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

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Imido–hydrido complexes (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**1**) and (ArN)Mo(H)$_2$(PMe_3)$_3$ (**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 $RCH_2N(BCat)_2$. 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)(PMe_3)$_2$; whereas for complex **2** stoichiometric reactions suggest initial addition of HBCat to form the agostic complex Mo(H)$_2$(PMe_3)$_3$(η^3-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 = catehol, 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] imines[10] 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)(PMe_3)$_3$ (**1**; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).[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)-$MoCl_2(PMe_3)_3$[14] 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)$MoH_2(PMe_3)_3$ (**2**, Scheme 1). **2** can be prepared from (ArN)$MoCl_2(PMe_3)_3$ 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

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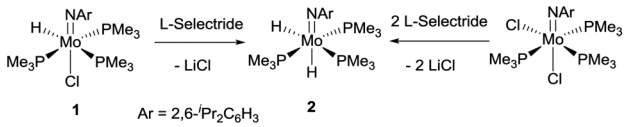


Scheme 1 Synthesis of $(ArN)MoH_2(PMe_3)_3$ (**2**).

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 $^{31}P\{^1H\}$ 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 $^2J_{P-P}$ = 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 ($^2J_{H-H}$ = 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 $^2J_{H-P}$ = 46.2 and 60.6 Hz and $^2J_{H-P}$ = 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.

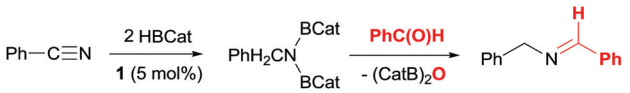
Catalytic reactivity of $(ArN)Mo(H)(Cl)(PMe_3)_3$ (1) and $(ArN)MoH_2(PMe_3)_3$ (2)

Catalysis by $(ArN)Mo(H)(Cl)(PMe_3)_3$ (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 ($^iPr_2C(O)$, $Ph_2C(O)$, cyclohexanone, PhC(O)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 MeC(O)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*-PhCH=CHBCat and ethylbenzene in addition to the expected product $PhCH_2CH_2BCat$. 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)	*t*	Yield[c], %	TON[d]
1	$^iPr_2C(O)$	91	$^iPr_2CHOBCat$	20 h	91	18
2	$Ph_2C(O)$	100	$Ph_2CH(OBCat)$	30 min	100	20
3	PhC(O)Me	99	PhCH(OBCat)Me	15 min	99	20
4	4-Nitroacetophenone	100	4-NO_2-C_6H_4-CH(OBCat)Me	1 h	100	20
5	Cyclohexanone	100	CyOBCat	1 h	100	20
6	MeC(O)OEt	100	EtOBCat	2 h	100	20
7	$PhCH{=}CH_2$	100	$PhCH_2CH_2BCat$	20 h	32	20
			trans-PhCH=CHBCat		53	
			$PhCH_2CH_3$		15	
8	1-Hexene	70	HexBCat	60h	55	14
			2-Hexene		8	
			3-Hexene		7	
9	3-Hexyne	94	EtCH=C(Et)BCat	21 h	94	19
10	PhC≡CH	99	*trans*-PhCH=CHBCat	20 h	99	20
11	MeCN	100	$EtN(BCat)_2$	12 h	100	20
12	PhCN	100	$PhCH_2N(BCat)_2$	12 h	100	20
13	5-Hexynenitrile	50	*trans*-$NC(CH_2)_3CH$=CHBCat	20 h	50	10
		92	*trans*-$NC(CH_2)_3CH$=CHBCat	48 h	92	18
14	4-Acetylbenzonitrile	100	4-CN-C_6H_4-CH(OBCat)Me	12 h	67	20
			4-$(CatB)_2NCH_2$-C_6H_4-CH(OBCat)Me		33	
15	Acrylonitrile	65	$CatBCH_2CH_2CN$	48 h	55	13
			$CatBCH_2(CH_2)_2N(BCat)_2$		10	
16	3-(2-Oxocyclohexyl)propanenitrile	100	2-$NC(CH_2)_2$-C_6H_{10}-OBCat	5 min	100	20
		100	2-$NC(CH_2)_2$-C_6H_{10}-OBCat	48 h	32	20
			2-$(CatB)_2N(CH_2)_3$-C_6H_{10}-OBCat		68	
17	$Ph_2C(O)$/PhCN (1/1)	100	$Ph_2CH(OBCat)$	12 h	67	20
			$Ph_2CH_2N(BCat)_2$		33	

[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 PhC≡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 C≡N bond, *i.e.* $RCH_2N(BCat)_2$ (R = Me, Ph; Table 1, entries 11 and 12).[13] Moreover, $PhCH_2N(BCat)_2$ was found to react easily with benzaldehyde to give the corresponding imine $PhCH_2N{=}CHPh$ with the release of $(CatB)_2O$. 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-acetylbenzonitrile, 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 $Ph_2C{=}O$ and PhCN afforded both $Ph_2CH(OBCat)$ and $Ph_2CH_2N(BCat)_2$ (entry 17). In contrast, the hydroboration of 5-hexynenitrile takes place selectively on the alkyne moiety to give *trans*-$NC(CH_2)_3CH{=}CHBCat$, leaving the nitrile group unreacted (Table 1, entry 13).

Catalysis by $(ArN)MoH_2(PMe_3)_3$ (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 → 80; $^{i}Pr_2C(O)$: TOF 0.9 → 48; benzophenone: TOF 40 → 76; cyclohexanone: TOF 20 → 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*-PhCH=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)	*t*	Yield[c], %	TON[d]
1	PhC(O)Me	100	PhCH(OBCat)Me	15 min	>99	20
2	4-Nitroacetophenone	100	$4\text{-}NO_2\text{-}C_6H_4\text{-}CH(OBCat)Me$	15 min	>99	20
3	$Ph_2C(O)$	95	$Ph_2CH(OBCat)$	15 min	95	19
4	$^{i}Pr_2C(O)$	100	$^{i}Pr_2CH(OBCat)$	25 min	>99	20
5	Cyclohexanone	94	CyOBCat	25 min	94	19
6	MeC(O)OEt	99	EtOBCat	19 h	99	20
7	1-Hexene	93	HexBCat	24 h	85	19
			2-Hexene		3	
			3-Hexene		5	
8	$PhCH{=}CH_2$	100	$PhCH_2CH_2BCat$	60 h	25	20
			trans-PhCH=CHBCat		24	
			$PhCH_2CH_3$		51	
9	PhC≡CH	100	*trans*-PhCH=CHBCat	48 h	>99	20
10	MeCN	74	$EtN(BCat)_2$	24 h	74	15
11	PhCN	99	$PhCH_2N(BCat)_2$	24 h	99	20
12	$^{t}BuCN$	76	$^{t}BuCH_2N(BCat)_2$	24 h	76	15
13	Acrylonitrile	92	$CH_3CH(BCat)CN$	20 h	92	18
14	5-Hexynenitrile	42	*trans*-$NC(CH_2)_3CH{=}CHBCat$	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}H-NMR yields based on internal standard (tetramethylsilane). [d] Turnover numbers were calculated at maximum conversion.

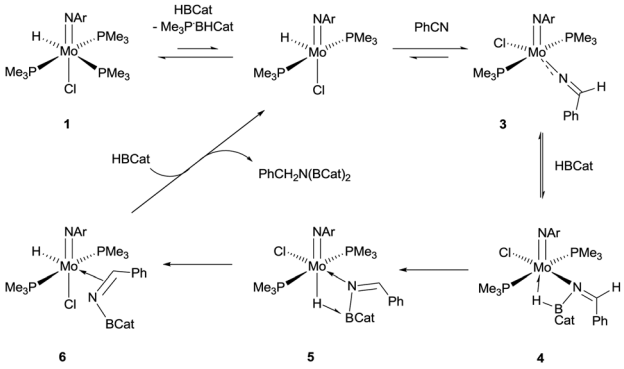
showed conversion of 3-hexyne to EtCH═C(Et)BCat with the TOF of 0.9 (Table 1, entry 9).

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 CH_3CN, 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$(CH_2)_3$CH═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.* CH_3CH(Bcat)CN (92%, Table 2, entry 13), whereas the **1**-catalysed reaction gives a mixture of CatB$(CH_2)_2$CN and CatB$(CH_2)_3$N(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 BH_3 and B_2Cat_3 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-hexinenitrile 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 $PMe_3{\cdot}BH_3$ adduct.[17]

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

Stoichiometric reactivity of (ArN)Mo(H)(Cl)$(PMe_3)_3$ (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)-$MoCl_2(PMe_3)_3$ [14] and (ArN)Mo$(H)_2(PMe_3)_3$ (**2**) was observed by NMR. No products of oxidative addition of borane to Mo, akin to (ArN)Mo(Cl)$(H)_2$(BCat)$(PMe_3)_2$ or its derivative (ArN)Mo(Cl)-(BCat)$(PMe_3)_x$ (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 vinyledeneamide derivative (ArN)Mo(Cl)(N═CHPh)$(PMe_3)_2$ (**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-enenitrile, 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 methylenamide species was further substantiated by X-ray



Scheme 3 Catalytic transformation of nitriles to imines.

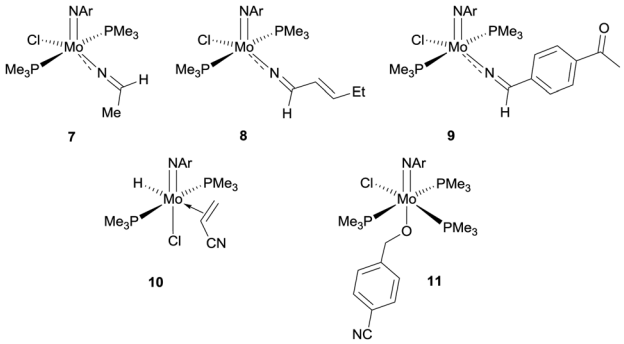
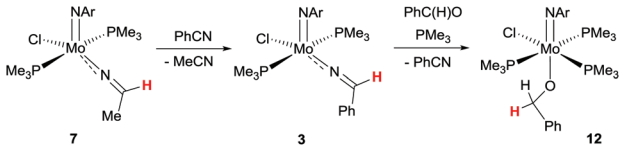


Fig. 1 Methylenamide complexes **7–9** and products of the reactions of **1** with acrylonitrile and 4-formylbenzonitrile, **10** and **11**, respectively.

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 ^{1}H–^{13}C HSQC NMR to the corresponding ^{1}H resonances) in their ^{1}H and ^{13}C 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 ArN^{2-} (Mo═N–C 175.0(3)°)[13] donates 6ē.

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 Cp_2*Sc(NCHR).[19c] A similar reactivity pattern was also observed upon the treatment of benzylideneamide **3** with benzaldehyde, which in the presence of PMe_3 leads to the exclusive formation of the benzoxy complex (ArN)Mo(Cl)(OBn)$(PMe_3)_3$ (**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-acetylbenzonitrile and 4-formylbenzonitrile to give 4-acetylbenzylideneamide 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)H[12]), one can assume that for both keto- and aldonitriles the reactions proceed *via* initial insertion of the nitrile group into the Mo–H bond. For 4-formylbenzonitrile, this insertion can be followed by intermolecular hydrogen transfer to the formyl moiety to form the more thermodynamically stable complex **11**.

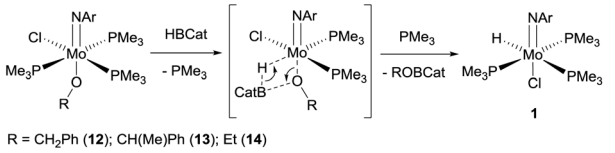
The reaction of complex **3** with HBCat was followed by NMR spectroscopy at low temperature. At −30 °C, the formation of a mixture of two bis(phosphine) compounds (**4** and **5** in Scheme 3) was observed. One of the products was tentatively formulated as the agostic amido-borane adduct (ArN)Mo(Cl){κ^3-N(=CHPh)(CatB-H···)}(PMe$_3$)$_2$ (**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 PMe$_3$ ligands giving rise to a singlet at δ −0.9 ppm in ^{31}P NMR; (ii) ^{1}H NMR revealed a downfield imine signal at δ 8.91 ppm, coupled in ^{1}H–^{13}C HSQC NMR to the ^{13}C NMR resonance at δ 172.0 ppm; (iii) ^{11}B 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 B_2H_6).

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 ^{1}H NMR spectrum of **5** reveals a broad upfield hydride signal at δ −2.94 ppm and a downfield imine ^{1}H resonance at δ 8.31 ppm, coupled in ^{1}H–^{13}C HSQC NMR to the ^{13}C NMR signal at δ 154.2 ppm. A series of ^{1}H, ^{1}H{^{31}P} and ^{1}H{^{11}B} 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 ^{11}B nucleus. Unfortunately, we could not measure the B–H coupling constant from the very broad signal in ^{11}B NMR. The two non-equivalent PMe$_3$ ligands give rise to two mutually coupled doublets at δ −1.4 ppm and δ −13.0 ppm in the ^{31}P NMR spectrum. The large value of $^2J_{P–P}$ = 212.0 Hz suggests the *trans* arrangement of the phosphine ligands in **6**. The ^{11}B 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**, presumable 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}-(PMe$_3$)$_2$ (**5**, Scheme 3) having non-equivalent PMe$_3$ 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}(PMe$_3$)$_2$ (**6**; Scheme 3), the structure of which was suggested on the basis of multinuclear NMR spectroscopy. Thus, the ^{31}P NMR spectrum of **6** shows two non-equivalent PMe$_3$ 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 ^{1}H 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 ^{1}H–^{13}C 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 ^{1}H–^{31}P HSQC NMR; $^2J_{H–P}$ = 45.0 and 50.9 Hz), suggesting the *cis* disposition of the hydride and imido ligands. The ^{11}B NMR spectrum of **6** shows a downfield signal at δ 15.3 ppm.

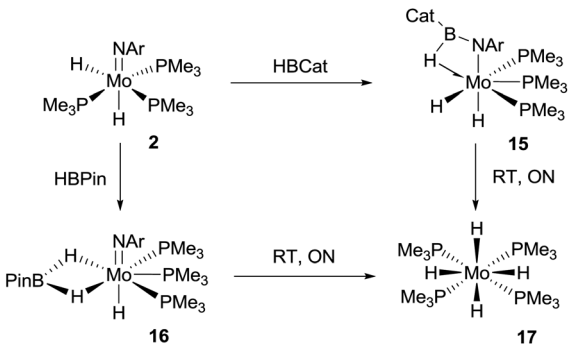
No further intermediates were observed upon addition of another equivalent of HBCat to complex **6**. Only the release of PhCH$_2$N(BCat)$_2$ and formation of a mixture of the hydrido–chloride **1** and (ArN)MoCl$_2$(PMe$_3$)$_3$ [14] together with a small amount of unknown decomposition products were 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 methylenamide 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)Mo(Cl)(OBn)(PMe$_3$)$_3$ (**12**; generated from **1** and PhC(O)H),[12] or (ArN)Mo(Cl)(OCH(Me)Ph)(PMe$_3$)$_3$ (**13**; generated from **1** and PhC(O)Me) or (ArN)Mo(Cl)(OEt)-(PMe$_3$)$_3$ [12,23] (**14**; generated from **1** and ethyl acetate) with HBCat immediately regenerates the complex **1** and gives the corresponding hydroboration products, PhCH$_2$OBCat, PhCH(OBCat)Me and EtOBCat, respectively.[24] A small amount of (ArN)MoCl$_2$(PMe$_3$)$_3$ [14] 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



R = CH_2Ph (**12**); CH(Me)Ph (**13**); Et (**14**)

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



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

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-formylbenzonitrile, 4-acetylbenzonitrile) 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)(η^2-O═CRH)(PMe_3)$_2$, which in the presence of a large excess of RHC(O) rearranges slowly (≥5 h) into an alkoxy complex *via* dissociation of PMe_3.[12] Addition of excess borane could significantly accelerate this process through the formation of a PMe_3–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.

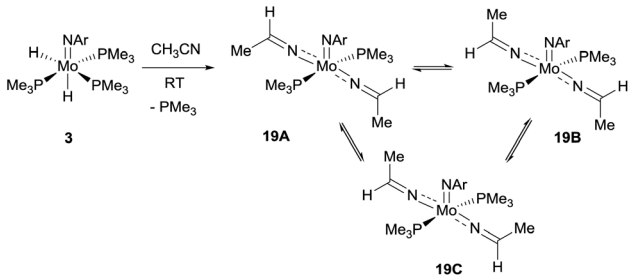
Stoichiometric reactivity of (ArN)MoH_2(PMe_3)$_3$ (2). To further identify the potential catalytically active species in the hydroboration reactions, stoichiometric reactions between complex **2**, unsaturated organic molecules and HBR (R = Cat, Pin) were studied. At ambient temperature, NMR scale reaction 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)$_2$(PMe_3)$_3$(η^3-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 ^{1}H 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 ^{11}B nucleus, the hydride signal at δ −1.82 ppm resolves into a broad doublet, presumably, due to coupling to the *trans*-PMe_3 ligand ($^2J_{H-P}$ = 15.2 Hz). Also, ^{11}B NMR showed the presence of a four-coordinate boron species exhibiting a signal at δ −0.59 ppm (*vs.* 29 ppm for HBCat). The ^{31}P{^{1}H} 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 ^{1}H–^{31}P 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] Treatment 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 ^{1}H 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 ^{1}H{^{11}B} NMR spectrum. The ^{11}B 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(η^2-H_2BPin)(H)(PMe_3)$_3$ (**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 $MoH_4(PMe_3)_4$ (**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.

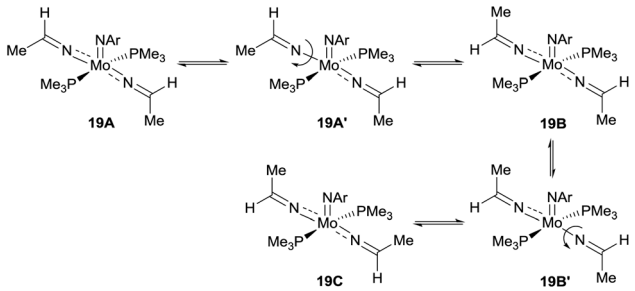
On the other hand, treatment of the dihydride complex **2** with ketones resulted in complex reaction mixtures. In the reaction mixture obtained upon mixing **2** with cyclohexanone, we identified a species tentatively assigned the structure (ArN)Mo(H)(OCy)(PMe_3)$_3$ (**18**) on the basis of analogy of its spectral features with the compound (ArN)Mo(Cl)(OCy)(PMe_3)$_3$ [12b] and the correlation of its ^{31}P signals in the ^{1}H–^{31}P 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)$_2$(PMe_3)$_2$ (**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 ^{1}H EXSY NMR ($\Delta S^{\neq}$ = −12.0 ± 2.8 kcal mol^{-1}, $\Delta H^{\neq}$ = 12.3 ± 1.1 kcal mol^{-1}). The negative entropy of activation suggests an intramolecular exchange mechanism.

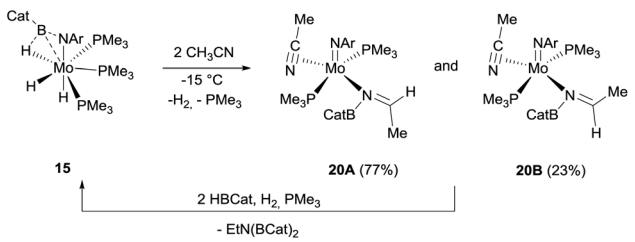
All three isomers of **19** were characterised by NMR spectroscopy and their ^{1}H NMR spectra revealed the presence of downfield imine resonances at δ 8.13 ppm (for **19A**), 8.12 and 7.70 ppm (for **19B**) and 7.66 ppm (for **19C**). These imine



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 ^{1}H–^{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 ^{1}H–^{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 ^{1}H NMR spectra of **19**, we suggest that the Mo=N–Ar fragment is almost linear and the imido ligand acts as a 6ē donor. If this assumption is true, complex **19** can be thought of as a stable 18ē 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 M=NC bond (σ + dative π) into a single Mo–N=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, $EtN(BCat)_2$. 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 °C, **15** reacts with 2 equiv. of CH_3CN to give $(ArN)Mo(-N(Bcat)=CHMe)(\eta^2\text{-}N\equiv CCH_3)(PMe_3)_2$ (**20**) as a mixture of two isomers (Scheme 9; ≈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 ^{1}H 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 ^{1}H–^{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)	t	Yield, %[c]	TON[d]
1	PhC(O)Me	100	PhCH(OBCat)Me	10 min	>99	20
2	4-Nitroacetophenone	95	4-O_2N-C_6H_4-CH(OBCat)Me	10 min	95	19
3	$Ph_2C(O)$	99	$Ph_2CH(OBCat)$	10 min	99	20
4	$^{i}Pr_2C(O)$	90	$^{i}Pr_2CH(OBCat)$	25 min	90	18
5	Cyclohexanone	99	CyOBCat	10 min	9	20
6	1-Hexene	82	HexBCat	24 h	79	16
			2-Hexene + 3-hexene		3	
7	$PhCH=CH_2$	87	$PhCH_2CH_2BCat$	24 h	4	17
			trans-PhCH=CHBCat		77	
			$PhCH_2CH_3$		6	
8	PhC≡CH	99	*trans*-PhCH=CHBCat	24 h	99	20
9	MeCN	99	$EtN(BCat)_2$	12 h	99	20
10	PhCN	99	$PhCH_2N(BCat)_2$	12 h	99	20
11	^{t}BuCN	90	$^{t}BuCH_2N(BCat)_2$	9 h	90	18
12	5-Hexynenitrile	95	*trans*-$NC(CH_2)_3CH=CHBCat$	36 h	95	19

[a] 5 mol% of **15**, 22 °C, C_6D_6, substrate/HBCat = 1/1 (1/2 for entries 9–11). [b] Conversion of organic substrate. [c] ^{1}H 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-NR_2 (about 26 ppm) and the four-coordinate catecholborane-imine adducts CatBH*N(R)=CR_2 (−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 ^{31}P-NMR spectra for both isomers of **20** show broad signals for the PMe_3 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 η^2-N≡CCH_3 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 CaH_2. Benzene-d_6 and toluene-d_8 were dried by distillation over K/Na alloy. NMR spectra were obtained with Bruker DPX-300 (^{1}H: 300 MHz; ^{13}C: 75.5 MHz; ^{31}P: 121.5 MHz; ^{11}B: 96.3 MHz) and Bruker DPX-600 (^{1}H: 600 MHz; ^{2}D: 92.1 MHz; ^{13}C: 151 MHz; ^{31}P: 243 MHz; ^{11}B: 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)$(PMe_3)_3$ (**1**)[12] and (ArN)Mo(Cl)-(N=CHPh)$(PMe_3)_2$ (**3**)[13] were prepared according to the previously published procedures. Compounds (ArN)Mo-$(H)_2(PMe_3)_3$ (**2**) and $Mo(H)_2(PMe_3)_3(\eta^3$-NAr-HBCat) (**15**) are unstable at room temperature whereas compounds (ArN)Mo-$(H)_2(PMe_3)_3$ (**2**) and (ArN)Mo(Cl)(N=CHMe)$(PMe_3)_2$ (**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)$(PMe_3)_2$ (3) with HBCat

A: Room temperature reaction. A solution of HBCat (3.5 μl, 0.033 mmol) in 0.6 ml of C_6D_6 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)(η^2-N(BCat)=CHPh)$(PMe_3)_2$ (**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 ^{31}P–^{31}P EXSY NMR spectrum of complex **6** revealed an intramolecular exchange of the PMe_3 ligands; however, addition of PhCN to a solution of **6** in C_6D_6 does not afford CatBN=CHPh. On the other hand, addition of a stoichiometric mixture of PhCN and HBCat to a solution of **6** in C_6D_6 leads to slow (2 days) conversion of **6** into **3** and formation of $PhCH_2N(BCat)_2$.

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. N_2 solution of **3** (23.5 mg, 0.042 mmol) in 0.6 ml of C_6D_6 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){η^3-N(=CHPh)-(CatB-H···}$(PMe_3)_2$ (**4**), and (ArN)Mo(H)(Cl)(η^1-N(BCat)=CHPh)-$(PMe_3)_2$ (**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){η^2-CatBN=CHPh}$(PMe_3)_2$ (**6**). Addition of another equivalent of HBCat affords $PhCH_2N(BCat)_2$ and a mixture of **1**, $(ArN)MoCl_2(PMe_3)_3$[14] and unknown decomposition products.

*(ArN=)Mo(Cl){η^3-N(=CHPh)(CatB-H···}$(PMe_3)_2$ (**4**).* ^{1}H NMR (600 MHz; 225 K; PhMe-d_8; δ, ppm): 8.91 (br s, 1H, C*H*Ph); 8.08 (d, $^3J_{H-H}$ = 7.4 Hz, 2H, *o*-H, CH*Ph*); 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, 2*CH*, *Ar*N, overlapping with *CH* (*Ar*N) of **3**); 1.39 (br m, 6H, 2CH_3, *Ar*N); 1.29 (bm, 6H, 2CH_3, *Ar*N); 1.24 (br m, 18H, 2 PMe_3). $^{31}P\{^1H\}$ NMR (243 MHz; 225 K; PhMe-d_8; δ, ppm): −0.9 (br s, *P*Me_3). $^{11}B\{^1H\}$ NMR (193 MHz; 253 K; PhMe-d_8; δ, ppm): 2.3 (br s, H*B*Cat). ^{11}B NMR (193 MHz; 283 K; PhMe-d_8; δ, ppm): 2.2 (br d, $^1J_{B-H} \approx 55$ Hz; H*B*Cat). $^{13}C\{^1H\}$ NMR (151 MHz; 253 K; PhMe-d_8; δ, ppm): 172.0 (s, N=*C*HPh, found by $^1H-^{13}C$ HSQC NMR); 129.7 (s, *o*-C, CH*Ph*); 27.5 (s, *CH*, *Ar*N); 23.8 (s, CH_3, *Ar*N); 23.6 (s, CH_3, *Ar*N); 14.3 (vt, $^1J_{C-P}$ = 24 Hz, 2 *trans*-PMe_3).

(ArN)Mo(H)(Cl)(η^1-N(BCat)=CHPh)(PMe_3)$_2$ ***(5)***. ^1H NMR (600 MHz; 225 K; PhMe-d_8; δ, ppm): 8.31 (br s, 1H, N=C*H*Ph); 6.63–7.37 (m, overlapping aromatic signals of HBCat, **2**, **4**, and **5**); 4.12 (br s, 1H, *CH*, *Ar*N); 3.92 (br s, 1H, *CH*, *Ar*N); 1.32 (br m, 6H, 2CH_3, *Ar*N); 1.29 (d, $^2J_{H-P}$ = 8.4 Hz, 9H, PMe_3); 1.21 (br m, 6H, 2CH_3, *Ar*N); 0.87 (d, $^2J_{H-P}$ = 8.1 Hz, 9H, PMe_3); −2.94 (br m, 1H, Mo*H*). $^{31}P\{^1H\}$ NMR (243 MHz; 225 K; PhMe-d_8; δ, ppm): −1.4 (d, $^2J_{P-P}$ = 212.0 Hz, *P*Me_3); −13.0 (d, $^2J_{P-P}$ = 212.0 Hz, *P*Me_3). ^{11}B NMR (193 MHz; 253 K; PhMe-d_8; δ, ppm): 10.1 (br s, *B*Cat). ^{11}B NMR (193 MHz; 283 K; PhMe-d_8; δ, ppm): 10.2 (br s, *B*Cat). $^{13}C\{^1H\}$ NMR (151 MHz; 253 K; PhMe-d_8; δ, ppm): 154.2 (s, N=*C*HPh, found by $^1H-^{13}C$ HSQC NMR); 27.2 (s, *CH*, *Ar*N); 26.9 (s, *CH*, *Ar*N); 25.7 (bs, CH_3, *Ar*N); 25.2 (s, CH_3, *Ar*N); 13.1 (d, $^1J_{C-P}$ = 22.8 Hz, PMe_3); 12.7 (d, $^1J_{C-P}$ = 21.7 Hz, PMe_3).

ArN)Mo(H)(Cl){η^2-CatBN=CHPh}(PMe_3)$_2$ ***(6)***. ^1H NMR (600 MHz; 295 K; PhMe-d_8; δ, ppm): 7.65 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, *o*-H, CH*Ph*, major isomer); 7.45 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, *o*-H, CH*Ph*, minor isomer); 7.06 (m, Mo*H* of major isomer, obscured by aromatic signals, found by $^1H-^{31}P$ HSQC NMR); 6.9–7.3 (m, overlapping aromatic signals of CPh and NAr of **2**, **5**, **6**, and (ArN)$MoCl_2(PMe_3)_3$); 6.91 (m, 2H, B*Cat*, major isomer); 6.78 (m, 2H, B*Cat*, major isomer); 6.73 (br m, Mo*H* of minor isomer, found by $^1H-^{31}P$ HSQC NMR); 5.00 (dd, $^3J_{H-P}$ = 3.0 Hz; 1H, N=C*H*Ph, major isomer); 4.39 (br s, 1H, N=C*H*Ph, minor isomer); 4.22 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, *CH*, *Ar*N, major isomer); 4.13 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, *CH*, *Ar*N, major isomer); 3.98 (br m, 1H, *CH*, *Ar*N, minor isomer); 3.84 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, *CH*, *Ar*N, minor isomer); 1.80 (d, $^2J_{H-P}$ = 10.1 Hz, 9H, PMe_3, major isomer); 1.72 (d, $^2J_{H-P}$ = 10.1 Hz, 9H, PMe_3, minor isomer); 1.35 (bm, 9H, PMe_3, minor isomer); 1.24 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, 2CH_3, *Ar*N, major isomer); 1.20 (d, $^2J_{H-P}$ = 9.9 Hz, 9H, PMe_3, major isomer); 1.18 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, 2CH_3, *Ar*N, major isomer). $^{31}P\{^1H\}$ NMR (243 MHz; 295 K; PhMe-d_8; δ, ppm): 2.4 (d, $^2J_{P-P}$ = 88.5 Hz, *P*Me_3, both isomers); −5.2 (d, $^2J_{P-P}$ = 88.5 Hz, *P*Me_3, both isomers). ^{31}P NMR (selectively decoupled from methyl groups at 1.20 ppm in the ^1H NMR spectrum; 243 MHz; 295 K; PhMe-d_8; δ, ppm): 2.4 (dd, $^2J_{P-P}$ = 88.5 Hz, $^2J_{P-H}$ = 50.9 Hz, *P*Me_3); −5.2 (br m, *P*Me_3). ^{31}P NMR (selectively decoupled from methyl groups at 1.80 ppm in the ^1H NMR spectrum; 243 MHz; 295 K; PhMe-d_8; δ, ppm): 2.4 (br m, *P*Me_3); −5.2 (dd, $^2J_{P-P}$ = 88.5 Hz, $^2J_{P-H}$ = 45.0 Hz, *P*Me_3). ^{11}B NMR (193 MHz; 295 K; PhMe-d_8; δ, ppm): 15.3 (br s, *B*Cat). $^1H-^{13}C$ HSQC NMR (*f*1: 300 MHz; *f*2: 75.5 MHz; *J* = 145 Hz; 296 K; PhMe-d_8; ^{13}C projection for major isomer; δ, ppm): 128.9 (*o*-C, C*Ph*); 62.9 (N=*C*HPh); 27.2 (*C*H, *Ar*N); 26.6 (*C*H, *Ar*N); 24.9 (CH_3, *Ar*N); 24.8 (CH_3, *Ar*N); 17.5 (PMe_3); 17.1 (PMe_3).

Preparation of (ArN)$Mo(H)_2(PMe_3)_3$ (2)

(ArN)$Mo(Cl)_2(PMe_3)_3$ [14] (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-d_8; 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, Mo*H* (*trans*- to PMe_3)); 1.35 (m, 21H, 4 CH_3 of N*Ar* and PMe_3); 1.49 (br m, 18H, 2 PMe_3); 2.08 (m, overlapping with residual toluene-d_8 signal, $^2J_{H-P}$ = 43.2 Hz, $^2J_{H-H}$ = 7.2 Hz, 1H, Mo*H* (*trans*- to NAr), found by $^1H-^1H$ COSY and $^1H-^{31}P$ HSQC NMR); 4.43 (sept, $^3J_{H-H}$ = 6.6 Hz, 2H, 2 *CH*, N*Ar*); 6.91–7.32 (m, overlapping with residual toluene-d_8 resonances, 3H, *m*-H and *p*-H of N*Ar*). $^1H\{^{31}P\}$ NMR (600 MHz; toluene-d_8; 243 K; selected resonances; δ, ppm): −5.31 (d, $^2J_{H-H}$ = 7.2 Hz, 1H, Mo*H*); 1.38 (s, 9H, PMe_3); 1.50 (s, 18H, 2 PMe_3); 2.09 (d, $^2J_{H-H}$ = 7.2 Hz, 1H, Mo*H*). $^{31}P\{^1H\}$ NMR (243 MHz; toluene-d_8; 247 K; δ, ppm): 14.8 (d, $^2J_{P-P}$ = 19.4 Hz, 2P, 2 *P*Me_3); 13.1 (t, $^2J_{P-P}$ = 19.4 Hz, 1P, *P*Me_3). $^1H-^{13}C$ HSQC NMR (*f*1: 600 MHz; *f*2: 151 MHz; toluene-d_8; 243 K; ^{13}C projection; selected resonances; δ, ppm): 124.9, 122.0, 121.9, (*m*-C and *p*-C, N*Ar*); 26.3 (*C*H, N*Ar*); 26.2 (CH_3, N*Ar*); 25.9 (PMe_3), 25.0 (CH_3, N*Ar*); 24.2 (PMe_3). IR (nujol): 1620 cm^{-1} (broad, medium, Mo–H).

Preparation of $Mo(H)_2(PMe_3)_3(\eta^3$-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-d_8; 244 K; δ, ppm): −6.03 (dt, $^2J_{H-P}$ = 39.6 Hz, $^2J_{H-P}$ = 88.2 Hz, 1H, Mo*H*); −2.79 (t, $^2J_{H-P}$ = 59.9 Hz, 1H, Mo*H*); −1.82 (bs, 1H, ArN–B–*H*–Mo agostic); 0.86 (d, $^2J_{H-P}$ = 7.3 Hz, 9H, PMe_3); 1.33 (bs,6H, 2 ^{i}Pr-CH_3 of *Ar*N); 1.35 (d, $^2J_{H-P}$ = 9.0 Hz, 18H, 2 PMe_3); 1.55 (d, $^2J_{H-P}$ = 6.2 Hz, 6H, 2 ^{i}*Pr*-CH_3 of *Ar*N); 3.45 (sept, 2H, 2 ^{i}Pr-*CH* of *Ar*N); 6.97–6.8 (br m, 4H, B*Cat*). $^1H\{^{31}P\}$ NMR (243 MHz, toluene-d_8, 243 K; δ, ppm): −6.03 (bs, Mo*H*); −2.79 (bs, Mo*H*). $^{31}P\{^1H\}$ NMR (243 MHz, toluene-d_8, 243 K; δ, ppm): 2.54 (t, $^2J_{P-P}$ = 17.0 Hz, 1P, *P*Me_3); 23.9 (d, $^2J_{P-P}$ = 17.0 Hz, 2P, 2 *P*Me_3). $^1H-^{13}C$ HSQC NMR (*f*1: 600 MHz; *f*2: 151 MHz; toluene-d_8, 243 K; ^{13}C projection; selected resonances; δ, ppm): 125.0, 123.0, 121.9 (*m*-C and *p*-C, N*Ar*); 112.0, 122.3

(*Cat*B); 26.8 (^{i}Pr-*C*H, N*Ar*); 25.2 (2 P*Me*$_3$); 24.8 (P*Me*$_3$); 23.7 (*C*H$_3$, N*Ar*); 23.5 (*C*H$_3$, N*Ar*); ^{11}B NMR (192.6 MHz; toluene-d$_8$, 243 K; δ, ppm): −0.59 (br s, ArN-*B*Cat).

NMR reaction of (ArN)Mo(H)$_2$(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, (ArN)Mo(η^2-H$_2$BPin)(H)(PMe$_3$)$_3$ (**16**), was observed. ^{1}H NMR (600 MHz; toluene-d$_8$; 244 K; δ, ppm): −6.89 (q, $^2J_{H-P}$ = 63 Hz, 1H, Mo*H*); −4.13 (br s, 2H, η^2-PinB*H*$_2$); 1.10 (d, $^2J_{H-P}$ = 7.3 Hz, 18H, 2 P*Me*$_3$); 1.20 (d, $^2J_{H-P}$ = 8 Hz, 9H, P*Me*$_3$); 1.27 (s, 12 H, Me of Bpin); 1.36 (br s, 12H, ^{i}Pr-*CH*$_3$ of N*Ar*); 3.62 (sept, $^3J_{H-H}$ = 6.2 Hz, 2H, ^{i}Pr-*CH* of NAr). ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; 243 K; δ, ppm): 50.0 (br s, 2P, 2 *P*Me$_3$); 12.7 (s, 1P, *P*Me$_3$). ^{11}B NMR (192.6 MHz; toluene-d$_8$; 243 K; δ, ppm): −3.6 (bs, H$_2$*B*Pin).

NMR reaction of (ArN)Mo(H)$_2$(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 °C to show the formation of (ArN)Mo(N=CHMe)$_2$(PMe$_3$)$_2$ (**19**) as a mixture of three isomers in the ratio of 1 : 0.7 : 0.1 by ^{1}H NMR. Major isomer: ^{1}H NMR (600 MHz; toluene-d$_8$; 258 K; δ, ppm): 8.13 (q, 2H, 2 N=*CH*CH$_3$); 4.67 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*); 2.24 (br s, 6H, 2 N=CH*CH*$_3$); 1.39 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, 4*CH*$_3$, N*Ar*); 1.11 (m, 18H, 2 P*Me*$_3$). ^{1}H–^{13}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 (CH$_3$*C*H=N); 26.9 (^{i}Pr *C*H, N*Ar*); 24.5 (*C*H$_3$CH=N); 23.9 (^{i}Pr *C*H$_3$, N*Ar*); 13.8 (P*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; 258 K; δ, ppm): 1.31 (br s, 2 *P*Me$_3$). Second major isomer: ^{1}H NMR (600 MHz; toluene-d$_8$; 258 K; δ, ppm): 8.12 (q, 1H, N=*CH*CH$_3$); 7.70 (br q, 1H, N=*CH*CH$_3$); 4.52 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*); 2.13 (br s, 6H, 2 N=CH*CH*$_3$); 1.42 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, 4*CH*$_3$, N*Ar*); 1.12 (m, 18H, 2 P*Me*$_3$). ^{1}H–^{13}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 (CH$_3$*C*H=N); 27.2 (^{i}Pr *C*H, N*Ar*); 26.1 (*C*H$_3$CH=N); 23.3 (^{i}Pr *C*H$_3$, N*Ar*); 13.9 (P*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; 258 K; δ, ppm): 2.42 (br s, 2 *P*Me$_3$). Minor isomer: ^{1}H NMR (600 MHz; toluene-d$_8$; 258 K; δ, ppm): 7.66 (q, 2H, 2 N=*CH*CH$_3$); 4.40 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*); 2.10 (br s, 6H, 2 N=CH*CH*$_3$); 1.49 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, 4*CH*$_3$, N*Ar*); 1.11 (m, 18H, 2 P*Me*$_3$). ^{1}H–^{13}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 (CH$_3$*C*H=N); 27.1 (^{i}Pr *C*H, N*Ar*); 24.2 (*C*H$_3$CH=N); 24.7 (^{i}Pr *C*H$_3$, NAr); 13.8 (P*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; 258 K; δ, ppm): 2.41 (br s, 2 *P*Me$_3$).

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

NMR reaction of Mo(H)$_2$(PMe$_3$)$_3$(η^3-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 °C to show the presence of (ArN)Mo{N(BCat)=CHMe}(η^2-CH$_3$CN)(PMe$_3$)$_2$ (**20**) as a mixture of two isomers (≈3 : 1 ratio by NMR). Evolution of H$_2$ gas was also observed. Major isomer: ^{1}H NMR (600 MHz; toluene-d$_8$; 270 K; δ, ppm): 7.38 (q, $^3J_{H-H}$ = 4.3 Hz, 1H, N(BCat)=*CH*CH$_3$); 6.83 (m, 2H, *Cat*B); 6.74 (m, 2H, *Cat*B); 4.02 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, *CH*, N*Ar*); 3.08 (br s, 3H, NC*CH*$_3$); 2.72 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, *CH*, N*Ar*); 1.65 (br d, $^3J_{H-H}$ = 4.3 Hz, 3H, N(BCat)=CH*CH*$_3$); 1.57 (d, $^3J_{H-H}$ = 6.7 Hz, 3H, *CH*$_3$, N*Ar*); 1.53 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, *CH*$_3$, N*Ar*); 1.32 (d, $^2J_{P-H}$ = 7.7 Hz, 9H, P*Me*$_3$); 1.18 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, *CH*$_3$, N*Ar*); 0.93 (d, $^2J_{P-H}$ = 7.7 Hz, 9H, P*Me*$_3$); 0.72 (d, $^3J_{H-H}$ = 6.7 Hz, 3H, *CH*$_3$, N*Ar*). ^{1}H–^{13}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 (N(BCat)=*C*HCH$_3$); 121.2 (*Cat*B); 111.2 (*Cat*B); 27.9 (*C*H, Ar); 26.3 (*C*H, Ar); 25.2 (*C*H$_3$, Ar); 23.4 (*C*H$_3$, Ar); 23.5 (*C*H$_3$, Ar); 21.7 (*C*H$_3$CH=N); 20.8 (*C*H$_3$CN); 18.2 (P*Me*$_3$), 14.6 (P*Me*$_3$). ^{1}H–^{13}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$_3$*C*N). ^{31}P{^{1}H} NMR (243 MHz, toluene-d$_8$, 270 K; δ, ppm): 10.5 (d, $^2J_{P-P}$ = 177.6 Hz, *P*Me$_3$), −1.86 (d, $^2J_{P-P}$ = 177.6 Hz, *P*Me$_3$). ^{11}B{^{1}H} NMR (192.6 MHz, toluene-d$_8$, 270 K; δ, ppm): 13.3 (vb s). Minor isomer: ^{1}H NMR (600 MHz; toluene-d$_8$; 270 K; δ, ppm): 8.56 (br s, 1H, N(BCat)=*CH*CH$_3$); 3.42 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*); 2.88 (br s, 3H, NC*CH*$_3$); 2.62 (br s, 3H, N=CH*CH*$_3$); 1.50 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, *CH*$_3$, N*Ar*); 1.44 (d, $^2J_{P-H}$ = 7.0 Hz, 9H, P*Me*$_3$), 1.29 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, *CH*$_3$, N*Ar*), 0.92 (obscured by the major isomer, P*Me*$_3$). ^{1}H–^{13}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 (*C*H$_3$, N*Ar*), 20.5 (*C*H$_3$CN), 21.3 (*C*H$_3$CH=N), 18.1 (P*Me*$_3$), 15.6 (*C*H$_3$, N*Ar*). ^{31}P{^{1}H} NMR (243 MHz, toluene-d$_8$, 258 K; δ, ppm): 9.0 (d, $^2J_{P-P}$ = 167.2 Hz, *P*Me$_3$), −4.46 (d, $^2J_{P-P}$ = 167.2 Hz, *P*Me$_3$). 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 EtN(BCat)$_2$ and regeneration of the starting complex **15**.

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