{1a}^{\mathrm{obs}} = k_1[\mathrm{HBpin}]^{b} \qquad (7)$$

whereas

$$k_2^{\mathrm{obs}} = k_{2a}^{\mathrm{obs}}[\mathrm{Os}]^{c} \qquad (8)$$

and

$$k_{2a}^{\mathrm{obs}} = k_2[\mathrm{HBpin}]^{d} \qquad (9)$$

Values of k_1^{obs} and k_2^{obs} obtained according to eqs 3-5 for the respective concentrations of catalyst precursor and borane, in the studied temperature range, are collected in Table 2.

Table 2. Kinetic Data for the Dihydroboration of 3-Phenylpropanenitrile (7.6 x 10^{-2} M in Toluene-d_8 Promoted by 1

T (K)	**1** (10^3 M)	HBpin (M)	k_1^{obs} (10^4 s^{-1})	k_{1a}^{obs} (10^2 M^{-1}s^{-1})	k_1 (10^2 M^{-2}s^{-1})	k_2^{obs} (10^4 s^{-1})	k_2 (10^4 M^{-1}s^{-1})
353	7.6	1.52	(3.0 ± 0.1)	(3.9 ± 0.4)	(2.6 ± 0.3)	(4.4 ± 0.4)	(2.9 ± 0.3)
353	6.9	1.52	(2.7 ± 0.1)	(3.9 ± 0.4)	(2.6 ± 0.3)	(4.4 ± 0.4)	(2.9 ± 0.3)
353	6.1	1.52	(2.5 ± 0.1)	(4.1 ± 0.4)	(2.7 ± 0.3)	(4.5 ± 0.5)	(3.0 ± 0.3)
353	5.3	1.52	(2.1 ± 0.1)	(4.0 ± 0.4)	(2.6 ± 0.3)	(4.5 ± 0.5)	(3.0 ± 0.3)
353	4.6	1.52	(1.9 ± 0.1)	(4.1 ± 0.4)	(2.7 ± 0.3)	(4.5 ± 0.5)	(2.9 ± 0.3)
353	7.6	1.93	(3.5 ± 0.1)	(4.6 ± 0.5)	(2.4 ± 0.2)	(6.3 ± 0.6)	(3.3 ± 0.3)
353	7.6	2.34	(4.1 ± 0.2)	(5.3 ± 0.5)	(2.3 ± 0.2)	(7.3 ± 0.7)	(3.1 ± 0.3)
353	7.6	2.62	(4.7 ± 0.2)	(6.1 ± 0.6)	(2.3 ± 0.2)	(8.7 ± 0.9)	(3.3 ± 0.3)
353	7.6	3.03	(5.4 ± 0.1)	(7.1 ± 0.7)	(2.4 ± 0.2)	(10.0 ± 1.0)	(3.3 ± 0.3)
344	7.6	1.52	(1.4 ± 0.1)	(1.9 ± 0.2)	(1.2 ± 0.1)	(2.6 ± 0.3)	(1.7 ± 0.2)
348	7.6	1.52	(2.2 ± 0.1)	(2.9 ± 0.3)	(1.9 ± 0.2)	(3.4 ± 0.3)	(2.2 ± 0.2)
362	7.6	1.52	(6.1 ± 0.3)	(8.0 ± 0.8)	(5.3 ± 0.5)	(8.7 ± 0.9)	(5.7 ± 0.6)
369	7.6	1.52	(10.9 ± 0.6)	(14.2 ± 1.4)	(9.4 ± 0.9)	(15.3 ± 1.5)	(10.1 ± 1.0)

A plot of log(k_1^{obs}) versus log[Os] for a borane concentration of 1.52 M yields a straight line of slope 0.9 (Figure S87). Thus, the values of k_{1a}^{obs} given in Table 2 were obtained from eq 6 for $a = 1$. Similarly, the plot of log(k_{1a}^{obs}) versus log[HBpin] yields a straight line of slope 0.9 (Figure S88), indicating that also $b = 1$ in eq 7. Accordingly, the plot of k_{1a}^{obs} versus [HBpin] (Figure 2) provides a value of $2.3 \pm 0.2 \times 10^{-2}$ M^{-2} s^{-1} for k_1 at 353 K. The activation parameters obtained from the Eyring analysis (Figure 3) are $\Delta H^{\ddagger} = 19.3 \pm 2.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.3 \pm 7.0$ cal mol^{-1} K^{-1}, which yield a $\Delta G^{\ddagger}$ value of 22.7 ± 4.6 kcal mol^{-1} at 298 K.

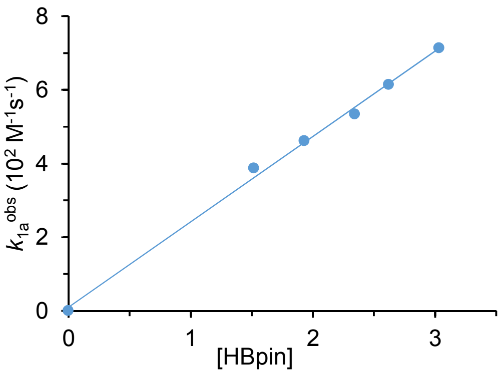


Figure 2. Plot of k_{1a}^{obs} versus [HBpin] for the monohydroboration of $PhCH_2CH_2CN$ (7.6×10^{-2} M) with HBpin promoted by **1** (7.6×10^{-3} M) in toluene-d_8 at 353 K.

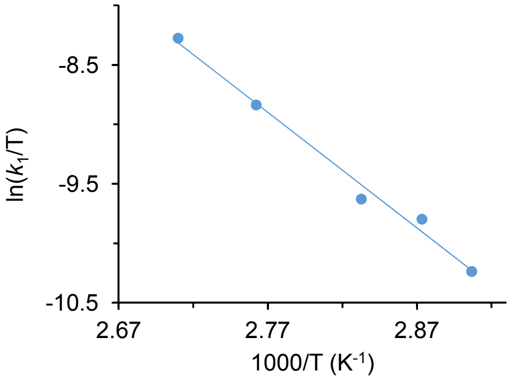


Figure 3. Eyring plot for the monohydroboration of $PhCH_2CH_2CN$ promoted by **1** in toluene-d_8.

Rate constant k_2^{obs} is independent of the concentration of the catalyst precursor within the experimental error (Figure 4), in agreement with $c = 0$ in eq 8; i. e., $k_2^{obs} = k_{2a}^{obs}$. This result firmly demonstrates that, in contrast to the monohydroboration of the nitrile, the hydroboration of the borylimine is a metal-free stoichiometric reaction. On the contrary to eq 8, the plot of $\log(k_{2a}^{obs})$ versus log[HBpin] yields a straight line of slope 1.2 (Figure S89), in accordance with $d = 1$ in eq 9. Thus, the plot of k_2^{obs} versus [HBpin] (Figure 5) provides a value of $3.3 \pm 0.3 \times 10^{-4}$ M^{-1} s^{-1} for k_2 at 353 K. In this case, the activation parameters obtained from the corresponding Eyring analysis (Figure 6) are $\Delta H^{\ddagger} = 17.1 \pm 2.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -26.4 \pm 6.5$ cal mol^{-1} K^{-1}, which yield a $\Delta G^{\ddagger}$ value of 24.9 ± 4.6 kcal mol^{-1} at 298 K.

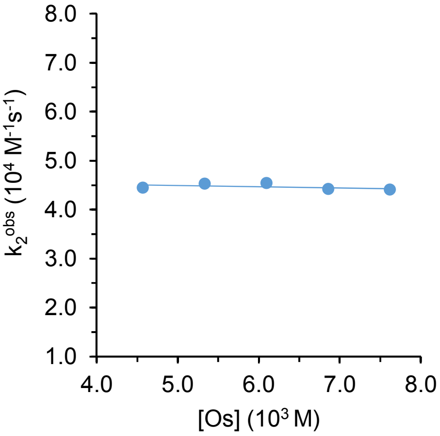


Figure 4. Plot of k_2^{obs} versus [Os] for the transformation of $PhCH_2CH{=}CNBpin$ into $PhCH_2CH_2CN(Bpin)_2$ in toluene-d_8 at 353 K).

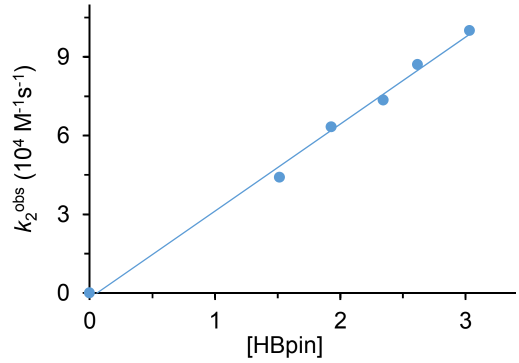


Figure 5. Plot of k_{2a}^{obs} versus [HBpin] for the transformation of $PhCH_2CH{=}CNBpin$ into $PhCH_2CH_2CN(Bpin)_2$ in toluene-d_8 at 353 K.

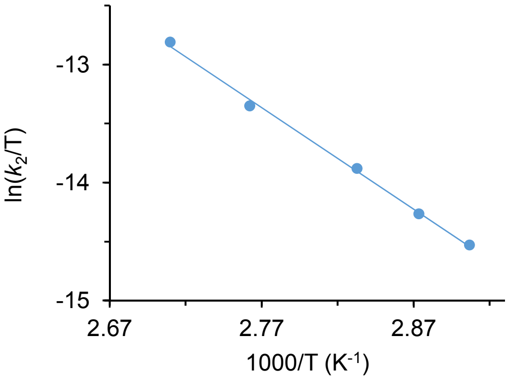
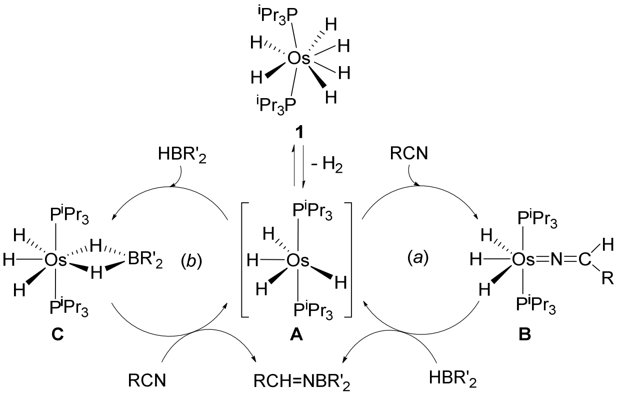


Figure 6. Eyring plot for the transformation of $PhCH_2CH{=}CNBpin$ into $PhCH_2CH_2CN(Bpin)_2$ in toluene-d_8.

Mechanism of the Monohydroboration. The stoichiometric reactions of the hexahydride **1** with alkyl nitriles and HBR_2 boranes have been previously studied. Alkyl nitriles afford trihydride-azavinylidene derivatives $OsH_3(=N=CHR)(P^iPr_3)_2$,[23] whereas boranes give trihydride-dihydrideborate compounds $OsH_3\{\kappa^2\text{-}H,H\text{-}(H_2BR'_2)\}(P^iPr_3)_2$.[25] In both cases, the reactions take place via the unsaturated tetrahydride intermediate $OsH_4(P^iPr_3)_2$ (**A**), which lies in equilibrium with the hexahydride. So, at the first glance, the monohydroboration of the C-N triple bond could take place through two different routes: (a) azavinylidene or (b) dihydrideborate. The former should involve the initial formation of trihydride-azavinylidene intermediates **B** which could subsequently react with the boranes to give the borylimines and regenerate the tetrahydride **A**. In the second one, the coordination of a borane to the latter should lead to trihydride-dihydrideborate compounds **C**, which could subsequently react with the nitriles to yield the borylimines and recover the tetrahydride (cycles *a* and *b*, respectively, in Scheme 3). Both mechanisms are consistent with the kinetic results, although the rate determining step in each cycle should be different. While the reactions of the trihydride-azavinylidene intermediates **B** with the boranes should be the slow step for the azavinylidene route, the reactions of the trihydride-dihydrideborate species **C** with the nitriles should be the step with the highest activation energy for the dihydrideborate route.

Scheme 3. Possible Catalytic Cycles for the Nitrile Monohydroboration Promoted by 1



Previous DFT calculations have suggested that the insertion of the alkyl nitriles into one of the Os-H bonds of tetrahydride **A**, to afford trihydride-azavinylidene **B**, has to overcome a barrier of about 18 kcal mol^{-1},[23] while the coordination of the borane to the unsaturated species **A** is a barrierless process. According to this, under the same conditions, the formation of dihydrideborate intermediates **C** should be kinetically favored with respect to azavinylidene species **B** and therefore cycle *b* should be the predominant one in the catalysis. In order to confirm this preference, we studied three different competitive reactions pivalonitrile-HBpin at 60 ºC, pivalonitrile-HBcat at 50 ºC, and 3-phenylpropanenitrile-HBpin at 30 ºC. In all cases the treatment of **1** with these equimolecular nitrile-borane combinations leads to mixtures of the hexahydride precursor and the trihydride-dihydrideborate compounds. No traces of the alternative trihydride-azavinylidene complexes were detected.

Once the preference for cycle *b* was experimentally confirmed, we decided to analyze the reactions of the dihydrideborate intermediates **C** with the nitriles. Complexes **C** are coordinatively saturated species. Two ways are the most probable for their activation: rupture of one of the Os–H–B bridges by direct nucleophilic attack of the nitrile to the boron atom and dissociation of a hydrogen molecule. To gain more insight into it, we carried out DFT calculations at the dispersion-corrected PCM(toluene)-B3LYP-D3/def2-SVP level (see computational details in the Supporting Information) using dihydridepinacolborate and acetonitrile as models of dihydrideborate and nitrile, respectively. The changes in free energy (ΔG) were calculated in toluene at 298.15 K and 1 atm.

The nucleophilic attack of the nitrile to the boron atom of the dihydrideborate **C** produces a tetrahydride-nitrileborane adduct (see Figure S90), which lies 24.7 kcal mol^{-1} above the separate reactants **C** + MeCN. This intermediate has to overcome an additional barrier of 7.7 kcal mol^{-1} to yield the borylimine, i.e., the activation energy through this pathway of 32.4 kcal mol^{-1} is too high compared to that observed experimentally. So, it can be safely ruled out.

We then turned our attention to the alternative pathway involving an initial H_2 release. Figure 7 shows the computed energy profile for this dissociative route, whereas Scheme 4 gathers all the intermediates involved in the catalytic cycle. The creation of a coordination vacancy in the saturated dihydrideborate **C** by dissociation of a hydrogen molecule takes place through the

Kubas type dihydrogen ($d_{H\text{-}H}$ = 0.923 Å)[20] σ-borane ($d_{B\text{-}H}$ = 1.351 Å)[25] intermediate **D**, which lies 6.3 kcal mol^{-1} above the initial dihydrideborate **C**. The dissociation of the coordinated dihydrogen molecule, to afford the unsaturated species **E**, produces a destabilization of 6.8 kcal mol^{-1}. Therefore, the H_2 release is an endergonic process (ΔG_R = 13.1 kcal mol^{-1}). The coordination of the nitrile to **E** is a strongly exergonic process (ΔG_R = –7.5 kcal mol^{-1}) and leads to the key intermediate of the process **F**, which lies 5.6 kcal mol^{-1} above the trihydride-dihydrideborate **C**. The insertion of the coordinated nitrile into the Os–B bond of the Os-σ-borane unit of **F** initially gives **G**, which subsequently evolves to **H**, by rupture of the boron-hydride interaction. The regioselectivity of the insertion is consistent with the nucleophilicity of the nitrogen atom and the electrophilicity of the carbon atom of the nitrile.[26] The computed barrier for this step is 15.9 kcal mol^{-1}; i. e., 21.5 kcal mol^{-1} with respect to the separate reactants **C** + MeCN, and constitutes the rate-determining step of the transformation. The value is fully consistent with that experimentally obtained from Figure 3. The coordination of the previously released hydrogen molecule to the unsaturated center of **H** affords the bis(Kubas-type dihydrogen) intermediate **I** ($d_{H\text{-}H}$ = 0.899 and 0.920 Å), which undergoes an almost barrierless ($\Delta G^{\neq}$ = 2 kcal mol^{-1}, via $TS_{I\text{-}J}$) homolytic cleavage of both dihydrogen ligands to give the pentahydride **J**, having a typical dodecahedral structure of the eight-coordinate osmium-polyhydrides.[27] Final reductive elimination via $\mathbf{TS_{J\text{-}K}}$ ($\Delta G^{\neq}$ = 9.5 kcal mol^{-1}) followed by dissociation of the readily formed borylimine regenerates the active tetrahydride catalyst **A**.

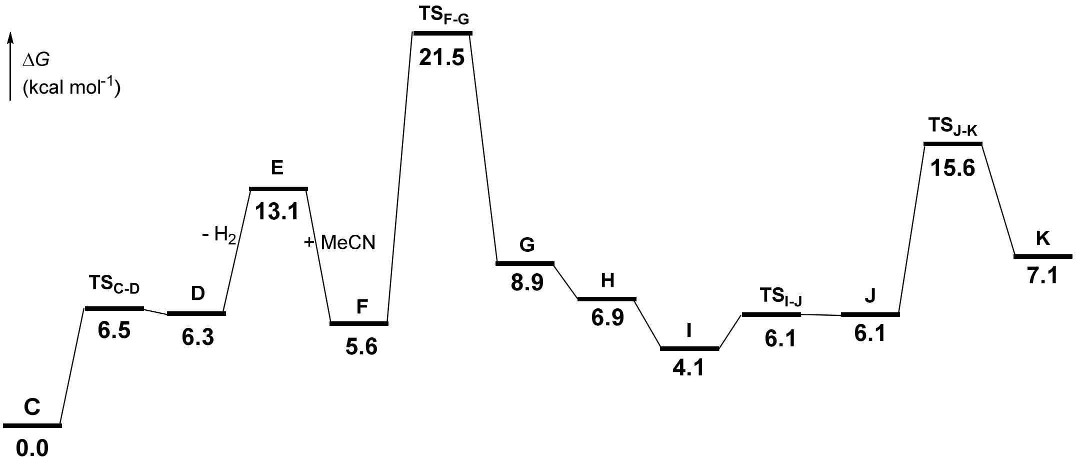
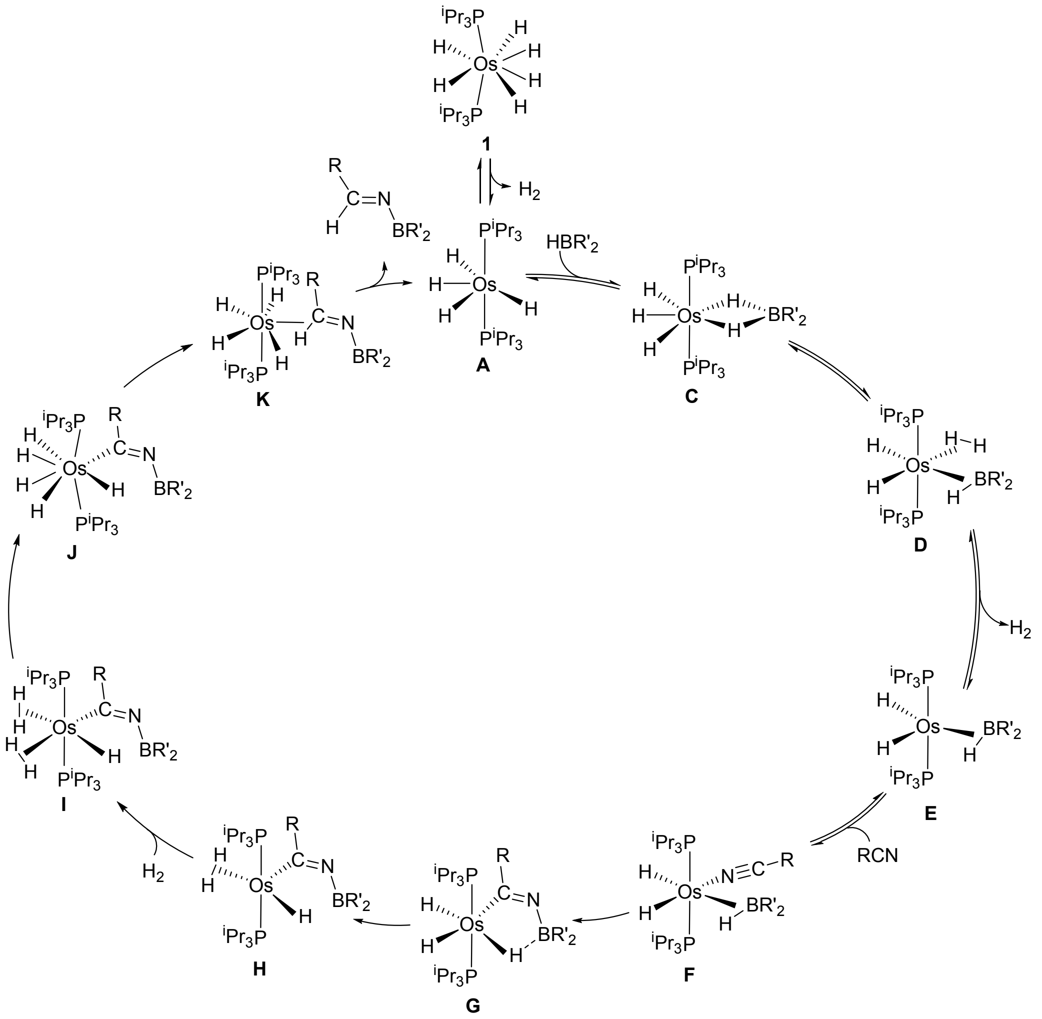


Figure 7. DFT-Computed energy profile for the catalytic monohydroboration of acetonitrile with HBpin via the dissociative route. Relative free energies (Δ*G*, at 298.15 K) are given in kcal mol^{-1} and were computed at the PCM(toluene)-B3LYP-D3/def2-SVP level.

Scheme 4. Catalytic Cycle for the Monohydroboration of Alkyl Nitriles Promoted by 1



Concluding remarks

This work reveals the discovery of the first catalyst of a 5d metal for the preparation of diborylamines through the addition of pinacolborane or catecholborane to the C-N triple bond of nitriles. Accordingly, we have demonstrated that the hexahydride complex $OsH_6(P^iPr_3)_2$ efficiently promotes the dihydroboration of alkyl nitriles of unfunctionalized linear and branched chains, and functionalized chains with methoxide, trifluoromethyl, aryl, pyridyl, benzoyl, or cyanide groups. The *N*,*N*-diborylamines, including thirteen new products not described so far, are generally isolated in high yields. A detailed kinetic study of the catalysis points out that the dihydroboration is a process consisting of two consecutive irreversible reactions, namely the catalytic metal-promoted monohydroboration of the nitrile to afford the borylimine followed by the metal-free stoichiometric hydroboration of the latter to give the diborylamine.

The formation of the borylimine takes place through saturated trihydride-dihydroborate intermediates $OsH_3\{\kappa^2\text{-}H,H\text{-}(H_2BR_2)\}(P^iPr_3)_2$ (BR_2 = Bpin, Bcat), which are generated by coordination of the boranes to the true catalyst, the tetrahydride $OsH_4(P^iPr_3)_2$. DFT calculations suggest that these intermediates evolve to unsaturated σ-borane species, which coordinate the nitrile. By comparing the overall computed barrier with the activation energy experimentally obtained for the monohydroboration reaction, it is found that the insertion of the C-N triple bond of the coordinated nitrile into the Os–B bond of the osmium-σ-borane unit constitutes the rate determining step of the catalysis. The process is regio-directed by the nucleophilicity of the nitrogen atom and the electrophilicity of the carbon atom of the nitrile.

In summary, a very efficient catalyst of a 5d transition element for the dihydroboration of a wide range of alkyl nitriles has been discovered and the mechanism of the catalysis has been established by combination of experimental and computational evidence.

Experimental Section

General Information. All reactions were performed with rigorous exclusion of air at an argon/vacuum manifold using standard Schlenk-tube or glovebox techniques. Toluene and pentane were obtained oxygen- and water-free from an MBraun solvent purification apparatus. Complex **1** was prepared according to the published method.[28] Nitriles were purchased from commercial sources and distilled in a Kugelrohr distillation oven. NMR spectra were recorded on a Bruker ARX 300, Bruker Avance 300 MHz, or a Bruker Avance 400 MHz instruments.

Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}), external H_3PO_4 (^{31}P{^{1}H}), $BF_3·OEt_2$ (^{11}B), or $CFCl_3$ (^{19}F). Coupling constants are given in Hertz. High-resolution (HR-MS) electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). DFT computational details are given in the Supporting Information.

General Procedure for the Catalytic Hydroboration of Nitriles with Pinacolborane. The particular nitrile (0.17 mmol), pinacolborane (50 μL, 0.34 mmol), and mesitylene (24 μL, 0.17 mmol) were added to an NMR tube containing a solution of **1** (4.4 mg, 8.5 x 10^{-3} mmol, 5 mol%) in 0.5 mL of C_7D_8, under argon atmosphere. The mixture was heated at 60 ºC, in an oil bath, for 24 h. After this time ^{1}H NMR were measured and yields were calculated based on the integration of characteristic peaks of the amines formed against the methyl resonances of the internal standard. After the crude was checked by ^{1}H NMR, the reaction mixture was transferred to a vial in the glove box and the solvent was removed under vacuum. A saturated solution of the mixture in pentane was kept at -30 ºC for 24 h; during this time colorless crystals of the diborylamines appeared, which were characterized by ^{1}H and ^{13}C{^{1}H} NMR. The unpublished diborylamines were also characterized by HR-MS. It should be noted that diborylamines are sensitive to moisture. Thus, its characterization and isolation were performed with rigorous exclusion of air.

General Procedure for the Catalytic Hydroboration of Nitriles with Catecholborane. The respective nitrile (0.23 mmol), catecholborane (50 μL, 0.46 mmol), and mesitylene (32 μL, 0.23 mmol) were added to an NMR tube containing a solution of **1** (5.9 mg, 1.15 x 10^{-2} mmol, 5 mol%) in 0.5 mL of C_7D_8, under argon atmosphere. The mixture was heated at 50 ºC, in an oil bath, for 24 h. During the reaction the diborylamines precipitated in the reaction media. The mixture was transferred to a vial in the glove box and the solvent was removed under vacuum.

The remaining white solid was washed with pentane (3 x 0.5 mL) and dried under vacuum. The resulting diborylamines were characterized by ^{1}H and ^{13}C{^{1}H} NMR. It should be noted that diborylamines are sensitive to moisture. Thus, its characterization and isolation were performed with rigorous exclusion of air.

Kinetic Experiments. An NMR tube was charged in the glovebox with 3-phenylpropanenitrile (0.038 mmol, 0.076 M), HBpin (110 – 220 μL, 0.76 – 1.52 mmol, 1.52 – 3.45 M), complex **1** (2.3 x 10^{-3} – 3.8 x 10^{-3} mmol, 4.6 x 10^{-3} – 7.6 x 10^{-3} M), and mesitylene (0.038 mmol, 0.076 M) as an internal standard and the total volume was made to 0.5 mL with C_7D_8. Complex **1** was taken from a stock solution 0.023 M in C_7D_8. 3-Phenylpropanenitrile and mesitylene were added from a stock solution 0.38 M of both in C_7D_8. All the experiments were done changing either the borane or catalyst concentration keeping constants the other reagents. All NMR data were recorded on a Bruker ARX300 operating at 300.13 MHz (^{1}H) and were recorded at 353 K unless stated otherwise. ^{1}H NMR spectra were recorded at regular intervals of 5 min during 2 h (or until 90 % of nitrile was transformed) and changes in the area of nitrile and products resonances were monitored. Rate constants k_1^{obs} were obtained according to eq 3 by plotting ln([RCN]/[RCN]$_0$) versus time for the different concentrations of **1** and HBpin. Rate constants k_2^{obs} were obtained according to eq 5 by least-squares adjustment.

ASSOCIATED CONTENT

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

Analytical data of the diborylamines, NMR spectra, plots of log(k_1^{obs}) vs log[Os], log(k_{1a}^{obs}) vs log[HBpin], and log(k_2^{obs}) vs log[HBpin], computational details and energies of computed structures (PDF)

Cartesian coordinates of calculated structures (XYZ)

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Notes

The authors declare no competing financial interest.

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