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# A Ru<sup>II</sup>–N-heterocyclic carbene (NHC) complex from metal–metal singly bonded diruthenium(I) precursor: Synthesis, structure and catalytic evaluation

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ABSTRACT

A mononuclear Ru(II)–N-heterocyclic carbene (NHC) complex [Ru<sup>II</sup>(CO)<sub>2</sub>(κ<sup>2</sup>C,N-BIN)(H<sub>2</sub>O)Br][OTf] (OTf = trifluoromethane sulphonate)(1) has been synthesized in high-yield by the oxidative cleavage of the metal-metal singly-bonded diruthenium(I) precursor [Ru<sub>2</sub>(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>(OTf)<sub>2</sub>] with 1,8-naphthyridine functionalized NHC precursor 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (BIN·HBr) at room temperature. Compound 1 catalyzes transfer hydrogenation of ketones to alcohols, and carbene-transfer from ethyl diazoacetate to a variety of substrates. It is shown to be an excellent catalyst for the insertion of carbene into the O-H and N-H bonds of alcohols and amines. © 2010 Elsevier B.V. All rights reserved.

1. Introduction

N-heterocyclic carbenes (NHC) have emerged as a useful class of ligands in the development of homogeneous organic [1] and organometallic catalysts [2]. These are strong  $\sigma$ -donors, sterically and electronically tunable, and form thermally stable compounds with different metal ions. Such qualities have rendered NHC ligands as surrogates to phosphines in organometallic catalysis [3]. Last few decades have witnessed an extensive exploration of metal-NHC complexes as catalysts for a wide variety of organic transformations including olefin metathesis [4], hydrosilylation [5], hydroformylation [6], hydrogenation [7], copolymerization [8], and C–C [9] and C–N [10] coupling reactions and asymmetric transformations [11]. In general, NHCs are shown to be good ancillary ligands; however, recent reports on the reductive elimination of corresponding imidazolium salt from NHC-Pd<sup>II</sup>-alkyl complex have cast doubt on an all-out 'spectator' description [12].

The complexation protocols in NHC chemistry are mainly based on the following routes: 1. the complexation of the free, preisolated NHC with metal; 2. in situ deprotonation of the azolium salt by base, either exogenous or embedded in the metal precursor, and subsequent metal-complexation; 3. use of basic Ag<sub>2</sub>O to generate a Ag-NHC complex, followed by the NHC transfer to a late transition metal via transmetallation [13]. Recently, Cu<sup>I</sup>-NHC complexes have

been shown to transfer NHC to Au, Pd and Ru [14]. Several other procedures have also been developed in recent years [15].

Oxidative addition of C2-H bond of imidazolium cations to lowvalent metal complex is a facile but less explored path. Advantage of this protocol is that no base is required for the activation. Nolan [16] and Crabtree [17] independently proposed oxidative addition of the imidazolium C–H to Pd(0) for the synthesis of Pd<sup>II</sup>-NHC compounds. Isolation of a hydride complex  $[Pt(H)(dmiy)(PR_3)_2]BF_4$ (dmiy = 1,3-dimethylimidazolin-2-ylidene and R = Phenyl, Cyclohexyl) by Cavell, following a similar procedure, provides support for this hypothesis [18]. Subsequently several reports have appeared implicating oxidative addition pathway for the activation process [19]. Though this method is successfully employed for lowvalent electron-rich coordinatively unsaturated Group 10 metal complexes, there are limited examples known for other metals [20].

The prospect of functionalization at the N atoms and in the backbone of imidazole has brought about a new dimension in NHC chemistry [21]. Hetero-arene derivatized NHC ligands exhibit wide diversity in ligand topology and binding mode, offering greater control over the coordination environment of metal and its catalytic activities [22]. Introduction of 1,8-naphthyridine (NP) unit in NHC afforded 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene (BIN) which exhibits diversity in metal-carbene chemistry by virtue of its multiple binding sites and topological flexibility (Fig. 1) [23]. We have recently demonstrated multifaceted coordination of this NP-NHC hybrid ligand BIN generating a host of transition metal complexes involving W, Ag, Pd, Ir and Rh are synthesized [24]. However, our efforts to access a mononuclear





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Fig. 1. Schematic representation of 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl) imidazol-2-ylidene (BIN).

ruthenium complex remained thus far unsuccessful from a variety of conventional mononuclear Ru<sup>II</sup> precursors such as Ru<sub>2</sub>(p-cyme-ne)<sub>2</sub>Cl<sub>4</sub>, Ru<sub>2</sub>(Cp<sup>\*</sup>)<sub>2</sub>Cl<sub>4</sub>, [Ru(COD)Cl<sub>2</sub>]<sub>2</sub> and Ru(PPh<sub>3</sub>)<sub>3</sub>(CO)(H)<sub>2</sub>.

In this contribution, we report oxidative cleavage of the metal-metal single bond in the diruthenium(I) precursor [Ru<sub>2</sub>-(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>(OTf)<sub>2</sub>] affording [Ru<sup>II</sup>(CO)<sub>2</sub>( $\kappa^2$ C,N-BIN)(H<sub>2</sub>O)Br][OTf] (OTf = trifluoromethane sulphonate) (**1**). The catalytic activities of this complex are evaluated with special emphasis on the carbene-transfer reactions from ethyl diazoacetate (EDA).

# 2. Results and discussions

2.1. Synthesis and characterization of aqua-bromo-dicarbonyl-[1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene] ruthenium(II) trifluomethylsulphonate (1)

The NP substituted NHC-ligand precursor 1-benzyl-3-(5,7dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (BIN·HBr) was obtained by the direct linkage between 2-imidazolyl-1,8naphthyridine and benzyl bromide as reported earlier [24]. Room temperature treatment of  $[Ru_2(CO)_4(CH_3CN)_6][OTf]_2$  with two equivalents of BIN·HBr in dichloromethane provided a mononuclear Ru(II)–carbene complex **1** (Scheme 1) in high-yield (80%).

Formation of **1** involves metal-oxidation from Ru<sup>I</sup> to Ru<sup>II</sup> accompanied by the metal-metal bond cleavage, clearly suggesting an 'oxidative addition' step in the mechanism. Homolytic oxidative scission of the diruthenium(I) system in presence of BIN·HBr results in a mononuclear ruthenium(II) species incorporating one chelated BIN and two carbonyl ligands. Two incipient vacant sites are subsequently occupied by one bromide from NHC precursor and an adventitious water molecule providing **1**.

Detail of the molecular structure was established by single crystal X-ray diffraction studies. Molecular structure of the complex **1**, as depicted in Fig. 2, reveals the chelate binding of the ligand involving carbene carbon and nitrogen atom of the naphthyridine unit. The Ru1–C23 and Ru1–N2 bond distances of the C^N BIN are 2.013(5) Å and 2.194(4) Å. The octahedral coordination sphere about ruthenium atom is fulfilled by a bromide and two carbonyl ligands, while the sixth position is occupied by a water molecule. The water molecule occupies the position *trans* to the carbene carbon atom (C23) with a Ru–O distance of 2.158(3) Å which is



**Fig. 2.** ORTEP diagram (50% probability thermal ellipsoid) of the cationic unit [Ru  $(CO)_2(\kappa^2C,N-BIN)(H_2O)Br|^+$  in compound **1** with important atoms labeled. Hydrogen atoms omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ru1–C23 2.013(5), Ru1–N2 2.194(4), Ru1–O3 2.158(3), Ru1–Br1 2.5151(7), Ru1–C1 1.901(6), Ru1–C2 1.892(5), N3–C23 1.374(6), N4–C23 1.348(6), N2–C17 1.361(6), N2–C20 1.332(6), N1–C12 1.329(6), N3–C20 1.405(6), N3–C21 1.392(6), N4–C22 1.399(7), N4–C24 1.453(7), C1–O1 1.118(7), C2–O2 1.122(6). N4–C23–N3 104.5(4), C2–Ru1–C1 90.5(2), C2–Ru1–C23 97.7(2), C1–Ru1–C23 92.89(19), C1–Ru1–O3 93.06(18), C2–Ru1–O3 90.66(18), C23–Ru1–O3 169.69(16), C23–Ru1–N2 77.20(17), C23–Ru1–Br1 91.08(12), O3–Ru1–Br1 83.37(10), C20–N2–C17 117.0(4), C12–N1–C17 118.0(4), C23–N3–C20 128.8(4), N2–C20–N3 114.3(4), N1–C17–N2 115.9(4). Dihedral Angles (deg): N2–C20–N3–C23 1.8(6), Ru1–C23–N4–C24 0.6(8).

comparable with other Ru<sup>II</sup>-aqua complexes carrying NHC-ligands [25].

All ligand protons have been assigned in the <sup>1</sup>H NMR spectra for complex **1**. Protons of the coordinated BIN show marginal shifts reflecting its coordination to the metal. The methylene protons undergo geminal coupling (<sup>2</sup>J<sub>HH</sub> = 16 Hz), appearing as a doublet of doublet at  $\delta$  5.55 ppm with characteristic 'roof' shape, which indicate their inequivalent chemical environment. The <sup>13</sup>C NMR signal corresponding to the carbene carbon atom (NC<sub>Im</sub>N) undergoes considerable downfield shift, appearing at 178.9 ppm. Such a large shift ( $\Delta\delta$  42.7 ppm) is credited to the highly deshielded chemical shielding tensor associated with the diamino carbenes [26]. Two carbonyl carbon atoms resonate at 194.2 and 187.3 ppm. The ESI-MS spectrum of **1** reveals the molecular ion signal at *m*/*z* 571 (20%). The base signal which is attributed to the dehydrated molecular ion [M – H<sub>2</sub>O]<sup>+</sup> appears at *m*/*z* 553.

# 2.2. Catalysis

Ru–NHC complexes constitute an important class of molecules in the field of catalysis [27], known to catalyze numerous organic transformations such as metathesis [4], hydrogenation [7], C–H bond activation and C–C bond formation [9], tandem catalytic reactions [28], and cyclopropanation reactions of alkenes with diazo compounds [29]. Examination of the molecular structure of **1** reveals a metal-coordinated water which is trans to the carbene unit, presumably labile and offers accessible site for substrate binding. Accordingly, we evaluated the catalytic properties of **1** for



Scheme 1. Synthesis of  $[Ru(CO)_2(\kappa^2C,N-BIN)(H_2O)Br][OTf]$  (1).

#### Table 1

Transfer hydrogenation reaction of ketones catalyzed by 1.ª



Entry	Ketone	Yield (%) <sup>b</sup>
1	Benzophenone	85
2	Acetophenone	83
3	2-Methylacetophenone	80
4	4-Methoxyacetophenone	79
5	3-Nitroacetophenone	77
6	2,4-Dimethoxyacetophenone	77
7	2-Fluroacetophenone	76
8 <sup>c</sup>	Acetylthiazole	65
9 <sup>c</sup>	Acetylpyridine	59
10 <sup>d</sup>	Acetylpyrrole	<1

 $^a$  Reaction conditions: 1 mmol substrate, 1 mol% 1, 0.5 mL 0.1 M KOH in  $^i$  PrOH, 30 °C, 5 h, unless mentioned otherwise.

<sup>b</sup> Isolated yield.

<sup>c</sup> 12 h, 80 °C.

<sup>d</sup> 24 h, 80 °C.

transfer hydrogenation reaction and carbene-transfer reactions. The results are discussed in the preceding sections.

#### 2.2.1. Catalytic transfer hydrogenation reaction

Complex **1** showed moderate activity in the transfer hydrogenation reaction of aromatic and heteroaromatic ketones to the corresponding secondary alcohols from <sup>i</sup>PrOH/KOH at room temperature. For aromatic ketones, yields exceed 75% irrespective of the substituents on the phenyl groups (entries 1–7, Table 1). The catalyst exhibits diminished activity towards the heteroaromatic ketones; acetylpyridine and acetylthiazole afforded moderate yields (55–65%) at elevated temperature (entries 8 and 9). No conversion was observed for acetylpyrrole (entry 10) even after prolonged heating.

# 2.2.2. Carbene-transfer reactions

Transition metal—catalyzed transfer of carbene moiety from an aliphatic diazo source to organic substrates has received considerable interests in the last few decades [30]. These reactions are mostly catalyzed by rhodium and copper catalysts [31]. Recently Ru<sup>II</sup>–NHC complexes found their applications in this field, though the studies are limited to cyclopropanation reactions. We subjected complex **1** for the carbene-transfer reactions from ethyl diazoacetate (EDA).

To examine the reactivity of **1** towards EDA, the latter was added to a methylene chloride solution of **1** resulting in the rapid formation of the olefins diethyl maleate and diethyl fumarate in 80:20 ratio (Scheme 2). Complete decomposition of EDA was observed in less than 2 h (EDA/catalyst **1**: 100/1). In the absence of **1**, no dimer formed and the chlorinated product ethyl 1,2-dichloropropanoate was observed after 16 h of stirring. This observation is consistent with the formation of metal—carbene adduct from EDA with the extrusion of nitrogen. Furthermore, observed selectivity in the olefin products is indicative of possible stereoselectivity in the product from the carbene-transfer reactions catalyzed by **1**.

#### 2.2.3. Cyclopropanation of olefins

Reaction of EDA with alkene is among the conventional reactions to evaluate the efficiency of the catalysis in carbene-transfer reactions. Room temperature addition of a 1.5 mmol of EDA to a dichlormethane solution of **1** (1 mol%) and substituted olefins (10 mmol) resulted in the formation of the cis and trans cyclopropanes (Scheme 3, Table 2). Dilute EDA solution and excess olefins were added to minimize the dimerization of EDA relative to the desired cyclopropane products. Products were identified by GC and <sup>1</sup>H NMR, and yields were obtained by isolation of the products or by integration of peaks in the GC traces relative to that of an internal standard.

Styrene gave moderate cyclopropanation yield (60%) in 6 h (entry 1). Substituted styrenes containing electron donating substituent provided slightly better conversion (entries 2 and 3) compared to those containing electron withdrawing substituent (entry 4). The  $\beta$ -substituted styrenes were also examined for cyclopropanations.  $\beta$ -Methylstyrene (entry 5) afforded a conversion similar to styrene derivatives; whereas, cinnamonitrlie (entry 6) gave very poor conversion (<5%). Even a longer duration and higher temperature did not improve the conversion. Among all compounds studied in this work, ethyl vinyl ether afforded the best conversion (90%) (entry 7) though the selectivity is poor (55:45). The cyclic aliphatic alkenes had shown slightly lower reactivity (entries 8–11). Longer reaction times improved the yields only marginally. In case of the cyclic dialkene 1,5-cyclooctadiene, cyclopropanation occurred in one double bond (entry 11).



Scheme 2. Dimerization of EDA catalyzed by 1.



Scheme 3. Cyclopropanation reaction catalyzed by 1.

## Table 2

Complex 1 catalyzed cyclopropanation of alkene.<sup>a</sup>



Entry	Reactant	Product	Time (h)	Conversion <sup>b</sup>	Yield (%) <sup>c</sup>
1		COOEt	6	62	60
2	MeO	MeO	6	70	66
3			6	65	62
4	F	F-COOEt	6	59	55
5		COOEt	6	65	60
6		CN COOEt	6	<5	_
7 <sup>d</sup>		COOEt	6	90	70
8	$\bigcirc$	COOEt	8	62	55
9	$\bigcirc$	COOEt	8	58	50
10 <sup>e</sup>		COOEt	10	58	56
11	$\bigcirc$	COOEt	10	55	50

<sup>a</sup> Reaction conditions: 1.5 mmol EDA in 3 mL dichloromethane was slowly added to the mixture of 10 mmol alkene, 1 mol% 1 in 5 mL dichloromethane at 40 °C. E/Z ratio: in <sup>b</sup> Determined by GC–MS after reaction.
 <sup>c</sup> Combined yields of E and Z isomer after chromatography.

<sup>d</sup> E/Z ratio 55:45.

<sup>e</sup> E/Z ratio 60:40.

#### 2.2.4. Ylide formation and aldehyde-olefination

Aldehyde—olefination via reaction with the ylide is one of the important synthetic transformations in synthetic organic chemistry. Classically Wittig and its numerous variants are used for this process [32]. Multistep synthetic methods, low selectivity and possible epimerization of base-sensitive substrates are the major shortcomings of the ylide generation. Development of metal-mediated carbene-transfer reactions have appeared as a potential substitute for these widely used classical methods [33]. The carbene-transfer ability of **1** was tested in the aldehyde—olefination reactions. Carbenes are transferred to tertiary phosphines providing corresponding phosphorous ylides which subsequently participate in the olefination reaction. The reactions were carried out with variety of

#### Table 3

Olefination of aldehydes with EDA catalyzed by 1.<sup>a</sup>

 $\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$ 

Entry	Aldehyde	Product	Temp. (°C)	Time (h)	Conversion <sup>b</sup>	E/Z (%) <sup>c</sup>	Yield (%) <sup>c</sup>
1	O2N NO2	O <sub>2</sub> N NO <sub>2</sub> COOEt	25	1	100	99/1	95
2	0 <sub>2</sub> N	O <sub>2</sub> N COOEt	25	2	95	98/2	92
3		COOEt NO2	25	2	85	99/1	80
4	NC	NC	60	6	88	91/9	82
5	F <sub>3</sub> C	F <sub>3</sub> C COOEt	25	2	85	93/7	80
6	Br	Br	60	6	83	98/2	75
7	0	COOEt	60	6	75	92/8	73
8	ОН	COOEt	60	6	60	99/1	54

aldehydes (1 mmol) using 1.5 mmol ethyl diazoacetate (EDA), 1.2 mmol of PPh<sub>3</sub>, 1 mol% catalyst in toluene.

Treatment of benzaldehyde with EDA/PPh<sub>3</sub>/catalyst **1** in toluene at 60 °C provided ethyl cinnamate in 75% conversion after 6 h of reaction time with an E/Z ratio of 92:8. Purification of the product by silica gel column chromatography with petroleum ether/ethyl acetate (9:1 v/v) afforded 73% isolated yield (entry 7) and the product was characterized by NMR. Ethyl maleate and fumarate were also observed in GC–MS as side products resulting from the dimerization of carbene although the combined yields are less than 10%. All results are collected in Table 3.

Among the aldehydes studied, those containing electron withdrawing groups were found to be more reactive as compared to 

 Table 3 (continued)

Entry	Aldehyde	Product	Temp. (°C)	Time (h)	Conversion <sup>b</sup>	E/Z (%) <sup>c</sup>	Yield (%) <sup>c</sup>
9	o	COOEt	60	6	70	93/7	60
10	Me <sub>2</sub> N	Me <sub>2</sub> N COOEt	60	6	55	96/4	47
11	MeO	MeO	60	10	38	97/3	30
12	0	COOEt	60	6	~10		10

<sup>a</sup> Reaction conditions: To a stirred solution of 1 mol % complex **1**, 1 mmol aldehyde, and 1.2 mmol of Ph<sub>3</sub>P in 5 mL of toluene at room temperature was added drop-wise a solution of 1.5 mmol of EDA in 3 mL of toluene.

<sup>b</sup> Determined by GC-MS after reaction.

<sup>c</sup> Combined yields of E and Z isomer after chromatography.



Scheme 4. Reaction of p-nitrobenzaldehyde with EDA in absence of 1.

aldehydes with electron donating groups. Incorporation of nitro groups in aromatic ring provided higher yield and E-selectivity. Quantitative conversion (100%) of product was achieved for 2,4-dinitrobenzaldehyde (entry 1) at ambient temperature in 1 h with excellent selectivity (99:1). Similar conversion and selectivity was also observed for p-nitrobenzaldehyde (entry 2). o-Nitrobenzaldehyde and p-trifluoromethylbenzaldehyde showed similar conversion (85%) with slightly less E-selectivity for the later (93:7) (entries 3 and 5). Only 53% conversion was achieved for p-cyanobenzaldehyde at room temperature; increase of temperature and reaction time drastically improved conversion to 88% (entry 4). Electron-rich aldehyde exhibited reduced reactivity. Lower conversions (<70%) were observed for o-hydroxy, p-tolyl and p-(N,N-dimethyl)aminobenzaldehyde after 6 h of reaction time and at elevated temperature (60 °C) (entries 8, 9, 10). p-methoxybenzaldehyde (entry 11) was found to be the least reactive among the aromatic aldehydes, and the reaction could be completed only after prolonged reaction time (10 h). Excellent E-selectivities were observed in every case. The aliphatic aldehyde 2-phenylacetaldehyde was found to be inactive and only  $\sim 10\%$  conversion was observed (entry 12).

The presence of triphenylphosphine was found to be essential for this reaction. No olefin was observed in absence of triphenylphosphine. Invariably, the formation of triphenylphosphine oxide was observed from GC–MS. The reaction is catalytic since no olefination product was observed without the application of the catalyst under identical conditions. Azine was identified as the only product when p-nitrobenzaldehyde was reacted with EDA for 2 days in absence of catalyst (Scheme 4).

Based on this information, a catalytic cycle is proposed in Scheme 5 [33d]. In the initial step, EDA reacts with the ruthenium (II) catalyst **1** and forms a metal-carbenoid intermediate [ $Ru^{II} = CH$  (COOEt)] with the extrusion of N<sub>2</sub>. In the next step, the incipient

carbene is transferred to the phosphine resulting in the phosphorane,  $Ph_3P = CHCOOEt$ . The ylide then undergoes Wittig type reaction with aldehyde to produce the new olefin and phosphine oxide. The intermediacy of the phosphorane is confirmed by a controlled experiment, where the phosphorane was identified by <sup>31</sup>P NMR spectroscopy in absence of aldehyde. Involvement of the Wittig type reaction in the process also explains the higher reactivity of the electron deficient aldehydes which make the carbonyl carbon more electronegative facilitating the nucleophilic attack of the ylide carbon to aldehyde. It should be pointed out that the formation of ylide that is catalyzed and not the subsequent Wittig reaction.

### 2.2.5. Carbene insertion into N–H and O–H bonds

Transition metal-mediated insertion reaction of carbenes into polar N–H and O–H bonds have become a convenient method for



Scheme 5. Mechanism for Ru(II) catalyzed aldehyde olefination reaction.

N-H Insertion 
$$R_1 \xrightarrow{H} R_2 + H \xrightarrow{N_2} CO_2Et \xrightarrow{1 \mod \% 1} DCM \xrightarrow{R_1} CO_2Et$$

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...

α-aminocarboxylicacid ester

O-H Insertion 
$$R_1 \xrightarrow{O} H \xrightarrow{+} H \xrightarrow{N_2} CO_2Et \xrightarrow{1 \mod \% 1} DCM \xrightarrow{R_1} O \xrightarrow{CO_2Et} CO_2Et$$

Scheme 6. Carbene insertion reaction into N–H and O–H bonds catalyzed by 1.

#### Table 4

Complex 1 catalyzed insertion of carbene into N-H and O-H bonds.<sup>a</sup>





<sup>a</sup> Reaction conditions: 1.5 mmol EDA in 3 mL dichloromethane was slowly added to the mixture of 1 mmol amine or alcohol, 1 mol% 1 in 5 mL dichloromethane at 40 °C and the reaction was continued for 6 h.

the synthesis of  $\alpha$ -amino and  $\alpha$ -alkoxycarboxylic acid derivatives [34]. The N–H bonds of aromatic and aliphatic amine, as well as the O–H bonds of aliphatic alcohols, were functionalized. The reactions were carried out with variety of primary/secondary amines and alcohols (1 mmol) using 1.5 mmol ethyl diazoacetate (EDA) and 1 mol% catalyst in DCM (Scheme 6).

The results are collected in Table 4. This reaction was found to be excellent for aromatic amines and aliphatic alcohols. The insertions of EDA into the N–H bond of primary aromatic amines (entries 1, 2 and 3) and that into O–H bond of primary aliphatic alcohols (entries 7 and 8) were found to be very high exceeding 90%. Aliphatic secondary amines (entries 4 and 5) and alcohols (entry 9) show relatively less activity with a conversion ~80%, while benzyl amine shows least activity (entry 6).

# 3. Conclusion

We have reported a new high-yield synthetic protocol for accessing metal-NHC complex from metal-metal singly bonded dimetal precursor. Oxidative addition of the imidazolium C2–H bond into  $[Ru^{1}_{2}(CO)_{4}(CH_{3}CN)_{6}][OTf]_{2}$  afforded  $[Ru^{II}(CO)_{2}(\kappa^{2}C,N-BIN)(H_{2}O)Br][OTf]$  (1). The NHC ·HBr addition occurs at the expense of the metal-metal bond cleavage. Complex 1 exhibits good activities in catalyzing transfer hydrogenation of ketone to alcohols. It is also shown to be a carbene-transfer catalyst from EDA to various organic substrates. The best results are obtained for carbene insertion into O–H and N–H bonds of alcohols and amines.

## 4. Experimental section

## 4.1. General procedures, materials and physical measurements

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. RuCl<sub>3</sub>·H<sub>2</sub>O was purchased from Arora Matthey, India. The compounds Ru<sub>2</sub>(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>(OTf)<sub>2</sub> [35] and 1-Benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide [24] were synthesized following the literature procedure. Substrates for catalysis were purchased from commercial suppliers and used as received.

<sup>1</sup>H NMR spectra were obtained on JEOL JNM-LA 500 MHz spectrometers. <sup>1</sup>H NMR chemical shifts were 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<sup>-1</sup> on a Vertex 70 Bruker spectrophotometer. ESI-MS was recorded on a Waters Micromass Quattro

Micro triple-quadrupole mass spectrometer. ESI-MS of compound **1** was recorded in acetonitrile. GC–MS experiments were performed on an Agilent 7890A GC and 5975C MS system.

4.2. Synthesis of aqua-bromo-dicarbonyl-[1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene]ruthenium(II) trifluomethyl-sulphonate (1)

1-Benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (42 mg, 0.106 mmol) was added to a dichloromethane solution of Ru<sub>2</sub>(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>6</sub>(OTf)<sub>2</sub> (45 mg, 0.052 mmol) and stirred at room temperature for 6 h. Resulting greenish-yellow solution was concentrated under reduced pressure and diethyl ether was added to induce precipitation. The yellowish-brown solid was washed with diethyl ether and dried under vacuo. Crystals suitable for X-ray diffraction were grown by layering petroleum ether over a concentrated dichloromethane solution of the compound. Yield: 56 mg (80%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 293K): 8.998-8.976 (1H, d, J = 8.75 Hz, NP), 8.20 (1H, d, J = 2.3 Hz, Im), 8.07 (1H, d, J = 8.75 Hz, NP), 7.52 (s, 1H, NP), 7.434–7.33(6H, m, Im, Ph), 5.55 (2H, dd, *J* = 50 Hz, *J* = 16 Hz, methylene), 2.77 (3H, s, Me), 2.73 (3H, s, Me). <sup>13</sup>C NMR (127.7 MHz, CD<sub>3</sub>CN, 293K): 194.2 (CO), 187.3 (CO), 178.9 (NCN<sub>Im</sub>), 165.7 (NCN<sub>NP</sub>), 154.2 (NCC<sub>NP</sub>), 153.8 (NCC<sub>NP</sub>), 147.99 (CCC<sub>NP</sub>), 141.9 (CH<sub>NP</sub>), 134.7 (CH<sub>Ph</sub>), 129.1 (CH<sub>Ph</sub>), 128.6 (CH<sub>Ph</sub>), 127.3 (CH<sub>Ph</sub>), 125.9 (CH<sub>NP</sub>), 125.2 (CH<sub>Im</sub>), 120.4 (CCC<sub>NP</sub>), 119.2 (CH<sub>NP</sub>), 110.7 (CH<sub>Im</sub>), 54.5 (CH<sub>2</sub>Ph), 24.8 (CH<sub>3</sub>), 17.5 (CH<sub>3</sub>). IR (KBr) data (cm<sup>-1</sup>): v(CO): 2073 (s), 2011 (s),; v(OTf): 1257. ESI-MS, m/z (fragment): 594 [M-H<sub>2</sub>O + CH<sub>3</sub>CN]<sup>+</sup>, 571 [M]<sup>+</sup>, 553  $[M - H_2O]^+$ , 525  $[M - H_2O - CO]^+$  where M is Ru(CO)<sub>2</sub>(BIN)(H<sub>2</sub>O)Br. Anal. Calcd for C23H20N4F3SO6BrRu: C, 38.45; H, 2.80; N, 7.80. Found: C, 38.55; H, 2.97; N, 7.87.

## 4.3. General procedures for catalysis

#### 4.3.1. Transfer hydrogenation

Aromatic ketone (1 mmol) and **1** (0.01 mmol) were placed in a Schlenk flask and the vessel was flushed with nitrogen. 12 mL 2-propanol was added to the mixture and stirred for 5 min. 0.5 mL of 0.1 M KOH in 2-propanol was added to the mixture. Reaction was continued under the conditions mentioned in Table 1. After completion of reaction, as monitored by GC, the reaction mixture was evaporated and the crude product was purified by silica gel column chromatography using 10% ethyl acetate/petroleum ether.

# 4.3.2. Cyclopropanation reaction

3 mL dichloromethane solution of EDA (1.5 mmol, 0.14 mL) was added drop-wise to the mixture of alkene (10 mmol) and catalyst **1** (0.01 mmol) in dichloromethane under nitrogen atmosphere over a period of 30 min. Then the solution was stirred for 6 h at room temperature. The progress of the reaction was monitored by GC. After the reaction was over, the reaction mixture was extracted with diethyl ether (3 × 20 mL). The ethereal solution was washed with brine (3 × 10 mL) and dried over MgSO<sub>4</sub> and filtered. After removing the solvent under vacuum, the product was purified by chromatography on a silica gel column using a mixture hexane/EtOAc as eluent.

#### 4.3.3. Aldehyde–olefination reaction

3 mL toluene solution of EDA (1.5 mmol, 0.14 mL) was added drop-wise to the mixture of triphenylphosphine (1.2 mmol, 314 mg), aldehyde (1 mmol) and catalyst **1** (0.01 mmol) in toluene over a period of 30 min under nitrogen atmosphere. The reactions were performed under the conditions mentioned in Table 3. The progress of the reaction was monitored by GC. After the reaction was over, the resulting mixture was cooled to room temperature, then it was extracted with diethyl ether (3  $\times$  20 mL). The ethereal solution was washed with brine (3  $\times$  10 mL) and dried over MgSO<sub>4</sub> and filtered. After removing the solvent under vacuum, the product was purified by chromatography on a silica gel column using a mixture hexane/EtOAc as eluent.

# 4.3.4. N–C bond formation

3 mL dichloromethane solution of EDA (1.5 mmol, 0.14 mL) was drop-wise added to the mixture of amine (1 mmol) and catalyst **1** (0.01 mmol) in dichloromethane under nitrogen atmosphere over a period of 30 min. Then the solution was stirred for 6 h at 40 °C. The progress of the reaction was monitored by GC. After the reaction was over, the reaction mixture was extracted with diethyl ether (3  $\times$  20 mL). The ethereal solution was washed with brine (3  $\times$  10 mL) and dried over MgSO<sub>4</sub> and filtered. After removing the solvent under vacuum, the product was purified by chromatography on a silica gel column using a mixture hexane/EtOAc as eluent.

# 4.3.5. O–C bond formation

3 mL dichloromethane solution of EDA (1.5 mmol, 0.14 mL) was drop-wise added to the mixture of alcohol (1 mmol) and catalyst **1** (0.01 mmol) in dichloromethane under nitrogen atmosphere over a period of 30 min. Then the solution was stirred for 6 h at 40 °C. The progress of the reaction was monitored by GC. After the reaction was over, the reaction mixture was extracted with diethyl ether (3 × 20 mL). The ethereal solution was washed with brine (3 × 10 mL) and dried over MgSO<sub>4</sub> and filtered. After removing the solvent under vacuum, the product was purified by chromatography on a silica gel column using a mixture hexane/EtOAc as eluent.

## 4.4. X-ray data collections 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-K $\alpha$  radiation ( $\lambda_{\alpha}$  = 0.71073 Å). The frames were indexed, integrated and scaled using SMART and SAINT software package [36], and the data were corrected for absorption using the SADABS program [37]. The

Table	25
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Crystallographic data and	pertinent refinement	parameters for <b>1</b> .

Empirical formula	C <sub>23</sub> H <sub>18</sub> BrF <sub>3</sub> N <sub>4</sub> O <sub>6</sub> SRu
Formula weight	716.45
Crystal system	Triclinic
Space group	P-1
a (Å)	8.2654(7)
b (Å)	10.2658(9)
<i>c</i> (Å)	16.3288(14)
$\alpha$ (deg)	95.5860(10)
$\beta$ (deg)	91.7690(10)
$\gamma$ (deg)	107.6390(10)
$V(Å^3)$	1311.4(2)
Ζ	2
$\rho_{\text{calcd}}$ (g cm <sup>-3)</sup>	1.814
$\mu ({\rm mm}^{-1})$	2.269
F(000)	708
Reflections	
Collected	11700
Independent	6247
Observed $[I > 2\sigma(I)]$	5127
No. of variables	354
GooF	1.102
R <sub>int</sub>	0.0242
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0480$
	$wR_2 = 0.1235$
R indices (all data) <sup>a</sup>	$R_1 = 0.0644$
• •	$wR_2 = 0.1542$

 $\label{eq:rescaled} ^a \ R_1 = \Sigma \|F_o| - |F_c\|/\Sigma |F_o| \ \text{with} \ F_o^2 > 2\sigma(F_o^2). \ \text{w} \\ R_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma |F_o^2|^2]^{1/2}.$ 

structures were solved and refined using SHELX suite of programs [38] while additional crystallographic calculations were performed by the programs PLATON [39]. Figures were drawn using ORTEP32 [40]. 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 of the coordinated water molecule were not included in the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data and pertinent refinement parameters for **1** are presented in Table 5.

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# Appendix A. Supplementary material

CCDC-793941 contains the supplementary crystallographic data for compound **1**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

#### Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.11.003.

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