



Cite this: *Chem. Commun.*, 2017, 53, 7333

Received 25th March 2017,
Accepted 5th May 2017

DOI: 10.1039/c7cc02281f

rsc.li/chemcomm

Hydroboration of alkynes and nitriles using an α -diimine cobalt hydride catalyst†

Hagit Ben-Daat,^a Christopher L. Rock,^a Marco Flores,^a Thomas L. Groy,^a
Amanda C. Bowman^b and Ryan J. Trovitch[✉]^a

Addition of NaEt₃BH to (Ph₂PP^rDI)CoCl₂ affords the corresponding monohydride, (Ph₂PP^rDI)CoH. X-ray diffraction and DFT calculations indicate that this compound possesses a radical monoanion α -DI chelate and a Co(II) centre. Notably, (Ph₂PP^rDI)CoH catalyzes the hydroboration of alkynes and dihydroboration of nitriles under mild conditions.

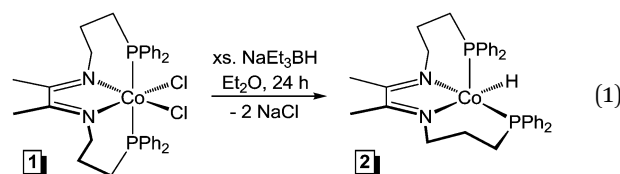
First popularized by Miyaura and Suzuki,¹ alkenyl boronate esters have remained vital precursors for highly functionalized organic molecules due to their utility in palladium-catalyzed cross-coupling reactions.² These reagents have traditionally been prepared by adding Grignard or organolithium reagents to trialkyl borates;³ however, the direct⁴ and metal-catalyzed⁵ hydroboration of alkynes have emerged as alternative, atom-efficient synthetic routes. For precursors that do not easily undergo direct hydroboration, it is desirable from a cost and sustainability perspective to utilize hydroboration catalysts which feature Earth abundant first transition series metals.⁶

There has been explosive growth in the development of cobalt-catalyzed alkene hydroboration over the last three years;⁷ however, relatively few examples of cobalt-mediated alkyne hydroboration have been reported. In 2015, it was determined that the bis(imino)pyridine cobalt alkyl complex, (2,6-iPr₂PhPDI)CoCH₃, affords *E*-alkenyl boronate esters following terminal alkyne hydroboration while cyclohexyl-substituted (CyPDI)CoCH₃ yields *Z*-alkenyl boronate esters with turnover frequencies (TOFs) of up to 6 h^{−1} at 23 °C.⁸ Zuo and Huang subsequently reported that *in situ* activation of (IPO)CoCl₂ with 2 equiv. of NaEt₃BH allows for alkyne dihydroboration TOFs of up to 3 h^{−1} (6 h^{−1} based on pinacol borane, HBPIn).⁹ Most recently, it was found that the supporting ligand can

control selectivity for either alkyl or alkenyl boronate esters during cobalt catalyzed 1,6-enyne cyclization (TOFs up to 4 h^{−1}).¹⁰ For these examples, TOF has been inferred from general reaction conditions and may not represent the upper activity limit.

In this contribution, we describe the synthesis and characterization of an α -diimine (DI) cobalt hydride complex that mediates alkyne hydroboration with TOFs of up to 900 h^{−1} at ambient temperature. Furthermore, we report modest TOFs for Co-catalyzed dihydroboration of nitriles to yield diborylamines.

An equimolar quantity of Ph₂PP^rDI¹¹ was added to CoCl₂ in acetonitrile solution and stirring at 25 °C for 24 h afforded a dark red product identified as (Ph₂PP^rDI)CoCl₂ (**1**, eqn (1)). This compound was found to exhibit broad ¹H NMR resonances that suggest two ligand coordination modes (one set predominates at −20 °C, see ESI†) and was determined to have a magnetic moment of 2.8 μ_B at 25 °C (by Evans method in acetonitrile-*d*₃ and magnetic susceptibility balance). Single crystals of **1** grown at −35 °C were then analysed by X-ray diffraction. Although high quality data could not be obtained (*R* = 0.0984), two unique molecules in the unit cell were found to possess a κ^4 -Ph₂PP^rDI chelate and *cis*-chloride ligands (Fig. S1 of the ESI†). DI ligands including Ph₂PP^rDI,^{11,12} are known to behave in a redox non-innocent manner when coordinated to low-valent first row metals;¹³ however, the N=C [1.273(10), 1.303(10), 1.306(9), and 1.287(9) Å] and C=C [1.492(10) and 1.501(11) Å] distances determined for **1** suggest an unreduced Ph₂PP^rDI chelate and Co(II) centre.¹⁴ To confirm this assignment, an electron paramagnetic resonance (EPR) spectrum of this compound was collected at 9.4 GHz and 113 K, which revealed a broad and nearly isotropic signal extending over 90 mT, consistent with a low-spin ⁵⁹Co(II) (*d*⁷, *S*_{Co} = 1/2, *I*_{Co} = 7/2) electronic structure (Fig. S3 of the ESI†).



^a School of Molecular Sciences, Arizona State University, Tempe, Arizona, 85287, USA. E-mail: ryan.trovitch@asu.edu; Tel: +1 480 727 8930

^b Department of Chemistry and Biochemistry, Colorado College, Colorado Springs, Colorado, 80903, USA

† Electronic supplementary information (ESI) available: X-ray crystallographic information for **2**, computational results, experimental details, and supporting spectroscopic data. CCDC 1539444. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc02281f

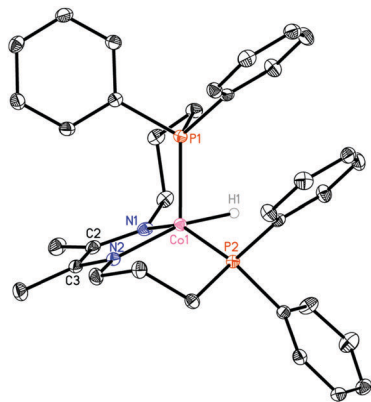


Fig. 1 Solid state structure of **2** at 30% probability ellipsoids. Hydrogen atoms except H1 are omitted for clarity. For complete atom listing and metrical parameters see Fig. S2 and Table S2, ESI†

Adding 2.2 equiv. of NaEt₃BH to **1** afforded a dark green product identified as (^{Ph₂PP^r}DI)CoH (**2**, eqn (1)). The ¹H NMR spectrum of diamagnetic **2** was found to feature left-to-right chelate inequivalence and a doublet of doublets at –19.80 ppm, indicative of a Co–H resonance that is split by two inequivalent phosphine environments. This was corroborated by the ³¹P NMR spectrum, which features two broadened resonances at 75.33 and 50.59 ppm. Taken together, the data suggest that complex **2** possesses a square pyramidal geometry consisting of apical and equatorial phosphine donors.

A single crystal of **2** was then analysed by X-ray diffraction. The solid state structure of this complex (Fig. 1) is consistent with its observed solution phase behaviour. A pseudo square pyramidal geometry is evident with P(1)–Co(1)–N(1), P(1)–Co(1)–N(2), P(1)–Co(1)–P(2), and P(1)–Co(1)–H(1) angles of 93.82(5), 115.86(5), 114.437(19), and 78.9(7)°, respectively. The Co–H distance of 1.439(19) Å is shorter than expected based on the sum of low-spin Co and H covalent radii (1.57 Å).¹⁵ Importantly, the N(1)–C(2) and N(2)–C(3) distances of 1.347(2) and 1.357(2) Å, respectively, are elongated relative to unreduced DI ligand values (1.29 Å).¹⁴ Moreover, contraction of the C(2)–C(3) distance to 1.401(3) Å is suggestive of single electron DI reduction and a Co(II) metal centre.¹⁴

To gain additional support for this electronic structure assignment, DFT calculations were conducted on **2**. An unrestricted Kohn–Sham (UKS) calculation converged to the restricted Kohn–Sham (RKS) solution, which features highly mixed molecular orbitals (e.g., the HOMO possesses 28% Co character, Fig. S4, ESI†). A broken symmetry calculation [BS(1,1)] was then performed, revealing a low-spin Co(II) metal centre that is antiferromagnetically coupled to a DI based electron (*S* = 0.66). The spin density plot for this solution features a charge of +0.74 on the metal and an overall charge of –0.72 on the DI backbone (Fig. 2, left). The RKS and BS(1,1) solutions reasonably match the experimental metrical parameters determined for **2** (Table S5, ESI†), and the BS(1,1) solution was found to be 1.2 kcal mol^{–1} lower in energy. Performing single point UKS and BS(1,1) calculations using the solid state structure coordinates revealed a smaller preference for BS(1,1) of 0.6 kcal mol^{–1}. Given this

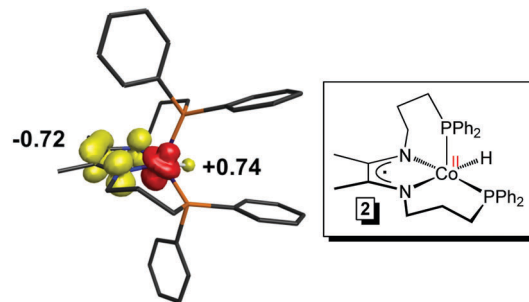


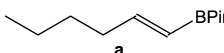
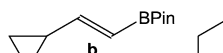
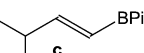
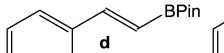
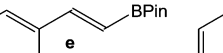
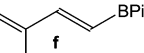
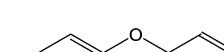
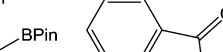
Fig. 2 Mulliken Spin density plot of BS(1,1) solution (left) and updated electronic structure of **2** (right).

slight preference, the electronic structure of **2** is consistent with a low-spin Co(II) centre that is antiferromagnetically coupled to a DI radical anion (Fig. 2, right). Comparable DI ligand non-innocence has been observed for (^{2,6-iPr₂Ph}DI)Co(η³-allyl), which is an efficient alkene hydroboration catalyst.^{7f}

Having characterized **2**, the hydroboration activity of this compound was evaluated (Table S6, ESI†). Adding an equimolar quantity of 1-hexyne and HBPin to 5 mol% **2** in benzene-*d*₆ solution resulted in 81% conversion (average of 5 trials) to the *E*-alkenyl boronate ester after 2 h at 25 °C. Longer reaction times did not improve the conversion rate, suggesting that borane consumption was limiting turnover. Therefore, the same transformation was conducted in the presence of 1.25 equiv. of HBPin and greater than 99% conversion was observed. To optimize the reaction conditions, the catalyst loading was lowered to 1.0 mol%, which also allowed for complete 1-hexyne hydroboration after 2 h (Table 1, entry a). Adding 2.2 equiv. of HBPin did not result in further reduction of the alkene and attempted hydroboration of 1-hexene revealed no conversion after 24 h.

Under these conditions, the **2**-catalyzed hydroboration of seven additional substrates was conducted. Alkynes featuring secondary alkyl substitution, cyclopropylacetylene and cyclohexylacetylene (Table 1, b and c), were hydroborated in 2 h at 25 °C. Likewise,

Table 1 Hydroboration of alkynes using 1.0 mol% **2**

R–C≡C + 1.25 HBPin $\xrightarrow[25\text{ }^{\circ}\text{C, 2 h}]{1.0\text{ mol\% } \mathbf{2}, \text{ benzene-}d_6}$ R–CH=CH–BPIn		
		
99% Conv.	99% (61% ^a)	99% (89%)
		
99% (96%)	99% (81%)	99% (69%)
		
58%	70% 99% ^b	

^a Isolated yields shown in parenthesis. ^b Conversion after 6 h.

2 was found to efficiently hydroborate phenylacetylenes (d–f) in the presence of HBPIn, affording the respective *E*-alkenyl boronate ester in good yield. Lower conversion was noted for phenyl propargyl ether (g, 58%) and *N*-propargylphthalimide (h, 70%) after 2 h; however, the latter was fully hydroborated after 6 h. For Table 1 entries a–f, the TOF for **2**-mediated alkyne hydroboration is 49 h^{−1}.

To further optimize this reaction, the hydroboration of aliphatic alkynes in neat HBPIn was performed using 0.1 mol% **2**. Starting with 1-hexyne (Table 2, a), 90% conversion was noted after 1 h at 25 °C, equating to an alkyne hydroboration TOF of 900 h^{−1}. Allowing this reaction to stir for 2 h afforded *trans*-1-hexen-1-ylboronic acid pinacol ester in 93% yield following purification by silica gel column chromatography. No conversion was noted in the absence of catalyst (Table S6, entry 10, ESI†). Similarly, the hydroboration of 1-octyne, 5-methyl-1-hexyne, and 4-phenyl-1-butyne afforded the respective *E*-alkenyl boronate ester (b–d). For each entry in Table 2, **2**-mediated alkyne hydroboration was achieved with a TOF of 495 h^{−1}.

Knowing that **2** is capable of hydroborating alkynes, this catalyst was also screened for nitrile hydroboration activity. Adding an equimolar mixture of benzonitrile and HBPIn to 1.0 mol% **2** in benzene-*d*₆ and monitoring the reaction by ¹H NMR spectroscopy revealed partial conversion to a new, non-alkene product after 6 h at 25 °C. Additional conversion was noted after 24 h; however, it became clear that HBPIn was being consumed prior to complete benzonitrile reduction. Repeating this experiment with 2.2 equiv. HBPIn revealed selective conversion to the *N,N*-diborylated product after 24 h at 60 °C (Table 3, entry a), and recrystallization from pentane afforded a modest 45% yield. No conversion was noted in the absence of catalyst.

After determining that **2** is active for benzonitrile dihydroboration, six additional substrates were screened. Unfunctionalized examples such as acetonitrile (b) and 4-phenylbutyronitrile (c) were efficiently converted under these conditions, as were ether-, dimethylamine-, and diphenylphosphine-substituted variants (d–f), demonstrating that donor groups do not inhibit **2**-catalyzed nitrile dihydroboration. Interestingly, when 4-acetylbenzonitrile hydroboration was attempted using 2.2 equiv. HBPIn, an exothermic reaction ensued. After 30 min, analysis by ¹H NMR spectroscopy revealed complete ketone reduction with partial nitrile dihydroboration, indicating that **2** is likely a highly active

Table 3 Dihydroboration of nitriles using 1.0 mol% **2** at 60 °C

$\text{R}-\text{C}\equiv\text{N} + 2.2 \text{ HBPIn} \xrightarrow[\text{60 } ^\circ\text{C, 24 h}]{1.0 \text{ mol\% } \mathbf{2} \text{ benzene-}d_6}$	
	a 99% (45%) ^a
	b 99% (43%)
	c 99% (72%)
	d 99% (88%)
	e 99% (30%)
	f 99% (45%)
	g ^b 99% (33%)

^a Isolated yields in parenthesis. ^b Trial conducted with 3.3 equiv. HBPIn.

carbonyl hydroboration catalyst. Repeating this trial with 3.3 equiv. of HBPIn allowed greater than 99% conversion to the trihydroborated product (g). As with a–f, a modest isolated yield was recorded following recrystallization. For each entry in Table 3, **2** was found to mediate nitrile dihydroboration with a TOF of 4 h^{−1}.

Although metal mediated imine hydroboration has been fairly well-documented,¹⁶ few catalysts for nitrile dihydroboration have been described. In 2012, Nikonov and co-workers reported that (2,6-¹Pr₂C₆H₃N)MoH(Cl)(PMe₃)₃ catalyzes the dihydroboration of acetonitrile and benzonitrile in the presence of catechol borane (HBCat) at 5 mol% loading after 12 h at 22 °C.¹⁷ Subsequently, this catalyst and related compounds, (2,6-¹Pr₂C₆H₃N)MoH₂(PMe₃)₃ and (η³-2,6-¹Pr₂C₆H₃NHBCat)MoH₂(PMe₃)₃ were found to reduce an expanded nitrile scope with HBCat.¹⁸ A loading of 5 mol% was also used by Szymczak and co-workers when investigating the substrate scope and functional group tolerance of [(BH₃PI)Ru(PPh₃)₂]-[K(18-crown-6)] catalyzed nitrile dihydroboration at 45 °C using HBPIn.¹⁹ Several variants of this catalyst also exhibited activity for this transformation. In 2016, Hill and co-workers achieved nitrile dihydroboration using HBPIn and a butylmagnesium β-diiminate catalyst at 60 °C.²⁰ Despite using a 10 mol% catalyst loading, propionitrile was converted to the *N,N*-diborylpropylamine after only 30 min. More recently, [(*p*-cymene)RuCl₂]₂ was found to mediate the slow dihydroboration of benzonitrile at ambient temperature, with complete turnover after 24 h at 60 °C.²¹ A broad substrate scope was effectively reduced with HBPIn over 15–36 h. It can be said that the nitrile dihydroboration activity achieved for **2** is largely comparable to what has been reported for other catalysts known to mediate this transformation.

In summary, the synthesis, electronic structure, and catalytic hydroboration activity of a DI-supported Co hydride catalyst,

Table 2 Hydroboration of alkynes in neat HBPIn using 0.1 mol% **2**

$\text{R}-\text{C}\equiv\text{C}-\text{H} + 1.25 \text{ HBPIn} \xrightarrow[\text{25 } ^\circ\text{C, 2 h}]{0.1 \text{ mol\% } \mathbf{2} \text{ benzene-}d_6}$	
	a 90% ^a 99% (93%) ^b
	b 99% (44%)
	c 99% (85%)
	d 99% (84%)

^a Conversion after 1 h. ^b Isolated yields shown in parenthesis.

(^{Ph₂PP_r}DI)CoH, has been described. This complex was found to possess a distorted square pyramidal geometry in addition to a radical anionic DI chelate that is antiferromagnetically coupled to low-spin Co(II). Importantly, this compound has been found to catalyze ambient temperature alkyne hydroboration to yield the respective *E*-alkenyl boronate esters with TOFs of up to 900 h⁻¹. The first cobalt catalyzed dihydroboration of nitriles to yield *N,N*-diborylamines has also been reported.²²

Acknowledgement is made to Arizona State University and Colorado College for support in the form of start-up funding. The authors declare no competing financial interests.

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