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Double and Single Hydroboration of Nitriles Catalyzed by a Ruthenium−Bis(silyl)xanthene Complex: Application to One-Pot Synthesis of Diarylamines and *N*-Arylimines

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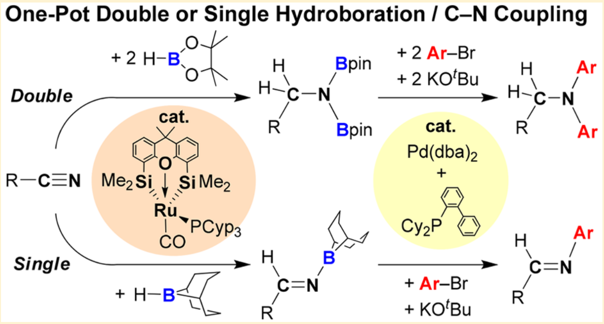
Supporting Information

ABSTRACT: A ruthenium complex bearing a bis(silyl)xanthene chelate ligand xantsil, i.e. Ru[κ^3(*Si,O,Si*)-xantsil](CO)(PCyp$_3$) (**1a**, Cyp = cyclopentyl), was found to catalyze both double and single hydroboration reactions of nitriles with pinacolborane (HBpin) and 9-borabicyclo[3.3.1]nonane (9-BBN) to give bis(boryl)amines **2** and *N*-borylimines **3**, respectively, in mostly >99% yields. By combination of these reactions with subsequent palladium-catalyzed deborylative C−N coupling reactions of **2** and **3** with a 1:1 mixture of bromoarenes and KO^{t}Bu, one-pot synthetic routes to tertiary *N,N*-diarylamines **4** and *N*-arylaldimines **5** from nitriles were developed.



Reduction of C≡N bonds of nitriles is a useful method to synthesize amines and imines. Amines are widely used as medicines, agrochemicals, etc.,[1] whereas imines are important as starting materials for organic synthesis, building blocks of supramolecules, etc.[2] Hydroboration reactions of nitriles giving either amine or imine derivatives selectively[3,4] are regarded as efficient methods for this nitrile reduction. In the last several years, double hydroboration reactions of nitriles with HBpin or catecholborane (HBcat) to give *N,N*-bis(boryl)amines have been investigated by use of transition-metal, rare-earth-metal, or main-group-element compounds as catalysts.[3] In sharp contrast with these catalytic reactions, uncatalyzed reactions of nitriles with alkyl- or arylboranes have been known to lead to single hydroboration to give *N*-borylimines.[4] Interestingly, to the best of our knowledge, catalysts that are active for both of these double and single hydroboration reactions have not been reported.

In this work, as the catalyst for hydroboration of nitriles, we employed a 16-electron ruthenium complex having a xanthene-based bis(silyl) chelate ligand xantsil ((9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)),[5] i.e. Ru[κ^3(*Si,O,Si*)-xantsil](CO)(PCyp$_3$) (**1a**), which was recently developed by us.[5c] Strong σ-donating ability of two silyl-ligand moieties of xantsil in **1a** is expected to make the metal center electron-rich and facilitate the oxidative addition of hydroboranes to the Ru center. Moreover, the Si,O,Si-type tridentate xantsil ligand of **1a** can function as a hemilabile ligand due to the weak coordination of the xanthene oxygen. Complex **1a** is therefore considered to generate 14-electron active species with two vacant coordination sites on the metal center, which can accept both nitrile and hydroborane molecules at the same time. In this study, we found that **1a** became a selective catalyst for both double and single hydroboration reactions of nitriles using HBpin and 9-BBN, respectively.

Furthermore, because *N*-borylated amines and imines obtained by double and single hydroboration reactions of nitriles possess labile B−N bonds, they are expected to serve as precursors for the syntheses of organic nitrogen compounds.[3,4,6] However, conversion reactions of these hydroboration products via B−N bond cleavage are still very limited, and most of them are hydrolysis or alcoholysis reactions.[3a−c,g,j,n,4a−d] The only known C−N bond forming reaction from the hydroboration products is a conversion of bis(boryl)amines to aldimines by treatment with benzaldehyde.[3a−c] In addition, Buchwald et al. previously reported that a reaction of triaminoboranes with bromoarenes and NaO^{t}Bu catalyzed by Pd(dba)$_2$/P(*o*-tolyl)$_3$ (a 1:2 mixture, dba = dibenzylideneacetone) afforded *N*-arylamines via C−N bond formation.[6] We applied this protocol to C(aryl)−N coupling reactions of the hydroboration products using a palladium−phosphine catalyst [a 1:2−4 mixture of Pd(dba)$_2$ and 2-(dicyclohexylphosphino)biphenyl (CyJohnPhos)],[7] and successfully prepared *N,N*-diarylamines and *N*-arylimines by a one-pot procedure from nitriles.

In the presence of 5 mol % of Ru−xantsil complex **1a**, 4-(trifluoromethyl)benzonitirile reacted with 2 equiv of pinacolborane (HBpin) in cyclohexane-d_{12} at 40 °C to give *N,N*-bis(boryl)amine **2a** quantitatively via double hydroboration (Table 1, entry 1). The single-hydroboration product, i.e. *N*-borylimine (4-CF$_3$C$_6$H$_4$)CH═NBpin, was not obtained even when one equivalent of HBpin was used. Catalytic activity of **1a** toward this reaction was compared against that of related

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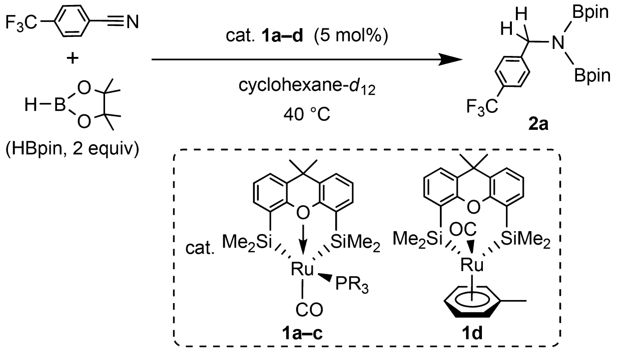
Table 1. Double Hydroboration of 4-$CF_3C_6H_4C{\equiv}N$ with HBpin Catalyzed by Complexes 1a−d[a]



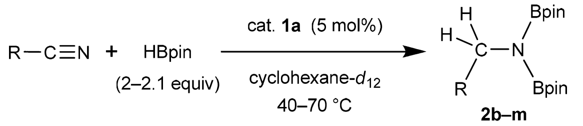
entry	cat.	time (h)	NMR yield of **2a** (%)[b]
1	**1a** (R = Cyp)	4	>99
2	**1b** (R = Cy)	4	>99
3	**1c** (R = Pyrr)	24	23
4	**1d**	24	>99

[a] Conditions: 4-$CF_3C_6H_4C{\equiv}N$ (0.15 mmol), HBpin (0.30 mmol), and catalyst (7 μmol, 5 mol %) in cyclohexane-d_{12} (0.5 mL) at 40 °C. [b] Based on 4-$CF_3C_6H_4C{\equiv}N$.

Ru−xantsil complexes, i.e. 16-electron complexes having different phosphine ligands Ru[κ^3(*Si*,*O*,*Si*)-xantsil](CO)(PR_3) (R = Cy (cyclohexyl) (**1b**)[5b] and Pyrr (1-pyrrolidinyl) (**1c**)[5d]) and also an 18-electron η^6-toluene complex Ru[κ^2(*Si*,*Si*)-xantsil](CO)(η^6-toluene) (**1d**)[5a] (entries 2−4). The reaction catalyzed by trialkylphosphine complex **1b** for 4 h at 40 °C afforded **2a** quantitatively (entry 2), which shows that the catalytic activity of **1b** is comparable with that of **1a** (entry 1). On the other hand, when complex **1c** having a less electron-donating triaminophosphine ligand was employed as a catalyst, even after a longer reaction time (24 h), **2a** was obtained in only 23% NMR yield (entry 3). This result implies that the hydroboration reaction is accelerated when the metal center of the catalyst becomes more electron-rich. η^6-Toluene complex **1d** was also found to catalyze this reaction to give **2a** quantitatively (entry 4), but the reaction was slower than those with catalysts **1a** and **1b**.

Bis(boryl)amine **2a** was prepared in a gram scale by a reaction in THF at 60 °C for 24 h using 0.2 mol % of complex **1a** as a catalyst (see eq S1 in the Supporting Information). In this reaction, product **2a** was formed nearly quantitatively and, from the reaction mixture, 1.04 g of **2a** was isolated in 83% yield. This amount of catalyst (0.2 mol %) is smaller than those of previously reported homogeneous catalysts for double hydroboration of nitriles (0.5−10 mol %),[3] and this fact clearly demonstrates the high catalytic activity of **1a**.

Table 2. Scope of Nitriles for the Double Hydroboration Catalyzed by 1a[a]



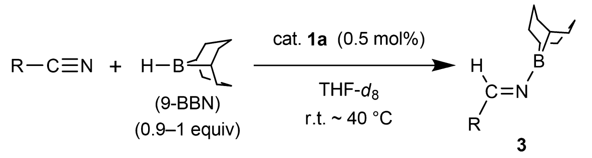
entry	R	product	temp (°C)	time (h)	NMR yield of 2 (%)[b,c]
1	4-ClC_6H_4	**2b**	40	4	>99
2	Ph	**2c**	60	4	>99
3	4-MeC_6H_4	**2d**	60	12	>99
4	4-$OMeC_6H_4$	**2e**	60	12	>99
5	3-MeC_6H_4	**2f**	60	12	>99
6	2-$CF_3C_6H_4$	**2g**	60	6	>99 (63)
7	2-ClC_6H_4	**2h**	60	9	>99 (61)
8	2-MeC_6H_4	**2i**	60	24	>99
9	2-$OMeC_6H_4$	**2j**	60	96	51 (43)
10	Mes	**2k**	70	360	62 (7)
11	^{t}Bu	**2l**	60	1	>99
12	Me	**2m**	60	3	>99

[a] Conditions: nitrile (0.14−0.15 mmol), HBpin (0.30 mmol), and catalyst **1a** (7 μmol, 5 mol %) in cyclohexane-d_{12} (0.5 mL). [b] Based on nitrile. [c] Isolated yields are shown in parentheses.

Scope of nitriles for the double hydroboration was explored by use of $PCyp_3$ complex **1a** (5 mol %), which is, as has been mentioned, one of the most active Ru−xantsil complex catalysts **1a** and **1b**. In most cases, hydroboration products **2** were obtained in >99% NMR yields (Table 2). The reactions of benzonitrile and its *para*- or *meta*-substituted derivatives gave the corresponding bis(boryl)amines **2b−f** quantitatively (entries 1−5). The reaction rates for the benzonitrile derivatives having an electron-withdrawing CF_3 or Cl group at the *para*-position (entry 1 in Table 1 and that in Table 2) are higher than those for the corresponding compounds having an electron-donating Me or OMe group (entries 3 and 4 in Table 2). We also examined the reactions of *ortho*-substituted benzonitriles (five examples involving mesitylnitrile, entries 6−10) whose C≡N groups are sterically hindered, and hence, these nitriles have been rarely used as substrates for the double hydroboration.[3c,f,i−k] As a result of the experiments, bis(boryl)amines **2g−k** involving three novel compounds **2h**, **j**, and **k** were obtained in high to moderate yields (entries 6−10). For the reaction of a certain benzonitrile derivative having a CF_3, Cl, or Me group at an *ortho*-position (entries 6−8), a longer reaction time was required for complete conversion of the nitrile compared with the reaction of that having the same group at the *para*-position (entry 1 in Table 1 and entries 1 and 3 in Table 2). Nevertheless, NMR yields of products **2g** and **2i** (>99% each, entries 6 and 8) are significantly improved in comparison with the corresponding ones (**2g**: 50%[3c] and **2i**: 59% (isolated yield)[3f] or 86%[3k]) reported for the reactions using other catalysts. Furthermore, 2-$OMeC_6H_4C{\equiv}N$ with an electron-donating OMe group at an *ortho*-position and bulkier MesC≡N were also doubly hydroborated, although the reactions were slower and the NMR yields (51 and 62%) of bis(boryl)amines **2j** and **2k** were lower (entries 9 and 10). These results clearly show that the increase of steric hindrance around a nitrile C≡N group retards the progress of the double hydroboration. Aliphatic nitriles (R = ^{t}Bu and Me) also underwent double hydroboration to give bis(boryl)amines **2l** and **2m** quantitatively (entries 11 and 12).

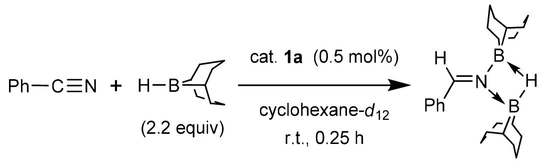
To clarify whether complex **1a** also functions as a catalyst for single hydroboration of nitriles, we examined the catalytic reaction using commercially available dialkylborane, 9-borabicyclo[3.3.1]nonane (9-BBN). In the presence of 0.5 mol % of **1a**, nitriles RC≡N (R = 4-$CF_3C_6H_4$, Ph, 4-$OMeC_6H_4$, and ^{t}Bu) reacted with 9-BBN (0.9−1 equiv for the monomer) in THF-d_8 at room temperature ∼ 40 °C to give single hydroboration products, i.e. *N*-borylimines **3**, quantitatively (Table 3). When 2.2 equiv of 9-BBN were used for the hydroboration of PhC≡N in the presence of **1a** as a catalyst, an *N*-borylimine·9-BBN adduct **3b·9-BBN**[4a] was formed quantitatively (eq 1, reaction solvent: cyclohexane-d_{12}),[8] and further heating of the reaction mixture at 60 °C did not give

Table 3. Single Hydroboration of Nitriles with 9-BBN Catalyzed by 1a[a]



entry	R	product	temp (°C)	time (h)	NMR yield of 3 (%)[b,c]
1	4-$CF_3C_6H_4$	**3a**	40	0.5	>99 (98)
2	Ph	**3b**	40	0.5	>99
3	4-$OMeC_6H_4$	**3c**	40	0.5	>99
4	^{t}Bu	**3d**	rt	0.25	>99

[a]Conditions: nitrile (0.14–0.15 mmol), 9-BBN (0.14 mmol for the monomer), and catalyst **1a** (0.7 μmol, 0.5 mol %) in THF-d_8 (0.5 mL). [b]Based on 9-BBN. [c]Isolated yield of **3a** is shown in parentheses.



(1)

3b•9-BBN

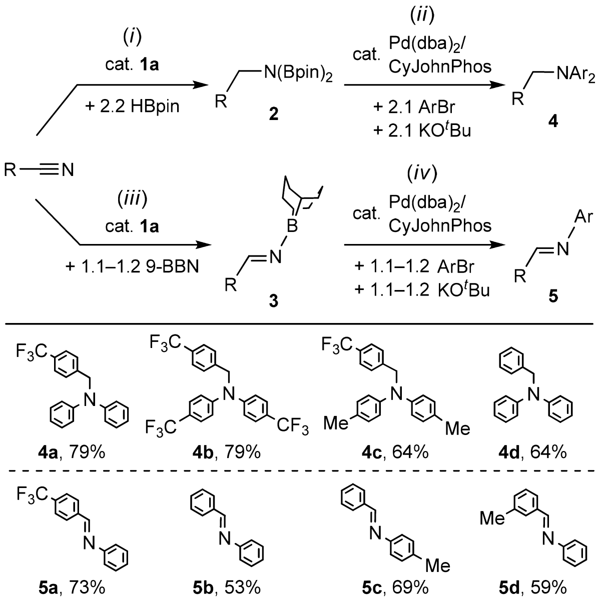
the double hydroboration product, i.e. bis(boryl)amine $PhCH_2N(BC_8H_{14})_2$. This is possibly because a further reaction of **3b** with catalyst **1a** is inhibited by bulkiness of the boryl group. In comparison with the previous report for the uncatalyzed single hydroboration reaction of nitriles with 9-BBN,[4a] the reaction catalyzed by **1a** proceeded under milder conditions. For example, the reaction of 4-$OMeC_6H_4C{\equiv}N$ with 9-BBN in the absence of catalyst needs heating at much higher temperature (110 °C) and for a longer time (20 h).[4a]

To obtain insights into mechanisms for the catalytic hydroboration reactions, we examined a stoichiometric reaction of **1a** with 1 equiv of 4-trifluoromethylbenzonitirile (eq S2 in the Supporting Information). The reaction completed at room temperature within 0.25 h to give a 16-electron nitrile complex Ru[κ^2(*Si*,*Si*)-xantsil](CO)($PCyp_3$)-[$N{\equiv}C(C_6H_4$-4-$CF_3)$] (**6**) quantitatively via dissociation of the xanthene oxygen and coordination of the nitrile. The structure of **6** was determined by X-ray crystal structure analysis (see the Supporting Information). On the other hand, reaction of **1a** with excess HBpin (ca. 10 equiv) at room temperature was much slower, in which only ca. 5% of **1a** reacted to give 9,9-dimethyl-4,5-bis(dimethylsilyl)xanthene (xantsilH_2) after 24 h (eq S3 in the Supporting Information). These results imply that the first step of the catalytic hydroboration reaction is the formation of a nitrile complex such as **6**. On the basis of these results and taking into account a previously proposed mechanism for ruthenium-catalyzed double hydroboration reported by Gunanathan et al.,[3d] we propose a possible mechanism for the hydroboration of nitriles catalyzed by **1a** as shown in Scheme S1 (see the Supporting Information).

As novel conversion reactions of hydroboration products **2** and **3** via B–N bond cleavage, we developed palladium-catalyzed C(aryl)–N coupling reactions shown in Table 4.[6,7] After the double hydroboration of nitriles with HBpin (2.2 equiv) catalyzed by **1a** (2 mol %) in THF, to the resulting mixture containing bis(boryl)amine **2** were added bromoarenes (2.1 equiv), phosphine CyJohnPhos (5 mol %) and Pd(dba)$_2$ (2 mol %) as catalyst precursors,[7] and base KO^{t}Bu (2.1 equiv) in this order. The mixture was then heated at 60 °C for 12 h to give *N*,*N*-diarylamines **4**, involving novel compounds **4b** and **4c**, in 64–79% isolated yields. *N*-Arylimines **5** were also synthesized in 53–73% isolated yields by a similar C–N coupling reaction of single hydroboration products **3** obtained from nitriles and 9-BBN (1.1–1.2 equiv) in the presence of 0.5–0.7 mol % of catalyst **1a**. In this coupling reaction, 1.1–1.2 equiv each of bromoarenes and KO^{t}Bu were used. It is noteworthy that the hydroboration and C–N coupling reactions can be successively performed in one pot without isolation of intermediary hydroboration products **2** and **3**.[9]

In summary, we demonstrated that 16-electron ruthenium–bis(silyl)xanthene chelate complex **1a** functions as a highly active catalyst for both the double and single hydroboration reactions of nitriles to give **2** and **3** in perfect selectivity. These products **2** and **3** were also found to be converted into tertiary diarylamines **4** and *N*-arylaldimines **5** by subsequent palladium-catalyzed deborylative C–N coupling reactions. These hydroboration and successive C–N coupling reactions can be conveniently done in one pot.

Table 4. One-Pot Synthesis of *N*,*N*-Diarylamines 4 or *N*-Arylimines 5 from Nitriles by Double or Single Hydroboration and Subsequent C–N Coupling[a]



[a]Conditions for synthesis of **4**: (i) nitrile (0.29 mmol), HBpin (0.63 mmol), catalyst **1a** (7 μmol, 2 mol %), 40–60 °C, THF; (ii) bromoarenes (0.61 mmol), KO^{t}Bu (0.61 mmol), Pd(dba)$_2$ (6.1 μmol, 2 mol %), CyJohnPhos (14 μmol, 5 mol %), 60 °C, 12 h, THF. For synthesis of **5**: (iii) nitrile (0.099–0.29 mmol), 9-BBN (0.12–0.32 mmol for the monomer), catalyst **1a** (0.7–1.4 μmol, 0.5–0.7 mol %), 1 h, rt, THF; (iv) bromoarenes (0.11–0.32 mmol), KO^{t}Bu (0.12–0.32 mmol), Pd(dba)$_2$ (2.1–6 μmol, 2 mol %), CyJohnPhos (4–14 μmol, 4–8 mol %), 60 °C, 12 h, THF. [b]Isolated yields based on nitriles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00064.

Experimental procedures, proposed mechanism for hydroboration, crystal structure analysis, and NMR spectra of products (PDF)

Accession Codes

CCDC 1893612 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(8) During the initial stage of the catalytic single-hydroboration reaction of $PhC\equiv N$ with 9-BBN, adduct **3b·9-BBN** was observed in the reaction mixture by ^{1}H and ^{11}B NMR spectroscopy.

(9) We also confirmed that C−N coupling reactions of *isolated* double and single hydroboration products **2a** and **3a** with bromobenzene and KO^{t}Bu catalyzed by $Pd(dba)_2$/CyJohnPhos gave **4a** and **5a**, respectively (see eqs S4 and S5 in the Supporting Information).