

A Rh^{III}–N-heterocyclic carbene complex from metal–metal singly bonded [Rh^{II}–Rh^{II}] precursor

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Abstract. Metal–metal singly bonded [Rh₂(CO)₄(acac)₂][OTf]₂ (**1**) has been synthesized and characterized by spectroscopic and analytical techniques. A density functional theory (DFT) optimized structure has been computed for the unbridged centro-symmetric structure. Reaction of **1** with PIN.HBr results in the [Rh(PIN)₂(H₂O)Br][OTf]₂ (**2**) in high yield. The reaction involves metal–oxidation from Rh^{II} to Rh^{III} accompanied by the metal–metal bond cleavage. The X-ray structure of **2** has been determined which reveals the incorporation of two N-heterocyclic carbene (NHC) ligands to each rhodium. This work demonstrates the general utility of the metal–metal bonded compounds for the easy synthesis of metal–NHC compounds.

Keywords. Naphthyridine; rhodium; N-heterocyclic carbene; metal–metal bond; oxidative addition.

1. Introduction

N-heterocyclic carbenes (NHC) have ubiquitous presence in contemporary organometallic chemistry.¹ These strong σ -donating and highly stable molecules are gradually diminishing the use of phosphine in homogeneous catalysis.² However, principal drawback lies in the inherent difficulty in their ready generation and subsequent metalation. The complexation protocols in NHC chemistry are mainly based on the following routes: (i) the complexation of the free, pre-isolated NHC with the metal; (ii) *in situ* deprotonation of the azolium C–H by base, either exogenous or embedded in the metal precursor, and subsequent metal-complexation; (iii) use of basic Ag₂O to generate a Ag–NHC complex, followed by the NHC transfer to a late transition metal via transmetalation.³ Recently, Cu^I–NHC complexes have been shown to transfer NHC to Au, Pd and Ru.⁴ Several other procedures have also been developed in recent years.⁵

We have recently introduced a new approach for the synthesis of metal–NHC complexes which employs metal–metal bonded compounds as the precursors. A mononuclear Ru^{II}–NHC complex was synthesized via oxidative cleavage of the Ru^I–Ru^I single bond in an unsupported diruthenium(I) precursor [Ru₂(CO)₄(CH₃CN)₆][BF₄]₂.⁶ Use of the acetate bridged precursor [Ru₂(CO)₄(CH₃CO₂)₂] did not lead to metal–metal bond cleavage, instead, provided NHC incorporated diruthenium(I) compounds in which the metal–metal single bond remains intact.⁷

In this chemistry, the naphthyridine-functionalized NHC ligands 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene (BIN) and 1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene (PIN) were employed.⁸

In our continuing effort to examine the suitability of metal–metal bonded compounds for accessing metal–NHC compounds, we report here the synthesis of a new metal–metal singly-bonded unsupported dirhodium(II) complex [Rh₂(CO)₄(acac)₂][OTf]₂ (OTf = trifluoromethanesulphonate) (**1**), and its reaction with PIN.HBr to obtain [Rh^{III}(PIN)₂(H₂O)Br][OTf]₂ (**2**).

2. Experimental

2.1 General procedures and materials

All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk vessel and vacuum line techniques. Solvents were dried by conventional methods, distilled under nitrogen and deoxygenated prior to use. RhCl₃.xH₂O was purchased from Arora Matthey, India. 1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (PIN.HBr) was synthesized following the reported procedure.⁸

2.2 Physical measurements

¹H NMR spectra were obtained on JEOL JNM-LA 500 MHz spectrometers. ¹H NMR chemical shifts were

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referenced to the residual hydrogen signal of the deuterated solvents. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with dry diethyl ether and dried in vacuum for at least 48 h prior to elemental analyses. Infrared spectra were recorded in the range of 4000–400 cm^{-1} on a Vertex 70 Bruker spectrophotometer. ESI-MS were recorded on a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer using acetonitrile as solvent. UV-Visible spectra were recorded using a Jasco V-670 UV/Vis absorption spectrophotometer. Cyclic voltammetric studies were performed on a BAS Epsilon electrochemical workstation in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The working electrode was a BAS Pt disk electrode, the reference electrode was Ag/AgCl and the auxiliary electrode was a Pt wire. The ferrocene/ferrocenium couple occurs at $E_{1/2} = +0.51$ (70) V versus Ag/AgCl under the same experimental conditions. The potentials are reported in volts (V); the ΔE ($E_{p,a} - E_{p,c}$) values are in millivolts (mV) at a scan rate 100 mVs^{-1} .

2.3 Syntheses

2.3a $[\text{Rh}(\text{CO})_2(\text{acac})(\text{OTf})]$ (**1**): AgOTf (95 mg, 0.37 mmol) was added to a yellow CH_2Cl_2 solution (15 mL) of $[\text{Rh}(\text{CO})_2(\text{acac})]$ (100 mg, 0.34 mmol). Resulting black suspension was stirred at room temperature for 3 h and the mixture was filtered through a pad of celite. Orange-yellow filtrate was concentrated under reduced pressure and hexane was added to induce precipitation. The greenish-brown solid was washed with hexane and dried in vacuo. Yield: 105 mg (70%). ^1H NMR (500 MHz, CD_3CN , 292K): δ 5.70 (s, 1H, CH_{acac}), 2.11 (s, 6H, 2 Me_{acac}). ^{13}C NMR (125.77 MHz, CD_3CN , 292K): δ 178.5 (d, $^1J_{\text{RhC}} = 71$ Hz, CO), 100.3 (CH), 30.0 (CH_3). ^{19}F NMR (470.6 MHz, CD_3CN , 292K): δ -79.22. IR (CH_2Cl_2) data (cm^{-1}): $\nu(\text{CO})$: 2075 (s), 2027 (s), 2002 (s), 1563 (m, acac), 1523 (s, acac); $\nu(\text{C}-\text{CO}-\text{C})$: 1150–1083 (s, acac); $\nu(\text{OTf})$: 1259. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_{14}\text{F}_6\text{S}_2\text{Rh}_2$: C, 23.60; H, 1.73. Found: C, 23.41; H, 1.68.

2.3b $[\text{Rh}(\text{PIN})_2(\text{H}_2\text{O})\text{Br}][\text{OTf}]_2$ (**2**): 1-Isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (90 mg, 0.26 mmol) and $[\text{Bu}_4\text{N}][\text{OTf}]$ (103 mg, 0.26 mmol) was added to an acetonitrile solution (15 mL) of $[\text{Rh}_2(\text{CO})_4(\text{acac})_2][\text{OTf}]_2$ (50 mg, 0.06 mmol) and stirred at room temperature for 12 h.

Resulting yellow solution was concentrated under reduced pressure and diethyl ether was added to induce precipitation. The yellow solid was washed with diethyl ether and dried under vacuum. Yield: 100 mg (75%). ^1H NMR (500 MHz, CD_3CN , 292K): δ 9.12 (d, $J = 10$ Hz, 1H, NP), 8.92 (d, $J = 10$ Hz, 1H, NP), 8.61 (s, 1H, NP), 8.48 (dd, $J = 9$, $J = 2.5$ Hz, 1H, Im), 8.39 (m, 2H, NP, Im), 8.14 (d, $J = 10$ Hz, 1H, NP), 7.90 (dd, $J = 9$, $J = 2.5$ Hz, 1H, Im), 7.60 (s, 1H, NP), 7.42 (dd, $J = 9$, $J = 2.5$ Hz, 1H, Im), 6.26 (m, 1H, methyne), 3.47 (m, 1H, methyne), 2.87 (s, 3H, Me), 2.83 (s, 3H, Me), 2.59 (s, 3H, Me), 1.63 (s, 6H, Me), 1.41 (s, 6H, Me), 1.35 (s, 3H, Me). ^{13}C NMR (125.77 MHz, CD_3CN , 292K): δ 185.3 (d, $^1J_{\text{RhC}} = 78$ Hz, NCN_{Im}), 180.5 (d, $^1J_{\text{RhC}} = 71$ Hz, NCN_{Im}), 165.5 (NCN_{NP}), 165.1 (NCN_{NP}), 154.9 (NCC_{NP}), 154.1 (NCC_{NP}), 152.9 (NCC_{NP}), 151.7 (NCC_{NP}), 146.5 (CCC_{NP}), 143.4 (CCC_{NP}), 141.4 (CH_{NP}), 140.2 (CH_{NP}), 133.9 (CH_{NP}), 126.7 (CH_{Im}), 122.1 (CCC_{NP}), 119.9 (CH_{NP}), 113.2 (CH_{Im}), 54.6 (CH), 27.2 (CH_3), 25.8 (CH_3), 25.1 (CH_3), 21.7 (CH_3), 21.5 (CH_3), 17.7 (CH_3), 17.5 (CH_3). ESI-MS, m/z (fragment): 883 $[\text{M}-\text{OTf}]^+$. Anal. Calcd for $\text{C}_{34}\text{H}_{36}\text{BrF}_6\text{N}_8\text{O}_7\text{RhS}_2$: C, 39.66; H, 3.52; N, 10.88. Found: C, 38.98; H, 3.37; N, 10.33.

2.4 X-ray data collection and refinement

Single crystal X-ray structural studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda_\alpha = 0.71073$ Å). The frames were indexed, integrated and scaled using SMART and SAINT software package,⁹ and the data were corrected for absorption using the SADABS program.¹⁰ The structures were solved and refined using SHELX suite of programs¹¹ as implemented in X-seed,¹² while additional crystallographic calculations were performed by the programs PLATON.¹³ Figures were drawn using ORTEP32.¹⁴ The hydrogen atoms were included into geometrically calculated positions in the final stages of the refinement and were refined according to 'riding model'. Hydrogen atoms were not assigned for the coordinated and crystal water molecules. CCDC-833295 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data and pertinent refinement parameters for **2** are presented in table 1.

Table 1. Crystallographic data and pertinent refinement parameters for 2·CH₂Cl₂·H₂O.

	2·CH ₂ Cl ₂ ·H ₂ O
Empirical formula	C ₃₅ H ₃₈ BrCl ₂ F ₆ N ₈ O ₈ RhS ₂
Formula weight	1130.57
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	12.454(5)
<i>b</i> (Å)	12.921(5)
<i>c</i> (Å)	14.959(5)
α (deg)	96.564(5)
β (deg)	110.511(5)
γ (deg)	95.155(5)
<i>V</i> (Å ³)	2217.9(14)
<i>Z</i>	2
ρ_{calcd} (g cm ⁻³)	1.693
μ (mm ⁻¹)	1.584
<i>F</i> (000)	1136
Reflections	
Collected	20164
Independent	10686
Observed [<i>I</i> > 2 σ (<i>I</i>)]	7009
No. of variables	576
GooF	1.069
<i>R</i> _{int}	0.0509
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0652
	0.1576
<i>R</i> indices (all data) ^a	0.1109
	0.2090

3. Results and discussions

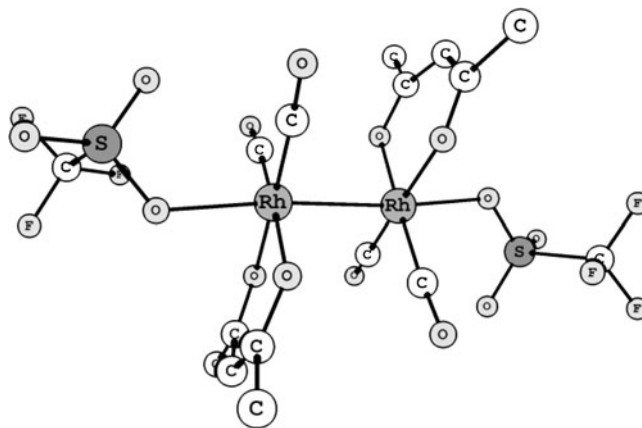
3.1 An unsupported metal–metal bonded compound [Rh₂(CO)₄(*acac*)₂][OTf]₂ (**1**)

Reaction of Rh₂(OAc)₄ with PIN.HBr did not provide a clean product. It was realized that the unbridged metal–metal bonded compounds are the most suitable for the facile oxidative cleavage.^{6,7} Accordingly, we sought to synthesize an unsupported dirhodium(II) compound **1**, following an identical procedure recently reported for the [Ir₂(CO)₄(*acac*)₂][OTf]₂ by Hughes and coworkers.¹⁵ Reaction of AgOTf with [Rh^I(CO)₂(*acac*)] in 1:1 ratio in CH₂Cl₂ afforded **1** in good yield. IR spectrum shows three carbonyl absorptions at 2075, 2027 and 2002 cm⁻¹ typical for a paddlewheel ‘M₂(CO)₄’ species.¹⁶ The *acac* exhibits sharp carbonyl bands at 1563 and 1523 cm⁻¹. The ¹H NMR spectrum shows the methine and methyl protons of *acac* as sharp singlets at δ 5.70 and 2.11 ppm, respectively, whereas the corresponding carbon atoms resonate at δ 100.3 (CH) and 30 (CH₃) ppm. The carbonyl carbons exhibit signal at δ 178.5 (*J*_{Rh–C} = 71 Hz). The presence of triflate

anions is confirmed by its characteristic IR absorption at 1259 cm⁻¹ (figure S1), and by the ¹⁹F NMR resonance at δ –79.22 ppm.

The UV-Vis spectrum of **1** is rather unremarkable. This is understandable considering the electronic nature of the compound. An intense UV-Vis absorption occurs at 210 nm which is accounted for the intra-ligand π – π^* transitions. In addition, two weak absorptions at 255 and 325 nm are observed which probably originate from [Rh–Rh] $d\pi$ – $d\pi$ orbital to ligand acceptor orbitals (figure S2).¹⁷ The cyclic voltammogram of **1** shows two irreversible oxidations at *E*_{p,a} = +0.78 and +1.15 V which are attributed to Rh₂^{II,II} → Rh₂^{II,III} → Rh₂^{III,III} (figure S3). Two irreversible reductions are observed at *E*_{p,c} = –0.61 and –0.94 V, the first one at lower negative potential is based on the dirhodium(II) unit and the following one is most likely due to ligand reduction. The reduction of the [Rh^{II}–Rh^{II}] core at an accessible cathodic potential leading to infinite Rh chain complexes have been widely reported.¹⁸

Appropriate single crystals of **1** for structure determination could not be obtained. The spectroscopic and analytical data suggest a metal–metal bonded {Rh(CO)₂(*acac*)} dimer structure for **1**. A DFT optimized structure for **1** has been computed (figure 1). It has a paddlewheel structure with C_i symmetry. The unsupported Rh–Rh bond distance is 2.692 Å with two axial sites occupied by the triflate anions. Two triflate oxygens makes a linear arrangement with the Rh–Rh vector with (TfO)O–Rh–Rh–O(OTf) dihedral angle 174.5°. The *acac* ring is planar, however, it makes an angle 21° with the O–Rh–O plane. NBO analysis shows that the HOMO consists of the ligands *acac* and triflates (80%) with significant contributions from the dirhodium based orbital (20%). On the contrary, the LUMO primarily originates from the out-of-phase interaction of the d_{z²} orbitals of each rhodium

**Figure 1.** DFT optimized structure for compound **1**.

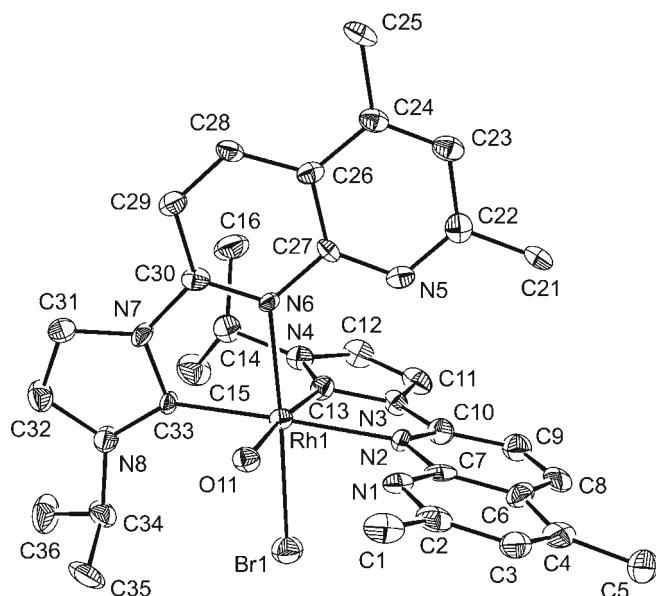


Figure 2. ORTEP diagram (50% probability thermal ellipsoid) of the cationic unit $[\text{Rh}^{\text{III}}(\kappa^2\text{C,N-PIN})_2(\text{H}_2\text{O})\text{Br}]^+$ in compound **2** with important atoms labelled. Hydrogen atoms omitted for the sake of clarity.

(total contributions 70%) with participations from the coordinated oxygen atoms of triflates (30%) (figure S4).

3.2 Accessing $[\text{Rh}(\text{PIN})_2(\text{H}_2\text{O})\text{Br}][\text{OTf}]_2$ (**2**) from metal–metal bonded compound **1**

Room temperature treatment of **1** with PIN.HBr in the presence of tetrabutylammonium trifluoromethanesulphonate (TBAOTf) provided a mononuclear Rh(III) compound $[\text{Rh}(\text{PIN})_2(\text{H}_2\text{O})\text{Br}][\text{OTf}]_2$ (**2**) in high yield.

The reaction involves metal-oxidation from Rh^{II} to Rh^{III} accompanied by the metal–metal bond cleavage. The molecular structure of **2** has been established by X-ray crystallography. The coordination geometry of the rhodium is best described as pseudo octahedral comprising of two *cis* oriented PIN ligands, one water molecule and a bromide (figure 2). Chelate binding of both ligands involves carbene carbon and nitrogen atoms of the naphthyridine unit. The Rh1–C13, Rh1–C33 and Rh1–N2, Rh1–N6 bond distances are 1.965(6), 1.997(5) Å and 2.139(5), 2.117(5) Å, respectively. The water molecule occupies the position *trans* to the carbene carbon atom (C13) with a Rh–O distance of 2.142(4) Å (table 2).

Four imidazole protons and six aromatic NP protons from two PIN ligands are assigned in the ^1H NMR spectrum of compound **2**. Protons of the coordinated PIN show marginal shifts reflecting its coordination to the metal. One of the two methyne protons (H34) undergoes considerable downfield shift with a shift difference ($\Delta\delta$) of 1.11 ppm compared to the uncoordinated ligand precursor. This is due to its interaction with the bromide with $\text{H34}\cdots\text{Br1}$ distance of 2.595 Å calculated from X-ray geometry. On the contrary, the second methyne proton (H14) shifts downfield by $\Delta\delta$ 1.68 ppm which is attributed to its interaction with the π electron cloud of one of the imidazole rings. Molecular structure reveals that the H14 is placed 2.86 Å above the imidazole ring from the second ligand. The diamagnetic shift of one of the naphthyridine methyl signal (C21H_3) with a shift difference ($\Delta\delta$) of 1.36 ppm compared to the uncoordinated ligand precursor is credited to the shielding effect exerted by the naphthyridine π electron cloud

Table 2. Relevant metrical parameters for compound **2**.

Bond length (Å)			
Rh1–C13	1.965(6)	Rh1–O11	2.142(4)
Rh1–C33	1.997(5)	Rh1–Br1	2.445(1)
Rh1–N6	2.117(5)	Br1–H34	2.5946
Rh1–N2	2.139(5)	O11–N1	2.630(7)
Bond angle (°)			
C13–Rh1–C33	103.0(3)	O11–Rh1–Br1	90.04(12)
C13–Rh1–N6	91.2(2)	C13–Rh1–Br1	88.15(18)
C33–Rh1–N6	78.8(2)	N6–Rh1–Br1	176.50(13)
C13–Rh1–N2	78.6(2)	C30–N6–C27	120.1(5)
C33–Rh1–N2	177.8(2)	C10–N2–C7	116.7(5)
N6–Rh1–N2	102.67(18)	N8–C33–N7	105.0(5)
C13–Rh1–O11	173.6(2)	N4–C13–N3	105.9(5)
Dihedral angle (°)			
N2–C10–N3–C13	–0.9(8)	C33–N6–N2–Rh1	1.23(17)
N6–C30–N7–C33	–6.2(8)	C33–C13–N2–Rh1	–0.90(13)

to the methyl group. The $C21 \cdots X_{NP}$ (X_{NP} = centroid of the naphthyridine ring) is 3.68 Å, as obtained from the molecular structure of **2**. The 1H NMR spectrum of compound **2** with above mentioned interactions is presented in figure 3. The ^{13}C NMR signal corresponding to the two carbene carbon atoms ($NC_{Im}N$) appear as two doublets at 185.3 and 180.5 ppm with Rh–C coupling constants 68 and 71 Hz, respectively.

3.3 Tentative mechanism

We have proposed a tentative mechanism for the formation of compound **2** which involves the cleavage of the $Rh^{II}-Rh^{II}$ single bond with concomitant

increase in the metal oxidation state by one unit. The *acac* on each metal deprotonates PIN.HBr generating the free carbene. Subsequent metalation of the NHC ligands possibly leads to the formation of an unsupported complex $[Rh_2(PIN)_2(CO)_4Br_2]$ (scheme 1). An isoelectronic and isostructural diruthenium(I) complex $[Ru_2(PIN)_2(CO)_4Br_2]$ has been isolated and structurally characterized by employing $[Ru_2(CH_3COO)_2(CO)_4]$ as the precursor.⁷

Incorporation of the second PIN proceeds through the oxidative addition of the C2–H of PIN.HBr to the metal–metal bond. Stone *et al.* first reported the synthesis of NHC-metal complexes following oxidative addition pathway during early 1970s.¹⁹ Nolan²⁰ and Crabtree²¹ independently proposed C2–H

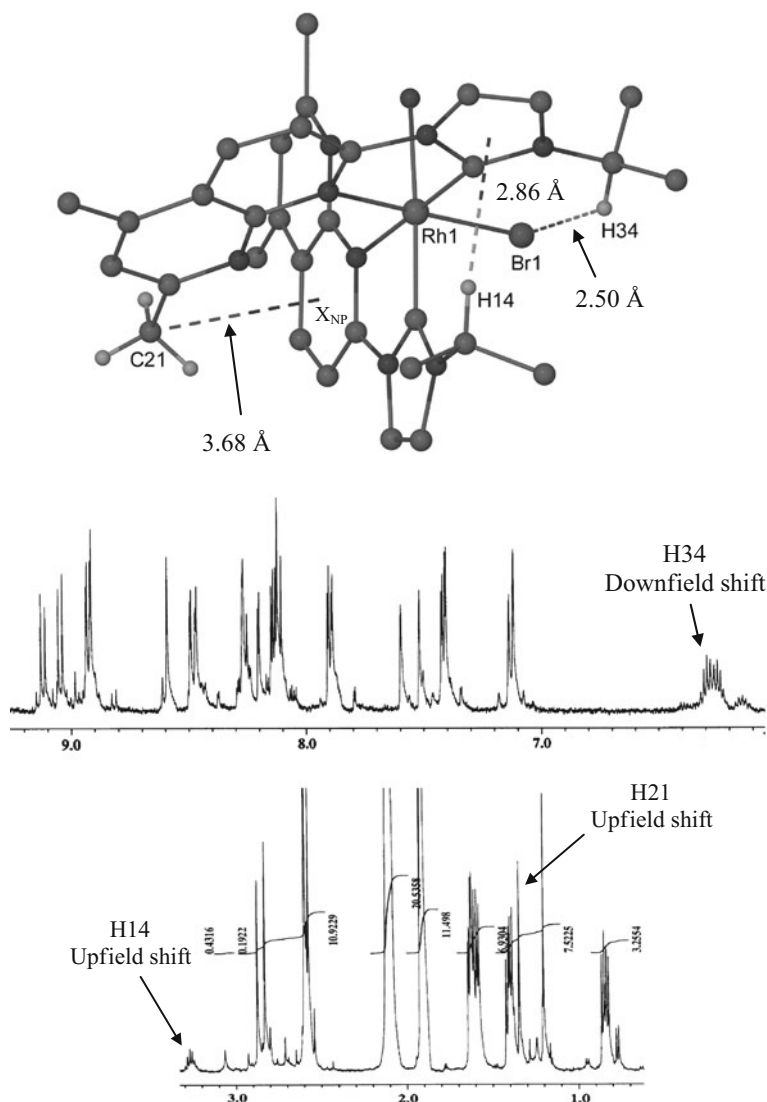
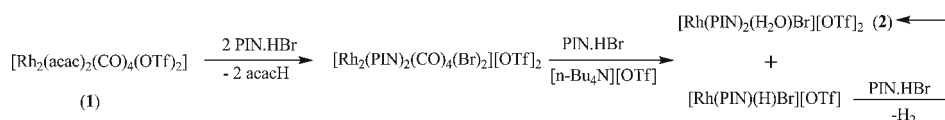


Figure 3. 1H NMR spectra of **2** in CD_3CN . Figure at the top shows the different types of interactions dictating observed proton signal shift.



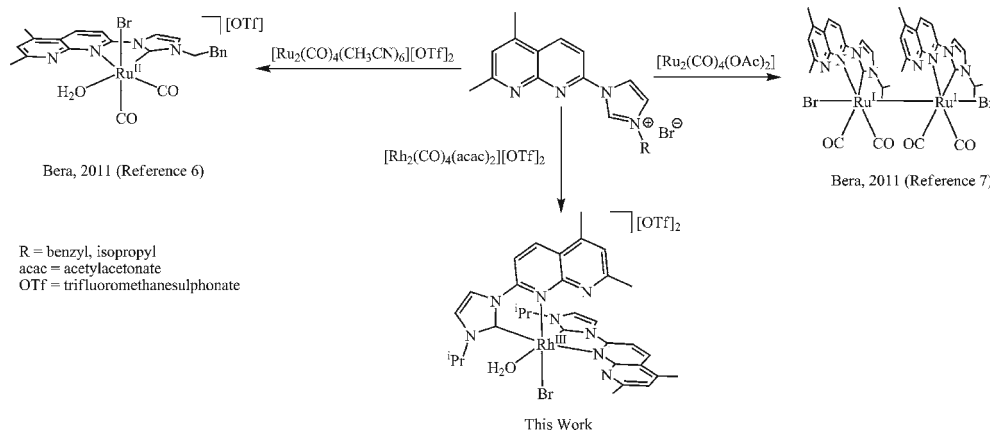
Scheme 1. Proposed mechanism for the high-yield synthesis of **2**.

oxidative addition of the imidazolium C–H to Pd(0) for the synthesis of Pd^{II}-NHC compounds. Isolation of a hydride complex [Pt(H)(dmiy)(PR₃)₂]₂BF₄ (dmiy = 1,3-dimethylimidazolin-2-ylidene and R = phenyl, cyclohexyl) by Cavell, following a similar procedure, provides support for this hypothesis.^{22,23} Several other reports have also appeared implicating oxidative addition pathway for the activation process.²⁴ In the present case, the PIN.HBr undergoes oxidative addition across the Rh^{II}–Rh^{II} bond resulting in its cleavage leading to the formation of two Rh^{III} compounds, one of which contain two PIN ligands and the another with one PIN and one hydride (scheme 1). Coordination of another equivalent of PIN.HBr to the hydride complex followed by the abstraction of the C2–H proton by the hydride with the exclusion of molecular hydrogen gives back compound **2**. This hydrogen elimination process possibly occurs in a concerted fashion involving the metal-hydride and the C2–H proton. The high yield of this reaction can be explained by this mechanism (scheme 1).

4. Conclusion

We summarize this work in the context of our broad research interest on the reactivity of NHC precursors

with metal–metal singly bonded compounds (scheme 2). Reaction of PIN.HBr with [Ru₂^I(OAc)₂(CO)₄] allowed the site-selective incorporation of NHC providing [Ru₂^I(PIN)₂(CO)₄Br₂]. The reaction involves the direct deprotonation of C2–H by acetate and subsequent metalation. In the absence of any base, the primary pathway is the oxidative addition of the C2–H to each metal. Accordingly, oxidative cleavage of the metal–metal bond in [Ru₂(CH₃CN)₆(CO)₄][OTf]₂ afforded [Ru^{II}(CO)₂(BIN)(H₂O)Br][OTf]. In the present work, we have examined the parallel chemistry with isoelectronic dirhodium(II) system. A new metal–metal singly bonded [Rh₂^I(CO)₄(acac)₂][OTf]₂ (**1**) has been synthesized following the protocol reported for the Ir congener. Compound **1** has been characterized by spectroscopic and analytical measurements. A DFT optimized structure has also been computed. Reaction of **1** with PIN.HBr results in the [Rh^{III}(PIN)₂(H₂O)Br][OTf]₂ (**2**) in high yield. Incorporation of two PIN ligands to each Rh most likely proceeds in two steps; the PIN is generated via deprotonation of PIN.HBr aided by the *acac*, followed by the chelation of the ligand. The second ligand adds to the metal by oxidative cleavage of the Rh^{II}–Rh^{II} single bond followed by dehydrogenation. Clearly, the present work validates our contention on the use of metal–metal bonded compounds in the efficient generation of metal–NHC compounds.



Scheme 2. Reactivity of metal–metal bonded compounds with NHC precursor ligands.

Supplementary material

Figures S1–S4 and table S1 can be found in www.ias.ac.in/chemsci as electronic supporting information.

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