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## Introduction

Coordinatively unsaturated ruthenium complexes have received much attention due to their involvement in ruthenium catalysed organic transformations. Ruthenium can adopt a wide range of coordination geometries and oxidation states and because of this ruthenium compounds are found to be effective catalysts for a variety of organic reactions including ring closing metathesis,<sup>1</sup> C-H activation,<sup>2-4</sup> activation of carbon-carbon multiple bonds<sup>2</sup> and C-C bond formation,<sup>2</sup> Oppenauer oxidation<sup>5</sup> and transfer hydrogenation.<sup>6</sup> It has been emphasized in the literature that, 16 electron cationic species are the active catalyst. Thus, in recent years, some 16 electron cationic stable species have been isolated and characterised structurally.7-9 Ruthenium(II) phosphine complexes are widely used as catalysts for various types of organic transformations. A large number of compounds with tertiary phosphines of all types, including bi- and tridentate ones have been synthesised.<sup>10,11</sup> Ruthenium complexes with diphosphine ligands have been shown to be effective catalysts for various organic transformations.12

The structure of metal complexes plays a pivotal role on their catalytic properties. Thus, control of ligand orientation on metal centre determines the efficacy of the complexes as catalysts. Ligand controlled metal catalysis has been shown to be one of the most important factors for producing regio- and stereoselective products.<sup>13-15</sup>

Synthesis, structure and catalytic properties of

catalytically active [Ru(dppp)<sub>2</sub>Cl][BPh<sub>4</sub>]: ruthenium

The compound,  $[Ru(dppp)_2(CH_3CN)Cl][BPh_4]$  (1) has been synthesised from the precursor complex,  $[Ru(PPh_3)_3Cl_2]$ . The complex has been structurally characterised. The complex has been found to be an

efficient catalyst for the homocoupling of alkynes in the presence of silver salts. The complex can also

catalyse homocoupling of alkynes and subsequent alkyne-azide cycloaddition. The catalytically active

species,  $[Ru(dppp)_2Cl][BPh_4]$  (2) and one of the intermediate complexes,  $[Ru(dppp)_2(CCPh)_2]$  (6), have

 $[Ru(dppp)_{2}(CH_{3}CN)Cl][BPh_{4}]$  and isolation of

catalysed alkyne homocoupling and tandem

alkyne-azide cycloaddition\*

been isolated and structurally characterised.

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Diynes are useful starting materials in synthetic organic chemistry. Number of natural products having anti-bacterial, anti-cancer and anti-HIV activities contain 1,3-diyne moiety.16 Conjugated divnes afford important functional materials like non-linear optical materials and organic conducting materials.17 The coupling of terminal alkynes was first reported by Glaser and Hay, independently, which involves copper(1) as catalyst or reagents.18 Numerous studies performed on this reaction allowed its further improvements. In all these modified methods a large amount of bases like pyridine, N,N,N',N'-tetramethylethylenediamine, piperidine etc. are used.18 This was followed by reports on palladium catalysed cross coupling of 1haloalkynes and terminal alkynes.18,19 Recently complexes of iron,20a cobalt,20b nickel20c and gold20d have been used for coupling of terminal alkynes. It may be noted that, the copper catalysed reactions suffer from the use of large amount of base and the palladium catalysed reactions are not atom economical. In iron catalysed reactions extra preparation step of alkynyl Grignard is required. In nickel catalysed reaction lithium salt of alkyne is required and the catalyst loading is high. Similarly, in cobalt and gold catalysed reactions the catalyst loading is high.

Butadiyenes have been used for the synthesis of heterocycles like thiophene and triazoles and other heterocycles.<sup>21</sup> Synthesis of complex molecules by transition metal catalysed one pot tandem reactions has gained importance over last few decades. This is because such reactions are considered to be greener.<sup>22</sup>

Ruthenium complexes have been shown to catalyse head to head dimerization of alkynes to en-ynes.<sup>23</sup> Also ruthenium complexes have been found to be efficient catalysts for alkyneazide cycloaddition reaction.<sup>24</sup> It may be noted that, synthesis of



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#### Paper

4,5-disubstituted triazoles by alkyne–azide cycloaddition is rare. There are only two reports in the literature for the synthesis of alkynyl triazoles and they have been predicted to be important intermediates in pharmaceutical industries.<sup>25,26</sup> Thus we thought to design a catalytic system for tandem reaction for the preparation of alkynyl triazole. Herein we report synthesis and structure of [Ru(dppp)<sub>2</sub>(CH<sub>3</sub>CN)Cl][BPh<sub>4</sub>] (1) and first example of ruthenium catalysed Glaser–Hay<sup>18</sup> coupling of terminal alkynes and synthesis and structure of the catalytically active species, [Ru(dppp)<sub>2</sub>Cl][BPh<sub>4</sub>] (2) and isolation and structural characterization of the reaction intermediate *trans*-[Ru(dppp)<sub>2</sub>(CCPh)<sub>2</sub>] (6). The ruthenium complex, 1 has also been utilized for one pot synthesis of 4-substituted-5-alkynyl 1,2,3-trazole.

### **Results and discussion**

### Synthesis and characterization of [Ru(dppp)<sub>2</sub>(CH<sub>3</sub>CN)Cl] [BPh<sub>4</sub>] (1) and [Ru(dppp)<sub>2</sub>Cl][BPh<sub>4</sub>] (2)

The complex,  $[Ru(dppp)_2(CH_3CN)Cl][BPh_4]$  (1) has been synthesised from the reaction of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> with diphenylphosphinopropane (dppp) in 1:2.5 ratio in acetonitrile in the presence of NaBPh<sub>4</sub>. This can also be prepared form the reaction of  $RuCl_3 \cdot nH_2O$  with excess of dppp in the presence of NaBPh<sub>4</sub>. The complex, [Ru(dppp)<sub>2</sub>Cl][BPh<sub>4</sub>] (2) has been synthesised by heating a solution of 1 in toluene at 100 °C. The complexes have been characterised by elemental analyses, IR, and <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. The elemental analyses agree well with the formulations of the compounds. The <sup>1</sup>H NMR spectrum of 1 shows multiplet in the region 6.87 to 7.85 ppm due to aromatic protons. The signals for  $P-CH_2$  protons appear at 2.75 ppm (broad) and at 2.51 ppm (multiplet). The signals of -CH<sub>3</sub> protons of the acetonitrile ligand and the C-CH<sub>2</sub>-C protons appear at 2.09 ppm (broad). The <sup>31</sup>P NMR spectrum of the complex shows a singlet at 36.5 ppm. The spectral features are similar to those reported for ruthenium complexes of bidentate phosphine ligands.12 The <sup>1</sup>H NMR spectrum of 2 shows a multiplet in the region 2.57-2.63 (4H) ppm due to the methylene protons of the P-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-P moiety. The signal for methylene protons of the P-CH<sub>2</sub> group appears at, 3.26 ppm (br, 8H) and the signals for aromatic protons appear at 6.8-7.4 (m, 60H). The <sup>31</sup>P NMR spectrum of 2 shows two singlets at, 36.8 and at 47.6 ppm. In addition, a singlet appears at -0.1 ppm. This may be due to some impurity.

### Structural characterization of [Ru(dppp)<sub>2</sub>(CH<sub>3</sub>CN)Cl][BPh<sub>4</sub>] (1) and [Ru(dppp)<sub>2</sub>Cl][BPh<sub>4</sub>] (2)

The complex, **1** crystallizes in triclinic space group  $P\bar{1}$  (Table S1, ESI<sup>†</sup>). The asymmetric unit contains one cationic ruthenium complex (Fig. 1) and one tetraphenylborate anion. The ruthenium center is in a distorted octahedral coordination environment. The basal positions are occupied by four phosphorus from two dppp ligands, P1, P2, P3 and P4 {P1-Ru1 = 2.4025(15) Å; P2-Ru1 = 2.4247(14) Å; P3-Ru1 = 2.4750(14) Å; P4-Ru1 = 2.4428(15) Å}. The axial positions are occupied by one chloride, Cl1 {Cl1-Ru1 = 2.4222(13) Å} and an acetonitrile nitrogen {N1-



Fig. 1 ORTEP view of  $[Ru(dppp)_2(CH_3CN)Cl]^+$  cation in 1. Hydrogen atoms have been omitted for clarity.

 $Ru1 = 2.003(4) \text{ Å} \$  (Table S2, ESI†). The  $BPh_4^-$  anion is found outside the coordination sphere and does not show any bonding interaction with ruthenium(II) center.

The complex,  $[Ru(dppp)_2Cl][BPh_4]$  (2) crystallizes in monoclinic space group P21/a (Table S1, ESI<sup>†</sup>). The asymmetric unit consists of a complex cation,  $[Ru(dppp)_2Cl]^+$  and the anion  $BPh_4^-$  (Fig. 2). The ruthenium center is in a trigonal bypyramidal coordination environment. The basal positions are occupied by two phosphorus atoms, P1 and P3 {P1-Ru1 = 2.263(2) Å, P3-Ru1 = 2.280(2) Å} form two different dppp ligands and a chloride ion, Cl1 {Cl1-Ru1 = 2.394(2) Å}. The axial positions are occupied by two phosphors atoms, P2 and P4 {P2-Ru1 = 2.429(2) Å, P4-Ru1 = 2.416(2) Å}. The Ru1-P2 and Ru1-P4 bond distances as well as P2-Ru1-P4 bond angle {P4-Ru1-P2 = 173.11(7)°} (Table S2, ESI<sup>†</sup>) clearly shows that, the ruthenium centre is in distorted trigonal bipyramidal coordination environment.

### Studies of catalytic properties of [Ru(dppp)<sub>2</sub>(CH<sub>3</sub>CN)Cl][BPh<sub>4</sub>] (1)

Ruthenium(II) complexes have been shown to be capable of activating alkynes *via* vinylidene complex formation or  $\pi$ -complex formation towards nucleophilic addition reactions.<sup>27</sup> Also it may be noted that, ruthenium complexes of  $\eta^1$  coordinated alkynes have been reported.<sup>28</sup> We have been working on



Fig. 2 ORTEP view of  $[Ru(dppp)_2Cl]^+$  cation in 2. Hydrogen atoms have been omitted for clarity.

activation of alkyne *via* vinylidene complex and  $\pi$ -complex formation towards nucleophilic addition reactions.<sup>29</sup> We were interested in activation of alkynes by ruthenium(II) complexes *via* the formation of  $\eta^1$  coordinated alkynes.

Silver salts are known to form acetylide very easily and in number of catalytic reactions these acetylides have been used.<sup>30</sup> Thus it is expected that silver salts will react with phenylacetylene to produce silver acetylide, which in turn react with in situ generated pentacoordinated cationic ruthenium complex  $[Ru(dppp)_2Cl]^+$  to produce ruthenium coordinated  $\eta^1$  alkyne. We were interested in studying its catalytic properties towards Glaser-Hay coupling and subsequent alkyne-azide cycloaddition reaction. Thus, coupling of phenylacetylene (3a) was chosen as a model reaction. The coupling reaction of 3a was carried out in the presence of a catalytic amount of 1 (1 mol%) in the presence of silver salts (3 mol%) and air at various solvents at different temperature for the optimization of the reaction (Table 1). It has been found that, DMF is the best solvent and  $Ag(NO_3)$  is the ideal co-catalyst and the optimum temperature was found to be 90 °C. It may be noted that, the reaction carried out in degassed DMF under argon atmosphere failed to afford the desired product. Similarly, in the absence of silver salts no product formation could be detected. Also, we could not get any product from the reaction of phenylacetylene in the absence of 1 but in the presence of only  $Ag(NO_3)$ . However, reaction carried out only in the presence of 1 gives corresponding ene-yene. Thus it is clear that, presence of 1 as well as silver(I) and air is essential for the reaction.

Having established the optimum condition, we were interested in studying the scope of the reaction. Thus, a number of alkynes were subjected to the coupling reaction

Table 1 Optimization of coupling of phenyl acetylene catalyzed by 1 and  $\mathsf{Ag}(\mathsf{I})^{\alpha}$ 

<hr/>	[1] Ag(I), solvent, △			
3a		4a		

Entry	Solvent	Temp. (°C)	<i>T</i> (h)	Yield <sup><math>b</math></sup> (%)	Ag(1)
	_				
1	Toluene	90	24	—	—
2	Toluene	90	5	75	$Ag_2(CO_3)$
3	DMSO	90	5	65	$Ag_2(CO_3)$
4	DMF	90	5	87	$Ag_2(CO_3)$
5	DMF	90	2	93	Ag(OAc)
6	DMF	60	1	38	Ag(OAc)
7	DMF	90	0.5	90	Ag(OAc)
8	DMF	70	1	80	$Ag(NO_3)$
9	DMF	90	0.75	95	$Ag(NO_3)$
10	DMF	25	24	_	$Ag(NO_3)$
11	DMF	90	0.5	95	$Ag(NO_3)$
12	DMSO	90	2	75	$Ag(NO_3)$
13	DMF	90	24	_	$Ag(NO_3)^c$
14	DMF	90	24	_	$Ag(NO_3)^a$
15	DMF	90	0.5	95	$Ag(NO_3)^e$

<sup>*a*</sup> Reaction conditions: phenylacetylene (1.0 mmol), **1** (1 mol%) Ag(i) (3 mol%) in solvent (5.0 cm<sup>3</sup>). <sup>*b*</sup> Isolated. <sup>*c*</sup> In the absence of **1**. <sup>*d*</sup> Under argon atmosphere. <sup>*e*</sup> Complex **2** as catalyst instead of complex **1**.

Table 2 Homocoupling of alkynes catalyzed by 1<sup>a</sup>



 $^a$  Reaction conditions: alkyne (1.0 mmol), 1 (0.01 mmol), AgNO<sub>3</sub> (0.03 mmol), DMF (5.0 cm<sup>3</sup>), temp. (90 °C).  $^b$  Yields are isolated.

and the coupling products were isolated in good to excellent yield (Table 2).

As mentioned we were interested in tandem reaction of homocoupling of alkynes and subsequent cycloaddition reaction with azide. Accordingly, in a separate reaction first phenylacetylene was taken in DMF and to this complex 1 (2 mol%) and  $Ag(NO_3)$  (5 mol%) was added and the reaction mixture was heated for 30 min. To this was then added NaN<sub>3</sub> and the reaction mixture was heated for 8 h. The reaction mixture on usual workup afforded, 4-phenyl-5-phenylethylyne-1H-[1,2,3]triazole (5a) in 85% yield. In order to check the involvement of Ag(1) in the reaction, a separate reaction was done using isolated coupled product and NaN<sub>3</sub> in the presence of only 1 and the corresponding triazole could be isolated in good yield. In another reaction the preformed coupled product was reacted with  $NaN_3$  only in the presence of  $Ag(NO_3)$ . In this case no triazole formation could be detected. Similarly, reaction between preformed divene with NaN<sub>3</sub> in the absence of 1 failed to give any product under the employed reaction condition. Thus, it is clear that, the cycloaddition reaction is catalysed by the ruthenium complex, 1. The reaction was generalized using number of alkynes and triazoles were isolated in good yields (Table 3). It may be noted that, when alkyl azide was used instead of sodium azide, we could not detect any triazole formation. Thus it is clear that, polarity of azide is very important in this case.

### Mechanistic investigation

We next proceeded to examine the mechanism of the coupling reaction. As it has been mentioned, in solution, the complex looses the hemilabile acetonitrile ligand and forms catalytically active trigonal bipyramidal complex, [Ru(dppp)<sub>2</sub>Cl]<sup>+</sup>. A model reaction was carried out with phenyl acetylene in the presence



 $^a$  Reaction conditions: alkyne (1.0 mmol), NaN\_3 (2.0 mmol), DMF (5.0 cm³), temp. (90 °C).  $^b$  Yields are isolated.

of catalytic amount of  $[Ru(dppp)_2Cl][BPh_4]$  and we could isolate the coupled product in high yield (Table 1, entry 15). No appreciable difference between the catalytic activity of **1** and **2** could be observed. This is expected, as **1** looses  $CH_3CN$  very easily in solution to produce **2**. Thus it is clear that,  $[Ru(dppp)_2Cl]^+$  is the active species.

In order to probe the role of silver, complex **1** was treated with phenylacetylene and  $Ag(NO_3)$  in 1:2:2 ratio in DMF and the mixture was heated for 5 min. The reaction solution on standing afforded a few crystals of *trans*-[Ru(dppp)<sub>2</sub>(CCPh)<sub>2</sub>] (**6**), which has been characterised by spectroscopic techniques and single crystal X-ray crystallography (Fig. 3). In this reaction probably both *trans*- and *cis*-complexes are produced and the *trans*-product being more stable crystallizes out. Number of *trans*-bis acetylide complexes containing diphosphine ligands have been synthesised starting form *trans*-dichloro and dihydrido complexes of ruthenium.<sup>28</sup> However, in one of the reports it has been shown that, *cis*-Ru(PMe<sub>3</sub>)<sub>4</sub>Me<sub>2</sub> reacts with terminal alkynes to afford both *cis*- and *trans*-[Ru(PMe<sub>3</sub>)(CCR)<sub>2</sub>], the *trans*-product being the minor product.<sup>28a</sup> Thus it is clear that,



Fig. 3 ORTEP view of  $[Ru(dppp)_2(CCPh)_2]$  (6). Hydrogens have been omitted for clarity.

during reaction the diacetylide complexes can undergo isomerization.

The <sup>31</sup>P NMR spectrum of the complex shows a singlet at 38.3 ppm, In addition to this a singlet appear at 0.1 ppm. This may be due to some impurity (Fig. S5, ESI<sup>†</sup>).

The complex, *trans*-[Ru(dppp)<sub>2</sub>(CCPh)<sub>2</sub>] (6) crystallizes in triclinic space group  $P\bar{1}$  (Table S1, ESI<sup>†</sup>). The Ruthenium center is in a distorted octahedral coordination environment. The basal positions are occupied by four phosphorus atoms, P1, P2, P3, P4 {P1-Ru1 = 2.394(2) Å, P2-Ru1 = 2.3826(19) Å, P3-Ru1 = 2.405(2) Å, P4-Ru1 = 2.4096(19) Å} (Table 2). The axial positions are occupied by two carbon atoms, C55 and C63, of coordinated phenyl acetylene {C55-Ru1 = 2.041(7) Å, C63-Ru1 = 2.037(7) Å}.

In a separate reaction, **1** was treated with phenyl acetylene and Ag(NO<sub>3</sub>) in DMF in 1 : 2 : 2 ratio and was heated for 5 min and the reaction was quenched by the addition of water and the product was extracted by ethyl acetate. The ethyl acetate extract was evaporated and <sup>31</sup>P NMR spectrum of the isolated products was recorded in CDCl<sub>3</sub> (Fig. S6, ESI<sup>†</sup>). The <sup>31</sup>P NMR spectrum of the solution shows two singlets at 25.2 and at 23.0 ppm, along with two singlets at 47.6 and 36.5 ppm due to **2**. The singlets at 25.2 and at 23.0 ppm can be assigned to the species, *cis*-[Ru(dppp)<sub>2</sub>(CCR)<sub>2</sub>]. In addition to these signals, three singlets were observed at 1.5, 0.2, -1.2 ppm. These signals are due to some decomposed product. We could not observed any signal due to *trans*-[Ru(dppp)<sub>2</sub>(CCR)<sub>2</sub>].

Based upon these observations it is suggested that, in solution complex 1 looses acetonitrile ligand to produce the pentacoordinated complex  $[Ru(dppp)_2Cl]^+$ . The complex first reacts with two equivalent of Ag(CCR) to produce the comparatively less stable *cis*- $[Ru(dppp)_2(CCR)_2]$  complex and a very small amount of *trans*- $[Ru(dppp)_2(CCR)_2]$ . The reactive *cis*- $[Ru(dppp)_2(CCR)_2]$  undergoes reductive elimination to give the



 $\label{eq:scheme1} \begin{array}{l} \mbox{Suggested mechanism of alkyne homocoupling catalyzed} \\ \mbox{by 1}. \end{array}$ 

coupled product and Ru(0). The Ru(0) complex is oxidized by aerial oxygen to produce Ru( $\pi$ ) back (Cycle A, Scheme 1). It is also possible that, Ag<sup>+</sup> oxidizes Ru(0) to Ru( $\pi$ ) and metallic silver is produced, which undergoes aerial oxidation (Cycle B, Scheme 1). It may be noted that, in couple of occasions we could see the formation of silver mirror after prolonged heating. In the complex **6**, the two phenyl acetylides are *trans* to each other and that is why no reductive elimination takes place when the complex **6** is heated.

It is suggested that, the cycloaddition reaction proceeds by the mechanism suggested in the literature for  $[Cp*RuCl(PPh_3)_2]$ catalysed azide–alkyne cycloaddition reaction.<sup>24c</sup> The source of proton is the water generated in coupling reaction of alkyne.

### Experimental

Solvents and reagents used were reagent grade products. <sup>1</sup>H NMR spectra were recorded on Bruker Avance II (400 and 200 MHz) spectrometers. The <sup>31</sup>P (161.98 MHz) NMR spectra were recorded on Bruker Avance II spectrometer (<sup>1</sup>H frequency: 400 MHz). HRMS of the newly synthesised compounds were recorded on Waters TOF MS in ESI+ mode in methanol water mixture.

# Synthesis of $[Ru(dppp)_2(CH_3CN)Cl][BPh_4]$ (1) {dppp = 1,3-bis (diphenylphosphino)propane}

A sample of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (1.03 g; 1.2 mmol) and 1,3-bis(diphenylphosphino)propane (1.03 g; 2.5 mmol) were dissolved in distilled acetonitrile (10 mL) and the reaction solution was refluxed for about 5 h. The colour of the reaction solution turned brown to light yellow. The reaction solution was then filtered and NaBPh4 (0.41 g; 1.2 mmol) was added. The solution was concentrated over a water bath. A yellow, crystalline solid separated out. The separated solid was filtered and washed with hexane (3-4 times) and dried in vacuum. The compound was finally recrystallised from acetonitrile. Yield: 1.0 g (76%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 1.99 (br, 3H), 2.08 (s, 4H), 2.24 (qt, J = 7.6, 9.2 Hz, 4H), 2.6 (br doublet, J = 17.8 Hz, 4H), 6.89-7.84 (m, 60H); <sup>31</sup>P NMR (161.98 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 34.033$ ppm; IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 522, 697, 747, 1090, 1381, 1608, 2369, cm<sup>-1</sup>; elemental analysis: calcd 2958, 3057 for C<sub>80</sub>H<sub>75</sub>BClNP<sub>4</sub>Ru: C 72.70, H 5.72, N 1.06; found: C 72.75, H 5.92, N 1.09.

### Synthesis of [Ru(dppp)<sub>2</sub>Cl][BPh<sub>4</sub>] (2)

A sample of [Ru(dppp)<sub>2</sub>(CH<sub>3</sub>CN)Cl][BPh<sub>4</sub>] (0.66 g; 0.5 mmol) was dissolved in 3 mL of toluene and heated for 1 hour at 100 °C. The yellow solutions turned brown. On standing for 2–3 h, at room temperature a dark brown power separated out. The powder was filtered and washed with hexane. The compound was finally crystallised from dichloromethane–diethyl ether layer. Yield: 0.5 g; 79%. Elemental analysis calculated for C<sub>78</sub>H<sub>72</sub>BClP<sub>4</sub>Ru (mol. wt. = 1280.63): C, 73.15; H, 5.67; found: C, 73.20; H, 5.75; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 2.57–2.63 (m, 4H), 3.26 (br, 8H), 6.8–7.4 (m, 60H); <sup>31</sup>P NMR (161.98 MHz,

CDCl<sub>3</sub>, ppm):  $\delta = -0.08$ , 36.8 and 47.6 ppm; IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 507, 697, 738, 1088, 1433, 1479, 1575, 2860, 2924, 3054.

#### Homo coupling of alkyne catalysed by 1

In a round bottomed flask 1 (1 mol% with respect to alkyne), alkyne (1 mmol),  $AgNO_3$  (3–5 mol%) and DMF (5 mL) was taken. The reaction mixture was stirred at 90 °C under air for required time. The solvent was removed under vacuum and the product was isolated by column chromatography on silica gel using *n*-hexane as an eluent, giving 80–98% yield (99% purity by <sup>1</sup>H NMR). Spectral data of the compounds are given in ESI.<sup>†</sup>

## Homo coupling of alkyne followed by alkyne-azide cycloaddition catalysed by 1

After the completion of homo-coupling reaction, in this round bottomed flask 1 mmol of NaN<sub>3</sub> was added and stirred at 90 °C for 6–8 h. The conversion of 1,3-dialkyne was monitored by TLC. The solvent was removed under vacuum and the product was isolated by column chromatography on silica gel using *n*-hexane and ethylacetate mixture as an eluent, giving 70–85% yield. Spectral data of the compounds are given in ESI.†

### Isolation of [Ru(dppp)<sub>2</sub>(CCPh)<sub>2</sub>] (6)

The complex  $[Ru(dppp)_2(CH_3CN)Cl][BPh_4]$  (0.33 g; 0.25 mmol) was treated with phenylacetylene and AgNO<sub>3</sub> in 1 : 2 : 2 ratio in DMF and the mixture was heated for 5 min. The reaction solution on standing afforded a few crystals of *trans*- $[Ru(dppp)_2(CCPh)_2]$ , which has been structurally characterised by single crystal X-ray crystallography. Yield: 0.03 g (10%).

#### Single crystal data collection and refinements

Single crystal X-ray data of **1**, **2** and **6** were collected on Bruker Smart APEX system that uses graphite monochromated Mo K $\alpha$ radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct method and refined by least square method on  $F^2$  employing WinGx<sup>31</sup> package and the relevant programs (SHELX-97 (ref. 32) and ORTEP-3 (ref. 33)) implemented therein. Non-hydrogen atoms were refined anisotropically and hydrogen atoms on Catoms were fixed at calculated positions and refined using a riding model. For **6** PLATON SQUEEZE was used for removing disordered solvent molecule.

### Conclusions

In conclusion, we have successfully synthesised and characterised a new simple cationic ruthenium complex,  $[Ru(dppp)_2(CH_3CN)CI][BPh_4]$ . The complex can efficiently catalyse homocoupling of alkyne in the presence of silver(1) salts and air. This is the first report on ruthenium(II) catalysed oxidative coupling of alkynes. The catalytically active species,  $[Ru(dppp)_2CI][BPh_4]$  has been isolated and structurally characterised. One of the intermediate complex,  $[Ru(dppp)_2(CCPh)_2]$ has been isolated and structurally characterised. This complex can also catalyse cycloaddition reaction between sodium azide and alkynes and thus it has been used for tandem synthesis of 4-substituted-5-alkynyl-1,2,3-triazoles. The catalyst loading is low (1 mol%) and the complex is stable to air and moister.

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