RSC Advances

Graphical Abstract

The air and moister stable cationic Ru(II) compound, [Ru(dppp)$_2$(CH$_3$CN)Cl][BPh$_4$], has been synthesized. It is an efficient catalyst for coupling of alkynes in the presence of air and Ag(NO$_3$). Also, it has been found to catalyze alkyne – azide cycloaddition reaction with sodium azide and it can be used for tandem synthesis of 4-substituted-5-alkynyl-1,2,3-triazoles.

ARTICLE TYPE

Synthesis, Structure and Catalytic Property of [Ru(dppp)₂(CH₃CN)Cl][BPh₄] and Isolation of Catalytically Active [Ru(dppp)₂Cl][BPh₄]: Ruthenium Catalysed Alkyne Homocoupling and Tandem Alkyne – Azide Cycloaddition

5 **Uttam Kumar Das,[a] Rajesh K. Jena and Manish Bhattacharjee*[a]**

The compound, [Ru(dppp)₂(CH₃CN)Cl][BPh₄] (**1**) has been synthesised from the precursor complex, [Ru(PPh₃)₃Cl₂]. The complex has been structurally characterised. The complex has been found to be an
10 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][BPh₄] (**2**) and one of the intermediate complexes, [Ru(dppp)₂(CCPh)₂] (**6**), have been isolated and structurally characterised.

Introduction

15 Coordinatively unsaturated ruthenium complexes have received much attention due to their involvement in ruthenium catalysed organic transformations. Ruthenium can adopt wide range of coordination geometry and oxidation states and because of this ruthenium compounds are found to be effective catalysts for
20 varity of organic reactions including ring closing metathesis,[1] C-H activation,[2-4] activation of carbon carbon multiple bonds[2] and C-C bond formation,[2] Oppenauer oxidation[5] and transfer hydrogenation.[6] It has been emphasized in the literature that, 16 electron cationic species are the active catalyst. Thus, in recent
25 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
30 have been synthesised.[10, 11] 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
35 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.[13-15]

Diynes are useful starting materials in synthetic organic
40 chemistry. Number of natural products having anti-bacterial, anti-cancer and anti-HIV activities contain 1,3-diyne moiety.[16] Conjugated diynes 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
45 Hay, independently, which involves copper(I) 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'-tetramethylethylendiamine, pipreridine etc. are used.[18] This was
50 followed by reports on palladium catalysed cross coupling of 1-haloalkynes and terminal alkynes.[18, 19] Recently complexes of iron,[20a] cobalt,[20b] nickel[20c] and gold[20d] 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
55 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.

60 Butadiyenes have been used for the synthesis of heterocycles like thiophene and triazoles and other heterocycles.[21] 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.[22]

65 Ruthenium complexes have been shown to catalyse head to head dimerization of alkynes to en-ynes.[23] Also ruthenium complexes have been found to be efficient catalysts for alkyne – azide cycloaddtion reaction.[24] It may be noted that, synthesis of 4,5-disubstituted triazoles by alkyne – azide cycloaddition is rare.
70 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.[25, 26] Thus we thought to design a catalytic system for tandem reaction for the preparation of alkynyl triazole. Herein we report synthesis and
75 structure of [Ru(dppp)₂(CH₃CN)Cl][BPh₄] (**1**) and first example of ruthenium catalysed Glaser – Hay[18] coupling of terminal alkynes and synthesis and structure of the catalytically active species, [Ru(dppp)₂Cl][BPh₄] (**2**) and isolation and structural

characterization of the reaction intermediate *trans*-[Ru(dppp)₂(CCPh)₂] (**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)₂(CH₃CN)Cl][BPh₄] (1) and [Ru(dppp)₂Cl][BPh₄] (2)

The complex, [Ru(dppp)₂(CH₃CN)Cl][BPh₄] (**1**) has been synthesised from the reaction of $RuCl_2(PPh_3)_3$ with diphenylphosphinopropane (dppp) in 1:2.5 ratio in acetonitrile in the presence of $NaBPh_4$. This can also be prepared form the reaction of $RuCl_3 \cdot nH_2O$ with excess of dppp in the presence of $NaBPh_4$. The complex, [Ru(dppp)₂Cl][BPh₄] (**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 ^1H and ^{31}P NMR spectroscopy. The elemental analyses agree well with the formulations of the compounds. The ^1H NMR spectrum of **1** shows muliplet 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_3 protons of the acetonitrile ligand and the C – CH_2 – C protons appear at 2.09 ppm (broad). The ^{31}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 ^1H NMR spectrum of **2** shows a multiplet in the region 2.57-2.63 (4H) ppm due to the methylene protons of the P-CH₂-CH_2-CH₂-P moiety. The signal for methylene protons of the P- CH_2 group appears at, 3.26 ppm (br, 8H) and the signals for aromatic protons appear at 6.8-7.4 (m, 60H). The ^{31}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)₂(CH3CN)Cl][BPh₄] (1) and [Ru(dppp)₂Cl][BPh₄] (2)

The complex, **1** crystallizes in triclinic space group P-1 (Table S1, ESI). The asymmetric unit contains one cationic ruthenium complex (Figure 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 – Ru1 = 2.003(4) Å} (Table S2, ESI). The BPh₄⁻ anion is found outside the coordination sphere and does not show any bonding interaction with ruthenium(II) center.

The complex, [Ru(dppp)₂Cl][BPh₄] (**2**) crystallizes in monoclinic space group P21/a (Table S1, ESI). The asymmetric unit consists of a complex cation, [Ru(dppp)₂Cl]⁺ and the anion BPh₄⁻ (Figure 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, ESIS) clearly shows that, the ruthenium centre is in distorted trigonal bipyramidal coordination environment.
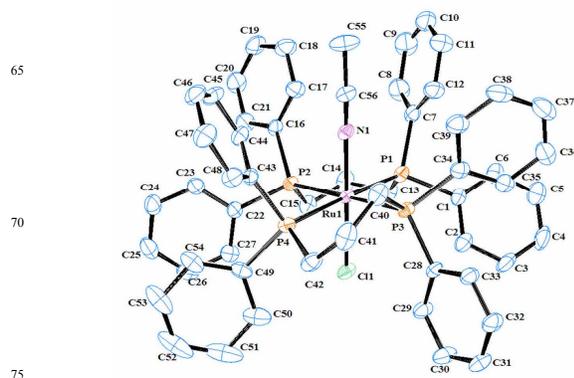

Figure 1 ORTEP view of [Ru(dppp)₂(CH₃CN)Cl]⁺ cation in **1**. Hydrogen atoms have been omitted for clarity.
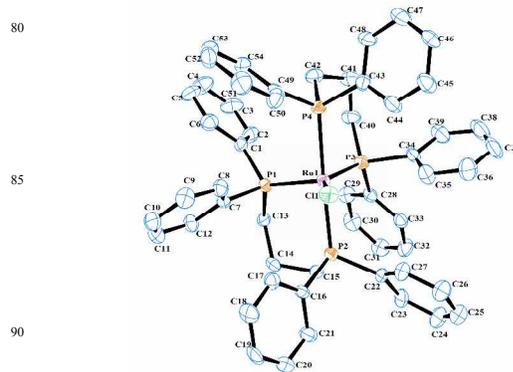

Figure 2 ORTEP view of [Ru(dppp)₂Cl]⁺ cation in **2**. Hydrogen atoms have been omitted for clarity.

Studies of Catalytic Properties of [Ru(dppp)₂(CH₃CN)Cl][BPh₄] (1)

Ruthenium(II) complexes have been shown to be capable of activating alkynes via vinylidene complex formation or π - complex formation towards nucleophilic addition reactions.[27] Also it may be noted that, ruthenium complexes of η¹ coordinated alkynes have been reported.[28] We have been working on activation of alkyne via vinylidene complex and π - complex formation towards nucleophilic addition reactions.[29] We were interested in activation of alkynes by ruthenium(II) complexes via the formation of η¹ coordinated alkynes.

Silver salts are known to form acetylide very easily and in number of catalytic reactions these acetylides have been used.[30] 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 η¹ 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.

Table 1 Optimization of coupling of phenyl acetylene catalyzed by **1** and Ag(I)[a]
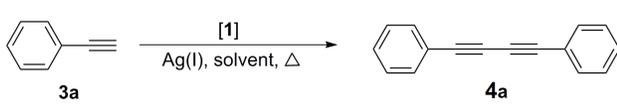
| Entry	Solvent	Temp (°C)	T (hr)	Yield (%)[b]	Ag(1)
1	Toluene	90	24	-	-
2	Toluene	90	5	75	Ag$_2$(CO$_3$)
3	DMSO	90	5	65	Ag$_2$(CO$_3$)
4	DMF	90	5	87	Ag$_2$(CO$_3$)
5	DMF	90	2	93	Ag(OAc)
6	DMF	60	1	38	Ag(OAc)
7	DMF	90	0.5	90	Ag(OAc)
8	DMF	70	1	80	Ag(NO$_3$)
9	DMF	90	0.75	95	Ag(NO$_3$)
10	DMF	25	24	-	Ag(NO$_3$)
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$_3$)[d]
15	DMF	90	0.5	95	Ag(NO$_3$)[e]

[a]Reaction conditions: phenylacetylene (1.0 mmol), **1** (1 mol%) Ag(I) (3 mol%) in solvent (5.0 cm^3), [b]isolated,[c]in the absence of **1**. [d]under argon atmosphere.[5]complex **2** as catalyst instead of complex **1**

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 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 mins. To this was then added NaN$_3$ and the reaction mixture was heated for 8 hrs. 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(I) in the reaction, a separate reaction was done using isolated coupled product and NaN$_3$ 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 diyene with NaN$_3$ 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.

Table 2 Homocoupling of alkynes catalyzed by **1**
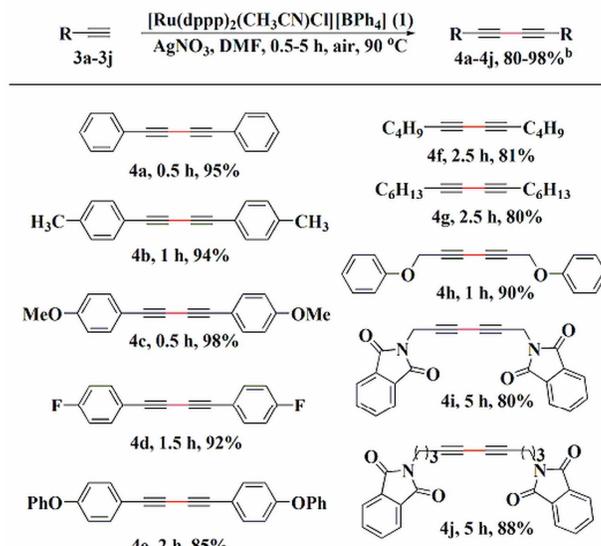
[a]Reaction conditions: alkyne (1.0 mmol), **1** (0.01 mmol), AgNO$_3$ (0.03 mmol), DMF (5.0 cm^3), temp 90 °C. [b]yields are isolated

Table 3 Alkyne – azide cyclization catalyzed by 1
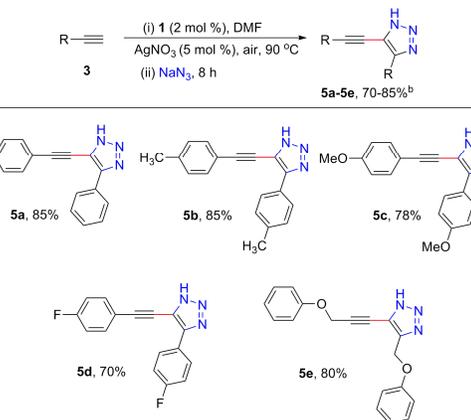
[a]Reaction conditions: alkyne (1.0 mmol), NaN$_3$ (2.0 mmol), DMF (5.0 cm^3), temp 90 °C. [b]yields are isolated

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, $[Ru(dppp)_2Cl]^+$. A model reaction was carried out with phenyl acetylene in the presence 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 mins. The reaction solution on standing afforded a few crystals of *trans*-$[Ru(dppp)_2(CCPh)_2]$ (**6**), which has been characterised by spectroscopic techniques and single crystal X-ray crystallography (Figure 2). 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.[28] However, in one of the reports it has been shown that, *cis*- $Ru(PMe_3)_4Me_2$ reacts with terminal alkynes to afford both *cis –* and *trans –* $[Ru(PMe_3)(CCR)_2]$, the *trans –* product being the minor product.[28a] Thus it is clear that, during reaction the diacetylide complexes can undergo isomerization.
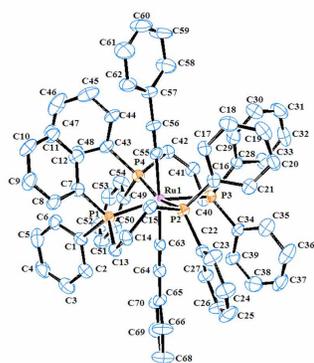

Figure 2 ORTEP view of $[Ru(dppp)_2(CCPh)_2]$ (**6**). Hydrogens have been omitted for clarity

The ^{31}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 (Figure S5, supplementary material).
The complex, *trans*-$[Ru(dppp)_2(CCPh)_2]$ (**6**) crystallizes in triclinic space group P-1 (Table S1, ESI). 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 $Ag(NO_3)$ in DMF in 1:2:2 ratio and was heated for 5 mins and the reaction was quenched by the addition of water and the product was extracted by ethyl acetate. The CH_2Cl_2 extract was evaporated and ^{31}P NMR spectrum of the isolated products was recorded in $CDCl_3$ (Figure S6, supplementary material). The ^{31}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* -$[Ru(dppp)_2(CCR)_2]$. 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*- $[Ru(dppp)_2(CCR)_2]$.

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 coupled product and Ru(0). The Ru(0) complex is oxidized by aerial oxygen to produce Ru(II) back (Cycle A, Scheme 4). It is also possible that, Ag^+ oxidizes Ru(0) to Ru(II) and metallic silver is produced, which undergoes aerial oxidation (Cycle B, Scheme 4). 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 acetyildes are *trans* to each other and that is why no reductive elimination takes place when the complex **6** is heated.
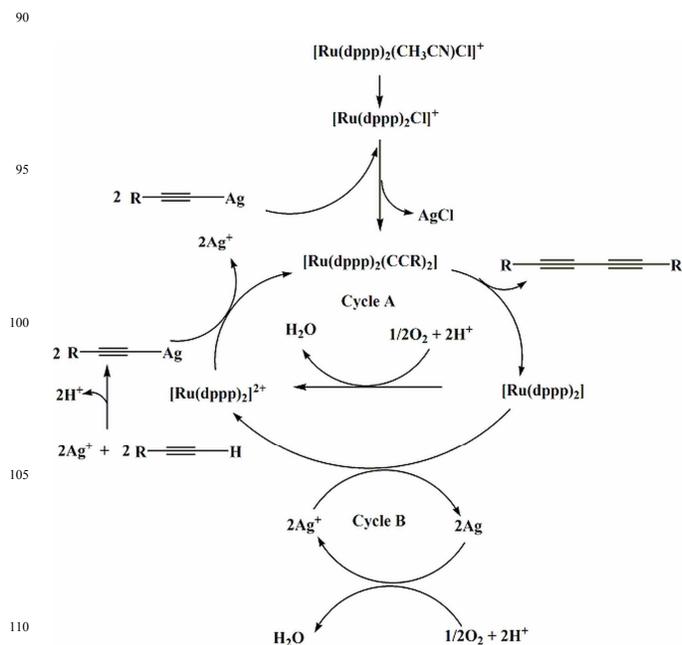
Scheme 1 Suggested mechanism of alkyne homocoupling catalyzed by **1**

It is suggested that, the cyloaddition reaction proceeds by the mechanism suggested in the literature for $[Cp^*RuCl(PPh_3)_2]$

catalysed azide – alkyne cycloaddition reaction.[24c] The source of proton is the water generated in coupling reaction of alkyne.

Experimntal

Solvents and reagents used were reagent grade products. ^{1}H NMR spectra were recorded on Bruker Avance II (400 and 200 MHz) spectrometers. The [31]P (161.98 MHz) NMR spectra were recorded on Bruker Avance II spectrometer (^{1}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$_3$CN)Cl][BPh$_4$] (1){dppp = 1,3-Bis (diphenylephosphino)propane}

A sample of RuCl$_2$(PPh$_3$)$_3$ (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 hrs. The colour of the reaction solution turned brown to light yellow. The reaction solution was then filtered and NaBPh$_4$ (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: 1.0g (76%): ^{1}H NMR (400 MHz, CDCl$_3$, 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, 60 H); ^{31}P NMR (161.98 MHz, CDCl$_3$, ppm): δ = 34.033 ppm; IR (KBr): ν (cm^{-1}) = 522, 697, 747, 1090, 1381, 1608, 2369, 2958, 3057 cm^{-1} ; elemental analysis: calcd for C$_{80}$H$_{75}$BClNP$_4$Ru: C 72.70, H 5.72, N 1.06; found: C 72.75, H 5.92, N 1.09.

Synthesis of [Ru(dppp)$_2$Cl][BPh$_4$] (2)

A sample of [Ru(dppp)$_2$(CH$_3$CN)Cl][BPh$_4$] (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 hrs, 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$_{78}$H$_{72}$BClP$_4$Ru (Mol. Wt. = 1280.63): C, 73.15; H, 5.67; Found: C, 73.20; H, 5.75; ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 2.57-2.63 (m, 4H), 3.26 (br, 8H), 6.8-7.4 (m, 60H); ^{31}P NMR (161.98 MHz, CDCl$_3$, ppm): δ = -0.08, 36.8 and 47.6 ppm; IR (KBr): ν (cm^{-1}) = 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 mole %) 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 ^{1}H NMR). Spectral data of the compounds are given in supplementary material.

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$_3$ was added and stirred at 90 °C for 6-8 hrs. 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 ethyleacetate mixture as an eluent, giving 70-85% yield. Spectral data of the compounds are given in supplementary material.

Isolation of [Ru(dppp)$_2$(CCPh)$_2$] (6)

The complex [Ru(dppp)$_2$(CH$_3$CN)Cl][BPh$_4$] (0.33 g; 0.25 mmol) was treated with phenylacetylene and AgNO$_3$ in 1:2:2 ratio in DMF and the mixture was heated for 5 mins. 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: 0.03g (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 Kα radiation (λ = 0.71073 Å). The structure was solved by direct method and refined by least square method on F^2 employing WinGx[31] package and the relevant programs (SHELX-97[32] and ORTEP-3[33]) implemented therein. Non-hydrogen atoms were refined anisotropically and hydrogen atoms on C-atoms 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$_3$CN)Cl][BPh$_4$].   The   complex   can   efficiently catalyse homocoupling of alkyne in the presence of silver(I) salts and air. This is the first report on ruthenium(II) catalysed oxidative coupling of alkynes. The catalytically active species, [Ru(dppp)$_2$Cl][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.

Acknowledgment

Notes and references

[a] Department of Chemistry, Indian Institute of Technology, Kharagpur, Kharagpur 721302, India E-mail: mxb@iitkgp.ac.in

1 R. H. Grubbs, S. Chang, *Tetrahedron*, **1998**, *39,* 2805.

2 B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067.

3 S. Busch, W. Leitner, *Chem. Cmmun.* **1999**, 2305.

4 G. C. Hsu, W. P. Kosar, W. D. Jones, *Organometallics* **1994**, *13,* 385.

5 S. Gauthier, R. Scopelliti, K. Severin, *Organometallics* **2004**, *23*, 2769.

6 (a) C. Thoumazet, M. Melaimi, L. Ricard, F. Mathey, P. L. Floch, *Organometallics* **2003**, *22*, 1580. (b) S. Naskar, M. Bhattacharjee, *J. Organomet. Chem.* **2005**, *700*, 5006. (c) S. Naskar, M. Bhattacharjee, *Tetrahedron Lett.* **2007**, *48*, 465. (c) S. Naskar, M. Bhattacharjee, *Tetrahedron Lett.* **2007**, *48*, 3367.

7 M. J. Tenorio, K. Mereiter, M. C. Pureta, P. Valerga, *J. Am. Chem. Soc.* **2000**, *690*, 11230.

8 C. Gemel, K. Mereiter, R. Schmid, K. Krichner, *Organometallics*, **1997**, *16*, 5601.

9 Y. Yamagichi, H. Nagashima, *Organometallics* **2000**, *19*, 725.

10 (a) M. J. Burn, M. G. Fickes, F. J. Hollander, R. G. Bergman *et al*. *Organometallics* **1995**, *14,*137. (b) E. Fache, C. Santini, F. Senocq, J. M. Basset *J. Mol. Catal*. **1992**, *72,*331.

11 (a) P. S. Hallman, T. A. Stephenson, G. Wilkinson *Inorg. Synth.* **1970**, 12, 237. (b) P. S. Hallman, B. R. McGarvey, G. Wilkinson, *J. Chem. Soc. A* **1968**, (12), 3143. (c) L. D. Field, A. V. George, D. C. R. Hockless, G. R. Purches, A. H. White, *J . Chem. Soc Dalton Trans.* **1996**, 2011.(d) J . Chatt, R. G. Hayter, *J . Chem. Soc.* **1961**, 896. (e) J. Chatt, R. G. Hayter, *J. Chem. Soc.* **1961**, 2605. (f) L. D. Field, T. W. Hambley, B. C. K. Yau, *Inorg. Chem.* **1994,** *33*, 2009. (g) M. E. Woodhouse, F. D. Lewis, T. J. Marks *J. Am. Chem. Soc.* **1982**, *104*, 5586.

12 (a) O. Kröcher, R. A. Köppel, A. Baiker *Chem. Commun.* **1997**, 453. (b) J. A. van Rijn, M. Lutz, L. S. von Chrzanowski, A. L. Spek, E. Bouwman, E. Drent, *Adv. Synth. Catal.* **2009**, *351*, 1637. (c) M. T. Bautista, E. P. Cappellan, S. D. Drouin, R. H. Morris, C. T. Schweitzer, A. Sella, J. Zubkowski, *J. Am. Chem. Soc.* **1991**, *113*, 4876. (d) B. Chin, A. J. Lough, R. H. Morris, C. T. Schweitzer, C. D'Agostino, *Inorg. Chem.* **1994**, *33*, 6278.

13 (a) P W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, P. Dierkes *Chem. Rev.* **2000**. *100*. 2743. (b) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008,** *108,* 3351.

14 (a) R. Kumareswaran, M. Nandi, T. V. RajanBabu, *Org. Lett.* **200**3, *5*, 4345.(b) D. Zhao, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc*. **2006,** *118*, 14440.

15 H. Doucet, V. B. Martin, C. Bruneau, P. H. Dixneur, *J .Org. Chem* **1995,***60***,** 7247.

16 (a) W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang, A. Lei, *J. Am. Chem. Soc.* **2008**, *130*, 14713. (b) M. Gholami, R. R. Tykwinski, *Chem Rev.* . **2006**, *106*, 4997. (c) P. N. W. Baxter, R. Dali-Youcef, *J. Org. Chem.* **2005**, *70*, 4935. (d) J. A. Marsden, M. M. Haley,. *J. Org. Chem.* **2005**, *70*, 10213. (e) M. Ladika, T. E. Fisk, W. W. Wu, S. D. Jons, *J. Am. Chem. Soc*. **1994**, *116*, 12093. (f) S. F. Mayer, A. Steinreiber, R. V. A. Orru, K. Faber, *J. Org. Chem.* **2002**, *67*, 9115. (g) A. Stütz, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 320.

17 (a) A–C. Bédard, S. K. Collins, *J. Am. Chem. Soc.*, **2011**, *133*, 19976. (b) M. C. Baier, J. Huber, S. Mecking, *J. Am. Chem. Soc.*, **2009**, *131*, 14267. (c) P. Bolduc, A. Jacques, S. K. Collins, *J. Am. Chem. Soc.*, **2010**, *132*, 12790.

18 (a) C. Glaser, *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422. (b) C. Glaser, *Ann. Chem. Pherm.*, **1870**, *154*, 137. (c) A. H. Hay, *J. Org. Chem.* **1962**, *27*, 3320. (d) P. Siemsen, R. C. Livingston and F. Diederich, *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 2632 and references therein.

19 (a) W. Susanto, C–Y. Chu, W. J. Ang, T–C. Chou, L–C. Lo and Y. Lam, *J. Org. Chem.* **2012**, *77*, 2729. (b) J. H. Li, Y. Liang and X–D. Zhang, *Tetrahedron*, **2005**, *61*, 1903.

20 (a) K. Kude, S. Hayase, M. Kawatsura and T. Itoh, *Heteroatom Chem*. **2011**, *22*, 397. (b) M. E. Krafft, C. Hirosawa, N. Dalal, C. Ramsey and A. Stiegman, *Tetrahedron Lett*., **2001**, *42*, 7733. (c) J. D. Crowley, S. M. Goldup, N. D. Gowans, D. A. Leigh, V. E. Ronaldson and A. M. Z. Slawin, *J. Am. Chem. Soc*., **2010**, *132*, 6243. (d) M. N. Hopkinson, J. E. Ross, G.T. Giuffredi, A. D. Gee and V. Gouverneur, *Org. Lett.* **2010**, *12*, 4904.

21 (a) A, K. Mandadapu, S. K. Sharma, S. Gupta, D. G. V Krishna and B. Kundu, *Org. Lett*. **2011**, *13*, 3162. (b) L. Wang, X. Yu, X. Feng and M. Bao, *Org. Lett.* **2012**, *14*, 2418.

22 (a) Q. Nguyen, T. Nguyen and T. G. Driver, *J. Am. Chem. Soc.* **2013**, *135*, 620. (b) K. Takahashi, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.* **2012**, *134*, 18746. (c) W–J. Yoo, H. Miyamura and S. Kobayashi, *J. Am. Chem. Soc.* **2011**, *133*, 3095.

23 (a) J. Le Paih, F. Monnier, S. Dérien, P. H. Dixneuf, E. Clot and O. Eisenstein, *J. Am. Chem*., *Soc.* **2003**, *125*, 11964. (b) K. Melis, T. Opstal and F. Verpoort, *Eur. J. Org. Chem*. **2002**, 3779. (c) C. Slugovc, D. Doberer, C. Gemel, R. Schmid, K. Kirchner, B. Winkler, F. Stelzer, *Monatshefte Für Chemie* **1998**, *129*, 221

24 (a) M. Lamberti, G. C. Fortman, A. Poater, J. Broggi, A. M. Z. Slawin, L. Cavallo and S. P. Nolan, *Organometallics*, **2012**, *31*, 756. (b) L. Zhang, X. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin and G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 15998. (c) B. C. Boren, S. Narayan, L. K. Rasmussen, L. Zhang, H. Zhao, Z.; Jia, G. Lin and V. V. Fokin, *J. Am. Chem. Soc.* **2008**, *130*, 8923.

25 (a) I. N. Domnin, L. A. Remizova, G. L. Starova, F. Rominger, *Russ. J. Org. Chem.* **2009**, *45*, 1678. (b) T. H. Luu, B. J. Medos, E. R. Graham, D. M. Valle, R. McDonald, M. J. Ferguson, R. R. Tykwinski, *J. Org. Chem.* **2010**, *75*, 8498.

26 (a) J. Tang, X. Zhao and S. Zheng, *Cn. Pat.* 2012186932 20120328, **2012**. (b) D. An, D. Xie, X. Yu, Q. Su and L. Shi, *Cn. Pat.* 20121128711 20120427, **2012**.

27 C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1997**, 507.

28 (a) L. D. Field, A. M. Magill, S. J. Dalgarno, P. Jensen, *Eur. J. Inorg. Chem.* **2008**, 4248. (b) L. D. Field,A. M. Magill, T. K. Shearer, S. J. Dalgarno, M. M Bhadbhade,. *Eur. J. Inorg. Chem.* **2011**, 3503. (c) C – Y. Wong, C – M. Che, M. C. W. Chan, J. Han, K – H. Leung, D. L. Phillps, K – Y. Wong, N. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 13997.

29 (a) U. K. Das, M. Bhattacharjee, *J. Organomet. Chem.* **2012**, *700*, 78. (b) U. K. Das, M. Bhattacharjee, *Chem. Eur. J.* **2012**, *18*, 5180.

30 (a) Q–H. Wie, L–Y. Zhang, G–Q. Yin, L–X. Shi, Z–N. Chen, *J. Am. Chem. Soc.* **2004**, *126*, 9940. (b) C. He, S. Guo, J. Ke, H. Xu, H. Chen, A. Lei, *J. Am. Chem. Soc.* **2012**, *134*, 5766.

31 L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

32 G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

33 L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.