



Chelation-Assisted Reactions of Phosphine- and Olefin-Tethered Imidazolium Derivatives and Their Affiliated N-Heterocyclic Carbenes with Roper's Complex $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$

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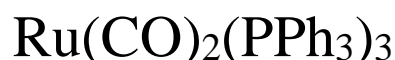
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Chelation-assisted reactions of phosphine- and olefin-tethered imidazolium derivatives and their affiliated N-heterocyclic carbenes with Roper's complex



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ABSTRACT. Complex $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, **1**, is a suitable starting compound for the generation of N-heterocyclic carbene complexes of Ru(0). Though monodentate NHCs are totally unreactive toward **1**, phosphine- or olefin-functionalized N-heterocyclic carbenes, as well as their imidazolium precursors, react with **1** under chelation assistance where the phosphine or the olefin are acting as directing groups. Reactions of 1-mesityl-3-(2-diphenylphosphinoeth-1-yl)-imidazolium bromide, $[\text{HL}^{1a}]^+\text{Br}^-$, 1-mesityl-3-(2-diphenylphosphinoeth-1-yl)-imidazolium tetrafluoroborate, $[\text{HL}^{1a}]^+\text{BF}_4^-$, and 1-(2,6-diisopropylphenyl)-3-(2-diphenylphosphinoeth-1-yl)-imidazolium bromide, $[\text{HL}^{1b}]^+\text{Br}^-$, with **1** give cationic hydrido species formulated as $[\text{RuH}\{\text{L}^{*1a-b}\}(\text{CO})_2(\text{PPh}_3)]^+\text{X}^-$ [**2a-b**]⁺**X**[−] (**a**, Ar = mesityl; **b**, Ar

= 2,6 diisopropylphenyl), in which abnormal activation (symbolized by the asterisk) at the C(4) position of the heterocycle has taken place to yield the bidentate ligands L^{*1a-b} . Deprotonation of $[HL^{1b}]^+$ with KOtBu gives the corresponding NHC/phosphine bidentate ligand, which reacts with **1** to give the chelated NHC/phosphine complex $Ru\{L^{1b}\}(CO)_2(PPh_3)$ (**3b**), the first analog of Roper's complex incorporating an NHC moiety. The olefin-functionalized imidazolium ligand 3-(but-3-enyl)-1-mesitylimidazolium bromide $[HL^{2a}]^+Br^-$ reacts with **1** *via* chelation-assisted C-H activation and H transfer to the olefin giving $Ru\{Ar(N_2C_3H_2)CH_2C(H)(CH_2CH_3)\}(CO)_2(PPh_3)Br$ (**4a**). Deprotonation of $[HL^{2a}]^+Br^-$ gives L^{2a} , which reacts with **1** to give $Ru\{L^{2a}\}(CO)_2(PPh_3)$ (**5a**). Its protonation with HBF₄ at $-80^\circ C$ gives a cationic NHC/olefin- hydrido- complex $[RuH\{L^{2a}\}(CO)_2(PPh_3)]^+BF_4^-$, $[6a]^+BF_4^-$. NMR data indicate the occurrence of a dynamic process involving a fast exchange between the hydride and the two terminal hydrogen atoms of the coordinated olefin, which can be rationalized in terms of the transient generation of an elusive higher energy NHC/alkyl- intermediate $[Ru\{Ar(N_2C_3H_2)CH_2CH_2C(H)CH_3\}(CO)_2(PPh_3)]^+BF_4^-$, $[7a]^+BF_4^-$. At temperatures above $-20^\circ C$, $[6a]^+BF_4^-$ is irreversibly converted into the isomerized NHC/olefin- hydrido- complex $[RuH\{Ar(N_2C_3H_2)CH_2CH=C(H)CH_3\}(CO)_2(PPh_3)]^+BF_4^-$, $[8a]^+BF_4^-$. Here again, NMR data reveal a dynamic process involving fast exchange between the hydride and the terminal hydrogen atom of the coordinated olefin, now through the intermediacy of the elusive cationic NHC/alkyl species $[Ru\{Ar(N_2C_3H_2)CH_2C(H)CH_2CH_3\}(CO)_2(PPh_3)]^+BF_4^-$, $[9a]^+BF_4^-$. Though none of the above unsaturated cationic alkyl intermediates $[7a]^+$ or $[9a]^+$ was observed, their occurrence could be inferred from trapping experiments. Indeed, the addition of LiCl or [PPN]Cl to the above mixture after equilibration at $25^\circ C$ leads to the formation of the chloride analog of **4a**. Protonation with HCl instead of HBF₄ allows capture of the first elusive intermediate $[7a]^+$ by the halide, which quenches the isomerization process and promotes a migratory CO insertion yielding the NHC/alkyl derivative $Ru\{Ar(N_2C_3H_2)CH_2CH_2C(H)(CH_3)C=O\}(CO)(PPh_3)$, **10a**. The X-ray structure analyses for **4** and **5** are included.

Introduction

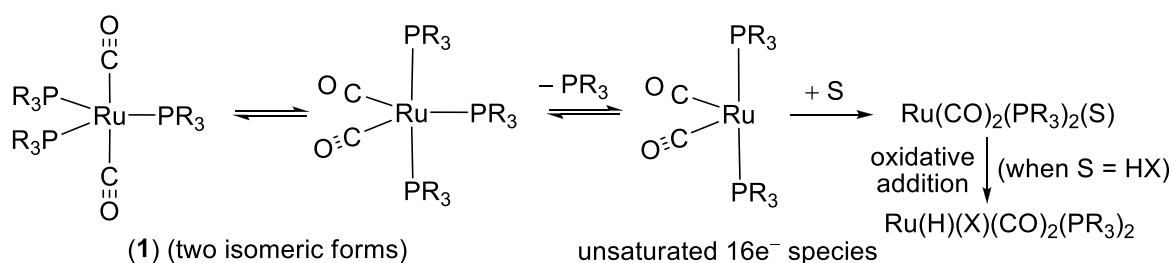
During the past fifteen years, N-heterocyclic carbenes (NHCs) have gained considerable significance in synthetic organometallic chemistry and catalysis,¹ essentially because of their ability to function as *powerful ancillary ligands* in a variety of catalytically active metal complexes,² and, albeit to a lower extent, as *reactive intermediates* in certain transition-metal catalyzed transformations of their imidazolium precursors.^{3,4}

In the chemistry of ruthenium(II), representative evidences for their major benefits as ligands are found in the development of “new generations” of Grubbs and Grubbs/Hoveyda catalysts.⁵ By contrast, studies of the interaction of NHCs with basic mono- or polynuclear carbonyl or carbonyl/phosphine derivatives of Ru(0) are only beginning to emerge. In the footsteps of the pioneering work of Lappert on reactions of the dimeric 1,3-dialkylimidazolin-2-ylidene with metal carbonyls,⁶ several authors have recently revisited the substitution reactions of $\text{Ru}_3(\text{CO})_{12}$, now using various stable N-heterocyclic carbenes as incoming ligands.^{7,8,9} Such reactions were found to be very dependent on the carbene steric and electronic properties, the faster and more efficient substitutions being observed with the more basic and less bulky ligands.⁷ Cabeza and co-workers were the first to report the isolation of a simple mono-substituted 1,3-dimesitylimidazol-2-ylidene tri-ruthenium carbonyl derivative, $\text{Ru}_3(\text{CO})_{11}(\text{IMes})$, obtained in 36% yield and exhibiting a normal coordination of the carbene through the C2 atom.^{7b} Quite unexpectedly, Whittlesey⁸ observed that a parallel substitution reaction involving the bulkier carbene 1,3-di-*tert*-butylimidazol-2-ylidene (*ItBu*) gives the substituted derivative $\text{Ru}_3(\text{CO})_{11}(\text{ItBu}^*)$ (81% yield) in which the ligand is bound to the metal through the backbone C4 atom of the heterocycle, thus reflecting the occurrence of an “abnormal” C-H activation¹⁰ accompanied by transfer of the activated H to the available C2 site.

Beyond the scope of cluster chemistry, where further irreversible transformations of these NHCs at contiguous metal centers are seen to occur *via* subsequent C-H activation reactions,^{7,8} the above trinuclear IMes complexes can be alternatively degraded with an excess of ligand to give $\text{Ru}(\text{NHC})(\text{CO})_4$ or $\text{Ru}(\text{NHC})_2(\text{CO})_3$ in low to moderate yields.^{8b,9} Better than such a multistep “cluster”

route, efficient methods for the incorporation of N-heterocyclic carbenes into mononuclear ruthenium carbonyl complexes have been proposed. They involve phosphine (or arsine) displacement from various Ru(II) precursors such as $\text{RuH}(\text{CO})\text{Cl}(\text{PCy}_3)_2$,¹¹ $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{CO})(\text{AsPh}_3)_3$,¹² or direct addition of the NHC to $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$.¹³ Further reduction of the resulting NHC/Ru(II) complexes to Ru(0) appears to be problematic and has been observed only under CO, again giving only access to the tricarbonyl derivative $\text{Ru}(\text{NHC})_2(\text{CO})_3$.^{8b,12} However, just like their phosphine analogues $\text{Ru}(\text{PR}_3)_2(\text{CO})_3$, such complexes are reluctant to CO loss, hence, they remain poorly reactive and of limited practical utility.

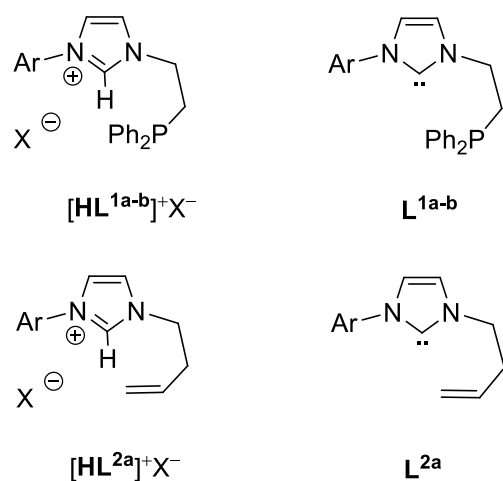
The particularly reactive benchmark derivative $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, known as Roper's complex,¹⁴ might appear as a suitable starting complex for the direct generation of Ru(0)/NHC complexes, especially since it is now readily available in good yield through a fast preparative procedure.¹⁵ This complex is fluxional and exists as a mixture of two rapidly interconverting isomers with a very low activation energy barrier (chart I).^{14,16} Its intrinsic high substitutional lability has been rationalized in terms of the transient generation of an unsaturated 16e^- species " $\text{Ru}(\text{CO})_2(\text{PR}_3)_2$ ",¹⁷ (chart 1) which has been even isolated in the case of the bulky phosphine PMe^tBu_2 , and is prone to add a variety of 2e^- donor substrates S within the time of mixing, giving simple substituted derivatives of the type $\text{Ru}(\text{CO})_2(\text{PR}_3)_2(\text{S})$ (S = basic phosphine, alkyne, olefin).^{17,18} With H_2 or HX type substrates possessing reactive H-element bonds (S = HCl, H-CCR, H-SiR₃), the transient Ru(0) adduct " $\text{Ru}(\text{CO})_2(\text{PR}_3)_2(\text{HX})$ " is not intercepted, since rapid oxidative addition of the H-element bond to the metal gives directly the Ru(II) species $\text{Ru}(\text{H})(\text{X})(\text{CO})_2(\text{PR}_3)_2$.¹⁸



The complex $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ was originally used as a pre-catalyst for the Murai reaction,¹⁹ an early example of *chelation-assisted* catalytic functionalization of substrates possessing unreactive C-H bonds.²⁰ In this context, our recent experimental modeling of a stepwise Ru-mediated stoichiometric hydro-acylation of an alkyne with a tethered aldehyde²¹ provides a hint that the same concept might be transposable to a broader range of coupling reactions.

In a preliminary set of experiments, it was found that monodentate 1,3-disubstituted imidazol-2-ylidenes (incorporating mesityl, cyclohexyl, or methyl substituents) are totally reluctant to react with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$. Indeed, IR monitoring indicated that no reaction occurs at room temperature, whereas sacrificial transformation of **1** into the thermodynamically more stable complex $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ occurs at high temperatures. We were thus prompted to examine whether the functionalization of one of the two heterocyclic nitrogen atoms by a potentially coordinating side arm would assist the incorporation of the heterocycle into the metal's coordination sphere.

Two parallel approaches are presented here. They deal respectively with two categories of hybrid heterocyclic ligands (see Chart II) differing in the nature of the “directing group”, namely, (i) a phosphine-tethered imidazolium and its affiliated NHC derivative, and (ii) an olefin-tethered imidazolium, and its NHC analog.



a: Ar = mesityl; **b:** Ar = 2,6 diisopropylphenyl
X = Br, BF_4

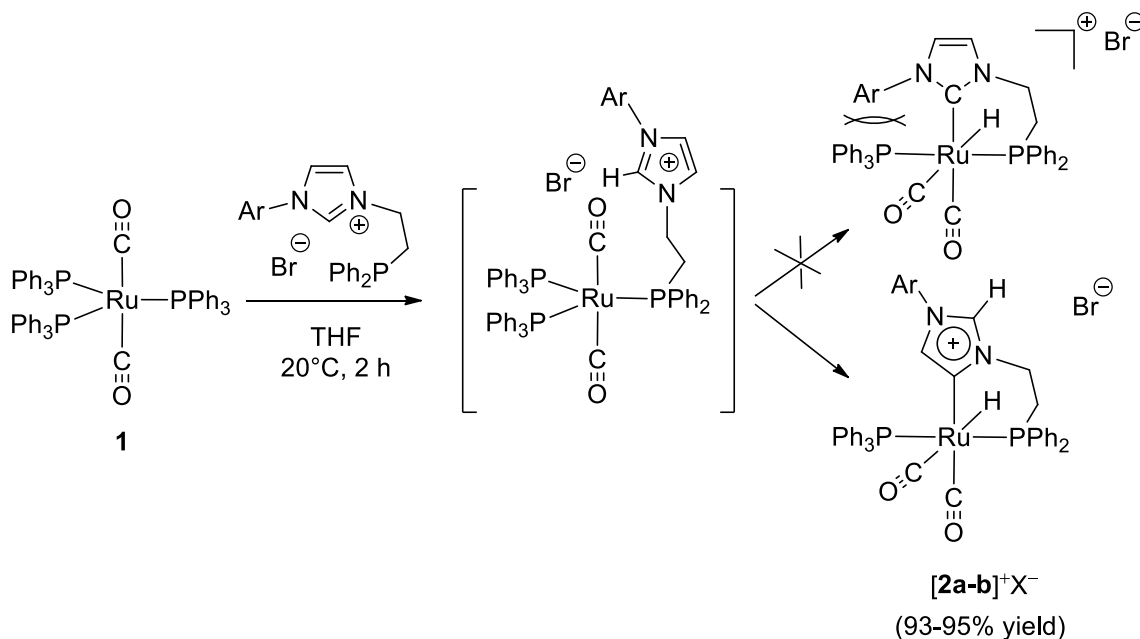
The propensity of a phosphine to act as a directing group susceptible to assist the interaction of an N-heterocycle with a metal center has been established for various metals,²² but rarely applied to the case of ruthenium.^{22b} In parallel, the ability of an olefin - a chemically reactive substrate - to play such a role, was proposed to account for the transition-metal catalyzed annulation of heterocycles, reported by Ellman⁴ for rhodium complexes, and by Cavell³ for nickel complexes. In light of such precedents, it was of interest to examine the possible transposition of such chelation-assisted reactions to the case of a benchmark ruthenium(0) complex.

Results and discussion

A. Phosphine-functionalized imidazolium derivatives

Both the mesityl (**a**) and 2,6-diisopropylphenyl (**b**) imidazolium derivatives²³ [**HL**^{1a-b}]⁺Br⁻ were found to react cleanly with Ru(CO)₂(PPh₃)₃ (**1**) in THF at room temperature over a period of two hours to give the related cationic hydrido species [RuH{L*^{1a-b}}(CO)₂(PPh₃)]⁺Br⁻ [**2a-b**]⁺Br⁻ (* indicates so-called abnormal coordination) in nearly quantitative yield ([**2a**]⁺Br⁻: 93% yield; [**2b**]⁺Br⁻: 95% yield) (Scheme 1). The occurrence of a Ru-H hydride signal (δ = -5.97 ppm for [**2a**]⁺Br⁻, δ = -5.94 ppm for [**2b**]⁺Br⁻), the persistence of the characteristic signal of the imidazolium proton linked to the C2 site at ca. 10 ppm ([**2a**]⁺Br⁻: δ = 10.05 ppm, [**2b**]⁺Br⁻: δ = 9.95 ppm), and the occurrence of a ¹³C resonance at 140 ppm for the C4 site of the heterocycle, clearly indicated that abnormal C-H activation at the backbone C4 site had taken place. Evidence that the two phosphorus centers are in *trans* position was obtained from the magnitude of the *J*_{PP} coupling constant (²*J*_{PP} = 226-227 Hz), whereas the presence of two IR ν (CO) stretching bands corroborated the fact that the two carbonyls are in *cis* position. All such spectroscopic data are consistent with the structure shown in Scheme 1.

Scheme 1. Chelation-assisted reaction of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with phosphine-tethered imidazolium salts, showing privileged abnormal C-H activation at the C4 site.



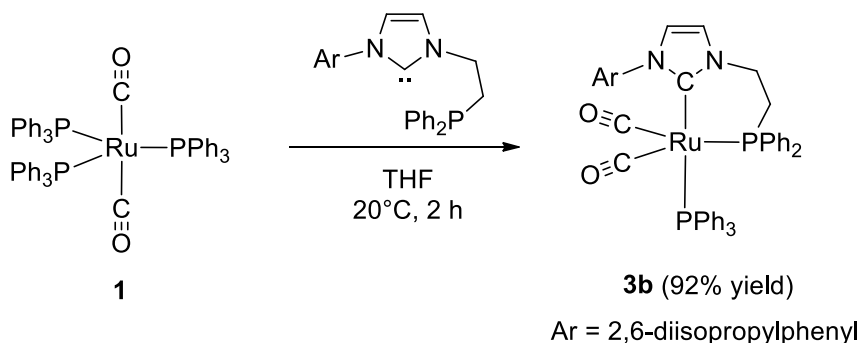
Abnormal C-H activation of imidazolium cations has been observed in various instances and is now well documented.¹⁰ In their studies of the coordination of hybrid imidazolium pyridine ligands to iridium, Crabtree and Eisenstein^{10e} reported the observation of an anion-dependent switch in selectivity between the activation of C2-H and C4-H positions, which was tentatively ascribed to the different acidities of the two sites. However, such an explanation cannot be transposed to the present case since we do observe that the reaction of $[\text{HL}^{1a}]^+\text{BF}_4^-$ with **1** still involves selective activation at the C4 position (as observed with complexes of other metals, particularly Ir(I)),^{22d,23e} possibly reflecting a slightly better steric accessibility of such a site.

B. Phosphine-functionalized NHC derivatives.

In line with the above results, we became interested in synthesizing the first Ru(0) analogs of Roper's complex $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ (**1**) incorporating a chelating N-heterocyclic carbene/phosphine ligand. The above phosphine-functionalized imidazolium derivatives $[\text{HL}^{1a-b}]^+\text{Br}^-$ were thus deprotonated by

KOtBu in THF for 10 minutes and subsequently transferred to a solution of complex **1**, followed by stirring at room temperature for 2 hours. With 1-(2,6-diisopropylphenyl)-3-(2-diphenylphosphinoethyl)-imidazolydene, **L^{1b}**, monitoring by infrared spectroscopy indicated the formation of one compound only, exhibiting two IR $\nu(\text{CO})$ stretching bands (1896(m), 1844(s) cm^{-1}). Whereas this IR pattern corresponds to a di-carbonyl ruthenium(0) complex possessing two CO ligands in *cis* position, the position of these bands at very low wavelength provides convincing evidence for the presence of a strongly basic ligand within the metal's coordination sphere.^{16,17} The new complex was subsequently isolated and indeed unambiguously formulated as $\text{Ru}\{\text{L}^{\text{1b}}\}(\text{CO})_2(\text{PPh}_3)$ (**3b**) (92% yield) based on NMR data. The occurrence of a normal coordination of the NHC through the C2 center was inferred from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra showing a doublet of doublet at $\delta = 185.9$ ppm for C2 and singlets at $\delta = 120.5$ ppm and $\delta = 123.6$ ppm for the backbone atoms C4 and C5. The relative position of the NHC ligand with respect to the two phosphorus centers was deduced from the magnitude of the $^2J_{\text{C2P}}$ coupling constants of 63 Hz, and 35 Hz associated with that signal, and from selective hetero-nuclear decoupling experiments revealing that the carbene is in a *trans* position relative to the PPh_3 ligand, and, inherently, in a *cis* position relative to the RPPH_2 arm, the latter two P nuclei being in a mutual *cis* position ($^2J_{\text{PP}} = 30$ Hz). Taken altogether, the spectroscopic data are fully consistent with the structure shown in Scheme 2 for **3b**. It should be mentioned that when the reaction was carried out with the mesityl-substituted ligand **L^{1a}**, the corresponding Ru(0) complex $\text{Ru}\{\text{L}^{\text{1a}}\}(\text{CO})_2(\text{PPh}_3)$ (**3a**) was also obtained in good yield (92%), but, curiously, the complex, apparently existing as a mixture of two inseparable isomeric forms as revealed by IR spectroscopy,^{17d} appeared to be rather unstable, which precluded its full characterization by NMR spectroscopy. This complex represents the first analogue of Roper's complex incorporating an N-heterocyclic carbene.

Scheme 2. Chelation-assisted reaction of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with a phosphine-functionalized N-heterocyclic carbene.



C. Olefin-functionalized imidazolium derivatives.

It was also of interest to determine whether an olefin - a chemically reactive donor ligand - could be used as a directing group for the chelation-assisted cleavage of an unreactive C-H bond onto a Ru center, with a view to the possibility of exploiting this for the annulation of heterocycles, known to be catalyzed by certain transition metals.^{3,4} We were thus led to prepare several olefin-functionalized imidazolium ligands, namely, 3-allyl-1-mesitylimidazolium bromide, and 3-(but-3-enyl)-1-mesitylimidazolium bromide (**[HL^{2a}]⁺Br⁻**), by simple nucleophilic substitution of allyl or homoallyl bromide respectively by 1-mesitylimidazole. We also prepared the saturated equivalent of the latter, namely, 3-butyl-1-imidazolium bromide, which we used in a preliminary blank experiment aimed at verifying that no C-H bond activation occurs when the nitrogen substituent of the imidazolium is a saturated aliphatic arm.

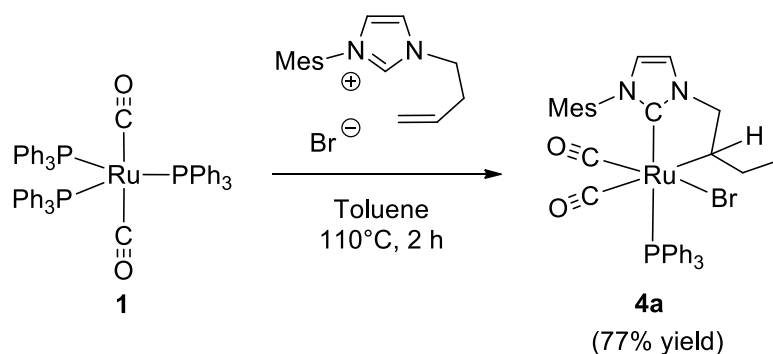
Preliminary assays using 3-allyl-1-mesityl imidazolium bromide as a potential substrate, did not lead to the expected C-H activation. Instead, its reaction with **1** afforded the known cationic allyl derivative $[\text{Ru}(\text{C}_3\text{H}_5)(\text{CO})_2(\text{PPh}_3)_3]^+\text{Br}^-$ via C-N bond cleavage²⁴ and concomitant recovery of 1-mesitylimidazole. With the aim to avoid such a splitting, we were thus prompted to start from the homo-allylic imidazolium salt, **[HL^{2a}]⁺Br⁻**, possessing one more carbon atom in its aliphatic chain. The latter was effectively found to react cleanly with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ (**1**) in toluene solution at 110°C over a period of two hours, giving a colourless complex which was fully characterized in solution and

isolated in crystalline form (77% yield) (see Scheme 3). The reaction was monitored by infrared spectroscopy, following the disappearance of the $\nu(\text{CO})$ stretching bands of complex **1** (1907, 1857 cm^{-1}) and the appearance of two $\nu(\text{CO})$ bands at 2012 and 1948 cm^{-1} indicative of the formation of a ruthenium(II) complex containing two carbonyl ligands in a *cis* position. Here, the disappearance of the imidazolium C2-H signal in the ^1H NMR spectra indicated that “normal” C-H oxidative addition at the C2 position had taken place. This is corroborated by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showing a doublet at $\delta = 183.2$ ppm for the carbene carbon atom, with an associated $^2J_{\text{CP}}$ coupling constant of 89 Hz indicative of a *trans* arrangement of the carbene relative to the remaining PPh_3 ligand. Furthermore, the absence of any hydride signal and the emergence of the characteristic signal of a Ru-CHR group in the ^{13}C NMR spectra at $\delta = 41.0$ ppm ($^2J_{\text{CP}} = 6.0$ Hz) strongly suggested that olefin insertion into the transient Ru-H bond had taken place. The new complex was unambiguously formulated as the hybrid NHC/alkyl derivative $\text{Ru}\{\text{Ar}(\text{N}_2\text{C}_3\text{H}_2)\text{CH}_2\text{C}(\text{H})(\text{CH}_2\text{CH}_3)\}(\text{CO})_2(\text{PPh}_3)\text{Br}$ (**4a**) on the basis of an X-ray structure analysis. An ORTEP drawing of the complex is shown in Figure 1, along with a selection of relevant interatomic distances and bond angles, whereas relevant crystallographic data are set out in Table 1. The X-ray analysis confirms the *cis* arrangement of the CO ligands, and the *trans* arrangement of the carbene carbon atom C3 relative to the remaining PPh_3 ligand. The coordination sphere of the ruthenium center is completed by a bromine atom *trans* to a first CO ligand, and an alkyl fragment *trans* to the second one. Clearly, it appears that the imidazolium/olefin ligand **L**^{2a} was converted into a chelating NHC/alkyl ligand forming a five-membered metallacycle with the ruthenium through additional bonding with C7. The five-membered metallacycle adopts an envelope conformation, C7 pointing away by 0.592 Å from the Ru1 / C3 / N2 / C6 plane. It appears that the carbene moiety is significantly tilted away from the ideal octahedral basis set ($\text{P1-Ru1-C3} = 169.67(7)^\circ$) reflecting both the steric strain within the five-membered metallacycle, and the steric repulsion between the mesityl ring and the carbonyl ligands in the equatorial plane. Given that **4a** possesses two stereogenic centers, namely, Ru1 and the alkyl carbon atom C7, the generation of two diastereoisomers can be anticipated. Actually, although the ^1H spectra appear

relatively limpid, the ^{31}P NMR spectra show, besides the main singlet at 26.0 ppm, an additional singlet at 26.4 ppm in an approximate 1:9 ratio, while some signals in the ^{13}C spectra show a very weak parent resonance (see experimental). Since the elemental analysis is reasonably good, this impurity may actually be the second diastereoisomer of **4a**. The isomer corresponding to the solid-state structure reported here is presumably the thermodynamically more stable one, where the ethyl group of the alkyl moiety is directed away from the bulky bromide ligand.

The formation of complex **4** could be reasonably understood in terms of a stepwise sequence involving: i) chelation-assisted activation of the C2-H bond of the cationic 3-(but-3-enyl)-1-mesitylimidazolium pro-ligand to give an elusive cationic NHC/olefin-hydrido-complex; ii) reversible hydride migration to the olefin giving an alkyl species; iii) migration of the double bond along the chain by reversible β -H elimination to afford the observed five-membered metallacycle; iv) capture of the bromide anion by the unsaturated cationic alkyl intermediate.

Scheme 3. Chelation-assisted reaction of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with an olefin-functionalized imidazolium derivative.



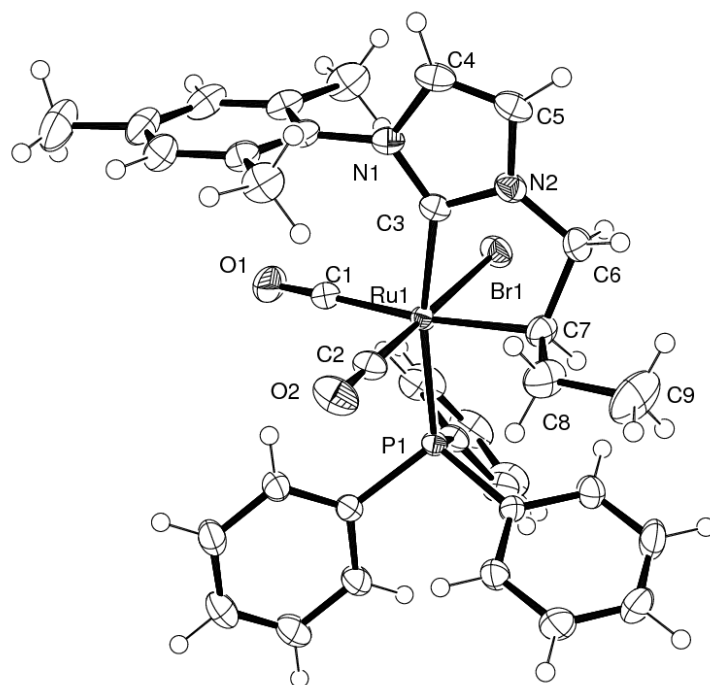


Figure 1: Perspective view of the alkyl complex **4a**. Ellipsoids are shown at the 50% probability level. Selected interatomic distances (Å) and bond angles (°): Ru1-Br1 2.5695(14); Ru1-P1 2.4220(14); Ru1-C1 1.937(3); Ru1-C2 1.843(3); Ru1-C3 2.071(2); Ru1-C7 2.197(3); C1-O1 1.126(3); C2-O2 1.126(3); N1-C3 1.354(3); N1-C4 1.393(3); N1-C11 1.431(3); N2-C3 1.344(3); N2-C5 1.382(3); N2-C6 1.457(3); C4-C5 1.337(4); C6-C7 1.531(4); C7-C8 1.524(4); C8-C9 1.535(4); Br1-Ru1-P1 91.01(3); Br1-Ru1-C1 88.94(7); Br1-Ru1-C3 84.81(6); Br1-Ru1-C7 86.93(7); P1-Ru1-C1 91.76(7); P1-Ru1-C2 91.91(8); P1-Ru1-C7 93.26(7); C1-Ru1-C2 93.37(11); C3-Ru1-C7 77.12(9); Ru1-C3-N1 138.35(17); Ru1-C3-N2 117.04(16); C3-N2-C6 118.6(2); N2-C6-C7 108.3(2); Ru1-C7-C6 107.65(16); Ru1-C7-C8 116.23(17); C6-C7-C8 110.8(2); Ru1-C1-O1 178.2(2); Ru1-C2-O2 179.9(3).

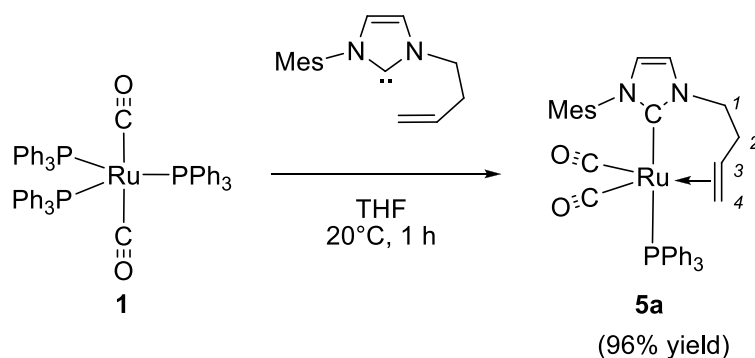
D. Olefin-functionalized NHC derivatives.

In further work, we were interested in the synthesis of a potentially hemilabile NHC/olefin Ru(0) complex.²⁵ In a one-pot reaction, the 3-(but-3-enyl)-1-mesitylimidazolium cation [**HL^{2a}**]⁺Br⁻ was deprotonated *in situ* by addition of KO^{*t*}Bu in THF at 0°C for a period of one hour,²⁶ then allowed to react with **1** at room temperature. The reaction, monitored by following the evolution of IR ν(CO) bands, appeared to be spectroscopically quantitative within one hour, producing a white solid, which was unambiguously identified on the basis of spectroscopic and crystallographic data as the new complex Ru{**L^{2a}**}(CO)₂(PPh₃) (**5a**) (96% yield) (Scheme 4).

The multiplicity and position of the ν(CO) bands for **5a** are indicative of the formation of a dicarbonyl Ru(0) complex, in which the CO ligands are in a *cis* position (two bands: 1947(m), 1879(s) cm⁻¹). In the

$^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the carbene carbon atom in **5a** is observed at $\delta = 185.8$ ppm and, as for **4a**, the associated $^2J_{\text{CP}}$ coupling constant of 87 Hz clearly shows that it occupies a *trans* position relative to the remaining PPh_3 ligand. NMR data are otherwise in agreement with the persistence of a but-3-ene-1-yl moiety (see experimental). Resonances attributable to the olefinic termination, however, appear to be significantly shifted up-field, as compared with the corresponding ones in the pro-ligand [**HL**^{2a}]⁺ ($^{13}\text{C}\{^1\text{H}\}$ NMR: $\Delta\delta\text{C}_4 = -83.1$ ppm, $\Delta\delta\text{C}_3 = -90.6$ ppm; ^1H NMR: $\Delta\delta\text{H}_{4(\text{ave.})} = -3.6$ ppm, $\Delta\delta\text{H}_3 = -3.2$ ppm), clearly showing coordination to Ru.

Scheme 4. Chelation-assisted reaction of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with an olefin-functionalized N-heterocyclic carbene.



The structure of this unique NHC/olefin Ru(0) 18 e^- complex is shown in Figure 2, along with a selection of interatomic distances and bond angles, whereas relevant crystallographic data are set out in Tables 1.

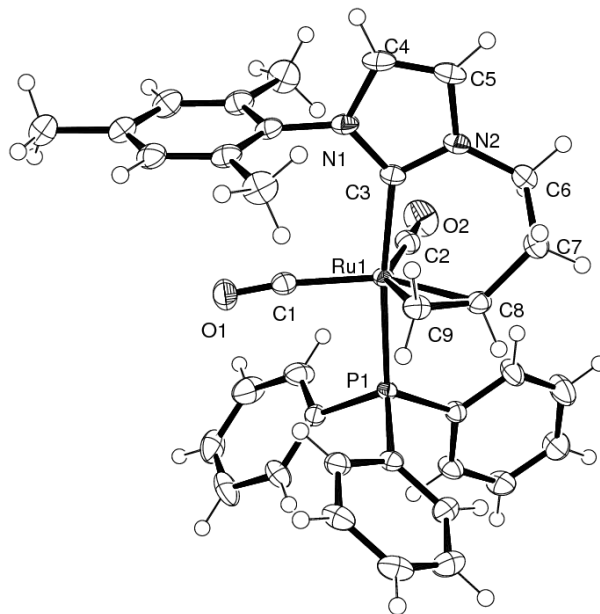


Figure 2: Perspective view of complex **5a**. Ellipsoids are shown at the 50% probability level. Selected interatomic distances (Å) and bond angles (°): Ru1-P1 2.3467(3); Ru1-C1 1.9148(14); Ru1-C2 1.8959(13); Ru1-C3 2.0775(12); Ru1-C8 2.2076(14); Ru1-C9 2.1838(13); N1-C3 1.3578(16); N1-C4 1.3910(19); C4-C5 1.336(2); N2-C5 1.3824(19); N2-C3 1.3611(17); N2-C6 1.4602(19); C6-C7 1.516(2); C7-C8 1.527(2); C8-C9 1.430(2); Ru1-C1-O1 172.91(12); Ru1-C2-O2 175.66(13); Ru1-C9-C8 71.90(8); Ru1-C8-C9 70.10(8); Ru1-C8-C7 120.25(9); C1-Ru1-C2 108.09(6); C1-Ru1-C9 103.39(5); C2-Ru1-C8 111.10(5); C1-O1 1.1484(18); C2-O2 1.1515(19); P1-Ru1-C1 89.08(4); C1-Ru1-C3 97.52(5); C3-Ru1-C8 86.15(5); C3-Ru1-C9 83.02(5); P1-Ru1-C8 87.54(4); P1-Ru1-C9 93.65(4); Ru1-C3-N2 122.48(9); N1-C3-N2 104.05(11).

The complex exhibits a trigonal bipyramidal geometry where the NHC unit and the remaining triphenylphosphine ligand occupy the two opposite apexes, whereas the two mutually *cis* carbonyl ligands and the η^2 terminal butenyl moiety occupy the three equatorial coordination sites. The carbene-to-ruthenium bond length in the present Ru(0) complex (Ru1-C3 = 2.0775(13) Å) is not significantly different from the corresponding bond in **4a** (**4a**: Ru1-C3 = 2.071(2) Å), and actually appears to fall within the typical range for Ru / NHC complexes.^{7,8,12} The butenyl C=C termination is bound in a slightly dissymmetrical fashion to Ru, the internal Ru-C bond being the longest one (Ru1-C8 = 2.2076(14) Å, Ru1-C9 2.1838(13) Å), whereas its coordination plane is slightly tilted off the equatorial plane ($\{\text{Ru1-C1-C2-CENT}_{\text{C8C9}}\}-\{\text{Ru1-C8-C9}\} = 11.3^\circ$). As expected, due to coordination, the C8-C9

bond distance (C8-C9 = 1.430(2) Å) is significantly longer than one would expect for an isolated C=C bond (1.299 Å).²⁷ Noticeably, the carbonyl ligand C1O1, which is located below the mesityl ring, is significantly bent away from the ring (Ru1-C1-O1 = 172.91(12); O1-C1-Ru1-C11 = -170.1(1)°) probably due to steric repulsion.

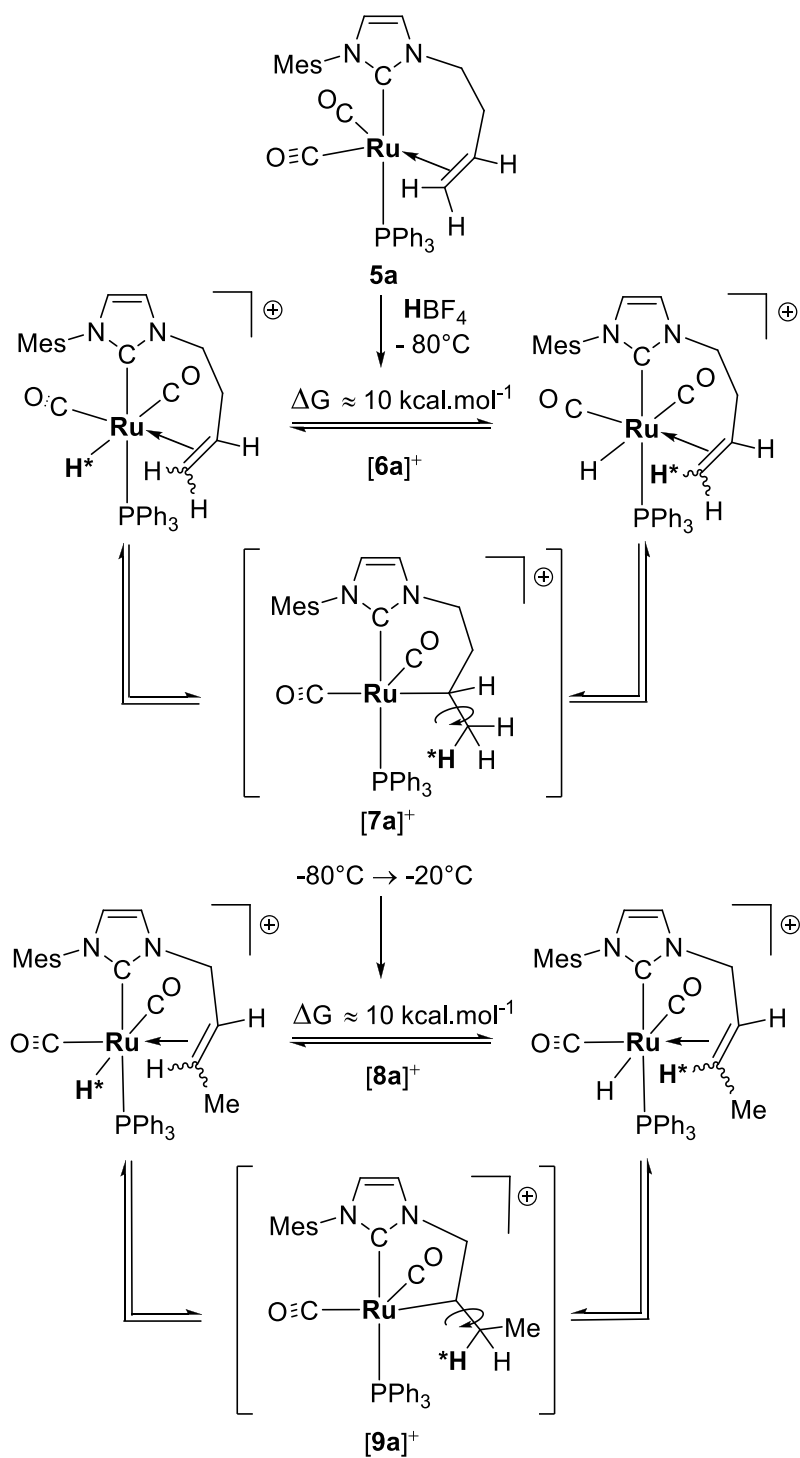
For comparative purposes, we remind that several olefin adducts of Roper's complex are known.^{14,28} In particular Kakiuchi^{28c} previously reported a parallel reaction of **1** with an olefin-functionalized phosphine, *o*-styryl-diphenylphosphine, leading to a structurally similar complex, Ru{Ph₂P(C₆H₄)CH=CH₂}(CO)₂(PPh₃). The IR ν(CO) bands of the present NHC/olefin species **5a** (ν(CO): 1947 (s), 1879 (s) cm⁻¹ (THF); ν(CO): 1941 (s), 1872 (s) cm⁻¹ (CDCl₃)) appear at lower stretching frequencies than those of the above-mentioned phosphine/olefin derivative (ν(CO) = 1965(m), 1899 (s) cm⁻¹ (CDCl₃)), corroborating the fact that the N-heterocyclic carbene acts as a better electron-donor than the phosphine. The observation that such frequencies are yet relatively high, illustrates the fact that the olefin plays an important role as a π acceptor, which also results in the above mentioned lengthening of the C=C double bond. It appears that the Ru(CO)₂(NHC)(PPh₃) fragment of the present complex relies heavily on its π-basicity for binding the ethylene, as previously noted by Caulton in the case of the unsaturated species Ru(CO)₂(P^tBu₂Me)₂.^{16,17} This may account for the relatively high stability of **5a**, as indicated, for example, by the fact that, unlike Roper's complex, it does not react with molecular hydrogen at atmospheric pressure. Such a behaviour is also in sharp contrast with the reported case of an olefin-functionalized NHC complex of Iridium, where the olefinic arm could be readily hydrogenated under one atmosphere of H₂ at 20°C.^{25b}

Since **5a** is the first NHC olefin complex of Ru(0), it appears as a convenient model to trace the elementary transformations of an olefin in the vicinity of a strongly basic Ru(0) center. In the context of the present work, we were interested in the identification of elusive intermediates generated through the metal-mediated transformation of the salt [HL^{2a}]⁺Br⁻ right after the key C-H bond activation step, on the way to the alkyl species **4a** (Scheme 3). Considering that C-H bond cleavage is expected to produce

a cationic carbene-hydrido-derivative as the first putative intermediate undetectable under thermal activation, it seemed obvious that such a complex could alternatively be generated at low temperature by simple protonation of **5a**, which effectively proved to be the case.

The addition of HBF₄ to **4a** was performed at –80°C, and monitored by NMR spectroscopy. The initial complex generated at low temperature was spectroscopically identified as the cationic hydrido NHC/olefin derivative [RuH{L^{2a}}(CO)₂(PPh₃)]⁺BF₄[–], [**6a**]⁺BF₄[–] (Scheme 5) exhibiting a ³¹P NMR signal at δ = 39.1 ppm. ¹H NMR data revealed, in particular, the occurrence of (i) two signals at δ = –0.66 ppm and δ = –0.11 ppm corresponding to the two terminal hydrogen atoms of the olefinic substituent of the NHC, and (ii) a hydride signal at δ = –7.80 ppm. Very characteristically, the latter three signals appeared to be relatively broad, as compared with those of the mesityl signals for instance, suggesting that the corresponding three protons were engaged in a fast exchange process on the NMR timescale. This was established by a selective 1D DPGSE-NOE experiment²⁹ revealing a selective enhancement of the terminal olefinic proton signals upon irradiation of the hydride signal at –7.80 ppm (Figure 3).³⁰ Examination of the coalescence between the hydride signal and the terminal olefinic protons signals (Δν = 3850 Hz, T_c ≈ 255 K)³¹ led to an estimated activation barrier of *ca.* 10 kcal.mol^{–1} for the relevant dynamic exchange process, which can be rationalized in terms of the transient generation of an elusive unsaturated higher energy NHC/alkyl- intermediate [Ru{Ar(N₂C₃H₂)CH₂CH₂C(H)CH₃}(CO)₂(PPh₃)]BF₄[–], [**7a**]⁺BF₄[–] (see Scheme 5). It is worth noting that this process constitutes somehow a low activation–energy pathway for an apparent *cis/trans* isomerisation of the coordinated olefinic arm.

Scheme 5: Protonation of **5a** with HBF₄ at low temperature.



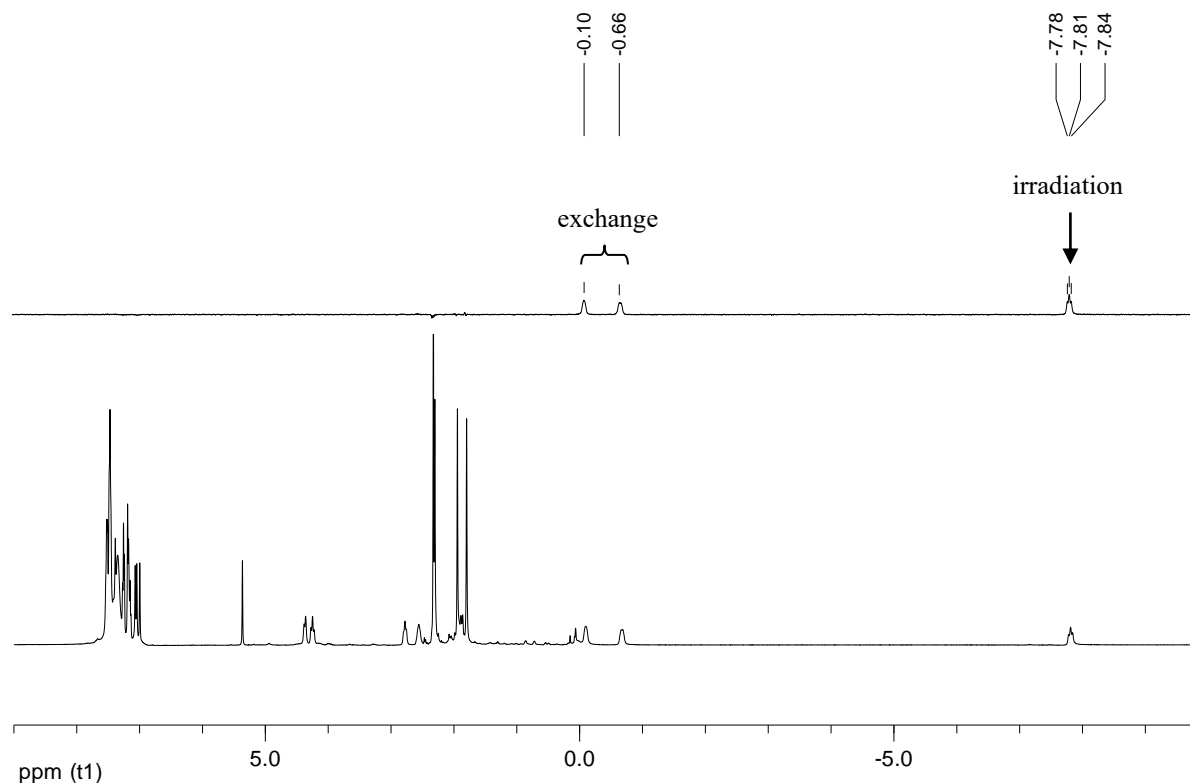


Figure 3: ^1H NMR reference spectrum for $[\mathbf{6a}]^+$ at 195 K and 1D selective DPGSE-NOE²⁹ experiment ($T_m = 100$ ms) (upper spectrum) providing evidence for the exchange process between the terminal olefinic protons ($\delta - 0.11$ and $- 0.66$ ppm) and the hydride ligand ($\delta - 7.80$ ppm).³⁰

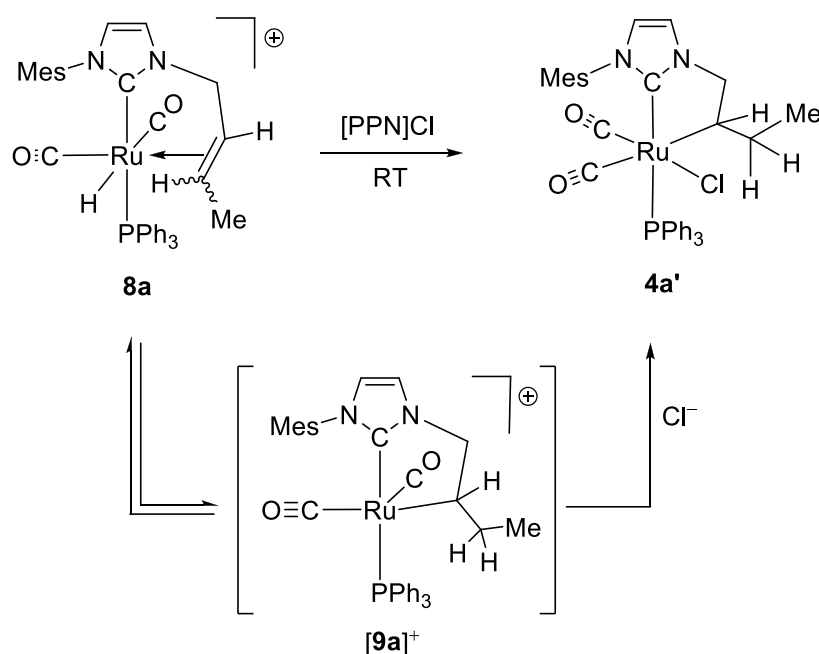
During the course of NMR experiments aimed at determining the activation barrier of the above process, we were led to observe that complex **6a** further evolves above -20°C in an irreversible manner. Indeed, as the temperature is raised above -20°C , NMR data actually indicate the progressive and gradual disappearance of $[\mathbf{6a}]^+\text{BF}_4^-$ with concomitant generation of a new hydrido NHC/olefin species characterized by a characteristic $^{31}\text{P}\{^1\text{H}\}$ NMR signal at $\delta = 35.2$ ppm (25°C). The new complex was formulated as $[\text{RuH}\{\text{Ar}(\text{N}_2\text{C}_3\text{H}_2)\text{CH}_2\text{CH}=\text{C}(\text{H})\text{CH}_3\}(\text{CO})_2(\text{PPh}_3)]^+\text{BF}_4^-$, $[\mathbf{8a}]^+\text{BF}_4^-$ on the basis of both ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data. As shown in scheme 5, $[\mathbf{8a}]^+$ is a new isomeric form of the previous species, differing from its antecedent $[\mathbf{6a}]^+$ by the position of the olefinic double bond along the functionalized arm. The ^1H NMR spectra, at 298K are indeed consistent with the presence of the coordinated olefinic arm “ $\text{CH}_2\text{CH}=\text{C}(\text{H})\text{Me}$ ” as revealed by the occurrence of an ABX pattern centered

at $\delta = 4.50$ ppm (2H, $-\text{CH}_2\text{CH}=\text{}$), a complex multiplet at $\delta = 2.55$ ppm ($-\text{CH}_2\text{CH}=\text{}$), a relatively sharp triplet at $\delta = 0.79$ ppm for the methyl group, and a very broad signal at $\delta = -1.26$ ppm for the remaining proton in geminal position. The corresponding hydride ligand appears as a very broad singlet at $\delta = -4.80$ ppm. The formation of this complex reflects the fact that, as the temperature is raised above 255 K, β -elimination from the intracyclic carbon atom of the elusive intermediate $[\mathbf{7a}]^+\text{BF}_4^-$ (Scheme 5) becomes more favourable than β -elimination from the exocyclic carbon atom. Noticeably, the observation of concurrent broadening of the resonances due to the terminal olefinic hydrogen atom and the hydride ligand indicates that these nuclei are, here also, involved in an exchange process, which was established by a 2D NOESY experiment. The present exchange process can be rationalized in terms of the existence of the elusive cationic NHC/alkyl intermediate $[\text{Ru}\{\text{Ar}(\text{N}_2\text{C}_3\text{H}_2)\text{CH}_2\text{C}(\text{H})\text{CH}_2\text{CH}_3\}(\text{CO})_2(\text{PPh}_3)]^+\text{BF}_4^-$, $[\mathbf{9a}]^+\text{BF}_4^-$ (Scheme 5), offering, like for $\mathbf{6a}$, a low activation–energy pathway for the *E/Z* isomerisation of the coordinated olefinic arm. Very characteristically, by lowering the temperature down to 178 K, the exchange process can be slowed down to an extent allowing the observation of the *two* isomers of $\mathbf{8a}$, corresponding to the generation of *E* and *Z* isomers of the coordinated olefin. Indeed, we do observe a splitting of the ^{31}P resonance at $\delta = 35.2$ ppm into two sharp singlets at $\delta = 36.7$ ppm and $\delta = 34.4$ ppm ($\approx 5:1$ ratio),³² along with a concomitant splitting of the hydride resonances into two still relatively broad signals at $\delta = -6.89$ ppm and $\delta = -7.15$ ppm ($\approx 10:1$ ratio). Examination of the de-coalescence/coalescence behavior of the ^{31}P NMR signals ($\Delta\nu = 484$ Hz; $T_c \approx 230$ K) finally gives an estimate of the free activation enthalpy of the exchange process ≈ 10 kcal.mol⁻¹.³¹

Interestingly, and even though none of the above unsaturated cationic alkyl intermediates $[\mathbf{7a}]^+$ or $[\mathbf{9a}]^+$ is directly observable, their existence could be inferred from trapping experiments, taking advantage of their intrinsic unsaturation. As shown in scheme 6, we were effectively led to observe that the addition of bis-triphenylphosphineiminium chloride (PPNCl), to the final mixture containing $[\mathbf{8a}]^+$, results in quasi-instantaneous chloride capture by the elusive unsaturated alkyl intermediate $[\mathbf{9a}]^+$ with

formation of the neutral alkyl species **4a'**, the chloro- equivalent of the previously isolated bromo-complex **4a**, obtained in a 1:1 mixture of diastereoisomers, different from that obtained through the thermal reaction (Scheme 3). Thus, the entire sequence displayed here provides a suitable model for the observed generation of the NHC/alkyl species upon reaction of **1** with $[\text{HL}^{2a}]^+\text{Br}^-$.

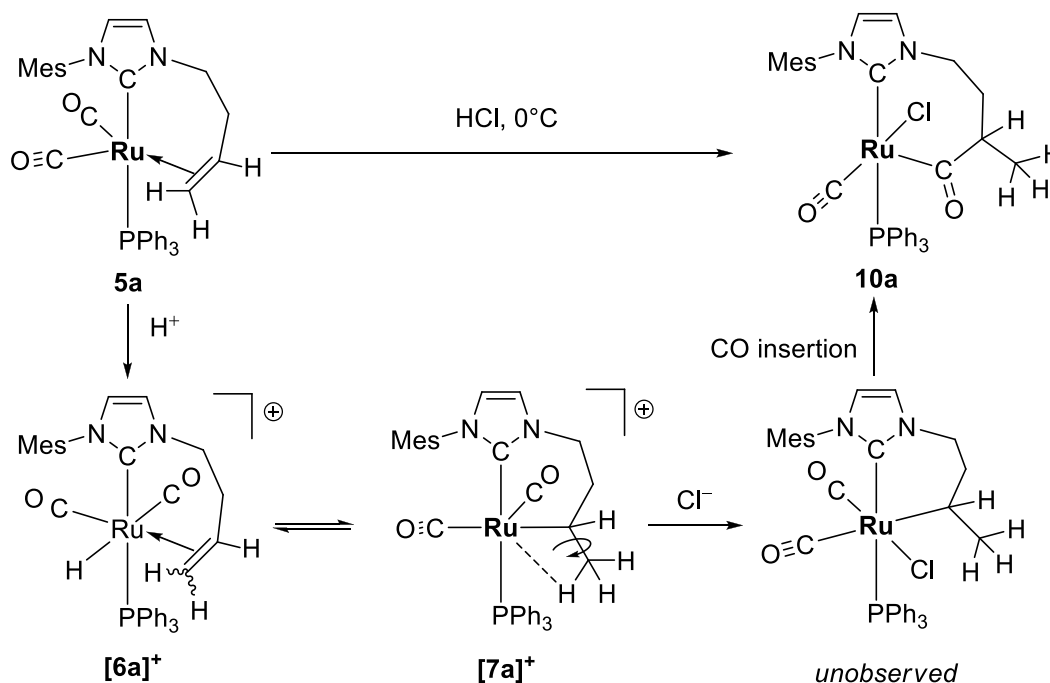
Scheme 6: Trapping of the elusive cationic alkyl intermediate by halide capture leading to the neutral alkyl species **4a'**.



Logically, addition of the halide ion Cl^- prior to the isomerisation of the olefinic arm, i.e. when $[\mathbf{6a}]^+$ is still present in solution, should give a neutral alkyl complex resulting from halide capture by $[\mathbf{7a}]^+$. This effectively happens when the protonation of **5a** is achieved at 0°C with HCl , since the potentially coordinating halide anion is immediately liberated in solution. As expected, (Scheme 7), quenching the vacant site by coordination of the halide *also quenches any possibility of β -elimination, thus blocking the isomerisation process*. Quite surprisingly, however, the anticipated neutral alkyl intermediate is not intercepted due to its immediate conversion into the 16 e^- NHC- acyl- $\text{Ru}(\text{II})$ complex

$\text{RuCl}\{\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2(\text{N}_2\text{C}_3\text{H}_2)\text{Mes}\}(\text{CO})(\text{PPh}_3)$ (**10a**) via a migratory CO insertion reaction (Scheme 7).

Scheme 7. Protonation of the hybrid NHC/olefin complex **5a** by HCl and generation of the NHC/acyl complex **10a**.



At first sight, the spontaneous conversion of an 18 e⁻ Ru(II) alkyl carbonyl complex into the corresponding formally unsaturated 16 e⁻ acyl derivative might appear as unexpected, though there are precedents for such a transformation in the literature, and in particular, in the case of comparable carbonyl phosphine complexes.³³ Besides, the reluctance of the closely related alkyl complex **4a'** to undergo migratory CO insertion is probably due to the high thermodynamic stability of its five-membered metallacyclic ring.

Conclusion

Chelation assistance is known to play an important role in stoichiometric and catalytic transformations of substrates possessing sterically hindered donor atoms or unreactive C-H bonds. In the present account, we have shown that phosphine-functionalized N-heterocyclic carbenes and, more surprisingly, olefin-functionalized N-heterocyclic carbenes, react cleanly with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ *via* pre-coordination of their functionalized arm, to give, respectively, chelating NHC/phosphine or NHC/olefin complexes of general formula $\text{Ru}(\text{CO})_2[\text{NHC/phosphine}](\text{PPh}_3)$ and $\text{Ru}(\text{CO})_2[\text{NHC/olefin}](\text{PPh}_3)$ in good to excellent yields. These new Ru(0) species represent the first isolated congeners of Roper's complex incorporating a strongly stabilizing N-heterocyclic carbene ligand. Their intrinsic reactivity deserves to be explored in future work.

Importantly, chelation assistance was also found to be a prerequisite to observe C-H activation from the parent hybrid imidazolium/phosphine or imidazolium/olefin ligands. Kinetic preference for *abnormal vs normal C-H activation* of the heterocycle was observed in the case of the imidazolium/phosphine ligand, but such a preference may not be systematic since it can be determined by the steric bulk of the nitrogen substituents. Normal coordination at the C2 center takes place if the imidazolium precursor is de-protonated prior to complexation. Normal coordination was also observed with the imidazolium/olefin ligand bearing the same substituents. In that case, the elusive hydrido intermediate was not intercepted under the temperature conditions of such an activation reaction, because of rapid H transfer to the olefin to give a new NHC/alkyl Ru(II) complex. Nevertheless, the principal cationic isomeric hydrido olefinic intermediates sequentially generated in such a transformation were identified in an NMR experiment following the evolution of $\text{Ru}(\text{CO})_2[\text{NHC/olefin}](\text{PPh}_3)$ in the presence of a proton source. It was shown that the isomerisation of the metal-mediated olefinic arm takes place through elusive high energy cationic intermediates which are not directly observable, but, because of their unsaturation, can be quenched by incoming nucleophilic anions. It is noteworthy that the interconverting intermediate complexes detected here are closely related to those postulated by Cavell in the nickel-catalyzed annulation of heterocycles, except that the final CC bond forming reaction involving the carbene center does not occur in the case of

ruthenium. Unlike what was observed with nickel, once an N-heterocyclic carbene becomes coordinated to Ru, it systematically behaves as an excellent strongly stabilizing ancillary ligand and is thus unlikely to be subsequently engaged in any further reductive CC bond forming reaction involving its carbene center.

Experimental

General considerations. All manipulations were performed under an inert atmosphere of dry nitrogen by using vacuum line and Schlenk tube techniques. THF and diethyl ether were distilled from sodium/benzophenone and toluene was distilled from sodium. Pentane, hexane and dichloromethane were dried over CaH_2 and subsequently distilled. Deuterated solvents (dichloromethane, benzene and chloroform) were dried over CaH_2 , vacuum distilled, degassed by three freeze-pump-thaw cycles, and stored under a nitrogen atmosphere in Teflon valve ampoules. NMR spectra were recorded on Bruker AC200, WM250, AV300, AV400, or AV500 spectrometers. ^1H and ^{13}C chemical shifts (δ) are given in ppm (the residual peak of deuterated solvents was used as reference). ^{31}P chemical shifts are reported in ppm. Infrared spectra were obtained on a Perkin Elmer 1725 FT-IR spectrometer for solutions and on a Perkin Elmer GX 2000 FT-IR spectrometer (ATR mode) for solids. Microanalyses were performed by the micro analytical Service of the Laboratoire de Chimie de Coordination and MS spectra by the mass spectrometry service of the Paul Sabatier University. Melting points were obtained with a Stuart Scientific Melting Point apparatus SMP1. Compounds $\text{Ru}(\text{CO})_3\text{Cl}_2(\text{thf})$,³⁴ and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$,¹⁵ were prepared using our previously published synthetic procedures. 1-Mesitylimidazole was prepared according to a literature procedure.³⁵ The hybrid phosphine/imidazolium salts 1-mesityl-3-(2-diphenylphosphinoeth-1-yl)-imidazolium bromide, $[\text{HL}^{1a}]^+\text{Br}^-$ 1-mesityl-3-(2-diphenylphosphinoeth-1-yl)-imidazolium tetrafluoroborate, $[\text{HL}^{1a}]^+\text{BF}_4^-$ and 1-(2,6-diisopropylphenyl)-3-(2-diphenylphosphinoeth-1-yl)-imidazolium bromide $[\text{HL}^{1b}]^+\text{Br}^-$ were prepared using procedures established by some of us.²³

3-Allyl-1-mesitylimidazolium bromide. 3-Bromopropene (370 μ L, 4.25 mmol) was added to a solution of 1-mesitylimidazole (750 mg, 4 mmol) in toluene (5 mL). The mixture was heated in an oil bath at 100°C for 20 hours during which time a white precipitate appeared. After cooling, Et₂O (10 mL) was added and the overlaying solution was filtered through cannula. The white solid residue was washed with Et₂O (2 x 10 mL) and dried *in vacuo* to yield the imidazolium salt as a white powder (928 mg, 75%). mp: 225°C; ¹H NMR (250 MHz, CDCl₃): δ 10.42 (s, 1H, CH_{Im-2}), 7.81 (t, 1H, *J*_{HH} = 1.6 Hz, CH_{Im-4/5}), 7.23 (t, 1H, *J*_{HH} = 1.7 Hz, CH_{Im-4/5}), 7.03 (s, 2H, CH_{mes}), 6.15 (m, 1H, =CH), 5.56 (s, 1H, =CH₂), 5.49 (br s, 1H, =CH₂), 5.42 (d, 2H, *J*_{HH} = 6.7 Hz, N-CH₂), 2.35 (s, 3H, CH_{3 para}), 2.09 (s, 6H, CH_{3 ortho}). ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ 141.4 (C_{para}), 138.1 (CH_{Im-2}), 134.2 (C_{ortho}), 130.5 (=CH), 129.9 (CH_{mes}), 123.2 (CH_{Im-4/5}), 122.8 (CH_{Im-4/5}), 122.4 (=CH₂), 52.4 (CH₂), 21.1 (CH_{3 para}), 17.7 (CH_{3 ortho}). MS (ESI): *m/z* (%) 227.3 (100) [M - Br]⁺, 187.3 (4) [M - Br - allyl]⁺. FT-IR (ATR): 3078, 2972, 1608, 1557, 1541, 1486, 1443, 1202, 1162, 1067, 1043, 1021, 990, 937, 924, 877, 760, 729, 669, 638, 582, 559, 526 cm⁻¹.

3-Allyl-1-mesitylimidazolium tetrafluoroborate. 3-Allyl-1-mesitylimidazolium bromide (150 mg, 0.49 mmol) and sodium tetrafluoroborate (108 mg, 0.98 mmol) were placed in an Erlenmeyer. CH₂Cl₂ (20 mL) and H₂O (10 mL) were added. The mixture was poured into a separatory funnel and vigorously stirred. The organic layer was extracted, dried over Na₂SO₄, filtered and evaporated to dryness by rotary evaporation. The white residue was washed with Et₂O (5 mL) to give a white solid (131 mg, 85 %). ¹H NMR (250 MHz, CDCl₃): δ 8.80 (br s, 1H, CH_{Im-2}), 7.81 (t, 1H, *J*_{HH} = 1.7 Hz, CH_{Im-4/5}), 7.21 (t, 1H, *J*_{HH} = 1.7 Hz, CH_{Im-4/5}), 6.99 (s, 2H, CH_{mes}), 6.08 (m, 1H, =CH), 5.47 (m, 2H, =CH₂), 5.01 (d, 2H, *J*_{HH} = 6.4 Hz, N-CH₂), 2.33 (s, 3H, CH_{3 para}), 2.05 (s, 6H, CH_{3 ortho}). ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ 141.3 (C_{para}), 136.7 (CH_{Im-2}), 134.4 (C_{ortho}), 130.2 (=CH), 129.8 (CH_{mes}), 123.7 (CH_{Im-4/5}), 123.2 (CH_{Im-4/5}), 122.7 (=CH₂), 52.4 (CH₂), 21.1 (CH_{3 para}), 17.2 (CH_{3 ortho}).

3-(But-3-enyl)-1-mesitylimidazolium bromide, [HL^{2a}]⁺Br⁻ 4-Bromobut-1-ene (210 μ L, 2.05 mmol) was added to a solution of 1-mesitylimidazole (382 mg, 2.05 mmol) in THF (5 mL). The mixture was heated in an oil bath at 70°C for 20 hours. The product precipitates along the reaction course. After

cooling, Et₂O (10 mL) was added and the overlaying solution was evacuated through a filtering cannula. The white solid residue was washed with Et₂O (2 x 10 mL) and dried *in vacuo* to yield the imidazolium salt as a white powder (584 mg, 89%). mp: 143°C; ¹H NMR (400 MHz, CDCl₃): δ 10.19 (br s, 1H, CH_{Im-2}), 8.10 (br s, 1H, CH_{Im-4/5}), 7.17 (s, 1H, CH_{Im-4/5}), 6.95 (s, 2H, CH_{mes}), 5.94 (m, 1H, J_{HH} = 7.2 Hz, J_{HH} = 10.1 Hz, =CH), 5.02 (br s, 1H, =CH₂), 4.91 (br d, 1H, J_{HH} = 7.4 Hz, =CH₂), 4.80 (t, 2H, J_{HH} = 6.3 Hz, N-CH₂), 2.70 (td, 2H, J_{HH} = 6.3 Hz, J_{HH} = 6.4 Hz, =C-CH₂), 2.27 (s, 3H, CH_{3 para}), 1.98 (s, 6H, CH_{3 ortho}). ¹³C{¹H} NMR (100.4 MHz, CDCl₃): δ 141.2 (C_{para}), 137.7 (CH_{Im-2}), 134.2 (C_{ortho}), 132.9 (=CH), 130.7 (C_{ipso}), 129.8 (CH_{mes}), 123.5 (CH_{Im-4/5}), 123.1 (CH_{Im-4/5}), 119.4 (=CH₂), 49.1 (CH₂), 34.9 (CH₂), 21.1 (CH_{3 para}), 17.5 (CH_{3 ortho}). MS (ESI): m/z (%) 241.3 (100) [M - Br]⁺, 187.3 (34) [M - Br - homoallyl]⁺. FT-IR (ATR): 3055, 1561, 1546, 1487, 1459, 1433, 1202, 1158, 1067, 1039, 1001, 993, 931, 875, 838, 762, 667 cm⁻¹.

3-(But-3-enyl)-1-mesitylimidazolium tetrafluoroborate, [HL^{2a}]⁺BF₄⁻. Compound [HL^{2a}]⁺Br⁻ (862 mg, 2.68 mmol) and sodium tetrafluoroborate (323 mg, 2.95 mmol) were placed in a Schlenk tube containing a small stirring bar. Then CH₂Cl₂ (10 mL) and H₂O (10 mL) were added. After 2 hours of vigorous stirring, the product was extracted with CH₂Cl₂ (3 x 10 mL). The organic layer was successively washed with water (2 x 10 mL), dried over Na₂SO₄ and filtered in a Schlenk tube. The solvent was removed *in vacuo* and the white residue was washed with distilled Et₂O, to give a very hygroscopic white powder (474 mg, 54 %). ¹H NMR (250 MHz, CDCl₃): δ 8.72 (br s, 1H, CH_{Im-2}), 7.76 (br s, 1H, CH_{Im-4/5}), 7.18 (s, 1H, CH_{Im-4/5}), 6.96 (s, 2H, CH_{mes}), 5.94 (tdd, 1H, J_{HH} = 7.1 Hz, J_{HH} = 10.3 Hz, J_{HH} = 14.5 Hz, =CH), 5.02 (br s, 1H, =CH₂), 4.96 (br d, 1H, J_{HH} = 8.8 Hz, =CH₂), 4.47 (t, 2H, J_{HH} = 6.3 Hz, N-CH₂), 2.62 (q, 2H, J_{HH} = 6.3 Hz, =CH-CH₂), 2.29 (s, 3H, CH_{3 para}), 1.96 (s, 6H, CH_{3 ortho}). ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ 141.2 (C_{para}), 136.4 (CH_{Im-2}), 134.4 (C_{ortho}), 132.8 (=CH), 130.6 (C_{ipso}), 129.7 (CH_{mes}), 123.7 (CH_{Im-4/5}), 123.5 (CH_{Im-4/5}), 119.4 (=CH₂), 49.1 (CH₂), 34.6 (CH₂), 21.0 (CH_{3 para}), 17.1 (CH_{3 ortho}).

3-Butyl-1-mesitylimidazolium bromide. 4-Bromobutane (290 μL, 2.7 mmol) was added to a solution of 1-mesitylimidazole (500 mg, 2.7 mmol) in THF (5 mL). The mixture was heated in an oil

bath at 70°C for 20 hours during which time a white precipitate appeared. After cooling, Et₂O (10 mL) was added and the overlaying solution was filtered through cannula. The white solid residue was washed with Et₂O (2 x 10 mL) and dried *in vacuo* to yield the imidazolium salt as a white powder (251 mg, 30 %). mp: 174-175°C; ¹H NMR (250 MHz, CDCl₃): δ 10.50 (s, 1H, CH_{Im-2}), 7.83 (br s, 1H, CH_{Im-4/5}), 7.21 (t, 1H, *J*_{HH} = 1.7 Hz, CH_{Im-4/5}), 7.08 (s, 2H, CH_{mes}), 4.75 (t, 2H, *J*_{HH} = 7.2 Hz, N-CH₂), 2.35 (s, 3H, CH_{3 para}), 2.08 (s, 6H, CH_{3 ortho}), 1.99 (m, 2H, CH₂), 1.46 (m, 2H, CH₂), 0.99 (t, 3H, *J*_{HH} = 7.3 Hz, CH₃). ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ 141.3 (C_{para}), 138.4 (CH_{Im-2}), 134.2 (C_{ortho}), 130.7 (C_{ipso}), 129.9 (CH_{mes}), 123.2 (CH_{Im-4/5}), 122.9 (CH_{Im-4/5}), 50.1 (CH₂), 31.5 (CH₂), 21.1 (CH_{3 para}), 19.4 (CH₂), 17.6 (CH_{3 ortho}), 13.6 (CH₃). MS (ESI): *m/z* (%) 243.3 (100) [M - Br]⁺. FT-IR (ATR): 3056, 3005, 2958, 2932, 2872, 1560, 1543, 1488, 1460, 1449, 1376, 1200, 1158, 1110, 1066, 1037, 1047, 863, 751, 668, 639, 583 cm⁻¹.

Dicarbonylhydrido[1-mesityl-3-(2-diphenylphosphino-κP-eth-1-yl)-imidazol-4-ylidene-κC⁴](triphenylphosphine)ruthenium(II) bromide, [2a]⁺Br⁻. Compounds [HL^{1a}]⁺Br⁻ (48 mg, 0.10 mmol) and **1** (94 mg, 0.10 mmol) were reacted in THF (10 mL) at room temperature. The light yellow mixture was stirred for 2 h, and THF was then removed *in vacuo*. The resulting residue was washed with pentane (2 x 10 mL) and dried to yield the complex as a white powder (84 mg, 93%). ¹H NMR (500 MHz, CDCl₃): δ 9.95 (d, 1H, *J*_{HH} = 1.4 Hz, CH_{Im-2}), 7.80 - 7.88 (m, 2H, CH_{PPh2}), 7.50 - 7.58 (m, 14H, CH_{PPh2}), 7.40 - 7.46 (m, 9H, CH_{PPh3}), 6.92 (s, 1H, CH_{mes}), 6.88 (s, 1H, CH_{mes}), 6.00 (ddt, 1H, *J*_{HH} = 4 Hz, *J*_{HH} = 9 Hz, *J*_{HH} = 30 Hz, N-CH₂), 5.72 (d, 1H, *J*_{HH} = 1.4 Hz, CH_{Im-5}), 4.77 (ddt, 1H, *J*_{HH} = 4 Hz, *J*_{HH} = 9 Hz, *J*_{PH} = 30 Hz, N-CH₂), 2.75 (m, 1H, P-CH₂), 2.94 (m, 1H, P-CH₂), 2.30 (s, 3H, CH_{3 para}), 1.89 (s, 3H, CH_{3 ortho}), 1.45 (s, 3H, CH_{3 ortho}), - 5.97 (t, 1H, *J*_{PH} = 21 Hz, Ru-H). ³¹P{¹H} NMR (202.5 MHz, CDCl₃): δ 43.02 (d, *J*_{PP} = 227 Hz, PPh₃), 39.8 (d, (d, *J*_{PP} = 227 Hz, PPh₂)). ¹³C NMR (125.8 MHz, CDCl₃): δ 196.4 (t, *J*_{CP} = 11 Hz, CO), 196.1 (t, *J*_{CP} = 11 Hz, CO), 143.4 (dd, *J*_{CP} = 15 Hz, *J*_{CP} = 17 Hz, C_{Im-4}), 140.1 (C_{p-mes}), 137.8 (CH_{Im-2}), 135.9 (dd, *J*_{CP} = 47.1 Hz, *J*_{CP} = 3.1 Hz, C_{ipso PPh2}), 135.7 (dd, *J*_{CP} = 43.5 Hz, *J*_{CP} = 2.0 Hz, C_{ipso PPh2}), 16.9 (CH_{3 ortho}), 134.9 (dd, *J*_{CP} = 43.3 Hz, *J*_{CP} = 2.8 Hz, C_{ipso PPh3}), 134.5 (C_{o-mes}), 134.0 (C_{o-mes}), 133.2 (d, *J*_{CP} = 10.8 Hz, CH_{PPh3}), 132.9 (d, *J*_{CP} = 19.4 Hz, CH_{PPh2}), 132.8

(d, $J_{CP} = 12.0$ Hz, CH_{PPh_2}), 131.6 ($C_{ipso-mes}$), 131.2 (d, $J_{CP} = 10.5$ Hz, CH_{PPh_2}), 130.7 (d, $J_{CP} = 2.2$ Hz, CH_{PPh_2}), 130.3 (d, $J_{CP} = 1.8$ Hz, CH_{PPh_3}), 129.2 (CH_{mes}), 129.0 (CH_{mes}), 128.2 (d, $J_{CP} = 6$ Hz, CH_{Im-5}), 128.9 (d, $J_{CP} = 7.0$ Hz, CH_{PPh_2}), 128.6 (d, $J_{CP} = 9.5$ Hz, CH_{PPh_3}), 47.2 (N- CH_2), 29.5 (d, $J_{CP} = 33$ Hz, P- CH_2), 20.7 (CH_3_{para}), 17.4 (CH_3_{ortho}). MS (FAB, MNBA matrix) m/z (%): 789 (100) $[M - Br - CO]^+$, 761 (94) $[M - Br - 2CO]^+$, 497 (73) $[M - Br - 2CO - PPh_3]^+$, 819 (18) $[M - Br]^+$. FT-IR ($\nu(CO)$, THF): 2041 (s), 1987 (vs) cm^{-1} . HRMS: m/z calcd for: $C_{46}H_{43}N_2O_2P_2Ru$: 819.1843; found : 819.1849.

Dicarbonylhydrido[1-mesityl-3-(2-diphenylphosphino- κP -eth-1-yl)-imidazol-4-ylidene- κC^4](triphenylphosphine)ruthenium(II) tetrafluoroborate, $[2a]^+BF_4^-$. Compounds $[HL^{1a}]^+BF_4^-$ (30 mg, 62 μmol) and **1** (60 mg, 62 μmol) were reacted in THF (5 mL) at room temperature. The light yellow mixture was stirred for 1 hour, then THF was removed *in vacuo*. The resulting residue was washed with pentane (5 mL) and dried to yield the complex as a white powder (42 mg, 75%). 1H NMR (200 MHz, $CDCl_3$): δ 8.71 (d, 1H, $J_{HH} = 1$ Hz, CH_{Im-2}), 6.89 - 7.96 (m, CH_{PPh_3} , CH_{mes}), 5.75 (s, 1H, CH_{Im-5}), 5.22 (s, 1H, N- CH_2), 4.77 (m, 1H, N- CH_2), 2.81 (m, 1H, P- CH_2), 2.71 (m, 1H, P- CH_2), 2.31 (s, 3H, CH_3_{para}), 1.83 (s, 3H, CH_3_{ortho}), 1.43 (s, 3H, CH_3_{ortho}), -5.98 (t, 1H, $J_{HH} = 21$ Hz, Ru- H). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 46.7 (d, $J_{PP} = 226$ Hz, PPh_2), 43.0 (d, $J_{PP} = 226$ Hz, PPh_3). FT-IR ($\nu(CO)$, CH_2Cl_2): 2042 (s), 1992 (vs) cm^{-1} .

Dicarbonylhydrido[1-(2,6-diisopropylphenyl)-3-(2-diphenylphosphino- κP -eth-1-yl)-imidazol-4-ylidene- κC^4](triphenylphosphine)ruthenium(II) bromide, $[2b]^+Br^-$. Compounds $[HL^{1b}]^+Br^-$ (56 mg, 110 μmol) and **1** (100 mg, 110 μmol) were reacted in THF (10 mL) at room temperature. The light yellow mixture was stirred for 2 h, then THF was removed *in vacuo*. The resulting residue was washed with pentane (2 x 10 mL) and dried to yield the complex as a white powder (95 mg, 95%). 1H NMR (500 MHz, CD_2Cl_2): δ 10.03 (d, 1H, $J_{HH} = 1$ Hz, CH_{Im-2}), 7.40 - 7.86 (m, 26H, CH_{PPh_3} , CH_{PPh_2} , CH_{p-DIPP}), 7.20 (d, 1H, $J_{HH} = 7.8$ Hz, CH_{m-DIPP}), 7.17 (d, 1H, $J_{HH} = 7.8$ Hz, CH_{m-DIPP}), 6.00 (ddt, 1H, $J_{HH} = 3.9$ Hz, $J_{HH} = 13.2$ Hz, $J_{HP} = 30.2$ Hz, N- CH_2), 5.71 (d, 1H, $J_{HH} = 1$ Hz, CH_{Im-5}), 4.77 (ddt, 1H, $J_{HH} = 3.9$ Hz, $J_{HH} = 13.2$ Hz, $J_{HP} = 19.8$ Hz, N- CH_2), 2.75 (br t, 1H, $J_{HH} = 12.7$ Hz, P- CH_2), 2.89 - 2.98 (m, 1H, P- CH_2), 1.99 (h, 1H, $J_{HH} = 6.8$ Hz, CH_{iPr}), 1.69 (h, 1H, $J_{HH} = 6.8$ Hz, CH_{iPr}), 1.20 (d, 3H, $J_{HH} = 6.8$

Hz, CH₃), 1.05 (d, 3H, $J_{\text{HH}} = 6.8$ Hz, CH₃), 0.70 (d, 3H, $J_{\text{HH}} = 6.3$ Hz, CH₃), 0.80 (d, 3H, $J_{\text{HH}} = 6.8$ Hz, CH₃), -5.94 (t, 1H, $J_{\text{PH}} = 21$ Hz, Ru-H); ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂): δ 42.7 (d, $J_{\text{PP}} = 226$ Hz, PPh₃), 39.6 (d, $J_{\text{PP}} = 226$ Hz, PPh₂); ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): δ 198.9 (t, $J_{\text{CP}} = 11$ Hz, CO), 23.5 (CH₃), 196.5 (t, $J_{\text{CP}} = 11.0$ Hz, 145.5 (C_{DIPP}), CO), 145.2 (C_{DIPP}), 143.2 (dd, $J_{\text{CP}} = 14.7$ Hz, $J_{\text{CP}} = 15.7$ Hz, C_{Im-4}), 138.4 (CH_{Im-2}), 135.9 (dd, $J_{\text{CP}} = 47.1$ Hz, $J_{\text{CP}} = 3.5$ Hz, C_{ipso PPh2}), 135.7 (dd, $J_{\text{CP}} = 43.1$ Hz, $J_{\text{CP}} = 2.3$ Hz, C_{ipso PPh2}), 134.9 (dd, $J_{\text{CP}} = 46.1$ Hz, $J_{\text{CP}} = 3.1$ Hz, C_{ipso PPh3}), 133.3 (d, $J_{\text{CP}} = 10.8$ Hz, CH_{o-PPh3}), 132.8 (d, $J_{\text{CP}} = 11.3$ Hz, CH_{o-PPh2}), 131.1 (d, $J_{\text{CP}} = 10.4$ Hz, CH_{o-PPh2}), 130.9 (C_{ipso DIPP}), 130.7 (CH_{p-DIPP}, CH_{p-PPh2}), 130.3 (d, $J_{\text{CP}} = 1.6$ Hz, CH_{p-PPh3}), 129.6 (d, $J_{\text{CP}} = 6$ Hz, CH_{Im-5}), 128.9 (d, $J_{\text{CP}} = 9.6$ Hz, CH_{m-PPh2}), 128.8 (d, $J_{\text{CP}} = 10.2$ Hz, CH_{m-PPh2}), 128.5 (d, $J_{\text{CP}} = 9.6$ Hz, CH_{m-PPh3}), 124.1 (CH_{m-DIPP}), 123.9 (CH_{m-DIPP}), 47.9 (N-CH₂), 29.5 (d, $J_{\text{CP}} = 33$ Hz, P-CH₂), 28.4 (CH_{iPr}), 28.1 (CH_{iPr}), 24.6 (CH₃), 24.1 (CH₃), 23.9 (CH₃). MS (FAB, MNBA matrix): m/z (%) 831 (100) [M - Br - CO]⁺, 803 (70) [M - Br - 2 CO]⁺, 861 (30) [M - Br]⁺. FT-IR (ν(CO), THF): 2042 (s), 1991 (vs) cm⁻¹. HRMS: m/z calcd for: C₄₉H₄₉N₂O₂P₂Ru: 861.2313; found: 861.2357.

Dicarbonyl[1-(2,6-diisopropylphenyl)-3-(2-diphenylphosphino-κP-eth-1-yl)-imidazol-2-ylidene-κC²](triphenylphosphine)ruthenium(0), 3b. KO^tBu (29 mg, 0.25 mmol) and [HL^{1b}]⁺Br⁻ (115 mg, 0.22 mmol) were reacted in THF (12 mL) for 10 min at room temperature before being transferred by cannula to a solution of **1** (199 mg, 210 μmol) in THF (28 mL). The mixture was stirred for 2 hours and THF was then removed *in vacuo*. The residue was washed with pentane (15 mL) and the overlaying solution was evacuated through a cannula. The product was then dissolved in CH₂Cl₂ and filtered through Celite. After evaporation of the solvents, the product was washed with pentane (2 x 15 mL) to give an air sensitive pale yellow powder (166 mg, 92%). ¹H NMR (500 MHz, CD₂Cl₂): δ 7.44 (t, 1H, $J_{\text{HH}} = 7.5$ Hz, CH_{p-DIPP}), 7.28 (d, 2H, $J_{\text{HH}} = 7.8$ Hz, CH_{m-DIPP}), 7.18 (q, 4H, $J_{\text{HH}} = 7.5$ Hz, CH_{m-PPh2}), 7.06-7.12 (m, 19H, CH_{PPh3}, CH_{p-PPh2}, CH_{o-PPh2}, CH_{Im-4/5}), 6.86 (d, 1H, $J_{\text{HH}} = 1.7$ Hz, CH_{Im-4/5}), 4.62 (dt, 2H, $J_{\text{HH}} = 21$ Hz, $J_{\text{HH}} = 5$ Hz, N-CH₂), 2.69 (h, 2H, $J_{\text{HH}} = 6.8$ Hz, CH_{iPr}), 2.30 (t, 2H, $J_{\text{HH}} = 5$ Hz, P-CH₂), 1.43 (d, 6H, $J_{\text{HH}} = 6.8$ Hz, CH₃), 1.03 (d, 6H, $J_{\text{HH}} = 6.8$ Hz, CH₃). ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂): δ 31.5 (d, $J_{\text{PP}} = 29$ Hz, PPh₂), 57.5 (d, $J_{\text{PP}} = 29$ Hz, PPh₃). ¹³C{¹H} NMR (125.8 MHz,

CD₂Cl₂): δ 218.0 (t, J_{CP} = 18.5 Hz, CO), 185.9 (dd, J_{CP} = 35 Hz, J_{CP} = 63 Hz, N₂C), 147.1 (C_{O-DIPP}), 143.0 (d, J_{CP} = 22.9 Hz, C_{ipso} PPh₂), 137.7 (C_{ipso} DIPP), 134.0 (d, J_{CP} = 11.6 Hz, CH_{O-PPh_3}), 132.4 (d, J_{CP} = 13.7 Hz, CH_{O-PPh_2}), 130.0 (d, J_{CP} = 9.4 Hz, CH_{Im-PPh_3}), 129.4 ($CH_{Im-DIPP}$), 128.4 (CH_{P-PPh_3}), 127.8 (CH_{P-PPh_2}), 127.5 (d, J_{CP} = 7.4 Hz, CH_{Im-PPh_2}), 123.6 ($CH_{Im-4/5}$), 123.4 ($CH_{Im-DIPP}$), 120.5 ($CH_{Im-4/5}$), 51.0 (d, J_{CP} = 10.2 Hz, N-CH₂), 34.1 (d, J_{CP} = 19.0 Hz, P-CH₂), 28.6 (CH_{iPr}), 25.5 (s, CH₃), 22.3 (CH₃). MS (FAB, MNBA matrix): m/z (%): m/z (%) 860 (4) [M]⁺, 831 (10) [M - CO]⁺, 803 (11) [M - 2CO]⁺, 567 (35) [M - CO - PPh₃]⁺, 538 (100) [M - 2CO - PPh₃]⁺. FT-IR (ν (CO), THF): 1896 (m), 1844 (s) cm⁻¹.

Bromodicarbonyl[1-mesityl-3-(but-1-yl- κ C²)-imidazol-2-ylidene- κ C²](triphenylphosphine)-ruthenium(II), 4a. Compounds **1** (100 mg, 0.11 mmol) and [HL^{2a}]⁺Br⁻ (34 mg, 0.11 mmol) were reacted in toluene (3 mL) for 2 hours at 110°C. After cooling, toluene was evaporated; the residue was washed with pentane (2 x 10 mL) and dried *in vacuo* to yield the product as an off-white powder (61 mg, 77%). Crystallization from CH₂Cl₂/pentane gave colourless crystals suitable for an X-ray diffraction experiment. ¹H NMR (300 MHz, CDCl₃): δ 7.50-7.75 (br m, 5H, CH_{PPh_3}), 7.30-7.40 (br s, 10H, CH_{PPh_3}), 7.24 (s, 1H, $CH_{Im-4/5}$), 7.02 (s, 1H, CH_{mes}), 6.96 (s, 1H, CH_{mes}), 6.84 (s, 1H, $CH_{Im-4/5}$), 4.57 (dd, 1H, J_{HH} = 11.7 Hz, J_{HH} = 7.8 Hz, N-CH₂), 3.91 (br d, 1H, J_{HH} = 11.7 Hz, N-CH₂), 3.49 (q, 2H, J_{HH} = 7.2 Hz, CH₂-CH₃), 2.34 (s, 6H, CH₃ ortho), 2.03 (s, 3H, CH₃ para), 1.60 (m, 1H, Ru-CH), 1.38 (t, 3H, J_{HH} = 7.2 Hz, CH₂-CH₃). ³¹P{¹H} NMR (121.4 MHz, CDCl₃): δ 26.4 (s, PPh₃, minor isomer), 26.0 (s, PPh₃, major isomer). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 199.8 (d, J_{CP} = 10.6 Hz, CO), 191.5 (d, J_{CP} = 9.1 Hz, CO), 183.2 (d, J_{CP} = 88.8 Hz, N₂C), 139.2 (C_{mes}), 137.7 (C_{mes}), 136.3 (C_{mes}), 135.4 (C_{mes}), 140.0 (d, J_{CP} = 10.2 Hz, CH_{PPh_3} , major), 133.9 (d, J_{CP} = 39 Hz, C_{ipso} PPh₃), 133.9 (d, J_{CP} = 10.1 Hz, CH_{PPh_3} , minor), 129.7 (d, J_{CP} = 2.0 Hz, CH_{PPh_3}), 128.7 (CH_{mes} , major), 128.4 (CH_{mes}), 128.0 (d, J_{CP} = 9.2 Hz, CH_{PPh_3} , minor), 127.9 (d, J_{CP} = 9.3 Hz, CH_{PPh_3} , major), 122.5 (d, J_{CP} = 3.6 Hz, $CH_{Im-4/5}$), 119.7 (d, J_{CP} = 1.8 Hz, $CH_{Im-4/5}$, major), 119.6 (d, J_{CP} = 2 Hz, $CH_{Im-4/5}$, minor), 53.0 (CH₂-CH₃), 57.1 (d, J_{CP} = 4.1 Hz, NCH₂), 41.0 (d, J_{CP} = 6.0 Hz, Ru-CH), 21.1 (CH₃ ortho), 17.4 (CH₃ para), 8.0 (CH₂-CH₃). MS (ESI): m/z (%) 661.2 (100) [M - Br]⁺, 633.2 (55) [M - Br - CO]⁺. FT-IR (ν (CO), CH₂Cl₂): 2021, 1948

cm⁻¹. Anal. calcd for C₃₆H₃₇BrN₂O₂PRu (740.63): C, 58.38; H, 4.90; N, 3.78; found : C, 58.63; H, 4.60; N, 3.75.

Note: complex **4a'**, the chloro-analog of **4a**, was not fully characterized; it was just identified on the basis of the close similarity of its ¹H NMR and IR spectra with those of **4a**, listed above.

Dicarbonyl[1-mesityl-3-(η^2 -but-3-en-1-yl)-imidazol-2-ylidene- κ C²](triphenylphosphine)-ruthenium(0), 5a. KO^tBu (48 mg, 0.43 mmol) and 3-(but-3-enyl)-1-mesitylimidazolium bromide (130 mg, 0.40 mmol) were weighed and placed in a Schlenk tube. THF (20 mL) was syringed into the Schlenk tube and the mixture was stirred for 1 hour at 0°C. Then, the complex Ru(CO)₂(PPh₃)₃ (384 mg, 0.40 mmol) was added and the cool bath was taken off. After 1 hour at room temperature, volatiles were removed *in vacuo*. The residue was washed with pentane (15 mL) and the overlaying solution was filtered through cannula. The product was then dissolved in CH₂Cl₂ and filtered through Celite. Solvents were evaporated and the residue was washed with pentane (2 x 10 mL) to obtain a white solid (258 mg, 96 %). Colourless crystals suitable for an X-ray diffraction study were obtained by slow diffusion of hexane in a solution of complex in toluene. ¹H NMR (300 MHz, C₆D₆): δ 7.92-7.98 (m, 6H, CH_{PPh3}), 7.47-7.50 (m, 2H, CH_{PPh3}), 7.27 (s, 1H, CH_{PPh3}), 6.93-7.16 (m, CH_{PPh3} + mes), 6.22 (d, 1H, *J*_{HH} = 1.5 Hz, CH_{Im-4/5}), 6.09 (d, 1H, *J*_{HH} = 1.5 Hz, CH_{Im-4/5}), 4.17 (td, 1H, ²*J*_{H1b/H1a} = 12.2 Hz, ³*J*_{H1b/H2a} = 12.8 Hz, ³*J*_{H1b/H2b} = 2.5 Hz, N-CH₂), 3.39 (td, 1H, ²*J*_{H1a/H1b} = 12.2 Hz, ³*J*_{H1a/H2a} = 2.9 Hz, ³*J*_{H1a/H2b} = 2.3 Hz, N-CH₂), 2.79 (m, 1H, =CH), 2.53 (tdd, 1H, ³*J*_{H2b/H1a} = 2.3 Hz, ³*J*_{H2b/H3} = 9.3 Hz, ²*J*_{H2b/H2a} = 13.5 Hz, ³*J*_{H2b/H1b} = 2.5 Hz, =CH-CH₂), 2.32 (s, 3H, CH₃ mes), 2.26 (s, 3H, CH₃ mes), 2.11 (s, 3H, CH₃ mes), 1.62 (tdd, 1H, ²*J*_{H2a/H2b} = 13.5 Hz, ³*J*_{H2a/H1a} = 2.9 Hz, ³*J*_{H2a/H3} = 3.6 Hz, ³*J*_{H2a/H1b} = 12.8 Hz, =CH-CH₂), 1.50 (ddd, 1H, ²*J*_{H4b/H4a} = 1.5 Hz, *J*_{H4bP} = 6.6 Hz, ³*J*_{H4b/H3} = 8.6 Hz, =CH₂), 1.28 (ddd, 1H, ²*J*_{H4a/H4b} = 1.5 Hz, *J*_{H4a/P} = 5.5 Hz, ³*J*_{H4a/H3} = 9.6 Hz, =CH₂). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ 58.4 (s, PPh₃). ¹³C{¹H} NMR (75.4 MHz, CD₂Cl₂): δ 211.7 (d, *J*_{CP} = 14.9 Hz, CO), 208.8 (d, *J*_{CP} = 12.3 Hz, CO), 185.8 (d, *J*_{CP} = 87.0 Hz, N₂C), 138.8 (C_{mes}), 136.9 (C_{mes}), 17.8 (CH₃ mes), 136.2 (C_{mes}), 135.2 (d, *J*_{CP} = 38.3 Hz, C_{ipso} PPh₃), 134.0 (d, *J*_{CP} = 10.9 Hz, CH_O-PPh₃), 133.7 (d, *J*_{CP} = 19.6 Hz, CH_O-PPh₃), 129.1 (d, *J*_{CP} = 1.95 Hz, CH_P-PPh₃), 128.8 (s, CH_{mes}), 128.7 (CH_{mes}), 127.5 (d, *J*_{CP} = 9.2 Hz, CH_m-PPh₃), 120.7 (d, *J*_{CP} = 3.2 Hz,

$\text{CH}_{\text{Im-4/5}}$), 120.4 (d, $J_{\text{CP}} = 2.5$ Hz, $\text{CH}_{\text{Im-4/5}}$), 57.4 (N- CH_2), 42.3 (d, $J_{\text{CP}} = 2.6$ Hz, $=\text{CH}$), 36.3 (d, $J_{\text{CP}} = 2.9$ Hz, $=\text{CH}_2$), 31.3 (d, $J_{\text{CP}} = 1.1$ Hz, CH- CH_2), 20.8 (CH_3_{mes}), 18.0 (CH_3_{mes}). MS (FAB, MNBA matrix): m/z (%) 661 (6) $[\text{M}]^+$, 632 (30) $[\text{M} - \text{CO}]^+$, 604 (100) $[\text{M} - 2\text{CO}]^+$, 418 (20) $[\text{M} - \text{NHC}(\text{olefin})]^+$, 363 (33) $[\text{M} - \text{NHC}(\text{olefin}) - 2\text{CO}]^+$. FT-IR ($\nu(\text{CO})$, THF): 1947, 1879 cm^{-1} . Anal. calcd for $\text{C}_{36}\text{H}_{37}\text{N}_2\text{O}_2\text{PRu} \cdot 0.4 \text{CH}_2\text{Cl}_2$: C, 62.84; H, 5.48; N, 4.03; found: C, 62.84; H, 5.16; N, 3.93.

Dicarbonyl-hydrido-[1-mesityl-3-(η^2 -but-3-en-1-yl)-imidazol-2-ylidene- κC^2](triphenylphosphine)ruthenium(II) tetrafluoroborate, $[\mathbf{6a}]^+\text{BF}_4^-$

Sample preparation: In a NMR tube, a solution of compound **5a** (30 mg, 46 μmol) in CD_2Cl_2 (1 mL) was cooled to -78°C . To this solution, $\text{HBF}_4 \cdot \text{OEt}_2$ (7 μL , 50 μmol , 1.1 eq) was slowly added and NMR spectra were recorded. NMR ^1H (500 MHz, 195 K, CD_2Cl_2): δ 7.46 - 7.56 (m, 9H, $\text{CH}_{\text{o-Ph}}$, $\text{CH}_{\text{p-Ph}}$), 7.38 (br s, 1H, CH_{Im}), 7.34 (br s, 6H, $\text{CH}_{\text{m-Ph}}$), 7.07 (s, 1H, CH_{mes}), 7.05 (s, 1H, CH_{mes}), 7.01 (br s, 1H, CH_{Im}), 4.26 (t, 1H, $J_{\text{HH}} = 12.5$ Hz, N- CH_2), 4.73 (m, 1H, N- CH_2), 2.78 (t, 1H, $J_{\text{HH}} = 12.5$ Hz, $=\text{CH}-\text{CH}_2$), 2.56 (br s, 1H, $=\text{CH}$), 2.18 (s, 3H, CH_3_{mes}), 1.98 (m, 1H, $=\text{CH}-\text{CH}_2$), 1.95 (s, 3H, CH_3_{mes}), 1.80 (s, 3H, CH_3_{mes}), -0.11 (m, 1H, $=\text{CH}_2$), -0.66 (m, 1H, $=\text{CH}_2$), -7.80 (t, 1H, $J_{\text{HH}} = 15.0$ Hz, Ru- H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, 195 K, CD_2Cl_2) δ 39.1 (s, PPh_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, 195 K, CD_2Cl_2) δ 201.0 (d, $J_{\text{CP}} = 15.1$ Hz, CO), 191.4 (d, $J_{\text{CP}} = 7.5$ Hz, CO), 167.8 (d, $J_{\text{CP}} = 83.0$ Hz, N_2C), 140.7 (C_{mes}), 136.3 (C_{mes}), 135.4 (C_{mes}), 133.6 ($\text{CH}_{\text{m-Ph}}$), 131.5 ($\text{CH}_{\text{p-Ph}}$), 129.6 (CH_{mes}), 129.5 (CH_{mes}), 129.3 (d, $J_{\text{CP}} = 10.0$ Hz, $\text{CH}_{\text{o-Ph}}$), 124.3 ($\text{CH}_{\text{Im4/5}}$), 123.0 ($\text{CH}_{\text{Im4/5}}$), 56.4 (N- CH_2), 32.9 (d, $J_{\text{CP}} = 5.0$ Hz, $=\text{CH}$), 28.6 ($=\text{CH}-\text{CH}_2$), 21.2 (CH_3_{mes}), 18.1 (CH_3_{mes}), 18.0 (CH_3_{mes}), 9.3 (m, $=\text{CH}_2$). $^{11}\text{B}\{^1\text{H}\}$ NMR (160.5 MHz, 195 K, CD_2Cl_2) δ -1.2 (s, BF_4).

Dicarbonyl-hydrido-[1-mesityl-3-(η^2 -but-3-en-1-yl)-imidazol-2-ylidene- κC^2](triphenylphosphine)ruthenium(II) trifluoromethanesulfonate, $[\mathbf{6a}]^+\text{TfO}^-$.³⁰

Sample preparation: In a NMR tube, a solution of compound **5a** (26.7 mg, 40.3 μmol) in CD_2Cl_2 (0.6 mL) was cooled to -78°C . To this solution, TfOH (4 μL , 44.3 μmol , 1.1 eq) was slowly added and NMR spectra were recorded. ^1H NMR (500 MHz, 195 K, CD_2Cl_2): δ 7.52 - 7.13 (m, CH_{Im} , CH_{Ph}), 7.07 (s, 1H,

CH_{mes}), 7.04 (s, 1H, CH_{mes}), 6.99 (br s, 1H, CH_{Im}), 4.37 (m, 1H, N- CH_2), 4.26 (t, 1H, $J_{HH} = 12.5$ Hz, N- CH_2), 2.78 (t, 1H, $J_{HH} = 12.5$ Hz, =CH- CH_2), 2.56 (br s, 1H, =CH), 2.30 (s, 3H, CH_3_{mes}), 1.94 (s, 3H, CH_3_{mes}), 1.88 (m, 1H, =CH- CH_2), 1.80 (s, 3H, CH_3_{mes}), -0.10 (m, 1H, = CH_2), - 0.67 (m, 1H, = CH_2), - 7.81 (t, 1H, $J_{HH} = 15.6$ Hz, Ru- H).

Dicarbonyl-hydrido-[1-mesityl-3-(η^2 -but-2-en-1-yl)-imidazol-2-ylidene- κC^2](triphenylphosphine)ruthenium(II) tetrafluoroborate, [8a]⁺BF₄⁻

A solution of compound **5a** (26.1 mg, 40 μ mol) in CH₂Cl₂ (2 mL) was cooled to 0°C. To this solution, HBF₄.OEt₂ (6 μ L, 44 μ mol, 1.1 eq). was slowly added The mixture was stirred for 1 hour and CH₂Cl₂ was then removed *in vacuo*. The residue was washed with pentane (2 x 5 mL) and the overlaying solution was evacuated through cannula. The white powder was dissolved in CD₂Cl₂ (0.75 mL) and NMR spectra were recorded. ¹H NMR (300 MHz, 298 K, CD₂Cl₂): δ 7.49 - 7.60 (m, 10H, CH_{p-Ph} , CH_{m-Ph} , $CH_{Im-4/5}$), 7.31 - 7.38 (m, 6H, CH_{o-Ph}), 7.15 (s, 1H, CH_{mes}), 7.12 (s, 1H, CH_{mes}), 7.04 (m, 1H, $J_{HH} = 1.2$ Hz, $CH_{Im-4/5}$), 4.56 (dd, 1H, $J_{HH} = 14.2$ Hz, $J_{HH} = 4.2$ Hz, N- CH_2), 4.44 (d, 1H, $J_{HH} = 14.1$ Hz, N- CH_2), 2.55 (m, 1H, (-CH₂CH=), 2.39 (s, 3H, CH_3_{mes}), 2.09 (s, 3H, CH_3_{mes}), 1.92 (s, 3H, CH_3_{mes}), 0.79 (t, 3H, $J_{HH} = 5.7$ Hz, CH_3), -1.26 (br s, 1H, =C(H)CH₃), - 4.80 (br s, 1H.). ¹H NMR (500 MHz, 195 K, CD₂Cl₂) : δ 7.54 - 7.05 (m, $CH_{Im-4/5}$, CH_{Ph}), 4.52 - 4.21 (m, N- CH_2), 2.35 - 1.86 (CH_3_{mes}), 2.29 (-CH₂CH=), 0.71 (=C(H)CH₃, isomer Z/E), 0.69 ((=C(H)CH₃, isomer E/Z) ³¹P{¹H} NMR (121.5 MHz, 298K, CD₂Cl₂) δ 35.2 (s, PPh₃). ³¹P{¹H} NMR (121.5 MHz, 195 K, CD₂Cl₂) δ 36.7 (s, PPh₃, Z or E isomer), 34.4 (s, PPh₃, E or Z isomer). ¹³C{¹H} NMR (75.5 MHz, 298K, CD₂Cl₂): δ 199.1 (d, $J_{CP} = 13.0$ Hz, CO), 191.8 (d, $J_{CP} = 10.0$ Hz, CO), 173.4 (d, $J_{CP} = 80.8$ Hz, N₂C), 140.7 (C_{p-mes}), 133.2 d, $J_{CP} = 11.4$ Hz, CH_{o-Ph}), 133.2 d, $J_{CP} = 11.4$ Hz, CH_{o-Ph}), 131.4 d, $J_{CP} = 2.3$ Hz, CH_{p-Ph}), 130.1 (d, $J_{CP} = 45.8$ Hz, $C_{ipso-Ph}$), 129.7 (CH_{mes}), 129.6 (CH_{mes}), 129.3 (d, $J_{CP} = 10.2$ Hz, CH_{m-Ph}), 125.1 (d, $J_{CP} = 2.9$ Hz, $CH_{Im-4/5}$), 121.1 (d, $J_{CP} = 1.0$ Hz, $CH_{Im-4/5}$), 53.5 (d, $J_{CP} = 3.6$ Hz, N- CH_2), 38.7 (d, $J_{CP} = 3.6$ Hz, =CH), 20.8 (CH_3_{mes}), 17.5 (CH_3_{mes}), 17.2 (CH_3_{mes}), 10.8 (CH_3). ¹¹B{¹H} NMR (128.4 MHz, CD₂Cl₂): δ - 1.12 (s, BF₄). FT-IR (ν (CO), CH₂Cl₂): 2033 (m), 1962 (s) cm⁻¹.

Carbonylchloro[1-mesityl-3-(3-methyl-4-oxo-but-1-yl- κ C²)-imidazol-2-ylidene-

κ C²](triphenylphosphine)ruthenium(II), 10a. A solution of compound **5a** (30 mg, 0.045 mmol) in THF (2.5 mL) was cooled to 0°C. To this solution, HCl (1M in Et₂O) was slowly added. The light yellow mixture was stirred for an hour and then evaporated to dryness. The resulting residue was washed with Et₂O (2 x 5 mL). The product was isolated as a bright yellow powder (29 mg, 92%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.42 (m, 3H, CH_{PPh₃}), 7.34 (m, 12H, CH_{PPh₃}), 7.25 (s, 1H, CH_{Im-4/5}), 7.06 (br s, 2H, CH_{mes}, CH_{Im-4/5}), 6.99 (s, 1H, CH_{mes}), 5.11 (dt, 1H, $J_{HH} = 4.0$ Hz, $J_{HH} = 13.9$ Hz, N-CH₂), 3.98 (dd, 1H, $J_{HH} = 4.5$ Hz, $J_{HH} = 14.2$ Hz, N-CH₂), 3.16 (m, 1H, CH₂-CH), 2.42 (s, 3H, CH_{3 mes}), 2.22 (s, 3H, CH_{3 mes}), 2.05 (m, 1H, CH-CH₂), 1.98 (s, 3H, CH_{3 mes}), 1.81 (dt, 1H, $J_{HH} = 3.2$ Hz, $J_{HH} = 12.6$ Hz, CH-CH₂), 0.93 (d, 3H, $J_{HH} = 6.5$ Hz, CO-CH₃). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ 32.3 (s, PPh₃). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ 242.8 (d, $J_{CP} = 6.0$ Hz, C=O_{acyl}), 200.7 (d, $J_{CP} = 13.8$ Hz, CO), 184.0 (d, $J_{CP} = 99.0$ Hz, N₂C), 139.0 (C_{para}), 136.0 (C_{ortho}), 135.8 (C_{ipso-mes}), 135.7 (C_{ortho}), 134.0 (d, $J_{CP} = 11$ Hz, CH_{O-PPh₃}), 133.6 (d, $J_{CP} = 37$ Hz, C_{ipso PPh₃}), 129.6 (d, $J_{CP} = 3.0$ Hz, CH_{p-PPh₃}), 129.2 (CH_{mes}), 129.1 (CH_{mes}), 127.9 (d, $J_{CP} = 9.1$ Hz, CH_{m-PPh₃}), 122.6 (d, $J_{CP} = 3.6$ Hz, CH_{Im-4/5}), 122.1 (d, $J_{CP} = 2.4$ Hz, CH_{Im-4/5}), 59.8 (d, $J_{CP} = 1.9$ Hz, CH₃-CH), 48.0 (N-CH₂), 37.2 (CH-CH₂), 21.0 (CH_{3 mes}), 18.6 (CH_{3 mes}), 18.5 (CH_{3 mes}), 7.1 (CO-CH₃). MS (FAB, MNBA matrix): m/z (%) 660 (1) [M - Cl]⁺, 630 (6) [M - CO - 2H]⁺, 602 (17) [M - 2CO - 2H]⁺, 241 (100) [NHC(olefin)]⁺. FT-IR (ν (CO), ATR) 1930 (s), 1644 (m) cm⁻¹.

X-ray Diffraction Studies. Crystals of **4a**, and **5a** suitable for X-ray diffraction were obtained through recrystallization from CH₂Cl₂/pentane (**4a**), or toluene/pentane (**5a**) solutions. Data were collected on a Bruker D8 APEX II diffractometer. All calculations were performed on a PC-compatible computer using the WinGX system.³⁶ Full crystallographic data are given in Table 1. The structures were solved by using the SIR92 program,³⁷ which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXL97

program.³⁸ Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Ru, Br, and P atoms were included in Fc. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms – except hydrogen atoms attached to C8 and C9 in the structure of **5a** – were set in idealized position (R_3CH , C-H = 0.96 Å; R_2CH_2 , C-H = 0.97 Å; RCH_3 , C-H = 0.98 Å; $C(sp^2)-H$ = 0.93 Å; U_{iso} 1.2 or 1.5 time greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and their position were refined as “riding” atoms. The olefinic hydrogen atoms attached to C8 and C9 in **5a** were inferred from a Fourier difference map calculated in the final stage of the refinement. Their position were ultimately refined holding their U_{iso} 1.2 time greater than the U_{eq} of the associated carbon atom; this led to acceptable C-H bond lengths.

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SUPPORTING INFORMATION PARAGRAPH: CIF files giving crystallographic data and including a full list of interatomic bond lengths and angles for the reported complexes **4a**, and **5a**. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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- 31) The activation energy barrier was estimated using the approximation of the Eyring equation: $\Delta G^\ddagger = RT_c(22.96 + \ln T_c/\Delta \nu)$, where T_c (K) is the coalescence temperature of two sets signals separated by $\Delta \nu$ (Hz).
- 32) The observation of a ratio between *Z* and *E* isomers different from 1:1 reflects the fact that the formation of one isomer is kinetically favored over the second one. Since we could not reach $^2J_{HH}$ coupling constants between the protons attached to the C=C bond in any of the two isomers, we could not determine which one is actually the favored one.
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SYNOPSIS TOC (Word Style "SN_Synopsis_TOC").

The phosphine and olefinic arms of functionalized imidazolium cations serve as directing groups in the chelation-assisted C-H bond cleavage of such ligands onto a Ru(0) center. In the olefin case, all cationic intermediates involved in the subsequent Ru-mediated H transfer to the olefinic arm have been identified by NMR in a model reaction carried out on the new Ru(0) complex $\text{Ru}\{\text{NHC}/\text{olefin}\}(\text{CO})_2(\text{PPh}_3)$ at low temperature.

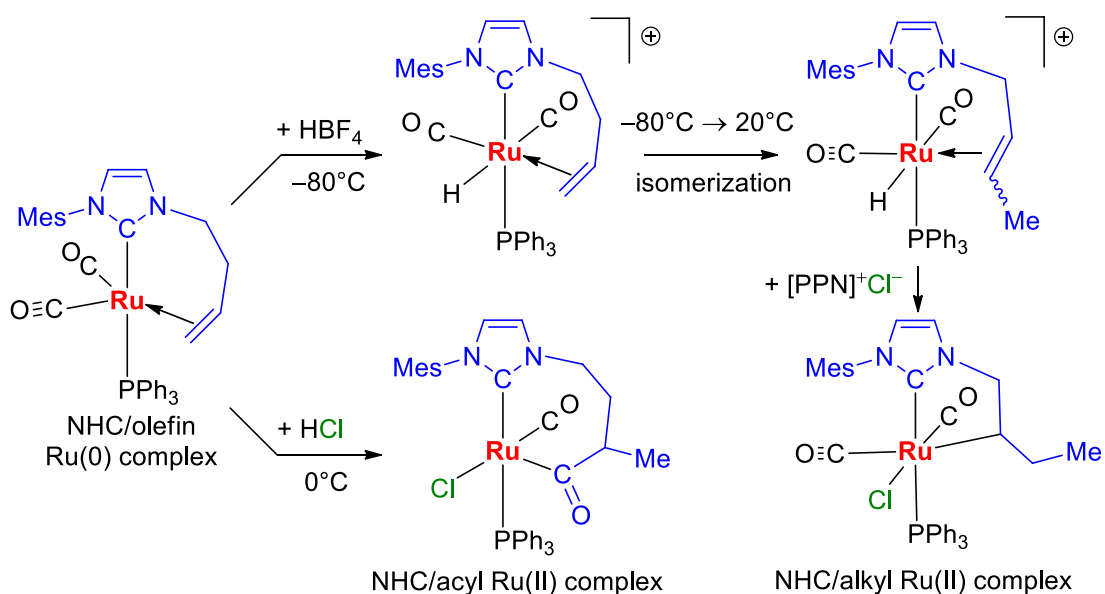


Table 1. Crystal data and structure refinement parameters, for complexes **4a**, and **5a**.

Complex	4a	5a.C₇H₈
Empirical formula	C ₃₆ H ₃₆ BrN ₂ O ₂ PRu	C ₄₃ H ₄₃ N ₂ O ₂ Ru
M_r	740.61	751.83
T/ K	180	180
$\lambda / \text{\AA}$	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group (no.)	P 2 ₁ /n (# 14)	P 2 ₁ /n (# 14)
$a/ \text{\AA}$	13.534(7)	9.7482(4)
$b/ \text{\AA}$	12.260(6)	16.8095(7)
$c/ \text{\AA}$	19.840(2)	22.2652(9)
$\beta/ ^\circ$	93.96(3)	95.755(2)
$V/ \text{\AA}^3$	3284(2)	3630.0(3)
Z	4	4
$D_c/ \text{g.cm}^{-3}$	1.498	1.376
μ/ mm^{-1}	1.777	0.515
$F(000)$	1504	1560
$\theta_{\text{max}}/ ^\circ$	30.50	30.51
Completeness to θ_{max} (%)	0.99	0.99
Index range, hkl	-19<h<19 -17<k<17 -28<l<28	-13<h<13 -24<k<24 -31<l<31
Reflections collected	56655	247950
Independant reflections	10026	11056
Data/restraints/parameters	10026/0/392	11056/0/456
GOF	0.964	1.11
$R [I>2\sigma(I)]$	0.0342	0.0247
$R_w [I>2\sigma(I)]$	0.0909	0.0588

Table 1 (continued)

R (all data)	0.0451	0.0310
R_w (all data)	0.0963	0.0631
$\Delta\rho_{\max/\min}/\text{e}\cdot\text{\AA}^{-3}$	-1.54/0.63	-0.33/0.41