Mechanism of the Ru-Allenylidene to Ru-Indenylidene Rearrangement in Ruthenium Precatalysts for Olefin Metathesis

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KEYWORDS: Olefin Metathesis, Mechanism, Computational studies, DFT, Ruthenium, Indenylidene, Allenylidene,

Supporting Information Placeholder

ABSTRACT: The intramolecular allenylidene $RuCl_2(PR_3)_2(C{=}C{=}CPh_2)$ to indenylidene $RuCl_2(PR_3)_2(Ind)$ rearrangement occurring during the synthesis of Ru-based precatalysts for olefin metathesis is presented. In the absence of acid the ring closure via C-H activation was shown to be unfavoured for energy barriers up to 70 kcal/mol. Thus, it turned out to be HCl (or acids in general) that plays a crucial role during the indenylidene formation as the upper energy barrier decreases to reasonable 35 kcal/mol. Moreover, we proved computationally that depending on the nature of the phosphine the intramolecular rearrangement is either facilitated (PPh_3) or slightly hampered (PCy_3) which is in line with experimental results.

INTRODUCTION

The evolution of well-defined ruthenium-alkylidene complexes contributed to make olefin metathesis as a many faceted reaction to form C=C double bonds for several different applications.[1] Typical representatives of this type of (pre-)catalysts are Grubbs- or Hoveyda-type catalysts and consist of five ligands (carbene, two neutral ligands, two anionic ligands) which are arranged around the ruthenium centre. During the years a large number of alternative ligands were tested with the aim of improving already accomplished systems in terms of thermal stability and efficiency.[2] One of the most important developments was the introduction of N-heterocyclic carbenes (NHC) in place of less reactive systems based on phosphines.[3,4] However, the specific nature of the initial Ru-ylidene bond also attracted attention, and several motifs were investigated. During this search, the transformation of $(RuCl_2(\eta^6\text{-arenes}))_2$ with phosphine and prop-2-yn-1-ol led to the first (cationic) ruthenium complex bearing an allenylidene ($Ru{=}C{=}C{=}CR_2$) moiety.[5] Changing the precursor to the (neutral) catalyst $RuCl_2(PPh_3)_{3\text{-}4}$, it was first (wrongly) believed to also provide allenylidene complexes.[6] However, later works proved an intramolecular rearrangement leading to the indenylidene ($RuCl_2(PPh_3)_2(Ind)$) complex.[7] A new class of ruthenium catalysts evolved by exchanging the triphenylphosphine in a second step by diverse neutral ligands[8] resulting in diverse ruthenium indenylidene complexes bearing *bis*phosphanes,8[a,9] NHCs,8[a,8b,9] arenes[10] and Schiff Bases[11] (*cf.* Figure 1, above). Their activity is comparable to the one of Grubbs-type systems (as in ring opening metathesis polymerization[12]),[13] although a somewhat decreased initiation rate was reported for indenylidene complexes in favour of a higher stability.[14] Further advancement of this family of catalysts arose by introducing chelating indenylidene ligands equipped with electron donating properties. Similar to Hoveyda type catalysts this family bears high thermal stability associated with a high catalytic activity.[15] Recently it was even found that this type of ligands is prone to re-activate decomposed Hoveyda-type catalysts.[16]

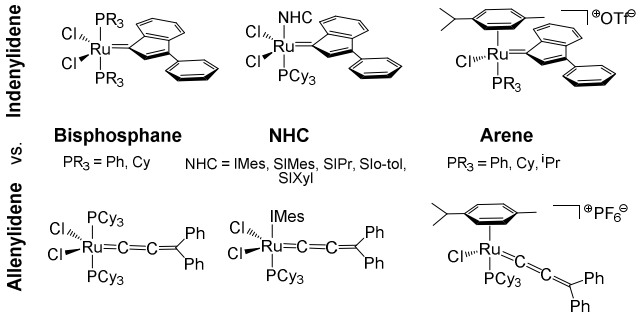


Figure 1. Typical representatives for indenylidene (above) and allenylidene (below) (pre-)catalysts.

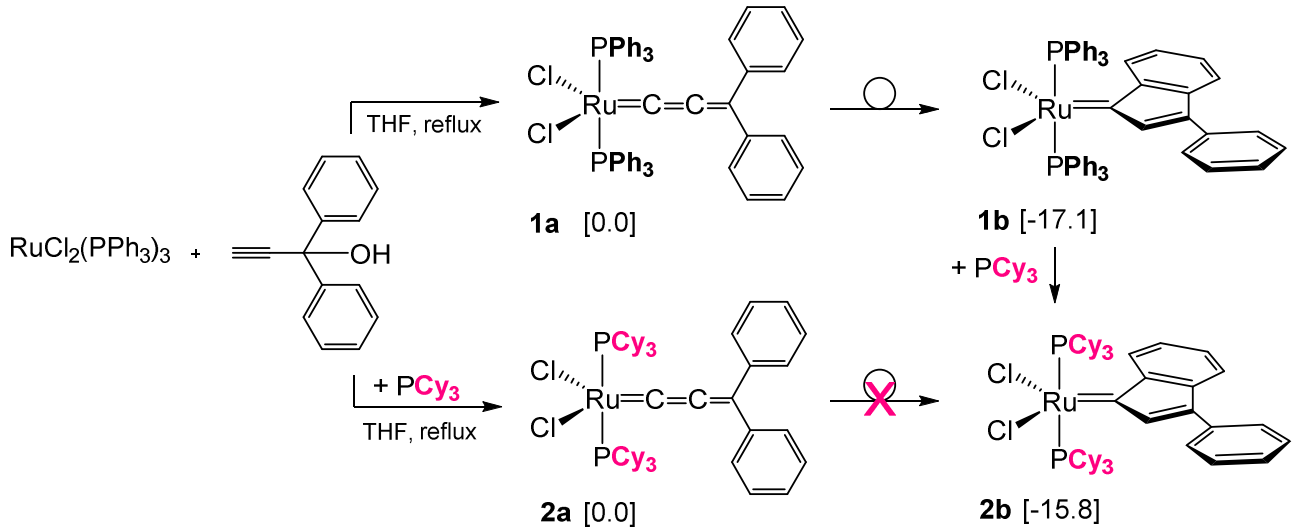
In contrary, allenylidene complexes (*cf.* Figure 1, below) are not as present in productive metathesis applications

although they also bear good catalytic properties associated with an easy accessibility from commercial reagents.[17] Their formation is mainly dependent on the nature of the substituents on the Ru.[18] When starting from the neutral $RuCl_2(PPh_3)_{3\text{-}4}$ precursor and diphenyl prop-2-yn-1-ol, the allenylidene species is not isolatable and the reaction ends up in an indenylidene complex. In turn, when adding PCy_3 during the reaction, the allenylidene species is unable to precede its rearrangement towards the indenylidene species.

This report describes the mechanism of the formation of the indenylidene species from the allenylidene species in ruthenium *bis*-phosphane complexes, pointing out the fundamental role of a protic acid, typically HCl, added to the reaction media to promote the transformation, and the reason for the hindered indenylidene formation in presence of PCy_3.

COMPUTATIONAL DETAILS

All the DFT static calculations were performed with the Gaussian09 set of programs.[19] For geometry optimization, the well-established and computationally fast GGA functional BP86 was used.[20] Geometry optimizations were performed without symmetry constraints, while the located stationary points were characterized as minima or transition state by analytical frequency calculations. The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, P, and Cl (SVP keyword in Gaussian).[21] For Ru, we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set contracted (standard SDD keywords in Gaussian 09).[22] Zero point energies and thermal corrections calculated at the BP86 level were added to the M06 in solvent energies[23] to approximate free energies in solvent using the triple-ζ valence plus polarization basis set for main group atoms (TZVP keyword in Gaussian). Since entropic contribution calculated within the ideal gas approximation at P = 1 atm is likely exaggerating the expected values for the dissociative steps in the condensed phase,[14b,24,27c] all the thermochemical analyses were performed at P = 1354 atm and T = 298.15 K, as suggested by Martin et al.[25] Solvent effects were included with the polarizable continuous solvation model PCM using THF as solvent.[26] The M06 energy calculations were carried out with the scf=tight, and integral(grid=ultrafinegrid) keywords. This approach was recently shown to be particularly effective in the modelling of Ru-promoted olefin metathesis.[27]



Scheme 1. Experimental routes to obtain *bis*-phosphine allenylidene and/or indenylidene ruthenium complexes.

RESULTS AND DISCUSSION

Bearing in mind experimental outcomes regarding the fundamental step corresponding to the ring closure of the allenylidene moiety of $RuCl_2(PPh_3)_2(C{=}C{=}CPh_2)$ (**1a**) to form the indenyl skeleton of $RuCl_2(PPh_3)_2(Ind)$ (**1b**) the following assertions can be retained: first, ring formation occurs under harsh reaction conditions in THF at 90°C starting from $RuCl_2(PPh_3)_{3\text{-}4}$ and diphenyl propargyl alcohol,8[a] whereas it was found that the allenylidene to indenylidene formation occurs preferentially in the presence of a protic acid. The second observation is connected to tricyclohexyl (PCy_3): the simultaneous addition of PCy_3 under the previous described reaction condition prevents rearrangement towards the indenylidene complex **2b** and terminates at the stage of $RuCl_2(PCy_3)_2(C{=}C{=}CPh_2)$ **2a** with the consequence that the *bis*-tricyclohexylphosphane indenylidene complex **2b** is only observed when exchanging the phosphine of **1b** by PCy_3 in a second step (see Scheme 1). DFT calculations were envisaged to unravel the mechanism to obtain indenylidene from *bis*-phosphane allenylidene precatalysts **1a** and **2a**. The thermodynamic stability of the indenylidene species with PPh_3 (**1**: -17.1 kcal/mol) and with PCy_3 (**2**: -15.8 kcal/mol) complexes relative to the starting allenylidene complexes suggests a clear exothermicity towards the indenylidene complex in both cases, indicating that the reason for the hindered ring

closure of the *bis*-PCy_3 species cannot be ascribed to the thermodynamic equilibrium but to the energy barriers within the intramolecular rearrangement mechanism. The reaction profile of allenylidene to indenylidene arrangement (**A**) was investigated for *bis*-PPh_3 (**1**) and *bis*-PCy_3 (**2**) Ru complexes. Moreover, the dissociative pathway for each species (PPh_3 (**3**) and PCy_3 (**4**)) was considered. The mechanism and respective energy values (ΔG in kcal/mol) of the non-HCl catalyzed reaction pathway are summarized in Figure 2 (left) and

Table 1. Starting from the [Ru=C=C=CPh_2] moiety (**I**), the first step involves the proton transfer from the *ortho*-carbon of the aromatic ring to the α-carbon of the allenylidene moiety (**A-I-II**). The corresponding transition state displays the highest barrier of the reaction pathway, 71.2 kcal/mol for **1** and 71.3 kcal/mol for **2**. These high energy values are clearly due to the bending of about 60° of the linear C_α=C_β=C_γ allene (Ru-C_{ortho}(arene) = 5.31 Å) to reach a reasonable Ru-C_{ortho} (arene) distance of 2.21 Å, which consequently allows C-H activation and concomitant hydrogen transfer. The structure ends up in the deformed cyclic intermediates **1-A-II** and **2-A-II**, 20.5 and 25.7 kcal/mol above the starting allenylidene species. A second hydrogen transfer from the C_α to the C_β through transition state **A-II-III** costs 49.9 and 50.8.kcal/mol for **1** and **2,** and leads to intermediate **A-III**, bearing a conjugated ring system with partial charges on the Ru and C_α atom. The final step towards $RuCl_2(PR_3)_2$(Ind) **A-IV** will be reached by binding the two carbons (C_α and C_{ortho}(arene)) by overcoming barriers of 12.4 (**1**) and 18.5 kcal/mol (**2**).

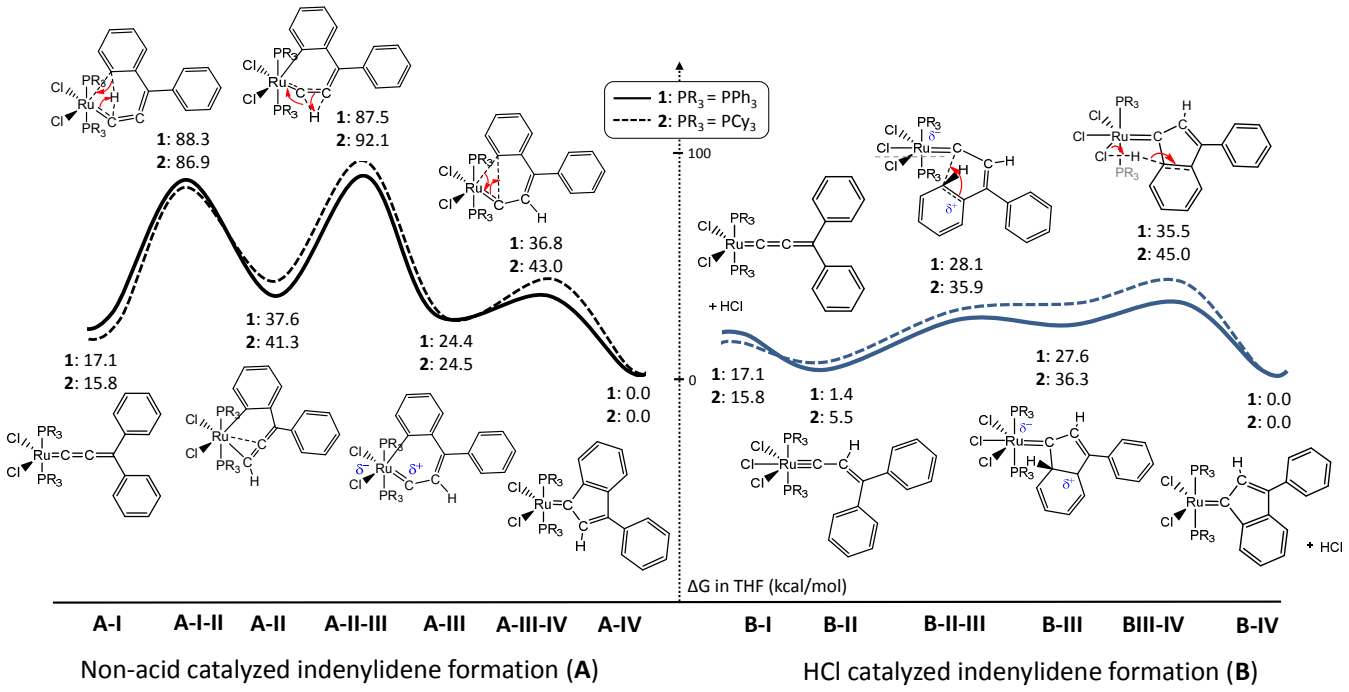


Figure 2. Mechanism without HCl (**A**: left) and HCl catalyzed (**B**: right) intramolecular allenylidene-indenylidene rearrangement for *bis*-PPh_3 (**1**) and *bis*-PCy_3 (**2**) complexes with respective energy values in kcal/mol.

Table 1. Relative energies (kcal/mol) for non-acid catalyzed indenylidene formation (**A**) for complexes **1-4**.

	A-I	**A-I_{diss}**	**A-I-II**	**A-II**	**A-II-III**	**A-III**	**A-III-IV**	**A-IV_{diss}**	**A-IV**
1	17.1	-	88.3	37.6	87.5	24.4	36.8	-	0.0
2	15.8	-	86.9	41.3	92.1	24.5	43.0	-	0.0
3	17.1	38.6	101.2	53.4	100.6	35.6	51.3	15.5	0.0
4	15.8	31.7	100.8	42.9	100.2	29.9	46.3	10.1	0.0

Table 2. Relative energies (kcal/mol) for HCl catalyzed indenylidene formation (**B**) for complexes **1-4**.

	B-I	**B-I$_{diss}$**	**B-II**	**B-II-III**	**B-III**	**B-III-IV**	**B-IV$_{diss}$**	**B-IV**
1	17.1	-	1.4	28.1	27.6	35.5	-	0.0
2	15.8	-	5.5	35.9	36.3	45.0	-	0.0
3	17.1	38.6	16.0	33.8	33.4	41.1	15.5	0.0
4	15.8	31.7	-0.3	23.0	20.6	27.2	10.1	0.0

The rate determining step is defined by the energy barrier **A-I-II** and suggests that both ring closures (starting either from *bis*-PPh_3 **1** or *bis*-PCy_3 **2** Ru allenylidene) are similar and differ by only 0.1 kcal/mol. However, considering that the energy barrier for this step is higher than 70 kcal/mol, this route seems to be experimentally not accessible. The same conclusion holds when one phosphine is removed from the ruthenium centre. Although energy barriers of **3** (one PPh_3 removed) and **4** (one PCy_3 removed) are comparable to the ones of reaction pathways **1** and **2**, the energy needed to dissociate one phosphine from $RuCl_2(PR_3)_2(C{=}C{=}CPh_2)$ (21.5 and 15.9 kcal/mol) has to be considered. Consequently, the upper energy point (**A-I-II**) lies in both cases at least 80 kcal/mol above **A-I**, making also this pathway experimentally impossible to occur.

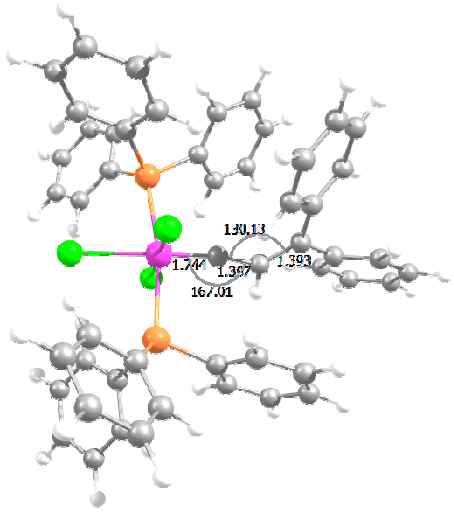


Figure 3. Geometry of the key intermediate **B-II** for **1**. Distances in Å, angles in deg.

In 2007 Schanz et al[28] stated that the presence of HCl or other acids is the key for enabling the indenylidene formation. Previously successfully implemented syntheses may have benefited from impurities as acidic $HPPh_3^+$, a cationic byproduct during the synthesis of the precursor $RuCl_2(PPh_3)_{3\text{-}4}$.[29] In Figure 2 both mechanisms (left: no acid cocatalyst (**A**)) and right: HCl-catalyzed (**B**)) are compared showing that the presence of HCl decreases the energy barriers drastically (respective values can be found in

Table 2). In presence of HCl, maximum energy barriers of around 35 kcal/mol were found. These barriers can be easily overcome at elevated reaction temperatures. Starting from the allenylidene complex $RuCl_2(PR_3)_2(C{=}C{=}CPh_2)$ (**B-I**), the reaction consists of HCl coordination (**B-II**): chloride coordinates on the ruthenium centre and the C_β carbon is protonated engendering a ruthenium carbyne species.[30] The new structure **B-II** is associated with an energy release of 15.7 (**1**) and 10.3 kcal/mol (**2**). Additionally, this coordination involves the formation of a conjugated alkenylcarbyne complex leading to a 50 degree bend of the C_α-C_β=C_γ angle and a concomitant sharp reduction of the C_α-C_{ortho}(arene) distance from 3.81 to 3.04 Å, which facilitates the arene-allene bond formation in the next transition step **B-II-III**. The C_{ortho}(arene)-hydrogen lifts up and allows the corresponding double bond to coordinate to the positively charged C_α. Energy barriers for this step were found to be 26.7 and 30.4 kcal/mol for **1** and **2**, respectively. The geometry of the key intermediate **B-II** for **1** is shown in Figure 3.

The unstable next stationary intermediate **B-III**, bearing a positively charged indenylium moiety, was found to be 0.5 kcal/mol more stable (**1**) and 0.4 kcal/mol (**2**) less stable with respect to the previous transition state. The final release of HCl (**B-III-IV**) from intermediate **B-III** costs 7.9 (**1**) and 8.7 kcal/mol (**2**) before ending up into the $RuCl_2(PR_3)_2$(Ind) (**B-IV**) involving an energy release of 35.5 (**1**) and 45.0 kcal/mol (**2**) when referring to **B-III-IV**. The upper energy point of the HCl catalyzed mechanism is defined by the highest transition state (**B-III-IV**) which defines an overall barrier of 34.1 (**1**) and 39.5 kcal/mol (**2**) with respect to the most stable intermediate of the pathway, **B-II**.

Hence, the reaction pathway involving the *bis*-PPh_3 species **1** seems to remain the most beneficial route for facilitating an intramolecular allenylidene to indenylidene rearrangement because the overall barrier from species **1** is 5.4 kcal/mol lower in energy than for complex **2**. Values for phosphine dissociative pathways can be found in

Table 2. Generally, phosphine dissociation of **2** (leading to complex **4**) better stabilizes the reaction pathway by releasing 16.1 kcal/mol from **B-I** to **B-II** whereas the same step releases just 1.1 kcal/mol for PPh_3 (**3**). However, the maximum energy barriers **B-II** to **B-III-IV** only differ by 2.4 kcal/mol in favour of **3** amounting in 25.1 kcal/mol for this transition compared to 27.5 kcal/mol for **4**. However, one has to bear in mind that that a dissociative pathway for **3** and for **4** is unlikely to occur as 1-2 equivalents of phosphine will be released during the reaction with $RuCl_2(PPh_3)_{3\text{-}4}$ catalyst dealing with **3** and additional 2.3

equivalent of tricyclohexylphospine will be present in case of **4**. Thus, the reaction pathway involving the *bis*-PPh_3 species **1** seems to remain the most beneficial route for facilitating an intramolecular allenylidene to indenylidene rearrangement. However, we cannot be sure about the observed reactivity difference between these two phosphines till new experiments trap the free phosphine once dissociated.

To test the coordinating capability of the solvent, THF, although the dissociation of an anionic ligand is always delicate,[31] we envisaged calculations substituting a chloride ligand of intermediate **II** by a THF molecule of the HCl catalysed mechanism. However, the corresponding optimised species are 16.6, 23.9, 20.9, and 19.8 kcal/mol higher in energy, for systems **1**-**4**, respectively.

CONCLUSION

In summary, we have investigated the allenylidene to indenylidene rearrangement with four neutral Ru allenylidenes complexes (**1**, **2**, **3**, **4**) via non-acid catalyzed (**A**) and HCl catalyzed (**B**) pathways. It was shown that in the absence of any acid getting the indenylidene species via C-H activation is disadvantageous, with energy barriers of at least 70 kcal/mol to form the arene-Ru bond. In agreement with experimental findings, our calculations suggest that the role of HCl on the indenylidene formation pathway is crucial for decreasing the highest energy barrier up to 35 kcal/mol. The main reason for this large decrease in the energy profile is connected to the formation of a carbyne intermediate **B-II** through protonation of the C_β carbon. Formation of this intermediate results in a large reduction of the C_{ortho} (arene) and C_α (allene) distance which consequently also reduces the energy barrier for the rate determining step **B-III-IV** to the reasonable amount of 34.1 kcal/mol for **1**. Even though the phosphine dissociation cannot be excluded, if we exclude the dissociative pathways for **3** and **4** to occur experimentally due to an excess of phosphine present during the reaction, our data suggest a preferential ring closure with the triphenylphosphine containing complexes **1**. The buried volume $\%V_{Bur}$ describing the sterical bulkiness of the ligand sphere amounts 26.5,[32] for **1** is exceeded by the bulkier tricyclohexylphosphine analogue **2**, with a $\%V_{Bur}$ of 28.1. These values help to rationalize why the allenylidene to indenylidene rearrangement is more facile with triphenylphosphine instead of tricyclohexylphosphine.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information provides the Cartesian coordinates of all species discussed in this work, as .xyz files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

A.P. thanks the Spanish MINECO for a project CTQ2014-59832-JIN, and European Commission for a Career Integration Grant (CIG09-GA-2011-293900). E.P. gratefully acknowledges the receipt of the "Chemical Monthly Fellowship" financed by Springer Verlag, the Austrian Academy of Sciences (ÖAW), and the Gesellschaft Österreichischer Chemiker (GÖCH).

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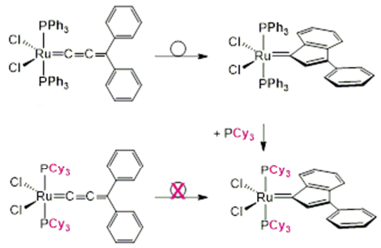
Graphical Abstract



The mechanism of formation of the indenylidene from the allenylidene in ruthenium bisphosphane complexes