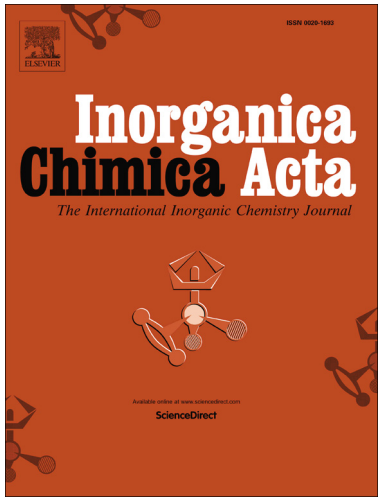

Research paper

Remote Coordination Approach for Electronic Tuning of a Rhodium(I)-N-Heterocyclic Carbene (NHC)–Complex

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Remote Coordination Approach for Electronic Tuning of a Rhodium(I)-N-Heterocyclic Carbene (NHC)–Complex

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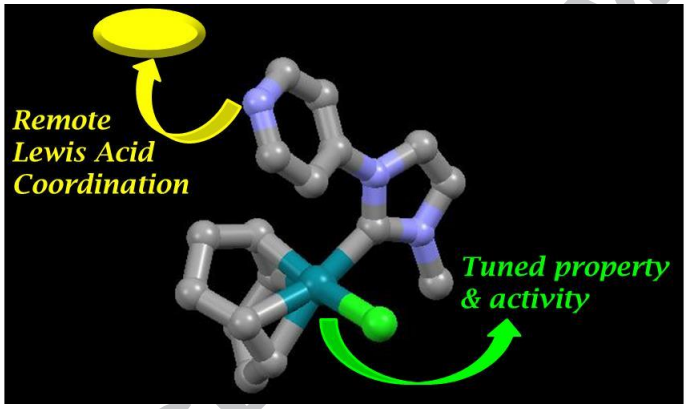
Dedication: This work is dedicated to Professor Rabindranath Mukherjee on the occasion of his 65th birthday.

Abstract

A simple Lewis acid coordination at the remote binding site installed within a modular N-heterocyclic carbene (NHC) ligated rhodium(I) complex could induce desired electronic influence and thereby enhance the activity of the complex in a model styrene hydroboration reaction.

Graphical Abstract



Keywords

N-Heterocyclic carbene (NHC) / Remote coordination / Rhodium / Lewis acid / Hydroboration

Highlights

- A monodentate NHC-rhodium(I) complex was designed with remote free pyridine ligand
- Lewis acid coordination at the free pyridine site modulates electronic property of the rhodium center
- Remote coordination thus alters catalytic activity of the complex

1. Introduction

Regulating property and function of a molecule with external stimuli (light, pH, electric potential, chemical species etc.) represents an alternative and attractive strategy [1], in parallel to the traditional methods of covalent backbone modification, requiring extensive synthesis, to bring about the desired changes. The key to such stimuli-controlled regulatory effect is to design a dynamically reversible molecular platform with a stimuli-responsive functionality which can tune the requisite stereoelectronic property of the system with utmost precision and delicacy leading to switchable modification. However, this is a conceptual challenge to the synthetic chemists in contrast to the existence of many such biological systems. Nevertheless, chemists succeeded in designing such reversible systems primarily via capitalizing the redox property of a metal or ligand, and introducing pH, light or chemo-sensitive functional group into the ligand backbone [1]. In the field of catalysis, this promising strategy led to the inception of a rapidly-developing research area of "artificial switchable catalysis" [1]. In the past, organometallic chemists applied redox-active and chemo-active phosphine- and nitrogen-based ligands to design remote-controlled catalysis [1]. Very recently, influenced by an all-round tremendous success of N-heterocyclic carbene (NHC) ligands, the idea of introducing stimuli-sensitive functional groups onto NHCs to achieve switchable catalysis has received much attention. The major successes so far are in the domain of light-, redox-, and pH-responsive systems as developed by many leading research groups including our group [2, 3]. In parallel, we have programmed our efforts to apply a "*remote coordination approach*" as a platform to regulate electronic property and catalytic activity of metal–NHC complexes [4]. We have demonstrated how a reversible coordination (by acid or metal center) at a remote pyridine site of a metal-bound NHC ligand could fine-tune the electronic property of the active center which is considered as prerequisite for switchable catalysis. Notably, in supramolecular chemistry, "*weak-link approach*" utilises coordination-induced structural changes and resulting allosteric effect to tune catalysis [5]. Several other catalytic and stoichiometric reactions, such as polymerization [6], hydrogenation [7], reductive elimination [8] etc. were also found to be triggered by the strategy of remote Lewis acid binding. Herein, we demonstrate the tuning of electronic property of a rhodium(I)–NHC complex consisting of a free-pyridine site via remote-coordination approach, followed by its effect in catalytic alkene-hydroboration reaction (Fig. 1).

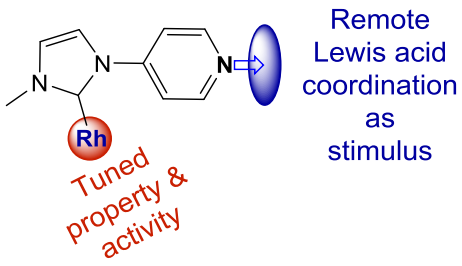


Fig. 1. Lewis acid coordination at a remote site as a stimulus for tuning property and activity at an active catalytic metal center of a metal-NHC complex

2. Experimental

2.1. General methods and materials

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AVANCE III 400 MHz NMR spectrometer at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H spectra, 77.2 ppm for $^{13}C\{^{1}H\}$ spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for ^{1}H-^{1}H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), m (multiplet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. Electrochemical experiments were done using CHI 620E Electrochemical Analyzer. Deuterated solvents and $RhCl_3.xH_2O$ were purchased from Aldrich. $[RhCl(COD)]_2$ [9], compound **1** [4a], complex **2** [4a], $[IrCp^*Cl_2]_2$ [10], and $[RhCp^*Cl_2]_2$ [11] were synthesized according to reported procedures.

*2.2. Synthesis of Complex **3***

A mixture of **2** (60 mg, 0.2 mmol) and $[RhCl(COD)]_2$ (49 mg, 0.1 mmol) in degassed CH_2Cl_2 (10 mL) was stirred under N_2 for 24 h. The reaction mixture was then filtered through a Celite plug and the solvent was removed under vacuum, resulting in the desired product as a solid compound. The compound was purified by precipitation from CH_2Cl_2-hexane. Pale yellow solid thus obtained was dried *in vacuo*. Yield: 80 mg (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.81 (d, J = 6.1 Hz, 2H, CH_{pyr}), 8.36 (d, J = 6.1 Hz, 2H, CH_{pyr}), 7.21 (d, J = 1.9 Hz, 1H, CH_{imz}), 7.04 (d, J = 1.9 Hz, 1H, CH_{imz}), 5.18 (m, 1H, CH_{COD}), 5.04 (m, 1H, CH_{COD}), 4.26 (s, 3H, CH_{3imz}), 3.23 (m, 1H, CH_{COD}), 2.52 (m, 1H, CH_{COD}), 2.45-2.17 (m_{broad}, 3H, CH_{2COD}), 1.90-1.55 (m_{broad}, 5H, CH_{2COD}). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 185.7 (d, J_{Rh-C} = 51.0 Hz, N*C*N), 151, 146.9, 123.9, 120.2, 118.6, 99.2 (d, J_{Rh-C} = 7 Hz, *C*H_{COD}), 98.7 (d, J_{Rh-C} = 7 Hz, *C*H_{COD}), 68.9-68.7 (2 doublets, *C*H_{COD}), 39.0, 33.4, 32.0, 29.2, 28.6. HRMS (ESI, positive ion): M^+ = 370.0803 (calculated 370.0790 for $[C_{17}H_{21}N_3Rh]^+$. Anal. Calcd for $C_{17}H_{21}ClRhN_3$ (%): C, 50.32; H, 5.22; N, 10.36. Found: C, 49.81; H, 5.17; N, 9.48).

*2.3. Single crystal X-ray diffraction analysis of **3***

Crystals of complex **3** suitable for single-crystal X-ray diffraction were obtained by diffusing hexane into the CH_2Cl_2 solution of complex **3** at ambient temperature. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at low temperature. Structure was solved with direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97 [12]. Full crystallographic data of **3** (CCDC 995437) can be obtained free of charge from The Cambridge Crystallographic data Center via www.ccdc.cam.ac.uk/data_request/cif.

*2.4. Remote coordination of Lewis acid $B(C_6F_5)_3$ to Complex **3***:

With tris pentafluorophenylborane ($B(C_6F_5)_3$): Complex **3** (3 mg, 7.4 µmol) and tris pentafluorophenylborane (3.6 mg, 7.4 µmol) was added to an NMR tube and dissolved in $CDCl_3$ (0.5 mL). The mixture was shaken well and the coordination was monitored by ^{1}H NMR spectroscopy.

2.5. Electrochemical studies

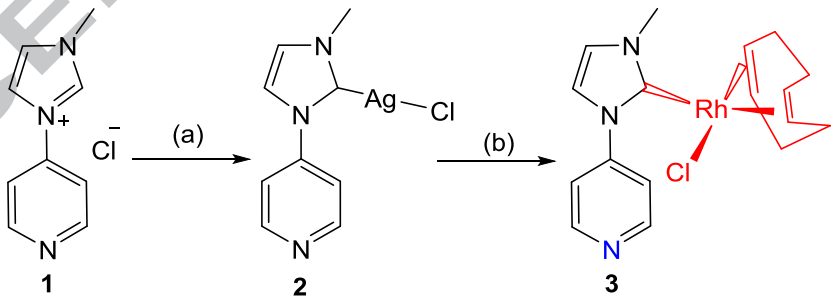
The electrochemical measurements were carried out by a CHI Instrument (CHI 620E Electrochemical Analyzer) at ambient temperature using a three electrode configuration (working electrode: Pt disk (1 mm diameter); counter electrode: a Pt wire; reference electrode: saturated calomel electrode, SCE). All the samples were prepared in dry acetonitrile (MeCN) and deoxygenated for 5 minutes with nitrogen gas before starting the actual experiments. 1.0 mM solution of complex **3** and 0.02 mM solution of $B(C_6F_5)_3$ were used for the study. A 0.1 M solution of $[NBu_4]PF_6$ in dry DCE was used as the supporting electrolyte. Ferrocene ($E_{1/2}$, Fc/Fc^+ = 0.436 volts vs SCE) was used as external calibration standard for all the measurements.

2.6. Catalytic studies

In a 5 mL Schlenk tube complex **3** (0.005 mol) or a mixture of complex **3** (0.005 mmol) and $B(C_6F_5)_3$ (0.005 mmol) was taken and DCE (2 mL) was added to it. After that styrene (0.5 mmol) and mesitylene (0.5 mmol; used as an internal NMR standard) were added to the flask. Next, pinacolborane (1.25 mmol) was added quickly and the mixture was started to stir at 30 °C. After the desired time intervals, small volumes of aliquots were withdrawn, dissolved in $CDCl_3$, and the yields of the various products were determined by ^1H NMR spectroscopy.

3. Results and discussion

The modular Rh^I–NHC complex, **3** was synthesized by employing the versatile silver transmetalation route. Thus, a reaction of the Ag–NHC complex **2** with 0.5 equiv. of rhodium(I) dimer, $[(1,5\text{-COD})RhCl]_2$ in dichloromethane at ambient temperature afforded the Rh^I–NHC complex **3** exclusively in excellent yield (Scheme 1). It is noteworthy that the free pyridine appended within the ligand did not coordinate to rhodium(I) center and hence could be utilized for further controlled coordination of suitable Lewis acids to tune the electronic property of the central metal. A similar Rh^I-NHC complex was reported previously for binding of Zinc(II)-complexes [13]. Our group previously explored this ligand in the context of catalytic annulation reactions wherein a bimetallic Rh^{III}-NHC complex was synthesized consisting of the remote pyridine coordination by a Cp^*Rh^{III}-fragment [14].



Scheme 1. Synthesis of complex **3**. Reaction conditions: (a) Ag_2O, CH_2Cl_2-CH_3OH, 27 °C, 4 h, dark. (b) $[Rh^ICl(COD)]_2$, CH_2Cl_2, 27 °C, 24 h.

Full characterization of complex **3** was accomplished by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, high resolution electrospray ionization mass spectroscopy (HR ESI-MS) and single-crystal X-ray diffraction analyses. The ^1H NMR spectrum of **3** in $CDCl_3$ exhibited two doublets at 8.81 and 8.36 ppm respectively

with a coupling constant value of 6.1 Hz which correspond to the two sets of pyridyl backbone protons. Four non-equivalent olefinic COD resonances at 5.18, 5.04, 3.23 and 2.52 ppm suggested a restricted rotation of the NHC motif around the Rh–$C_{carbene}$ bond in **3**. Moreover, the strong *trans* influencing NHC ligand resulted in more downfield shifts of the corresponding *trans*-olefinic protons (at 5.18 and 5.04 ppm) as compared to the *cis* ones (at 3.23 and 2.52 ppm) (Fig. 2). The characteristic $^{13}C\{^{1}H\}$ NMR signal of the Rh–$C_{carbene}$ carbon appeared at a much downfield region of 185.7 ppm as a doublet ($J_{Rh\text{-}C}$ = 51 Hz) due to coupling with the Rh atom. As in the ^{1}H NMR spectrum, the olefinic COD carbons *trans* to NHC resonated at more downfield region (99.2 and 98.7 ppm) than those *cis* to it (68.9-68.7 ppm) (see Supplementary Information). The characteristic NMR chemical shift values (e.g., Rh-Carbene carbon) were found similar to the previously reported Rh(COD)(NHC) complexes [13,15,16,17] The positive ion electrospray ionization (ESI) mass spectrum of **3** exhibited a major intense peak at m/z = 370.0803 assigned to $[M-Cl]^{+}$ (calcd for $[\mathbf{3}-Cl]^{+}$ 370.0790) (see Supplementary Information). A single crystal X-ray diffraction study of complex **3** unambiguously confirmed the structural arrangement within the molecule (Fig. 3). The coordination geometry around the d^{8}, $16e^{-}$ rhodium(I) center is square-planar arranged with the NHC-carbon, the bidentate COD, and the chloro ligands. The distance between metal center and olefinic group of COD which is *trans* to NHC group is much longer than other olefinic part as expected from stronger *trans* influence of NHC compared to the chloro ligand. The Rh(I)–$C_{carbene}$ bond distance of 2.011(3) Å is slightly shorter than that reported for analogous Rh(I) complexes [13,15,16,17].

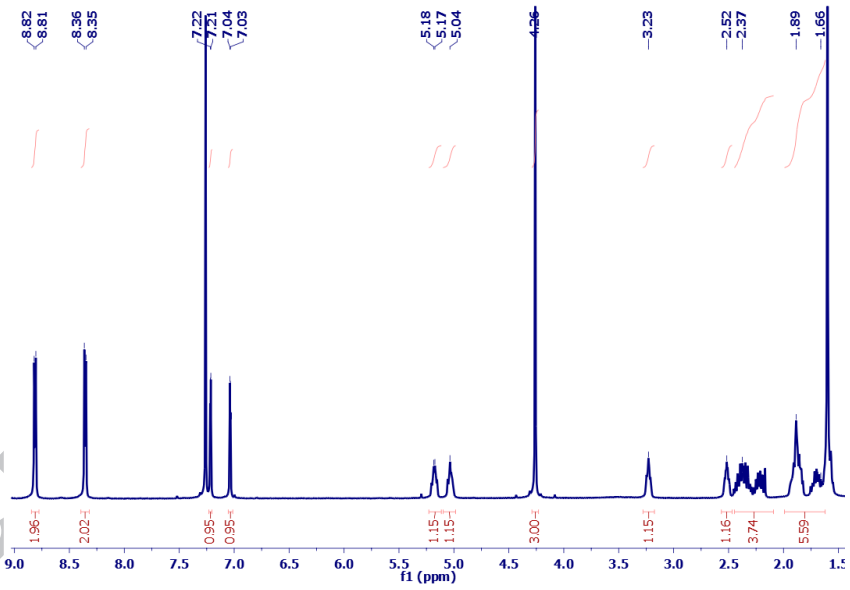


Fig. 2. ^{1}H NMR spectrum of complex **3** (400 MHz, $CDCl_3$, 300 K).

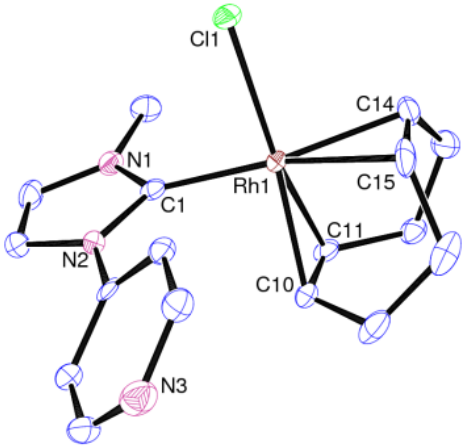
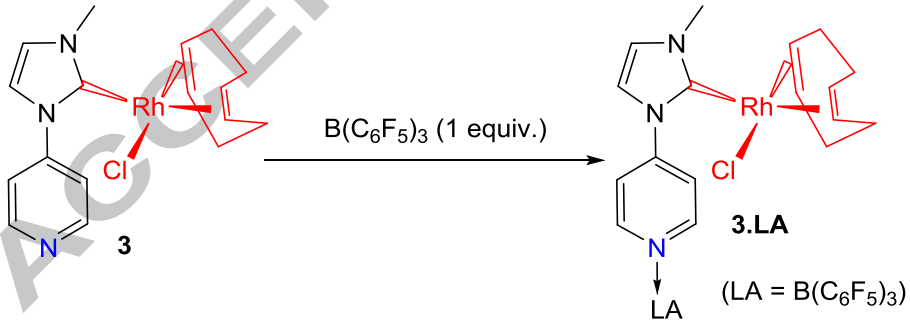


Fig. 3. Molecular structure of complex **3**. Selected bond lengths (Å) and angels (deg): C1–Rh1 = 2.011(3), Cl1–Rh1 = 2.4013(9), C10–Rh1 = 2.113(4), C11–Rh1 = 2.118(3), C14–Rh1 = 2.174(4), C15–Rh1 = 2.191(4), N1–C1–N2 = 103.7(3), C1–Rh1–Cl1 = 87.93(10), N1–C1–Rh1 = 128.2(3), N2–C1–Rh1 = 128.1(3). CCDC 1465253, contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Next we sought to investigate the remote coordination of Lewis acid $B(C_6F_5)_3$, at the free pyridine site of **3** leading to the proposed formation of the adduct **3.LA** (LA = Lewis acid, $B(C_6F_5)_3$) and its influence on the electronic property of **3** (Scheme 2). The ^1H NMR spectroscopic monitoring of such remote coordination effect showed a good degree of downfield shifts of the pyridyl protons as well as the imidazole backbone protons of the NHC–pyridyl scaffold in complex **3** upon gradual addition of incremental amounts of $B(C_6F_5)_3$ in $CDCl_3$ at ambient temperature (Fig. 4). This fact suggested a plausible coordination of $B(C_6F_5)_3$ to the open pyridine ligand and thereby inducing a substantial electron-deficiency into the system. Presumably, addition of one equivalent of Lewis acid completed the formation of the proposed **3·LA** adduct (Scheme 2) and after that no more change was observed (Figure 4).



Scheme 2. Coordination of Lewis acid $B(C_6F_5)_3$ to the free pyridine site of **3**.

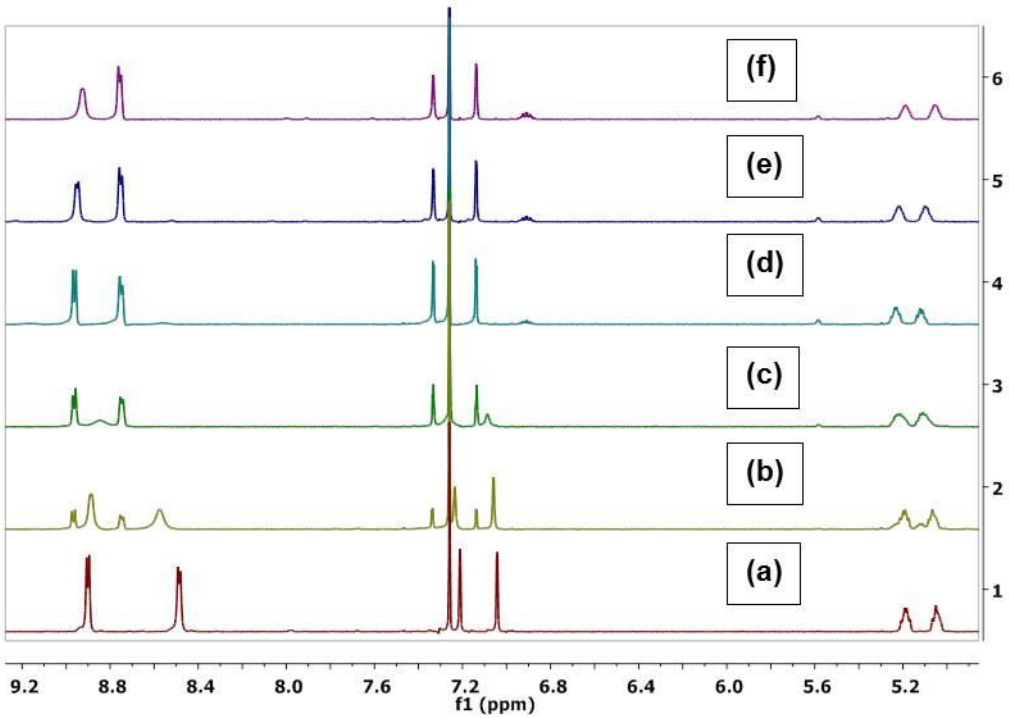


Fig. 4. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) monitoring for controlled addition of $B(C_6F_5)_3$ to complex **3**: (a) free complex, (b) 0.25 equiv., (c) 0.50 equiv., (d) 1.0 equiv., (e) 1.25 equiv., and (f) 1.50 equiv. of $B(C_6F_5)_3$.

After this NMR spectroscopic experiment, influence of such effect toward electronic perturbation directly at the metal center (Rh) of complex **3** was evaluated further by electrochemical method which is an extremely sensitive probe. The half-wave potential ($E_{1/2}$) values of the Rh^{I}/Rh^{II} redox couple for free complex **3** [16,17], and the $B(C_6F_5)_3$-coordinated **3**, derived from differential pulse voltammetry (DPV) are shown in Fig. 5 (obtained via gradual addition of a 0.02 mM solution of $B(C_6F_5)_3$ to a 1.0 mM solution of complex **3**). It was clearly evident from the study that coordination at the remote pyridine site generated an electron-poor, less-donating NHC ligand compared to the free system. This trend was ascertained from the higher Rh^{I}/Rh^{II} redox potential values in $B(C_6F_5)_3$-coordinated **3** ($E_{1/2}$ = 0.752 V vs SCE in acetonitrile) by 40 mV compared to the free complex **3** ($E_{1/2}$ = 0.712 V vs SCE in acetonitrile).

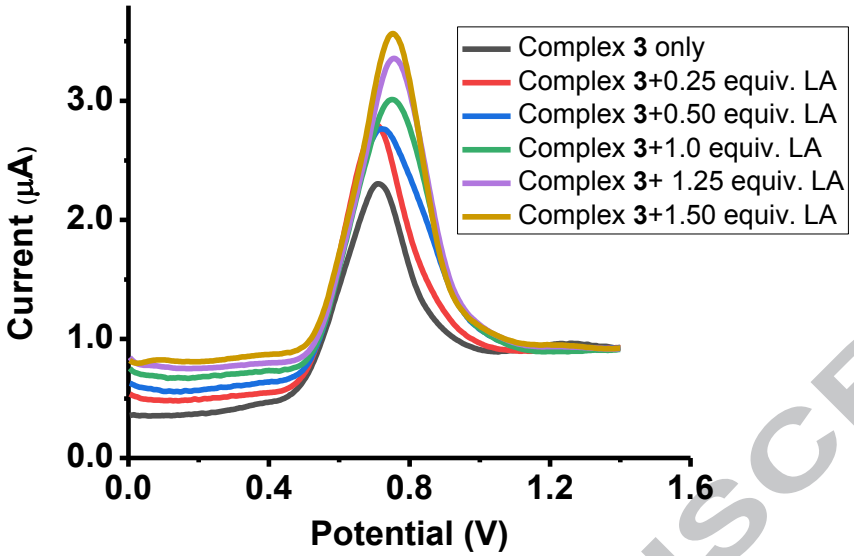


Fig. 5. DPV plots of complex **3** and its coordination study with $B(C_6F_5)_3$(1 mM of complex **3** and 0.02 mM of $B(C_6F_5)_3$ in dry MeCN with 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte; Ferrocene ($E_{1/2}$, Fc/Fc^+ = 0.427 V vs. SCE) was used as external calibration standard). The additional peak at the higher positive potential 1.2 V (vs SCE) for complex **3** might be due to the Cl-dissociated solvated complex [18].

Attempts were made to isolate the proposed **3**·$B(C_6F_5)_3$ adduct (Scheme 2) and characterize the same. After a few attempts, it was isolated and characterized by ^1H and ^{19}F NMR spectroscopy and also by CHN analysis (see Supplemenatry Information). The changes in the ^1H and ^{19}F NMR chemical shift values for the adduct from the free complex **3** and free $B(C_6F_5)_3$ respectively, suggested the formation of the proposed adduct. Moreover, as expected, in the ^1H NMR spectrum, the corresponding chemical shifts of the characteristic protons matched well with the same as observed during the in-situ solution studies described above.

Finally, a control complex **4** has been synthesized in which the 4-pyridyl substituent of the NHC ligand was replaced with a phenyl group, and some control NMR and DPV experiments were performed. As expected, during the ^1H NMR spectroscopic monitoring, addition of the Lewis acid $B(C_6F_5)_3$ to the solution of the control complex **4** effectively did not show shifts of the characteristic protons of the phenyl ring and the imidazole ring, except some broadening effect as observed for the phenyl protons at 8.15 ppm (see Supplementary Information). Similarly, in the DPV experiment, the shift of redox potential for the control complex **4** upon addition of Lewis acid $B(C_6F_5)_3$ (LA) was found to be negligible (see Supplementary Information). These experiments suggested that for complex **3**, the pyridine coordination was relevant for the observed electronic effect upon Lewis acid addition.

After confirming the proposed remote-coordination-induced tuning of electronic property at the metal center in complex **3** as demonstrated above, a model catalytic reaction was conducted to examine the feasibility of translating such modulation into practical application. Rh(I)-catalyzed hydroboration of styrene with pinacolborane (HBPin) was selected for this model study. As is evident from Fig. 6, the catalytic activity was substantially increased with **3**•$B(C_6F_5)_3$ catalyst system as compared to **3**. However the selectivity was not influenced much. The enhancement of activity might be due to an accelerated

reductive elimination step (proposed to be rate-determining in this type of olefin-hydroboration catalysis)[19,20] with the electron-deficient catalytic metal center in **3**•$B(C_6F_5)_3$. A detailed investigation toward the mechanistic aspect of such an accelerating effect will be the subject of future study.

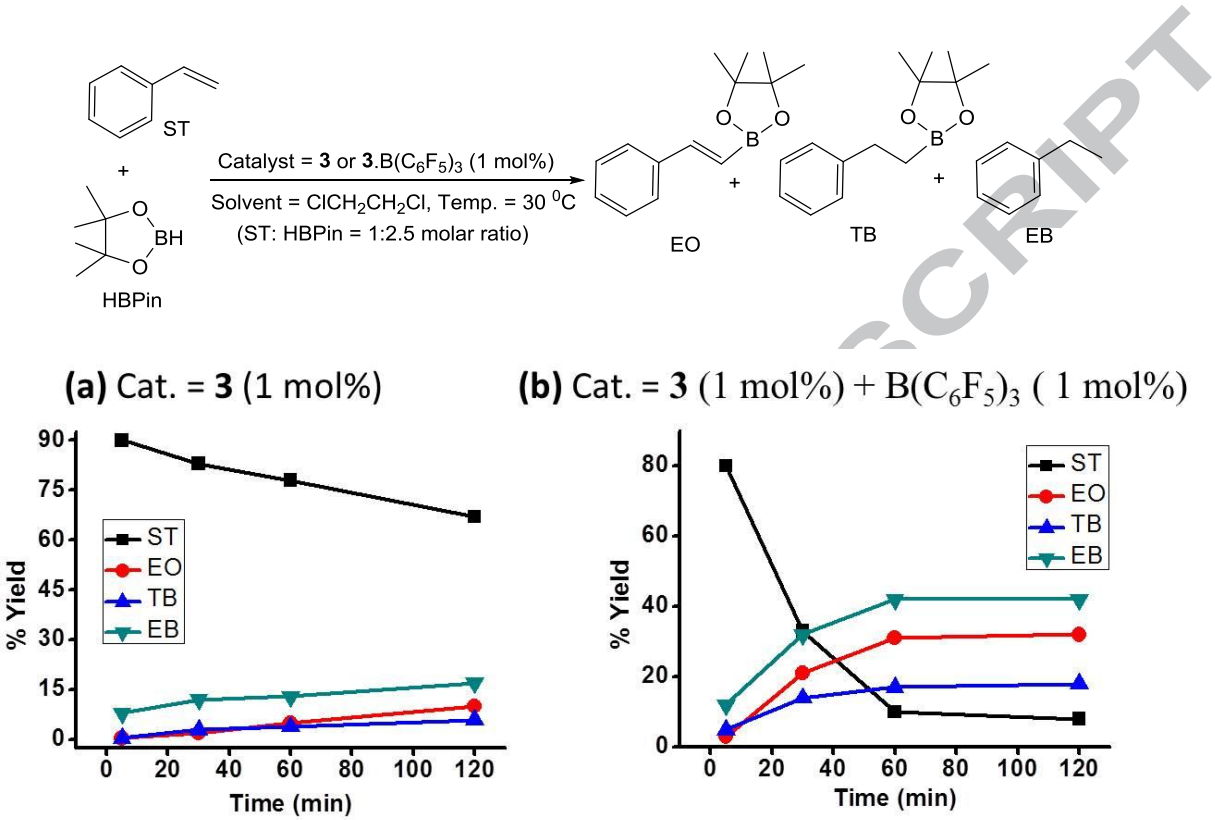


Fig. 6. Catalytic hydroboration results. Yields were calculated by ^{1}H NMR spectroscopy using an internal standard. No conversion of styrene was observed in the absence of catalyst (with only $B(C_6F_5)_3$), or in the absence of catalyst+$B(C_6F_5)_3$.

4. Conclusion

In conclusion, this study demonstrated a simple strategy of remote coordination of chemical entity to tune the electronic property of a metal complex, thus avoiding any pre- or post-synthetic structural modification within the ligand backbone. It was observed that such coordination resulted in electron-deficiency at the central metal center, as probed by NMR spectroscopy and electrochemical analysis. Finally, it was also found that activity of the metal center toward a model catalytic styrene hydroboration reaction could be influenced via such strategy. An in-depth understanding of the actual mechanistic details as well as expanding this useful approach toward other application are the next goal of our laboratory.

Acknowledgements

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Appendix

Supplementary content

Supplementary information containing spectral traces are available.

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