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Influence of increasing steric demand on isomerization of terminal alkenes catalyzed by bifunctional ruthenium complexes

Alexey V. Smarun, Wahyu Shahreel, Steven Pramono, Shin Yi Koo, Lai Yoong Tan, Rakesh Ganguly, Dragoslav Vidović*

School of Physical and Mathematical Sciences, Division of Chemistry and Biological Chemistry, Nanyang Technological University, 21 Nanyang Link, 637371, Singapore

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ABSTRACT

Preparation of a series of cyclopentadienyl- and imidazolyl-phosphine-containing Ru-based complexes bearing a different degree of the Cp-ring methylation has been attempted. According to experimental and structural data the steric factors prevented the formation of the last complex in the series that contains permethylated Cp ring. These complexes were then subjected to alkene isomerization using 1-hexene. The rate of isomerization decreased, in general, with the increase in the Cp-ring methylation suggesting that the initial alkene coordination and/or imidazolyl N decoordination steps are restricted in the overall mechanism.

1. Introduction

Carbon-carbon double bond migration is one of the most common types of redox isomerization reactions. Due to potential quantitative atom economy it represents a highly attractive method towards compounds that are otherwise hardly accessible via conventional methods [1]. Established procedures for alkene isomerization either require potent acidic/basic/radical [2–4] or photochemical [5] treatment of olefin precursors. However, in most cases, harsh reaction conditions are required leading to intolerance of some functional groups. In contrast, transition metal catalyzed reactions of alkene isomerization require milder conditions, show higher tolerance towards functional groups together with better selectivity and tunability. Decades of development of different transition metal-based catalytic systems has allowed isomerization of wide range of functionalized alkenes [6]. These catalytic systems found wide application in selective carbon-carbon double bond migration over one position while tolerating a majority of functional groups [7–9]. However, only few catalysts were capable of more extensive isomerization of olefins in which the double bond was moved over several positions along a hydrocarbon chain. Up to date, the best performance was demonstrated by ruthenium(II) bifunctional catalyst [**1**][PF_6] (Fig. 1) containing chelating imidazolyl-phosphine ligand which was introduced by Grotjahn's group in 2007 [10]. Small loadings of catalyst [**1**][PF_6] (0.05–5%) efficiently produced new alkenes in high yields and exclusively in *E*-configuration at room temperature. In addition, for its outstanding ability to migrate a double bond up to 30 carbon positions in unsaturated alcohols it was titled as an “alkene zipper”.

The superb performance of catalyst $\mathbf{1}^+$ allowed its application as a useful synthetic tool towards a number of monoisomerized alkenes [11]. However, selective double bond migration over one position along an alkene chain with $\mathbf{1}^+$ could only be achieved if further isomerization was either impossible or restricted by the substrate's steric hindrance. Without these factors, i.e. in cases of linear terminal alkenes, catalyst $\mathbf{1}^+$ lacked control and produced a mixture of internal isomers [12]. This problem was resolved by introducing significant steric bulk into the structure of the catalyst by changing cyclopentadienyl (Cp) ring in complex $\mathbf{1}^+$ with bulkier pentamethylcyclopentadienyl (Cp^*) ring yielding a mixture of complexes [**2**][PF_6] and [**3**][PF_6] (Fig. 1 [13]). Even though all attempts to isolate pure chelating complex [**3**][PF_6] have failed, a mixture of both complexes [**2**][PF_6] and [**3**][PF_6] of any composition resulted in controlled monoisomerization of linear alkenes. For example, using 1-heptene as a substrate, almost 1:1 mixture of internal isomers 2- and 3-heptene was produced by catalyst [**1**][PF_6]. Meanwhile, the catalytic $\mathbf{2}^+/\mathbf{3}^+$ system selectively formed 2-

* Corresponding author.
E-mail address: dvidovic@ntu.edu.sg (D. Vidović).

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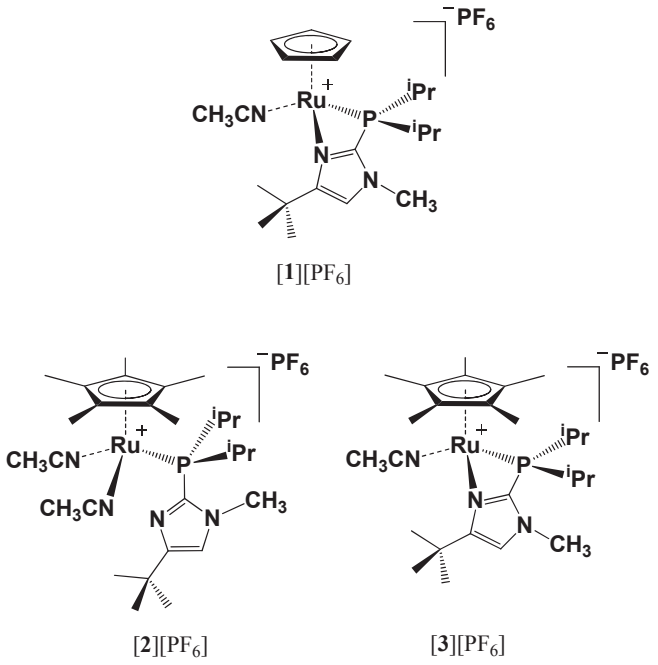
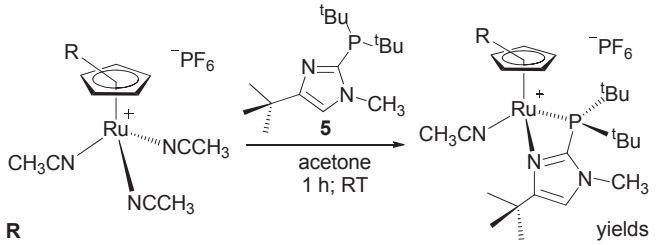


Fig. 1. Grotjahn's "alkene zipper" [**1**][PF_6] and sterically demanding complexes [**2**][PF_6] and [**3**][PF_6].

heptene with >95% yield. Thus, these results prompted us to study the influence of increasing the steric demand around the ruthenium centre in $\mathbf{1}^+$ on the isomerization rates of alkenes. The steric demand around $\mathbf{1}^+$ was enhanced by (i) introducing *tert*-butyl (^{t}Bu) groups at the phosphine ligand and (ii) varying the degree of Cp methylation.

2. Results and discussion

Grotjahn's group [13] showed that the most appropriate method to obtain the target Ru-catalysts (e.g. [**1**][PF_6], [**2**][PF_6] and [**3**][PF_6]) involved the synthesis of the corresponding tri(acetonitrile) precursors. Therefore, our initial goal was to prepare all possible precursors ([**4a**][PF_6]-[**4h**][PF_6], Scheme 1) required for the current investigation. The preparation of three key precursors [**4a**][PF_6] [14], [**4b**][PF_6] [15] and [**4h**][PF_6] [14] (Scheme 1) have already been reported using unique synthetic methodologies. We then explored



R		yields
H	[**4a**][PF_6]	[**6a**][PF_6] 84%
Me	[**4b**][PF_6]	[**6b**][PF_6] 83%
1,2-Me_2	[**4c**][PF_6]	[**6c**][PF_6] 79%
1,3-Me_2	[**4d**][PF_6]	[**6d**][PF_6] 78%
1,2,3-Me_3	[**4e**][PF_6]	[**6e**][PF_6] 82%
1,2,4-Me_3	[**4f**][PF_6]	[**6f**][PF_6] 79%
1,2,3,4-Me_4	[**4g**][PF_6]	[**6g**][PF_6] 90%
1,2,3,4,5-Me_5	[**4h**][PF_6]	[**6h**][PF_6] ---

Scheme 1. General synthetic procedure.

each method for the synthesis of the remaining precursors ([**4c**][PF_6]-[**4g**][PF_6]) and came to the conclusion that the method reported for [**4b**][PF_6] [15] was the most viable. This method involved the reduction of $RuCl_3 \cdot (H_2O)_x$ (X = 1.5–2.6) with cyclohexadiene to produce dimeric [(benzene)$RuCl_2$]$_2$, which was then treated with the lithium salt of the corresponding cyclopentadienes. After replacing chloride with PF_6^- anion the sandwich complexes ([Cp^RRu(benzene)][PF_6], R = various degree of methylation) were exposed to UV light in acetonitrile to yield the target precursors. Detailed synthetic procedures are described in the Experimental section. It is also noteworthy that apart from full spectroscopic characterization, several benzene- and tri(acetonitrile)-containing compounds have also been characterized by single crystal X-ray diffraction (Fig. 2). The most significant structural changes which occurred by replacing the benzene with three acetonitrile ligands were shortening of the Ru-$Cp_{(centroid)}$ distance from the average value of 1.81 Å to about 1.78 Å. This is not surprising as the benzene substituent is a stronger *trans*-ligand than acetonitrile leading to stronger Cp-Ru bonds in the acetonitrile complexes.

After synthesis and detailed characterization, compounds [**4**][PF_6] were individually reacted with imidazolyl-phosphine ligand (^{t}Bu$_2$P-C(NMe)(NC^{t}Bu)(CH), **5**, Scheme 1) bearing bulky *tert*-butyl substituents on phosphorus atom in order to prepare the target compounds $\mathbf{6}^+$. According to ^{31}P NMR spectroscopy all reaction mixtures, except for the reaction involving [**4h**][PF_6], resulted in the formation of only one new species. In each case the initial δ_P signal for **5** (- 0.5 ppm) was replaced by a sharp downfield signal found between δ_P 54.1–58.2 ppm. After workup complexes [**6a**][PF_6]-[**6g**][PF_6] were obtained in high yields and great purity and were fully characterized by multinuclear NMR spectroscopy, mass spectrometry as well as elemental analysis. At this point it is worth mentioning that all our attempts to prepare complex [**6h**][PF_6] by reacting its precursor [**4h**][PF_6] with **5** were unsuccessful even though numerous reaction conditions have been examined. Initial assessment suggested steric factors were responsible for this observation which further was supported by structural and additional experimental evidence (see below).

Even before we elucidated structural features of the majority of the synthesized complexes [**6**][PF_6] it was possible to assess whether the imidazolyl-phosphine ligand was coordinated in a chelating or monodentate manner. As already discussed, Grotjahn and co-workers prepared a catalyst system for alkene monoisomerization ($\mathbf{2}^+ + \mathbf{3}^+$, Fig. 1) in which the monodentate form $\mathbf{2}^+$ was preferred over the chelating form $\mathbf{3}^+$ [13]. Analysis of the ^{13}C NMR data revealed strong influence of the coordination mode of the imidazolyl-phosphine ligand on the δ_C values and the J_{PC} coupling constants involving carbon atoms at the C2 and C4 positions of the imidazolyl ring as indicated it Table 1. Ligand chelation ($\mathbf{2}^+ \rightarrow \mathbf{3}^+$) resulted in downfield shifting of both δ_C signals associated with C2 ($\mathbf{2}^+$: 142.5 ppm; $\mathbf{3}^+$: 148.3 ppm) and C4 ($\mathbf{2}^+$: 151.7 ppm; $\mathbf{3}^+$: 153.1 ppm). On the other hand, the J_{PC} coupling for C2 ($\mathbf{2}^+$: 58.0 Hz; $\mathbf{3}^+$: 28.5 Hz) was approximately halved while for C4 ($\mathbf{2}^+$: 7.8 Hz; $\mathbf{3}^+$: 14.3 Hz) it was almost doubled. For complexes $\mathbf{6a}^+$–$\mathbf{6g}^+$ the values for δ_C signals associated with the C2 (ave. 149.2 ppm) and C4 (ave. 152.6 ppm) as well as for the corresponding J_{PC} coupling constants (ave. 20.6 and 13.6 Hz, for C2 and C4, respectively) strongly suggested the chelating binding mode for ligand **5**, which was further supported by structural analysis (Fig. 3).

Samples of single crystals for [**6c**][PF_6], [**6e**][PF_6], and [**6g**][PF_6] suitable for structural determination were grown from the respective acetone solutions by slow diffusion of ether. For compounds $\mathbf{6b}^+$, $\mathbf{6d}^+$, and $\mathbf{6f}^+$ it was necessary to exchange the PF_6^- anion with $BAr^f_4^-$ ($Ar^f = C_6H_3(CF_3)_2$-3,5) and then allow pentane to slowly diffuse into respective THF solutions. As data for $\mathbf{6b}^+$

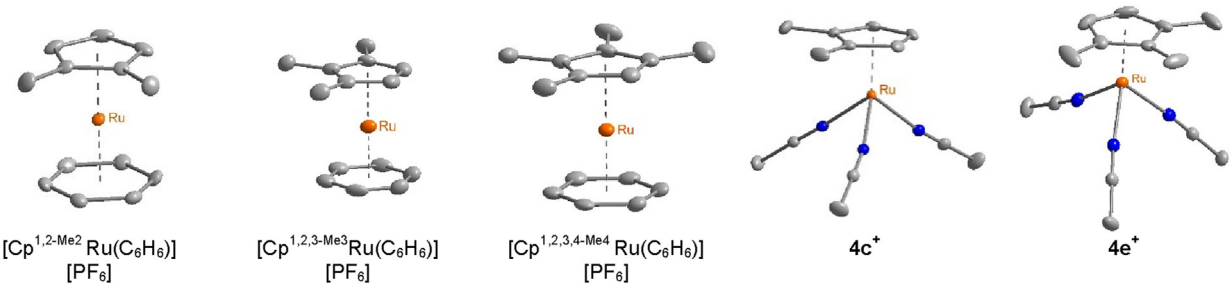
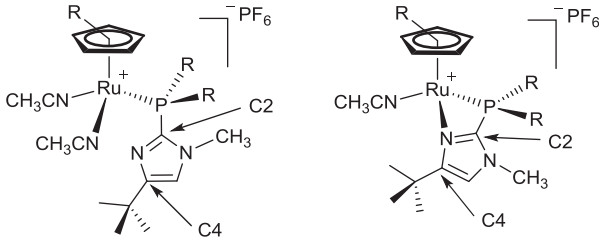


Fig. 2. Molecular structures for $[Cp^{1,2\text{-}Me2}Ru(C_6H_6)][PF_6]$, $[Cp^{1,2,3\text{-}Me3}Ru(C_6H_6)][PF_6]$, $[Cp^{1,2,3,4\text{-}Me4}Ru(C_6H_6)][PF_6]$, [**4c**][$PF_6$] and [**4e**][$PF_6$] as drawn at the 30% probability level. All hydrogen atoms, counterions as well as the second molecules found in the asymmetric unit have been omitted for clarity.

Table 1
The values for the ^{13}C NMR (δ_C) chemical shifts (ppm) and the J_{PC} coupling constants (Hz) for C2 and C4 atoms for various complexes.



	C2	C4
	δ_C (ppm) J_{PC} (Hz)	δ_C (ppm) J_{PC} (Hz)
2$^+$	142.5 58.0	151.7 7.8
3$^+$	148.3 28.5	153.1 14.3
6a$^+$	149.3 20.9	152.5 13.3
6b$^+$	149.3 20.6	152.4 13.4
6c$^+$	149.4 20.8	152.4 12.9
6d$^+$	149.2 20.2	152.8 13.4
6e$^+$	149.2 21.4	152.6 13.4
6f$^+$	149.1 19.7	152.7 14.5
6g$^+$	149.2 20.3	152.8 13.8

showed a high degree of molecular disorder, structural parameters for this complex are not included in further discussion. For the remaining five complexes Table 2 lists the selected bond lengths and angles. All structurally analysed complexes have distinctive distorted octahedral three-legged piano-stool structures with bulky chelating imidazolyl-phosphine ligands occupying two coordination sites. The average Ru-P bond distance (2.38 Å) for **6c**$^+$-**6g**$^+$ is in a good agreement with complexes that incorporate P^tBu_2-containing chelating ligands [16–18]. The Ru-$Cp_{(centroid)}$ bond distance vary from 1.804(1) Å for **6c**$^+$ to 1.820(1) Å for **6g**$^+$ which is longer than the same distances observed for the corresponding precursors **4c**$^+$ (1.775(2) Å) and **4d**$^+$ (1.779(2) Å). This slight elongation could be explained by the fact that two acetonitrile ligands have been replaced by a more basic (i.e. a better *trans* influence [19]) and more sterically encumbered ligand i.e. **5**. On the other hand, the imperfect correlation among complexes **6**$^+$ regarding the same structural parameter could be explained by

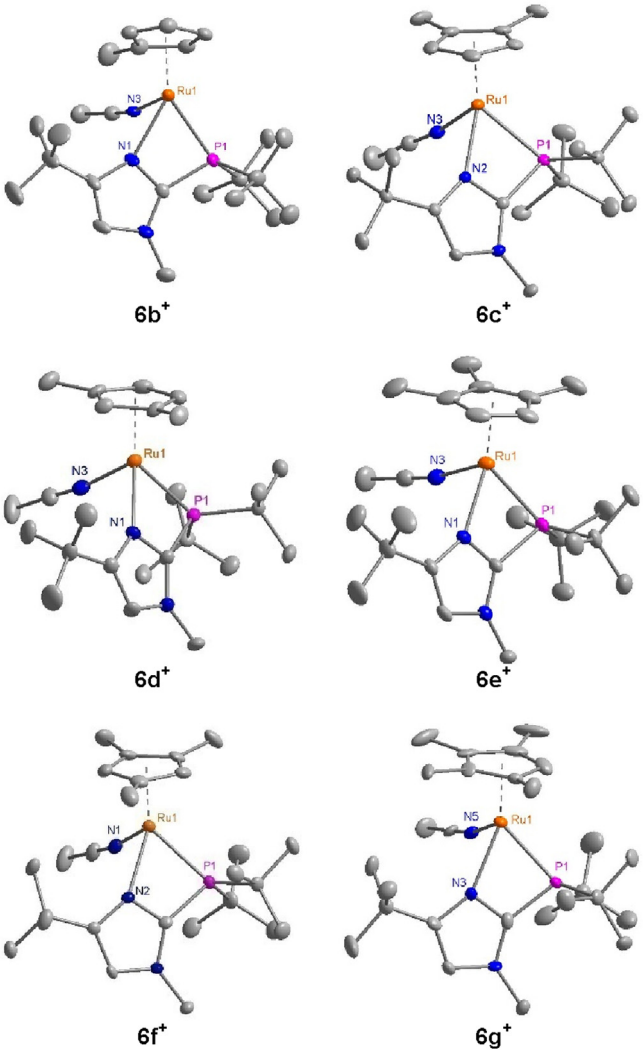


Fig. 3. Molecular structures for **6b**$^+$–**6g**$^+$. All hydrogen atoms, counterions as well as second molecules in the asymmetric unit have been omitted for clarity.

competing steric and electronic effects. The addition of methyl groups on the Cp ring would favour stronger Ru-Cp bonds but the resulting increase in the steric demand would favour elongation of the same bonds. In fact, both the Ru-N_{Im} (N_{Im}: imidazolyl N coordinated to Ru) and Ru-N_{AcN} (N_{AcN}: acetonitrile N coordinated to Ru) bond distances follow this imperfect pattern (Table 2). More evidence about increased steric bulk around the Ru centre was gathered by analysing the Cp tilt angle which we defined as the

Table 2
Selected bond distances (Å) and bond angles (°) for **6c**$^+$, **6d**$^+$, **6e**$^+$, **6f**$^+$, and **6g**$^+$.

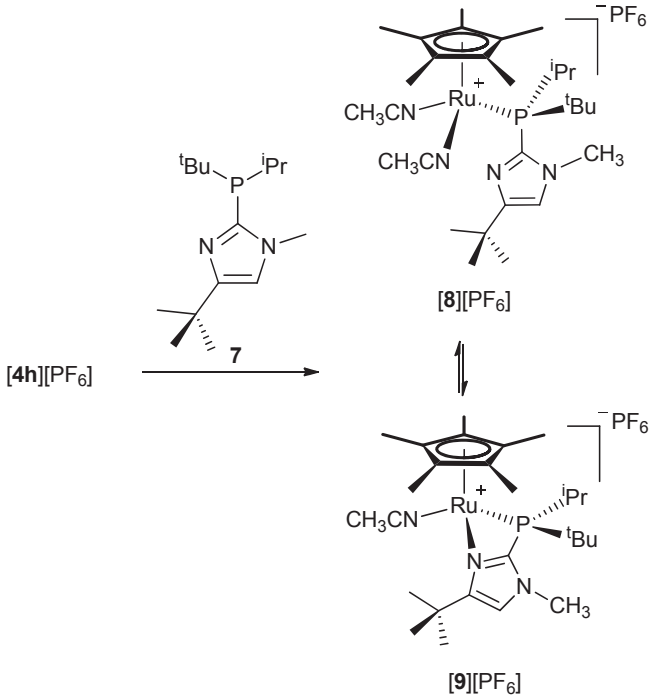
	6c$^+$	**6d**$^+$	**6e**$^+$	**6f**$^+$	**6g**$^+$
Ru-P	2.401(1) 2.383(1)	2.398(2)	2.380(1)	2.394(1)	2.373(3) 2.369(3)
Ru-N_{Im}[a]	2.206(2) 2.181(2)	2.210(4)	2.222(3)	2.261(3)	2.253(8) 2.246(8)
Ru-N_{AcN}[b]	2.064(2) 2.061(2)	2.067(4)	2.069(3)	2.065(4)	2.087(8) 2.075(8)
Ru-$Cp_{(centr.)}$	1.804(1) 1.800(1)	1.818(1)	1.807(1)	1.809(1)	1.820(1) 1.813(1)
Cp tilt[c,d]	1.6(2) 0.9(2)	2.8(3)	3.0(3)	1.7(2)	7.9(5) 5.6(5)

[a] N_{Im} is the imidazolyl N atom.
[b] N_{AcN} is the acetonitrile N atom.
[c] Defined as C^x-$Cp_{(centroid)}$-Ru, where C^x is one of the C atoms of the Cp ring.
[d] The results are reported as the difference between the largest and smallest angle formed by C^x-$Cp_{(centroid)}$-Ru.

difference between the largest and smallest angle formed by C^x-$Cp_{(centroid)}$-Ru where C^x is one of the C atoms in the Cp ring. The tilt angle progressively increased from the average value of 1.3(3)° for **6c**$^+$ to 3.0(3)° for **6e**$^+$. It then dropped to 1.7(2)° for **6f**$^+$ which is presumably due to the presence of two vacant but non-adjacent Cp sites for **6f**$^+$ in comparison to **6e**$^+$ creating a slight steric relief. On the other hand, the average tilt angle significantly increased to 6.5(7)° for **6g**$^+$ with the only vacant site positioned directly above the phosphine moiety. Nevertheless, crystal packing effects should not be completely disregarded as they could have not only influenced the position of the Me groups but also the observed tilt angles. However, it is still strongly believed that a certain correlation still exists with respect to increased steric demand and the degree of the Cp ring methylation.

All abovementioned structural evidence would then suggest that steric encumbrance is highly likely responsible for inability of precursor **4h**$^+$ to coordinate ligand **5** to form target complex **6h**$^+$. In order to experimentally test this hypothesis we decided to slightly reduce the steric encumbrance of ligand **5** by substituting one of the ^{t}Bu group with ^{i}Pr. This new ligand (**7**, Scheme 2) was then reacted with **4h**$^+$ and according to ^{31}P NMR spectroscopy a coordination complex was formed. The δ_P signal associated with **7** (- 8.6 ppm) was replaced with a downfield signal at δ_P 40.7 ppm which is consistent with coordination of **5** to the other tri(-acetonitrile) precursors. However, this new δ_P signal was observed to be much broader than the same signals observed for **6a**$^+$-**6g**$^+$ suggesting a dynamic process in the solution. Indeed, after an acetone-d_6 sample of this new reaction mixture was cooled down to − 80 °C identification of two major compounds, with δ_P values of 45.7 and 34.8 ppm, was possible. As the difference between the δ_P values for these two newly identified species ($\Delta\delta_P = 10.9$ ppm) was quite similar for the **2**$^+$/**3**$^+$ system ($\Delta\delta_P = 8.4$ ppm) we assigned the δ_P 45.7 ppm signal to monodentate species **8**$^+$ while the δ_P 34.8 ppm signal to chelating complex **9**$^+$ (Scheme 2). Even though numerous unsuccessful attempts have been made to further characterize the newly formed complexes it is quite evident that steric encumbrance was responsible for the lack of ligand **5** coordination to **4h**$^+$. It seems that only a slight ligand-based structural change, modifying **5** to form **7**, was necessary to alleviate enough steric strain leading to ligand coordination. However, due to the absence of full spectroscopic characterization of this newly created system, it was omitted from the subsequent isomerization studies.

Our next aim was to examine the influence of increasing steric bulk in **6**$^+$ with respect to isomerization of terminal alkenes. For this purpose we chose 1-hexene because it would also allow us to investigate whether any of the prepared complexes would show selectivity with respect to isomerization of this particular substrate to the other two possible isomers i.e. 2- vs 3-hexene. The experiments were set up by adding the terminal alkene to an acetone-d_6 solution containing one of [**6**][PF_6] (2% mol) complexes at 60 °C and the isomerization was followed by ^{1}H NMR spectroscopy. First of all, all complexes were capable of isomerizing 1-hexene but the reaction rates were influenced by the steric encumbrance of the



Scheme 2. Observed equilibrium.

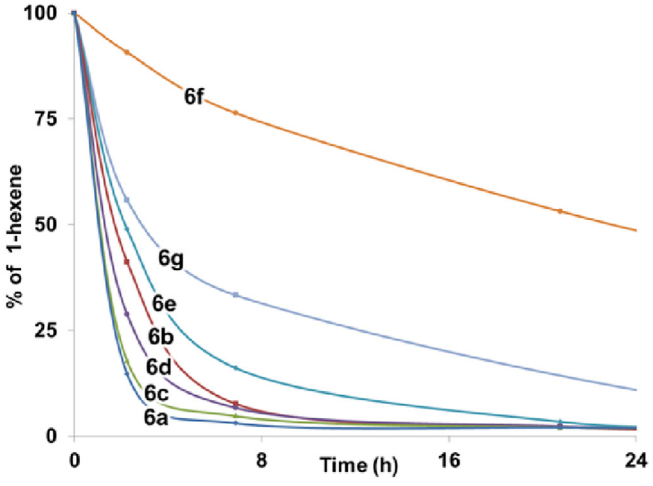
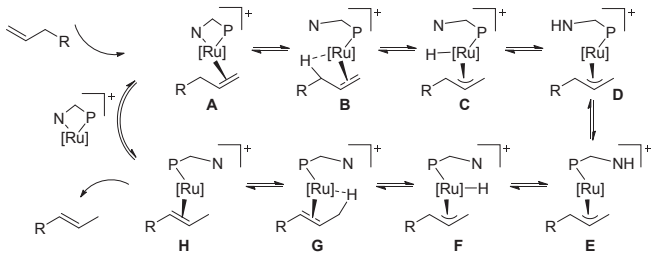


Fig. 4. Reaction profiles of 1-hexene isomerization by various complexes **6**$^+$ (2% mol) in acetone-d_6 at 60 °C. The lines serve as a visual tool to observe reaction progress.



Scheme 3. The proposed mechanism of alkene isomerization with ruthenium bifunctional catalysts.

investigated complexes (Fig. 4). While complexes **6a**$^+$–**6d**$^+$ completed substrate isomerization within 10 h, the three remaining and most sterically demanding complexes needed more time (about 24h for **6e**$^+$ and over 36 h for **6g**$^+$) or did not complete the isomerization within more than 4 days (**6f**$^+$) [20]. These observations suggested that, in general, enhancing the steric bulk by increasing the amount of Cp methylation decreased the isomerization rate. If we examine the proposed mechanism of alkene isomerization catalyzed by ruthenium bifunctional catalysts [10,21] (Scheme 3) the alkene coordination (**A**) and subsequent imidazolyl moiety decoordination (**B**) are probably the two steps mostly affected by steric factors. The increased steric bulk would not only slow down the alkene coordination by repelling the substrate but it would also make the opening of the PN chelate more difficult due to the clash between the ^{t}Bu groups and the Cp ring [22]. The decoordination of the imidazolyl moiety could be slow as a result of the large ^{t}Bu groups forcing the chelate closed. This is similar to what is seen by Shaw's work with cyclometallation using P^{t}Bu$_2$ ligands [23]. It is also worth mentioning that **6b**$^+$ and **6f**$^+$ are the only anomalies with respect to this hypothesis as the isomerization rates observed for **6a**$^+$ through **6d**$^+$ are very similar and certainly fall within the experimental error. Even though several structural parameters (Table 2) indicated that unique property of **6f**$^+$ (the non-adjacent vacant sites on the Cp ring) allowed this complex to alleviate some of the steric strain it does not necessarily imply that this complex is less sterically demanding than **6g**$^+$, with respect to the alkene coordination. On the contrary, it is believed that partial alleviation of the steric strain in **6f**$^+$ compared to **6g**$^+$ resulted in higher stability and, hence, lesser flexibility/reactivity of the former. This, in turn, led to alienation of the initial alkene coordination to **6f**$^+$. On the other hand, the observed structural deformity increased the structural flexibility of **6g**$^+$, which presumably translated into a higher probability for the alkene coordination and the subsequent isomerization.

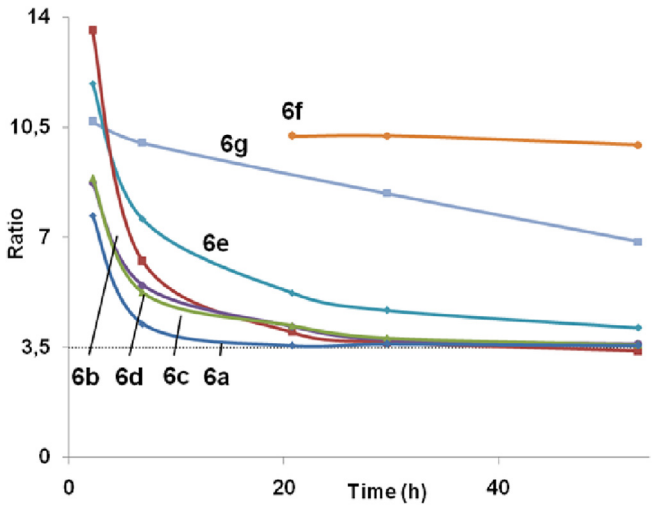


Fig. 5. Ratios between 2-hexene and 3-hexene produced in a course of 1-hexene isomerization by means of 2 mol % **6**$^+$ in acetone-d$_6$ at 60 °C. The lines serve as a visual tool to observe reaction progress.

In order to determine whether any of the prepared complexes **6**$^+$ was capable of selectively isomerizing 1-hexene to either 2- or 3-hexene the ratio of these two isomers was followed with the reaction progress (Fig. 5). Initially, the reaction mixture contained a higher amount of 2-hexene over 3-hexene. This was not surprising considering that the terminal alkene is less sterically demanding and, hence, has a higher propensity to coordinate to the Ru centre than 2-hexene. After majority of 1-hexene was isomerized to 2-hexene then the amount of 3-hexene started increasing until the ratio levelled off at a value of about 3.5 for the system isomerized by **6a**$^+$-**6d**$^+$ (Fig. 4). This seems to be the thermodynamic ratio between these two internal alkenes as virtually the same ratio was reached when only *E*-3-hexene was isomerized with **6a**$^+$ [24]. It is also believed that the same ratio would have been reached for the other Ru complexes (**6e**$^+$, **6f**$^+$ and **6g**$^+$) if more time was given. It is also noteworthy that other terminal alkenes have been attempted (e.g. 1-heptene and 1-octene) but there was no improvement with respect to isomerization selectivity. Thus, it appears that prepared complexes **6**$^+$ are not specific enough with respect to isomerization of terminal alkenes in comparison to the **2**$^+$/**3**$^+$ system. This is presumably due to a higher coordination propensity of terminal than internal alkenes in the coordination sphere of **2**$^+$/**3**$^+$ in comparison to complexes **6**$^+$.

In conclusion, we have synthesized a series of Cp- and imidazolyl-phosphine-containing ruthenium complexes by varying the degree of Cp methylation. All the prepared complexes **6a**$^+$-**6g**$^+$ were fully characterized by multinuclear NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction. According to extensive experimental and structural data the most sterically demanding complex **6h**$^+$ could not be synthesized due to the steric clash between the permethylated Cp ring and ligand **5**. The obtained complexes were then investigated with respect to terminal alkene isomerization and even though no selectivity was obtained it was evident that increase in steric bulk, in general, decreased the rate of the isomerization.

3. Experimental section

3.1. General methods

All experiments were performed under dry nitrogen or argon atmosphere using standard Schlenk and/or drybox techniques. Unless specified otherwise, all commercially available reagents were used as received without further purification. Hexane, diethyl ether and THF were distilled over sodium/benzophenone under N_2 atmosphere. Acetonitrile/acetonitrile-d$_3$ and acetone/acetone-d$_6$ were distilled over CaH_2 and B_2O_3, respectively, under N_2 atmosphere. Dried solvents were then degassed by means of either reduced pressure or saturation with inert gas. Degassed solvents were further stored over 4 Å molecular sieves (except acetone/acetone-d$_6$).

3,4-dimethyl-2,4-cyclopentadiene [25], 2,3,4,5-tetramethyl-2,4-cyclopentadiene [26], phosphine–imidazolyl ligand ^{t}Bu$_2$PIm, **5**, (Im = 4-*tert*-butyl-1-methylimidazol-2-yl) [27], [CpRu(NCCH$_3$)$_3$][PF$_6$], [**4a**][PF$_6$] [14], [Cp'Ru(NCCH$_3$)$_3$][PF$_6$], [**4b**][PF$_6$] [15], [Cp*Ru(NCCH$_3$)$_3$][PF$_6$], [**4h**][PF$_6$] [14], and [(C$_6$H$_6$)RuCl$_2$]$_2$ [28] were prepared according to published preparatory methods. 2,3,5-Trimethyl-2,4-cyclopentadiene was synthesized from 3,4-dimethyl-2-cyclopentenone using an adaptation of the same

method used for the synthesis of 1,2,3,4,5-pentamethyl-2,4-cyclopentadiene [29]. Complexes [CpRu(^{i}Pr$_2$PIm)(NCCH$_3$)]PF$_6$, [**1**][PF$_6$] [10] and [Cp*Ru(^{i}Pr$_2$PIm)(NCCH$_3$)]PF$_6$, [**2**][PF$_6$]/[**3**][PF$_6$] [13] were obtained using methods similar to those described in literature. Phosphine–imidazolyl ligand ^{i}Pr^{t}BuPIm, **7**, was synthesized from ^{i}Pr^{t}BuPCl using an adaptation of the same method used for the synthesis of ligand **5** [27].

NMR spectra were recorded at 25 °C on either Brüker Avance 500 (500 MHz listed below for ^{1}H = 499.9 MHz, ^{13}C{^{1}H} = 125.7 MHz and for ^{31}P{^{1}H} = 202.3 MHz) or JEOL ECA 400 (400 MHz listed below for ^{1}H = 399.8 MHz and 100 MHz for ^{13}C{^{1}H} = 100.5 MHz). ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million to low field relative to tetramethylsilane and referenced to residual solvent resonances (^{1}H NMR: 2.05 ppm for acetone-d$_6$ and 1.95 for acetonitrile-d$_3$; ^{13}C NMR: 29.84 ppm for acetone-d$_6$ and 1.32 for acetonitrile-d$_3$). ^{31}P{^{1}H} NMR chemical shifts were referenced to an external 85% aqueous H_3PO_4 capillary placed in the solvent.

Mass spectrometric analysis was performed on a QTOF Premier instrument (Waters, Milford, MA) operating in positive mode. The LC-MS data were acquired in centroid mode from *m/z* values of 100–1000 in MS scanning using Waters MassLynx software. Elemental analysis was performed with Elementar vario MICRO cube analyzer. It should be, however, noted that on average five runs were needed in order to obtain satisfactory analysis presumably due to air/moisture sensitivity of the newly synthesized compounds.

3.2. Synthesis of lithium salts of the corresponding cyclopentadienes

For Cp^{R}Li (R = 1,2-Me$_2$, 1,2,4-Me$_3$ and 1,2,3,4-Me$_4$) the isolated cyclic dienes were reacted with 1.0 equiv of n-BuLi, in hexane and isolated as white solids in almost quantitative yields.

For Cp^{R}Li (R = 1,2,4-Me$_3$) the following procedure was followed: 1,2,3-Trimethylcyclopenta-1,3-diene was synthesized by modifying the method described by Mironov et al. [30]. A distillation apparatus fitted with a 15 cm Vigreux column was flushed with nitrogen for 30 min. A 250 mL reaction flask was equipped with a stirring bar and charged with the mixture of 2,3,4-trimethylcyclopent-2-en-1-ol and 3,4,5-trimethylcyclopent-2-en-1-ol (6.52 g, 51.7 mmol) obtained from the previous step. A 100 mL receiving flask was charged with 50 mL anhydrous ether and 5 g $MgSO_4$ which were stirred during the whole distillation process with the magnetic stirring bar. The mixture of alcohols was then heated to 230 °C. A mixture of Cp^{R}H, 3-methylene-2,4-dimethylcyclopentene, and water was collected into the receiving flask where the latter was trapped with the desiccant. After completion of the reaction, the ether solution was isolated by means of filtration and stirred with another portion of $MgSO_4$ for an hour. Then the colorless solution was filtered off into a Schlenk flask, degassed by bubbling nitrogen through it and cooled to −78 °C. n-BuLi solution (20 mL, 2 M in cyclohexane) was added dropwise and the mixture was left in the acetone bath overnight, allowed to be slowly heated to room temperature. A white solid of Cp^{R}Li was isolated by filtration, washed twice with 10 mL hexane, dried under vacuum and was stored in a glovebox. Yield: 1.645 g (28%).

For Cp^{R}Li (R = 1,3-Me$_2$) 1,3-Dimethylcyclopentadienyl lithium was synthesized from 1,3-dimethylcyclopent-2-en-1-ol using the analogous procedure as for Cp^{R}Li (R = 1,2,4-Me$_3$). Yield: 38%.

3.3. General procedure for the synthesis of [Cp^{R}Ru(C$_6$H$_6$)][PF$_6$] (R = 1,2-Me$_2$, 1,3-Me$_2$, 1,2,3-Me$_3$, 1,2,4-Me$_3$ and 1,2,3,4-Me$_4$)

All ruthenium benzene complexes [Cp^{R}Ru(C$_6$H$_6$)][PF$_6$] (R = 1,2-Me$_2$, 1,3-Me$_2$, 1,2,3-Me$_3$, 1,2,4-Me$_3$ and 1,2,3,4-Me$_4$) were synthesized using modified method for synthesis of [Cp^{Me}Ru(C$_6$H$_6$)][PF$_6$] [15]. [(C$_6$H$_6$)RuCl$_2$]$_2$ and lithium salt 1.05 equiv Cp^{R}Li (R = 1,2-Me$_2$, 1,3-Me$_2$, 1,2,3-Me$_3$, 1,2,4-Me$_3$ and 1,2,3,4-Me$_2$) were put together in a Schlenk flask and cooled to 0 °C. Ice cold acetonitrile (20 mL) was then added to the mixture. The vigorously stirred suspension was left in an ice bath to warm slowly overnight. The solution was then isolated by filtration and solvent was removed *in vacuo*. The resulting solid was washed twice with ether (10 mL) and hexane (10 mL) and dried under vacuum to afford crude [Cp^{R}Ru(C$_6$H$_6$)]Cl which was used without further purification. Then, in a 250 mL Schlenk flask [Cp^{R}Ru(C$_6$H$_6$)]Cl was suspended in degassed water (150 mL). The solution was then filtered and added to a 3 mL aqueous solution of KPF_6 (3.35 eq.) upon which a light precipitate formed immediately. The mixture was allowed to stir overnight. After the suspension was cooled to 0 °C, the solid was isolated by filtration, washed with ice cold water (10 mL) and dried *in vacuo* for several hours. The obtained solid was then recrystallized from a 1:1 acetonitrile/ether mixture, filtered, washed twice with ether (10 mL) and hexane (10 mL) and dried under vacuum to afford the desired product.

3.3.1. [Cp$^{1,2\text{-}Me2}$Ru(C$_6$H$_6$)][PF$_6$]

[(C$_6$H$_6$)RuCl$_2$]$_2$ (1.472 g, 2.94 mmol), 1,2-dimethylcyclopentadienyl lithium salt (Cp$^{1,2\text{-}Me2}$Li, 590 mg, 5.89 mmol) and KPF_6 (1.89 g, 10.3 mmol). Yield: 768 mg (42%, light brown powder.). ^{1}H NMR (500 MHz, acetonitrile-d$_3$) 6.01 (s, 6H, C$_6$H$_6$), 5.29 (s, 2H, Cp-CH), 5.11 (s, 1H, Cp-CH), 2.02 ppm (s, 6H, Cp-CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, acetonitrile-d$_3$) δ 99.1 (s, Cp-$\underline{C}$CH$_3$), 86.4 (s, C$_6$H$_6$), 81.2 (s, Cp-$\underline{C}$H), 77.4 (s, Cp-$\underline{C}$H), 11.3 ppm (s, Cp-$\underline{C}$H$_3$). Anal. Calcd for $C_{13}H_{15}F_6PRu$: C, 37.42; H, 3.62. Found: C, 37.46; H, 3.60. HRMS: *m/z* (M)$^+$ = (Calculated for $RuC_{13}H_{15}$, 273.0217) found 273.0196.

3.3.2. [Cp$^{1,3\text{-}Me2}$Ru(C$_6$H$_6$)][PF$_6$]

[(C$_6$H$_6$)RuCl$_2$]$_2$ (800 mg, 1.60 mmol), 1,3-dimethylcyclopentadienyl lithium salt (Cp$^{1,3\text{-}Me2}$Li, 336 mg, 3.36 mmol), and KPF_6 (2.0 g, 10.9 mmol). Yield: 726 mg (56%, light brown powder). ^{1}H NMR (500 MHz, acetonitrile-d$_3$) δ 6.03 (s, 6H, C$_6$H$_6$), 5.38 (s, 1H, Cp-CH), 5.24 (s, 2H, Cp-CH), 1.98 ppm (s, 6H, Cp-CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, acetonitrile-d$_3$) δ 99.1 (s, Cp-$\underline{C}$CH$_3$), 86.5 (s, C$_6$H$_6$), 82.9 (s, Cp-$\underline{C}$H), 80.7 (s, Cp-$\underline{C}$H), 12.8 ppm (s, Cp-$\underline{C}$H$_3$). Anal. Calcd for $C_{13}H_{15}F_6PRu$: C, 37.42; H, 3.62. Found: C, 37.45; H, 3.64. HRMS: *m/z* (M)$^+$ = (Calculated for $RuC_{13}H_{15}$, 273.0217) found 273.0226.

3.3.3. [Cp$^{1,2,3\text{-}Me3}$Ru(C$_6$H$_6$)][PF$_6$]

[(C$_6$H$_6$)RuCl$_2$]$_2$ (1.186 g, 2.37 mmol), 1,2,3-trimethylcyclopentadienyl lithium salt (Cp$^{1,2,3\text{-}Me3}$Li, 541 mg, 4.74 mmol), and KPF_6 (2.093 g, 11.4 mmol). Yield: 959 mg (40%, light brown powder). ^{1}H NMR (400 MHz, acetonitrile-d$_3$) δ 5.88 (s, 6H, C$_6$H$_6$), 5.11 (s, 2H, Cp-CH), 1.97 (s, 3H, Cp-CH$_3$), 1.95 ppm (s, 6H, Cp-CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, acetonitrile-d$_3$) δ 100.1 (s, Cp-$\underline{C}$CH$_3$), 88.0 (s, C$_6$H$_6$), 80.4 (s, Cp-$\underline{C}$H), 13.0 (s, Cp-$\underline{C}$H$_3$), 10.9 ppm (s, Cp-$\underline{C}$H$_3$). Anal. Calcd for$C_{14}H_{17}F_6PRu$: C, 38.99; H, 3.97. Found: C, 39.00; H, 4.02. HRMS: *m/z* (M)$^+$ = (Calculated for $RuC_{14}H_{17}$, 287.0374) found 287.0376.

3.3.4. [Cp$^{1,2,4\text{-}Me3}$Ru(C$_6$H$_6$)][PF$_6$]

[(C$_6$H$_6$)RuCl$_2$]$_2$ (493 mg, 0.98 mmol). 1,2,4-trimethylcyclopentadienyl lithium salt (Cp$^{1,2,3\text{-}Me3}$Li, 225 mg, 1.97 mmol), and KPF_6 (1.09 g, 5.92 mmol). Yield: 466 mg (61%, light brown powder). ^{1}H NMR (400 MHz, acetonitrile-d$_3$) δ 5.96 (s, 6H, C$_6$H$_6$), 5.30 (s, 2H, Cp-CH), 1.98 (s, 6H, Cp-CH$_3$), 1.93 ppm (s, 3H, Cp-CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, acetonitrile-d$_3$) δ 98.3 (s, Cp-$\underline{C}$CH$_3$),

96.8 (s, Cp-$\underline{C}CH_3$), 86.7 (s, C_6H_6), 82.65 (s, Cp-$\underline{C}H$), 12.7 (s, Cp-$\underline{C}H_3$), 11.2 ppm (s, Cp-$\underline{C}H_3$). Anal. Calcd for $C_{14}H_{17}F_6PRu$: C, 38.99; H, 3.97. Found: C, 39.04; H, 3.99. HRMS: *m/z* $(M)^+$ = (Calculated for $RuC_{14}H_{17}$, 287.0374) found 287.0372.

3.3.5. $[Cp^{1,2,3,4\text{-}Me4}Ru(C_6H_6)][PF_6]$

$[(C_6H_6)RuCl_2]_2$ (1.0 g, 2.0 mmol), tetramethylcyclopentadienyl lithium salt ($Cp^{1,2,3,4\text{-}Me4}Li$, 538 mg, 4.19 mmol), and KPF_6 (1.98 g, 10.8 mmol). Yield: 908 mg (63%, brown powder). ^1H NMR (400 MHz, acetonitrile-d_3) δ 5.82 (s, 6H, C_6H_6), 5.19 (s, 1H, Cp-CH), 1.95 (s, 6H, Cp-CH_3), 1.91 ppm (s, 6H, Cp-CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetonitrile-d_3) δ 99.6 (s, Cp-$\underline{C}CH_3$), 98.0 (s, Cp-$\underline{C}CH_3$), 88.3 (s, C_6H_6), 82.5 (s, Cp-$\underline{C}H$), 12.8 (s, Cp-$\underline{C}H_3$), 11.3 ppm (s, Cp-$\underline{C}H_3$). Anal. Calcd for $C_{15}H_{19}F_6PRu$: C, 40.45; H, 4.30. Found: C, 40.38; H, 4.26. HRMS: *m/z* $(M)^+$ = (Calculated for $RuC_{15}H_{19}$, 301.0530) found 301.0513.

3.4. General procedure for the synthesis of $[Cp^RRu(NCCH_3)_3][PF_6]$ (**[4c]**$[PF_6]$: R = 1,2-Me_2; **[4d]**$[PF_6]$: R = 1,3-Me_2; **[4e]**$[PF_6]$: R = 1,2,3-Me_3, **[4f]**$[PF_6]$: R = 1,2,4-Me_3; **[4g]**$[PF_6]$: R = 1,2,3,4-Me_4)

Ruthenium *tris*-acetonitrile complexes [**4c**][PF_6] - [**4g**][PF_6] were synthesized using modified method for synthesis of $[Cp^{Me}Ru(CH_3CN)_3]PF_6$, [**4b**][$PF_6$] [15]. 50 mL Schlenk-type quartz vessel was charged with $[Cp^RRu(C_6H_6)]PF_6$ and 40 mL acetonitrile. The solution was irradiated with UV-light (low pressure Hg lamp, 15 W, 254 nm) for several days until no starting material was detectable by ^1H NMR spectroscopy. The solution was then filtered and solvent was removed under reduced pressure. The obtained solid was then recrystallized from 1:1 acetonitrile/ether mixture, isolated by filtration, washed twice with ether (10 mL) and hexane (10 mL) and finally dried *in vacuo* to afford the desired product.

3.4.1. **[4c]**$[PF_6]$

550 mg of $[Cp^{1,2\text{-}Me2}Ru(C_6H_6)][PF_6]$. Yield: 530 mg (87%, yellow powder). ^1H NMR (500 MHz, acetone-d_6) δ 4.16 (m, 1H, Cp-CH), 4.02 (m, 2H, Cp-CH), 2.54 (br s, 9H, $NCCH_3$), 1.70 ppm (s, 6H, Cp-CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 125.1 (s, N$\underline{C}CH_3$), 83.7 (s, $\underline{C}CH_3$), 70.4 (s, CH), 65.6 (s, CH), 10.1 (s, Cp-CH_3), 2.3 ppm (s, NC$\underline{C}H_3$). Anal. Calcd for $C_{13}H_{18}F_6N_3PRu$: C, 33.77; H, 3.92; N, 9.09. Found: C, 33.65; H, 3.94; N, 9.10. HRMS: *m/z* $(M\text{-}CH_3CN)^+$ = (Calculated for $RuC_{11}H_{15}N_2$, 277.0279) found 277.0282, $(M\text{-}2CH_3CN)^+$ = (Calculated for $RuC_9H_{12}N$, 236.0013) found 236.0014.

3.4.2. **[4d]**$[PF_6]$

550 mg of $[Cp^{1,3\text{-}Me2}Ru(C_6H_6)][PF_6]$. Yield: 500 mg (82%, yellow powder). ^1H NMR (400 MHz, acetone-d_6) δ 3.93 (m, 2H, Cp-CH), 3.78 (m, 1H, Cp-CH), 2.51 (br s, 9H, $NCCH_3$), 1.65 ppm (s, 6H, Cp-CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 124.8 (s, N$\underline{C}CH_3$), 91.4 (s, $\underline{C}CH_3$), 65.0 (s, CH), 61.9 (s, CH), 12.0 (s, Cp-CH_3), 2.3 ppm (s, NC$\underline{C}H_3$). Anal. Calcd for $C_{13}H_{18}F_6N_3PRu$: C, 33.77; H, 3.92; N, 9.09. Found: C, 33.67; H, 3.88; N, 9.07. HRMS: *m/z* $(M\text{-}2CH_3CN)^+$ = (Calculated for $RuC_9H_{12}N$, 236.0013) found 236.0020.

3.4.3. **[4e]**$[PF_6]$

550 mg of $[Cp^{1,2,3\text{-}Me3}Ru(C_6H_6)][PF_6]$. Yield: 456 mg (75%, yellow powder). ^1H NMR (400 MHz, acetone-d_6) δ 3.90 (s, 2H, Cp-CH), 2.51 (br s, 9H, $NCCH_3$), 1.66 (s, 6H, Cp-CH_3), 1.63 ppm (s, 3H, Cp-CH_3). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6) δ 126.1 (s, N$\underline{C}CH_3$), 87.9 (s, $\underline{C}CH_3$), 78.3 (s, $\underline{C}CH_3$), 66.2 (s, CH), 12.0 (s, Cp-CH_3), 9.6 (s, Cp-CH_3), 3.6 ppm (s, NC$\underline{C}H_3$). Anal. Calcd for $C_{14}H_{20}F_6N_3PRu$: C, 35.30; H, 4.23; N, 8.82. Found: C, 35.36; H, 4.27; N, 8.86. HRMS: *m/z* $(M\text{-}2CH_3CN)^+$ = (Calculated for $RuC_{10}H_{14}N$, 250.0170) found 250.0182.

3.4.4. **[4f]**$[PF_6]$

550 mg of $[Cp^{1,2,4\text{-}Me3}Ru(C_6H_6)][PF_6]$. Yield: 480 mg (79%, yellow powder). ^1H NMR (400 MHz, acetone-d_6) δ 3.74 (s, 2H, Cp-CH), 2.48 (br s, 9H, $NCCH_3$), 1.60 (s, 6H, Cp-CH_3), 1.57 ppm (s, 3H, Cp-CH_3). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6) δ 124.4 (s, N$\underline{C}CH_3$), 90.9 (s, $\underline{C}CH_3$), 84.0 (s, $\underline{C}CH_3$), 62.8 (s, $\underline{C}H$), 11.8 (s, Cp-CH_3), 10.1 (s, Cp-CH_3), 2.2 ppm (s, NC$\underline{C}H_3$). Anal. Calcd for $C_{14}H_{20}F_6N_3PRu$: C, 35.30; H, 4.23; N, 8.82. Found: C, 35.30; H, 4.20; N, 8.83. HRMS: *m/z* $(M\text{-}CH_3CN)^+$ = (Calculated for $RuC_{12}H_{17}N_2$, 291.0435) found 291.0464, $(M\text{-}2CH_3CN)^+$ = (Calculated for $RuC_{10}H_{14}N$, 250.0170) found 250.0188.

3.4.5. **[4g]**$[PF_6]$

The preparation of this compound has already been reported in the literature [31] by a different method. It is also believed that the reported ^1H NMR is not correct so we report it here. 550 mg of $[Cp^{1,2,3,4\text{-}Me4}Ru(C_6H_6)][PF_6]$. Yield: 497 mg (82%, yellow powder). ^1H NMR (400 MHz, acetone-d_6) δ 3.68 (s, 1H, Cp-CH), 2.48 (br s, 9H, $NCCH_3$), 1.60 (s, 6H, Cp-CH_3), 1.58 ppm (s, 6H, Cp-CH_3).

3.5. General procedure for the synthesis of $[Cp^RRu(^tBu_2P\text{-}Im)][PF_6]$ (Im = 4-tert-butyl-1-methylimidazol-2-yl; **[4a]**$[PF_6]$: R = H; **[4b]**$[PF_6]$: R = Me; **[4c]**$[PF_6]$: R = 1,2-Me_2; **[4d]**$[PF_6]$: R = 1,3-Me_2; **[4e]**$[PF_6]$: R = 1,2,3-Me_3, **[4f]**$[PF_6]$: R = 1,2,4-Me_3; **[4g]**$[PF_6]$: R = 1,2,3,4-Me_4)

These complexes were synthesized using modified method for synthesis of complex $[CpRu(^iPr_2P\text{-}Im)(CH_3CN)][PF_6]$ ([**1**][PF_6]) [10]. $^tBu_2P$-Im (1.2 equiv, as a 0.167 M stock solution in hexane) was transferred into a 5 mL Schlenk flask and all volatiles were removed *in vacuo* after which phosphine was re-dissolved in 3 mL of acetone. This solution was then added to the solution of complex $[Cp^RRu(CH_3CN)_3][PF_6]$ in 5 mL of acetone and reaction mixture was stirred for 1 h. The solution was concentrated *in vacuo* until a precipitate started to form, after which an excess of hexane (25 mL) was added with vigorous stirring. The mixture was stirred overnight, solid was then isolated by filtration, washed three times with hexane (10 mL) and dried under vacuum to afford the desired complex.

3.5.1. **[6a]**$[PF_6]$

2.5 mL (0.42 mmol) of $^tBu_2P$-Im and 150 mg (0.35 mmol) of [**4a**][PF_6]. Yield: 184 mg (84%, yellow-brown powder). ^1H NMR: (500 MHz, acetone-d_6) δ 7.08 (s, 1H, Im-$\underline{C}H$), 4.60 (s, 5H, Cp), 3.88 (s, 3H, N$\underline{C}H_3$), 2.46 (s, 3H, NCC$\underline{H}_3$), 1.50 (br s, 9H, P-^{t}Bu), 1.47 (br s, 9H, P-^{t}Bu), 1.43 ppm (s, 9H, Im-^{t}Bu). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6) δ 152.5 (d, J = 13.3, $\underline{C}C_4H_9$), 149.3 (d, J = 20.9, N$\underline{C}$P), 128.5 (sl br s, N$\underline{C}CH_3$), 120.6 (s, Im-$\underline{C}H$), 71.2 (Cp-$\underline{C}H$), 35.6 (s, N$\underline{C}H_3$), 31.4 (s, NC$\underline{C}(CH_3)_3$), 2.9 ppm (s, NC$\underline{C}H_3$). Note: several resonance signals related to carbon atoms in *tert*-butyl moieties are not listed due to overlapping with solvent peak at 29.8 ppm. $^{31}P\{^1H\}$ NMR (202.38 MHz, acetone-d_6) δ 59.0 ppm. Anal. Calcd for $C_{23}H_{39}F_6N_3P_2Ru$: C, 43.53; H, 6.19; N, 6.62. Found: C, 43.63; H, 6.13; N, 6.61. HRMS: *m/z* $(M\text{-}CH_3CN)^+$ = (Calculated for $RuC_{21}H_{36}N_2P$, 449.1660) found 449.1671.

3.5.2. **[6b]**$[PF_6]$

1.76 mL (0.29 mmol) of $^tBu_2P$-Im and 110 mg (0.25 mmol) of [**4b**][PF_6]. Yield: 132 mg (83%, yellow-brown powder). ^1H NMR (500 MHz, acetone-d_6) δ 7.06 (s, 1H, Im-$\underline{C}H$), 4.76 (v br s, 2H, Cp-$\underline{C}H$), 4.46 (s, 2H, Cp-$\underline{C}H$), 3.86 (s, 3H, N$\underline{C}H_3$), 2.50 (s, 3H, NCC$\underline{H}_3$), 1.80 (s, 3H, Cp-$\underline{C}H_3$), 1.46 (br s, 18H, P-^{t}Bu), 1.41 ppm (s, 9H, Im-^{t}Bu). Note: resonance signal of cyclopentadienyl proton at 4.76 ppm is barely visible presumably due to coalescence. $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6) δ 152.4 (d, J = 13.4, $\underline{C}C_4H_9$), 149.3 (d, J = 20.6, N$\underline{C}$P), 127.1

(sl br s, NCCH$_3$), 120.2 (s, Im-CH), 93.6 (br s, Cp-CCH$_3$), 75.2 (br s, Cp-CH), 70.3 (br s, Cp-CH), 36.1 (d, J = 8.0, NCH$_3$) 35.2 (s, NCC(CH$_3$)$_3$), 31.2 (s, PC(CH$_3$)$_3$), 30.2 (s, PC(CH$_3$)$_3$), 12.3 (s, Cp-CH$_3$), 2.8 ppm (s, NCCH$_3$). Note: several resonance signals related to carbon atoms in *tert*-butyl moieties are not listed due to overlapping with solvent peak at 29.8 ppm. ^{31}P{^{1}H} NMR (202.38 MHz, acetone-d$_6$) δ 58.8 ppm. Anal. Calcd for $C_{24}H_{41}F_6N_3P_2Ru$: C, 44.44; H, 6.37; N, 6.48. Found: C, 44.31; H, 6.32; N, 6.49. HRMS: *m/z* (M-CH$_3$CN)$^+$ = (Calculated for $RuC_{22}H_{38}N_2P$, 463.1816) found 463.1833.

3.5.3. [6c][PF$_6$]

1.71 mL (0.29 mmol) of ^{t}Bu$_2$P-Im and 110 mg (0.24 mmol) of [**4c**][PF$_6$]. Yield: 125 mg (79%, yellow-brown powder). ^{1}H NMR (500 MHz, acetone-d$_6$) δ 7.06 (s, 1H, Im-CH), 4.66 (v br s, 2H, Cp-CH), 4.08 (t, J = 2.1 Hz, 1H, Cp-CH), 3.87 (s, 3H, NCH$_3$), 2.58 (s, 3H, NCCH$_3$), 1.76 (br s, 6H, Cp-CH$_3$), 1.49 (br s, 9H, P-^{t}Bu), 1.47 (br s, 9H, P-^{t}Bu), 1.40 ppm (s, 9H, Im-^{t}Bu). Note: resonance signal of cyclopentadienyl proton at 4.66 ppm is barely visible presumably due to coalescence. ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d$_6$) δ 152.4 (d, J = 12.9, CC$_4$H$_9$), 149.4 (d, J = 20.8, NCP), 127.2 (sl br s, NCCH$_3$), 120.1 (s, Im-CH), 96.0 (br s, Cp-CCH$_3$), 75.0 (br s, Cp-CH), 72.3 (br s, Cp-CH), 36.4 (br s, NCH$_3$), 35.3 (s, NCC(CH$_3$)$_3$), 31.2 (s, PC(CH$_3$)$_3$), 10.9 (s, Cp-CH$_3$), 3.0 ppm (s, NCCH$_3$). Note: several resonance signals related to carbon atoms in *tert*-butyl moieties are not listed due to overlapping with solvent peak at 29.8 ppm. ^{31}P{^{1}H} NMR (202.38 MHz, acetone-d$_6$) δ 59.0 ppm. Anal. Calcd for $C_{25}H_{43}F_6N_3P_2Ru$: C, 45.31; H, 6.54; N, 6.34. Found: C, 45.25; H, 6.48; N, 6.36. HRMS: *m/z* (M-CH$_3$CN)$^+$ = (Calculated for $RuC_{23}H_{40}N_2P$, 477.1973) found 477.1976.

3.5.4. [6d][PF$_6$]

1.71 mL (0.29 mmol) of ^{t}Bu$_2$P-Im and 110 mg (0.24 mmol) of [**4d**][PF$_6$]. Yield: 123 mg (78%, yellow-brown powder). ^{1}H NMR (500 MHz, acetone-d$_6$) δ 7.11 (s, 1H, Im-CH), 4.57 (s, 1H, Cp-CH), 4.14 (br s, 2H, Cp-CH), 3.90 (s, 3H, NCH$_3$), 2.52 (s, 3H, NCCH$_3$), 1.75 (s, 6H, Cp-CH$_3$), 1.53 (s, 9H, P-^{t}Bu), 1.50 (s, 9H, P-^{t}Bu), 1.37 ppm (s, 9H, Im-^{t}Bu). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d$_6$) δ 152.8 (d, J = 13.4, CC$_4$H$_9$), 149.2 (d, J = 20.2, NCP), 127.3 (sl br s, NCCH$_3$), 120.6 (s, Im-CH), 72.6 (s, Cp-CH), 72.6 (s, Cp-CH), 35.7 (d, J = 9.0, NCH$_3$), 35.7 (s, NCC(CH$_3$)$_3$), 31.4 (s, PC(CH$_3$)$_3$), 30.2 (s, PC(CH$_3$)$_3$), 12.8 (s, Cp-CH$_3$), 2.9 ppm (s, NCCH$_3$). Note: several resonance signals related to carbon atoms in *tert*-butyl moieties are not listed due to overlapping with solvent peak at 29.8 ppm. ^{31}P{^{1}H} NMR (202.38 MHz, acetone-d$_6$) δ 58.0 ppm. Anal. Calcd for $C_{25}H_{43}F_6N_3P_2Ru$: C, 45.31; H, 6.54; N, 6.34. Found: C, 45.24; H, 6.47; N, 6.37. HRMS: *m/z* (M-CH$_3$CN)$^+$ = (Calculated for $RuC_{23}H_{40}N_2P$, 477.1973) found 477.1979.

3.5.5. [6e][PF$_6$]

1.66 mL (0.28 mmol) of ^{t}Bu$_2$P-Im and 110 mg (0.23 mmol) of [**4e**][PF$_6$]. Yield: 128 mg (82%, yellow-brown powder). ^{1}H NMR (400 MHz, acetone-d$_6$) δ 7.01 (s, 1H, Im-CH), 4.19 (s, 2H, Cp-CH), 3.85 (s, 3H, NCH$_3$), 2.52 (s, 3H, NCCH$_3$), 1.78 (br s, 6H, Cp-CH$_3$), 1.71 (s, 3H, Cp-CH$_3$), 1.48 (s, 9H, P-^{t}Bu), 1.44 (s, 9H, P-^{t}Bu), 1.35 ppm (s, 9H, Im-^{t}Bu). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d$_6$) δ 152.6 (d, J = 13.4, CC$_4$H$_9$), 149.2 (d, J = 21.4, NCP), 127.1 (s, NCCH$_3$), 120.6 (s, Im-CH), 87.6 (s, Cp-CCH$_3$), 67.2 (s, Cp-CH), 36.5 (s, NCH$_3$), 35.5 (s, NCC(CH$_3$)$_3$), 31.1 (s, PC(CH$_3$)$_3$), 30.2 (s, PC(CH$_3$)$_3$), 12.0 (s, Cp-CH$_3$), 8.6 (s, Cp-CH$_3$), 3.0 ppm (s, NCCH$_3$). Note: several resonance signals related to carbon atoms in *tert*-butyl moieties are not listed due to overlapping with solvent peak at 29.8 ppm. ^{31}P{^{1}H} NMR (202.38 MHz, acetone-d$_6$) δ 58.0 ppm. Anal. Calcd for $C_{26}H_{45}F_6N_3P_2Ru$: C, 46.15; H, 6.70; N, 6.21. Found: C, 46.05; H, 6.77; N, 6.23. HRMS: *m/z* (M-CH$_3$CN)$^+$ = (Calculated for $RuC_{24}H_{42}N_2P$, 491.2129) found 491.2151.

3.5.6. [6f][PF$_6$]

1.66 mL (0.28 mmol) of ^{t}Bu$_2$P-Im and 110 mg (0.23 mmol) of [**4f**][PF$_6$]. Yield: 123 mg (79%, dark-green powder). ^{1}H NMR (500 MHz, acetone-d$_6$) δ 7.11 (s, 1H, Im-CH), 4.47 (s, 2H, Cp-CH), 3.88 (s, 3H, NCH$_3$), 2.55 (s, 3H, NCCH$_3$), 1.68 (s, 6H, Cp-CH$_3$), 1.66 (s, 3H, Cp-CH$_3$), 1.53 (s, 9H, P-^{t}Bu), 1.50 (s, 9H, P-^{t}Bu), 1.47 ppm (s, 9H, Im-^{t}Bu). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d$_6$) δ 152.7 (d, J = 14.5, CC$_4$H$_9$), 149.1 (d, J = 19.7, NCP), 127.5 (s, NCCH$_3$), 120.8 (s, Im-CH), 87.6 (s, Cp-CCH$_3$), 82.1 (s, Cp-CCH$_3$), 72.8 (s, Cp-CH), 35.9 (d, J = 6.8, NCH$_3$), 35.4 (s, NCC(CH$_3$)$_3$), 31.5 (s, PC(CH$_3$)$_3$), 30.2 (s, PC(CH$_3$)$_3$), 12.3 (s, Cp-CH$_3$), 11.5 (s, Cp-CH$_3$), 3.1 ppm (s, NCCH$_3$). Note: several resonance signals related to carbon atoms in *tert*-butyl moieties are not listed due to overlapping with solvent peak at 29.8 ppm. ^{31}P{^{1}H} NMR (202.38 MHz, acetone-d$_6$) δ 56.8 ppm. Anal. Calcd for $C_{26}H_{45}F_6N_3P_2Ru$: C, 46.15; H, 6.70; N, 6.21. Found: C, 46.06; H, 6.74; N, 6.21. HRMS: *m/z* (M-CH$_3$CN)$^+$ = (Calculated for $RuC_{24}H_{42}N_2P$, 491.2129) found 491.2138.

3.5.7. [6g][PF$_6$]

1.61 mL (0.27 mmol) of ^{t}Bu$_2$P-Im and 110 mg (0.22 mmol) of [**4g**][PF$_6$]. Yield: 139 mg (90%, dark-brown powder). ^{1}H NMR (500 MHz, acetone-d$_6$) δ 7.10 (s, 1H, Im-CH), 4.24 (s, 1H, Cp-CH), 3.88 (s, 3H, NCH$_3$), 2.53 (s, 3H, NCCH$_3$), 1.80 (br s, 6H, Cp-CH$_3$), 1.65 (s, 6H, Cp-CH$_3$), 1.53 (s, 9H, P-^{t}Bu), 1.50 (s, 9H, P-^{t}Bu), 1.45 ppm (s, 9H, Im-^{t}Bu). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d$_6$) δ 152.8 (d, J = 13.8, CC$_4$H$_9$), 149.2 (d, J = 20.3, NCP), 127.4 (s, NCCH$_3$), 120.7 (s, Im-CH), 87.2 (s, Cp-CCH$_3$), 70.1 (s, Cp-CH), 36.1 (d, J = 8.0, NCH$_3$), 35.6 (s, NCC(CH$_3$)$_3$), 31.3 (s, PC(CH$_3$)$_3$), 30.2 (s, PC(CH$_3$)$_3$), 12.0 (s, Cp-CH$_3$), 9.8 (s, Cp-CH$_3$), 3.0 ppm (s, NCCH$_3$). Note: several resonance signals related to carbon atoms in *tert*-butyl moieties are not listed due to overlapping with solvent peak at 29.8 ppm. ^{31}P{^{1}H} NMR (202.38 MHz, acetone-d$_6$) δ 54.72 ppm. Anal. Calcd for $C_{27}H_{47}F_6N_3P_2Ru$: C, 46.95; H, 6.86; N, 6.08. Found: C, 46.97; H, 6.87; N, 6.10. HRMS: *m/z* (M-CH$_3$CN)$^+$ = (Calculated for $RuC_{25}H_{44}N_2P$, 505.2286) found 505.2295.

3.5.8. [8][PF$_6$]/[9][PF$_6$]

Mixture of compounds **8**$^+$ and **9**$^+$ was obtained following the modified procedure as for the synthesis of complexes **6**$^+$. Ligand **7** (4.56 mL, 0.055 M, 0.25 mmol) was reacted with 105 mg (0.21 mmol) of [**4h**][PF$_6$]. Yield: 109 mg (76%, dark-brown powder). ^{31}P{^{1}H} NMR (202.38 MHz, acetone-d$_6$) δ 40.7 ppm.

3.6. General procedure for isomerization of 1-hexene

In a typical reaction of 1-hexene isomerization, 2 mol% of complex [**6**][PF$_6$] was transferred into a J Young NMR tube. The complex was dissolved in 0.80 mL of acetone-d$_6$ followed by 0.05 mL (0.4 mmol) of 1-hexene. After the tube was sealed all its contents were thoroughly mixed together and the tube was heated to 60 °C in using an oil bath. The reaction progress was followed by ^{1}H NMR spectroscopy.

Author information

The authors declare no competing financial interests.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://

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