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Catalytic hydroboration by an imido-hydrido complex of Mo(IV)†

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The imido-hydrido complex (ArN)Mo(H)(Cl)(PMe_3)$_3$ catalyses a variety of hydroboration reactions, including the first example of catalytic addition of HBCat to nitriles to form the bis(borylated) amines $RCH_2N(BCat)_2$. The latter species easily undergoes chemoselective coupling with aldehydes R′C(O)H to yield imines $RCH_2N{=}C(H)R'$.

Hydroboration of unsaturated substrates is a reaction of immense importance for organic chemistry.[1,2] Whereas, alkyl and aryl boranes add to multiple C–C, C–O, and C–N bonds easily, the hydroboration by deactivated boranes, such as HBCat (Cat = catechol), calls for the application of transition metal catalysis, which to date is mostly done by late transition metals (Rh, Ir etc).[2,3] The latter are notorious for their high cost and toxicity. While early metals are usually both cheaper and more environmentally benign, only a few catalytic examples are known, and those are mostly limited to Ti and Zr.[4] Stoichiometric reactions of HBCat with olefins have been shown for Nb and Ta metallocene complexes.[5] Much less is known about catalytic hydroboration of carbonyl derivatives,[6,7] with no reported examples for esters and nitriles.[8]

We have recently reported catalytic and mechanistic studies on hydrosilylation reactions mediated by the imido-hydrido complex (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**1**; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), including one of the first examples of nitrile hydrosilylation.[9] Believing that HBCat may exhibit even superior reactivity patterns due to its enhanced Lewis acidity, we elected to study the hydroboration catalysed by **1**. Here we report the results of these efforts, including an insight into the mechanism and observation of unusual B–H···M agostic and borylimino intermediates.

Complex **1** shows catalytic activity in a diversity of hydroboration processes (Table 1). Thus, ketones (^{i}Pr$_2$C(O), Ph$_2$C(O), PhC(O)Me[10]), and esters, MeC(O)OEt, are easily converted to the corresponding boryl ethers (Table 1, entries 1–4). Addition of HBCat to alkenes[4b–g,5] and alkynes[4a,h–i] (styrene, 3-hexyne, and phenylacetylene) in the presence of **1** (5 mol%) affords the boro-substituted alkanes and alkenes, respectively (Table 1, entries 5–7); albeit the **1**-catalysed reaction with styrene also gives large amounts of *trans*-PhCH=CHB(Cat) and ethylbenzene. In contrast, **1** showed reduced or no catalytic activity in the hydroboration of 1-hexene, cyclohexene, α-methylstyrene, 1-octyne and PhC≡CHCH$_3$. The last but not the least, the hydroboration of nitriles (MeCN and PhCN) catalysed by **1** (5 mol%) leads to products of double addition of HBCat across the C≡N bond, $RCH_2N(BCat)_2$ (Table 1, entries 8 and 9).

Since nitriles react faster than ketones and alkynes we also tried polyfunctional compounds. Hydroboration of acrylonitrile, 3-(2-oxocyclohexyl)propanenitrile, 4-acetyl-benzonitrile, and a mixture of PhCN/Ph$_2$C(O) (1 : 1) was not chemoselective.[11] In contrast, addition of HBCat to 5-hexyne-nitrile occurs selectively on the alkyne moiety, leaving the nitrile group unreacted.[11]

Importantly, the products of nitrile hydroboration, $RCH_2N(Bcat)_2$, easily react with aldehydes to give imines $RCH_2N{=}CHR'$. Taken together, these novel hydroboration and coupling reactions constitute a useful synthetic transformation of nitriles to imines.[12] This reaction is remarkable in that it proceeds chemoselectively with aldehydes but not with ketones.

In order to elucidate the mechanism of nitrile hydroboration, we studied the stoichiometric reactivity of **1**.[13] Addition of nitriles to **1** results in the methylenamide derivatives *trans*-(ArN)Mo(Cl)(N=CHR)(PMe_3)$_2$ (**2–5**; Scheme 1). It is noteworthy that unlike catalytic reactions (*vide supra*) insertion of the C≡N bond into the Mo–H bond is chemoselective, tolerating ketone and non-conjugated alkene functionalities.

Table 1 Catalytic hydroboration with HBCat mediated by **1**[a]

Entry	Substrate	Product(s)	*t*, h	Yield, %[b]
1	^{i}Pr$_2$C(O)	(^{i}Pr)$_2$CH(OBCat)	24	91
2	Ph$_2$C(O)	Ph$_2$CH(OBCat)	24	100
3	PhC(O)Me	PhCH(OBCat)Me	24	99
4	MeC(O)OEt	EtOBCat	24	100
5	PhCH=CH$_2$	PhCH$_2$CH$_2$BCat	20	32
		PhCH=CHBCat		53
		PhCH$_2$CH$_3$		15
6	3-hexyne	EtCH=C(Et)BCat	24	94
7	PhC≡CH	PhCH=CHBCat	20	99
8	MeCN	EtN(BCat)$_2$	12	100
9	PhCN	PhCH$_2$N(BCat)$_2$	12	100

[a] Conditions: 5 mol% of **1**, 22 °C, C_6D_6, substrate/HBCat = 1 : 1 (1 : 2 ratio for entries 4, 8 and 9), C_{subst} = 0.4 M. [b] NMR yields.

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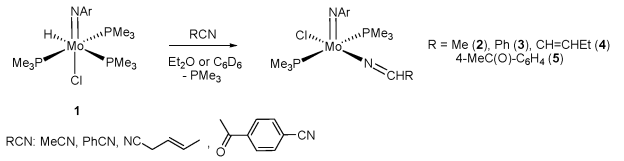
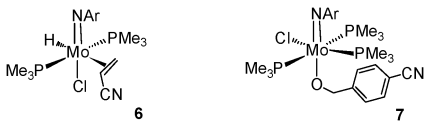
† Electronic supplementary information (ESI) available: Experimental details, full table for catalytic hydroboration reactions. CCDC 836951. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14508h



Scheme 1 Preparation of methylenamide complexes of Mo.

Control reactions of **1** with 1 : 1 mixtures of PhCN and ketones (acetone, acetophenone, and cyclohexanone) result in the exclusive formation of **3**.[14] In contrast, reactions of **1** with acrylonitrile and 4-formylbenzonitrile afford complexes **6** and **7**, respectively.



Compounds **2–7** were characterized by spectroscopic methods (IR, NMR) and X-ray diffraction for **3** (Fig. 1). Complex **3** has a distorted trigonal bipyramidal structure, with two *trans* PMe_3 ligands occupying the apical positions. The Mo1–N2–C13 bond angle is almost linear (172.3(4)°) suggesting that the [N═CHPh] fragment acts as a 4e donor[15] stabilizing the 18e valence shell, assuming that the linear imide ArN^{2-} (Mo1–N1–C1 175.0(3)°) also donates 6e. Compounds **2–5** and **7** give rise to diagnostic imine proton (7.09–7.43 ppm) and carbon signals (145.4–153.5 ppm) in their ^1H and ^{13}C NMR spectra, respectively.

Interestingly, the addition of PhCN to the methyl derivative **2** leads to a slow (24 h at RT) release of acetonitrile to form complex **3**, indicating α-CH bond activation in the methylenamide ligand. To the best of our knowledge, such a reversible nitrile insertion into an early metal–hydride bond has been previously observed only for complex $Cp^*_2Sc(N{=}CHR)$.[15c] The possibility of α-CH activation in the methylenamide ligand was further confirmed by the reaction of **3** with benzaldehyde, which in the presence of PMe_3 leads to exclusive formation of the benzoxy derivative $(ArN)Mo(Cl)(OBn)(PMe_3)_3$ (**8**).[9] However, no transfer hydrogenation was observed in reactions of **3** with acetone or acetophenone even upon heating up to 60 °C. Such a difference in the reactivity of **3** towards aldehydes and ketones allows us to explain the difference in chemoselectivity of the

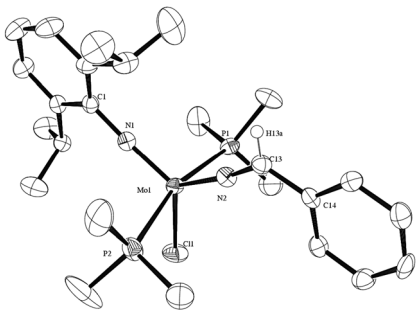


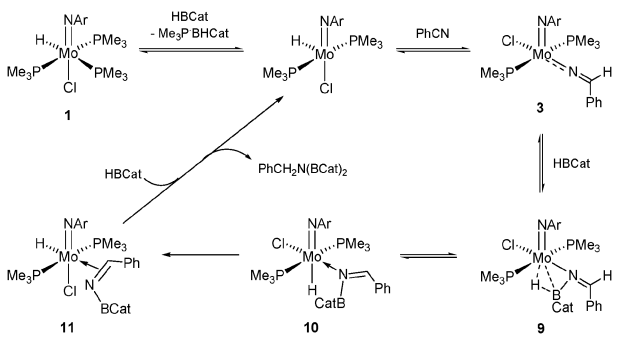
Fig. 1 Molecular structure of **3** (bond lengths in Å, angles in °). Hydrogen atoms except H13a are omitted. Mo1–N1 1.761(4), Mo1–N2 1.843(4), N2–C13 1.279(6), C1–N1–Mo1 175.0(3), C13–N2–Mo1 172.3(4), P1–Mo1–P2 164.60(5), Cl1–Mo1–N2 122.42(13), N1–Mo1–N2 116.45(17).

stoichiometric reactions of **1** with 4-acetylbenzonitrile and 4-formylbenzonitrile to give **5** and **7**, respectively.[16]

The reaction of **3** with HBCat was followed by NMR spectroscopy at low temperature. At −30 °C, the formation of a mixture of two bis(phosphine) compounds was observed. One of the products has a C_s symmetric NMR structure with two equivalent PMe_3 ligands giving rise to a singlet at −0.9 ppm in ^{31}P NMR. ^1H NMR revealed a downfield imine signal at 8.92 ppm, coupled in ^1H–^{13}C HSQC to the ^{13}C NMR signal at 172.0 ppm. Also, ^{11}B NMR showed the presence of a 4-coordinate boron centre exhibiting a doublet at 2.2 ppm (*vs.* 29 ppm for HBCat) with reduced B–H coupling ($J_{B-H} \approx 55$ Hz).[17] These spectroscopic features indicate an agostic borane structure tentatively formulated as the amido-borane adduct $(ArN{=})Mo(Cl)\{\kappa^3\text{-}N(=CHPh)(CatB\text{–}H\cdots)\}(PMe_3)_2$ (**9**; Scheme 2).[18]

The second product (**10**) in the mixture is produced from **9** upon gentle increase of temperature. However, all attempts to find a temperature regime for the full conversion of **9** were unsuccessful. The ^1H NMR spectrum of **10** at −50 °C shows a downfield imine signal at 8.31 ppm (s, coupled in ^1H–^{13}C HSQC NMR to the ^{13}C NMR signal at 154.2 ppm) and a broad upfield hydride resonance at −2.94 ppm. The two non-equivalent PMe_3 groups give rise to two mutually coupled doublets at −1.4 ppm and −13.0 ppm in the ^{31}P NMR spectrum, with the large $^2J_{P-P}$ = 212.0 Hz suggesting *trans*-arrangement. The ^{11}B NMR spectrum revealed the presence of an essentially 3-coordinate boron centre, which gives rise to a broad signal at 10.2 ppm, not coupled to the hydride at −2.94 ppm. All together these features are consistent with the formation of a κ^1-(*N*-boryl)imine derivative (ArN)-$Mo(H)(Cl)\{\kappa^1\text{-}N(BCat){=}CHPh\}(PMe_3)_2$ (**10**; Scheme 2). The non-equivalency of phosphines is then explained by the restricted rotation around the Mo–N bond at −50 °C.

Heating to 25 °C leads to disappearance of **9** and **10** and formation of $(ArN)Mo(H)(Cl)\{\eta^2\text{-}CatBN{=}CHPh\}(PMe_3)_2$ (**11**; Scheme 2). The ^{31}P NMR spectrum of this species shows two mutually coupled doublets at 2.4 and −5.2 ppm ($^2J_{P-P}$ = 88.5 Hz). The ^1H NMR spectrum of **11** revealed an upfield imine proton at 5.00 ppm (dd, $^3J_{H-P}$ = 3.1 Hz), diagnostic for the η^2-N═CHPh moiety, which is further supported by a significant upfield shift of the ^{13}C NMR resonance for the imine carbon (62.9 ppm, found by ^1H–^{13}C HSQC NMR). The MoH signal, in contrast, is shifted downfield to 7.06 ppm (found by ^1H–^{31}P HSQC NMR; $^2J_{H-P}$ = 45.0 and 50.9 Hz), suggesting the *cis* disposition of the hydride and imido ligands,



Scheme 2 Suggested mechanism for the hydroboration of PhCN.

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as in the parent complex **1**.[9] The downfield ^{11}B NMR signal at 10.1 ppm indicates a 3-coordinate boron.

Addition of another equiv. of HBCat to **11** does not allow for the observation of any further intermediates. Only the release of $PhCH_2N(BCat)_2$ and formation of a mixture of **1**, $(ArN)MoCl_2(PMe_3)_3$[19] and unknown decomposition products was observed. How the borylimine part of **11** is reduced into amine still remains unclear. But it is clear that this last step of a possible catalytic cycle (Scheme 2) is assisted by HBCat.

On the other hand, **1** reacts with HBCat very sluggishly: after 24 h at room temperature only ~20% conversion of **1** to a mixture of $(ArN)MoCl_2(PMe_3)_3$[19] and a highly fluxional dihydride complex $(ArN)MoH_2(PMe_3)_3$ (**12**) was observed by NMR. No oxidative addition of borane to Mo and formation of a Mo boryl complex, such as $(ArN)Mo(Cl)(BCat)(PMe_3)_x$ (x = 2, 3),[20] takes place.

A similar mechanism can be also suggested for the hydroboration of carbonyl compounds. Indeed, we found that the reaction of HBCat with $(ArN)Mo(Cl)(OBn)(PMe_3)_3$[9] (**8**), formed upon the reaction of **1** with PhC(O)H, immediately regenerates complex **1**. For nitriles bearing carbonyl substituents, the insertion of the C=O and C≡N moieties into the Mo–H bond of **1** becomes competitive in the presence of large excess of HBCat[21] resulting in the loss of chemoselectivity of hydroboration under catalytic conditions.

In conclusion, complex **1** was found to catalyse a variety of hydroboration reactions, including the so far unknown catalytic addition of HBCat to nitriles to form bis(boryl) amines. The latter compounds can be easily converted to imines by the reaction with aldehydes. The hydroboration of nitriles proceeds *via* a series of novel agostic borylamido and borylimino complexes.

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