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Addition of pyrroles onto terminal alkynes catalyzed by a dinuclear ruthenium (II) complex

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ABSTRACT

The addition of pyrroles onto alkynes has been catalyzed by a dinuclear ruthenium complex, Ru2(CO)4(PPh3)2Br4, resulting in the formation of geminal 2-vinylpyrroles in high yields under mild conditions. Further functionalization with pyrroles or alkynes to afford dipyrrolmethanes or 2,5-bis(vinyl)pyrroles via the vinyl functional group can readily be achieved. A mechanism involving cationic ruthenium complexes was proposed based on the product regioselectivity, deuteration and infrared spectroscopic studies carried out on the catalytic process.

1. Introduction

The synthesis of functionalized pyrroles is highly sought after due to its importance in the study of natural products, biologically active compounds and material science [1]. Various synthetic methods, including the Knorr [2], Paal-Knorr [3], Hantzsch [4], Piloty-Robinson [5] and aza-Wittig [6] synthesis have been reported for the production of functionalized pyrroles. In addition to these methods, direct functionalization of pyrrole has also been achieved via pyrrolyl C–H bond activation route [7], generating much interest due to the ability to selectively functionalize organic molecules. Subsequent addition of the activated site across alkynes provides an elegant one-step reaction towards the formation of vinylpyrroles (Scheme 1), which otherwise required multiple steps [8]. The resulting vinylpyrrole can further be modified via its unsaturated bond to produce a variety of useful pyrrolic products [9], and even dipyrromethanes [10].

Although a wide variety of metal catalysts, including gold [11], nickel [12], indium [13], palladium [14], rhodium [15] and ruthenium [16] has been shown to catalyze the hydroarylation of N heterocyclic compounds, it is only recently that palladium and ruthenium complexes have been shown to catalyze the addition of pyrroles onto unactivated alkynes [17]. Due to a lack of *gem*-selective pyrrole hydroarylation systems as highlighted by Gao et al. [18], it is therefore desirable to develop a regioselective system for the exclusive formation of geminal hydroarylation products.

We have recently found that the bromoruthenium carbonyl dimer, $Ru_2(CO)_4Br_4L_2$ (L = CO or PPh_3), catalyzes the hydroarylation of pyrroles even at room temperature. The reaction proceeds regioselectively to give geminal products in high yields (99%). It was noted that although the ruthenium dimer has been shown to catalyze hydroamination reactions, the formation of N-vinylpyrroles (hydroamination products) were not observed [19]. The selective nature of the system led us to propose $Ru_2(CO)_4Br_4L_2$ as an excellent alternative catalyst to existing pyrrole hydroarylation systems in producing 2-vinylpyrroles. Interestingly, by reacting vinylpyrroles with pyrroles or alkynes to give the unique dipyrromethanes or 2,5-bis(vinyl)pyrroles respectively, we have demonstrated the usefulness of the system for the development of functionalized pyrroles. The products obtained are believed to have potential applications in wide variety of areas.

2. Experimental section

2.1. General procedures

Triruthenium Dodecacarbonyl, $Ru_3(CO)_{12}$ (Aldrich, 99%), was recrystallized from cyclohexane before use. Phenylacetylene (98%), 1-hexyne (98%), propargyl alcohol (99%), pyrrole (98%), 1-methylpyrrole (99%) and 1-phenylpyrrole (99%) were obtained from Alfa Aesar, and used without further purification. IR spectra were collected with liquid samples in a cell with CaF_2 windows and

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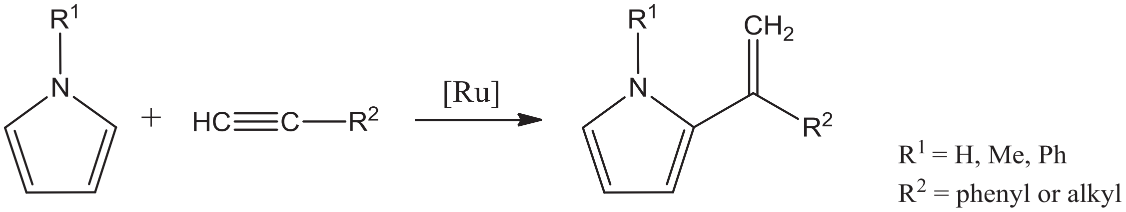


Scheme 1. Markovnikov addition of pyrrole across a terminal alkyne occurs in the presence of a ruthenium catalyst to produce vinylpyrrole.

0.1 mm pathlength, with a Shimadzu IR Prestige-21 spectrometer. ^{1}H NMR spectra were recorded with a Bruker AMX 500 Fourier Transform Spectrometer at room temperature, using $CDCl_3$ as solvent. The chemical shifts were referenced to tetramethylsilane. Organic product yields were calculated from the ^{1}H NMR spectra using reagent grade toluene as internal standard. Mass spectra of the organic products are recorded with a Finnigan Mat 95XL-T spectrometer.

The ruthenium complex, $Ru_2(CO)_4(PPh_3)_2Br_4$ and $Ru_2(CO)_6Br_4$, were prepared from $Ru_3(CO)_9(PPh_3)_3$ and $Ru_3(CO)_{12}$ respectively according to literature methods and characterised by FTIR spectroscopy [20].

2.1.1. Synthesis of $Ru_3(CO)_9(PPh_3)_3$

$Ru_3(CO)_{12}$ (0.5 g, 0.78 mmol) was refluxed with excess PPh_3 in hexane until a dark violet precipitate was formed. The residue was recrystallized using $CHCl_3$-hexane to give needle-like crystals (1 g, 0.75 mmol).

υ(CO) ($CHCl_3$): 2041 (vw), 1972 (sh), 1969 (vs). ^{31}P NMR: 36.9 ppm.

2.1.2. Synthesis of $Ru_2(CO)_4(PPh_3)_2Br_4$

$Ru_3(CO)_9(PPh_3)_3$ (0.5 g, 0.37 mmol) was dissolved in cold benzene, before excess Br_2 was added. The initial purple ruthenium turned dark yellow immediately. The solvent and unreacted Br_2 were then removed under reduced pressure, and a cold trap was installed to prevent the corrosive vapours from entering the vacuum pump. At this point, the residue contains a majority of $Ru(CO)_3(PPh_3)Br_2$. This was redissolved in enough $CHCl_3$ to give a saturated solution, which was heated at 50 °C for 30 min. Hexane was then added to precipitate the product. The product was recrystallized from a $CHCl_3$-Hexane solvent pair to give the yellow product (0.35 g, 0.30 mmol).

(Found: C 41.3, H 2.7, Br 27.2$C_{40}H_{30}O_4Br_4P_2Ru_2$ requires C 41.6, H 2.6, Br 27.4); ^{31}P NMR 41.3 ppm; υ(CO): ($CHCl_3$) 2070 (s), 2012S (s) cm^{-1}.

2.1.3. Synthesis of $Ru_2(CO)_6Br_4$

$Ru_3(CO)_{12}$ (0.2 g, 0.31 mmol) was dissolved in sufficient benzene, before excess Br_2 was added. The solution turned pale yellow immediately. The solvent and unreacted Br_2 were then removed under reduced pressure, and a cold trap was installed to prevent the corrosive vapours from entering the vacuum pump. Hexane was added to the residue and heated at 50 °C until a yellow precipitate forms. The yellow precipitate was collected and recrystallized using $CHCl_3$-Hexane.

(Found: C 10.4, Br 46.4$C_6O_6Br_4Ru_2$ requires C 10.2, Br 46.3); υ(CO): ($CHCl_3$) 2138 (s), 2078 (s) cm^{-1}.

2.1.4. Typical procedure for catalytic reaction

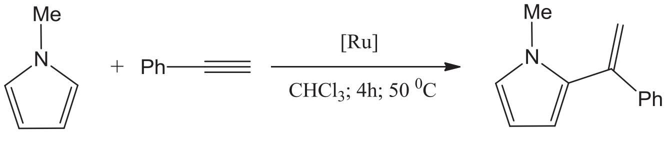
Pyrrole (10 mmol) and alkyne (1 mmol) was added to a $CHCl_3$ solution (1 mL) containing the catalyst (20 μmol). The reaction mixture was then reacted at either room temperature (25 °C) or at 50 °C. Sampling was carried out at 30 min intervals. The reaction was stopped after 4 h (or longer hours, if necessary) before excess hexane was added to precipitate the catalyst. The solvent from the filtrate was removed under reduced pressure, and the remaining contents were passed through a silica gel column, using $CHCl_3$:Hexane (3:1 v/v) solvent pair as eluant.

3. Results and discussion

Synthesis of $Ru_2(CO)_4(PPh_3)_2Br_4$ can easily be achieved and the obtained product can be purified conveniently. The complex was found to be stable under normal atmospheric conditions. It was found that the dinuclear ruthenium complex [21], $Ru_2(CO)_4(PPh_3)_2Br_4$, was able to catalyze the addition of pyrroles across terminal alkynes with high efficiency (turnover number of 50 over 4 h) (Table 1, entry 1). The reaction proceeds at relatively mild conditions, hence does not require any sophisticated setup. The analogous bromoruthenium carbonyl dimer [21], $Ru_2(CO)_6Br_4$, was also able to catalyze the same reaction, although its activity was much lower when compared to the phosphine complex (Table 1, entry 2). Our preliminary observations suggest that the lower activity of the carbonyl was probably due to electronic rather than steric effect, as otherwise the system that contains bulky phosphines will produce a lower yield. As the ruthenium dimer is known to generate active ruthenium intermediates which are electron-deficient, the presence of strong σ-donating phosphines would promote their formation to a larger extent than carbonyl ligands.

In contrast, the mononuclear analogue [22], $Ru(CO)_2(PPh_3)_2Br_2$, was found to be inert towards the same reaction (Table 1, entry 3). Such an observation is expected due to the strong coordinating property of PPh_3, which hinders the generation of a vacant site on the metal centre, especially at low reaction temperatures. On the

Table 1
Ruthenium-catalyzed hydroarylation of N-methylpyrrole, **1a**, with **2a**[a]



1a **3a**

Entry	Catalyst	% Yield[b]
1	$Ru_2(CO)_4(PPh_3)_2Br_4$	99
2	$Ru_2(CO)_6Br_4$	15[c]
3	$Ru(CO)_2(PPh_3)_2Br_2$	0
4	$Ru_3(CO)_{12}$	0
5	$Ru_3(CO)_{12}/NH_4PF_6$	20
6	$Ru_3(CO)_9(PPh_3)_3$	0
7	$[Ru_2(CO)_4(CH_3COO)_2]_n$	2

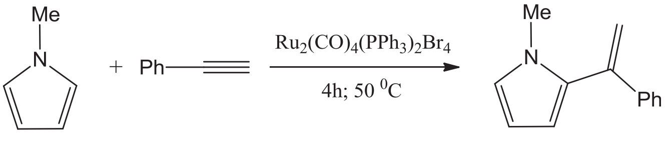
[a] Reactions were carried out based on **1a** (10 mmol) and **2a** (1 mmol) with 2% catalytic loading.
[b] Total yield w.r.t. amount of **2a** used.
[c] The low yield was due to further reaction of the product to give **5** in 25% yield.

contrary, the Br-bridged dinuclear $Ru_2(CO)_4(PPh_3)_2Br_4$ complex can readily dissociate to give, for example, the16-electron $Ru(CO)_2(PPh_3)Br_2$ species, which will then allow for substrate coordination and subsequent catalysis.

When other ruthenium complexes, such as $Ru_3(CO)_{12}$, $Ru_3(CO)_9(PPh_3)_3$ [23] and $[Ru_2(CO)_4(CH_3COO)_2]_n$ [24] were used, the catalysis did not proceed efficiently (Table 1, entry 4–7). In the case of $Ru_3(CO)_{12}$, the addition of acidic salt $NH_4^+PF_6^-$ was required to obtain substantial yield [18]. This presumably suggests that Ru-catalyzed hydroarylation involves the formation of ionic species, which are responsible for any catalytic activity.

Optimization of the system has been performed by studying the effect of various solvents on the catalytic process. Use of solvent is necessary especially when the ruthenium complex does not dissolve readily in the substrate. A variety of solvents, including THF, CH_3CN and $CHCl_3$ has been used with the yields of the organic products recorded in Table 2. As expected, the incomplete dissolution of the ruthenium complex in neat substrates, which corresponded to a lower catalytic loading, led to a lower product yield (Table 2, entry 1). When coordinating solvents (THF and CH_3CN) were used instead, a drastic drop in efficiency was observed (Table 2, entry 3 and 4). We reasoned that the coordinating nature of THF and CH_3CN induced increased competition between solvent and substrates for binding sites on the ruthenium centre, which resulted in the reaction being hindered. The degree of inhibition is proportional to the coordinating strength of the solvent, with the stronger CH_3CN ligand inactivating the reaction completely.

Table 2
Catalytic reaction of **1a** and **2a** carried out in different solvents[a]



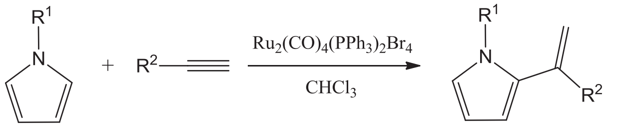
1a **3a**

Entry	Solvent[b]	% Yield[c]
1	Neat	74
2	$CHCl_3$	95
3	THF	15
4	CH_3CN	0

[a] Reactions were carried out based on **1a** (10 mmol) and **2a** (1 mmol) with 2% catalytic loading.
[b] 1 mL of solvent was sufficient to homogenize the reaction mixture.
[c] Total yield w.r.t. amount of **2a** used.

Addition of pyrroles across alkyne was observed in the presence of $Ru_2(CO)_4(PPh_3)_2Br_4$ catalyst, although excess amount of the pyrrole is required (Table 3). A mild reaction condition was sufficient to initiate the reaction using N-methylpyrrole (**1a**) and phenylacetylene (**2a**) to give the 2-vinylpyrrole product **3a** (Table 3, entry 1–2). The reaction can further be optimized by slightly increasing the temperature (Table 3, entry 3–4). When the reaction of **1a** with other alkynes was examined, it was noted that the yield of the products were lower when aliphatic alkynes were used (Table 3, entry5–7). The reduced reactivity is likely to be caused by electronic factors since even 1-hexyne (**2b**) and propargyl alcohol (**2c**), which are relatively less bulky than **2a**, suffers from low efficiency. There was no reaction between **1a** and 3-methyl-1-pentyn-3-ol (**2d**) (Table 3, entry 7). The reaction does not proceed with internal alkynes, such as 3-hexyne and diphenylacetylene, even at elevated temperatures and longer reaction times.

Table 3
$Ru_2(CO)_4(PPh_3)_2Br_4$-catalyzed hydroarylation of pyrroles, **1**, with alkynes, **2**[a]



1 **2** **3**

1a: R^1 = Me
1b: R^1 = Ph
1c: R^1 = H

2a: R^2 = Ph
2b: R^2 = ^{n}Bu
2c: R^2 = CH_2OH
2d: R^2 = C(Me)(Et)OH

3a: R^1 = Me; R^2 = Ph
3b: R^1 = Me; R^2 = ^{n}Bu
3c: R^1 = Me; R^2 = CH_2OH
3d: R^1 = Me; R^2 = C(Me)(Et)OH
3e: R^1 = Ph; R^2 = Ph
3f: R^1 = H; R^2 = Ph

Entry	1	2	Temp/°C	Time/h	3	%Yield of **3**[b]
1	**1a**	**2a**	25	0.5	**3a**	48
2	**1a**	**2a**	25	4	**3a**	89(86)
3	**1a**	**2a**	50	0.5	**3a**	65
4	**1a**	**2a**	50	4	**3a**	99(97)
5	**1a**	**2b**	50	4	**3b**	27
6	**1a**	**2c**	50	4	**3c**	14
7	**1a**	**2d**	50	4	**3d**	0
8	**1b**	**2a**	50	0.5	**3e**	5
9	**1b**	**2a**	50	4	**3e**	21(15)
10	**1c**	**2a**	50	0.5	**3f**	7[c]
11	**1c**	**2a**	50	4	**3f**	0[c]

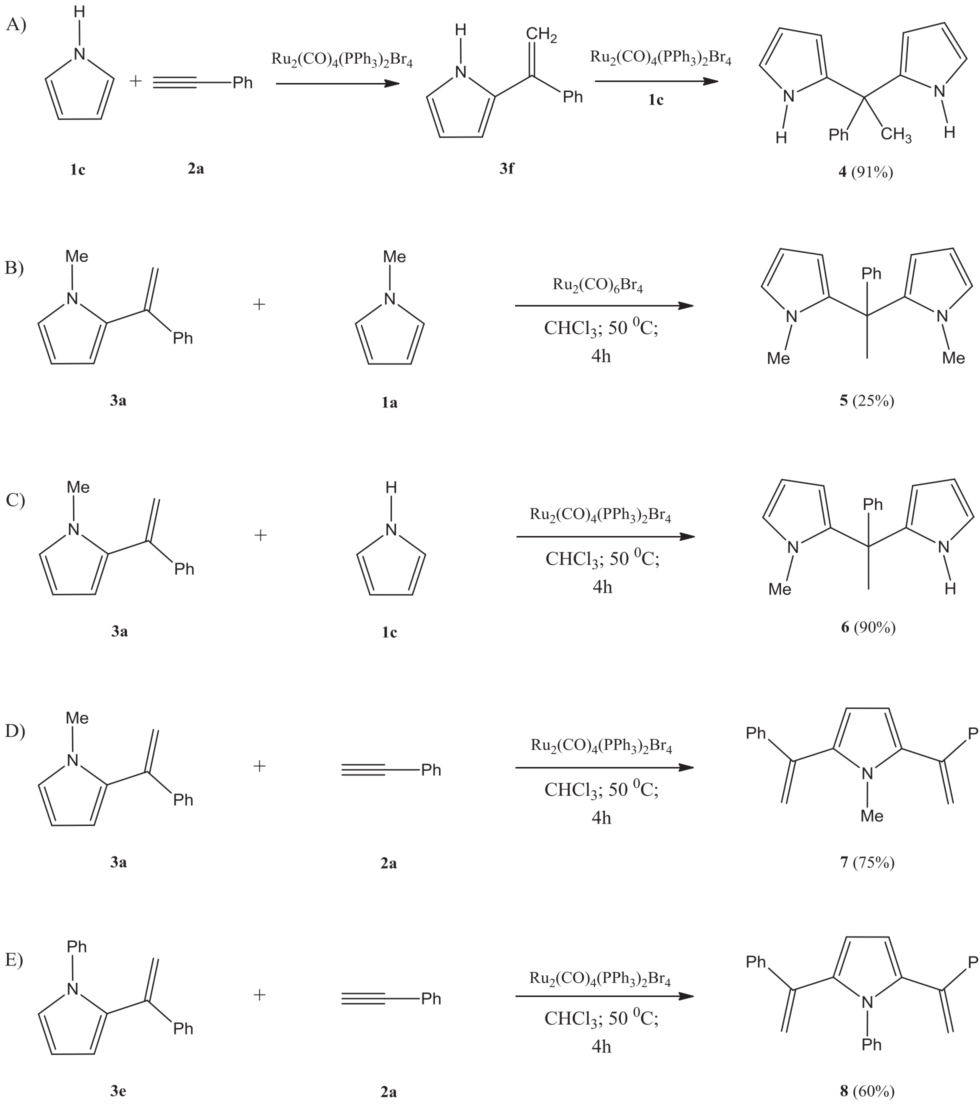
[a] Reactions were carried out based on pyrrole (10 mmol) and alkyne (1 mmol) with 2% catalytic loading.
[b] Total yield w.r.t. amount of alkyne used. Isolated yields are in parentheses.
[c] Further reaction of **3f** gave the double addition product **4** in 91% yield.

N-phenylpyrrole (**1b**) adds across **2a** to produce the corresponding 2-vinylpyrrole **3e**, albeit with a lower yield (Table 3, entry 8 and 9). It is reasonable for the more electron-deficient **1b** to have a lower yield, since the catalysis is most likely to proceed via an electrophilic aromatic substitution pathway if the pyrrole acts as the nucleophile [17,25]. The low yield can also be caused by steric factors, with the relatively more bulky phenyl group on **1b** hindering the reaction.

1c reacted with **2a** to produce the corresponding vinylpyrrole product **3f** (Table 3, entry 10 and 11). However the catalysis did not stop upon formation of **3f**. Instead the product underwent further reaction immediately to give the double addition product (dipyrromethane), **4** (Scheme 2, part A). Due to the reactivity of **3f** in the system, it could not be isolated to give a pure sample for analysis, with its existence being detected only at the initial stages of the reaction. We believed the lack of steric bulk on the N-atom of **1c** was responsible for the rapid formation of **4**. For the case of **1a**, the additional methyl group together with the bulky ruthenium catalyst would restrict further reaction of **3a**. On the same note, using the less bulky $Ru_2(CO)_6Br_4$ catalyst will result in the formation of the double addition product **5** under the same reaction condition (Scheme 2, part B). It was noted that the yield of **5** can be increased by lengthening the reaction time. From the above examples, it is possible to selectively form either vinylpyrrole or dipyrromethane products by tuning the steric bulk of the system.

Hence, following the above explanation, it can be expected that **1c** will add to **3a** under the same condition. Indeed, the unique mixed pyrrole product, **6**, was formed when **1c** and **3a** were reacted in the presence of $Ru_2(CO)_4(PPh_3)_2Br_4$ catalyst (Scheme 2, part C). The formation of **6** joins a list of useful dipyrromethanes, and points towards the advantage of having a controlled system for developments in a wide variety of applications.

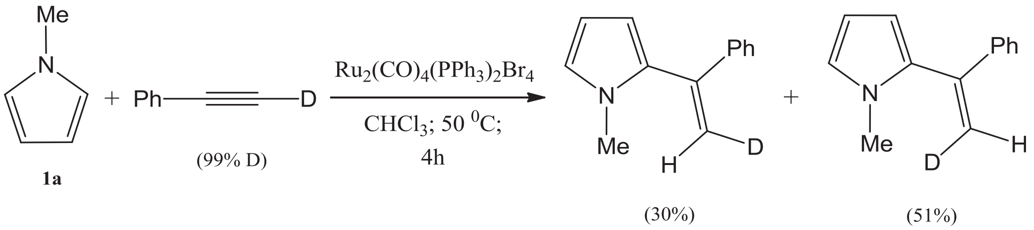
Next, it was observed that under a different set of reaction conditions, vinylpyrroles **3** can also add across an alkyne to give 2,5-bis(vinyl)pyrroles, **7** and **8** (Scheme 2, part D and E). The reaction can be controlled by simply adjusting the pyrrole-alkyne ratio to give the desired product. When the amount of pyrrole is sufficiently in excess of the alkyne (at least 10 equivalent of pyrrole to 1



Scheme 2. (A) **3f** reacts immediately upon formation with another molecule of pyrrole to give **4**. (B) Double addition involving **1a** can only take place using the less bulky $Ru_2(CO)_6Br_4$ catalyst. The yield can be improved to 70% if the reaction time is doubled to 8 h. (C) Addition of **1c** to **3a** can occur due to the lack of steric bulk on the incoming pyrrole. (D) Addition of **2a** to **3a** can occur when the pyrrole-alkyne ratio is reduced. (E) Similarly, addition of **2a** to **3e** can also occur.

equivalent of alkyne), **3** is formed exclusively. On the contrary, decreasing the ratio will give rise to the formation of 2,5-bis(vinyl) pyrroles. Based on our knowledge, synthesis of 2,5-bis(vinyl) pyrroles, such as **7** or **8**, is relatively unknown. Thus the obtained results will present an attractive platform for the synthesis of bis-functionalized pyrroles.

In an attempt to understand the reaction mechanism, deuterium studies were carried out using d^1-phenylacetylene. From the reaction of **1a** with PhCC-D, we have managed to obtain partial deuteration of the alkenyl proton alkenyl proton of 2-vinylpyrroles (Scheme 3). Since there was no sign of deuteration on the other positions of the product, it was clear that alkyne C-D bond cleavage did not occur during the reaction. This result is in contrast to other ruthenium systems studied by Yi et. al., where H/D exchange was observed at various positions on the product [18]. The lower chemical shift experienced by the deuterated product is a result of isotope shift effect (Fig. 1, δ 5.53 and 5.32 ppm, compared to 5.54 and 5.34 ppm of **3a**) [26]. The small amount of **3a** formed may be a result of a side reaction involving an H/D exchange of PhCC-D with atmospheric H_2O.



Scheme 3. Reaction of **1a** with d^1-phenylacetylene.

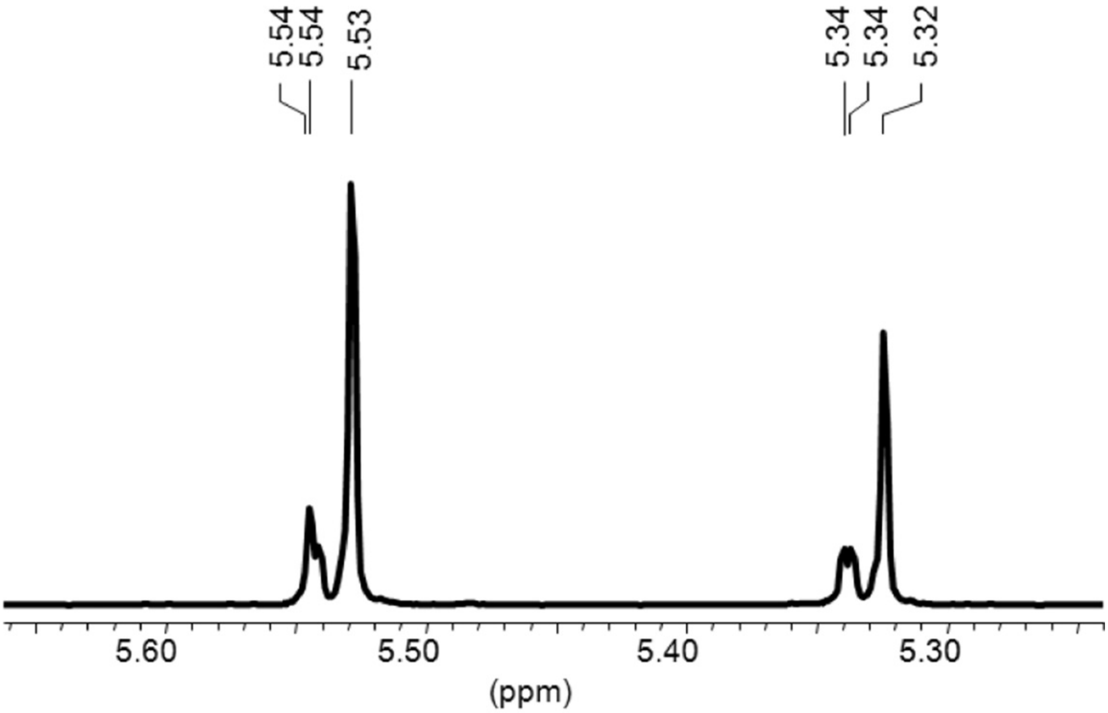


Fig. 1. Alkenyl region in the ^{1}H NMR spectrum showing the formation of deuterated 2-vinylpyrroles. The slight shift away from the non-deuterated product is caused by isotope shift effect.

Infrared spectra obtained after the reaction revealed 2 sets of peaks at (a) 2070 and 2013 cm^{-1}, and (b) 2056 and 1997 cm^{-1} corresponding to the starting ruthenium complex $Ru_2(CO)_4(PPh_3)_2Br_4$ and the inactive species $Ru(CO)_2(PPh_3)_2Br_2$ respectively (Fig. 2). The presence of $Ru(CO)_2(PPh_3)_2Br_4$ complex was probably due to the reaction of the dinuclear complex with free PPh_3 released from decomposed ruthenium intermediates. We believed that the active ruthenium species must have a short lifetime and hence eluded detection by FTIR spectroscopy.

As mentioned earlier, Ru-catalyzed pyrrole hydroarylation reactions most likely involve the formation of ionic species [18]. Hence, we first proposed the idea of ionic species being actively involved in our system (Scheme 4). Since pyrrole hydroarylation follows electrophilic aromatic substitution, formation of cationic ruthenium species would only favour the reaction. In addition, the electron-deficient intermediate can be stabilized by a strong σ-donating phosphine, which probably also accounts for a higher yield that was obtained when $Ru_2(CO)_4(PPh_3)_2Br_4$ was used. Formation of an ionic intermediate can also account for the exclusive formation of the Markovnikov product. In the mechanism, the cationic ruthenium species may be generated upon dissociation of the ruthenium dimer to the monomer species. This

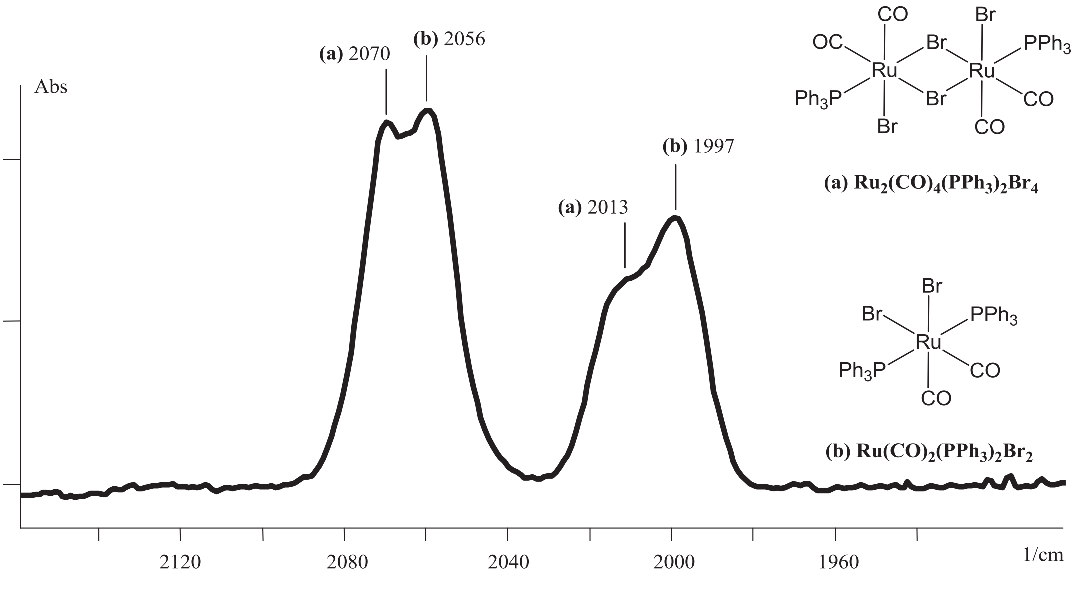
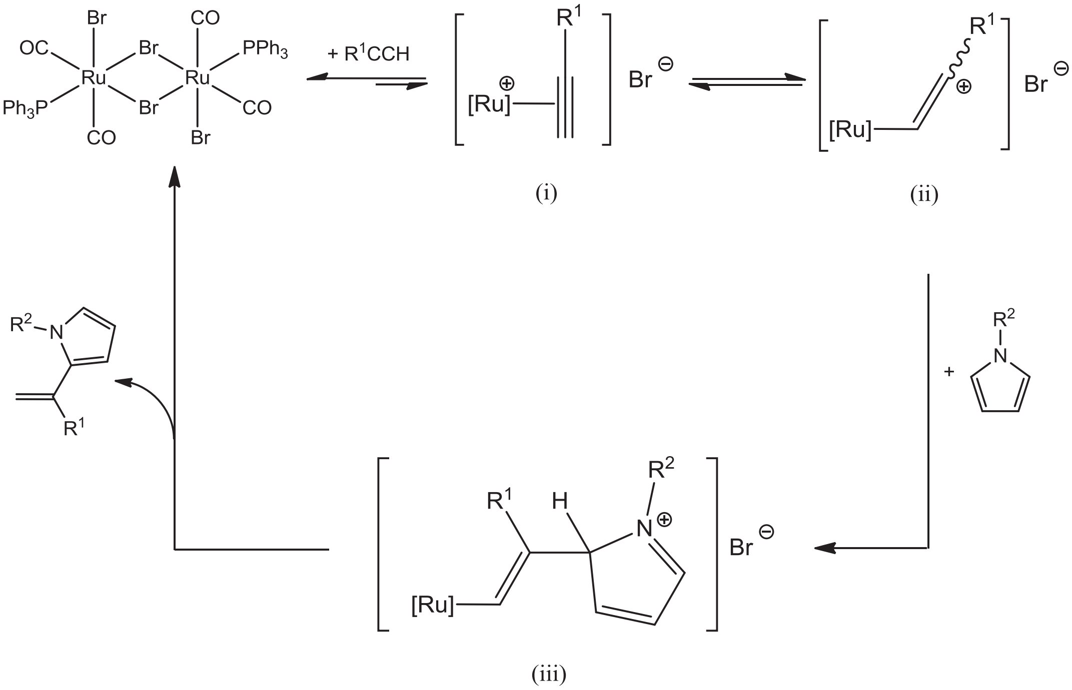


Fig. 2. FTIR spectrum obtained upon completion of the catalysis.



Scheme 4. Proposed mechanism for the reaction of pyrroles with alkynes.

is followed by the expulsion of a bromide ion upon alkyne coordination to give a species resembling intermediate **i**. Depending on the R group, either intermediate **i** or **ii** would be favoured for charge stabilization. When **2a** was used for example, the resultant benzyl carbocation formed would be relatively more stable than primary aliphatic carbocations, hence driving the reaction forward and accounting for the higher product yield associated with it. The effect of deuteration can also be accounted for by intermediate **ii**. The R group is able to move to either the cis or the trans position relative to C–D if PhC≡C–D is used as the substrate. Scheme 3 shows that the trans-position is slightly favoured. Subsequent step involving the attack of pyrrole onto **ii** would be driven by the electronic attraction between the electron-rich aromatic ring and the carbocation respectively. Ring substitution occurred exclusively at C-2 instead of the C-3 position due to a more extensive delocalization of the resultant positive charge throughout the pyrrole ring. Subsequent rearrangement within intermediate **iii** would form the addition product and complete the reaction cycle.

Apart from this pathway, we have also considered other similar mechanisms involving cationic ruthenium species. As the alkyne C–H bond was observed to have remained intact throughout the reaction, mechanisms involving the formation of ruthenium acetylide species cannot be applied to our system [27]. Also we ruled out the possibility of pyrrole being the first substrate to react with the ruthenium, as there was no observation reaction between pyrrole and the ruthenium starting material [28]. Lastly, we wish to emphasize that while the ionic mechanism was able to account for our experimental observations, we could not rule out any possibilities of the reaction occurring via neutral pathways.

4. Conclusions

The addition of pyrroles onto alkynes was catalyzed by the dinuclear $Ru_2(CO)_4(PPh_3)_2Br_4$ complex. Formation of 2-vinylpyrroles and 2,5-bis(vinyl)pyrroles have been achieved with high product yield. Further functionalization with pyrroles via the vinyl functional group can readily be achieved, as exemplified from the formation of the unprecedented 1-(1H-pyrrol-2-yl)-1-(1-methylpyrrol-2-yl)-1-phenylethane. A mechanism involving ionic species was proposed in an attempt to understand the process. The high regioselectivity of the system can be accounted for using the relatively stable carbocation formed from the resulting intermediates during the reaction.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2012.02.017.

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