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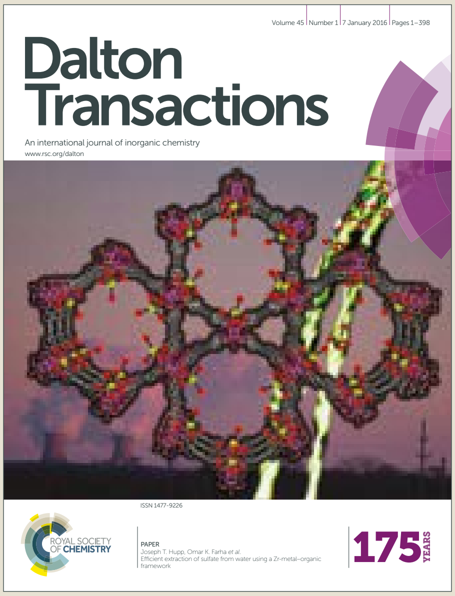

Volume 45 | Number 1 | 7 January 2016 | Pages 1–398

Dalton Transactions

An international journal of inorganic chemistry
www.rsc.org/dalton

ISSN 1477-9226

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COMMUNICATION

Hydrodebromination of Allylic and Benzylic Bromides with Water Catalyzed by Rhodium Porphyrin Complex

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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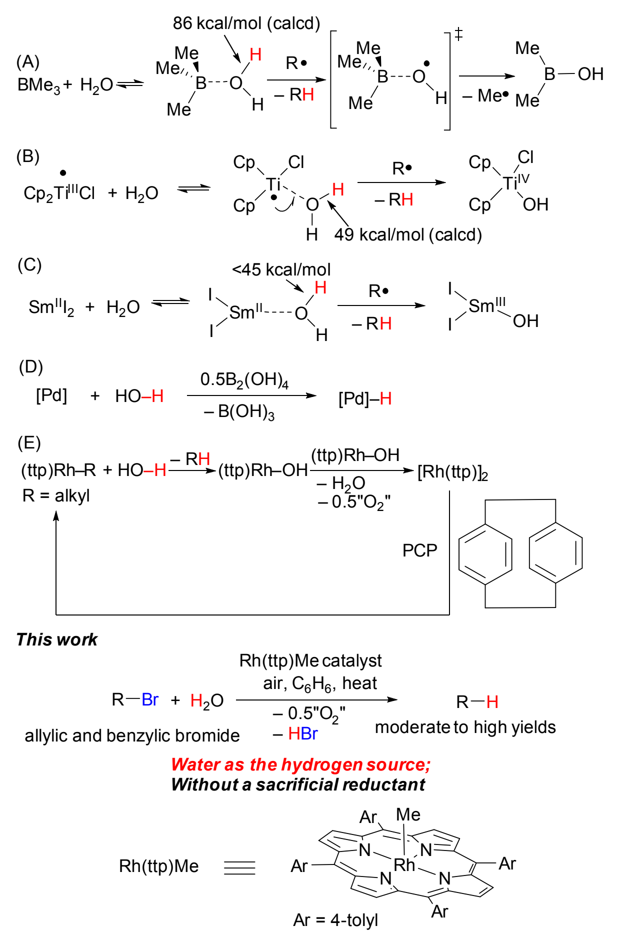
Hydrodebromination of allylic and benzylic bromides was successfully achieved by rhodium porphyrin complex catalyst with water without a sacrificial reductant. Mechanistic investigations suggest that the bromine atom abstraction via a rhodium porphyrin metalloradical operates to give the rhodium porphyrin alkyl species and the subsequent hydrolysis of the rhodium porphyrin alkyl species to hydrocarbon product is a key step to harness the hydrogen from water.

Hydrodebromination plays an indispensable role in synthetic organic chemistry. For instance, the bromide group can be removed by hydrodebromination with a hydrogen source.[1, 2] The hydrodeoxygenation of alcohols has also been accomplished via its bromide derivatives through hydrodebromination.[3] The common hydrogen sources in hydrodebromination are H_2 gas,[4] alcohols and alcoholates,[5, 6] formic acid and its salts,[7] organosilanes,[8, 9] metal hydrides,[10-13] borohydrides,[14-16] amines,[17-19] *etc*.[20]

Water, as a green, economically more attractive reducing agent, is generally believed unlikely to be the hydrogen source due to the high bond dissociation energy (BDE) of HO–H bond (118 kcal/mol).[21] Weakening the H–OH bond by the coordination of H_2O to a Lewis acid makes water as the hydrogen source possible. It has been recognized that alkylborane (Scheme 1A)[22, 23], $Cp_2Ti^{III}Cl$ (Scheme 1B),[24-28] and $Sm^{II}I_2$ (Scheme 1C)[29-31] are all effective Lewis acids to achieve considerable H–OH bond weakening through the coordination with H_2O. The low valent Lewis acid also functions as a stoichiometric reductant with Ti(III)/Sm(II) oxidized to a higher valent one. Most recently, the Pd-catalyzed hydrogenations of alkenes, alkynes and *N*-heteroaromatics using water as a stoichiometric hydrogen source have been achieved by employing $B_2(OH)_4/B_2pin_2$ as a sacrificial reductant via converting HO–H to [Pd]–H (Scheme 1D).[32, 33] To the best of our knowledge, catalytic hydrodebromination using water as the hydrogen source without a sacrificial reductant remains unknown.



Scheme 1 Common strategies to use water as the hydrogen source.

For the hydrodehalogenation with rhodium porphyrin catalysts, the Fu group has previously realized photocatalytic

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†Electronic Supplementary Information (ESI) available: Experimental procedures, ^1H NMR, ^{13}C NMR, and HRMS spectra, and X-ray crystallographic data. CCDC numbers for Rh(ttp)(*trans*-cinnamyl): 1813321; Rh(ttp)Br: 1813320. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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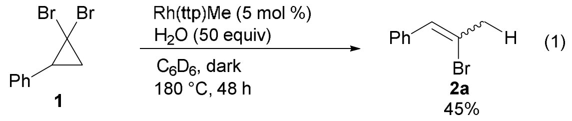
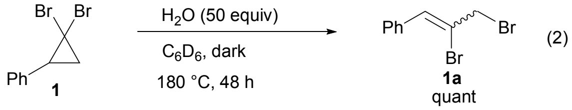
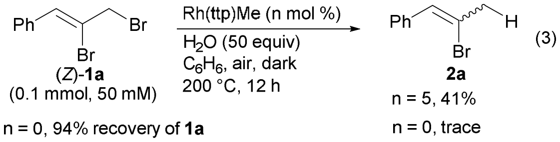
hydrodefluorination of perfluoroarene with silane as the sacrificial reductant.[34] Based on our earlier success of employing water as the hydrogen source for hydrogenating the carbon–carbon σ-bond of [2.2]paracyclophane (PCP) through the hydrolysis of Rh(ttp)(alkyl) (ttp = 5,10,15,20-tetratolylporphyrinato dianion) precatalyst and intermediates (Scheme 1E),[35, 36] herein, we disclose a rhodium porphyrin complex catalyzed hydrodebromination of allylic and benzylic bromides with water as the hydrogen source without a sacrificial reductant.

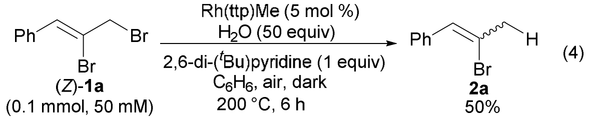
Initially, we aimed to conduct the selective C–C bond hydrogenation of the *gem*-dibromocyclopropane (**1**) with water catalyzed by rhodium porphyrin complex. However, the reaction of (2,2-dibromocyclopropyl)benzene (**1**) with water catalyzed by Rh(ttp)Me at 180 °C for 48 h gave the unexpected debromination product: (2-bromoprop-1-en-1-yl)benzene (**2a**) in 45% yield (eq 1). As **1** was reported to undergo thermal ring opening reaction with concomitant bromide migration to give the allylic bromide: (2,3-dibromoprop-1-enyl)benzene (**1a**) quantitatively (eq 2),[37, 38] we suspected that **2a** stemmed from **1a** through the hydrodebromination reaction with water.





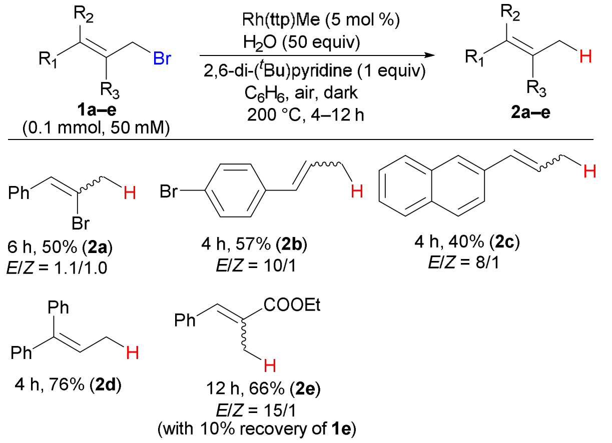
To validate the hypothesis, the allylic bromide (*Z*)-**1a** was reacted with water in the presence of Rh(ttp)Me catalyst. The hydrodebromination product **2a** was obtained in 41% yield under air at 200 °C for 12 h (eq 3). Without Rh(ttp)Me catalyst, only trace amount of **2a** was obtained with 94% recovery of **1a** (eq 3), and the catalytic role of Rh(ttp)Me was established.





With this initial success, the reaction conditions of temperature (180 °C, 200 °C) (Table S1 in the SI), atmosphere (air, N_2) (Table S1 in the SI), catalyst loading (0, 2.5, 5, 10 mol %) (Table S2 in the SI), solvent (C_6H_6, $PhCH_3$, $PhCF_3$, DME, EtOAc, tetrachloroethylene) (Table S3 in the SI), and additive (pH = 4.0/5.0/6.0/7.0/8.0/9.0 buffer, K_2CO_3, $CaCO_3$, pyridine, DIPEA, 2,6-di-(^{t}Bu)pyridine, phenylacetylene) (Table S4 in the SI) were then optimized using the model compound: (*Z*)-(2,3-dibromoprop-1-enyl)benzene ((*Z*)-**1a**), which gave the non-volatile product of (2-bromoprop-1-en-1-yl)benzene (**2a**) for ease of isolation. The optimal conditions were shown in eq 4 with **2a** obtained in 50% yield and trace amount of 2-bromo-3-phenylacrylaldehyde (**2a'**).

Table 1 Substrate scope of allylic bromides for the hydrodebromination[a,b]



[a]Reaction conditions: allylic bromides (0.1 mmol), Rh(ttp)Me (4.0 mg, 5.1 × 10^{-3} mmol), H_2O (90 μL, 5.0 mmol), 2,6-di-(^{t}Bu)pyridine (21 μL, 0.1 mmol), and benzene (2.0 mL) at 200 °C under air in Teflon screw capped pressure tubes. [b]NMR yield with 1,1,2,2-tetrachloroethane as the internal standard.

Under the optimal conditions, the substrate scope of allylic bromides was examined (Table 1). The hydrodebromination of **1a** and (*E*)-1-(4-bromophenyl)-1-propen-3-yl bromide (**1b**) occurred chemo-selectively with the retention of C(sp^2)–Br bonds to give isomeric **2a** and 4-bromo-*β*-methylstyrene (**2b**) respectively in moderate yields. With the *β*-unsubstituted allylic bromide: (*E*)-2-(3-bromoprop-1-en-1-yl)naphthalene (**1c**), the reaction also underwent smoothly to give 1-(2-naphthyl)propene (**2c**) in 40% yield. With the non-polymerizable alkene: (3-bromoprop-1-ene-1,1-diyl)dibenzene (**1d**), the hydrodebromination product of 1,1-diphenylpropene (**2d**) was obtained in a higher yield of 76%. Hydrodebromination also took place with the *β*-ester substituted allylic bromide: (*Z*)-ethyl 2-(bromomethyl)-3-phenylacrylate (**1e**) to give ethyl 2-methyl-3-phenylacrylate (**2e**) in 66% yield without the ester hydrolysis.

Hydrodebromination also worked well with less reactive benzylic bromides (Table 2). The hydrodebromination occurred smoothly both with 2-(bromomethyl)naphthalene (**3a**) and 4-*tert*-butylbenzyl bromide (**3b**) to afford 2-methylnaphthalene (**4a**) and 4-*tert*-butyltoluene (**4b**) in 60% and 66% yields, respectively. 9-Bromofluorene (**3c**) underwent the smooth hydrodebromination to give fluorene (**4c**) in 43% yield together with a minor amount of the homo-coupling co-product: 9,9'-bifluorene (**4c'**) in 9% yield. It suggests the existence of the 9-fluorenyl radical intermediate, which might be generated from the thermal homolytic cleavage of the relatively weak Rh–C bond of Rh(ttp)(9-fluorenyl)[21, 39] (BDE of (tmp)Rh–CH_2Ph (tmp = 5,10,15,20-tetra(2,4,6-trimethylphenyl) porphyrinato dianion): ~33 kcal/mol) or from the bromine atom abstraction of 9-bromofluorene via Rh^{II}(ttp)

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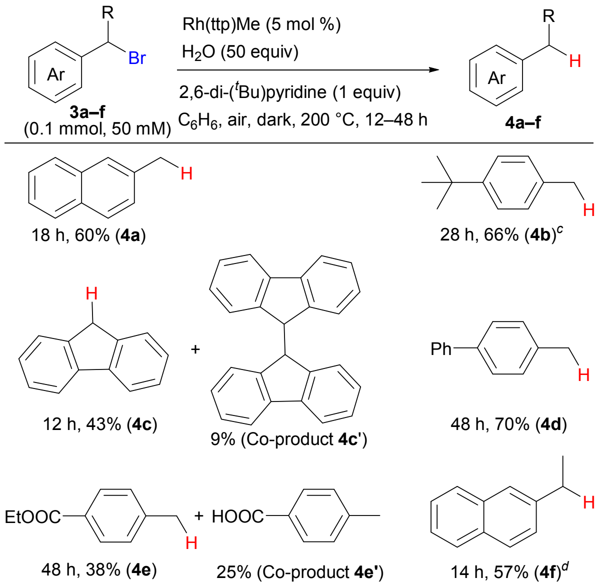
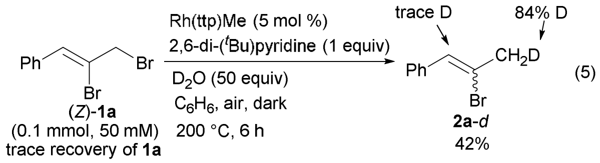
metalloradical.[40-43] The hydrodebromination worked smoothly with 4-phenyl-benzyl bromide (**3d**) to give 4-methyl-1,1'-biphenyl (**4d**) in 70% yield. For ethyl (4-bromomethyl)benzoate (**3e**) containing an ester group, the reaction gave the hydrodebromination product of ethyl 4-methylbenzoate (**4e**) in 38% yield. The ester hydrolysis product (**4e'**) was obtained in 25% yield, which might due to the catalytic effect of *in situ* formed HBr. For the benzylic bromide of 2-(1-bromoethyl)naphthalene (**3f**) bearing *β*-hydrogens, the hydrodebromination product of 2-ethylnaphthalene (**4f**) was obtained in 57% yield together with the elimination product of 2-vinylnaphthalene (**4f'**) in 7% yield.

Table 2 Substrate Scope of Benzylic Bromides for the Hydrodebromination[a,b]

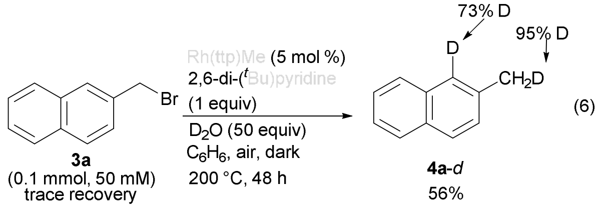


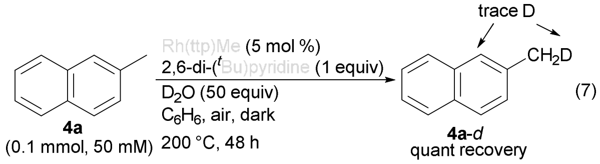
[a]Reaction conditions: benzylic bromides (0.1 mmol), Rh(ttp)Me (4.0 mg, 5.1 × 10^{-3} mmol), H_2O (90 μL, 5.0 mmol), 2,6-di-(^{t}Bu)pyridine (21 μL, 0.1 mmol), and benzene (2.0 mL) at 200 °C under air in Teflon screw capped pressure tubes. [b]NMR yield with 1,1,2,2-tetrachloroethane as the internal standard. [c]GC yield. [d]7% yield of 2-vinylnaphthalene (**4f'**).

To ascertain that water is the hydrogen source, the deuterium labeling experiment using D_2O was carried out. **2a**-*d* was obtained in 42% yield with 84% deuterium incorporation at the allylic position (eq 5), which is close to the theoretical 100% allylic mono-deuterium incorporation. Furthermore, the deuterium incorporations determined by MS analysis did not change with reaction time within the catalysis time scale (Figure S1 in the SI). This indicates the hydrodebromination product **2a** did not undergo product-H/D exchange with D_2O under the optimal reaction conditions. In addition, the proton signals of the allylic hydrogens of the trace amount of recovered **1a** appear at δ 4.45 (s, 2H, *Z* isomer), 4.41 (s, 2H, *E* isomer) as singlets (Figure S22 in the SI), which indicates that **1a** did not undergo starting material-H/D exchange with D_2O. Therefore, these results strongly support water as the hydrogen source.



The benzylic bromide of 2-(bromomethyl)naphthalene (**3a**) was also reacted with D_2O to afford **4a**-*d* in 56% yield with 73% deuterium at the naphthalene C-1 position and 95% deuterium at the benzylic position (eq 6), which is close to the theoretical 100% benzylic mono-deuterium incorporation. 80% deuterium at the benzylic position were also determined by quantitative ^{13}C NMR (eq S1 and Table S5 in the SI). There are mainly four isotopomers: d0-isotopologue in 5% composition, d1-isotopologue (with deuterium at the benzylic position in 26% or C-1 position in 14%), d2 isotopologue (with deuterium at both the benzylic and C-1 positions in 55% composition). (Table S6 and Figure S2 in the SI). As a control, little product-H/D exchange of 2-methylnaphthalene (**4a**) with D_2O was observed (eq 7). Thus, the hydrogen from water is established in the hydrodebromination of benzylic bromides. The 73% deuterium incorporation at the naphthalene C-1 position is likely resulted from the Rh(ttp)-catalyzed H/D exchange with D_2O via the intermediate of Rh(ttp)(2-naphthylmethyl) (**5**), which might undergo η^1–η^3 isomerization[44-48] for the deuterium incorporation at the naphthalene C-1 position (Scheme S5 in the SI).[35, 40, 49-51]





On the basis of the above findings, together with our previous mechanistic understandings of the C–Br bond activation[40-43] and Rh(ttp)-catalyzed hydrogenation of PCP with water,[35, 36, 52] a plausible mechanism is proposed (Scheme 2). Initially, Rh(ttp)Me undergoes hydrolysis to give Rh(ttp)OH and methane.[35, 53] At 200 °C, Rh(ttp)OH is unstable and decomposes to give the Rh^{II}(ttp) metalloradical and H_2O_2.[54] The indirect detection of H_2O_2 has been reported by the formation of Ph_3PO through the reaction of Rh(ttp)I with KOH with Ph_3P as a H_2O_2 trap.[54] H_2O_2 further disproportionates rapidly to give H_2O and O_2.[35, 55-57] The detection of O_2 is not possible as the reaction was conducted under air and in a small scale. The Rh^{II}(ttp) metalloradical is in an equilibrium with the $Rh^{II}_2(ttp)_2$ dimer,[58-60] which undergoes the disproportionation with H_2O to generate Rh(ttp)OH and Rh(ttp)H.[36, 61-64] Air-promoted dehydrogenative dimerization of Rh(ttp)H gives

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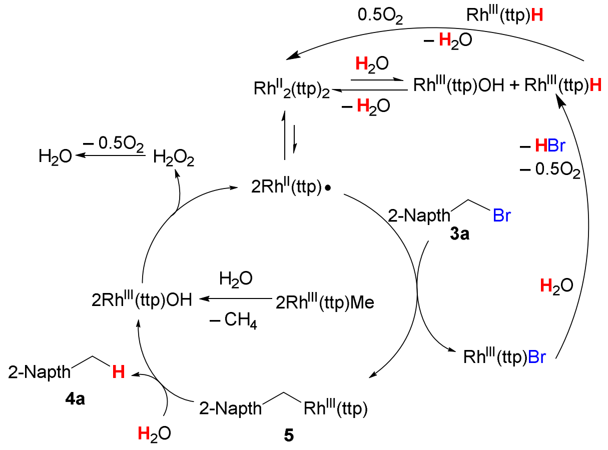
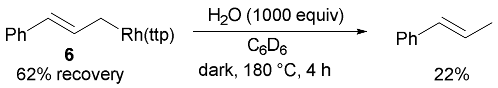
back to the $Rh^{II}{}_2(ttp)_2$ dimer.[65, 66] Abstraction of the bromine atom from 2-(bromomethyl)naphthalene (**3a**) via the $Rh^{II}(ttp)$ metalloradical affords Rh(ttp)Br and the Rh(ttp)(2-naphthylmethyl) intermediate (**5**).[40-43] Rh(ttp)Br further transforms into Rh(ttp)H in the presence of H_2O.[67] **5** undergoes hydrolysis with H_2O to give the final hydrodebromination product of 2-methylnaphthalene (**4a**) and regenerate Rh(ttp)OH to complete the catalytic cycle.[35, 36, 68]



Scheme 2 Proposed mechanism for the hydrodebromination reaction with water.

To examine whether allylic Rh(ttp) species undergo the hydrolysis process, Rh(ttp)(*trans*-cinnamyl) (**6**) was then chosen as a model compound and subject to the hydrolysis investigations. Indeed, Rh(ttp)(*trans*-cinnamyl) (**6**) underwent smooth hydrolysis at 180 °C for 4 h to give *trans-β*-methylstyrene in 22% yield with 62% recovery of **6** (eq 8). Hence, the hydrolysis of the allylic Rh(ttp) species is strongly supported to harness the hydrogen from water. In a previous reported model study, Rh(ttp)Bn has been shown to undergo hydrolysis to afford toluene, which is a key step for the incorporation of the hydrogen from water.[35, 64]



(8)

Furthermore, Rh(ttp)Br reacted with excess H_2O (1000 equiv) to give Rh(ttp)H in 27% yield at 180 °C for 52 h (eq 9). Therefore, Rh(ttp)Br can react with water to regenerate $Rh^{II}{}_2(ttp)_2$ for further catalysis.

$$\underset{\substack{2.5\ \text{mM}\\ 62\%\ \text{recovery}}}{\mathrm{Rh(ttp)Br}} + \underset{1000\ \text{equiv}}{\mathrm{H_2O}} \xrightarrow[\substack{-\,\mathrm{HBr}\\ -\,0.5\text{"}\mathrm{O_2}\text{"}}]{\substack{\mathrm{C_6D_6},\ \text{dark}\\ 180\ °\mathrm{C},\ 52\ \mathrm{h}}} \underset{27\%}{\mathrm{Rh(ttp)H}} \qquad (9)$$

In summary, the catalytic hydrodebromination of allylic and benzylic bromides was achieved to give the corresponding hydrodebromination products in moderate to good yields using H_2O as the convenient hydrogen source without a sacrificial reductant. The hydrolysis of Rh(ttp)(alkyl) species is proposed to be the key step to transfer the hydrogen from water to alkane.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Research Grants Council of Hong Kong SAR (14300214) and the Hong Kong PhD Fellowship (W. Y.) for financial support.

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67 Please see the following supporting experimental data (eq 9).

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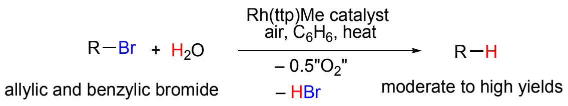
DOI: 10.1039/C8DT02168F



Water as the hydrogen source;
Without a sacrificial reductant

Rhodium porphyrin catalyzed Hydrodebormination of activated organic bromides with water