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ARTICLE

A Bromo-Capped Diruthenium(I,I) N-Heterocyclic Carbene Compound for *in situ* Bromine Generation with NBS: Catalytic Olefin Aziridination Reactions[ξ]

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A bromo-capped metal-metal bonded diruthenium (I,I) complex $Ru_2(CO)_4(PIN)_2Br_2$ (**1**) (PIN = 1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene) generates bromine with N-bromosuccinimide (NBS) at room temperature. Cycloalkene and stilbene are readily brominated by stoichiometric reactions with **1** and NBS. Analysis of the dibrominated products suggests the formation of cyclic bromonium intermediates indicating *in situ* Br_2 generation. Complex **2**, an iodide analogue of **1**, is also synthesized. Reaction of **2** with N-iodosuccinimide releases I_2, which is confirmed by the starch-iodine test. The catalytic utility of **1** is examined for bromination of phenol. Catalyst **1**, in combination with NBS and base, exhibits regioselectivity towards monobrominated products. Furthermore, efficient olefin aziridination is demonstrated utilizing catalyst **1** in the presence of NBS, K_2CO_3 and $TsNH_2$.

Introduction

Bromination of organic substrates is an important reaction in synthetic chemistry laboratory and in pharmaceutical industries. Traditionally molecular bromine has been used for bromination of various aromatic and aliphatic organic compounds.[1] In order to avoid the use of hazardous liquid bromine, several alternative methods have been developed.[2] Bromine carrying agents[3] (derivatives of pyridiniumperbromide, pentylpyridiniumtribromide, ammonium tribromide, N-bromosuccinimide) and oxidative brominating reagents[4] (H_2O_2-HBr, oxone-NaBr, $NaBrO_3$-NaBr) have conveniently replaced the direct use of molecular bromine. N-bromosuccinimide (NBS) is particularly useful because of its easy availablity and safe handling procedure. However, NBS and its derivatives often require activating agents to be effective especially for less reactive substrates.[5] NBS in combination with Bronsted acids[6] (like H_2SO_4, HCl, HBr), superacids[7] (CF_3SO_3H and BF_3-H_2O), silica supported heterogenous surfaces[8] (Amberlyst-15, $NaHSO_4$, $NaHCO_3$, and sulfonic acid functionalized silica) and Lewis acids[3h,9] ($Mg(ClO_4)_2$, LiBr, $FeCl_3$ and metal triflates) have been successfully employed for bromination reactions.

The aziridine motif is an important entity in organic chemistry.[10] It is a strained three-membered N-containing heterocycle widely used for the synthesis of versatile organic compounds of biological importance such as functionalized amines, β-lactams, amino acids, and natural products.[11] However, direct and convenient methods for aziridine synthesis are very few. Traditional routes require the pre-formation of imines or activation of alkene which necessarily increase the number of steps. Transition metal-catalysed olefin aziridination involves the use of nitrene precursors (e.g., iminophenyliodinanes such as TsN=IPh, or *in situ* variants).[12] Dirhodium(II,II) complexes catalyse such nitrene transfer reactions.[13] However, this protocol suffers from several drawbacks that include high catalyst loadings, use of expensive and limited shelf-life TsN=IPh, competing C-H insertion, poor selectivity and generation of iodobenzene and oxygenated hydrocarbons as by-products. Sharpless developed an effiecient bromine catalysed olefin aziridination using phenyltrimethylammonium tribromide as the brominating reagent.[14] Later Sudalai employed NBS as the bromine source for olefin aziridination.[15] Bromoamidation of olefins with $TsNH_2$ and NBS was achieved using catalytic amount of various Lewis acids.[16] Doyle's group reported an efficient and selective synthesis of aziridine by means of NBS activation with mixed-valent Rh_2(caprolactamate)$_4$Br.[17] This work prompted us to assess the efficacy of a metal-metal bonded diruthenium(I,I) complex for Lewis acid activation of NBS.

Metal dimers containing direct metal-metal bonds are increasingly being used to catalyse organic transformation reactions.[18] Metal-metal bonded species are also implicated as intermediates in catalytic reactions which were originally

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ξ Dedicated to Professor Kim R Dunbar on the occasion of her 60th Birthday

‡ G.S. and P.P. contributed equally to this work

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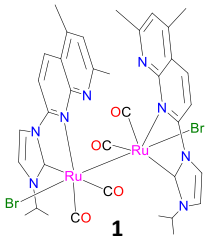
thought to involve single-metal species throughout.[19] Depending on the catalyst design and the nature of the reagents, reactions take place on equatorial platform or at site *trans* to the metal-metal bond.[20] Dirhodium(II,II) complexes are a prominent class of metal-metal bonded compounds which catalyse carbene and nitrene transfer reactions.[13] The reaction proceeds through the intermediacy of [Rh-Rh]=CR_2 or [Rh-Rh]=NR where the second Rh acts as a metallo-ligand. Berry offered a 2c-3e model to account for the higher electrophilicity advanced by the second metal.[21] Davies and Dikarev compared the reactivity of Rh/Rh vs Rh/Bi systems for styrene cyclopropanation and revealed higher reactivity of the Rh/Rh attributed to stronger metal-metal interaction.[22] We previously demonstrated a parallel carbene transfer chemistry using an isoelectronic diruthenium(I,I) complex wrapped with chelate-bound N-heterocyclic carbene (NHC) ligands at equatorial sites.[23] In this report, we examine the utility of the diruthenium(I,I) complex to generate bromine with NBS and its ability to catalyse bromine-mediated olefin aziridination reactions.

Results and discussion

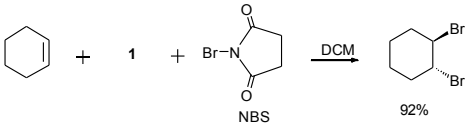
Compound 1 and olefin bromination with NBS

The 1,8-naphthyridine functionalized NHC-ligand precursor (**PIN.HBr**) was synthesized by quaternization of 2-imidazolyl-1,8-naphthyridine with isopropyl bromide. Treatment of **PIN.HBr** with $Ru_2(CH_3COO)_2(CO)_4$ in acetonitrile at room temperature provided the complex $Ru_2(CO)_4(\kappa^2C_2,N_1\text{-PIN})_2Br_2$ (**1**). Detailed characterization and structural description of **1** have been reported elsewhere.[23] Complex **1** (Scheme 1) consists of an unsupported metal-metal singly-bonded $[Ru(CO)_2]_2$ core stabilized by two chelate-bound PIN ligands, and two bromides occupy sites trans to the Ru-Ru bond.



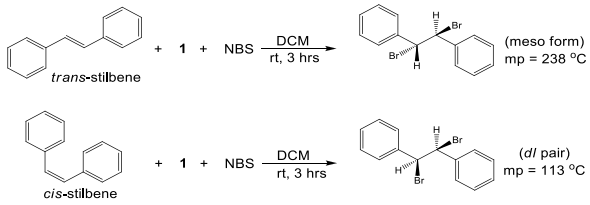
Scheme 1 Structure of diruthenium complex **1**.

The organobromine compounds are ideal bromine source in the presence of an activating agent. Complex **1** and NBS were reacted in stoichiometric amounts with olefins and the products are analyzed. Upon reaction of 0.50 mmol cyclohexene with 0.51 mmol of NBS and 0.50 mmol of complex **1** in dichloromethane, stereoselective *trans*-brominated product was obtained in 92% yield (Scheme 2). Two bromine atoms add to the opposite faces of the alkene across the double bond indicating the involvement of a cyclic bromonium ion intermediate. The dibromo product suggests *in situ* Br_2 generation as opposed to $Br^{\cdot}$ radical which would have given the allylic bromination product.[24]



Scheme 2 Stoichiometric reaction of **1** with NBS and cyclohexene.

In another experiment, complex **1** (0.5 mmol) was reacted in stoichiometric amount with *cis*- and *trans*-stilbene (0.5 mmol) in presence of NBS (0.51 mmol). *cis*-stilbene gave *d,l* stereoisomers 1,2-dibromo1,2-diphenylethane whereas meso-1,2-dibromo1,2-diphenylethane was obtained from bromination of *trans*-stilbene (Scheme 3). The melting points of *d,l* (rac) and meso forms of dibrominated stilbene are very different and that was used as a physical parameter for their identification. Melting point of *d,l* (rac) pair and meso form were observed to be 113 °C and 238 °C respectively. The *d,l* (rac) pair was also confirmed by HPLC (Fig. S6). Formation of different dibrominated products could be explained by invoking the intermediacy of a cyclic bromonium ion, which in turn suggests *in situ* Br_2 generation.



Scheme 3 Stereoselective dibrominated products from *trans*- and *cis*-stilbene.

In situ Generation of Iodine from an Iodide analogue of 1

Complex **2**, an iodide analogue of **1**, was synthesized. Reaction of ligand precursor **PIN.HI** in acetonitrile with $Ru_2(CH_3COO)_2(CO)_4$ in a 2:1 ratio afforded the complex $Ru_2(CO)_4(\kappa^2C_2,N_1\text{-PIN})_2I_2$ (**2**) in moderate yield 70%. Molecular structure of complex **2** closely resembles to that of **1** except that the axial bromides are replaced with iodides. The equatorial **PIN** and carbonyl ligands adopt a symmetrical anti-staggered conformation about the Ru–Ru bond. Only half of the molecule is located in the asymmetric unit (see, Fig. S4, for X-ray structure). The ^{1}H NMR spectrum of **2** shows a complex pattern probably because of the presence of different rotamers,[25] caused by the free rotation in solution along the unbridged metal-metal bond. The carbene carbon resonates at δ 173.2 ppm in the ^{13}C NMR spectrum (Fig. S2). ESI-MS of **2** exhibits a signal at *m/z* 947.0106, assigned for species $[M–CO–I]^+$ where M is $Ru_2(CO)_4(PIN)_2I_2$ (Fig. S3). Reaction of complex **2** with N-iodosuccinimide (NIS) led to I_2 generation that was confirmed by iodine-starch test. A dark blue color appeared upon addition of the starch solution to the reaction mixture. When tetrabutylammoniumiodide (Bu_4NI), a source of iodide, was reacted with NIS in presence of starch solution,

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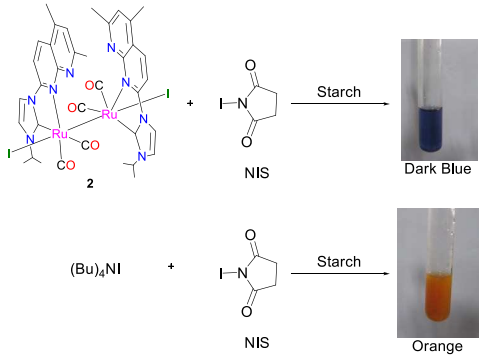
blue color was not observed (Scheme 4). Evidently, an iodide anion is not adequate to generate I_2 with NIS, rather a Lewis acidic metal center is required.

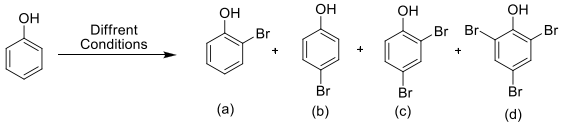


Scheme 4 Generation of I_2 from NIS and **2**.

Catalytic Studies

Bromination of Phenol. With a handful of evidences for *in situ* Br_2 generation under stoichiometric conditions, complex **1** was further evaluated for catalytic phenol bromination. Bromophenols are the key intermediates for various naturally occurring biologically active compounds and are also important for the synthesis of industrial chemicals.[26] The classical methods involve direct electrophilic bromination by molecular bromine or NBS in combination with additives.[27] Many of these methods suffer from several drawbacks such as the use of toxic reagents, harsh reaction conditions, low yields, and low chemo- and regioselectivity. Catalytic phenol bromination was carried out under different relevant conditions and the results are compared in Table 1 (Fig. S7a-d). Use of NBS and base in the absence of catalyst **1** led to only 15% conversion (entry 1). When liquid bromine was used, the reaction was fast and non-selective. The *para*-substituted and polybrominated products were major with *ortho*-bromophenol as minor product (entry 2). When 0.5 mmol of phenol was reacted with 1.0 mmol of NBS and 1.1 mmol of K_2CO_3 in presence of catalytic amount of complex **1** (5 mol%), mono-, di- and tribrominated products were observed in the ratio 69:11:20 (entry 3). Interestingly, in absence of base, the overall conversion was high with tribrominated compound as the major product (36%) (entry 4). Bromination of phenol *via* electrophilic substitution generates a molecule of HBr. In absence of base, the liberated catalytic amount of HBr activates NBS to produce Br_2 resulting in polybrominated product. Thus, catalyst **1** appears to facilitate controlled and regioselective bromination by slow generation of Br_2 in presence of base. It should be noted here that in addition to *in situ* Br_2 generation from NBS and **1**, there is another possibility of **1**-catalysed direct transfer of Br from NBS to phenol.

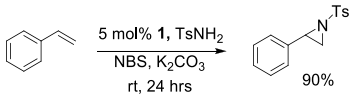
Table 1 Bromination of Phenol.



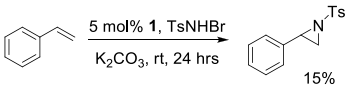
Entry	Different Conditions[a]	Total Conversion(%)	Product Distribution (%)[b]			
			(a)	(b)	(c)	(d)
1.	NBS (2.0 equiv.), K_2CO_3 (2.1 equiv.), 4 hrs	15	8	0	7	0
2.	Liq. Br_2, (2.1 equiv.), 3 hrs	96	4	24	39	29
3.	**1** (5 mol%), NBS (2.0 equiv.), K_2CO_3 (2.1 equiv.), 4 hrs	81	20	36	9	16
4.	**1** (5 mol%), NBS (2.0 equiv.), 4 hrs	97	15	24	22	36

[a] 1.0 equivalent of phenol is used; [b] Conversion determined by GC-MS.

Olefin Aziridination. Further, complex **1** was evaluated for aziridination of styrene at 5 mol% catalyst loading in the presence of *p*-toluene sulfonamide ($TsNH_2$) (0.5 mmol), NBS (0.5 mmol) and K_2CO_3 (1.1 mmol), which afforded the corresponding aziridine in 90% yield after 24 hrs (Scheme 5). In absence of the catalyst, 17% yield was obtained after 48 hrs. When catalyst **1** is reacted with TsNHBr in place of $TsNH_2$ and NBS, only 15% yield of the aziridine was observed (Scheme 6).



Scheme 5 Aziridination of olefins catalysed by **1**.



Scheme 6 Olefin aziridination reaction with TsNHBr.

To assess the influence of the equatorial and capping ligands, related diruthenium catalysts are also evaluated (Table S2). Axial bromides are removed from **1** by the use of $TlBF_4$ in acetonitrile solution (1:2 molar ratio) and the resultant solid was employed for the styrene aziridination reaction under optimized conditions. It was found that the catalyst lost its activity and gave only 18% yield. The acetate-bridged $Ru_2(CH_3COO)_2(CO)_4$ (**3**) gave 20% yield which is no better than the 17% yield achieved in absence of the catalyst. A bridge-chelate complex $Ru_2(CO)_4(OAc)(BIN)Br$ (**4**)[23] with one axial bromide gave 76% yield (Scheme 7). These observations reveal the importance of the axial bromides and the role of the

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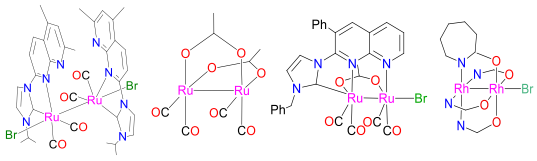
ancillary ligands for the catalytic activity. A mixed-valent dirhodium(II,III) catalyst **5**, generated *in situ* from the reaction of Rh_2(caprolactamate)$_4$ with NBS, featuring an axial bromide, catalyses olefin aziridination reaction. In contrast, the isoelctronic **1** is unsupported and unlikely to involve a mixed-valent species in the catalytic cycle.

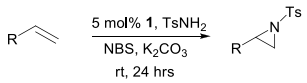


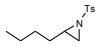
Scheme 7 Catalyst screening for olefin aziridination reaction.

Substrate scope

Catalyst **1** was evaluated for bromine catalysed aziridination using a wide range of olefins under optimized conditions and the results are summarized in Table 2. Both electron rich and electron deficeint aromatic olefins afforded high yields 85-92% (entries 2-5). Substitution patterns on the aromatic ring did not show any significant effect on the product formation - similar yields were obtained for *p/m*-methyl and *o/p*-fluorostyrenes. For *trans*-*β*-methylstyrene, the corresponding aziridine was obtained in 86% yield (entry 6). A polycyclic aromatic olefin was also examined to give moderate yield 60% (entry 7). The aziridination reaction was further extended to aliphatic olefins. Compared to the aromatic olefins, the aliphatic olefins gave lesser yields. Linear alkenes with different chain lengths afforded the corresponding aziridines (Yields: 77-80%, entries 8-10). Notably, cyclohexene and cyclooctene afforded the desired products without allylic amination (entries 11 and 12). For 1,5-cyclooctadiene, only one double bond underwent aziridination reaction and the product was obtained in modest yield of 60% (entry 13).

Table 2 Complex **1** catalysed aziridination of olefins[a].

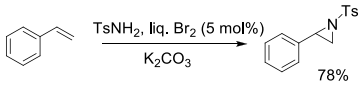


Entry	Substrate	Product	Yield %[b]
1.			90
2.			92
3.			88
4.			89
5.			85
6.			86[c]
7.			60
8.			78
9.			80
10.			77
11.			74
12.			80
13.			60

[a] 0.5 mmol olefin, 0.5 mmol NBS, 0.5 mmol $TSNH_2$ and 1.1 mmol K_2CO_3 in 5 ml DCM solution for 24 hrs. [b] Isolated yield. [c] Aziridine diastereoselectivity was determined by ^{1}H NMR prior to silica purification (*trans/cis*= 5:1).

Mechanistic Investigation

In order to gain insight into the reaction mechanism, a control experiment was performed where **1** and NBS were replaced with catalytic amount of liquid bromine for the model reaction. The corresponding aziridination product was isolated in 78% yield along with a small amount of 1,2-dibrominated by-product (Scheme 8). This suggests that the 'catalyst/NBS' combination acts as the source for 'positive bromine'[14a] to form a bromonium ion intermediate with olefin. Subsequent nucleophilic attack by $TsNH_2$ in presence of base followed by cyclization of the bromoamide product gives the desired aziridine. To garner evidence for bromonoium ion intermediacy, ^{1}H NMR study was performed. A 1:1 mixture of styrene and NBS in $CDCl_3$ revealed corresponding signals at δ 5.23, 5.74, 6.73 and 2.91 ppm. When 5 mol% of **1** and 1 equivalent of $TsNH_2$ were added to it, new signals at δ 3.55, 4.56, 5.21 and 7.59 ppm, characteristic of *β*–bromoamide, along with small peaks for TsNHBr[17] (δ 2.44, 7.84 ppm), appeared after 2 hrs strongly suggesting the intermediacy of a cyclic bromonium species. (Scheme S3, Fig. S8). Notably, in absence of base, the aziridine formation does not occur. Similarly, reaction with a different nucleophile NaN_3 in place of $TsNH_2$, gave the *β*–bromoazide product (Scheme 9).



Scheme 8 Olefin aziridination reaction with liquid bromine.

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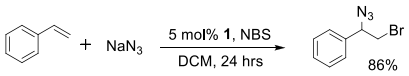
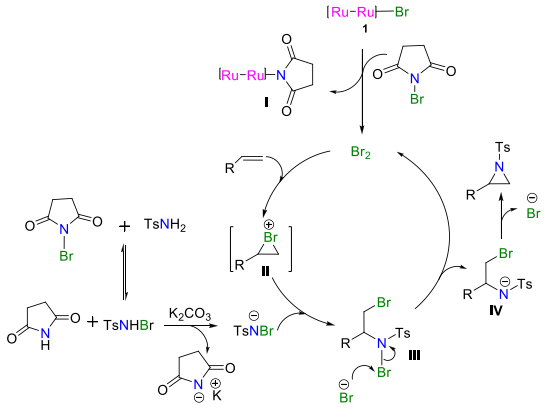


Scheme 9 Formation of the *β*-bromo azide product.

Based on the stoichiometric and control experiments described above, a bromine catalysed ionic mechanism is proposed.[14,17] At first, NBS reacts with complex **1** to generate Br_2 and **I**. The *in situ* generated Br_2 then reacts with olefin to give the cyclic bromonium ion intermediate **II**. Under the reaction conditions, NBS and $TsNH_2$ react to form an equilibrium mixture of TsNHBr and succinimide. In presence of K_2CO_3, a strong nucleophile $TsNBr^-$ is generated which attacks **II** to give the dibromo sulphonamide **III**. Attack of Br^- on the N-Br group of **III** gives an anionic intermediate **IV** with regeneration of Br_2 to close the catalytic cycle. Cyclization of **IV** gives the product with expulsion of a Br^- (Scheme 10).



Scheme 10 Proposed mechanism for bromine-mediated olefin aziridination catalysed by **1**.

An attempt was made to isolate and identify **I**. Stoichiometric reaction between complex **1** and NBS was carried out in 3 mL of dichloromethane for 3 hrs and then the reaction mixture was analyzed by ESI-MS. The ESI-MS data showed a mass peak at *m/z*: 522.0684 (z=1) which was assigned for $[M–Br]^+$ where M is $Ru(PIN)(CO)_2(C_4H_4O_2N)Br$ (Fig. 1). It is our assertion that Br_2 is oxidatively added to the Ru–Ru bond to give a mononuclear species.[28] Once Br_2 is generated by Lewis acid activation of NBS with catalyst **1**, the fate of the resulting complex does not change the catalytic cycle. This is in accordance with the proposed mechanism.

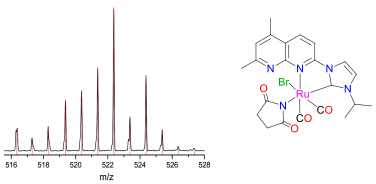


Fig. 1 Simulated (red line) and experimental mass distributions (black line) for $[M–Br]^+$ at m/z 522.0684 (z = 1) where M = $RuPIN(CO)_2(C_4H_4O_2N)Br$.

Conclusions

Development of milder brominating reagents has been considered as an important objective in green chemistry. NBS, in combination with an activating agent, is a convenient alternative to molecular bromine. Herein we show that a bromo-capped diruthenium(I,I) complex, containing metal-metal bond, activates NBS to afford 'positive bromine'. A diruthenium-iodide analog produces I_2 when reacted with NIS. It is thus likely that a parallel chemistry is operational for '**1**/NBS' combination to generate Br_2. Reactions with olefins and phenol give brominated products. Bromine catalysed olefin aziridination is achieved in the presence of base. This study reveals Lewis acid activation of NBS by a bromo-capped diruthenium compound and offers '**1**/NBS' as an effective brominating reagent.

Experimental Section

General Procedures

All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk-vessel and vacuum line techniques. NMR spectra were obtained on JEOL JNM–LA 500/400 MHz spectrometer. ^{1}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 compound was powdered, washed several times with dry diethyl ether, and dried in vacuum for at least 48 hrs prior to elemental analyses. ESI-MS were recorded on a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer. The GC-MS experiments were performed on an Agilent 7890A GC and 5975C MS. HPLC analyses were performed on Agilent 1200 series HPLC system using Daicel chiral column. Melting points were measured in open capillaries on a JSGW melting point apparatus.

Materials

Solvents were dried by conventional methods, distilled under nitrogen, and deoxygenated prior to use. $RuCl_3\ nH_2O$ (39% Ru) was purchased from Arora Matthey, India. All other chemicals were purchased from Sigma–Aldrich. The compound $Ru_2(CH_3COO)_2(CO)_4$[29] and 1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (**PIN.HBr**) were synthesized following the literature procedures.[30]

Synthesis of PIN.HI

The NP substituted NHC-ligand precursor 1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium iodide (**PIN.HI**) was obtained by the quaternization of 2-imidazolyl-1,8-naphthyridine with isopropyl iodide. In a pressure tube 300 mg (0.5 mmol) of 2-imidazolyl-5,7-dimethyl-1,8-naphthyridine and excess of isopropyl iodide (5 mL) were taken and dissolved in 5 mL of *p*-xylene. The reaction mixture was heated at 80 °C for 48 hrs. Dark gray colored precipitate appeared. The solvent was evaporated under vaccum and 20 mL of cold diethyl ether

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was added to furnish **PIN.HI** as the final product. The compund was filtered and washed with cold diethyl ether (3 X 10 mL) then dried under vacuum for 2 hrs and stored under nitrogen. Yield: 490 mg (93%). ^{1}H NMR (500 MHz, DMSO-D6, 294 K): δ 10.28 (s, 1H, Im), 8.95 (d, *J* = 9.1 Hz, 1H, NP), 8.69 (s, 1H, NP), 8.22 (d, *J* = 9.1 Hz, 1H, NP), 8.19 (s, 1H, Im), 7.52 (s, 1H, Im), 4.80 (m, 1H, CH^{i}Pr), 2.73 (s, 3H, CH_3-NP), 2.68 (s, 3H, CH_3-NP), 1.58 (d, 6H, *J* = 6.8 Hz, ^{i}Pr). ^{13}C NMR (125.8 MHz, DMSO-D6, 296.2 K): δ 164.7 (NCNNP), 153.5 (CCNNP), 147.8 (CCNNP), 139.9 (CCCNP), 135.3 (CCCNP), 124.9 (CCCNP), 122.4 (NCCIm), 121.5 (CCCNP), 120.1 (CCCNP), 112.7 (NImCC), 53.9 (CH^{i}Pr), 25.3 (CH_3NP), 22.7 ($CH_3{}^i$Pr), 18.4 (CH_3 NP). ESI–MS, *m/z*: 267.1611, (z=1),[M]$^+$.

Synthesis of 2

The ligand precursor **PIN.HI** (125 mg, 0.36 mmol) was added to an acetonitrile solution of $Ru_2(CH_3COO)_2(CO)_4$ (75 mg, 0.17 mmol). The mixture was stirred at 50 °C temperature for 48 hrs. The purple solution was concentrated under reduced pressure, and diethyl ether was added to induce precipitation. The purple precipitate was washed with diethyl ether and dried under vacuum. Crystals suitable for X-ray diffraction were grown by layering diethyl ether over a concentrated acetonitrile solution of **2** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 133 mg (70%). ^{1}H NMR (500 MHz, CD_3CN, 294 K): δ 8.86 - 8.69 (m, 1H, NP), 8.14 (s, 1H, Im), 8.02 -7.88 (m, 1H, NP), 7.52 - 7.50 (m, 1H, NP), 7.40 (s, 1H, Im), 5.86 - 5.81 and 5.52 - 5.48 (m, 1H, CH-^{i}Pr), 2.83 - 2.74 (m, 6H, CH_3-NP), 1.68 - 1.47 (m, 6H, ^{i}Pr). ^{13}C NMR (125.8 MHz, CD_3CN, 296.2 K): δ 202.9 (CO), 191.3 (CO), 173.2 (NCNIm), 166.4 (NCNNP), 155.2 (NNPCNIm), 147.8 (CCNNP), 140.3 (CCCNP), 126.3 (CCCNP), 125.6 (CCCNP), 122.7 (NCCIm), 120.8 (CCCNP),112.5 (NImCC), 111.5 (NImCC), 55.4 (CH^i*Pr*), 25.7 (CH_3 NP), 23.0 ($CH_3{}^i$Pr), 22.8 ($CH_3{}^i$Pr), 18.3 (CH_3 NP). IR (KBr, cm^{-1}): ν(CO) 2009, 1991, 1968, 1924. Anal. Calcd for $C_{36}H_{36}N_8O_4I_2Ru_2.CH_3CN$: C, 39.89; H, 3.43; N, 11.03. Found: C, 39.34; H, 3.37; N, 11.08. ESI-MS, m/z 947.0106 corresponding to [M–CO–I]$^+$, where M is $Ru_2(CO)_4(PIN)_2I_2$.

General procedure for stoichiometric reaction of olefin bromination

A mixture of olefin (0.5 mmol, 1 equiv.), **1** (0.5 mmol, 1 equiv.) and NBS (0.51 mmol, 1.0 equiv.) in 3.0 mL of dichloromethane solution was placed in an oven-dried reaction vessel. The color of the solution immediately changed to yellowish brown. The reaction vessel was capped with septum and stirred at room temperature for 3 hrs. Once the reaction is completed, the reaction mixture was diluted with ethyl acetate (EtOAc) and passed through a short column of silica and was subjected to GC-MS analysis. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography using silica (hexane/EtOAc 95/5). The isolated product was characterized by NMR spectroscopy.

General procedure for catalytic olefin aziridination

A flame dried reaction vessel equipped with a stir bar was charged with olefin (0.5 mmol, 1 equiv.), $TsNH_2$ (0.5 mmol, 1.0 equiv.), K_2CO_3 (1.05 mmol, 2.1 equiv.) and **1** (5 mol%, 0.05 equiv.) in 3.0 mL of dichloromethane solution. To the reaction mixture, NBS (0.5 mmol, 1.0 equiv.) was added and the color of the solution immediately changed to dark brown. The reaction vessel was capped with septum and stirred for 24 hrs. Completion of the reaction was monitored by TLC. After completion of reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using silica (hexane/EtOAc 95/5). The isolated product was characterized by NMR spectroscopy.

Procedure for ^{1}H NMR study

In a dry vessel, 0.15 mmol styrene and 0.15 mmol NBS were mixed together in 1.0 mL of $CDCl_3$ and stirred for 30 minutes. An aliquot of 0.5 mL was directly subjected to ^{1}H NMR spectroscopy. To the same mixture, 5 mol% **1** and 0.15 mmol $TSNH_2$ were added. After 2 hrs, an aliquot of 0.5 mL was analyzed by ^{1}H NMR.

Sub-stoichiometric reaction between complex 1 and NBS

20.0 mg (1.0 equiv) of complex **1** and 4.0 mg of NBS (1.1 equiv.) were taken in 3 mL of dry dichloromethane solution in a flame dried Schlenk tube. The reaction mixture was stirred for 3 hrs and then small aliquot of the reaction mixture was withdrawn and submitted for ESI-MS analysis.

Conflicts of interest

There are no conflicts to declare.

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