

## Synthesis of New Ruthenium Vinylidene Complexes: Characterization by NMR Techniques

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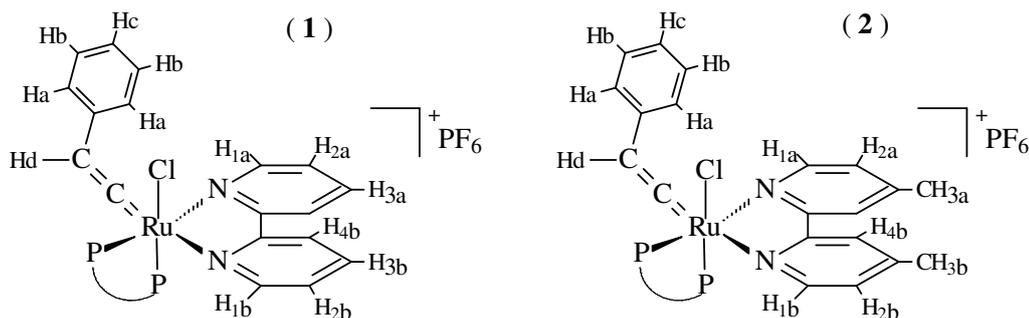
**Abstract:** The activation of several functional alkynes by ruthenium (II) complexes is one of the most important routes for synthesis of vinylidene complexes. Some metal vinylidenes ( $M=C=CHR$ ) have been used in many catalytic reactions of the following types: dimerisation of alkynes, nucleophilic addition and radical cycloaromatization. Direct coupling of 1-alkynes represents an easy route to unsaturated dimeric species, and these are valuable precursors for the synthesis of natural products as well as interesting building blocks for further organic modifications. Instead of using X-ray techniques, NMR experiments were used for characterization of these complexes. The  $^{31}P\{^1H\}$  NMR experiment shows two doublets for vinylidene complexes like  $[RuCl(dcybe)(bipy)(=C=CHPh)](PF_6)$  (**1**) and a singlet for  $[RuCl(PPh_3)_2(Mebipy)(=C=CHPh)](PF_6)$  (**2**). These signals suggest that **1** is a typical *cis* isomer while **2** is a *trans* isomer. The  $^1H-^{31}P$  HMBC experiments were quite effective to prove the presence of vinylidene group ( $P-Ru=C=CHR$ ) through of  $^4J_{H-P}$  for all compounds, and the  $^1H-^1H$  gCOSY experiment for these complexes showed, in detail, the correlation for the N-heterocyclic ligand. It was supposed that some hydrogens were downfield because of the effect of the electron density of the chlorine atom, which is a good  $\pi$  donor. Therefore, for both complexes, the chemical shifts were exchanged due to deshielded anisotropy effects from the vinylidene  $\pi$  system; DPFGSE-NOE was performed and the unambiguous assignment was possible. Thus, NMR techniques showed to be a powerful tool for the characterization of inorganic compounds.

The activation of several functional alkynes by ruthenium (II) complexes is one of the most important routes for synthesis of vinylidene complexes. Metal vinylidenes ( $M=C=CHR$ ) have emerged as useful precursors with unusual reactivity for a variety of organic reactions. With electrophilic ruthenium (II), complexes  $[RuCl_2(P)_2(N-N)]$  and  $[RuCl_2(P-P)(N-N)]$  {where P= triphenylphosphine ( $PPh_3$ ), P - P = 1,2-bis(dicyclohexylphosphine)ethane (dcybe), N-N = 2,2'-bipyridine (bipy) or 4,4'-dimethyl-2,2'-bipyridine (Mebipy)} in the presence of phenylacetylene and  $KPF_6$  react to order the activation of alkyne to afford ruthenium vinylidene complexes.

Metal vinylidenes have been applied in many catalytic reactions of the following types:

dimerization of alkynes, [2 + 2] cycloaddition, nucleophilic addition to alkynes and radical cycloaromatization. Direct coupling of 1-alkynes represents an easy route to unsaturated dimeric species, in particular, 1,3- and 1,4- disubstituted enynes. These are valuable precursors for the synthesis of natural products as well as interesting building blocks for further organic modifications.<sup>1</sup>

A similar procedure used to obtain precursors to vinylidene complexes was described by Batista and co-workers<sup>2</sup>, and the vinylidene complexes *cis*- $[RuCl(dcybe)(bipy)(=C=CHPh)](PF_6)$  (**1**) and *cis*- $[RuCl(dcybe)(Mebipy)(=C=CHPh)](PF_6)$  (**2**) (Figure 1) were obtained from the *trans*- $[RuCl(PPh_3)_2(bipy)(=C=CHPh)](PF_6)$  (**3**) and



**Figure 1.** Structures for complexes **1** and **2**.

from the *trans*-[RuCl(PPh<sub>3</sub>)<sub>2</sub>(Mebipy)(=C=CHPh)](PF<sub>6</sub>) (**4**), by exchanging the phosphine ligands.

Instead of using X-ray techniques we used NMR experiments to analyze these complexes. All NMR spectra were run on a Bruker Avance DRX 400, at 298K, using TMS and H<sub>3</sub>PO<sub>4</sub> (85%) as internal references for <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P respectively.

<sup>31</sup>P{<sup>1</sup>H} NMR spectra show two doublets for **1** (δ 61,8 and 58 ppm, <sup>2</sup>J<sub>PP</sub> = 14,2 Hz) and **2** (δ 56,8 and 53 ppm, <sup>2</sup>J<sub>PP</sub> = 14,5Hz) while for **3** and **4**, a singlet at δ 21 ppm and δ 22 ppm respectively is observed. These signals

suggest typical *cis* isomers for **1** and **2** and *trans* isomers for **3** and **4**. The chemical shift has a straightforward relationship with the basicity of the P-donor ligands.

<sup>1</sup>H-<sup>31</sup>P HMBC experiments were quite effective to prove the presence of a vinylidene group (P-Ru=C=CHR) through <sup>4</sup>J<sub>H,P</sub> for all compounds, which can be confirmed from the <sup>1</sup>H NMR triplet for each hetero coupling in the range from 3,3 to 3,7 Hz. The <sup>1</sup>H-<sup>1</sup>H gCOSY experiments for complexes **1** and **2** showed in detail the correlation for N-heterocyclic ligand and the aryl group from the acetylenic ligand, as described in Table 1.

**Table 1.** Chemical Shift, multiplicity and coupling constants for complexes **1** and **2**.

Complex 1		Complex 2	
Hydrogen	δ(ppm), m, J(Hz)	Hydrogen	δ(ppm),m, J(Hz)
H <sub>a</sub>	7,39 (d) 8,72	H <sub>a</sub>	7,39 (d) 8,3
H <sub>b</sub>	7,28 (t) 7,58	H <sub>b</sub>	7,27 (t) 7,54
H <sub>c</sub>	7,10 (t) 7,58	H <sub>c</sub>	7,09 (t) 7,54
H <sub>d</sub>	4,90 (t) 3,5	H <sub>d</sub>	4,8 (t) 3,7
H <sub>1a</sub>	9,91 (d) 5,46	H <sub>1a</sub>	9,69 (d) 5,68
H <sub>2a</sub>	7,55 (t) 5,46	H <sub>2a</sub>	7,31 (d) 5,34
H <sub>3a</sub>	8,05 (t) 7,99	Me <sub>a</sub>	2,53 (s)
H <sub>4a</sub>	8,34 (d) 7,99	H <sub>4a</sub>	8,16 (s)
H <sub>1b</sub>	8,85 (d) 5,38	H <sub>1b</sub>	8,64 (d) 5,68
H <sub>2b</sub>	7,97 (t) 5,38	H <sub>2b</sub>	7,73 (d) 5,51
H <sub>3b</sub>	8,20 (t) 7,99	Me <sub>b</sub>	2,59 (s)
H <sub>4b</sub>	8,38 (d) 7,99	H <sub>4b</sub>	8,18 (s)
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It is suggested that the hydrogens from H<sub>1a</sub> to H<sub>4a</sub> were downfield because of the electron density from the phosphine ligand, which is a good  $\pi$  donor. Therefore, for both complexes, the chemical shifts were confirmed by DPGSE-NOE, and it was found that H<sub>1a</sub> transfer magnetization to H<sub>2a</sub>, H<sub>a</sub> and H<sub>d</sub>, while H<sub>1b</sub> transfers only to H<sub>2b</sub>. These results show that H<sub>1a</sub> is more unshielded than H<sub>1b</sub>, which can be attributed to the deshielded anisotropy effect from the vinylidene  $\pi$  system. Thus, NMR techniques showed to be a powerful tool for the characterization of these compounds.

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### References

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