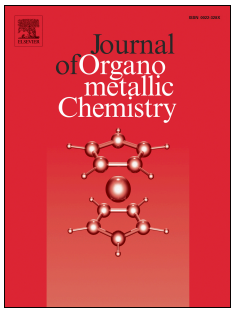


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# The reactivity of [{2-(diphenylphosphino)phenyl}methyl]-3-imidazol-2-ylidenes towards group VIII element precursors

**Jens Trampert, Yu Sun, Werner R. Thiel***

*Dedicated to Professor F. Ekkehardt Hahn on the occasion of his 65$^{th}$ birthday*

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**Abstract**

Phosphine functionalized imidazolium precursors were reacted with triiron(0)- resp. triruthenium(0)dodecacarbonyl in order to compare the reactivity of the Group VIII metals. Furthermore, [($\eta^6$-cymene)$RuCl_2$]$_2$ was treated in a transmetallation reaction with the silver(I) resp. copper(I) complexes of the corresponding imidazolylidenes possessing sterically largely different substituents at the NHC site, in order to evaluate the influence of these substituents on the catalytic activity of the ruthenium complexes.

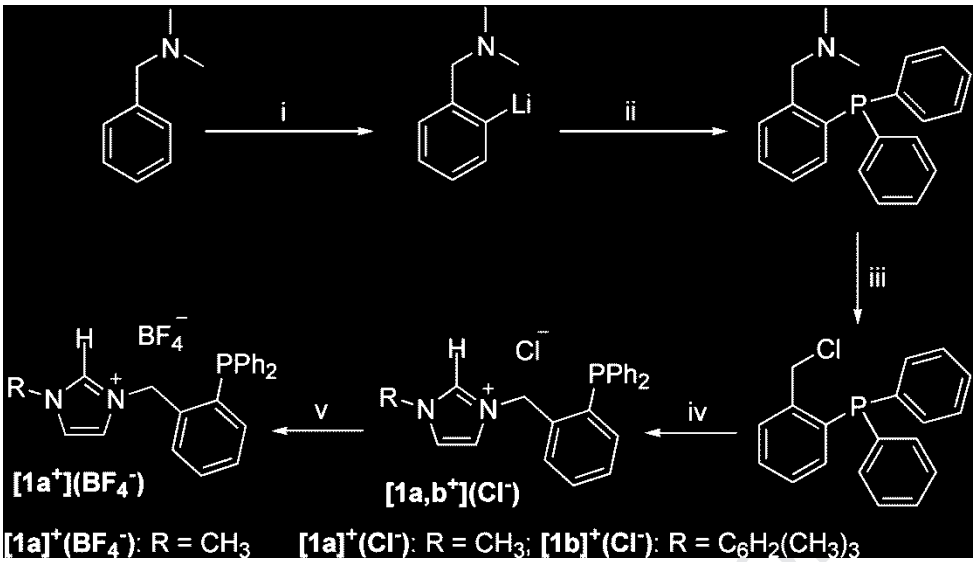
*Keywords*: NHC ligand • phosphine • ruthenium • iron • X-ray structure

**Introduction**

Transition metal complexes bearing *N*-Heterocyclic carbene ligands (NHC) have been known since the pioneering work of Wanzlick and Öfele published in 1968 [1]. However, detailed investigations on the coordination chemistry of NHC ligands, on the special properties of the metal-NHC [2] bond and on their use of NHC complexes in catalytic reactions [3] and in material chemistry [4] started in 1991 with the finding of the first stable NHC complex by Arduengo et al. [5]. Since imidazolium salts, the most common precursors of NHC ligands, are readily accessible, it took just a few years to fully develop the principles of the NHC coordination chemistry [6]. Along with this, combinations of the NHC fragment with other donor sites in chelating ligands rapidly became established leading to ligands possessing additional NHC [7], cyclopentadienyl [8], nitrogen [9], oxygen [9a,c,10], sulphur [11], phosphorus [12] or olefinic [13] donor centers.

Combinations of NHCs with additional phosphines are of special interest in this context. Phosphines as well as *N*-heterocyclic carbenes are good σ-donor and poor π-acceptor ligands, both stabilizing metal sites in lower oxidation states, which is of special interest for applications in catalysis. Nevertheless, the more directed lone pair of the NHC donors, makes them the harder Lewis-acids compared to phosphines, leading to a stronger *trans*-influence of the carbene. Connecting a phosphine group and an imidazole as the most common type of NHC precursor can either be performed directly [14] or via aliphatic [15] or aromatic [16] carbon based linker units.

A very simple route to a phosphine functionalized NCH precursor was published by Zhou et al. in 2005. They found that chloromethyl(2-(diphenylphosphino)benzene can be converted in high yields to the corresponding imidazolium chlorides **$1^{+}(Cl^{-})$** by reacting it with appropriate imidazoles.[17] The required chloromethyl derivative is accessible in a few steps from *N,N*-dimethylbenzylamine (Scheme 1).[18]



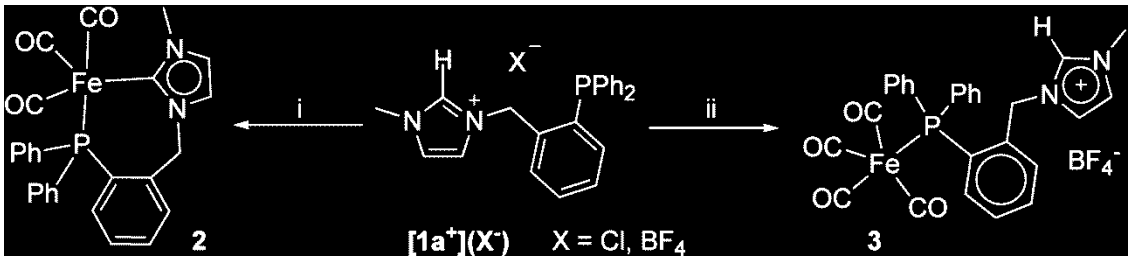

**Scheme 1.** i) 1.2 equiv. n-BuLi, $Et_2O$, r.t., 14 h, ii) 1.2 equiv. $Ph_2PCl$, $Et_2O$, -78 °C - r.t., 2 h, iii) 1.3 equiv. $ClCO_2Et$, benzene, refl., 2 h, iv) 1.0 equiv. *N*-substituted imidazole, MeCN, refl., 18 h, v) 1.2 equiv. $NaBF_4$, $CH_2Cl_2$, 18 h, r.t..

By following this strategy, NHC ligands with a broad variety of substituents R at the imidazolium ring can be obtained, which allows playing with the steric and electronic properties of the NHC ligand. Despite the fact that these ligand precursors are easily accessible, there are just few reports on their use for coordination to transition metal sites in the literature: The corresponding palladium(II) complexes bearing an *N*-aryl NHC [17,19] or an *N*-methyl NHC unit [20] turned out to be active catalysts in a series of C-C coupling reactions. Iridium, rhodium, and palladium complexes of this ligand type were investigated for C-H activation reactions [21]. An iridium COD complex (COD = cycloocta-1,5-diene) catalyzes the alkylation of amines with alcohols as the alkylating agents [22]. We recently published the reactivity of nickelocene towards imidazolium precursors of the type $\mathbf{1}^+$ [23]. Hereby cationic CpNi(II) complexes bearing chelating NHC-phosphine ligands are formed. Reacting them with cyanide leads to cleavage of the Ni-P bond. In ruthenium chemistry, the reactivity of NHC-phosphine ligands of type **1** towards $Ru(CO)_3Cl_2$ was investigated by Domski et al.. They found that the *N*-mesityl derivative gives the complex $(NHC)Ru(CO)_2(Cl)_2$ bearing a bidentate NHC ligand, while the corresponding *N*-phenyl ligand undergoes C-H activation in the *ortho*-position of the phenyl ring resulting in a tridentate coordination of the ligand to the $Ru(CO)_2Cl$ moiety [24] Cabeza et al. investigated the reactivity of NHC-phosphine ligands of type **1** with an *N*-

methyl substituent towards $Ru_3(CO)_{12}$ and published a bridging binding mode of the NHC ligand as long as the reactants were employed in an equimolar ratio [25]. Heating this product in tetrahydrofurane resulted in a carbon bridged hydrido cluster, with the hydrido ligands being delivered from the linking methylene group. Performing the same reaction in a 3:1 ratio (NHC vs. $Ru_3(CO)_{12}$) gave a mononuclear tricarbonylruthenium(0) complex. When the tetranuclear hydrido ruthenium carbonyl cluster $[\mathbf{1a}]^+[Ru_4(\mu\text{-}H)_3(CO)_{12}]^-$ (R = $CH_3$) was heated in toluene, the corresponding complex $[Ru_4(\mu\text{-}H)_4(\kappa_2\text{-}\mathbf{1})(CO)_{10}]$ was formed, wherein the NHC-phosphine ligand undergoes chelating coordination to one of the ruthenium centers [26].

**Results and discussion**

We here first report a series of novel ruthenium and iron compounds bearing NHC ligands of the type **1**, derived from $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$. By treating the methyl substituted imidazolium salt **$[\mathbf{1a}^+](Cl^-)$** (Scheme 1) with $Fe_3(CO)_{12}$ at elevated temperatures in toluene solution, the corresponding tricarbonyliron(0) complex **2** bearing a chelating NHC-phosphine ligand is formed readily in almost 50% yield (Scheme 2). Hereby the chloride anion - as the only base that is present - is essential for the formation of **2**. This hypothesis was proven by treatment of the same iron(0) precursor with the tetrafluoroborate salt **$[\mathbf{1a}^+](BF_4^-)$** (Scheme 1). By simply changing the basic chloride anion against the less basic tetrafluoroborate, a completely different product was formed: The cationic tetracarbonylphosphine iron(0) complex **3** was formed in 74% yield with tetrafluoroborate as the anion. The action of chloride as a base to deprotonate the imidazolium salt was also found for the formation of the nickel(II) complexes cited above [23]. In the absence of the basic anion, the nickelocene precursor stayed untouched.




**Scheme 2.** Synthesis of the iron carbonyl complexes **2** and **3**: i) X = $Cl^-$, 0.33 eq. $Fe_3(CO)_{12}$, toluene, refl., 18 h; ii) X = $BF_4^-$, 0.33 eq. $Fe_3(CO)_{12}$, toluene, refl., 18 h.

Compounds **2** and **3** could be obtained as single crystals by recrystallization from toluene (**2**, slow diffusion of pentane) resp. dichloromethane (**3**, slow diffusion of diethylether), which allowed to determine their solid state structures (Figure 1).

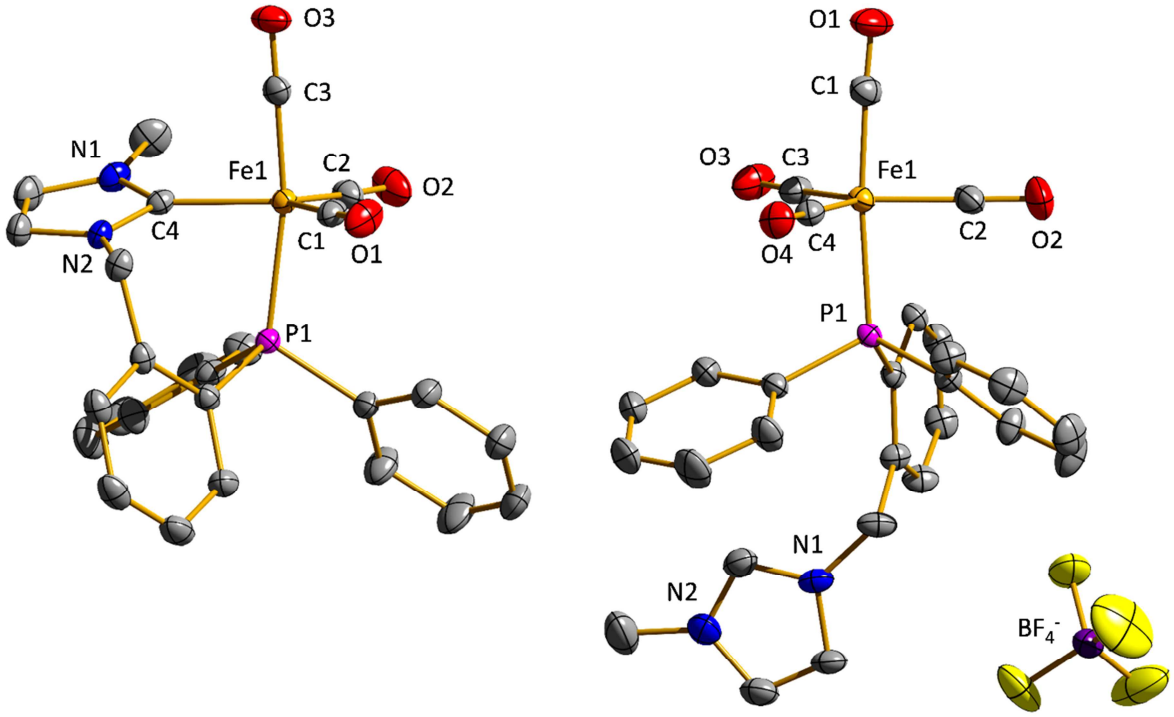
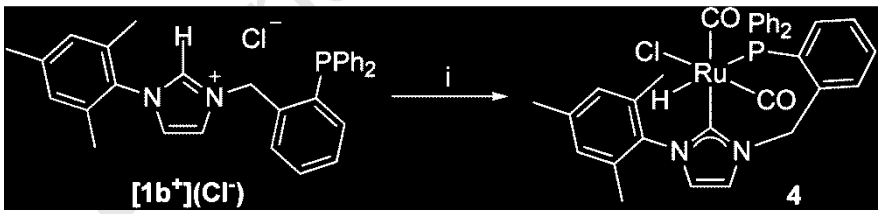



**Figure 1.** Molecular structures of compounds **2** (left) and **3** (right) in the solid state. The ellipsoids are at the 50% level. Selected bond lengths (Å) and angles (°) are listed. **2**: Fe1-P1 2.2196(4), Fe1-C1 1.7556(13), Fe1-C2 1.7675(13), Fe1-C3 1.7652(13), Fe1-C4 1.9795(13), O1-C1 1.1655(18), O2-C2 1.1578(18), O3-C3 1.1481(17), P1-Fe1-C1 91.56(4), P1-Fe1-C2 92.91(4), P1-Fe1-C3 168.79(4), P1-Fe1-C4 82.16(4), C1-Fe1-C2 120.16(6), C1-Fe1-C3 88.79(6), C1-Fe1-C4 125.90(5), C2-Fe1-C3 96.61(6), C2-Fe1-C4 113.83(6), C3-Fe1-C4 88.56(5), Fe1-C1-O1 177.83(12), Fe1-C2-O2 176.90(12), Fe1-C3-O3 176.99(12). **3**: Fe1-P1 2.2568(6), Fe1-C1

1.792(2), Fe1-C2 1.782(2), Fe1-C3 1.794(2), Fe1-C4 1.793(2), O1-C1 1.138(3), O2-C2 1.148(3), O3-C3 1.146(3), P1-Fe1-C1 174.41(8), P1-Fe1-C2 86.37(7), P1-Fe1-C3 92.50(7), P1-Fe1-C4 89.19(7), C1-Fe1-C2 88.10(10), C1-Fe1-C3 91.38(10), C1-Fe1-C4 92.87(10), C2-Fe1-C3 125.28(10), C2-Fe1-C4 120.31(10), C3-Fe1-C4 114.37(10), Fe1-C1-O1 177.3(2), Fe1-C2-O2 177.27(19), Fe1-C3-O3 177.90(19), Fe1-C4-O4 178.95(19).

Compound **2** crystallizes in a distorted trigonalbipyramidal coordination geometry, wherein the NHC donor is oriented in an equatorial and the phosphine donor in an axial position. Huttner et al. found a slightly longer Fe-$C_{Carbene}$ distance (2.007 Å) in the iron(II) compound (dmi)$Fe(CO)_4$ (dmi = *N*,*N*-dimethylimidazolylidene) [27], the difference might be explained by the chelating situation in compound **2**. The molecular structure of the cationic complex **3** is as expected similar to that of ($PPh_3$)$Fe(CO)_4$ [28], for which a Fe-P distance of 2.244(1) Å was reported. Only bulky substituents in the *ortho*-position of the phenyl substituents of the $PPh_3$ ligand lead to a pronounced elongation of the Fe-P distance in such complexes [29]. The $^{31}P\{^1H\}$ NMR resonances of compounds **2** and **3** are almost identical (δ = 67.6 and 66.5 ppm) speaking for similar donor properties of both phosphine sites. According to the solid state structure of compound **2**, the two protons of the methylene unit that connects the phosphine and the NHC donor sites are structurally inequivalent. However, there is no signal for these protons in the $^1H$ NMR spectrum of **2** which can be explained by the fact that there is a rapid equilibration at room temperature (according to the NMR time scale), thus these resonances are at the point of coalescence. In addition, a part of the phenyl resonances gives one broad signal, which supports this interpretation. By the way: the according signals in the $^{13}C$ NMR spectrum appear as sharp peaks, due to different time scales of $^{13}C$ and $^1H$ NMR spectroscopy. Such a rapid equilibration at room temp. is unexpected for seven-membered ring systems and can be assigned to a rapid dissociation/association equilibrium of probably the phosphine site, since Berry-rotation, which is often observed for five-coordinated metal complexes is not a suitable process to equilibrate the situation of the methylene and phenyl protons. The C=O stretching vibrations of compound **3** are found at higher energies (2049, 1979, 1921 $cm^{-1}$) than of compound **2** (1955, 1881, 1832 $cm^{-1}$), which is in agreement with the strong donating nature of the NHC moiety coordinating the iron site in **2**. This influence weakens the C=O bond by enhancing the π-backbonding to the carbonyl ligands.

In the following we investigated the reactivity of mixed *NHC*-phosphine ligands towards carbonyl precursors of the heavier group VIII element ruthenium. Cole et al. had reported the reactivity of $Ru_3(CO)_{12}$ against monodentate NHC ligands and found that the $Ru_3$ core often stays untouched.[30] In the presence of a large excess of a series of alkyl substituted imidazolylidenes, mononuclear complexes of the type $(NHC)_2Ru(CO)_3$ are formed. In accordance to the results of Cabeza et al.,[25] the reaction of $Ru_3(CO)_{12}$ with aryl substituted imidazolylidenes in a 1:3 ratio gave complexes of the type $(NHC)Ru(CO)_4$. However, treatment of $Ru_3(CO)_{12}$ with the dimesityl substituted imidazolium salt $[Mes_2Im^+]Cl^-$ in tetrahydrofurane solution led to the formation of $[(Mes_2Im)Ru(CO)_2(\mu^2\text{-}Cl)]_2$, a rather unique dimeric, chloride-bridged ruthenium(I) complex with a Ru-Ru single bond. We therefore started with treatment of $Ru_3(CO)_{12}$ with **[1b$^+$](Cl$^-$)** (see: Scheme 1) in a 1:3 ratio and found a completely different kind of reactivity compared to iron: Instead of deprotonation of the imidazolium salt by assistance of the chloride anion and the formation of a tetracarbonyl-NHC complex, the ruthenium precursor reacts under formal oxidative addition of HCl leading to the ruthenium(II) compound **4** in 73% yield (Scheme 3), which started to precipitate from the tetrahydrofurane solution shortly after the reaction was started.




**Scheme 3.** Synthesis of the ruthenium(II) complex **4**: i) 0.33 eq. $Ru_3(CO)_{12}$, tetrahydrofurane, refl., 18 h.

There are two mechanistic alternatives for the formation of **4**. We believe that a five-coordinate ruthenium(0) intermediate, structurally similar to iron complex **3**, should primarily be formed. This can either be followed by a (ruthenium assisted) deprotonation of the imidazolium moiety, wherein the chloride anion acts as the base and the NHC formed this way would then coordinate to the ruthenium(0) site under dissociation of a carbonyl ligand. Finally the liberated HCl would undergo oxidative addition to ruthenium again under dissociation of a carbonyl ligand. Alternatively a direct attack of the five-coordinate ruthenium(0) intermediate to the imidazolium moiety can be postulated. This would lead to

a six-coordinate ruthenium(II) hydrido cation with a chloride counter-anion. To achieve this, one carbonyl ligand has to be released first, otherwise a seven-coordinate, 20 VE intermediate would be formed. The ruthenium(II) hydrido intermediate should, due to its cationic nature rapidly undergo dissociation of a second carbonyl ligand which allows the coordination of the chlorido ligand.

Single crystals of compound **4** were obtained by slow diffusion of diethyl ether into a solution in dichloromethane, which allowed to elucidate its molecular structure by means of an X-ray structure analysis. Figure 2 shows the molecular structure of **4** in the solid state.

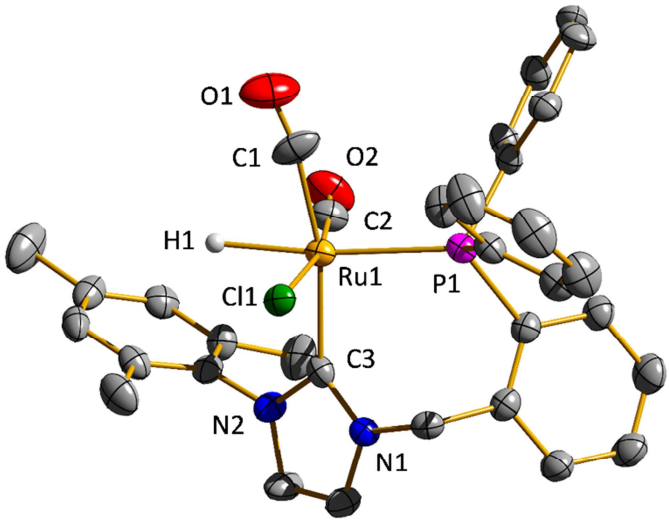



**Figure 2.** Molecular structure of compound **4** in the solid state. The ellipsoids are at the 50% level. Selected bond lengths (Å) and angles (°) are listed: Ru1-Cl1 2.4552(14), Ru1-P1 2.472(2), Ru1-C1 1.940(8), Ru1-C2 1.851(6), Ru1-C3 2.111(6), Ru1-H1 1.82(8), O1-C1 1.117(11), O2-C2 1.147(8), Cl1-Ru1-P1 94.77(5), Cl1-Ru1-C1 87.5(2), Cl1-Ru1-C2 168.4(2), Cl1-Ru1-C3 86.67(14), P1-Ru1-C1 96.3(2), P1-Ru1-C2 96.8(2), P1-Ru1-C3 95.23(18), C1-Ru1-C2 89.8(3), C1-Ru1-C3 167.5(3), C2-Ru1-C3 93.7(2), C2-Ru1-H1 85(2), C3-Ru1-H1 93(2), C1-Ru1-H1 76(2), Cl1-Ru1-H1 84(2), P1-Ru1-H1 172(2), Ru1-C1-O1 168.6(7), Ru1-C2-O2 175.6(7).

The position of the hydrido ligand could be determined from the structural data. However, the large standard deviation associated to the Ru-H bond keeps from discussing its length in more detail. The hydrido ligand is found in *trans*-orientation to the phosphine site, while the carbonyl ligands are oriented *cis* to each other. There is a pronounced difference in the Ru-

$C_{CO}$ bond distances: According to the much stronger *trans*-influence of the NHC site compared to the chlorido ligand, the Ru-C1 bond is by about 0.1 Å longer than the Ru-C2 distance. In addition, the carbonyl ligands are bent away from the bulky phosphine moiety towards the small hydrido ligand. It has to be mentioned at this point, that an attempt to recrystallize compound **4** from chloroform by slow diffusion of diethyl ether led to formation of the corresponding ruthenium(II)dichlorido complex. The molecular structure of this compound is presented in the Electronic Supporting Information. Compound **4** probably activates chloroform under cleavage of a C-Cl bond.

In addition, NMR and IR spectroscopy proved the molecular structure of compound **4**: The two expected C=O stretching vibrations are observed at 2031 and 1946 $cm^{-1}$. Compared to the iron(0) complexes discussed above, the $^{31}P\{^{1}H\}$ NMR resonance of **4** is shifted strongly to higher field ($\delta$ = 11.4 ppm). The presence of the hydrido ligand can be extracted from both, the proton-coupled $^{13}P$ NMR spectrum as well as from the $^{1}H$ NMR spectrum, where its resonance is observed with a chemical shift of -6.63 ppm (Figure 3). The evaluation gave a large $^{2}J_{PH}$ coupling constant of 129.8 Hz, which is in the typical range for a coupling between a hydrido and a phosphine ligand being in *trans*-orientation to each other at a ruthenium(II) site [31]. In contrast to compound **2**, there are two resonances for the protons of the methylene group (6.45 and 4.66 ppm, $^{2}J_{HH}$ = 14.5 Hz) with the typical large coupling constant of geminal protons. This proves, that the equilibration of these nuclei is slow with respect to the NMR time scale. Although the coordination number is higher than in compound **2**, which means that steric repulsion should be stronger, the phosphine site does not undergo dissociation probably caused by a stronger Ru-P bond due to the oxidation state +II of the ruthenium center.

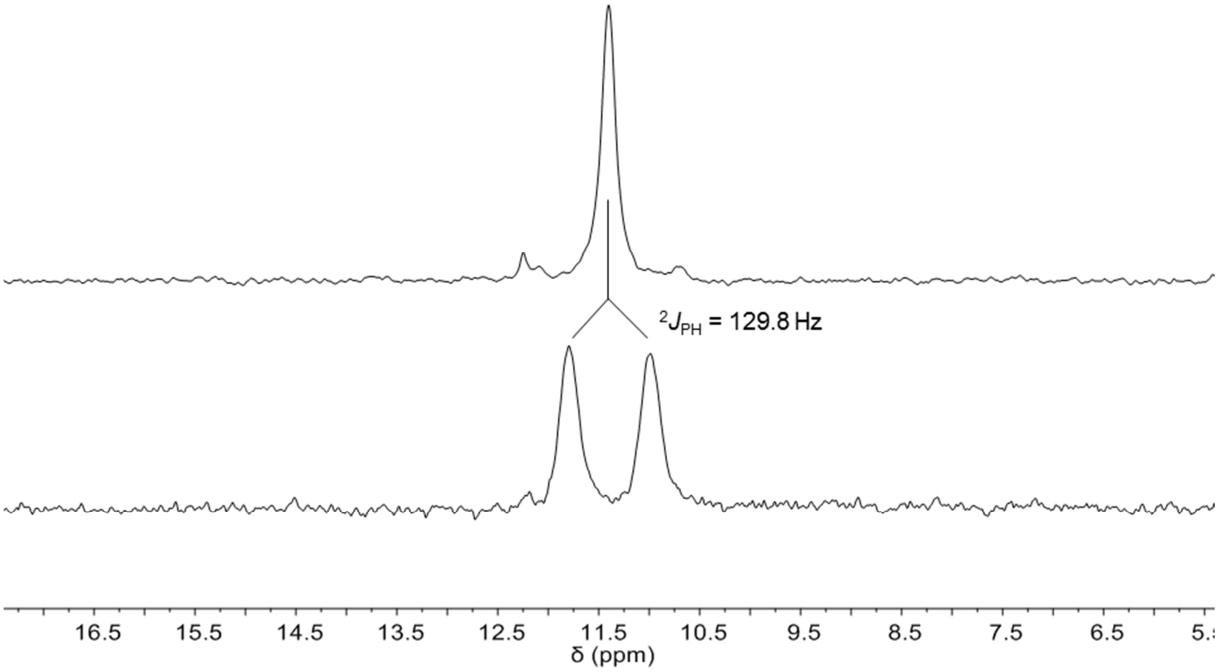
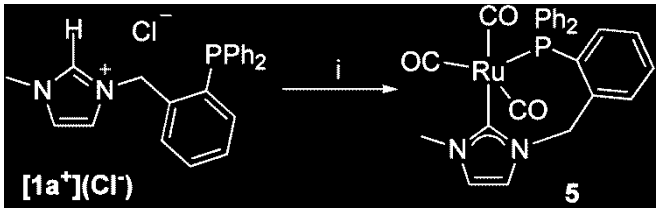



**Figure 3.** The de-coupled (top) and coupled $^{31}$P NMR spectrum (bottom) of compound **4** measured in $CD_2Cl_2$ solution.

In order to obtain a zero valent ruthenium complex for comparison with the iron complex **2**, an alternative synthesis route had to be employed. In-situ generation of the free NHC-phosphine ligand by deprotonation of **[1a$^+$](Cl$^-$)** (see: Scheme 1) with KHMDS (potassium hexamethyldisilazide) as the base in tetrahydrofurane solution followed by the addition of 0.33 equiv. of $Ru_3(CO)_{12}$ to this solution resulted in the formation of the ruthenium(0) complex **5** in more than 80% yield (Scheme 4).




**Scheme 4.** Two step synthesis of the ruthenium(0) complex **5** starting from **[1a$^+$](Cl$^-$)**: i) 1 equiv. of KHMDS, 0.33 equiv. of $Ru_3(CO)_{12}$, tetrahydrofurane, r.t., 20 h.

Recrystallization of compound **5** from toluene by slow diffusion of pentane yielded single crystals, which allowed to determine its molecular structure in the solid state (Figure 4).

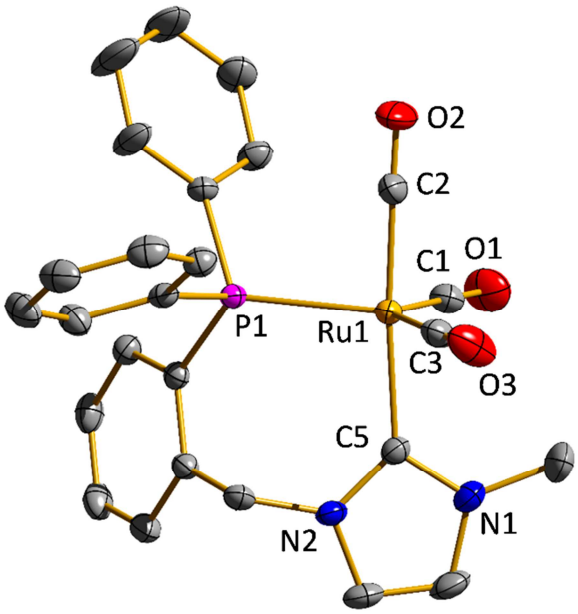
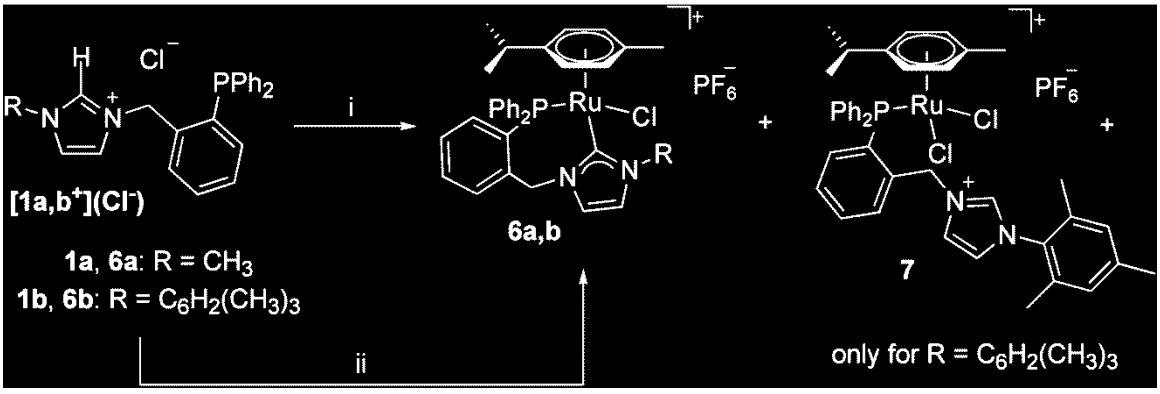



**Figure 4.** Molecular structure of compound **5** in the solid state. The ellipsoids are at the 50% level. Selected bond lengths (Å) and angles (°) are listed: Ru1-P1 2.3827(5), Ru1-C1 1.9064(19), Ru1-C2 1.901(2), Ru1-C3 1.8864(19), Ru1-C5 2.1221(18), O1-C1 1.153(2), O2-C2 1.140(2), O3-C3 1.159(3), P1-Ru1-C1 109.66(6), P1-Ru1-C2 87.48(6), P1-Ru1-C3 121.22(6), P1-Ru1-C5 97.43(5), C1-Ru1-C2 92.30(8), C1-Ru1-C3 129.12(8), C1-Ru1-C5 86.83(7), C2-Ru1-C3 89.61(8), C2-Ru1-C5 175.03(7), C3-Ru1-C5 87.15(7), Ru1-C1-O1 175.46(19), Ru1-C2-O2 179.09(17), Ru1-C3-O3 177.08(17).

Interestingly, the coordination of the NHC-phosphine ligand in **5** is opposite to the situation found for compound **2**: In the solid state structure of compound **5**, the NHC ligand is oriented in the axial and the phosphine donor is found in the equatorial position. It is hard to differ the electronic and steric influences on the thermodynamics of the two possible isomers. Maybe the longer Ru-$C_{NHC}$ bond allows the NHC site to occupy the axial position, which might be less favourable for the iron(0) complex **2**, since the NHC methyl group and the methylene unit are pointing towards the metal site. This argument is in agreement with the fact that the angle C1-Ru1-C3 (129.12(8) °) is much wider than the corresponding angle C1-Fe1-C2 (120.16(6) °) in compound **2** which reflects the steric impact of the NHC-ligand. The Ru-P in compound **5** is as expected shorter (2.3827(5) Å) than the Ru-P in compound **4** (Ru1-P1 2.472(2) Å), which is due to the strong *trans*-influence of the hydrido ligand in **4**.

The $^{31}$P NMR spectrum of compound **5** shows a significant shift of the phosphorous resonance ($\delta$ = 39.2 ppm) to lower field compared to the data of ruthenium(II) complex **4** ($\delta$ = 11.4 ppm). Compared to the iron(0) complex **2** ($\delta$ = 67.6 ppm), the resonance is shifted to higher field. In 1996 Kaupp published a detailed theoretical study on the contribution of a series of effects on the $^{31}$P NMR resonances of pentacarbonyl(phosphine) complexes of Group VI elements, which allows the interpretation of these differences [32]. In addition to the structural differences between the iron(0) complex **2** and its ruthenium(0) congener **5** discussed above, the dynamic behaviour of these compounds is different, too. The $^{1}$H NMR spectrum of **5** shows two (broadened) doublets with a coupling constant of 14.7 Hz which are assigned to two magnetically inequivalent methylene protons, which do not fully equilibrate at room temperature with respect to the NMR time scale. A part of the resonances of the phenyl groups is broadened too. The energies of the C=O stretching vibrations (1998, 1900, 1853 cm$^{-1}$) are observed at higher energies compared to the data of the structurally closely related iron complex **2** (1955, 1881, 1832 cm$^{-1}$) indicating a weaker $\pi$-back donation of the ruthenium centre.

The generation of silver NHC complexes by treatment of imidazolium salts with $Ag_2O$ opens up a well-established access to various transition metal NHC complexes by transmetallation.[33] Treatment of **[1a$^+$](Cl$^-$)** with $Ag_2O$ in dichloromethane, resulting in a dissolution of the black silver oxide and the formation of white AgCl in between 24 h, followed by addition of $[(\eta^6\text{-cymene})RuCl_2]_2$ and $KPF_6$ gives the expected ionic (cymene)ruthenium(II) NHC complex **6a** in 72% yield after work-up (Scheme 5) .




**Scheme 5**. Synthesis of the ruthenium(II) NCH complexes **6a,b** and **7**. i) 0.55 equiv. of $Ag_2O$, $CH_2Cl_2$, 18 h, r.t., 0.45 of equiv. $[(\eta^6\text{-cymene})RuCl_2]_2$, 18 h, r.t., 2 equiv. of $KPF_6$, 24 h, r.t.; ii)

1.0 equiv. of CuMes, tetrahydrofurane, 18 h r.t., 0.50 equiv. of $[(\eta^6\text{-cymene})RuCl_2]_2$, 18 h, r.t., $CH_2Cl_2$, sat. aqu. $KPF_6$.

In an analogous reaction, **[1b$^+$](Cl$^-$)** was treated with $Ag_2O$ and subsequently with $[(\eta^6\text{-cymene})RuCl_2]_2$ and $KPF_6$. However, the ligand reacted only partially, even by prolongation of the reaction time and under reflux conditions. Thus, according to NMR analysis of the raw product a mixture of the ionic chelate complex **6b** and compound **7** is obtained. It was not possible to obtain **6b** in pure form following this procedure. A few single crystals of compound **7** could be obtained, which allowed to elucidate its molecular structure. The structure can be found in the Supporting Information, since compound **7** also could not be obtained in pure form. The largely reduced reactivity of **[1b$^+$](Cl$^-$)** can be attributed to steric hindrance by the bulky mesityl substituent. Consequently, treatment of **[1b$^+$](Cl$^-$)** with well soluble and highly basic copper(I)mesityl gave the corresponding copper-NHC complex as transmetallation agent and finally provided access to pure **6b**.

Complex **6a** was obtained as single crystals by slow diffusion of diethylether into solutions of the compound in dichloromethane. Figure 5 presents its molecular structures in the solid state.

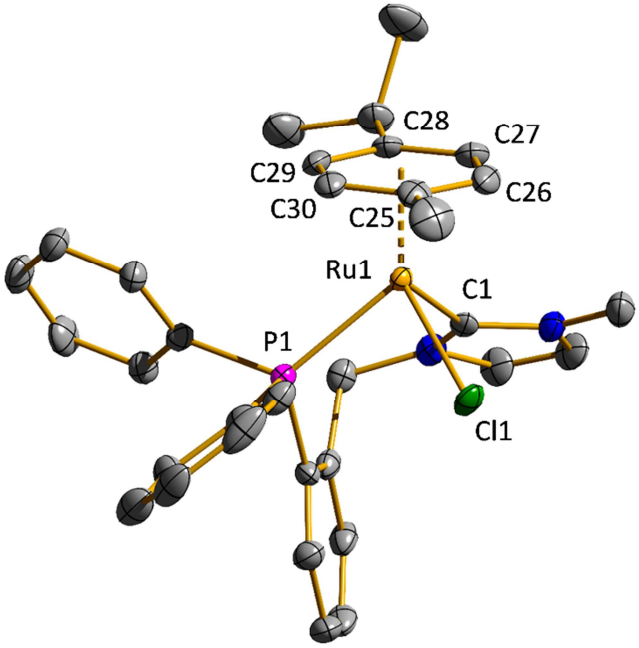



**Figure 5.** Molecular structure of compound **6a** in the solid state. Hydrogen atoms and the $PF_6^-$ anion are omitted for clarity. The ellipsoids are at the 50% level. Selected bond lengths

(Å) and angles (°) are listed. C* denotes the centroid of the cymene ligand. Ru1-Cl1 2.3943(10), Ru1-P1 2.3544(9), Ru1-C1 2.077(4), Ru1-C25 2.299(4), Ru1-C26 2.243(4), Ru1-C27 2.227(4), Ru1-C28 2.228(4), Ru1-C29 2.210(4), Ru1-C30 2.276(4), Ru1-C* 1.7464(3), Cl1-Ru1-P1 82.80(3), Cl1-Ru1-C1 84.66(12), Cl1-Ru1-C* 127.80(3), P1-Ru1-C1 94.84(11), P1-Ru1-C* 129.05(3), C1-Ru1-C* 123.9(1).

Complex **6a** occupies a pseudo tetrahedral coordination geometry with an $\eta^6$-coordinating cymene ligand, a chelating phosphine-NHC donor and a chlorido ligand. In addition, NMR spectroscopy proves the molecular structures of compounds **6a** and **6b**. As expected, the typical resonance at around 10 ppm of the proton bound at the imidazolium carbon atom C1 is not present in the $^1$H NMR spectra of **6a** and **6b**. Since the ruthenium(II) site is a center of chirality in **6a** and **6b**, the aromatic protons of the cymene ligands are diastereotopic (four doublets) as are the methyl groups of the cymene isopropyl substituent (two doublets). Furthermore, the protons of the methylene group are chemically inequivalent giving two doublets with a large $^2J_{HH}$ coupling constant of about 14.5 Hz for **6a**. The according resonances in the $^1$H NMR spectrum of **6b** are broad, indicating hindered rotation around the Ru-C* axis (C* = centroid of the cymene ligand due to the bulky mesityl substituent). Additionally, there are three resonances for the mesityl bound methyl groups in the $^1$H and the $^{13}$C NMR spectrum, which makes clear that the rotation around the N-$C_{mes}$ bond is strongly hindered, too. The $^{31}$P NMR resonances of **6a** and **6b** are observed at 24.6 resp. 22.4 ppm.

The ruthenium(II) complexes **6a** and **6b** were investigated for activity in the transfer hydrogenation of acetophenone with 0.5 mol-% of the catalyst, KOH as the base and isopropanol as the solvent and hydrogen source. The results are summarized in Table 1.

**Table 1**. Catalytic transfer hydrogenation of acetophenone.

| | yield of 1-phenylethanol / % [a] | |
|---|---|---|
| reaction time/ h | **6a** | **6b** |
| 1 | 87 | 0 |
| 2 | 96 | 10 |
| 3 | 100 | 18 |
| 4 | 100 | 29 |
| 8 | 100 | 52 |
| 24 | 100 | 90 |

a) 1.0 mmol of acetophenone, 0.5 mol-% of catalyst, 2.5 mol% of KOH, 5.0 mL of isopropanol, 82 °C, yields by GC analysis with measured response factors, tetradecane as the internal standard.

Obviously, **6a** is much more active than **6b**, which can be attributed to the steric influence of the substituents (methyl vs. mesityl) at the NHC ligand. While the substrate acetophenone is transferred to 1-phenylethanol with catalyst **6a** in about 2-3 h, it takes 24 for **6b** to reach 90% yield of the alcohol. Furthermore there is a period of induction of about 1 h for **6b**. If one assumes the reaction to proceed via a so-called “inner-sphere mechanism”, the coordination of isopropanolate, which is essential for the generation of the central ruthenium hydride intermediate, may be hindered in the case of **6b** due to the bulky mesityl substituent.

**Conclusion**

By reacting phosphine functionalized imidazolium precursors with triiron(0)- resp. triruthenium(0)dodecacarbonyl, a series of new iron and ruthenium carbonyl complexes with chelating phosphine-NHC ligands could be obtained. While, depending on the imidazolium counter anion, the iron compound gives tri- resp. tetracarbonyl complexes in the oxidation state 0, the use of ruthenium leads to an oxidative addition and therefore to a chlorido-hydridoruthenium(II) derivative. This is a remarkable difference in reactivity between iron and ruthenium. Only in case the carbene species is pre-formed in solution prior to the addition of triruthenium(0)dodecacarbonyl, a tricarbonylruthenium(0) complex was accessible. The free NHCs, generated by treatment of the phosphine functionalized

imidazolium precursors with either $Ag_2O$ or copper(I)mesityl, react with $[(\eta^6\text{-cymene})RuCl_2]_2$ under formation of cationic cymene complexes, which show largely different activities in the transfer hydrogenation of acetophenone depending on the bulkiness of the NHC substituent.

**Experimental section**

**General Remarks:** All reactions were carried out under an argon atmosphere using Schlenk techniques. The solvents were dried and degassed before use according to standard techniques. Other reagents were obtained from commercial suppliers and used as received. $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on BRUKER Spectrospin Avance 400 and 600 spectrometers at room temperature (unless otherwise denoted). The chemical shifts are referenced to internal solvent resonances and the assignment of the resonances refers to the numbering schemes provided in the Supporting Information to this manuscript. Infra-red spectra were recorded on a Perkin Elmer FT-ATR-IR spectrometer Spectrum 100 equipped with a diamond coated ZnSe window. Elemental analyses (C,H,N) were carried out with a vario MICRO cube elemental analyzer at the Analytical Department of Technische Universität Kaiserslautern. All commercially available starting materials were purchased from Sigma Aldrich and used without any further purification. Toluene and dichloromethane were dried in a MB-SPS solvent dryer. Tetrahydrofurane was dried over potassium/benzophenone, acetonitrile was dried over $CaH_2$. 1-Mesityl-1*H*-imidazol, (2-(chloromethyl)phenyl)diphenyl-phosphine and copper(I)mesityl were synthesized according to published procedures [34,35,36].

**1-(2-(Diphenylphosphino)benzyl)-3-methyl-1*H*-imidazol-3-ium chloride [1a$^+$](Cl$^-$):** 4.00 g (12.9 mmol) of (2-(chloromethyl)phenyl)diphenylphosphine and 1.10 g (12.2 mmol) of 1-methylimidazole were dissolved in 25 mL of acetonitrile and heated for 18 h under reflux. The solvent was removed and the residue was washed with diethylether and dried under vacuum. Colourless solid, yield: 4.19 g (87%). Elemental analysis calcd. for $C_{23}H_{22}ClN_2P\cdot(H_2O)_{0.9}$: C 67.53, H 5.86, N 6.85, found: C 67.62, H 5.94, N 6.85%. $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ 10.40 (s, 1H, H2), 7.75 (dd, $^3J_{HH}$ = 7.5 Hz, $J_{HP}$ = 4.5 Hz, 1H, H5), 7.46 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H6), 7.40-7.30 (m, 8H, H3, H6, $H_{Ph}$), 7.20-7.15 (m, 4H, $H_{Ph}$), 7.07 (t, $^3J_{HH}$ = 1.7 Hz, 1H, H3), 6.99 (ddd, $^3J_{HH}$ = 7.6 Hz, $J_{HP}$ = 4.2 Hz, $4J_{HH}$ = 1.1 Hz, 1H, H5), 5.78 (s, 2H,

H4), 3.94(s, 3H, H1). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 138.0, 137.1 (d, $J_{PC}$ = 25.8 Hz), 136.9 (d, $J_{PC}$ = 15.3 Hz), 134.7, 134.7 (d, $J_{PC}$ = 7.9 Hz), 133.8 (d, $J_{PC}$ = 19.7 Hz), 131.5 (d, $J_{PC}$ = 4.6 Hz), 130.5, 130.1, 128.9 (d, $J_{PC}$ = 7.2 Hz), 123.3, 121.4 (d, $J_{PC}$ = 4.3 Hz), 51.6 (d, $J_{PC}$ = 22.6 Hz), 36.5. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$): δ -17.32 (s). IR (ATR, $cm^{-1}$): $\tilde{\upsilon}$ 3053w, 2938w, 1571w, 1476w, 1434m, 1320w, 1196w, 1160m, 1112w, 1025w, 830w, 744s, 696s, 675m, 658m.

**1-(2-(Diphenylphosphino)benzyl)-3-methyl-1*H*-imidazol-3-ium tetrafluoroborate [1a$^+$](BF$_4^-$):** 2.00 g (5.09 mmol) of compound **1a** were dissolved in 25 mL of dichloromethane. 0.62 g (5.60 mmol) of odium tetrafluoroborate were added to the solution. The suspension was stirred at room temp. for 18 h. The solid residue was filtered off and the solvent was removed under vacuum. Colourless solid, yield: 2.11 g (93%). Elemental analysis calcd. for $C_{23}H_{22}BF_4N_2P$: C 62.19, H 4.99, N 6.31, found: C 62.12, H 5.14, N 6.24%. $^{1}H$ NMR (400.1 MHz, $CDCl_3$): δ 8.36 (s, 1H, H2), 7.62 (ddd, $^{3}J_{HH}$ = 7.5 Hz, $J_{HP}$ = 4.6 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, H5), 7.47 (td, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, H6), 7.37-7.28 (m, 7H, H6, $H_{Ph}$), 7.12 - 7.08 (m, 4H, $H_{Ph}$), 7.01-6.98 (m, 2H, H5, 3), 6.94 (t, $^{3}J_{HH}$ = 1.8 Hz, 1H, H3), 5.59 (s, 2H, H4), 3.61 (s, 3H, H1). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 137.3 (d, $J_{PC}$ = 15.6 Hz), 136.7 (d, $J_{PC}$ = 26.1 Hz), 136.7, 135.1, 134.7 (d, $J_{PC}$ = 7.9 Hz), 133.8 (d, $J_{PC}$ = 19.7 Hz), 131.9 (d, $J_{PC}$ = 4.7 Hz), 130.6, 130.4, 129.5, 128.9 (d, $J_{PC}$ = 7.3 Hz), 123.4, 121.7 (d, $J_{PC}$ = 2.3 Hz), 52.3 (d, $J_{PC}$ = 21.7 Hz), 36.2. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$): δ -17.86 (s). $^{19}F\{^{1}H\}$ NMR (376.5 MHz, $CDCl_3$): δ 151.6 (s). IR (ATR, $cm^{-1}$): $\tilde{\upsilon}$ 3154w, 1568w, 1478w, 1435m, 1330w, 1206w, 1155m, 1110m 1059s, 1013s, 852m, 783m, 752s, 698s.

**1-(2-(Diphenylphosphino)benzyl)-3-mesityl-1*H*-imidazol-3-ium chloride [1b$^+$](Cl$^-$):** 2.50 g (8.04 mmol) of (2-(chloromethyl)phenyl)diphenylphosphine and 1.50 g (8.05 mmol) of 1-mesityl-1*H*-imidazole were dissolved in 20 mL acetonitrile and heated for 18 h under reflux. Finally, the solvent was removed under vacuum and the bright yellow residue was purified by column chromatography (dichloromethane, methanol; product fraction at 7.3 % methanol). Colorless solid, yield: 3.24 g (81%). Elemental analysis calcd. for $C_{31}H_{30}ClN_2P\cdot(H_2O)_{0.4}$: C 73.84, H 6.16, N 5.56, found: C 74.07, H 6.12, N 5.22%. $^{1}H$ NMR (400.1 MHz, $CDCl_3$): δ 11.09 (s, 1H, H4), 8.38 (ddd, $^{3}J_{HH}$ = 7.6 Hz, $J_{HP}$ = 4.5 Hz, $^{4}J_{HH}$ = 0.9 Hz, 1H, H7), 7.88-7.87 (m, 1H, H5), 7.73 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, H8), 7.67-7.63 (m, 6H, $H_{Ph}$), 7.60 (td, $^{3}J_{HH}$ = 7.6 Hz,

$^4J_{HH}$ = 1.2 Hz, 1H, H8), 7.56-7.52 (m, 4H, $H_{Ph}$), 7.29 - 7.27 (m, 2H, H7, H5), 6.47 (s, 2H, H2), 5.58 (s, 2H, H6), 2.61 (s, 3H, H1), 2.30 (s, 6H, H3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 141.3, 138.9, 138.2 (d, $J_{PC}$ = 25.6 Hz), 136.5 (d, $J_{PC}$ = 14.1 Hz), 135.0 (d, $J_{PC}$ = 7.5 Hz), 134.4, 134.3, 133.9 (d, $J_{PC}$ = 19.5 Hz), 132.0 (d, $J_{PC}$ = 4.6 Hz), 130.9, 130.8, 130.0, 129.9, 129.5, 129.1 (d, $J_{PC}$ = 7.2 Hz), 122.6, 122.5 (d, $J_{PC}$ = 7.9 Hz), 51.1 (d, $J_{PC}$ = 21.8 Hz), 21.2, 17.7. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ -16.05 (s). IR (ATR, $cm^{-1}$): $\tilde{\nu}$ 2959w, 1561w, 1542m, 1478m, 1449m, 1436m, 1368w, 1280m, 1201m, 1194m, 1153m, 1072m, 1015m, 883m, 849m, 782m, 748s, 742s, 727s, 693s, 669m.

**1-(2-(Diphenylphosphino)benzyl)-3-methyl-2*H*-imidazol-2-ylidene(tricarbonyl)iron(0) (2):** 250 mg (0.64 mmol) of compound **[1a$^+$](Cl$^-$)** and 110 mg (0.22 mmol) of triirondodecarbonyl were suspended in 25 mL toluene and the reaction mixture was heated to reflux for 18 h. After this time period it was stirred for additional 4 h at room temp.. During this period, a brown precipitate formed in the solution, which was removed by filtration. The red filtrate was concentrated and a red, crystaline solid formed. The product was re-crystallized by slow diffusion of pentane into a saturated toluene solution. Red solid, yield: 155 mg (48%). Elemental analysis calcd. for $C_{26}H_{21}FeN_2O_3P$: C 62.92, H 4.27, N 5.64, found: C 62.96, H 4.50, N 5.53. $^1H$ NMR (400.1 MHz, $C_6D_6$): δ 7.66 (br, 4H, $H_{Ph}$), 7.11-6.96 (m, 7H, H4, $H_{Ph}$), 6.91 (t, $^3J_{HH}$ = 7.3 Hz, 1H, H5), 6.78 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H5'), 6.72-6.68 (m, 1H, H4), 6.09 (s, 1H, H2), 5.77 (s, 1H, H2'), 3.29 (s, 3H, H1), the resonance of H3 is missing due to equilibration effects. $^{13}C\{^1H\}$ NMR (100.6 MHz, $C_6D_6$): δ 189.1 (d, $J_{PC}$ = 25.0 Hz),, 140.5 (d, $J_{PC}$ = 13.8 Hz), 135.4 (d, $J_{PC}$ = 24.5 Hz), 129.9, 129.7 (d, $J_{PC}$ = 6.8 Hz), 129.6 (d, $J_{PC}$ = 1.5 Hz), 129.5, 129.0, 128.9, 128.6, 127.9, 125.7, 122.9, 120.9, 53.9 (d, $J_{PC}$ = 11.0 Hz), 38.6. $^{31}P\{^1H\}$ NMR (162.0 MHz, $C_6D_6$): δ 67.60 (s). IR (ATR, $cm^{-1}$): $\tilde{\nu}$ 2920w, 1955s, 1881s, 1832s, 1569m, 1481m, 1431m, 1365m, 1234s, 1186m, 1131m, 1090s, 1027m, 878w, 793w, 747s, 722m, 688s, 667s.

**[1-(2-(Diphenylphosphino)benzyl)-3-methyl-1*H*-imidazol-3-iumtetra(carbonyl)iron(0) tetrafluoroborate (3):** 397 mg (0.90 mmol) of compound **[1a$^+$](BF$_4^-$)** and 151 mg (0.30 mmol) of triirondodecarbonyl were suspended in 50 mL of toluene. The reaction mixture was heated to reflux for 18 h. While cooling down to room temp. an orange-brown precipitate formed, which was separated from the reaction mixture by filtration and washed with 20 mL of dichloromethane. After drying under vacuum the solid was re-crystallized by slow diffusion

of diethylether into a solution in dichloromethane. Orange solid, yield: 331 mg (74%). Elemental analysis calcd. for $C_{27}H_{22}BF_4FeN_2O_4P$: C 52.98, H 3.62, N 4.58, found: C 52.62, H 3.88, N 4.59%. $^1$H NMR (400.1 MHz, $CD_3CN$): δ 8.10 (s, 1H, H2), 7.68-7.35 (m, 14H, H6, H5, $H_{Ph}$), 7.28 (s, 1H, H3), 6.96 (s, 1H, H3'), 5.21 (s, 2H, H4), 3.77 (s, 3H, H1). $^{13}$C{$^1$H} NMR (100.6 MHz, $CD_3CN$): δ 214.2 (d, $J_{PC}$ = 18.0 Hz), 137.4, 136.5, 136.4 (d, $J_{PC}$ = 4.2 Hz), 133.9 (d, $J_{PC}$ = 10.7 Hz), 133.8, 133.5 (d, $J_{PC}$ = 3.7 Hz), 133.4 (d, $J_{PC}$ = 12.3 Hz), 132.7 (d, $J_{PC}$ = 2.5 Hz), 132.1 (d, $J_{PC}$ = 7.0 Hz), 130.5, 130.3 (d, $J_{PC}$ = 10.6 Hz), 125.1, 123.2, 52.1 (d, $J_{PC}$ = 6.0 Hz), 37.0. $^{31}$P{$^1$H} NMR (162.0 MHz, $CD_3CN$): δ 66.49 (s).$^{19}$F{$^1$H} NMR (376.5 MHz, $CD_3CN$): δ -151.46 (s). IR (ATR, cm$^{-1}$): $\tilde{\nu}$ 3159w, 2049s, 1979s, 1921s, 1575w, 1561w, 1435m, 1314w, 1199w, 1158m, 1051s, 1035s, 834m, 821m, 783m, 750s, 695s.

**1-(2-(Diphenylphosphino)benzyl)-3-mesityl-2*H*-imidazol-2-yliden(dicarbonyl)(chlorido)(hydrido)ruthenium(II) (4):** 233 mg (0.47 mmol) of compound **[1b$^+$](Cl$^-$)** were suspended in 20 mL of tetrahydrofurane. A solution of 100 mg (0.16 mmol) of triruthenium dodecacarbonyl in 10 mL of tetrahydrofurane was added. The reaction mixture was heated to reflux for 18 h. During the cooling process a colourless precipitate formed. Half of the solvent was removed under vacuum and the resulting solid was isolated by filtration, washed with diethylether and dried under vacuum. The product was re-crystallized by slow diffusion of diethylether into a saturated solution in dichloromethane. Colourless solid, yield: 224 mg (7 %). Elemental analysis calcd. for $C_{33}H_{30}ClN_2O_2PRu$: C 60.60, H 4.62, N 4.28, found: C 60.40, H 4.81, N 4.29%. $^1$H NMR (600.1 MHz, $CD_2Cl_2$): δ 7.57-7.43 (m, 7H, H7, $H_{Ph}$), 7.41-7.34 (m, 5H, H2, $H_{Ph}$), 7.17-7.05 (m, 4H, H7, H6, H4), 6.92 (s, 1H, H4'), 6.86 (d, $^4J_{HH}$ = 1.6 Hz, 1H, H2), 6.45 (d, $^2J_{HH}$ = 14.6 Hz, 1H, H5), 4.66 (d, $^2J_{HH}$ = 14.5 Hz, 1H, H5'), 2.35 (s, 3H, H3), 2.12 (s, 3H, H3'), 1.78 (s, 3H, H1), -6.63 (d, $^2J_{PH}$ = 129.8 Hz, 1H, RuH). $^{13}$C{$^1$H} NMR (150.9 MHz, $CD_2Cl_2$): δ 199.4 (d, $J_{PC}$ = 7.9 Hz), 198.9, 139.6, 137.5, 135.6 (d, $J_{PC}$ = 11.1 Hz), 135.5, 134.2, 133.1 (d, $J_{PC}$ = 11.6 Hz), 131.6, 131.2 (d, $J_{PC}$ = 7.1 Hz), 130.9, 130.1, 129.6, 129.5 (d, $J_{PC}$ = 4.6 Hz), 129.0 (d, $J_{PC}$ = 20.0 Hz), 128.9 (d, $J_{PC}$ = 20.5 Hz), 123.1, 122.4, 21.5, 19.3, 18.1. $^{31}$P{$^1$H} NMR (242.9 MHz, $CD_2Cl_2$): δ 11.41 (s). IR (ATR, cm$^{-1}$): $\tilde{\nu}$ 3130w, 3102w, 2031s, 1946s, 1588w, 1572w, 1481m, 1464m, 1434m, 1389m, 1282m, 1236m, 1186m, 1130m, 1087m, 1037w, 872w, 806m, 791m, 758m, 746s, 695s.

**1-(2-(Diphenylphosphino)benzyl)-3-methyl-2*H*-imidazol-2-ylidentri(carbonyl)ruthenium(0) (5):** 282 mg (0.72 mmol) of **[1a$^+$](Cl$^-$)** were suspended in 20 mL of tetrahydrofurane. Over a period of 15 min, a solution of 144 mg (0.72 mmol) of potassium hexamethyldisilazide in 10 mL of tetrahydrofurane was added. During the addition the colour of the reaction mixture turned slowly to orange. After further stirring the mixture for 90 min at room temp., a solution of 152 mg (0.24 mmol) of tririutheniumdodecacarbonyl in 15 mL tetrahydrofurane was added. The resulting suspension was stirred at room temp. for 18 h. The colourless precipitate formed was removed by filtration and the filtrate was concentrated to half of its volume. The resulting orange solid was washed with pentane and dried under vacuum. The raw product was re-crystallized by slow diffusion of pentane into a saturated solution in toluene. Yellow solid, yield: 320 mg (82%). Elemental analysis calcd. for $C_{26}H_{21}N_2O_3PRu$: C 57.67, H 3.91, N 5.17, found: C 57.62, H 4.05, N 5.09%. $^1$H NMR (400.1 MHz, $C_6D_6$): δ 7.96 (br, 2H, $H_{Ph}$), 7.61 (br, 2H, $H_{Ph}$), 7.09-6.99 (m, 7H, H4, $H_{Ph}$), 6.89 (t, $^3J_{HH}$ = 7.3 Hz, 1H, H5), 6.78 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H5'), 6.67 (ddd, $^3J_{HH}$ = 7.4 Hz, $J_{HP}$ = 4.4 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H4), 6.05 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H2), 5.83 (d, $^3J_{HH}$ = 1.9 Hz, 1H, H2), 5.70 (d, $^2J_{HH}$ = 14.2 Hz, 1H, H3), 3.51 - 3.46 (m, 4H, H3', H1). $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$): δ 214.2 (d, $J_{PC}$ = 8.3 Hz), 179.2 (d, $J_{PC}$ = 12.1 Hz), 139.7 (d, $J_{PC}$ = 15.4 Hz), 138.4 (d, $J_{PC}$ = 21.2 Hz), 134.8 (d, $J_{PC}$ = 17.0 Hz), 133.6 (d, $J_{PC}$ = 12.2 Hz), 132.1, 129.9 (d, $J_{PC}$ = 6.1 Hz), 129.6, 129.3, 129.2 (d, $J_{PC}$ = 4.4 Hz), 128.7 (d, $J_{PC}$ = 16.6 Hz), 127.9, 122.6, 120.4, 53.5 (d, $J_{PC}$ = 18.2 Hz), 39.8. $^{31}$P{$^1$H} NMR (162.0 MHz, $C_6D_6$): δ 39.15 (s). IR (ATR, cm$^{-1}$): $\tilde{\upsilon}$ 3060w, 1998s, 1900s, 1853s, 1661m, 1586m, 1571m, 1456m, 1434s, 1389m, 1352m, 1228m, 1163m, 1131m, 1088m, 1072m, 1000w, 918w, 746s, 724s, 687s.

**Chlorido(η$^6$-*p*-cymene)(1-(2-(diphenylphosphino)benzyl)-3-methyl-2*H*-imidazol-2-ylidene-ruthenium(II) hexafluorophosphate (6a):** 210 mg (0.53 mmol) of **[1a$^+$](Cl$^-$)** and 69.0 mg (0.30 mmol) of $Ag_2O$ were suspended in 20 mL of dichloromethane and stirred under exclusion of light for 18 h at room temp.. After filtration of the mixture, a solution of 150 mg (0.24 mmol) of [(η$^6$-cymene)$RuCl_2$]$_2$ in 10 mL of dichloromethane was added and the resulting mixture was stirred again under exclusion of light for further 18 h at room temp.. The precipitated AgCl was removed by filtration and 200 mg (1.09 mmol) of $KPF_6$ were added to the solution which was stirred for another 24 h. After removing the solvent under vacuum the resulting solid was recrystallized by slow diffusion of diethylether into a solution in dichloromethane. Yellow solid, yield: 295 mg (72%). Elemental analysis calcd. for $C_{33}H_{35}ClF_6N_2P_2Ru$: C 51.33, H

4.57, N 3.63, found: C 51.24, H 4.69, N 3.61. $^{1}$H NMR (400.1 MHz, $CD_2Cl_2$): δ 7.62-7.55 (m, 6H, $H_{Ph}$), 7.48 (tt, $^{4}J_{HH}$ = 1.4 Hz, $^{3}J_{HH}$ = 7.6 Hz, 1H, H5), 7.41-7.36 (m, 2H, H2, H4), 7.30-7.23 (m, 3H, H5, $H_{Ph}$), 7.16-7.10 (m, 3H, H2, $H_{Ph}$), 7.03-6.98 (m, 1H, H4'), 5.71 (dd, $^{4}J_{HH}$ = 1.2 Hz, $^{3}J_{HH}$ = 6.6 Hz, 1H, $H_{Cym}$), 5.66 (d, $^{2}J_{HH}$ = 14.1 Hz, 1H, H3), 5.60 (d, $^{3}J_{HH}$ = 6.0 Hz, 1H, $H_{Cym}$), 5.40-5.38 (m, 2H, $H_{Cym}$), 5.06 (d, $^{2}J_{HH}$ = 14.8 Hz, 1H, H3'), 3.96 (s, 3H, H1), 2.32 (hept, $^{3}J_{HH}$ = 6.9 Hz, 1H, H7), 2.17 (s, 3H, H6), 1.00 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, H8), 0.90 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, H8'). $^{13}$C{$^{1}$H} NMR (100.6 MHz, $CD_2Cl_2$): δ 167.7 (d, $J_{PC}$ = 22.5 Hz), 140.5 (d, $J_{PC}$ = 11.8 Hz), 137.8 (d, $J_{PC}$ = 44.7 Hz), 135.9, 135.3 (d, $J_{PC}$ = 9.8 Hz), 134.0, 133.4, 133.0 (d, $J_{PC}$ = 8.8 Hz), 132.6 (d, $J_{PC}$ = 2.2 Hz), 131.5, 131.0, 130.6 (d, $J_{PC}$ = 8.1 Hz), 129.9 (d, $J_{PC}$ = 7.4 Hz), 129.6 (d, $J_{PC}$ = 9.5 Hz), 128.8, 128.5 (d, $J_{PC}$ = 10.6 Hz), 128.3, 126.7, 123.0, 111.6, 106.2, 97.2, 94.5, 91.4, 89.9, 54.6 (d, $J_{PC}$ = 7.5 Hz), 39.8, 31.1, 23.2, 21.3, 18.3. $^{31}$P{$^{1}$H} NMR (162.0 MHz, $CD_2Cl_2$): δ = 24.60 (s), -144.39 (hept, $^{1}J_{PF}$ = 710.9 Hz). $^{19}$F{$^{1}$H} NMR (376.5 MHz, $CD_2Cl_2$): δ = -72.83 (hept, $^{1}J_{PF}$ = 711.1 Hz). IR (ATR, $cm^{-1}$): $\tilde{\upsilon}$ 2977w, 1577w, 1475w, 1436m, 1393m, 1324w, 1238m, 1175w, 1088m, 1031w, 829s, 755s, 729s, 696s.

**Chlorido(η$^{6}$-*p*-cymene)(1-(2-(diphenylphosphino)benzyl)-3-mesityl-2*H*-imidazol-2-ylidene-ruthenium(II) hexafluorophosphate (6b):** 69 mg (0.38 mmol) of copper(I)mesityl dissolved in further 3 mL tetrahydrofurane were added over a period of 10 min to a suspension of 188 mg (0.38 mmol) of **[1b$^{+}$](Cl$^{-}$)** in 10 mL of tetrahydrofurane. The reaction mixture was stirred for 18 h at room temp.. The resulting copper(II)-NHC complex was precipitated by addition of 15 mL of pentane and isolated by filtration to yield 150 mg of a light yellow solid that was dissolved in 15 mL of dichloromethane followed by the addition of 82 mg (0.14 mmol) of [(η$^{6}$-cymene)$RuCl_2$]$_2$. The resulting mixture was stirred at room temp. for further 20 h. The solution was reduced to half of its volume and cooled down to -35 °C for 12 h. The precipitate, which had formed, was filtered off and the filtrate was extracted twice with 5 mL of a saturated aqueous solution of $KPF_6$. The organic phase was dried over $Na_2SO_4$ and the solvent was removed under vacuum. Yellow-brownish solid, yield: 154 mg (65%). Elemental analysis calcd. for $C_{41}H_{43}ClF_6N_2P_2Ru\cdot(CH_2Cl_2)_{0.8}$: C 55.25, H 4.95, N 3.08, found: C 55.38, H 5.09, N 3.17. $^{1}$H NMR (400.1 MHz, $CDCl_3$): δ = 7.96-7.92 (m, 2H, $H_{Ph}$), 7.72 (dd, $^{3}J_{HH}$ = 6.9 Hz, $J_{PH}$ = 4.9 Hz, 1H, H6), 7.64-7.60 (m, 4H, H4, $H_{Ph}$), 7.54 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, H7), 7.30 (t, $^{3}J_{HH}$ = 7.6 Hz 1H, H7), 7.18-7.12 (m, 2H, H6, $H_{Ph}$), 7.02 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 2.5 Hz, 2H, $H_{Ph}$), 6.93 (d, $^{4}J_{HH}$ = 1.8 Hz, 1H, H4), 6.91 (s, 1H, H2), 6.75 (s, 1H, H2'), 6.55-6.50 (m, 2H, $H_{Ph}$), 5.94 (d,

$^{2}J_{HH}$ = 15.6 Hz, 1H, H5), 5.63 (br, 1H, $H_{Cym}$), 5.41 (d, $^{2}J_{HH}$ = 15.5 Hz, 2H, H5', $H_{Cym}$), 4.93 (br, 1H, $H_{Cym}$), 4.35 (br, 1H, $H_{Cym}$), 2.35-2.27 (m, 4H, H9, H3), 2.02 (s, 3H, H3'), 1.95 (s, 3H, H8), 1.65 (s, 3H, H1), 1.03 (d, $^{3}J_{HH}$ = 7.1 Hz, 3H, H10), 0.58 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, H10'). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 140.3 (d, $J_{PC}$ = 12.7 Hz), 139.1, 137.9, 137.7, 136.6, 135.8, 135.3, 134.8, 132.9 (d, $J_{PC}$ = 8.7 Hz), 132.3 (d, $J_{PC}$ = 1.9 Hz), 131.9 (d, $J_{PC}$ = 8.6 Hz), 131.3 (d, $J_{PC}$ = 8.8 Hz), 131.1 (d, $J_{PC}$ = 2.4 Hz), 129.2 (d, $J_{PC}$ = 6.5 Hz), 129.1 (d, $J_{PC}$ = 2.3 Hz), 128.9, 128.8, 128.5, 128.0 (d, $J_{PC}$ = 10.7 Hz), 127.7, 124.1, 54.9 (d, $J_{PC}$ = 7.1 Hz), 31.1, 23.8, 21.0, 20.0, 19.6, 19.6, 18.2. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$): δ 22.43 (s), -144.23 (hept, $^{1}J_{PF}$ = 712.8 Hz). $^{19}F\{^{1}H\}$ NMR (376.5 MHz, $CDCl_3$): δ -72.64 (d, $^{1}J_{FP}$ = 712.9 Hz). IR (ATR, $cm^{-1}$): $\tilde{\upsilon}$ 2925w, 1573w, 1482m, 1435m, 1385m, 1269m, 1234m, 1163w, 1090m, 1028w, 929w, 829s, 744s, 692s.

**Catalytic transfer hydrogenation:** Catalysis was carried out 15 mL in crimp-capped vials equipped with a magnetic stirring bar. After filling in the catalyst (0.5 mol-% with respect to acetophenone), the vials were closed with Teflon-coated septa caps and the vials were flushed with nitrogen gas. Then a solution of 0.05 mmol of KOH in 5 mL of isopropanol was added via a syringe. Since the amount of KOH is too small to be weighted correctly, 200 mL of a stock solution were prepared, and aliquots were taken from this solution. After addition of 1.00 mmol acetophenone by using a syringe, the vial was placed into a block of aluminum which had been pre tempered to 82 °C. To measure the conversion of the substrate, samples of about 0.1 mL were taken after 1, 2, 3, 4, 8 und 24 h, filtered over a short bed of silica and $MgSO_4$ and 50 µL of tetradecane were added as an external standard. Yields were determined by GC-FID analysis.

**X-ray structure analyses:** Crystal data and refinement parameters are collected in Table 2. All structures were solved using direct method with SIR92 [37], completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures [38]. Semi-empirical absorption corrections from equivalents (Multiscan) were carried out for complexes **2**-**5**, analytical numeric absorption corrections was applied on compound **6a** [39]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom H1 in the complex **4**, which is bound to Ru1, was located in the difference Fourier synthesis, and was then refined semi-freely with the help of a distance restraint, while constraining its *U*-value to 1.2 times the *U(eq)* value of Ru1. All other hydrogen atoms were

placed in calculated positions and refined by using a riding model. And the detailed information has been posted in the final CIF file. CCDC 1980356-1980360 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Table 2.** Crystallographic data, data collection and refinement.

| | **2** | **3** | **4** | **5** | **6a** |
|---|---|---|---|---|---|
| empirical formula | $C_{26}H_{21}FeN_2O_3P$ | $C_{27}H_{22}BF_4FeN_2O_4P$ | $C_{33}H_{30}ClN_2O_2PRu$ | $C_{26}H_{21}N_2O_3PRu$ | $C_{33}H_{35}ClF_6N_2P_2Ru$ |
| formula weight | 496.27 | 612.09 | 654.08 | 541.49 | 772.09 |
| crystal size [mm] | 0.37x0.25x0.25 | 0.534x0.328x0.285 | 0.30x0.09x0.04 | 0.470x0.355x0.258 | 0.390x0.350x0.180 |
| $T$ [K] | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| $\lambda$ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 1.54184 |
| crystal system | monoclinic | monoclinic | triclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ | C2/c |
| $a$ [Å] | 15.9395(2) | 9.5958(3) | 10.7497(9) | 9.2760(2) | 12.9158(1) |
| $b$ [Å] | 8.8558(1) | 20.7199(5) | 12.4462(9) | 13.8768(4) | 14.7534(2) |
| $c$ [Å] | 16.2401(2) | 14.0479(4) | 13.8730(9) | 18.3020(4) | 35.0814(3) |
| $\alpha$ [°] | 90 | 90 | 100.072(6) | 90 | 90 |
| $\beta$ [°] | 99.011(1) | 104.265(3) | 112.332(7) | 96.873(2) | 95.034(1) |
| $\gamma$ [°] | 90 | 90 | 110.085(7) | 90 | 90 |
| $V$ [Å$^3$] | 2264.11(5) | 2706.94(14) | 1509.6(3) | 2338.93(10) | 6659.04(12) |
| $Z$ | 4 | 4 | 2 | 4 | 8 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.456 | 1.502 | 1.439 | 1.538 | 1.540 |
| $\mu$ [mm$^{-1}$] | 0.768 | 0.681 | 0.693 | 0.769 | 5.986 |
| $\theta$-range [°] | 2.84-32.46 | 2.941-32.488 | 2.93-32.49 | 2.936-32.466 | 4.560-62.726 |
| refl. coll. | 28787 | 33327 | 17728 | 15124 | 19197 |
| indep. refl. | 7553 | 9092 | 9795 | 7664 | 5291 |
| | [$R_{int}$ = 0.0240] | [$R_{int}$ = 0.0437] | [$R_{int}$ = 0.0650] | [$R_{int}$ = 0.0212] | [$R_{int}$ = 0.0316] |
| data/restr./param. | 7553/0/299 | 9092/0/362 | 9795/0/367 | 7664/0/299 | 5291/141/443 |
| final $R$ indices [$I>2\sigma(I)$] [a] | 0.0340, 0.0808 | 0.0538, 0.1241 | 0.0850, 0.2081 | 0.0314, 0.0700 | 0.0333, 0.0945 |
| $R$ indices (all data) | 0.0398, 0.0834 | 0.0681, 0.1315 | 0.1200, 0.2315 | 0.0398, 0.0736 | 0.0367, 0.1149 |
| *GooF* [b] | 1.101 | 1.115 | 1.104 | 1.079 | 1.236 |
| $\Delta\rho_{max}/_{min}$ (e·Å$^{-3}$) | 0.445/-0.355 | 0.934/-0.781 | 3.477/-1.724 | 0.441/-0.621 | 1.058/-0.879 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $\omega R2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^2]^{1/2}$. [b] $GooF = [\Sigma\omega(F_o^2 - F_c^2)^2/(n\text{-}p)]^{1/2}$.

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**Scheme, Figure and Table captions**

**Scheme 1.** i) 1.2 equiv. n-BuLi, $Et_2O$, r.t., 14 h, ii) 1.2 equiv. $Ph_2PCl$, Et2O, -78 °C - r.t., 2 h, iii) 1.3 equiv. $ClCO_2Et$, benzene, refl., 2 h, iv) 1.0 equiv. *N*-substituted imidazole, MeCN, refl., 18 h, v) 1.2 equiv. $NaBF_4$, $CH_2Cl_2$, 18 h, r.t..

**Scheme 2.** Synthesis of the iron carbonyl complexes **2** and **3**: i) X = $Cl^-$, 0.33 eq. $Fe_3(CO)_{12}$, toluene, refl., 18 h; ii) X = $BF_4^-$, 0.33 eq. $Fe_3(CO)_{12}$, toluene, refl., 18 h.

**Figure 1.** Molecular structures of compounds **2** (left) and **3** (right) in the solid state. The ellipsoids are at the 50% level. Selected bond lengths (Å) and angles (°) are listed. **2**: Fe1-P1 2.2196(4), Fe1-C1 1.7556(13), Fe1-C2 1.7675(13), Fe1-C3 1.7652(13), Fe1-C4 1.9795(13), O1-C1 1.1655(18), O2-C2 1.1578(18), O3-C3 1.1481(17), P1-Fe1-C1 91.56(4), P1-Fe1-C2 92.91(4), P1-Fe1-C3 168.79(4), P1-Fe1-C4 82.16(4), C1-Fe1-C2 120.16(6), C1-Fe1-C3 88.79(6), C1-Fe1-C4 125.90(5), C2-Fe1-C3 96.61(6), C2-Fe1-C4 113.83(6), C3-Fe1-C4 88.56(5), Fe1-C1-O1 177.83(12), Fe1-C2-O2 176.90(12), Fe1-C3-O3 176.99(12). **3**: Fe1-P1 2.2568(6), Fe1-C1 1.792(2), Fe1-C2 1.782(2), Fe1-C3 1.794(2), Fe1-C4 1.793(2), O1-C1 1.138(3), O2-C2 1.148(3), O3-C3 1.146(3), P1-Fe1-C1 174.41(8), P1-Fe1-C2 86.37(7), P1-Fe1-C3 92.50(7), P1-Fe1-C4 89.19(7), C1-Fe1-C2 88.10(10), C1-Fe1-C3 91.38(10), C1-Fe1-C4 92.87(10), C2-Fe1-C3 125.28(10), C2-Fe1-C4 120.31(10), C3-Fe1-C4 114.37(10), Fe1-C1-O1 177.3(2), Fe1-C2-O2 177.27(19), Fe1-C3-O3 177.90(19), Fe1-C4-O4 178.95(19).

**Scheme 3.** Synthesis of the ruthenium(II) complex **4**: i) 0.33 eq. $Ru_3(CO)_{12}$, tetrahydrofurane, refl., 18 h.

**Figure 2.** Molecular structure of compound **4** in the solid state. The ellipsoids are at the 50% level. Selected bond lengths (Å) and angles (°) are listed: Ru1-Cl1 2.4552(14), Ru1-P1

2.472(2), Ru1-C1 1.940(8), Ru1-C2 1.851(6), Ru1-C3 2.111(6), Ru1-H1 1.82(8), O1-C1 1.117(11), O2-C2 1.147(8), Cl1-Ru1-P1 94.77(5), Cl1-Ru1-C1 87.5(2), Cl1-Ru1-C2 168.4(2), Cl1-Ru1-C3 86.67(14), P1-Ru1-C1 96.3(2), P1-Ru1-C2 96.8(2), P1-Ru1-C3 95.23(18), C1-Ru1-C2 89.8(3), C1-Ru1-C3 167.5(3), C2-Ru1-C3 93.7(2), C2-Ru1-H1 85(2), C3-Ru1-H1 93(2), C1-Ru1-H1 76(2), Cl1-Ru1-H1 84(2), P1-Ru1-H1 172(2), Ru1-C1-O1 168.6(7), Ru1-C2-O2 175.6(7).

**Figure 3.** The de-coupled (top) and coupled $^{31}P$ NMR spectrum (bottom) of compound **4** measured in $CD_2Cl_2$ solution.

**Scheme 4.** Two step synthesis of the ruthenium(0) complex **5** starting from **[1a$^+$](Cl$^-$)**: i) 1 equiv. of KHMDS, 0.33 equiv. of $Ru_3(CO)_{12}$, tetrahydrofurane, r.t., 20 h.

**Figure 4.** Molecular structure of compound **5** in the solid state. The ellipsoids are at the 50% level. Selected bond lengths (Å) and angles (°) are listed: Ru1-P1 2.3827(5), Ru1-C1 1.9064(19), Ru1-C2 1.901(2), Ru1-C3 1.8864(19), Ru1-C5 2.1221(18), O1-C1 1.153(2), O2-C2 1.140(2), O3-C3 1.159(3), P1-Ru1-C1 109.66(6), P1-Ru1-C2 87.48(6), P1-Ru1-C3 121.22(6), P1-Ru1-C5 97.43(5), C1-Ru1-C2 92.30(8), C1-Ru1-C3 129.12(8), C1-Ru1-C5 86.83(7), C2-Ru1-C3 89.61(8), C2-Ru1-C5 175.03(7), C3-Ru1-C5 87.15(7), Ru1-C1-O1 175.46(19), Ru1-C2-O2 179.09(17), Ru1-C3-O3 177.08(17).

**Scheme 5**. Synthesis of the ruthenium(II) NCH complexes **6a,b** and **7**. i) 0.55 equiv. of $Ag_2O$, $CH_2Cl_2$, 18 h, r.t., 0.45 of equiv. $[(\eta^6\text{-cymene})RuCl_2]_2$, 18 h, r.t., 2 equiv. of $KPF_6$, 24 h, r.t.; ii) 1.0 equiv. of CuMes, tetrahydrofurane, 18 h r.t., 0.50 equiv. of $[(\eta^6\text{-cymene})RuCl_2]_2$, 18 h, r.t., $CH_2Cl_2$, sat. aqu. $KPF_6$.

**Figure 5.** Molecular structure of compound **6a** in the solid state. Hydrogen atoms and the $PF_6^-$ anion are omitted for clarity. The ellipsoids are at the 50% level. Selected bond lengths (Å) and angles (°) are listed. C* denotes the centroid of the cymene ligand. Ru1-Cl1 2.3943(10), Ru1-P1 2.3544(9), Ru1-C1 2.077(4), Ru1-C25 2.299(4), Ru1-C26 2.243(4), Ru1-C27 2.227(4), Ru1-C28 2.228(4), Ru1-C29 2.210(4), Ru1-C30 2.276(4), Ru1-C* 1.7464(3), Cl1-Ru1-P1 82.80(3), Cl1-Ru1-C1 84.66(12), Cl1-Ru1-C* 127.80(3), P1-Ru1-C1 94.84(11), P1-Ru1-C* 129.05(3), C1-Ru1-C* 123.9(1).

**Table 1**. Catalytic transfer hydrogenation of acetophenone.

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**Highlights**

- A series of two novel iron(0), ruthenium(0) and ruthenium(II) complexes with chelating phosphine-NHC ligands synthesized and characterized
- There is a large difference in the reactivity of triiron(0)- resp. triruthenium(0)dodeca-carbonyl with respect to the imidazolium precursors; substitution vs. oxidative addition
- The reactivity of silver resp. copper metallated phosphine-NHC complexes against $[(\eta^6$-cymene)$RuCl_2]_2$ was investigated
- There is a largely different activity of the (cymene)ruthenium(II) in the transfer hydrogenation catalysis, which depends on the steric properties of the chelating ligand

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: