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β-Boration of α,β-unsaturated carbonyl compounds in ethanol and methanol catalyzed by CCC-NHC pincer Rh complexes

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ABSTRACT

Quantitative β-boration of α,β-unsaturated carbonyl compounds was achieved utilizing the eco-friendly solvent EtOH along with MeOH at room temperature in 1 h, by a CCC-NHC pincer Rh complex mixture. Substrates with β-substituents were successfully converted yielding challenging, quaternary C–B bonds. The air- and water-stable pre-catalyst **A**, identified as a mixture of iodo and chloro CCC-NHC pincer Rh amine complexes, was evaluated for catalytic activity. This report is the first example of a pincer Rh complex demonstrating catalytic activity in a 1,4-addition at room temperature.

1. Introduction

Organoborane compounds are highly sought after intermediates in organic synthesis. The facile transformation of the C–B bond into other functional groups such as alcohols, amines, and alkenes allows direct access to a wide range of organic molecules [1–4]. In 1997, a Pt catalyst was utilized in the first report of β-boration of α,β-unsaturated carbonyl compounds using a diboron reagent [5]. To date, the boration of α,β-unsaturated carbonyl compounds has been catalyzed with Pt [5–8], Pd [9,10], Rh [11–14], Cu [15–41], Ni [10,42,43], Fe [44], metal-free phosphines [45–47], and N-heterocyclic carbenes (NHCs) [48–51]. Subsequently, β-boration of α,β-unsaturated carbonyl compounds has become very useful due to the additional carbonyl contained in the product [6,11,17–22,42,44,52,53]. Oxidation of the product provides access to β-hydroxy compounds as an alternative to the aldol reaction or reduction of β-keto carbonyl compounds. β-Hydroxy carbonyl compounds are found widely in natural products and pharmaceuticals [54,55]. Additionally, β-boro-carbonyl compounds have been reported as being effective therapeutic agents in cancer treatment [56,57].

Cu systems have been the most commonly applied catalysts for β-boration of α,β-unsaturated carbonyl compounds. Noteworthy examples have been reported using strictly protic solvents such as MeOH [26] and H_2O [36,37,58–61]. In 2009, Santos reported the synthesis of an innovative sp^2–sp^3 diboron reagent and demonstrated its application in a Cu catalyzed β-boration of acyclic substrates [32]. In 2008, the first asymmetric catalysis for β-boration of acyclic compounds was reported using a chiral Cu phosphine complex [15], opening the path for innovative work such as asymmetric β-borations conducted in water [37,58–60] and the development of chiral β-tetrasubstituted carbon centers using β,β-substituted substrates [62–64]. Subsequently, other examples of asymmetric catalysis have been reported with Ni [10], Pd [10], Rh [11,12,14], and Cu [18,21,22,27–30,33–35,39,40,61,65,66]. Metal free-catalysis has also been developed, including asymmetric variants [47,49], such as a chiral NHC salt reported by Hoveyda [49,50,67].

Despite many reports utilizing various transition metals, base additives or high temperatures have been required for efficient rates, and limitations to acyclic α,β-unsaturated carbonyl substrates have been noted. In addition, very few cyclic products with boron-substituted quaternary carbon centers have been reported [48]. A catalyst that provides cyclic β-boro-carbonyl compounds containing quaternary carbon centers and can operate at room temperature without the need for an exogenous base provides a straight-

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forward methodology in the formation of C–B bonds as well as β-hydroxy carbonyl compound derived thereof.

Previously, we reported a mixture of the CCC-NHC pincer Rh complexes **1**/**2** (Scheme 1) that efficiently catalyzed 1,4-addition of aryl boronic acids to electron-deficient alkenes [68]. CCC-NHC pincer Rh complexes **1**/**2** (Scheme 1), along with added $NHMe_2$, produced excellent yields (>90%) with various Michael acceptors and arylboronic acids in protic solvents [68]. In looking toward the preparation of chiral variants, further attempts to optimize the synthesis of **1** led to a crude isolate (**A**) that was orange in color and was obtained reproducibly. We report herein, the characterization of mixture **A**, separate isolation and screening of the components and material **A** in the β-boration of cyclic and acyclic, α,β-unsaturated, electron-deficient alkenes. Furthermore, this report is among the few examples [69,70] in the literature of a pincer complex catalyzing 1,4-addition reactions at room temperature.

2. Results and discussion

2.1. Characterization of catalytically-active material *A*

The previously reported methodology for the synthesis of the CCC-NHC pincer Rh complexes was modified by switching the solvent to THF (Scheme 1) and using a careful work up procedure as detailed in the experimental procedure. This sequence reproducibly yielded an orange microcrystalline to powdery solid **A** that was highly catalytically active. Spectroscopic data indicated the orange mixture **A** consisted of two CCC-NHC pincer Rh complexes evidenced by two sets of diastereotopic, overlapping methylene signals (Fig. 1 and ESI) in the ^{1}H NMR spectrum and two carbene carbon signals coupled to Rh in the ^{13}C NMR spectra (Fig. 2 and ESI). Two Rh–$C_{aromatic}$ and Rh–$C_{carbene}$ doublets (Fig. 2) are observed in the ^{13}C NMR spectrum with identical Rh–$C_{carbene}$ and Rh–$C_{aromatic}$ doublet coupling values (^1J = 39 Hz and ^1J = 29 Hz, respectively) observed for **A**. These data indicated that the complexes were similar.

A dark orange solid was isolated from mixture **A** using silica gel chromatography. Spectroscopic data analysis of the isolated material lead to the assignment of axial amine adduct **1** as the structure [71], which has NMR peaks coincident with the major component of mixture **A**. Additionally, an orange X-ray quality crystal of **1** was grown by vapor diffusion (toluene/DCM) from mixture **A** (Fig. 3) [72]. The molecular structure was observed to be a distorted octahedron with the amine ligand in an axial position. The metric data (bond distances and angles) are typical for the CCC-NHC pincer ligand system Rh complexes.

Further analysis of the exact mass ESI-TOF spectrum of **A** contained a peak at *m*/*z* 537.0942 ([M − 2H]$^+$, corresponding to a theoretical mass for $C_{22}H_{30}N_5Cl_2Rh$ 537.0928) indicating a chloro

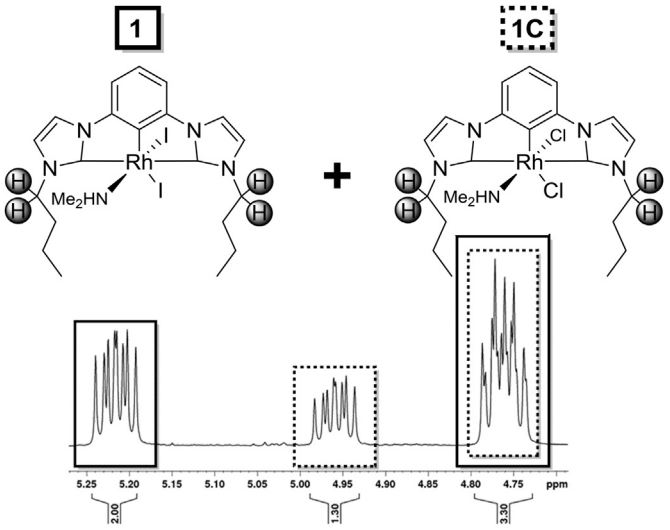


Fig. 1. Two sets of diastereotopic methylene peaks indicating a mixture of CCC-NHC pincer Rh complexes **1** and **1C** in **A**. The signal at 4.75 ppm is overlapping from both complexes.

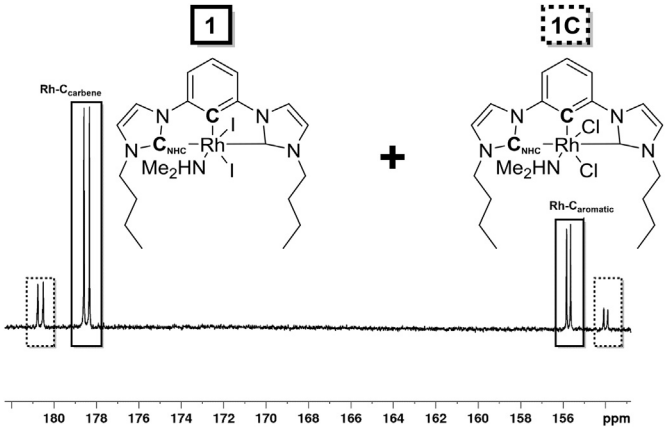
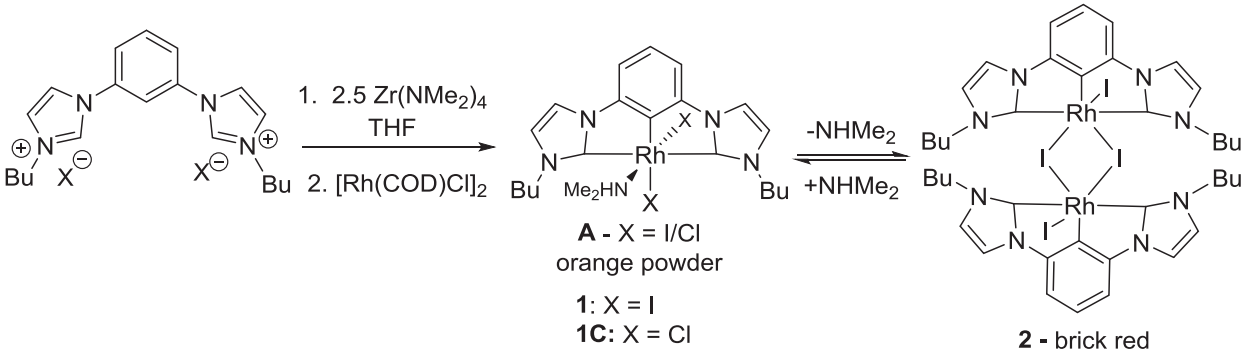


Fig. 2. Two Rh–$C_{aromatic}$ and Rh–$C_{carbene}$ doublets are observed in the ^{13}C NMR spectrum of **A**.

variant (**1C**). Spectroscopic data from the ^{13}C NMR also supported the assignment and similarities of the two species. Complex **1C** was then prepared independently by starting with the chloro-imidazolium salt (X = Cl, Scheme 1). It was analyzed to determine if the ^{1}H and ^{13}C NMR signals of this complex corresponded to



Scheme 1. Equilibrium of amine adduct and iodo-bridged dimer.

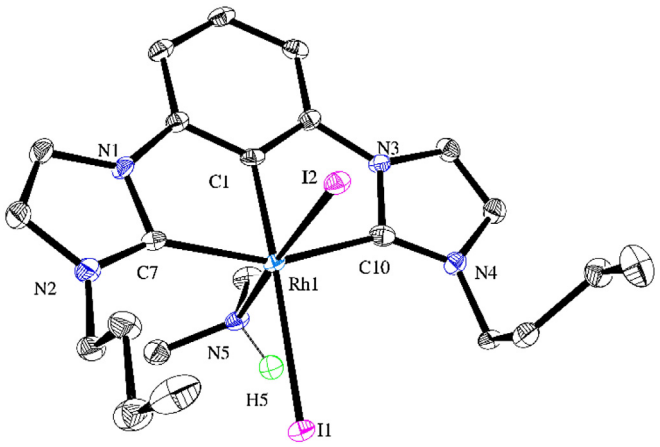


Fig. 3. Molecular structure 2-(1,3-bis(N-butylimidazol-2-ylidene)phenylene) (dimethylamine)bis(iodo) rhodium(III) (**1**). The hydrogens are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Rh(1)-C(1), 1.948(4); Rh(1)-C(10), 2.074(4); Rh(1)-C(7), 2.083(4); Rh(1)-N(5), 2.136(3); Rh(1)-I(2), 2.6610(4); Rh(1)-I(1), 2.8555(4); C(1)-Rh(1)-C(10), 78.41(15); C(1)-Rh(1)-C(7), 78.48(14); C(10)-Rh(1)-C(7), 156.61(14).

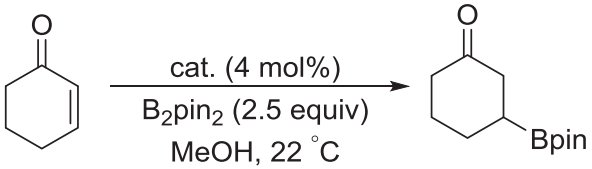
the second set of signals observed in the NMR spectra of **A**. Indeed, the spectrum for both **1** and **1C** match the ^{1}H and ^{13}C NMR signals observed for **A** (see ESI). For example, an integration value of 2 was set for the multiplet at 5.20 ppm (Fig. 2), a signal observed for diastereotopic methylene peaks, yet an integration value of 3.30 is observed for the other diastereotopic methylene signal at 4.75 ppm. This integral intensity is due to overlapping diastereotopic methylene peaks of **1** and **1C** at 4.75 ppm, while the other diastereotopic peak corresponding to the minor complex (**1C**), is slightly downfield at 4.95 ppm. Two doublets of doublets were observed at 1.59 and 1.64 ppm with identical coupling values (dd, $^{3}J_{H-H}$ = 1.2 Hz, $^{3}J_{Rh-H}$ = 6.3 Hz) in the ^{1}H NMR spectrum due to the unique heteronuclear coupling of NMR active ^{103}Rh to coordinated $NHMe_2$.

2.2. Catalytic activity

The activity of these Rh complexes was investigated in β-boration catalytic trials under optimized reaction conditions from our previous 1,4-addition report [68]. Isolated **A**, **1**, **1C**, and an independently prepared 2:1 ratio of **1** and **1C** were each examine with cyclohexenone and 2.5 equiv of B_2Pin_2 (Table 1). Only a 72% conversion to the borated product was observed in 1 h (entry 1) with **1**, compared to the 57% conversion observed in 1 h using the chloro adduct **1C** (entry 2). These conversions trends are analogous to our recent report on the halogen effects of CCC-NHC Zr and Hf pincer complexes in hydroamination/cyclization rates (I > Br > Cl) [73]. A 2:1 mixture of isolated **1** and **1C** provided the lowest conversion despite extended reaction times (entry 3). Despite the lower conversions of **1** and **1C** compared to **A** (Table 1, entry 4), these results are consistent to the report of Santos and co-workers, detailing the increased rate effect upon addition of amine base in β-boration of α,β-unsaturated carbonyl compounds [36]. While no exogenous based was added when using **A** in β-boration catalysis, excess $NHMe_2$ in freshly prepared **A** undoubtedly assists in accelerating the reaction rate. This would explain the decrease in catalytic efficiency observed when using "aged" **A** (i.e. was stored for several months). Using a five month old sample of **A** for the boration of cyclohexenone resulted in 83% conversion in 1 h (entry 5), compared to Table 1, entry 4, which provided quantitative conversion in 1 h with freshly prepared **A**.

Due to the superior performance of mixture **A**, it was further analyzed for catalytic activity in β-boration of acyclic and cyclic substrates due to the quantitative conversion obtained with cyclohexenone. Because high yields were observed previously for Michael addition products in a H_2O/MeOH solvent mixture [68], pre-catalyst loading optimization of **A** in β-boration reactions was conducted in MeOH with *trans*-3-nonen-2-one and B_2pin_2 (Table 2). Although the material **A** is a mixture, 2 mg (~4 mol %) were used in a catalytic trial. The molecular weight of amine adduct **1** (722.98 g/mol) was used as a surrogate for the entire sample to calculate pre-catalyst loading (mol %) for comparative purposes. Initially, 1.5 equiv of B_2pin_2 were used with *trans*-3-nonen-2-one, and a 34% conversion to the borated product was observed (entry 1). Previously, using 2.5 equiv of aryl boronic acids with α,β-unsaturated carbonyl compounds in 1,4-additions gave higher conversion. Therefore, the B_2pin_2 concentration was increased to 2.5 equiv, and as expected, conversion to the borated *trans*-3-nonen-2-one of >99% was observed in 1.5 h (entry 2). A sample from this crude reaction mixture was analyzed by exact mass spectrometry in order to determine possible decomposition of **A** (see SI). However, no evidence was observed to suggest regeneration of the imidazolium salts, which strongly suggests that

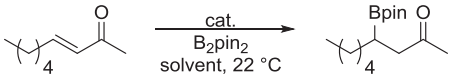
Table 1
β-boration with isolated CCC-NHC Rh complexes.[a]



Entry	Catalyst	Conv %[b]
1	**1**	72 (1 h)
2	**1C**	57 (1 h)
		>99 (5 h)
3	2:1 mixture of **1** and **1C**	17 (1 h)
		54 (5 h)
4	**A**	>99 (1 h)
5	**A**-5 months old	83 (1 h)

[a] 2-Cyclohexenone (0.0735 mmol), bis(pinacolato)diboron (0.184 mmol), cat. (2.94 μmol), and 0.700 mL of MeOH were added to a 1 dram vial with a magnetic stir bar, stirred at 22 °C.
[b] Conversion was determined by GC–MS analysis.

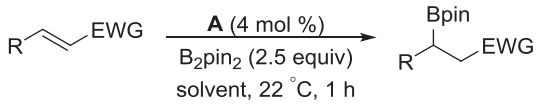
Table 2
Optimization of β-boration reaction conditions.[a]



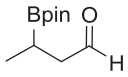
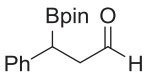
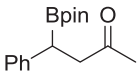
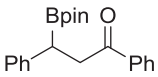
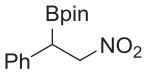
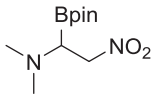
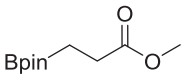
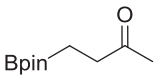
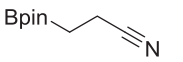
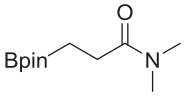
Entry	Solvent	Cat. (mol %)	B_2pin_2 (equiv)	Time	Conv %[b]
1	MeOH	**A** (4)	1.5	1 h	34
2	MeOH	**A** (4)	2.5	1 h	>99
3	MeOH	–	2.5	1 h	0
4	MeOH	$[Rh(COD)Cl]_2$ (4)	2.5	1 h	9
5	MeOH	$NHMe_2$ (4)	2.5	1 h	<3
6	MeOH	**A** (2)	2.5	1.5 h	>99
7	MeOH	**A** (4)	2.5	1 h	60[c]
8	EtOH	**A** (4)	2.5	1 h	93
9	H_2O	**A** (4)	2.5	1 h	>99

[a] T*rans*-3-nonen-2-one (0.0735 mmol), B_2pin_2, **A** (2.00 mg, ~2.94 μmol), and solvent (0.700 mL) were added to a 1 dram vial with a magnetic stir bar, sonicated for 1 min and stirred for 1 h at 22 °C.
[b] Conversion was determined by GC–MS analysis.
[c] Reaction was conducted at 0 °C.

Table 3
Scope of acyclic substrate reactivity in the β-boration with B_2pin_2.[a]



R = H, CH_3, Ph, NR_2 EWG = ald, ket, ester, amide, nitrile

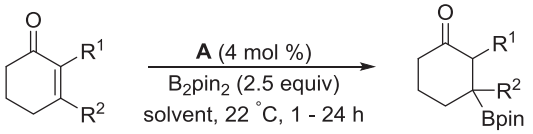
Entry	Product	MeOH conv %[b] (yield %)[c]	EtOH conv %[b] (yield %)[c]
1		>99 (86)	>99 (81)
2		>99 (86)	>99 (84)
3		96 (82)	84 (61)
4		81 (66)	49 (22)
5		0[d]	0[d]
6		0[d]	0[d]
7		>99 (90)	>99 (94)
8		>99 (93)	>99 (96)
9		0[d]	0[d]
10		>99 (84)	>99 (83)

[a] Acyclic α,β-unsaturated compound (0.0735 mmol), bis(pinacolato)diboron (0.184 mmol), **A** (2.00 mg, ~2.94 μmol), and 0.700 mL of MeOH were added to a 1 dram vial with a magnetic stir bar, and stirred for 1 h at 22 °C.
[b] Conversion was determined by GC–MS analysis.
[c] Isolated yield.
[d] After 24 h reaction time.

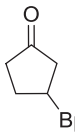
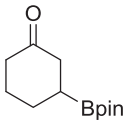
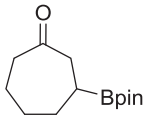
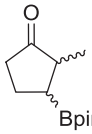
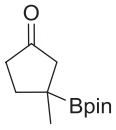
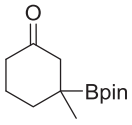
generation of a "free carbene" as the active catalyst is not occurring with these complexes. A control experiment without added **A** (entry 3) resulted in no reaction. Evaluating 4 mol % $[Rh(COD)Cl]_2$ dimer as a potential catalyst (entry 4) provided only 1 turnover (8-atom mol % Rh and 9% yield) in 1 h, thus eliminating extraneous starting material as the active catalyst. To demonstrate that the amine base was not the active catalyst, 4 mol % of $NHMe_2$ only produced <3% conversion (entry 5). The catalyst loading was lowered to examine the efficiency of **A** (entries 6 vs. 2). At 2 mol % (1 mg) pre-catalyst loading (entry 6), >99% conversion was observed in 1.5 h. The reaction was also conducted at 0 °C to determine the efficiency of the catalyst below rt (22 °C) (entry 7), which resulted in a respectable 60% conversion in only 1 h. High conversion was also observed using eco-friendly solvents, H_2O (>99%) and EtOH (>93%) (entries 8 and 9). These results are consistent with previous work of Yun and co-workers [26] and Fernández and co-workers [46], in which both demonstrated an enhanced rate of β-boration of α,β-unsaturated carbonyl compounds with the use of alcohol additives such as MeOH. Moreover, Santos clearly demonstrated, through detailed mechanistic studies, the ability of the amine base to activate a nucleophilic water molecule generating the sp^2–sp^3 diboryl adduct that participates in transmetalation [36]. Protic solvents MeOH and EtOH were used throughout the screening of activated acyclic and cyclic alkenes to evaluate the effect on the rate of conversion. Because >99% conversion was observed in 1 h with 4 mol % of **A** (entry 2, Table 3), the scope and limitations studies were conducted under these optimized conditions.

Utilizing the optimized reaction conditions, activated acyclic alkenes were examined (Table 3). Excellent conversions (>99%) of the aldehyde substrates (crotonaldehyde and cinnamaldehyde, entries 1 and 2) were observed in both MeOH and EtOH. *trans*-4-

Table 4
Scope of cyclic substrate reactivity in the β-boration with B_2pin_2.[a]



R^1,R^2 = H, CH_3

Entry	Product	MeOH conv %[b] (yield %)[c]	EtOH conv %[b] (yield %)[c]
1		>99 (90), 1 h	>99 (70) 1 h
2		>99 (88), 1 h	>99 (84) 1 h
3		>99 (91), 1 h	94 (90) 1 h
4		75, 1 h (*dr* = 1.1:1) 93 (71), 24 h (*dr* = 1:1)	70, 1 h (*dr* = 1.7:1) 80 (51), 24 h (*dr* = 1.6:1)
5		70, 1 h 86 (51), 24 h	57, 1 h 63 (40), 24 h
6		40, 1 h 51 (40), 24 h	26, 1 h 38 (25), 24 h

[a] Cyclic α,β-unsaturated compound (0.0735 mmol), bis(pinacolato)diboron (0.184 mmol), **A** (2.00 mg, ~2.94 μmol), and 0.700 mL of MeOH were added to a 1 dram vial with a magnetic stir bar, stirred for 1 or 24 h at 22 °C.
[b] Conversion was determined by GC–MS analysis.
[c] Isolated yield.

Phenyl-3-buten-2-one (entry 3) and chalcone (entry 4) had the least conversion in 1 h. Due to the lack of reported borated products containing nitro functionalities, *trans*-β-nitro styrene (entry 5) and 1-(dimethylamino)-2-nitroethylene (entry 6) were both screened. No product was observed for any of the nitro-containing substrates despite extended reaction time of 24 h. Ethyl acrylate (entry 7) exhibited excellent conversion (>99%) in both MeOH and EtOH. Methyl vinyl ketone (entry 8) was another acyclic substrate to show high conversion in MeOH and EtOH. Acrylonitrile (entry 9) was evaluated but no product was observed. Boration of *N*,*N*-dimethylacrylamide (entry 10) was successful (>99% conversion) in both MeOH and EtOH.

Previously, little success has been reported in borating cyclic enones with Rh catalysts. Reports include Rh(Phebox) [11] with 0% conversion of cyclohexenone and Wilkinson's catalyst with extended reactions times (12–13 h) and elevated temperature (80 °C) for the boration of cyclohexenone (78%) and cycloheptenone (75%) in good yields [13]. Thus, cyclic enones were evaluated under the optimized conditions with 4 mol % (2.00 mg) of **A**, and the results are presented in Table 4.

Conversions of >99% in just 1 h were observed for all three non-substituted cyclic substrates (entries 1–3) in MeOH and EtOH. This rate of conversion of cyclohexenone is comparable to catalytic reports with Cu (99%, 1 h) [36] and NHC (91%, 1 h) [48] catalysts. The rate of product formation with cycloheptenone (entry 3, >93%), in all solvents, is also comparable or faster than the best previous reports [13,48]. Only modest conversions were observed for the α-substituted, 2-methylcyclopent-2-en-1-one (entry 4) in 1 h, but upon extended reaction times improved conversions to the borated product were obtained. No significant diastereoselectivity was observed in the reactions with 2-methylcyclopent-2-en-1-one (entry 4). Excellent conversions have been reported for sterically hindered β-substituted cyclic enones in 1 h reaction times with Cu or NHC catalysts [36,48,49]. However, extended reaction times were required when pre-catalyst **A** was employed for both 2-methyl cyclopentenone (entry 5) and 2-methyl cyclohexenone (entry 6) in EtOH and MeOH, resulting in only fair to good conversions. After 1 h, moderate conversion (70%) was observed when using MeOH as a solvent for 3-methyl-2-cyclopentenone (entry 5), while less was observed in EtOH (57%). A drastic reduction in conversion rate was observed for 3-methyl-2-cyclohexenone (entry 6). This observation is consistent with Nishiyama [11] and co-workers' proposed catalytic cycle, which suggests that the steric congestion due to the methyl group hinders the boryl-insertion at the β-position.

3. Conclusions

In conclusion, the CCC-NHC pincer Rh complex mixture **A** catalyzed the β-boration of α,β-unsaturated activated alkenes at room temperature producing tertiary and quaternary carbon centers along with examples of quantitative conversion in just 1 h. The reported method does not require the exclusion of air or H_2O due to the stability of pre-catalyst **A**. To our knowledge, this is the first report of β-boration using a pincer complex catalyst to produce tertiary and quaternary β-substituted carbon centers at room temperature using MeOH or EtOH as the solvent. While complexes **1** and **1C** have been found to be the identity of the components in pre-catalyst **A**, **1**, **1C** and a mixture thereof was not as active a catalyst as the initial isolate **A**. CCC-NHC pincer amine Rh adduct **1** was characterized by X-ray Crystallography. The higher activity of initially isolated **A** is attributed to the presence of dimethyl amine.

4. Experimental section

4.1. Preparation of pre-catalyst *A*

The salt, 3-bis (1-butylimidazolium-3-yl) benzene iodide (0.150 g, 0.260 mmol), and tetrakis(dimethylamido)zirconium (0.173 g, 0.650 mmol) were weighed in under inert atmosphere and dry THF (15 mL) was added into a 50 mL flask. The mixture was stirred at room temperature for approximately 1 h or until a light yellow homogenous solution was obtained. Once the reaction became homogeneous, $[Rh(COD)Cl]_2$ (0.128 g, 0.260 mmol) was added to the flask and stirring continued at room temperature for another 12 h. Deionized water (1 mL) was added, and it was stirred vigorously for 10 min providing a white precipitate and a bright orange supernatant. The orange supernatant was filtered and the solvent was removed under reduced pressure yielding a dark orange solid. The solid was washed with hexanes (25 mL) and ether (25 mL) and dried to obtain dark orange/red solid (0.128 g, 68%). Orange X-ray quality crystals were grown by vapor diffusion

(toluene/DCM). Catalyst **A** mixture (two components: ratio ~2:1) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58–7.57 (m, 2.9H), 7.15–7.11 (m, 4.9H), 7.10–7.04 (m, 3H), 5.25–5.21 (m, 2H), 4.97–4.94 (m, 1.1H), 4.79–4.74 (m, 3.1H), 3.72 (m, 1H), 3.69 (m, 0.6H), 2.05–1.99 (m, 5.9H), 1.65–1.63 (dd, ^3J H–H = 1.2 Hz, ^3J Rh–H = 6.3 Hz, 3.1H), 1.61–1.56 (dd, ^3J H–H = 1.2 Hz, ^3J Rh–H = 6.3 Hz, 5.4H), 1.53–1.50 (m, 6.3H), 0.99–0.96 (m, 9H). ^{13}C {^{1}H} (150 MHz, $CDCl_3$): δ 180.6 (d, J = 39 Hz, Rh–$C_{carbene}$), 178.6 (d, J = 39 Hz, Rh–$C_{carbene}$), 155.9 (d, J = 29 Hz, Rh–$C_{aromatic}$), 154.1 (d, J = 29 Hz, Rh–$C_{aromatic}$), 145.8, 145.5, 124.0, 123.7, 121.6, 121.1, 115.8, 115.5, 108.6, 108.5, 51.7, 49.8, 44.6, 44.5, 33.6, 33.2, 20.1, 19.9, 14.1, 14.0. HRMS-ESI (m/z): $[M - I]^+$ calcd for $C_{22}H_{32}IN_5Rh$, 596.0752; found, 596.0740; $[M - I - NHMe_2]^+$ calcd for $C_{20}H_{25}IN_4Rh$, 551.0173; found, 551.0163; calcd for $C_{20}H_{25}I_2N_4RhNa$ $[M - NHMe_2 + Na]^+$ = 700.9116, found 700.9110; calcd for $C_{22}H_{30}Cl_2N_5Rh$ $[M - 2H]^+$ = 537.0928, found 537.0942.

4.2. Isolation of 2-((1,3-bis(N-butylimidazol-2-ylidene)phenylene) (dimethylamido)bis(iodo)) rhodium(III) (**1**)

A column was packed with 230–400 mesh silica gel using 1:1 (hexane: DCM). The column was initially eluted using 100% DCM followed by 2:98 (ethyl acetate:DCM) to isolate a dark orange solid, which had an R_f of 0.15. Isolated yield of the dark orange solid was 52 mg (26% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, J = 2.1 Hz, 2H), 7.17 (m, 1H), 7.11 (d, J = 7.7 Hz, 2H), 7.05 (d, J = 2.1 Hz, 2H), 5.24–5.21 (m, 2H), 4.76–4.71 (m, 2H), 3.75 (m, 1H, H_{N-H}), 2.01–1.99 (m, 4H), 1.62–1.59 (dd, $^3J_{H-H}$ = 1.2 Hz, $^3J_{Rh-H}$ = 6.3 Hz, 6H), 1.58–1.55 (m, 4H), 0.99–0.97 (t, J = 7.2 Hz, 6H). ^{13}C {^{1}H} (150 MHz, $CDCl_3$): δ 178.9 (d, J = 39 Hz, $C_{carbene-Rh}$), 156.2 (d, J = 29 Hz, $C_{aromatic-Rh}$), 145.7, 124.1, 121.7, 115.5, 108.7, 51.9, 44.6, 33.8, 20.0, 14.2. HRMS (ESI): Calculated for $C_{22}H_{32}IN_5Rh$ $[M - I + H]^+$ = 596.0752, found 596.0740; Calculated for $C_{20}H_{25}IN_4Rh$ $[M - NHMe_2, I]^+$ = 551.0173, found 551.0163.

4.3. Structure solution and refinement of 2-((1,3-bis(N-butylimidazol-2-ylidene)phenylene) (dimethylamido)bis(iodo)) rhodium(III) (**1**)

The structure was solved using ShelXS [74] and refined using ShelXL [75] full-matrix least-squares refinement. Molecular drawings and reports were generated using Olex2 [76]. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. In the final cycle of refinement 22,210 reflections (of which 6172 are observed with $I > 2\sigma(I)$) were used to refine 275 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 3.01%, 6.57%, 1.051, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

4.4. Synthesis of 2-((1,3-bis(N-butylimidazol-2-ylidene)phenylene) (dimethylamido)bis(chloro)) rhodium(III) (**1C**)

The salt, 1,3-bis(1-butylimidazolium-3-yl)benzene chloride (0.025 g, 0.0632 mmol), and tetrakis(dimethylamido)zirconium (0.018 g, 0.0695 mmol) were weighed under an inert atmosphere and combined with CD_2Cl_2 (0.8 mL) in a NMR tube. The mixture was kept at room temperature for approximately 1 h until a light yellow homogenous solution was obtained. Once the reaction became homogeneous, $[Rh(COD)Cl]_2$ (0.031 g, 0.0632 mmol) was added to the reaction mixture, and it was maintained at room temperature for another 12 h. The reaction mixture was then exposed to air for 10 min during which time a white precipitate formed leaving a bright orange supernatant. The orange supernatant was filtered and the solvent was removed under reduced pressure yielding a dark orange solid (0.028 g). A column was packed with 230–400 mesh silica gel using CH_2Cl_2. The column was initially eluted using CH_2Cl_2followed by 2:98 (MeOH: CH_2Cl_2) to the fractions were combined and concentrated yielding a dark orange solid (0.013 g, 38%), which had an R_f of 0.18. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, J = 2.1 Hz, 2H), 7.19 (m, 1H), 7.10 (d, J = 7.7 Hz, 2H), 7.06 (d, J = 2.1 Hz, 2H), 5.08–5.03 (m, 2H), 4.87–4.82 (m, 2H), 3.73 (s, br, 1H, H_{N-H}), 2.04–2.00 (m, 2H), 1.98–1.94 (m, 2H), 1.70–1.69 (dd, $^3J_{H-H}$ = 1.2 Hz, $^3J_{Rh-H}$ = 6.3 Hz, 6H), 1.58–1.54 (m, 4H), 1.03–1.01 (t, J = 7.2 Hz, 6H). ^{13}C {1H} (150 MHz, $CDCl_3$): δ 181.1 (d, J = 39 Hz, $C_{carbene-Rh}$), 155.7 (d, J = 29 Hz, $C_{aromatic-Rh}$), 146.1, 124.0, 121.0, 115.8, 108.8, 50.0, 45.7, 33.8, 20.2, 14.1. HRMS (ESI): Calculated for $C_{22}H_{32}ClN_5Rh$ $[M - Cl + H]^+$ = 504.1396, found 504.1380; Calculated for $C_{22}H_{33}ClN_5Rh$ $[M\text{-}Cl + Na]^+$ = 528.1372, found 528.1831.

4.5. General procedure for catalyses

A 1 dram vial containing a magnetic stir bar was charged with α,β-unsaturated compound (0.0735 mmol), bis(pinacolato)diboron (0.184 mmol), pre-catalyst **A** (2.00 mg, 2.94 μmol), and solvent (0.700 mL). The vial was closed and stirred vigorously for 1 h at 22 °C during which time a dark precipitate was observed to form. After 1 h, a 10 μL aliquot was passed through a short plug of celite and a 0.45 um PTFE filter. It was injected into the GC–MS to determine conversion. The crude reaction mixture was then filtered through a plug of celite. Volatiles were then removed under reduced pressure resulting in an oil. ^{1}H NMR and HRMS was taken of the crude product to confirm the borylated product. The crude product was then purified by silica gel chromatography to determine an isolated yield.

4.6. Catalysis using a 2:1 mixture of **1** and **1C**

A 2:1 ratio of 2-((1,3-bis(N-butylimidazol-2-ylidene)phenylene) (dimethylamido)bis(iodo)) rhodium(III) (**1**), and 2-((1,3-bis(N-butylimidazol-2-ylidene)phenylene) (dimethylamido)bis(chloro)) rhodium(III) (**1C**) (2.94 μmol total) were combined in a 1 dram vial with α,β-unsaturated compound (0.0735 mmol), bis(pinacolato) diboron (0.184 mmol), and solvent (0.700 mL). The general procedure for catalyses was then followed.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.11.010.

Author contributions

SWR and GKA contributed equally to the experimental data necessary for this work to be published.

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