



Cite this: *Dalton Trans.*, 2015, **44**, 18945

Received 30th July 2015,
Accepted 2nd October 2015
DOI: 10.1039/c5dt02945g

www.rsc.org/dalton

Imido–hydrido complexes of Mo(IV): catalysis and mechanistic aspects of hydroboration reactions†

Andrey Y. Khalimon,^{*a,b} Philip M. Farha^a and Georgii I. Nikonov^{*a}

Imido–hydrido complexes (ArN)Mo(H)(Cl)(PMe₃)₃ (**1**) and (ArN)Mo(H)₂(PMe₃)₃ (**2**) (Ar = 2,6-diisopropylphenyl) catalyse a variety of hydroboration reactions, including the rare examples of addition of HBCat to nitriles to form bis(borylated) amines RCH₂N(BCat)₂. Stoichiometric reactivity of complexes **1** and **2** with nitriles and HBCat suggest that catalytic reactions proceed *via* a series of agostic borylamido and borylamino complexes. For complex **1**, catalysis starts with addition of nitriles across the Mo–H bond to give (ArN)Mo(Cl)(N=CHR)(PMe₃)₂; whereas for complex **2** stoichiometric reactions suggest initial addition of HBCat to form the agostic complex Mo(H)₂(PMe₃)₃(η³-NAr-HBcat) (**16**).

Introduction

Reduction of unsaturated C–C, C–E, and E–E (where E – heteroatom) bonds is one of the most fundamental reactions in synthetic organic chemistry.^{1,2} Historically, the hydroboration reaction plays a major role in the reduction of unsaturated organic molecules. While addition of aryl and alkyl hydroboranes to multiple C–C, C–O, and C–N bonds is known to proceed quite easily,^{1,3} the use of deactivated hydroboranes such as HBCat and HBPIn (Cat = catechol, Pin = pinacol), requires transition metal catalysis^{2b} due to the significantly decreased Lewis acidity of the boron centre. Such reactions are mainly restricted to late transition systems, such as Rh, Ir, *etc.*^{2,4}

Due to the skyrocketing prices of heavy late transition metals and their recognised toxicity,⁵ the demand for cheaper and more environmentally benign surrogates has emerged. In this regard, early transition metals offer an appealing alternative as they are generally much cheaper and exhibit low toxicity. Nevertheless, compared to the late metal systems, application of early transition complexes in hydroboration catalysis is somewhat less studied.^{4d} The reported examples of catalytic hydroboration of unsaturated hydrocarbons by early transition metal complexes are mostly limited to Zr and Ti systems.⁶ Stoichiometric hydroboration of olefins with HBCat was also shown for Ta and Nb metallocene complexes.⁷ And

much less is known about the application of early transition metal systems in hydroboration of carbonyl compounds,^{4d,8,9} imines¹⁰ and nitriles.^{4d,11}

We have recently reported catalytic and mechanistic studies on the hydrosilylation reactions mediated by the Mo(IV) imido–hydrido complex (ArN)Mo(H)(Cl)(PMe₃)₃ (**1**; Ar = 2,6-*i*-Pr₂C₆H₃).¹² Taking into account the more hydridic nature of the H–B bond in hydroboranes such as HBCat and HBPIn, *vs.* hydrosilanes R_nSiH_{4–n}, coupled with the increased Lewis acidity of the boron centre *vs.* the silicon centre, we anticipated that the reactivity of **1** with hydroboranes would be enhanced compared to hydrosilanes. And indeed, **1** has been found to catalyse a variety of H–B addition reactions, including the first examples of hydroborations of nitriles.¹³ Moreover, our preliminary mechanistic studies suggested that these reactions proceed *via* agostic B–H...M intermediates. Here we present further details of stoichiometric and catalytic reactions of imido–hydrido complexes of Mo(IV), offering additional insights into the possible mechanism(s) of these reactions.

Results and discussion

Complex **1** was prepared from the dichloride precursor (ArN)MoCl₂(PMe₃)₃¹⁴ according to the previously published procedure and its spectroscopic and structural features have been reported previously.¹² Addition of an equivalent of *l*-selectride to **1** selectively affords the imido–dihydrido derivative (ArN)MoH₂(PMe₃)₃ (**2**, Scheme 1). **2** can be prepared from (ArN)MoCl₂(PMe₃)₃ directly *via* treatment with two equivalents of *l*-selectride.

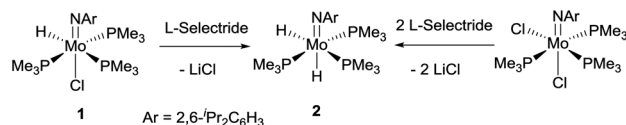
Complex **2** is unstable at room temperature, showing slow decomposition into a mixture of unidentified compounds even in the solid state over the course of several days, and

^aDepartment of Chemistry, Brock University, 500 Glenridge Ave., St. Catharines, ON L2S 3A1, Canada. E-mail: gnikonov@brocku.ca; Tel: +1 905 688 5550, ext 3350

^bDepartment of Chemistry, School of Science and Technology, Nazarbayev University, 53 Kabanbay Batyr Ave., Astana 010000, Kazakhstan.

E-mail: andrey.khalimon@nu.edu.kz; Tel: +7 7172 709102

† Electronic supplementary information (ESI) available: Additional experimental and spectroscopy details, general procedures for catalytic hydroboration reactions. See DOI: 10.1039/c5dt02945g



Scheme 1 Synthesis of $(\text{ArN})\text{MoH}_2(\text{PMe}_3)_3$ (**2**).

therefore defies isolation in the analytically pure state. Despite the instability, the dihydride **2** can be cleanly generated by the above procedure and the freshly prepared samples can be reliably characterised by multinuclear NMR and IR spectroscopy. Complex **2** is highly fluxional in solution and its room temperature NMR spectra exhibit only broad featureless resonances. However, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** recorded at -26°C shows two mutually coupled resonances for two sets of non-equivalent phosphine groups at δ 14.8 ppm (doublet) and 13.1 ppm (triplet) with $^2J_{\text{P-P}} = 19.4$ Hz. At -29°C , the ^1H NMR spectrum of **2** reveals two non-equivalent Mo-bound hydrides, which give rise to two mutually coupled ($^2J_{\text{H-H}} = 7.2$ Hz) resonances at δ -5.31 ppm (dtd) and 2.08 ppm (multiplet, overlapping with the resonance of toluene- d_8 , found by the ^1H - ^1H COSY and ^1H - ^{31}P HSQC NMR). In the ^1H - ^{31}P HSQC NMR spectra, these hydride signals are coupled to the ^{31}P signals with $^2J_{\text{H-P}} = 46.2$ and 60.6 Hz and $^2J_{\text{H-P}} = 43.2$ Hz, respectively. The presence of hydride ligands is also confirmed by the observation of the Mo-H stretch at

1620 cm^{-1} in the IR spectrum of **2**. Based on these spectroscopic features and on the analogy with the mono(hydride) derivative **1**,^{12,13} we suggest an octahedral structure for the dihydride **2**, with one of the hydride ligands occupying the apical position *trans* to the imido ligand. The second Mo-bound hydride of **2** lies in the equatorial position, being co-planar with all three PMe_3 ligands, as depicted in Scheme 1.

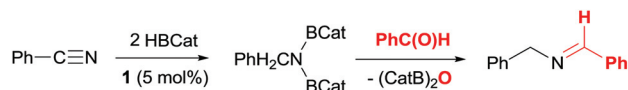
Catalytic reactivity of $(\text{ArN})\text{Mo}(\text{H})(\text{Cl})(\text{PMe}_3)_3$ (**1**) and $(\text{ArN})\text{MoH}_2(\text{PMe}_3)_3$ (**2**)

Catalysis by $(\text{ArN})\text{Mo}(\text{H})(\text{Cl})(\text{PMe}_3)_3$ (1**).** The imido-hydrido **1** has been found to catalyse a variety of hydroboration reactions (Table 1).¹³ Thus, the addition of HBCat to ketones ($^i\text{Pr}_2\text{C}(\text{O})$, $\text{Ph}_2\text{C}(\text{O})$, cyclohexanone, $\text{PhC}(\text{O})\text{Me}$,¹⁵ 4-nitroacetophenone) in the presence of 5 mol% of **1** affords the corresponding boronic esters in high yields (91–100%; Table 1, entries 1–5). Similarly, the ester $\text{MeC}(\text{O})\text{OEt}$ was converted into the ethoxy group of EtOBCat (entry 6). Alkenes (styrene, 1-hexene)^{6b-g,7} and alkynes (3-hexyne, phenylacetylene)^{6a,h,i} can be reduced to the boryl-substituted alkanes and alkenes, respectively (Table 1, entries 7–10). Interestingly, the **1**-catalysed reaction with styrene also gives *trans*- $\text{PhCH}=\text{CHBCat}$ and ethylbenzene in addition to the expected product $\text{PhCH}_2\text{CH}_2\text{BCat}$. The former product likely forms as a result of dehydrogenative addition of HBCat to styrene. In contrast, a reduced or no catalytic activity of the hydride **1** was observed in the hydroboration of 1-hexene, cyclohexene, α -methyl-

Table 1 Hydroboration of organic substrates with HBCat mediated by **1**^a

Entry	Substrate	Conversion ^b , %	Product(s)	<i>t</i>	Yield ^c , %	TON ^d
1	$^i\text{Pr}_2\text{C}(\text{O})$	91	$^i\text{Pr}_2\text{CHOBCat}$	20 h	91	18
2	$\text{Ph}_2\text{C}(\text{O})$	100	$\text{Ph}_2\text{CH}(\text{OBCat})$	30 min	100	20
3	$\text{PhC}(\text{O})\text{Me}$	99	$\text{PhCH}(\text{OBCat})\text{Me}$	15 min	99	20
4	4-Nitroacetophenone	100	4- NO_2 - C_6H_4 - $\text{CH}(\text{OBCat})\text{Me}$	1 h	100	20
5	Cyclohexanone	100	CyOBCat	1 h	100	20
6	$\text{MeC}(\text{O})\text{OEt}$	100	EtOBCat	2 h	100	20
7	$\text{PhCH}=\text{CH}_2$	100	$\text{PhCH}_2\text{CH}_2\text{BCat}$ <i>trans</i> - $\text{PhCH}=\text{CHBCat}$ PhCH_2CH_3	20 h	32 53 15	20
8	1-Hexene	70	HexBCat 2-Hexene 3-Hexene	60h	55 8 7	14
9	3-Hexyne	94	$\text{EtCH}=\text{C}(\text{Et})\text{BCat}$	21 h	94	19
10	$\text{PhC}\equiv\text{CH}$	99	<i>trans</i> - $\text{PhCH}=\text{CHBCat}$	20 h	99	20
11	MeCN	100	$\text{EtN}(\text{BCat})_2$	12 h	100	20
12	PhCN	100	$\text{PhCH}_2\text{N}(\text{BCat})_2$	12 h	100	20
13	5-Hexynenitrile	50	<i>trans</i> - $\text{NC}(\text{CH}_2)_3\text{CH}=\text{CHBCat}$	20 h	50	10
		92	<i>trans</i> - $\text{NC}(\text{CH}_2)_3\text{CH}=\text{CHBCat}$	48 h	92	18
14	4-Acetylbenzonitrile	100	4- CN - C_6H_4 - $\text{CH}(\text{OBCat})\text{Me}$ 4-(CatB) $_2\text{NCH}_2$ - C_6H_4 - $\text{CH}(\text{OBCat})\text{Me}$	12 h	67 33	20
15	Acrylonitrile	65	CatBCH $_2\text{CH}_2\text{CN}$ CatBCH $_2(\text{CH}_2)_2\text{N}(\text{BCat})_2$	48 h	55 10	13
16	3-(2-Oxocyclohexyl)propanenitrile	100	2- $\text{NC}(\text{CH}_2)_2$ - C_6H_{10} -OBCat	5 min	100	20
		100	2- $\text{NC}(\text{CH}_2)_2$ - C_6H_{10} -OBCat 2-(CatB) $_2\text{N}(\text{CH}_2)_3$ - C_6H_{10} -OBCat	48 h	32 68	20
17	$\text{Ph}_2\text{C}(\text{O})/\text{PhCN}$ (1/1)	100	$\text{Ph}_2\text{CH}(\text{OBCat})$ $\text{Ph}_2\text{CH}_2\text{N}(\text{BCat})_2$	12 h	67 33	20

^a 5 mol% of **1**, 22°C , C_6D_6 , substrate/HBCat = 1/1 (1/2 for entries 4, 9, 10, 12, and 15). ^b Conversion of organic substrate, except entries 12, 15 and 16 where the conversion of HBCat was calculated. ^c ^1H NMR yields based on internal standard (tetramethylsilane). ^d Turnover numbers were calculated at the maximum conversion.



Scheme 2 Transformation of nitriles to imines.

styrene, 1-octyne, and $\text{PhC}\equiv\text{CMe}$. Additionally, **1** was found to be active in the hydroboration of organic nitriles (MeCN and PhCN) leading to the products of double addition of HBCat across the $\text{C}\equiv\text{N}$ bond, *i.e.* $\text{RCH}_2\text{N}(\text{BCat})_2$ ($\text{R} = \text{Me}, \text{Ph}$; Table 1, entries 11 and 12).¹³ Moreover, $\text{PhCH}_2\text{N}(\text{BCat})_2$ was found to react easily with benzaldehyde to give the corresponding imine $\text{PhCH}_2\text{N}=\text{CHPh}$ with the release of $(\text{CatB})_2\text{O}$. Taken together, these novel hydroboration and coupling reactions present a useful synthetic transformation of nitriles to imines (Scheme 2).¹⁶ Noteworthy, the formation of imines from bis(boryl) amines proceeds only with aldehydes but not with ketones.

Lastly, **1**-catalysed addition of HBCat to polyfunctional compounds (4-acetylbenzotrile, acrylonitrile, and 3-(2-oxocyclohexyl)propanenitrile) were shown to be not chemoselective, affording mixtures of hydroboration products (Table 1, entries 14–16). In a similar vein, the hydroboration of an equimolar mixture of $\text{Ph}_2\text{C}=\text{O}$ and PhCN afforded both $\text{Ph}_2\text{CH}(\text{OBCat})$ and $\text{Ph}_2\text{CH}_2\text{N}(\text{BCat})_2$ (entry 17). In contrast, the hydroboration of 5-hexynenitrile takes place selectively on the alkyne moiety to give *trans*- $\text{NC}(\text{CH}_2)_3\text{CH}=\text{CHBCat}$, leaving the nitrile group unreacted (Table 1, entry 13).

Catalysis by $(\text{ArN})\text{MoH}_2(\text{PMe}_3)_3$ (2**).** Compared to **1**, the new imido-dihydrido complex **2** showed somewhat improved catalytic activity in hydroboration reactions. The results are summarised in Table 2. The scope of substrates for **2**-catalysed transformations is the same as for complex **1**. However, the

presence of the second hydride ligand in **2** often leads to drastic changes in the product distribution, selectivity, and the rate of the catalytic reactions. For example, the hydroboration of styrene with HBCat in the presence of 5 mol% of **2** affords a large amount of ethylbenzene (51% *vs.* 15% for the **1**-catalysed reaction; Table 1, entry 5 and Table 2, entry 8). Hydroboration of 1-hexene with HBCat catalysed by **2** (5 mol%) is more selective towards the hydroboration product with a higher turn-over number and frequency than the reaction catalysed by the hydrido-chloride **1**. For example, for complex **3** the TON of **19** with 93% conversion of 1-hexene to a mixture of HexBCat (85%), 2-hexene (3%) and 3-hexene (5%) was found (Table 2 entry 7) *vs.* the TON of **14** with 70% conversion of 1-hexene to a mixture of HexBCat (55%), 2-hexene (8%) and 3-hexene (7%) for complex **1** (Table 1, entry 7)).

A similar trend was also observed in the hydroboration of ketones by **2** (Table 2). Thus, switching from **1** to **2** in the hydroboration of 4-nitroacetophenone, di(isopropyl) ketone, benzophenone, and cyclohexanone with HBCat leads to a significant increase in TOF (4-nitroacetophenone: TOF 20 \rightarrow 80; $^i\text{Pr}_2\text{C}(\text{O})$: TOF 0.9 \rightarrow 48; benzophenone: TOF 40 \rightarrow 76; cyclohexanone: TOF 20 \rightarrow 46; compare Tables 1 and 2). In contrast, the turnover frequency for the hydroboration of ethyl acetate with complexes **1** and **2** decreases from 10 to 1.1, respectively (Tables 1 and 2). At the moment, we have no rationale for the latter observation.

On the other hand, the hydroboration of alkynes with the dihydride **2** is slower than with the hydrido-chloride **1**. Thus, the reaction of phenyl acetylene with 1 equiv. of HBCat in the presence of 5 mol% of **2** gives *trans*- $\text{PhCH}=\text{CHBCat}$ with the TOF of 0.3 *vs.* the TOF of 1.0 for the **1**-catalysed reaction (entry 9 in Table 2 *vs.* entry 10 in Table 1). Interestingly, **2** was found to be inactive in the hydroboration of 3-hexyne, whereas **1**

Table 2 Hydroboration of organic substrates with HBCat mediated by **2**^a

Entry	Substrate	Conversion ^b , %	Product(s)	<i>t</i>	Yield ^c , %	TON ^d
1	$\text{PhC}(\text{O})\text{Me}$	100	$\text{PhCH}(\text{OBCat})\text{Me}$	15 min	>99	20
2	4-Nitroacetophenone	100	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH}(\text{OBCat})\text{Me}$	15 min	>99	20
3	$\text{Ph}_2\text{C}(\text{O})$	95	$\text{Ph}_2\text{CH}(\text{OBCat})$	15 min	95	19
4	$^i\text{Pr}_2\text{C}(\text{O})$	100	$^i\text{Pr}_2\text{CH}(\text{OBCat})$	25 min	>99	20
5	Cyclohexanone	94	CyOBCat	25 min	94	19
6	$\text{MeC}(\text{O})\text{OEt}$	99	EtOBCat	19 h	99	20
7	1-Hexene	93	HexBCat 2-Hexene 3-Hexene	24 h	85 3 5	19
8	$\text{PhCH}=\text{CH}_2$	100	$\text{PhCH}_2\text{CH}_2\text{BCat}$ <i>trans</i> - $\text{PhCH}=\text{CHBCat}$ PhCH_2CH_3	60 h	25 24 51	20
9	$\text{PhC}\equiv\text{CH}$	100	<i>trans</i> - $\text{PhCH}=\text{CHBCat}$	48 h	>99	20
10	MeCN	74	$\text{EtN}(\text{BCat})_2$	24 h	74	15
11	PhCN	99	$\text{PhCH}_2\text{N}(\text{BCat})_2$	24 h	99	20
12	$^t\text{BuCN}$	76	$^t\text{BuCH}_2\text{N}(\text{BCat})_2$	24 h	76	15
13	Acrylonitrile	92	$\text{CH}_3\text{CH}(\text{BCat})\text{CN}$	20 h	92	18
14	5-Hexynenitrile	42	<i>trans</i> - $\text{NC}(\text{CH}_2)_3\text{CH}=\text{CHBCat}$	48 h	42	8

^a 5 mol% of **2**, 22 °C, C_6D_6 , substrate/HBCat = 1/1 (1/2 for entries 6, 10–12). ^b Conversion of organic substrate, except entry 4 where the conversion of HBCat was calculated. ^c $^1\text{H-NMR}$ yields based on internal standard (tetramethylsilane). ^d Turnover numbers were calculated at maximum conversion.

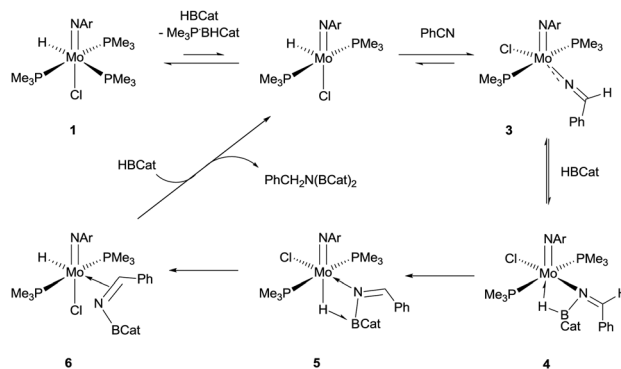
showed conversion of 3-hexyne to EtCH=C(Et)BCat with the TOF of 0.9 (Table 1, entry 9).

Lastly, hydroboration of nitriles with HBCat in the presence of 5 mol% of **2** is slightly less efficient when compared to catalyst **1**. Thus, a decrease in TOF values was observed for the hydroboration of CH₃CN, PhCN, and 5-hexynenitrile upon switching the catalyst from **1** to **2** (TOF 1.7 → 0.6, 1.7 → 0.8, 0.5 → 0.2, respectively; Tables 1 and 2). Similar to the **1**-catalysed reaction, the hydroboration of 5-hexynenitrile with **2** proceeds *via* selective addition of HBCat across the triple carbon–carbon bond to give *trans*-NC(CH₂)₃CH=CHBCat (Tables 1 and 2). Analogous reactivity was observed in the case of **2**-catalysed hydroboration of acrylonitrile, which gives rise to the product of HBCat addition across the C=C double bond, *i.e.* CH₃CH(BCat)CN (92%, Table 2, entry 13), whereas the **1**-catalysed reaction gives a mixture of CatB(CH₂)₂CN and CatB(CH₂)₃N(BCat)₂ (55% and 10%, respectively; Table 1, entry 15). The decrease in TON and TOF values for the hydroboration of nitriles with HBCat upon switching the catalyst from **1** to **2** can be attributed to the partial degradation of HBCat to BH₃ and B₂Cat₃ when complex **2** is used as the catalyst.¹⁷ Such a decomposition of HBCat was, for example, observed by NMR in the hydroboration of 5-hexynenitrile in the presence of **2**. We tentatively assign this behaviour to the higher lability of complex **2** that presumably has less tightly bound phosphines, which favours the formation of the PMe₃·BH₃ adduct.¹⁷

Stoichiometric reactivity of **1** and **2** and mechanistic insights into hydroboration catalysis

Stoichiometric reactivity of (ArN)Mo(H)(Cl)(PMe₃)₃ (1**).** To shed light on the mechanism of catalysis, stoichiometric reactions between complex **1** and unsaturated organic molecules and HBCat were studied.¹⁸ In our preliminary communication,¹³ we suggested a possible mechanism of the hydroboration of benzonitrile (Scheme 3) on the basis of studying individual steps under stoichiometric conditions. It is important to mention that the hydrido–chloride complex **1** reacts with HBCat very sluggishly: after 24 h at room temperature only *ca.* 20% conversion of **1** to a mixture of (ArN)MoCl₂(PMe₃)₃¹⁴ and (ArN)Mo(H)₂(PMe₃)₃ (**2**) was observed by NMR. No products of oxidative addition of borane to Mo, akin to (ArN)Mo(Cl)(H)₂(BCat)(PMe₃)₂ or its derivative (ArN)Mo(Cl)(BCat)(PMe₃)_x (*x* = 2 or 3), were detected. On the other hand, complex **1** readily reacts with PhCN (full conversion of **1** was achieved in 50 min at room temperature) to give the vinyldeaneamide derivative (ArN)Mo(Cl)(N=CHPh)(PMe₃)₂ (**3**; Scheme 3). A similar reactivity of complex **1** to yield products of nitrile insertion into the Mo–H bond was observed with MeCN, pent-3-enitrile, and 4-acetylbenzonitrile to give complexes **7–9**, respectively (Fig. 1). In contrast, reactions of **1** with acrylonitrile and 4-formylbenzonitrile afforded the olefin complex **10** and the product of aldehyde insertion into the M–H bond (**11**), respectively (Fig. 1).

Complexes **3** and **7–11** were characterised by spectroscopic methods (IR, NMR) and the formulation of complex **3** as a methyleneamide species was further substantiated by X-ray



Scheme 3 Catalytic transformation of nitriles to imines.

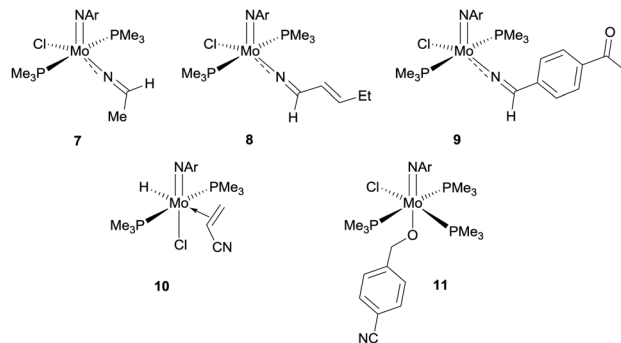
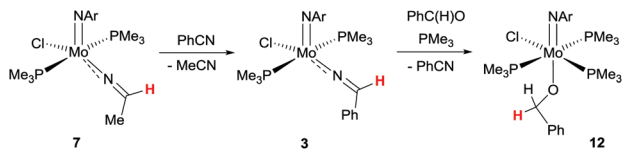


Fig. 1 Methyleneamide complexes **7–9** and products of the reactions of **1** with acrylonitrile and 4-formylbenzonitrile, **10** and **11**, respectively.

diffraction analysis described previously in a preliminary communication.¹³ Compounds **3**, **7–9** give rise to the diagnostic imine proton (δ 7.09–7.43 ppm) and carbon signals (δ 145.4–153.5 ppm; coupled in the ¹H–¹³C HSQC NMR to the corresponding ¹H resonances) in their ¹H and ¹³C NMR spectra, respectively. It is important to mention that the Mo–N=C bond angle in **3** is almost linear (172.3(4)°) suggesting that the [N=CHPh] fragment acts as a 4e donor.¹⁹ This coordination mode leads to the stable 18e valence shell, assuming that the linear imide ligand ArN²⁻ (Mo=N–C 175.0(3)°)¹³ donates 6e.

To our surprise, we found that complex **7** derived from acetonitrile reacts slowly (24 h at RT) with PhCN to form the benzylideneamide complex **3** *via* the release MeCN. This unusual reaction indicates the possibility of α -CH bond activation in the methyleneamide ligand (Scheme 4). We have recently reported a related reversible insertion of carbonyls into the M–H bond.²⁰ But to the best of our knowledge, the reversible insertion of nitriles into an early metal–hydride bond has been previously observed only for Cp₂*Sc(NCHR).^{19c} A similar reactivity pattern was also observed upon the treatment of benzylideneamide **3** with benzaldehyde, which in the presence of PMe₃ leads to the exclusive formation of the benzyloxy complex (ArN)Mo(Cl)(OBn)(PMe₃)₃ (**12**; Scheme 4)¹²



Scheme 4 H-transfer reactions in complexes 7 and 3.

along with the release of PhCN. In contrast, no transfer hydrogenation was observed in reactions of 7 with ketones (acetone and acetophenone) even upon heating up to 60 °C. This difference in reactivity of methyleneamide complexes towards aldehydes and ketones is reflected in the chemoselectivity of stoichiometric reactions of 1 with 4-acetylbenzimidazole and 4-formylbenzimidazole to give 4-acetylbenzimidazole complex 9 and (4-cyanophenyl)methoxy derivative 11, respectively (Fig. 1). Based on our observations that nitriles react faster with 1 than aldehydes (2 h for PhCN vs. 5–6 h for PhC(O)H¹²), one can assume that for both keto- and aldo-nitriles the reactions proceed *via* initial insertion of the nitrile group into the Mo–H bond. For 4-formylbenzimidazole, this insertion can be followed by intermolecular hydrogen transfer to the formyl moiety to form the more thermodynamically stable complex 11.

The reaction of complex 3 with HBCat was followed by NMR spectroscopy at low temperature. At –30 °C, the formation of a mixture of two bis(phosphine) compounds (4 and 5 in Scheme 3) was observed. One of the products was tentatively formulated as the agostic amido-borane adduct (ArN)MoCl(κ^3 -N(=CHPh)(CatB-H...))(PMe₃)₂ (4; Scheme 3)^{21,22} on the basis of the following spectroscopic features: (i) the complex has a C_s symmetric NMR-averaged structure with two equivalent PMe₃ ligands giving rise to a singlet at δ –0.9 ppm in ³¹P NMR; (ii) ¹H NMR revealed a downfield imine signal at δ 8.91 ppm, coupled in ¹H–¹³C HSQC NMR to the ¹³C NMR resonance at δ 172.0 ppm; (iii) ¹¹B NMR showed the presence of a four-coordinate boron centre exhibiting a doublet at δ 2.2 ppm (compare to δ 29 ppm for HBCat) with a reduced ¹J_{B–H} of ca. 55 Hz (compared to the ¹J_{B–H}(terminal) = 135.0 Hz and ¹J_{B–H}(bridging) = 46.0 Hz for B₂H₆).

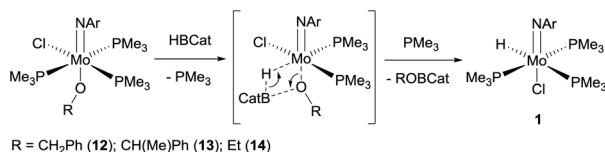
The second, fluxional product (5 in Scheme 3) was produced from 4 upon a gentle increase of temperature. However, all attempts to find a temperature regime for the complete conversion of 4 into 5 were unsuccessful. At –50 °C, the ¹H NMR spectrum of 5 reveals a broad upfield hydride signal at δ –2.94 ppm and a downfield imine ¹H resonance at δ 8.31 ppm, coupled in ¹H–¹³C HSQC NMR to the ¹³C NMR signal at δ 154.2 ppm. A series of ¹H, ¹H{³¹P} and ¹H{¹¹B} NMR experiments (Fig. S9 in ESI†) suggest some coordination of the Mo-bound hydride to the boron centre of the borylimine ligand of 5. This conclusion is supported by the significant sharpening of the hydride signal upon decoupling from the ¹¹B nucleus. Unfortunately, we could not measure the B–H coupling constant from the very broad signal in ¹¹B NMR. The two non-equivalent PMe₃ ligands give rise to two mutually

coupled doublets at δ –1.4 ppm and δ –13.0 ppm in the ³¹P NMR spectrum. The large value of ²J_{P–P} = 212.0 Hz suggests the *trans* arrangement of the phosphine ligands in 6. The ¹¹B NMR spectrum of 5 revealed the presence of a broad signal at δ 10.2 ppm, which is more downfield shifted in comparison with 4, presumably because of weaker B–H interaction. All together these features allow us to suggest the formation of a κ^1 -(*N*-boryl)imine complex (ArN)Mo(H)(Cl){ κ^1 -N(BCat)=CHPh}(PMe₃)₂ (5, Scheme 3) having non-equivalent PMe₃ groups because of restricted rotation about the Mo–N bond of the κ^1 -(*N*-boryl)imine ligand at –50 °C.

Increasing the temperature up to 25 °C leads to disappearance of complexes 4 and 5 and exclusive formation of (ArN)Mo(H)(Cl){ η^2 -CatBN=CHPh}(PMe₃)₂ (6; Scheme 3), the structure of which was suggested on the basis of multinuclear NMR spectroscopy. Thus, the ³¹P NMR spectrum of 6 shows two non-equivalent PMe₃ ligands, which give rise to two mutually coupled doublets at δ –5.2 ppm and 2.4 ppm with the ²J_{P–P} = 88.5 Hz. The ¹H NMR spectrum of 6 revealed an upfield imine proton resonance at δ 5.00 ppm (dd, ³J_{H–P} = 3.1 Hz), diagnostic for the η^2 -coordinated CatBN=CHPh, coupled in ¹H–¹³C HSQC NMR to an upfield shifted imine carbon resonance at δ 62.9 ppm. Similar to the parent hydrido–chloride complex 1, the Mo–H signal of 6 is shifted downfield to δ 7.06 ppm (found by ¹H–³¹P HSQC NMR; ²J_{H–P} = 45.0 and 50.9 Hz), suggesting the *cis* disposition of the hydride and imido ligands. The ¹¹B NMR spectrum of 6 shows a downfield signal at δ 15.3 ppm.

No further intermediates were observed upon addition of another equivalent of HBCat to complex 6. Only the release of PhCH₂N(BCat)₂ and formation of a mixture of the hydrido–chloride 1 and (ArN)MoCl₂(PMe₃)₃¹⁴ together with a small amount of unknown decomposition products were detected. The mechanism of addition of the second equivalent of HBCat to the boryl imine moiety of 6 to form bis(boryl) amine remains unknown. However, we suggest that this last step of a possible catalytic cycle (depicted in Scheme 3) is assisted by HBCat. One can assume that the reaction proceeds *via* insertion of the boryl imine into the Mo–H bond to form a boryl amide derivative, which can further react with HBCat in a manner similar to methyleneamide complexes (Scheme 3).

A similar mechanism can be also suggested for the hydroboration of carbonyl compounds as we found that the treatment of either (ArN)MoCl(OBn)(PMe₃)₃ (12; generated from 1 and PhC(O)H),¹² or (ArN)MoCl(OCH(Me)Ph)(PMe₃)₃ (13; generated from 1 and PhC(O)Me) or (ArN)MoCl(OEt)(PMe₃)₃^{12,23} (14; generated from 1 and ethyl acetate) with HBCat immediately regenerates the complex 1 and gives the corresponding hydroboration products, PhCH₂OBCat, PhCH(OBCat)Me and EtOBCat, respectively.²⁴ A small amount of (ArN)MoCl₂(PMe₃)₃¹⁴ was also observed by NMR, which can be indicative of a possible catalyst deactivation pathway. All attempts to elucidate any further intermediates were unsuccessful due to the high reactivity of complexes 12, 13 and 14 with HBCat even at –40 °C. Based on our previous study of hydrosilylation of carbonyl compounds and alcoholysis of

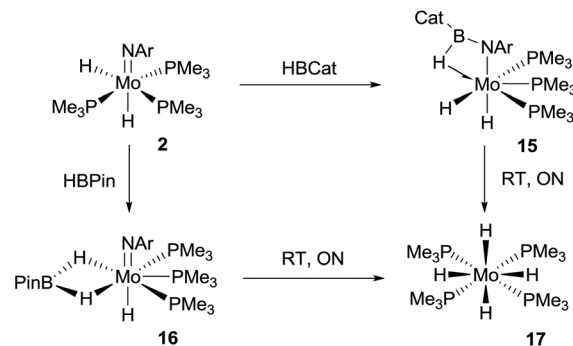


Scheme 5 Proposed mechanism for reactions of **12**, **13** and **14** with HBCat.

silanes mediated by complex **1**,¹² we tentatively suggest that the alkoxy derivatives **12**, **13** and **14** react with HBCat to furnish the corresponding hydroboration products *via* heterolytic splitting of the B–H bond (Scheme 5).

For nitriles having a carbonyl functionality (for example, 4-formylbenzoxonitrile, 4-acetylbenzoxonitrile) and for mixtures of nitriles with carbonyl compounds, the insertion of the C=O and C≡N moieties into the Mo–H bond of **1** becomes competitive in the presence of a large excess of HBCat. This suggestion stems from our previous observation that addition of aldehydes to **1** starts with the formation of the adduct *trans*-(ArN)Mo(H)(Cl)(η²-O=CRH)(PMe₃)₂, which in the presence of a large excess of RHC(O) rearranges slowly (≥5 h) into an alkoxy complex *via* dissociation of PMe₃.¹² Addition of excess borane could significantly accelerate this process through the formation of a PMe₃-borane adduct, making it competitive with (or even faster than) the formation of methylenamide derivatives (~2 h). This could be a possible explanation for the loss of chemoselectivity in the hydroboration reactions under catalytic conditions.

Stoichiometric reactivity of (ArN)MoH₂(PMe₃)₃ (2). To further identify the potential catalytically active species in the hydroboration reactions, stoichiometric reactions between complex **2**, unsaturated organic molecules and HBR (R = Cat, Pin) were studied. At ambient temperature, NMR scale reaction of **2** with HBCat results, within minutes, in the formation of a new tris(phosphine) complex, which was tentatively formulated as the agostic borane complex Mo(H)₂(PMe₃)₃(η³-NAr-HBCat) (**15**, Scheme 6).²⁵ This suggestion was made on the basis of the following spectroscopic features. Complex **15** is fluxional at room temperature; however, at –30 °C its ¹H NMR spectrum revealed three hydride resonances, at δ –6.03 ppm (dt, ²J_{H-P} = 39.6 Hz, ²J_{H-P} = 88.2 Hz), –2.79 ppm (t, ²J_{H-P} = 59.9 Hz) and –1.82 ppm (broad singlet). Upon decoupling from ¹¹B nucleus, the hydride signal at δ –1.82 ppm resolves into a broad doublet, presumably, due to coupling to the *trans*-PMe₃ ligand (²J_{H-P} = 15.2 Hz). Also, ¹¹B NMR showed the presence of a four-coordinate boron species exhibiting a signal at δ –0.59 ppm (*vs.* 29 ppm for HBCat). The ³¹P{¹H} NMR spectrum of **15** displays two mutually coupled resonances with 1 : 2 intensities: a triplet at δ 2.54 ppm (²J_{P-P} = 17.0 Hz) and a doublet at δ 23.9 ppm, coupled to two hydride signals at δ –6.03 ppm and –2.79 ppm in the ¹H–³¹P HSQC NMR spectrum. The agostic borane structure of **15** is further supported by the observation of a red-shifted B–H band at 2357 cm^{–1} in the IR spectrum (*vs.* ν(B–H) ≈ 2670 cm^{–1} for HBCat).²⁶ Treat-



Scheme 6 Reactions of complex **2** with HBCat and HBPIn.

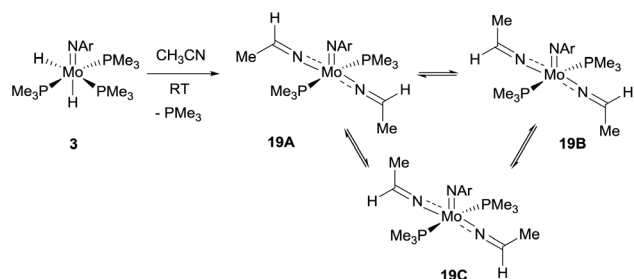
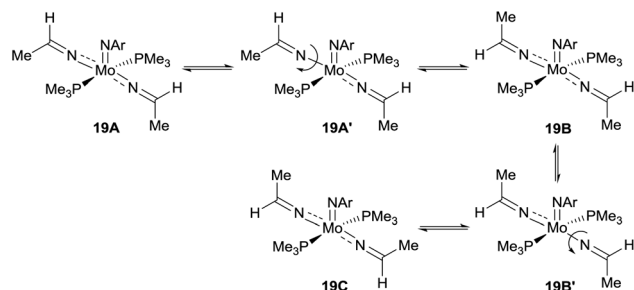
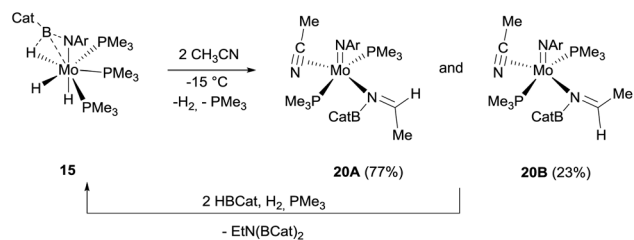
ment of **2** with the less Lewis acidic borane HBPIn results in the formation of another product, different in structure from the agostic complex **15**. The ¹H NMR spectrum of this species shows two hydride resonances at δ –6.89 ppm (q, 1H, ²J_{H-P} = 63 Hz) and –4.10 ppm (broad, 2H). The latter hydride signal appears as a sharp quartet (²J_{H-P} = 27 Hz) in the ¹H{¹¹B} NMR spectrum. The ¹¹B NMR spectrum of this species showed the presence of a four-coordinate boron centre with a signal at δ –3.62 ppm. These spectroscopic features indicate a borohydride structure tentatively formulated as (ArN)Mo(η²-H₂BPin)(H)(PMe₃)₃ (**16**, Scheme 6).

Both complexes **15** and **16** are not stable in solution and decompose after several hours at room temperature to the tetrahydride complex MoH₄(PMe₃)₄ (**17**, Scheme 6) previously reported by Brookhart *et al.*²⁷ Despite the instability, the agostic compound **15** can be generated on preparative scale in 82% yield by the reaction of the dihydride **2** with one equivalent of HBCat at –30 °C and can be stored at this temperature under inert atmosphere for several days.

On the other hand, treatment of the dihydride complex **2** with ketones resulted in complex reaction mixtures. In the reaction mixture obtained upon mixing **2** with cyclohexanone, we identified a species tentatively assigned the structure (ArN)Mo(H)(OCy)(PMe₃)₃ (**18**) on the basis of analogy of its spectral features with the compound (ArN)Mo(Cl)(OCy)(PMe₃)₃^{12b} and the correlation of its ³¹P signals in the ¹H–³¹P HSQC NMR with the Mo–H signal at δ 4.00 ppm. In contrast, a reaction of complex **2** with 2 equiv. of acetonitrile results in a double addition of MeCN and selective formation of bis(vinylideneamide) (ArN)Mo(N=CHMe)₂(PMe₃)₂ (**19**), obtained as an equilibrium mixture of three isomers in the ratio 1 : 0.7 : 0.1 (**19A**, **19B** and **19C**, respectively; Scheme 7).

The activation parameters for the exchange between the major isomers **19A** and **19B** were found through 1D ¹H EXSY NMR (ΔS[‡] = –12.0 ± 2.8 kcal mol^{–1}, ΔH[‡] = 12.3 ± 1.1 kcal mol^{–1}). The negative entropy of activation suggests an intramolecular exchange mechanism.

All three isomers of **19** were characterised by NMR spectroscopy and their ¹H NMR spectra revealed the presence of downfield imine resonances at δ 8.13 ppm (for **19A**), 8.12 and 7.70 ppm (for **19B**) and 7.66 ppm (for **19C**). These imine

Scheme 7 Reaction of complex **2** with acetonitrile.Scheme 8 Proposed mechanism for the exchange between isomers of **19**.Scheme 9 Reaction of complex **15** with CH_3CN .

proton signals were found to be coupled in ^1H - ^{13}C HSQC NMR to the imine ^{13}C resonances at δ 145.7 ppm (for **19A** and **19B**) and 145.8 ppm (for **19C**) and to the ^{31}P resonances at δ 1.31 ppm, 2.42 ppm and 2.41 ppm (for **19A**, **19B** and **19C**, respectively)²⁸ in ^1H - ^{31}P HSQC NMR.

Since all four Me groups of the ArN^{2-} ligand are equivalent and give rise to a sharp doublet in the ^1H NMR spectra of **19**, we suggest that the $\text{Mo}=\text{N}-\text{Ar}$ fragment is almost linear and the imido ligand acts as a $6e^-$ donor. If this assumption is true, complex **19** can be thought of as a stable $18e^-$ species, with each vinylideneamide ligand donating three electrons to molybdenum due to delocalisation of the nitrogen lone pair. As such, the interconversion of isomers is thought to occur by the transformation of the formal double $\text{M}=\text{NC}$ bond ($\sigma + \text{dative } \pi$) into a single $\text{Mo}-\text{N}=\text{C}$ bond (pure σ), followed by rotation (Scheme 8).

Addition of two equivalents of HBCat to **19** results in immediate formation of the hydroboration product, $\text{EtN}(\text{BCat})_2$. However, no recovery of the dihydride **2** was observed. NMR analysis of the reaction mixture showed the formation of a mixture of unknown products. Thus, in order to probe an alternative pathway for the hydroboration of acetonitrile, we studied the reaction of the agostic amido borane complex **15** with CH_3CN . At $-15\text{ }^\circ\text{C}$, **15** reacts with 2 equiv. of CH_3CN to give $(\text{ArN})\text{Mo}(-\text{N}(\text{BCat})=\text{CHMe})(\eta^2-\text{N}\equiv\text{CCH}_3)(\text{PMe}_3)_2$ (**20**) as a mixture of two isomers (Scheme 9; $\approx 3:1$ ratio by NMR). Formation of **20** is accompanied with the release of a molecule of PMe_3 and an equivalent of H_2 . In the ^1H NMR spectrum, both isomers of **20** give rise to characteristic imine proton resonances at δ 7.38 ppm (for **20A**) and 8.12 ppm (for **20B**), coupled in ^1H - ^{13}C HSQC NMR to the corresponding imine ^{13}C resonances at δ 151.8 ppm and 145.7 ppm, respectively. An η^2 -coordination mode of acetonitrile is suggested based on the diagnostic ^{13}C NMR signal at δ 203.1 ppm for the nitrile carbon nucleus.²⁹ The ^{11}B NMR spectrum of **20** showed the presence of a downfield signal at δ 13.3 ppm. While we could

Table 3 Hydroboration of organic substrates with HBCat mediated by **15**^a

Entry	Substrate	Conversion, % ^b	Product(s)	<i>t</i>	Yield, % ^c	TON ^d
1	PhC(O)Me	100	PhCH(OBCat)Me	10 min	>99	20
2	4-Nitroacetophenone	95	4-O ₂ N-C ₆ H ₄ -CH(OBCat)Me	10 min	95	19
3	Ph ₂ C(O)	99	Ph ₂ CH(OBCat)	10 min	99	20
4	ⁱ Pr ₂ C(O)	90	ⁱ Pr ₂ CH(OBCat)	25 min	90	18
5	Cyclohexanone	99	CyOBCat	10 min	9	20
6	1-Hexene	82	HexBCat	24 h	79	16
7	PhCH=CH ₂	87	2-Hexene + 3-hexene	24 h	3	17
			PhCH ₂ CH ₂ BCat		4	
			<i>trans</i> -PhCH=CHBCat		77	
			PhCH ₂ CH ₃		6	
8	PhC≡CH	99	<i>trans</i> -PhCH=CHBCat	24 h	99	20
9	MeCN	99	EtN(BCat) ₂	12 h	99	20
10	PhCN	99	PhCH ₂ N(BCat) ₂	12 h	99	20
11	^t BuCN	90	^t BuCH ₂ N(BCat) ₂	9 h	90	18
12	5-Hexynenitrile	95	<i>trans</i> -NC(CH ₂) ₃ CH=CHBCat	36 h	95	19

^a 5 mol% of **15**, 22 °C, C₆D₆, substrate/HBCat = 1/1 (1/2 for entries 9–11). ^b Conversion of organic substrate. ^c ^1H NMR yields based on internal standard (tetramethylsilane). ^d Turnover numbers were calculated at maximum conversion.

not find any literature data for the free *N*-borylimine CatB-N=CHR, this chemical shift falls between the signals for the boron amides CatB-NR₂ (about 26 ppm) and the four-coordinate catecholborane-imine adducts CatBH*N(R)=CR₂ (−19.2 ppm).¹⁰ Although not being clear-cut evidence, we believe that the boron chemical shift of 13.3 ppm is better consistent with the three-coordinate boron structure of **20** as depicted in Scheme 9. The ³¹P-NMR spectra for both isomers of **20** show broad signals for the PMe₃ groups at δ 1.31 ppm and 2.42 ppm (for **20A** and **20B**, respectively), suggesting the equivalency of phosphine ligands and, thus, the orientation of the η²-N=CCH₃ ligand coplanar with the Mo=N-Ar moiety.

Addition of two equiv. of HBCat to a freshly generated complex **20** results in immediate formation of the hydroboration product, EtNB(Cat)₂, and, in contrast to the reaction of **19** with HBCat, complete recovery of the starting dihydride **15** (Scheme 9). Moreover, when complex **15** was subjected to hydroboration reactions under catalytic conditions, it proved to be the most catalytically potent, when compared to complexes **1** and **2** (see Tables 1–3). Most importantly, complex **15** was found to be much more efficient in the hydroboration of nitriles (Table 3, entries 9–11). This result suggest that hydroboration of acetonitrile with HBCat more likely proceeds with the intermediacy of the agostic amido borane **15**, followed by the formation of complex **20** rather than through the bis(vinylideneamide) derivative **19**.

Conclusions

In conclusion, imido-hydrido complexes **1** and **2** were found to catalyse a variety of hydroboration reactions with HBCat, including a rare example of hydroboration of nitriles to give bis(boryl) amines. Mechanistic studies of hydroboration of nitriles suggest that reactions proceed *via* a series of agostic borylamido and borylamino complexes. No evident oxidative addition of HBCat to the Mo(IV) centre to form boryl complexes was observed.

Experimental

General methods and instrumentation

All manipulations were carried out under nitrogen atmosphere, using either conventional Schlenk techniques or an inert atmosphere MBraun glovebox. Dry solvents (THF, ether, hexane, dichloromethane, toluene, and acetonitrile) were obtained using Innovative Technologies Pure Solv. purification system. DME was dried over sodium/benzophenone; ethyl acetate was dried over CaH₂. Benzene-d₆ and toluene-d₈ were dried by distillation over K/Na alloy. NMR spectra were obtained with Bruker DPX-300 (¹H: 300 MHz; ¹³C: 75.5 MHz; ³¹P: 121.5 MHz; ¹¹B: 96.3 MHz) and Bruker DPX-600 (¹H: 600 MHz; ²D: 92.1 MHz; ¹³C: 151 MHz; ³¹P: 243 MHz; ¹¹B: 192.6 MHz) spectrometers. IR spectra were measured on an ATI Mattson FTIR spectrometer. Organic substrates were

purchased from Sigma-Aldrich and used without further purification. HBCat was additionally purified by distillation before use. (ArN)Mo(H)(Cl)(PMe₃)₃ (**1**)¹² and (ArN)Mo(Cl)(N=CHPh)(PMe₃)₂ (**3**)¹³ were prepared according to the previously published procedures. Compounds (ArN)Mo(H)₂(PMe₃)₃ (**2**) and Mo(H)₂(PMe₃)₃(η³-NAr-HBCat) (**15**) are unstable at room temperature whereas compounds (ArN)Mo(H)₂(PMe₃)₃ (**2**) and (ArN)Mo(Cl)(N=CHMe)(PMe₃)₂ (**7**) were isolated as viscous oils, which did not allow for elemental analysis to be performed. All catalytic, NMR scale reactions and kinetic experiments were done under nitrogen atmosphere using NMR tubes equipped with Teflon valves. The structures and yields of all hydroboration products were determined by NMR using tetramethylsilane as an internal standard.

NMR scale reaction of (ArN)Mo(Cl)(N=CHPh)(PMe₃)₂ (**3**) with HBCat

A: Room temperature reaction. A solution of HBCat (3.5 μl, 0.033 mmol) in 0.6 ml of C₆D₆ was added in one portion at room temperature to solid **3** (18.5 mg, 0.033 mmol). The mixture was immediately transferred into an NMR tube and left at room temperature for 10 min. During this time the colour of the mixture turned red. NMR analysis after 10 min showed formation of a difficult-to-separate mixture of the starting material and (ArN)Mo(H)(Cl)(η²-N(BCat)=CHPh)(PMe₃)₂ (**6**) (1:1). Addition of another equivalent of HBCat to the reaction mixture leads to full conversion of **3** into **6**. All attempts to isolate complex **6** were unsuccessful due to its instability. A ³¹P-³¹P EXSY NMR spectrum of complex **6** revealed an intramolecular exchange of the PMe₃ ligands; however, addition of PhCN to a solution of **6** in C₆D₆ does not afford CatBN=CHPh. On the other hand, addition of a stoichiometric mixture of PhCN and HBCat to a solution of **6** in C₆D₆ leads to slow (2 days) conversion of **6** into **3** and formation of PhCH₂N(BCat)₂.

B: Low temperature VT reaction. HBCat (3.6 μl, 0.033 mmol) was added in one portion at room temperature to a frozen in liq. N₂ solution of **3** (23.5 mg, 0.042 mmol) in 0.6 ml of C₆D₆ in an NMR tube. The mixture was warmed up to −30 °C and placed into an NMR spectrometer pre-cooled to −30 °C. The temperature was dropped down to −50 °C and the sample was warmed gradually and monitored by NMR spectroscopy. At −50 °C, NMR analysis revealed the presence of a mixture of the starting material **3**, (ArN)Mo(Cl){η³-N(=CHPh)-CatB-H...}(PMe₃)₂ (**4**), and (ArN)Mo(H)(Cl)(η¹-N(BCat)=CHPh)(PMe₃)₂ (**5**). Compound **4** is slowly transferred to **5** upon increase of the temperature of the reaction mixture. Warming the sample up to 25 °C leads to the formation of (ArN)Mo(H)(Cl){η²-CatBN=CHPh}(PMe₃)₂ (**6**). Addition of another equivalent of HBCat affords PhCH₂N(BCat)₂ and a mixture of **1**, (ArN)MoCl₂(PMe₃)₃¹⁴ and unknown decomposition products.

(ArN=)Mo(Cl){η³-N(=CHPh)(CatB-H...)}(PMe₃)₂ (**4**). ¹H NMR (600 MHz; 225 K; PhMe-d₈; δ, ppm): 8.91 (br s, 1H, CHPh); 8.08 (d, ³J_{H-H} = 7.4 Hz, 2H, *o*-H, CHPh); 6.63–7.37 (m, overlapping aromatic signals of HBCat, **2**, **4**, and **5**); 5.06 (br s, 1H,

H-B); 4.33 (br m, 2H, 2CH, ArN, overlapping with CH (ArN) of 3); 1.39 (br m, 6H, 2CH₃, ArN); 1.29 (bm, 6H, 2CH₃, ArN); 1.24 (br m, 18H, 2 PMe₃). ³¹P{¹H} NMR (243 MHz; 225 K; PhMe-d₈; δ, ppm): -0.9 (br s, PMe₃). ¹¹B{¹H} NMR (193 MHz; 253 K; PhMe-d₈; δ, ppm): 2.3 (br s, HBCat). ¹¹B NMR (193 MHz; 283 K; PhMe-d₈; δ, ppm): 2.2 (br d, ¹J_{B-H} ≈ 55 Hz; HBCat). ¹³C{¹H} NMR (151 MHz; 253 K; PhMe-d₈; δ, ppm): 172.0 (s, N=CHPh, found by ¹H-¹³C HSQC NMR); 129.7 (s, o-C, CHPh); 27.5 (s, CH, ArN); 23.8 (s, CH₃, ArN); 23.6 (s, CH₃, ArN); 14.3 (vt, ¹J_{C-P} = 24 Hz, 2 trans-PMe₃).

(ArN)Mo(H)(Cl)(η¹-N(BCat)=CHPh)(PMe₃)₂ (5). ¹H NMR (600 MHz; 225 K; PhMe-d₈; δ, ppm): 8.31 (br s, 1H, N=CHPh); 6.63–7.37 (m, overlapping aromatic signals of HBCat, 2, 4, and 5); 4.12 (br s, 1H, CH, ArN); 3.92 (br s, 1H, CH, ArN); 1.32 (br m, 6H, 2CH₃, ArN); 1.29 (d, ²J_{H-P} = 8.4 Hz, 9H, PMe₃); 1.21 (br m, 6H, 2CH₃, ArN); 0.87 (d, ²J_{H-P} = 8.1 Hz, 9H, PMe₃); -2.94 (br m, 1H, MoH). ³¹P{¹H} NMR (243 MHz; 225 K; PhMe-d₈; δ, ppm): -1.4 (d, ²J_{P-P} = 212.0 Hz, PMe₃); -13.0 (d, ²J_{P-P} = 212.0 Hz, PMe₃). ¹¹B NMR (193 MHz; 253 K; PhMe-d₈; δ, ppm): 10.1 (br s, BCat). ¹¹B NMR (193 MHz; 283 K; PhMe-d₈; δ, ppm): 10.2 (br s, BCat). ¹³C{¹H} NMR (151 MHz; 253 K; PhMe-d₈; δ, ppm): 154.2 (s, N=CHPh, found by ¹H-¹³C HSQC NMR); 27.2 (s, CH, ArN); 26.9 (s, CH, ArN); 25.7 (bs, CH₃, ArN); 25.2 (s, CH₃, ArN); 13.1 (d, ¹J_{C-P} = 22.8 Hz, PMe₃); 12.7 (d, ¹J_{C-P} = 21.7 Hz, PMe₃).

ArN)Mo(H)(Cl)(η²-CatBN=CHPh)(PMe₃)₂ (6). ¹H NMR (600 MHz; 295 K; PhMe-d₈; δ, ppm): 7.65 (d, ³J_{H-H} = 7.7 Hz, 2H, o-H, CHPh, major isomer); 7.45 (d, ³J_{H-H} = 7.7 Hz, 2H, o-H, CHPh, minor isomer); 7.06 (m, MoH of major isomer, obscured by aromatic signals, found by ¹H-³¹P HSQC NMR); 6.9–7.3 (m, overlapping aromatic signals of CPh and NAr of 2, 5, 6, and (ArN)MoCl₂(PMe₃)₃); 6.91 (m, 2H, BCat, major isomer); 6.78 (m, 2H, BCat, major isomer); 6.73 (br m, MoH of minor isomer, found by ¹H-³¹P HSQC NMR); 5.00 (dd, ³J_{H-P} = 3.0 Hz; 1H, N=CHPh, major isomer); 4.39 (br s, 1H, N=CHPh, minor isomer); 4.22 (sept, ³J_{H-H} = 6.7 Hz, 1H, CH, ArN, major isomer); 4.13 (sept, ³J_{H-H} = 6.7 Hz, 1H, CH, ArN, major isomer); 3.98 (br m, 1H, CH, ArN, minor isomer); 3.84 (sept, ³J_{H-H} = 6.7 Hz, 1H, CH, ArN, minor isomer); 1.80 (d, ²J_{H-P} = 10.1 Hz, 9H, PMe₃, major isomer); 1.72 (d, ²J_{H-P} = 10.1 Hz, 9H, PMe₃, minor isomer); 1.35 (bm, 9H, PMe₃, minor isomer); 1.24 (d, ³J_{H-H} = 6.7 Hz, 6H, 2CH₃, ArN, major isomer); 1.20 (d, ²J_{H-P} = 9.9 Hz, 9H, PMe₃, major isomer); 1.18 (d, ³J_{H-H} = 6.7 Hz, 6H, 2CH₃, ArN, major isomer). ³¹P{¹H} NMR (243 MHz; 295 K; PhMe-d₈; δ, ppm): 2.4 (d, ²J_{P-P} = 88.5 Hz, PMe₃, both isomers); -5.2 (d, ²J_{P-P} = 88.5 Hz, PMe₃, both isomers). ³¹P NMR (selectively decoupled from methyl groups at 1.20 ppm in the ¹H NMR spectrum; 243 MHz; 295 K; PhMe-d₈; δ, ppm): 2.4 (dd, ²J_{P-P} = 88.5 Hz, ²J_{P-H} = 50.9 Hz, PMe₃); -5.2 (br m, PMe₃). ³¹P NMR (selectively decoupled from methyl groups at 1.80 ppm in the ¹H NMR spectrum; 243 MHz; 295 K; PhMe-d₈; δ, ppm): 2.4 (br m, PMe₃); -5.2 (dd, ²J_{P-P} = 88.5 Hz, ²J_{P-H} = 45.0 Hz, PMe₃). ¹¹B NMR (193 MHz; 295 K; PhMe-d₈; δ, ppm): 15.3 (br s, BCat). ¹H-¹³C HSQC NMR (f1: 300 MHz; f2: 75.5 MHz; J = 145 Hz; 296 K; PhMe-d₈; ¹³C projection for major isomer; δ, ppm): 128.9 (o-C, CPh); 62.9 (N=CHPh); 27.2

(CH, ArN); 26.6 (CH, ArN); 24.9 (CH₃, ArN); 24.8 (CH₃, ArN); 17.5 (PMe₃); 17.1 (PMe₃).

Preparation of (ArN)Mo(H)₂(PMe₃)₃ (2)

(ArN)Mo(Cl)₂(PMe₃)₃¹⁴ (0.50 g, 0.9 mmol) was dissolved in ~25 mL of toluene and cooled -30 °C. THF solution of L-selectride (C = 1 M, 1.8 mL, 1.8 mmol) was added dropwise to the mixture. The colour of the solution almost immediately changed to a darker brown upon addition of L-selectride. The reaction was allowed to proceed for ~30 min until the bath was defrosted, and then allowed to react further at room temperature for 1 hour. The contents were filtered and extracted with toluene. All volatiles were removed under vacuum, resulting in dark brown viscous oil (0.41 g, 88% yield). The product is highly fluxional and unstable at room temperature (slowly decomposes into a mixture of unidentified products). Without decomposition, complex 2 can be stored at -30 °C under inert atmosphere. ¹H NMR (600 MHz; toluene-d₈; 244 K; δ, ppm): -5.31 (dtd, ²J_{H-P} = 60.6 Hz, ²J_{H-P} = 46.2 Hz, ²J_{H-H} = 7.2 Hz, 1H, MoH (trans- to PMe₃)); 1.35 (m, 21H, 4 CH₃ of NAr and PMe₃); 1.49 (br m, 18H, 2 PMe₃); 2.08 (m, overlapping with residual toluene-d₈ signal, ²J_{H-P} = 43.2 Hz, ²J_{H-H} = 7.2 Hz, 1H, MoH (trans- to NAr), found by ¹H-¹H COSY and ¹H-³¹P HSQC NMR); 4.43 (sept, ³J_{H-H} = 6.6 Hz, 2H, 2 CH, NAr); 6.91–7.32 (m, overlapping with residual toluene-d₈ resonances, 3H, m-H and p-H of NAr). ¹H{³¹P} NMR (600 MHz; toluene-d₈; 243 K; selected resonances; δ, ppm): -5.31 (d, ²J_{H-H} = 7.2 Hz, 1H, MoH); 1.38 (s, 9H, PMe₃); 1.50 (s, 18H, 2 PMe₃); 2.09 (d, ²J_{H-H} = 7.2 Hz, 1H, MoH). ³¹P{¹H} NMR (243 MHz; toluene-d₈; 247 K; δ, ppm): 14.8 (d, ²J_{P-P} = 19.4 Hz, 2P, 2 PMe₃); 13.1 (t, ²J_{P-P} = 19.4 Hz, 1P, PMe₃). ¹H-¹³C HSQC NMR (f1: 600 MHz; f2: 151 MHz; toluene-d₈; 243 K; ¹³C projection; selected resonances; δ, ppm): 124.9, 122.0, 121.9, (m-C and p-C, NAr); 26.3 (CH, NAr); 26.2 (CH₃, NAr); 25.9 (PMe₃), 25.0 (CH₃, NAr); 24.2 (PMe₃). IR (nujol): 1620 cm⁻¹ (broad, medium, Mo-H).

Preparation of Mo(H)₂(PMe₃)₃(η³-NAr-HBCat) (15)

2 (0.388 g, 0.724 mmol) was dissolved in 30 mL of diethyl ether and cooled to -30 °C. HBCat (77.2 μL, 0.724 mmol) was added to the solution via syringe. Immediate formation of a blue precipitate was observed. The latter was washed with small portions of cold ether and dried under vacuum (0.371 g, 82% yield). The product is fluxional at room temperature and decomposes after several hours. ¹H NMR (600 MHz; toluene-d₈; 244 K; δ, ppm): -6.03 (dt, ²J_{H-P} = 39.6 Hz, ²J_{H-P} = 88.2 Hz, 1H, MoH); -2.79 (t, ²J_{H-P} = 59.9 Hz, 1H, MoH); -1.82 (bs, 1H, ArN-B-H-Mo agostic); 0.86 (d, ²J_{H-P} = 7.3 Hz, 9H, PMe₃); 1.33 (bs, 6H, 2 ¹Pr-CH₃ of ArN); 1.35 (d, ²J_{H-P} = 9.0 Hz, 18H, 2 PMe₃); 1.55 (d, ²J_{H-P} = 6.2 Hz, 6H, 2 ¹Pr-CH₃ of ArN); 3.45 (sept, 2H, 2 ¹Pr-CH of ArN); 6.97–6.8 (br m, 4H, BCat). ¹H{³¹P} NMR (243 MHz, toluene-d₈, 243 K; δ, ppm): -6.03 (bs, MoH); -2.79 (bs, MoH). ³¹P{¹H} NMR (243 MHz, toluene-d₈, 243 K; δ, ppm): 2.54 (t, ²J_{P-P} = 17.0 Hz, 1P, PMe₃); 23.9 (d, ²J_{P-P} = 17.0 Hz, 2P, 2 PMe₃). ¹H-¹³C HSQC NMR (f1: 600 MHz; f2: 151 MHz; toluene-d₈, 243 K; ¹³C projection; selected resonances; δ, ppm): 125.0, 123.0, 121.9 (m-C and p-C, NAr); 112.0, 122.3

(CatB); 26.8 ($^1\text{Pr-CH}$, NAr); 25.2 (2 PMe_3); 24.8 (PMe_3); 23.7 (CH_3 , NAr); 23.5 (CH_3 , NAr); ^{11}B NMR (192.6 MHz; toluene- d_8 , 243 K; δ , ppm): -0.59 (br s, ArN-BCat).

NMR reaction of $(\text{ArN})\text{Mo}(\text{H})_2(\text{PMe}_3)_3$ (**2**) with HBPIn

HBPIn (5.2 μL ; 0.036 mmol) was added in one portion to a solution of **2** (18.5 mg; 0.036 mmol) in 0.6 mL of toluene- d_8 in an NMR tube. The reaction was monitored by NMR. The formation of a fluxional borohydride complex, $(\text{ArN})\text{Mo}(\eta^2\text{-H}_2\text{BPIn})(\text{H})(\text{PMe}_3)_3$ (**16**), was observed. ^1H NMR (600 MHz; toluene- d_8 ; 244 K; δ , ppm): -6.89 (q, $^2J_{\text{H-P}} = 63$ Hz, 1H, MoH); -4.13 (br s, 2H, $\eta^2\text{-PinBH}_2$); 1.10 (d, $^2J_{\text{H-P}} = 7.3$ Hz, 18H, 2 PMe_3); 1.20 (d, $^2J_{\text{H-P}} = 8$ Hz, 9H, PMe_3); 1.27 (s, 12 H, Me of Bpin); 1.36 (br s, 12H, $^1\text{Pr-CH}_3$ of NAr); 3.62 (sept, $^3J_{\text{H-H}} = 6.2$ Hz, 2H, $^1\text{Pr-CH}$ of NAr). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz; toluene- d_8 ; 243 K; δ , ppm): 50.0 (br s, 2P, 2 PMe_3); 12.7 (s, 1P, PMe_3). ^{11}B NMR (192.6 MHz; toluene- d_8 ; 243 K; δ , ppm): -3.6 (bs, H_2BPIn).

NMR reaction of $(\text{ArN})\text{Mo}(\text{H})_2(\text{PMe}_3)_3$ (**2**) with MeCN

MeCN (2.86 μL ; 0.055 mmol) was added in one portion to a solution of **2** (14.5 mg; 0.027 mmol) in 0.6 mL of toluene- d_8 in an NMR tube. The reaction was monitored by NMR and complete conversion was observed after several minutes at room temperature. The solution turned dark red. The obtained product is fluxional at room temperature, and therefore NMR analysis was performed at -15 $^\circ\text{C}$ to show the formation of $(\text{ArN})\text{Mo}(\text{N}=\text{CHMe})_2(\text{PMe}_3)_2$ (**19**) as a mixture of three isomers in the ratio of 1 : 0.7 : 0.1 by ^1H NMR. Major isomer: ^1H NMR (600 MHz; toluene- d_8 ; 258 K; δ , ppm): 8.13 (q, 2H, 2 $\text{N}=\text{CHCH}_3$); 4.67 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, 2CH, NAr); 2.24 (br s, 6H, 2 $\text{N}=\text{CHCH}_3$); 1.39 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, 4 CH_3 , NAr); 1.11 (m, 18H, 2 PMe_3). $^1\text{H}-^{13}\text{C}$ HSQC NMR (f_1 : 600 MHz; f_2 : 151 MHz; toluene- d_8 ; 258 K; ^{13}C projection; selected resonances; δ , ppm): 145.7 ($\text{CH}_3\text{CH}=\text{N}$); 26.9 ($^1\text{Pr CH}$, NAr); 24.5 ($\text{CH}_3\text{CH}=\text{N}$); 23.9 ($^1\text{Pr CH}_3$, NAr); 13.8 (PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz; toluene- d_8 ; 258 K; δ , ppm): 1.31 (br s, 2 PMe_3). Second major isomer: ^1H NMR (600 MHz; toluene- d_8 ; 258 K; δ , ppm): 8.12 (q, 1H, $\text{N}=\text{CHCH}_3$); 7.70 (br q, 1H, $\text{N}=\text{CHCH}_3$); 4.52 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, 2CH, NAr); 2.13 (br s, 6H, 2 $\text{N}=\text{CHCH}_3$); 1.42 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, 4 CH_3 , NAr); 1.12 (m, 18H, 2 PMe_3). $^1\text{H}-^{13}\text{C}$ HSQC NMR (f_1 : 600 MHz; f_2 : 151 MHz; toluene- d_8 ; 258 K; ^{13}C projection; selected resonances; δ , ppm): 145.7 ($\text{CH}_3\text{CH}=\text{N}$); 27.2 ($^1\text{Pr CH}$, NAr); 26.1 ($\text{CH}_3\text{CH}=\text{N}$); 23.3 ($^1\text{Pr CH}_3$, NAr); 13.9 (PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz; toluene- d_8 ; 258 K; δ , ppm): 2.42 (br s, 2 PMe_3). Minor isomer: ^1H NMR (600 MHz; toluene- d_8 ; 258 K; δ , ppm): 7.66 (q, 2H, 2 $\text{N}=\text{CHCH}_3$); 4.40 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, 2CH, NAr); 2.10 (br s, 6H, 2 $\text{N}=\text{CHCH}_3$); 1.49 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, 4 CH_3 , NAr); 1.11 (m, 18H, 2 PMe_3). $^1\text{H}-^{13}\text{C}$ HSQC NMR (f_1 : 600 MHz; f_2 : 151 MHz; toluene- d_8 ; ^{13}C projection; selected resonances; 258 K; δ , ppm): 145.8 ($\text{CH}_3\text{CH}=\text{N}$); 27.1 ($^1\text{Pr CH}$, NAr); 24.2 ($\text{CH}_3\text{CH}=\text{N}$); 24.7 ($^1\text{Pr CH}_3$, NAr); 13.8 (PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz; toluene- d_8 ; 258 K; δ , ppm): 2.41 (br s, 2 PMe_3).

Two equiv. of HBCat (5.76 μL , 0.054 mmol) were added to a solution of **19** resulting in the formation of hydroboration product $\text{EtN}(\text{BCat})_2$ and a mixture of unidentified, Mo-containing decomposition products.

NMR reaction of $\text{Mo}(\text{H})_2(\text{PMe}_3)_3(\eta^3\text{-NAr-HBCat})$ (**15**) with MeCN

MeCN (2.48 μL ; 0.048 mmol) was added in one portion to a solution of complex **15** (14.8 mg; 0.024 mmol) in 0.6 mL of toluene- d_8 in an NMR tube. The reaction was monitored by NMR and complete conversion was observed after several minutes at room temperature. Since the obtained product is fluxional at room temperature, NMR analysis was performed at -15 $^\circ\text{C}$ to show the presence of $(\text{ArN})\text{Mo}\{\text{N}(\text{BCat})=\text{CHMe}\}(\eta^2\text{-CH}_3\text{CN})(\text{PMe}_3)_2$ (**20**) as a mixture of two isomers ($\approx 3 : 1$ ratio by NMR). Evolution of H_2 gas was also observed. Major isomer: ^1H NMR (600 MHz; toluene- d_8 ; 270 K; δ , ppm): 7.38 (q, $^3J_{\text{H-H}} = 4.3$ Hz, 1H, $\text{N}(\text{BCat})=\text{CHCH}_3$); 6.83 (m, 2H, CatB); 6.74 (m, 2H, CatB); 4.02 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 1H, CH, NAr); 3.08 (br s, 3H, NCCH_3); 2.72 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 1H, CH, NAr); 1.65 (br d, $^3J_{\text{H-H}} = 4.3$ Hz, 3H, $\text{N}(\text{BCat})=\text{CHCH}_3$); 1.57 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 3H, CH_3 , NAr); 1.53 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CH_3 , NAr); 1.32 (d, $^2J_{\text{P-H}} = 7.7$ Hz, 9H, PMe_3); 1.18 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CH_3 , NAr); 0.93 (d, $^2J_{\text{P-H}} = 7.7$ Hz, 9H, PMe_3); 0.72 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 3H, CH_3 , NAr). $^1\text{H}-^{13}\text{C}$ HSQC NMR (f_1 : 600 MHz; f_2 : 151 MHz; toluene- d_8 ; 270 K; ^{13}C projection; selected resonances; δ , ppm): 151.8 ($\text{N}(\text{BCat})=\text{CHCH}_3$); 121.2 (CatB); 111.2 (CatB); 27.9 (CH, Ar); 26.3 (CH, Ar); 25.2 (CH_3 , Ar); 23.4 (CH_3 , Ar); 23.5 (CH_3 , Ar); 21.7 ($\text{CH}_3\text{CH}=\text{N}$); 20.8 (CH_3CN); 18.2 (PMe_3), 14.6 (PMe_3). $^1\text{H}-^{13}\text{C}$ HMBC NMR (f_1 : 600 MHz; f_2 : 151 MHz; toluene- d_8 ; 270 K; ^{13}C projection; selected resonances; δ , ppm): 203.8 (CH_3CN). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz; toluene- d_8 ; 270 K; δ , ppm): 10.5 (d, $^2J_{\text{P-P}} = 177.6$ Hz, PMe_3), -1.86 (d, $^2J_{\text{P-P}} = 177.6$ Hz, PMe_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (192.6 MHz; toluene- d_8 ; 270 K; δ , ppm): 13.3 (vb s). Minor isomer: ^1H NMR (600 MHz; toluene- d_8 ; 270 K; δ , ppm): 8.56 (br s, 1H, $\text{N}(\text{BCat})=\text{CHCH}_3$); 3.42 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, 2CH, NAr); 2.88 (br s, 3H, NCCH_3); 2.62 (br s, 3H, $\text{N}=\text{CHCH}_3$); 1.50 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, CH_3 , NAr); 1.44 (d, $^2J_{\text{P-H}} = 7.0$ Hz, 9H, PMe_3), 1.29 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, CH_3 , NAr), 0.92 (obscured by the major isomer, PMe_3). $^1\text{H}-^{13}\text{C}$ HSQC NMR (f_1 : 600 MHz; f_2 : 151 MHz; toluene- d_8 ; 270 K; ^{13}C projection; selected resonances; δ , ppm): 26.9 (CH_3 , NAr), 20.5 (CH_3CN), 21.3 ($\text{CH}_3\text{CH}=\text{N}$), 18.1 (PMe_3), 15.6 (CH_3 , NAr). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz; toluene- d_8 ; 258 K; δ , ppm): 9.0 (d, $^2J_{\text{P-P}} = 167.2$ Hz, PMe_3), -4.46 (d, $^2J_{\text{P-P}} = 167.2$ Hz, PMe_3). Two equivalents of HBCat (5.12 μL , 0.048 mmol) were added to a solution of complex **20**, resulting in the formation of hydroboration product $\text{EtN}(\text{BCat})_2$ and regeneration of the starting complex **15**.

Acknowledgements

This work was supported by NSERC (DG grant to GIN). GIN further thanks the CFI/OIT for a generous equipment grant. AYK thanks the OGS scholarship.

Notes and references

- H. C. Brown, *Hydroboration*, Wiley, NY, 1962.
- Selected reviews: (a) L. Tonks and J. M. Williams, *Contemp. Org. Synth.*, 1997, 353; (b) I. Beletskaya and A. Pelter, *Tetrahedron*, 1997, 53, 4957 and references therein; (c) T. Hayashi, in *Comprehensive Asymmetric Catalysis*, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer, NY, 1999, vol. 1, p. 349; (d) H. Braunschweig and M. Colling, *Coord. Chem. Rev.*, 2001, 223, 1; (e) C. M. Crudden and D. Edwards, *Eur. J. Org. Chem.*, 2003, 4695; (f) W. Carruthers and I. Coldham, *Modern Methods of Organic Synthesis*, Cambridge University Press, Cambridge, 4th edn, 2004, pp. 315–331; (g) C. Pubill-Ulldemolins, A. Bonet, C. Bo, H. Gulyas and E. Fernandez, *Org. Biomol. Chem.*, 2010, 8, 2667.
- (a) H. C. Brown, *Organic Synthesis via Boranes*, Wiley, New York, 1975; (b) A. Pelter, K. Smith and H. C. Brown, *Borane Reagents*, Academic Press, New York, 1988 and references therein.
- (a) D. Männig and H. Nöth, *Angew. Chem., Int. Ed. Engl.*, 1985, 24, 878; (b) K. Burgess and M. J. Ohlmeyer, *Chem. Rev.*, 1991, 91, 1179; (c) C. M. Vogels and S. A. Westcott, *Curr. Org. Chem.*, 2005, 9, 687; (d) C. C. Chong and R. Kinjo, *ACS Catal.*, 2015, 5, 3238 and references therein.
- For data on the toxicity of transition metals, see: http://www.ema.europa.eu/docs/en_GB/document_library/Scientific_guideline/2009/09/WC500003586.pdf.
- For examples of alkene and alkyne hydroborations, see: (a) D. A. Evans, A. R. Muci and R. Sturmer, *J. Org. Chem.*, 1993, 58, 5307; (b) K. Burgess and W. A. van der Donk, *Organometallics*, 1994, 13, 3616; (c) K. Burgess and W. A. van der Donk, *J. Am. Chem. Soc.*, 1994, 116, 6561; (d) E. A. Bijpost, R. Duchateau and J. H. Teuben, *J. Mol. Catal. A: Chem.*, 1995, 95, 121; (e) S. Pereira and M. Srebnik, *Organometallics*, 1995, 14, 3127; (f) S. Pereira and M. Srebnik, *Tetrahedron Lett.*, 1996, 37, 3283; (g) X. He and J. F. Hartwig, *J. Am. Chem. Soc.*, 1996, 118, 1696; (h) J. F. Hartwig, C. N. Muhoro, X. He, O. Eisenstein, R. Booque and F. Maseras, *J. Am. Chem. Soc.*, 1996, 118, 10936; (i) D. H. Motry, A. G. Brazil and M. R. Smith III, *J. Am. Chem. Soc.*, 1997, 119, 2743; (j) J. F. Hartwig and C. N. Muhoro, *Organometallics*, 2000, 19, 30; (k) Y. D. Wang, G. Kimball, A. S. Prashad and Y. Wang, *Tetrahedron Lett.*, 2005, 46, 8777.
- (a) D. R. Lantero, D. L. Ward and M. R. Smith III, *J. Am. Chem. Soc.*, 1997, 119, 9699; (b) D. R. Lantero, S. L. Miller, J.-Y. Cho, D. L. Ward and M. R. Smith III, *Organometallics*, 1999, 18, 235.
- Ketones: (a) D. A. Evans and A. H. Hoveyda, *J. Org. Chem.*, 1990, 55, 519; (b) C. W. Lindsley and M. DiMare, *Tetrahedron Lett.*, 1994, 35, 5141; (c) G. Giffels, C. Dreisbach, U. Kragl, M. Weiderding, H. Waldmann and C. Wandrey, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, 2005; (d) A. J. Blake, A. Cunningham, A. Ford, S. J. Teat and S. Woodward, *Chem. – Eur. J.*, 2000, 6, 3586; (e) I. Sarvary, F. Almqvist and T. Frejd, *Chem. – Eur. J.*, 2001, 7, 2158; (f) S.-G. Roh, Y.-C. Park, T.-J. Kim and J. H. Jeong, *Polyhedron*, 2001, 20, 1961; (g) P. Hegarty, R. Lau and W. B. Motherwell, *Tetrahedron Lett.*, 2003, 44, 1851; (h) M. Locatelli and P. G. Cozzi, *Angew. Chem., Int. Ed.*, 2003, 42, 4928; (i) S. G. Roh, J. U. Yoon and J. H. Jeong, *Polyhedron*, 2004, 23, 2063; (j) L. Koren-Selfridge, H. N. Londino, J. K. Vellucci, B. J. Simmons, C. P. Casey and T. B. Clark, *Organometallics*, 2009, 28, 2085; (k) A. A. Oluyadi, S. Ma and C. N. Muhoro, *Organometallics*, 2013, 32, 70.
- Esters: (a) S. C. Berk, K. A. Kreutzer and S. L. Buchwald, *J. Am. Chem. Soc.*, 1991, 113, 5093; (b) S. C. Berk and S. L. Buchwald, *J. Org. Chem.*, 1992, 57, 3751; (c) K. J. Barr, S. C. Berk and S. L. Buchwald, *J. Org. Chem.*, 1994, 59, 4323; (d) M. T. Reding and S. L. Buchwald, *J. Org. Chem.*, 1995, 60, 7884; (e) X. Verdagner, M. C. Hansen, S. C. Berk and S. L. Buchwald, *J. Org. Chem.*, 1997, 62, 8522; (f) L. Pehlivan, E. Méta, S. Laval, W. Dayoub, D. Delbrayelle, G. Mignani and M. Lemaire, *Eur. J. Org. Chem.*, 2011, 7400; (g) Z. Mao, B. T. Gregg and A. R. Cutler, *J. Am. Chem. Soc.*, 1995, 117, 10139; (h) D. Bezier, G. T. Venkana, L. C. Misal Castro, J. Zheng, T. Roisnel, J.-B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2012, 354, 1879; (i) K. Junge, B. Wendt, S. Zhou and M. Beller, *Eur. J. Org. Chem.*, 2013, 2061; (j) A. J. Ruddy, C. M. Kelly, S. M. Crawford, C. A. Wheaton, O. L. Sydora, B. L. Small, M. Stradiotto and L. Turculet, *Organometallics*, 2013, 32, 5581.
- Imines: R. T. Baker, J. C. Calabrese and S. A. Westcott, *J. Organomet. Chem.*, 1995, 498, 109.
- For uncatalysed addition of alkyl boranes and BH_3 to nitriles, see: (a) Y. Chujo, I. Tomita and T. Saegusa, *Macromolecules*, 1994, 27, 6714; (b) K. Wade, M. G. Davidson, M. A. Fox, W. R. Gill, T. G. Hibbert and J. A. H. Maceride, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1997, 124–125, 73; (c) D. Jaganyi and A. Mzinyati, *Polyhedron*, 2006, 25, 2730.
- (a) E. Peterson, A. Y. Khalimon, R. Simionescu, L. G. Kuzmina, J. A. K. Howard and G. I. Nikonov, *J. Am. Chem. Soc.*, 2009, 131, 908; (b) A. Y. Khalimon, O. G. Shirobokov, E. Peterson, R. Simionescu, L. G. Kuzmina, J. A. K. Howard and G. I. Nikonov, *Inorg. Chem.*, 2012, 51, 4300.
- A. Y. Khalimon, P. Farha, L. G. Kuzmina and G. I. Nikonov, *Chem. Commun.*, 2012, 48, 455.
- S. K. Ignatov, A. Y. Khalimon, N. H. Rees, A. G. Razuvaev, P. Mountford and G. I. Nikonov, *Inorg. Chem.*, 2009, 48, 9605.
- Uncatalysed reaction for acetophenone gives only 50% conversion after 2 days.
- Similar transformations are known for bis(silyl) amines. However, the reactions require either harsh conditions or the presence of a catalyst: (a) N. Duffaut and J. P. Dupin, *Bull. Soc. Chim. Fr.*, 1966, 10, 3205; (b) R. J. P. Corriu, V. Huynh, J. J. E. Moreau and M. Pataud-Sat, *J. Organomet. Chem.*, 1983, 225, 359; (c) T. Morimoto and M. Sekiya, *Chem. Lett.*, 1985, 1371.

- 17 For previous discussion of degradation of HBcat under catalytic conditions, see: S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker and J. C. Calabrese, *Inorg. Chem.*, 1993, **32**, 2175.
- 18 For the stoichiometric reactivity of **1** with carbonyls, see ref. 12.
- 19 (a) H. M. M. Shearer and J. D. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1973, 2629; (b) G. Erker, W. Fromberg, J. L. Atwood and W. E. Hunter, *Angew. Chem.*, 1984, **96**, 72; (c) J. E. Bercaw, D. L. Davies and P. T. Wolczanski, *Organometallics*, 1986, **5**, 443; (d) Y. Tanabe, H. Seino, Y. Ishii and M. Hidai, *J. Am. Chem. Soc.*, 2000, **122**, 1690; (e) M. F. C. Guedes da Silva, J. J. R. Frausto da Silva and A. J. L. Pombeiro, *Inorg. Chem.*, 2002, **41**, 219.
- 20 A. Y. Khalimon, S. K. Ignatov, A. I. Okhapkin, R. Simionescu, L. G. Kuzmina, Judith A. K. Howard and G. I. Nikonov, *Chem. – Eur. J.*, 2013, **19**, 8573.
- 21 For related agostic borylamides, see: (a) T. D. Forster, H. M. Tuononen, M. Parvez and R. Roesler, *J. Am. Chem. Soc.*, 2009, **131**, 6689; (b) D. Srimani, Y. Diskin-Posner, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2013, **52**, 14131.
- 22 For examples of agostic B–H complexes, see: (a) H. Braunschweg, R. D. Dewhurst, T. Herbst and K. Radacki, *Angew. Chem., Int. Ed.*, 2008, **47**, 5978; (b) Y. Gloaguen, G. Alcaraz, A.-F. Pécharman, E. Clot, L. Vendier and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2009, **48**, 2964.
- 23 (ArN) Mo(Cl)(OEt)(PMe₃)₃ (**14**) can be also prepared from the hydrido–chloride **1** by reaction with EtOH. See ref. 12.
- 24 For characterization of hydroboration products, see ESI.†
- 25 Similar to the reaction of complex **1** with HBCat, no product of oxidative addition of borane to Mo akin to (ArN)–Mo(H)(BCat)(PMe₃)_x (where x = 2 or 3) was detected.
- 26 Data from Sigma-Aldrich.
- 27 M. Brookhart, K. Cox, F. G. N. Cloke, J. C. Green, M. L. H. Green, P. M. Hare, J. Bashkin, A. E. Derome and P. D. Grebenik, *J. Chem. Soc., Dalton Trans.*, 1985, 423.
- 28 Since isomers of **19** are in fast exchange even at –15 °C, the PMe₃ resonances in the ³¹P NMR spectrum appear as broad singlets.
- 29 (a) A. B. Jackson, C. K. Schauer, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 2007, **129**, 10628; (b) A. Y. Khalimon, R. Simionescu, L. G. Kuzmina, J. A. K. Howard and G. I. Nikonov, *Angew. Chem., Int. Ed.*, 2008, **47**, 7701; (c) A. Y. Khalimon, R. Simionescu and G. I. Nikonov, *J. Am. Chem. Soc.*, 2011, **133**, 7033.