DOI: 10.1002/chem.200802569

# Methyleneimidazoline Complexes of Iridium, Rhodium, and Palladium from Selective C($sp^3$)–H Bond Activation

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**Abstract:** Palladium, iridium, and rhodium complexes of 2-methyleneimidazolines have been synthesized by selective phosphine-assisted activation of the 2-methyl C–H bonds in 2-methylimidazolium compounds. Metallacycles of various sizes were obtained in the reaction of phosphine-tethered 2-methylimidazolium compounds and [{M(cod)X}$_2$] (M = Rh or Ir; cod = 1,5-cyclooctadiene; X = alkoxyl or Cl). Representative complexes were characterized by X-ray crystallography. The selectivity for aliphatic C($sp^3$)H versus aromatic C($sp^2$)H activation could be adjusted by means of the steric bulk of the OR ligand, whereby a bulky OR group favors activation of the 2-methyl C($sp^3$)–H bond. Experimental results confirmed that a methyl C–H activation product (a seven-membered iridacycle) is the kinetic product, while the aryl C–H activation product (a six-membered iridacycle) is the thermodynamic product.

**Keywords:** carbene ligands · C–H activation · chelates · imidazolium compounds · transition metals

## Introduction

The last decade has witnessed great advances in ligand design to meet challenges in organometallic chemistry and catalysis.[1] The roles of these ligands can be ascribed to their donor capacity to stabilize transition metals and labilizing effects to facilitate the rate-limiting steps. In this context, neutral carbon-centered ligands have been widely used and are rapidly challenging the role of phosphine ligands.[2–4] The N-heterocyclic carbenes (NHCs) are representative of such ligands,[5] and NHC complexes have shown advantageous activity in palladium-catalyzed C–C coupling[6] and ruthenium-catalyzed olefin metathesis reactions.[7]

Various NHC ligands have been created with excellent electronic and steric tunability.[8,9] NHCs in the abnormal C4/5 binding mode (**A**, Figure 1), which are essentially zwitterionic and were first discovered by Crabtree and co-workers,[4] have received increasing attention.[10–12] NHCs in this abnormal binding mode are known to be more donating than the normal C2-bound NHCs.[12b,13] Analogously, metal complexes of ylides[14] (**B**, Figure 1) and 2-methyleneimidazolines[15–16] (**C**, Figure 1) are all zwitterionic in nature, and these ligands have been shown to be strong σ-donors. Examples of metal complexes of such ylidic ligands are still rather rare.

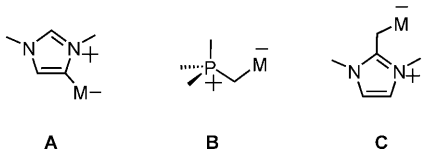


Figure 1. Complexes of C-centered ylidic ligands.

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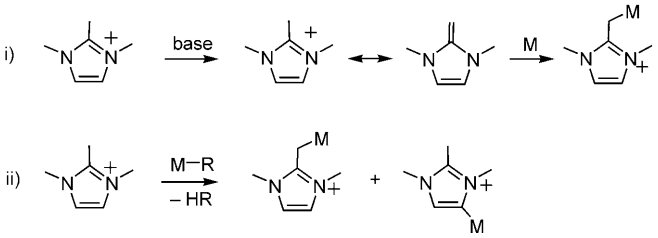
Complexation of 2-methyleneimidazoline moieties is expected because it is a formal organometallic version of the addition of enamines to an electrophilic carbonyl group. Indeed, palladium complexes stabilized by phosphine enamines on binapthyl backbones have been reported.[17] However, only very few examples of 2-methyleneimidazoline complexes are known,[15,16] and two synthetic methods have been utilized (Scheme 1). In method (i), 1,2,3-trimethylimidazolium iodide was deprotonated by a suitable base to give a ylidic 2-methyleneimidazoline, followed by treatment with transition metal compounds.[15] In method (ii), activation of the methyl C–H bond of a 2-methylimidazolium compound was mediated by a metal complex with an anionic R ligand; in this case only one example was reported.[16] One can imagine that selectivity of methyl C($sp^3$)–H versus backbone C4/5–H activation might be problematic if the C4/5 position is left unblocked. Indeed, in their studies of the reaction of [{Cp*$IrCl_2$}$_2$] (Cp* = η-$C_5Me_5$) and bis-imidazolium ions, Peris and co-workers observed low selectivity and rationalized this by computational methods.[16] Few experimental attempts have been made to explore the origin of this selectivity. It is thus important to investigate not only the thermodynamics of these two products but also the steric and electronic factors controlling the selective metalation of 2-methylimidazolium ions.



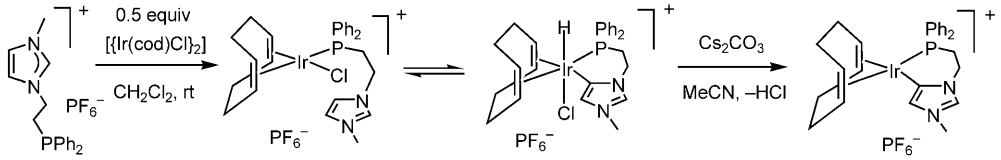

Scheme 1. Two synthetic methods for 2-methyleneimidazoline complexes.

We now report the synthesis and structures of palladium(II), iridium(I), and rhodium(I) 2-methyleneimidazoline complexes. Metalation can be exclusively directed to the 2-methyl groups of phosphine-tethered 2-methylimidazolium compounds. An iridium methyl C–H activation product is the kinetic product, while the abnormal carbene complex obtained from aryl C–H activation is the thermodynamic product.

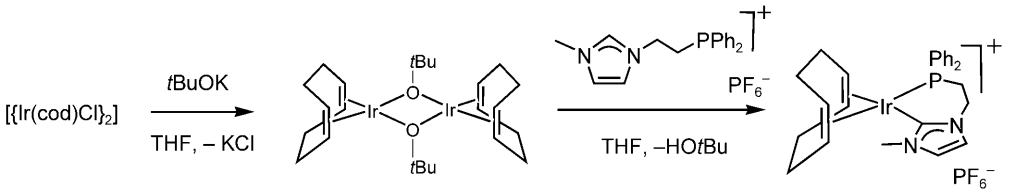
## Results and Discussion

We[12a] and others[12b] recently reported the synthesis of a series of iridium(III) abnormal NHC hydride complexes from highly selective oxidative addition of the C4/5–H bonds of phosphine-tethered imidazolium compounds (Scheme 2).[12a] These abnormal NHC hydrides can undergo base-promoted reductive elimination of HCl to afford the corresponding iridium(I) abnormal NHC complexes (Scheme 2).[12a] The corresponding iridium(I) normal NHC complex could be obtained from the reaction of [{Ir(cod)(O*t*Bu)}$_2$] (cod = 1,5-cyclooctadiene) and a phosphine-tethered imidazolium compound (Scheme 3).[12a,18] This method of metalation by metal alkoxides was initially developed by Herrmann and Köcher in the synthesis of $Ir^I$ and $Rh^I$ monodentate NHC complexes.[19]

The 2-methyl protons of 1,2,3-trimethylimidazolium compounds are more acidic than the aryl CH protons, as was evidenced by the isolation of 1,3-dimethyl-2-methyleneimidazoline after treatment of 1,2,3-trimethylimidazolium with base.[15a] In view of the relatively high acidity of the 2-methyl protons, we hypothesized that in situ generation of a 2-methyleneimidazoline ligand might also be possible. Indeed, addition of 1.05 equiv of *t*BuOK to a THF solution of [{Ir(cod)Cl}$_2$] (0.5 equiv) and ligand **1a** (1.0 equiv, −78 °C to RT) afforded a red solution, from which 2-methyleneimidazoline **2a** was isolated as the only product in 91% yield (Scheme 4. In agreement with other related reports,[12a,b] a phosphine intermediate was observed when **1a** and [{Ir(cod)Cl}$_2$] (0.5 equiv) were mixed at room temperature in THF ($\delta(^{31}P) = 19.9$ ppm). The exact mechanism of the C–H activation step and the role of *t*BuOK are not clear, since *tert*-butoxide could either act as an external base to directly

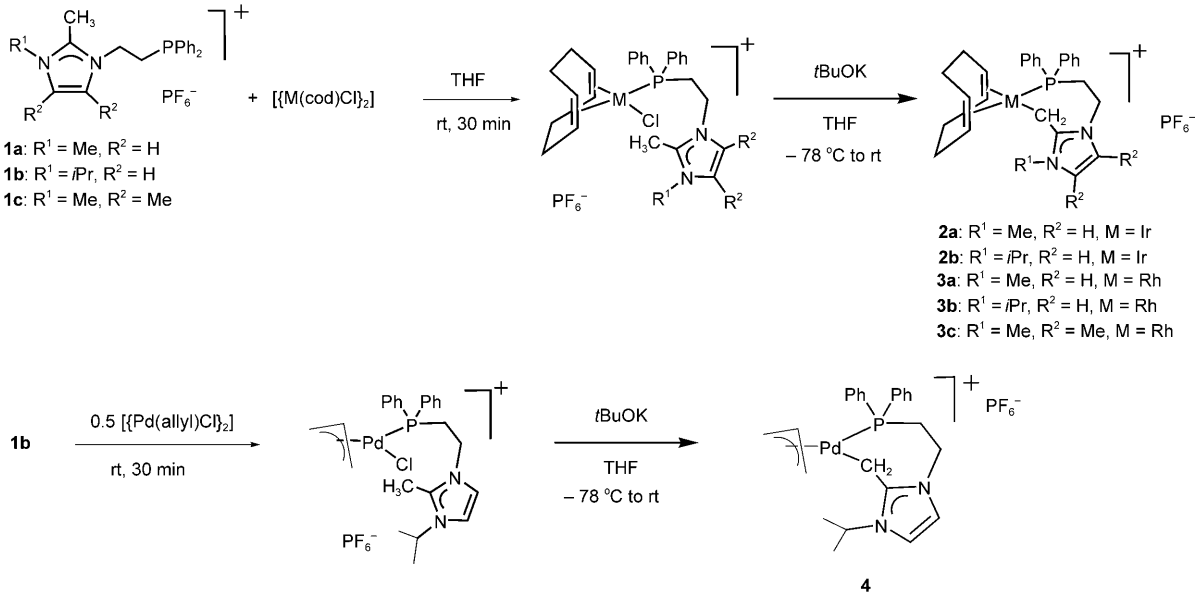



Scheme 2. Synthesis of $Ir^{III}$ and $Ir^I$ abnormal NHC complexes.[12a]




Scheme 3. Synthesis of an iridium(I) normal NHC complex.[12a,17]




Scheme 4. Synthesis of seven-membered metallacyclic 2-methyleneimidazoline complexes.

remove the acidic 2-methyl proton or as an internal base by substituting the chloro ligand and interacting with the 2-methyl C–H bond to eventually afford the same product.

Complex **2a** was characterized spectroscopically and crystallographically. In the $^1$H NMR spectrum ([D$_6$]acetone) of **2a**, the IrCH$_2$ protons resonate as a doublet ($\delta = 2.88$ ppm, $^3J_{P,H} = 1.8$ Hz), and the imidazolium backbone protons as two mutually coupled doublets at $\delta = 6.81$ and 6.38 ppm ($^3J_{H,H} = 2.1$ Hz), that is, no metalation took place at the C4/5 position. The fact that the IrCH$_2$ protons are equivalent also suggests that **2a** is $C_s$-symmetrical in solution. In the $^{13}$C NMR spectrum, the IrCH$_2$ carbon atom resonates characteristically at $\delta = 13.9$ ppm (d, $^2J_{P,C} = 5.0$ Hz). The scope of metalation in this mode was then extended to ligands **1b** and **1c** (Scheme 4) and to rhodium and palladium complexes by base treatment of a mixture of [{Ir(cod)Cl}$_2$] and ligand **1b** or **1c**, and by reaction of [{M(cod)(μ-O*t*Bu}$_2$] with the corresponding ligands. The characteristic NMR data are given in Table 1. In all cases, no corresponding six-membered abnormal NHC complexes could be detected by NMR spectroscopy.

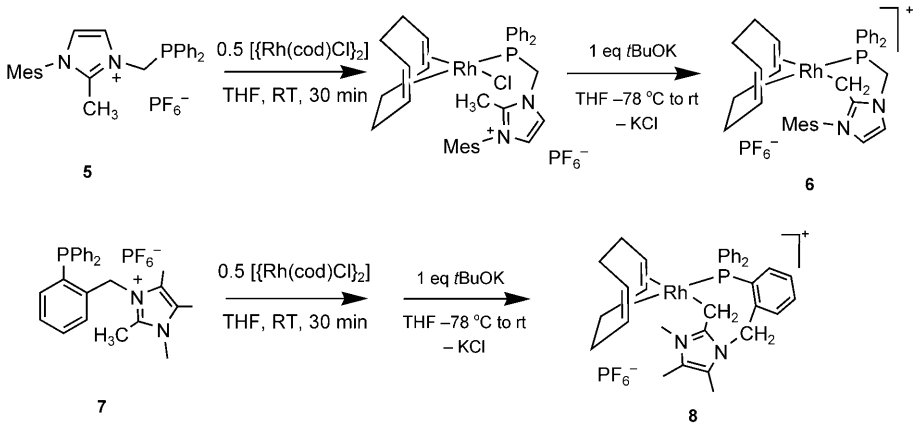
We thus further examined the metalation of other phosphine imidazolium compounds to prepare rhodium 2-methyleneimidazoline complexes with different ring sizes. Ligand **5** or **7** was treated with [{Rh(cod)Cl}$_2$] to afford the corresponding rhodium(I) phosphine complex in situ (Scheme 5). Subsequently, addition of *t*BuOK to the solution at −78 °C led to selective metalation at the desired 2-methyl position, forming either six-membered metallacyle **6** or eight-membered metallacyle **8**. Characteristic NMR signals of **6** and **8** are given in Table 1. In all cases, metalation took place exclusively at the 2-methyl position, instead of at the NCH$_3$ or linker group, on the basis of NMR analyses. In addition, although metalation at the imidazole backbone (C4/5) could have been expected for ligands **1a**,**b** and **5**, it is the high acidity of the 2-methyl protons that gives rise to this selectivity. No further deprotonation of such 2-methyleneimidazoline complexes could be observed when they were treated with an excess of *t*BuOK.

Table 1. Characteristic NMR data of 2-methyleneimidazoline complexes ($CD_2Cl_2$)

| | Yield [%] | MCH$_2$ | $^1$H imidazole C4/5-H (d, $^3J_{H,H}$) | $^{13}$C MCH$_2$ | $^{31}$P PPh$_2$ |
|---|---|---|---|---|---|
| **2a** | 91 | 2.88 (d, 1.8 Hz) | 6.81, 6.38 (2.1 Hz) | 13.9 (d, $J_{P,C} = 5.0$ Hz) | 15.4 (s) |
| **2b** | 88 | 2.96 (d, 1.7 Hz) | 6.97, 6.78 (2.0 Hz) | 13.9 (d, $J_{P,C} = 5.0$ Hz) | 13.2 (s) |
| **3a** | 92 | 2.09 (br) | 6.46, 6.03 (2.0 Hz) | 10.0 (dd, $J_{Rh,C} = 22.0$, $J_{P,C} = 8.0$ Hz) | 24.5 (d, 164.9 Hz) |
| **3b** | 91 | 2.13 (br) | 6.64, 6.35 (2.3 Hz) | 9.8 (dd, $J_{Rh,C} = 20.9$, $J_{P,C} = 8.2$ Hz) | 21.0 (d, 165.2 Hz) |
| **3c** | 94 | 2.08 (br) | – | 10.9 (dd, $J_{Rh,C} = 20.7$, $J_{P,C} = 7.9$ Hz) | 23.1 (d, 165.7 Hz) |
| **4** | 81 | poorly resolvable | 6.87. 6.62 (2.5 Hz) | −5.1 (d, $J_{P,C} = 9.5$ Hz) | 11.9 (s) |
| **6** | 93 | 1.82 (t, 3.2 Hz) | 6.72, 6.56 (2.2 Hz) | 12.7 (dd, $J_{Rh,C} = 19.2$, $J_{P,C} = 5.0$ Hz) | 74.2 (d, 186 Hz) |
| **8** | 65 | 1.65 (t, 4.0 Hz) | – | 8.51 (dd, $J_{Rh,C} = 23.3$, $J_{P,C} = 8.2$ Hz) | 26.0 (d, 159 Hz) |

Complexes **2a**, **3a**, and **6** were further characterized by X-ray crystallography (Figures 2–4 and Table 3). Each of these complexes has a square-planar geometry. The 2-methyleneimidazoline ligands behave very much like "carbon ylides", as evidenced by the end-on binding mode (Figures 2–4). Furthermore, the heterocyclic rings show all the structural attributes of imidazolium cations. Both **2a** (Figure 2) and **3a**




Scheme 5. Synthesis of rhodium 2-methylimidazoline complexes with different ring sizes.

slightly longer than typical aromatic C–C bonds and are close to C–C single bonds in length, which reinforces the ylidic character of the 2-methyleneimidazoline ligands.[15a]

Complex **6** cocrystallized with 0.5 equivalents of $CH_2Cl_2$. Two pseudo-enantiomers with slightly different bonds lengths and angles were detected in each asymmetric unit and only one is discussed here. The six-membered metallacycle in **6** adopts an "open-book" conformation (Figure 4), and this metallacycle must be fluxional and floppy in solution since both $RhCH_2$ and $NCH_2$ protons are equivalent in the $^1H$ NMR spectrum at room temperature. In contrast, as a result of a smaller ring size, the C9-M-P(1) (88.97(9)°) and Rh-C9-C10 angles (113.2(2)°) are smaller than those in **2a** or **3a**.

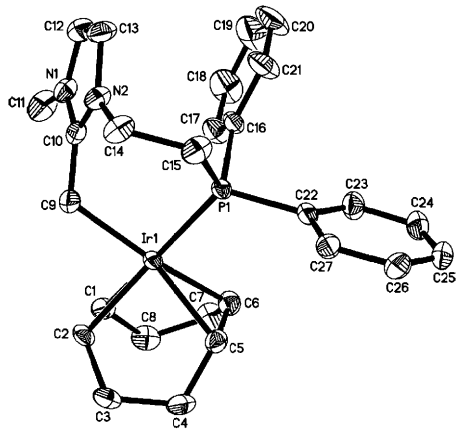



Figure 2. Molecular structure of **2a** (cation only) with thermal ellipsoids at 50% probability.

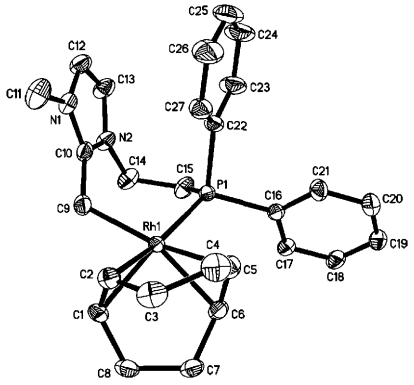



Figure 3. Molecular structure of **3a** (cation only) with thermal ellipsoids at 50% probability.

(Figure 3) adopt highly folded boat conformations and give nearly identical corresponding bond lengths and angles (Table 2). The metal–$CH_2$ distances are 2.145(3) and 2.147(2) Å for **2a** and **3a**, respectively, consistent with those reported for M–alkyl (M = Ir and Rh) bonds.[16,20] The C9–C10 bonds (1.449(4) Å for **2a** and 1.4450(3) Å for **3a**) are

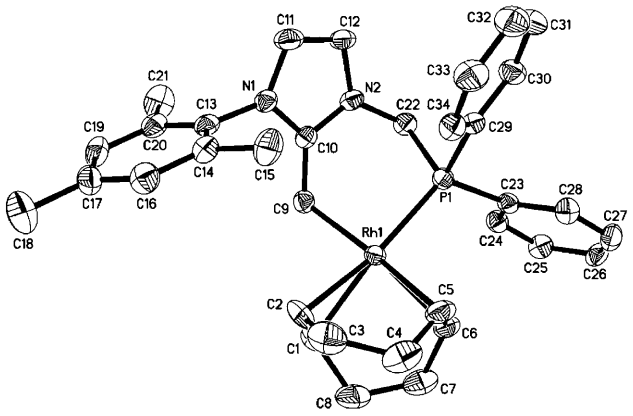



Figure 4. Molecular structure of **6**·0.5 $CH_2Cl_2$ (cation only) with thermal ellipsoids at 50% probability. Only one of the two independent molecules cocrystallized in the asymmetric unit is shown here.

Table 2. Selected bond lengths [Å] and angles [°] for **2a**, **3a**, and **6**·0.5 $CH_2Cl_2$.

| | **2a** | **3a** | **6**·0.5 $CH_2Cl_2$ |
|---|---|---|---|
| M–C9 | 2.145(3) | 2.147(2) | 2.141(3) |
| M–P1 | 2.2841(6) | 2.2816(5) | 2.2663(8) |
| C9–C10 | 1.449(4) | 1.450(3) | 1.431(4) |
| C9-M-P1 | 93.47(8) | 92.34(6) | 88.97(9) |
| M-C9-C10 | 120.69(19) | 121.06(14) | 113.2(2) |
| N1-C10-N2 | 106.1(2) | 106.33(17) | 106.5(3) |

To further understand the factors that control the selectivity of aliphatic versus aromatic C–H activation, we examined the effects of the anionic ligand (OR) in the reaction of [{Rh(cod)(OR)}$_2$] and **1a**. [{Rh(cod)(OR)}$_2$] (R = *t*Bu, Et, Me) was prepared in situ by treating [{Rh(cod)(OR)}$_2$] with two equivalents of NaOR or KOR. Ligand **1a** was then al-

Table 3. Crystallographic data for complexes **2a**, **3a**, and **6**·0.5 $CH_2Cl_2$.

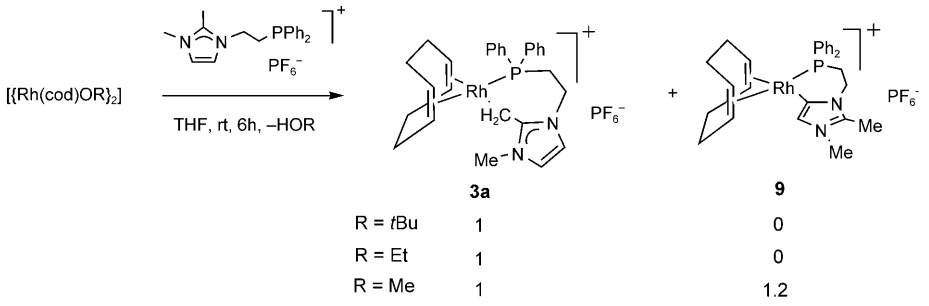
| | **2a** | **3a** | **6**·0.5 $CH_2Cl_2$ |
|---|---|---|---|
| empirical formula | $C_{27}H_{33}F_6N_2P_2Rh$ | $C_{27}H_{33}F_6N_2P_2Rh$ | $C_{34.5}H_{40}ClF_6N_2P_2Rh$ |
| formula weight [g mol$^{-1}$] | 753.69 | 664.40 | 796.98 |
| radiation, λ [Å] | | $Mo_{K\alpha}$, 0.71073 Å | |
| *T* [K] | | 173(2) | |
| crystal system | monoclinic | monoclinic | orthorhombic |
| space group | $P2_1/c$ | $P2_1/c$ | $Pna2_1$ |
| *a* [Å] | 10.3422(4) | 10.3242(4) | 19.7387(6) |
| *b* [Å] | 13.7466(5) | 13.7831(6) | 12.9197(3) |
| *c* [Å] | 19.3563(7) | 19.3904(8) | 27.3939(8) |
| *β* [°] | 96.117(2) | 96.086(2) | 90 |
| *V* [Å$^3$] | 2736.22(18) | 2743.7(2) | 6985.9(3) |
| *Z* | 4 | 4 | 8 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.830 | 1.608 | 1.516 |
| $\mu$ [mm$^{-1}$] | 5.058 | 0.800 | 0.717 |
| crystal size [mm] | 0.26×0.15×0.14 | 0.22×0.16×0.12 | 0.25×0.15×0.10 |
| no. of total/unique rflns | 41855/10269 | 69771/13999 | 198471/21335 |
| $R_{int}$ | 0.0398 | 0.0439 | 0.0541 |
| data, restraints, parameters | 10259, 0, 420 | 13999, 0, 344 | 21335, 1, 839 |
| *R*, $R_w$ (all data) | 0.0430, 0.0712 | 0.0540, 0.1125 | 0.0607, 0.0994 |
| GOF | 1.025 | 1.051 | 1.132 |

lowed to react with [{Rh(cod)(OR)}$_2$] in THF at room temperature. The NMR analysis of these products showed that only the C(sp$^3$)H activation product (**3a**) was obtained for R = *t*Bu or Et. However, for R = Me, C(sp$^2$)H activation product **9** is the major product (Scheme 6). $^1$H NMR analysis of the product mixture obtained for R = OMe also showed that the ratio of **3a** to **9** was essentially independent of time from 30 min to 1 day. Furthermore, heating (35 °C, 1 day) a solution of **3a** in $CD_2Cl_2$ or [$D_8$]THF in the presence of 3–5 equivalents of water or MeOH did not lead to formation of **9.** These results all point to the formation of **3a** and **9** from two parallel reactions, instead of conversion of one to the other. Attempts to isolate complex **9** from the product mixture failed. However, characteristic signals of **9** can be singled out from the $^1$H and $^{13}$C NMR spectra ($CD_2Cl_2$) of the mixture. The remaining C4/5−H of **9** resonates at $\delta$ = 6.10 ppm (s) and the $NCH_2$ signal shows up at $\delta$ = 5.08 ppm as a characteristic doublet of multiplets in the NMR spectrum. Two methyl groups with the correct signal integration were also detected at $\delta$ = 2.50 and 3.61 ppm. Importantly, the abnormal carbene signal of **9** resonates at $\delta$ = 149.9 ppm (dd, $^1J_{Rh,C}$ = 45 Hz, $^2J_{P,C}$ = 6.9 Hz), which is in line with an isostructural iridium complex.[12a] The fact that the ratio of **3a** to **9** decreases as the bulk of the R group decreases indicates that the selectivity of C(sp$^3$)H versus C(sp$^2$)H activation is likely controlled by the steric effects of these OR ligands. The conclusion that steric effect of the metal fragment is a key factor controlling the selectivity of C−H activation is consistent with recent theoretical studies on the C−H activation of 2-methylimidazolium compounds reported by Clot, Peris, and co-workers.[16]

It follows that strong C−H bonds often lead to even stronger C−M bonds.[21] However, the thermodynamics of the products obtained from cyclometalation of aliphatic versus aromatic C−H bonds can be hard to predict, particularly if the two metallacycles have the same ring size.[22] In evaluating the energetics of **3a** and **9** (or their isostructural iridium analogues), we reason that both a weaker M−$CH_2$ bond and a more floppy ring in **3a** (or **2a**) likely render it less thermodynamically stable.

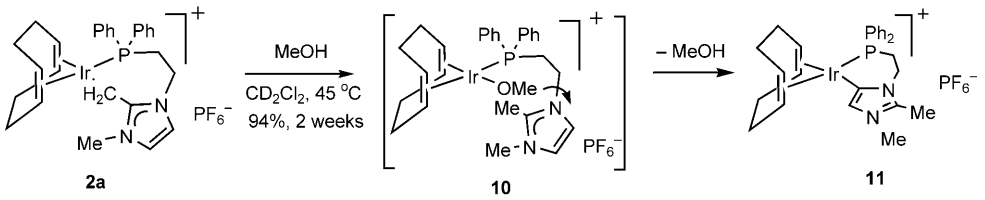
Although essentially no conversion of rhodium complex **3a** to **9** could be achieved when a solution of **3a** in $CD_2Cl_2$ was heated in the presence of MeOH or water, we did observe this type of conversion for the iridium analogue. Heating a solution of **2a** and MeOH in $CD_2Cl_2$ (5 equiv) at 45 °C in a sealed NMR tube slowly but rather cleanly gave abnormal carbene complex **11** in 94 % yield after two weeks. The identity of complex **11** was confirmed by an independent synthesis (Scheme 2):[12a] reaction of **1a** and [{Ir(cod)Cl}$_2$] gave an iridium hydride complex, which was treated with $Cs_2CO_3$ to alternatively yield **11**. We propose that **2a** undergoes protonolysis by MeOH to give iridium(I) phosphine methoxide intermediate **10**. Subsequent proton abstraction at the aryl CH group then gives the corresponding abnormal carbene **11** as the thermodynamic product (Scheme 7).

To examine the plausibility of the proposed conversion of **2a** to **11**, a phenyl-blocked phosphine imidazolium ion was allowed to react with [{Ir(cod)(OMe)}$_2$] in THF at room temperature (Scheme 8). Here the 2-phenyl group is a blocking group, and abnormal NHC complex **12** was isolated in high yield. In this reaction, an intermediate phosphine complex analogous to intermediate **10** (Scheme 7) was observed ($\delta$($^{31}$P) = 22.2 ppm), and in the absence of any 2-methyl group imidazole ring C4/5−H activation is the only pathway. These results reinforce the notion that a 2-methyl group of imidazolium ions might not be a good choice for an innocent blocking group in the preparation of abnormal NHC complexes and in ionic liquid applications.[23]

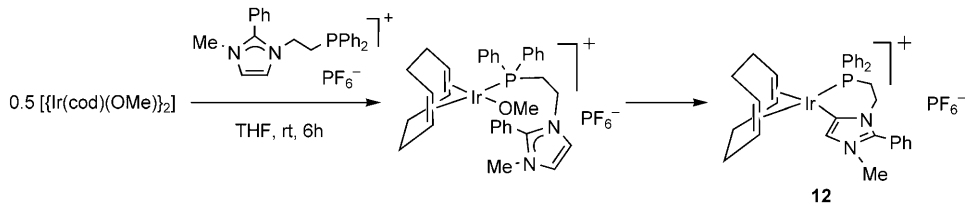



Scheme 6. Effects of alkoxide groups on the selectivity of C−H activation.




Scheme 7. Proposed conversion of **2a** to **11**.




Scheme 8. Synthesis of an iridium 2-methylimidazoline complex by using a phenyl blocking group.

## Conclusions

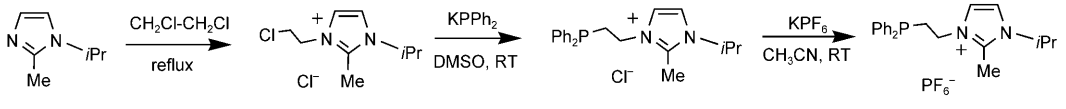
There are only a few reports on the synthesis and structures of transition metal complexes of 2-methyleneimidazoles. We have now synthesized iridium, palladium, and rhodium complexes stabilized by 2-methyleneimidazoles by selective activation of a 2-methyl C–H bond with chelation assistance by phosphine ligands. Metallacycles with six, seven, and eight members were obtained by reaction of phosphine-tethered 2-methylimidazolium ions (**1a–c**, **5**, and **7**) and $[\{M(cod)X\}_2]$ (M = Rh, Ir; X = alkoxyl, Cl) or $[\{Pd(allyl)Cl\}_2]$. Representative complexes were characterized by X-ray crystallography. The selectivity of aliphatic C($sp^3$)H versus aromatic C($sp^2$)H activation could be adjusted by means of the steric bulk of the OR ligand, which could be regarded as an internal base. A sterically bulkier OR ligand favors activation of the 2-methyl C–H bond. Experimental results also confirmed that a seven-membered iridium C($sp^3$)H activation product is the kinetic product, while the six-membered iridium abnormal carbene complex, resulting from the activation of a C($sp^2$)–H bond, is the thermodynamic product. Studies on catalytic applications of these 2-methylimidazoline complexes are underway.

## Experimental Section

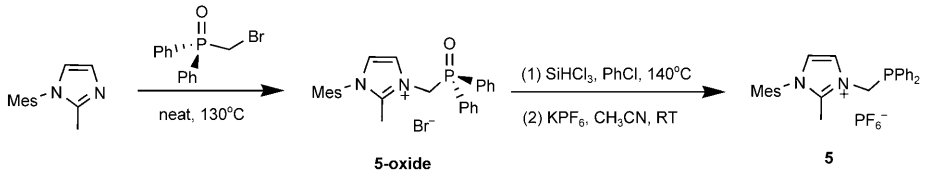
**General considerations**: All manipulations were carried out by standard Schlenk techniques or in a nitrogen-filled dry box, except where otherwise noted. All solvents were distilled under $N_2$ before use and were stored in a dry box. $CDCl_3$ was dried over 4 Å molecular sieves. $CD_2Cl_2$ and $[D_6]$DMSO were obtained in sealed ampoules from CIL and were used without further purification. Air-sensitive compounds were stored and weighed in a dry box. All other chemicals were purchased from Aldrich and used as received. Compound **1a** was synthesized by following a literature report.[12a] NMR spectra were recorded on a Bruker NMR spectrometer (300, 400, or 500 MHz) at 298 K unless otherwise specified. The chemical shifts are given as dimensionless $\delta$ values and is referenced to $SiMe_4$ for $^1H$ and $^{13}C$ NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University; HRMS spectra were obtained in an EI or ESI mode on a Finnigan MAT95XP GC/HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer.

**3-(2-Chloroethyl)-1-isopropyl-2-methylimidazolium chloride**: 1-Isopropyl-2-methylimidazole (1.0 g, 8.05 mmol) was dissolved in 1,2-dichloroethane (15 mL), and the mixture was stirred under reflux for 16 h. All volatile substances were removed under reduced pressure, and the residue obtained was washed with diethyl ether to give 3-(2-chloroethyl)-1-isopropyl-2-methylimidazolium chloride as a white solid. Yield: 85% (1.53 g, 6.8 mmol). $^1H$ NMR (400 MHz, $[D_6]$DMSO): $\delta = 7.99$ (s, 1H, imidazole H4/5), 7.91 (s, 1H, imidazole H4/5), 4.69 (septet, $J = 6.4$ Hz, 1H, CH of *i*Pr), 4.55 (t, $J = 5.0$ Hz, 2H, $CH_2$), 4.03(t, $J = 5.0$ Hz, 2H, $CH_2$), 2.67 (s, $CH_3$), 1.37 ppm (d, $J = 6.4$ Hz, 6H, $2CH_3$); $^{13}C$ NMR (100 MHz, $[D_6]$DMSO): $\delta = 144.4$, 122.8, 118.5, 50.6, 49.1, 43.7, 22.4, 10.2 ppm; HRMS (ESI$^+$): 187.1031; calcd for $[C_9H_{16}ClN_2^+]$ 187.1002.

**3-[2-(Diphenylphosphino)ethyl]-1-isopropyl-2-methylimidazolium chloride (1b-Cl)**: A solution of $KPPh_2$ in THF (0.5 M, 4.7 mL, 2.35 mmol) was added dropwise to a solution of 3-(2-chloroethyl)-1-isopropyl-2-methylimidazolium chloride (500 mg, 2.24 mmol) in DMSO (8 mL) . The mixture was stirred at room temperature for 5 h, followed by removal of DMSO under vacuum (ca. 0.01 mmHg). Methanol (5 mL) was then added to quench the reaction and was removed under reduced pressure. The residue was dissolved in dichloromethane and filtered to remove any insoluble material. The filtrate was evaporated under vacuum to dryness to afford **1b-Cl** as a white solid after successive washing with diethyl ether. Yield: 710 mg (1.9 mmol, 85%). $^1H$ NMR (500 MHz, $CDCl_3$): $\delta =$ 7.78 (d, $J = 2.1$ Hz, 1H, imidazole H4/5), 7.35–7.38(m, 4H, $PPh_2$), 7.34 (d, $J = 2.1$ Hz, 1H, imidazole H4/5), 7.30–7.32 (m, 6H, $PPh_2$), 4.63 (septet, $J = 6.6$ Hz, 1H, CH of *i*Pr), 4.45–4.50 (m, 2H, $NCH_2$), 2.69 (apparent t, $J = 7.2$ Hz, 2H, $PCH_2$), 2.68 ppm (s, 3H, $CH_3$), 1.43 (d, $J = 6.7$ Hz, 6H, $2CH_3$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -21.74$ ppm (s, $PPh_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 142.4$ (s, imidazole C2), 136.0 (d, $J_{P,C} =$ 11.5 Hz, *ipso*-$PPh_2$), 132.6 (d, $J_{P,C} = 19.3$ Hz, $PPh_2$), 129.4 (s, $PPh_2$), 128.9 (d, $J_{P,C} = 7.1$ Hz, $PPh_2$), 122.7 (s, C4/5), 117.6 (s, C4/5), 51.1 (s, CH of *i*Pr), 46.4 (d, $J_{P,C} = 20.9$ Hz, $CH_2$), 28.4 (d, $J_{P,C} = 15.7$ Hz, $CH_2$), 22.6 (s, $CH_3$ of *i*Pr) , 10.8 ppm (s, $CH_3$). No satisfactory microanalysis could be obtained



for **1b-Cl**) due to its hygroscopicity. The microanalysis of the $PF6^-$ salt gave satisfactory data (see data for **1b**).




5-oxide 5

**Compound 1b**: $KPF_6$ (900 mg, 4.9 mmol) was added to a solution of **1b-Cl** (300 mg, 0.81 mmol) in $CH_3CN$ (10 mL) and the mixture was stirred at room temperature for 8 h. Acetonitrile was then removed under reduced pressure and dichloromethane (15 mL) was added to the resulting residue. A clear solution was obtained after filtration. Removal of the solvent followed by addition of diethyl ether gave **1b** as a white solid in 96% yield (373 mg, 0.77 mmol). $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 7.37–7.40$ (m, 4H, $PPh_2$), 7.33–7.35 (m, 6H, $PPh_2$), 7.15 (d, $J = 2.2$ Hz, 1H, imidazole H4/5), 7.08 (d, $J = 2.2$ Hz, 1H, imidazole H4/5), 4.40 (septet, $J = 6.6$ Hz, 1H, CH of *i*Pr), 4.15–4.19 (m, 2H, $NCH_2$), 2.57 (apparent t, $J = 7.6$ Hz, 2H, $PCH_2$), 2.41 (s, 3H, $CH_3$), 1.38 ppm (d, $J = 6.6$ Hz, 6H, $2CH_3$); $^{31}P\{^1H\}$ NMR (201 MHz, $CDCl_3$): $\delta = -22.1$ (s, $PPh_2$), $-144.6$ ppm (septet, $J_{P,F} = 706$ Hz, $PF_6$); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta = 142.5$ (s, imidazole C2), 136.0 (d, $J_{P,C} = 11.5$ Hz, *ipso*-$PPh_2$), 132.6 (d, $J_{P,C} = 19.4$ Hz, $PPh_2$), 129.5 (s, $PPh_2$), 128.9 (d, $J_{P,C} = 7.1$ Hz, $PPh_2$), 121.5 (s, imidazole C4/5), 117.3 (s, imidazole C4/5), 51.0 (s, CH of *i*Pr), 46.0 (d, $J_{P,C} = 23$ Hz, $CH_2$), 28.4 (d, $J_{P,C} = 15.6$ Hz, $CH_2$), 22.1 (s, $CH_3$ of *i*Pr) , 9.4 ppm (s, $CH_3$); elemental analysis calcd (%) for $C_{21}H_{26}F_6N_2P_2$ (482.4): C 52.29, H 5.43, C 5.81; found: C 52.13, H 5.51, C 5.96.

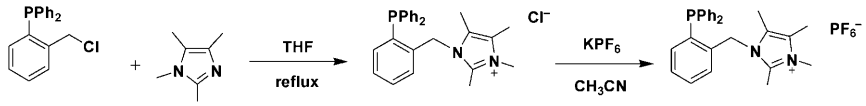
**3-(2-Chloroethyl)-1,2,4,5-teramethylimidazolium chloride**: 3-(2-chloroethyl)-1,2,4,5-teramethylimidazolium chloride was synthesized as a white solid in 86% yield by following a method directly analogous to that for 3-(2-chloroethyl)-1-isopropyl-2-methylimidazolium chloride. $^1H$ NMR (500 MHz, [D6]DMSO): $\delta = 4.56$ (t, $J = 5.8$ Hz, 2H, $NCH_2$), 4.00 (t, $J = 5.7$ Hz, 2H, $ClCH_2$), 3.66 (s, 3H, $CH_3$), 2.68 (s, 3H, $CH_3$), 2.29 (s, 3H, $CH_3$), 2.24 ppm (s, 3H, $CH_3$); $^{13}C$ NMR (125 MHz, [D6]DMSO): 144.1, 126.2, 125.4, 46.3, 43.3, 32.7, 10.8, 8.7, 8.5 ppm; HRMS ($ESI^+$): 187.1028; calcd for $[C_9H_{16}ClN_2^+]$: 187.1002.

**3-[2-(Diphenylphosphino)ethyl]-1,2,4,5-teramethylimidazolium chloride (1c-Cl)**: Compound **1c-Cl** was synthesized as a white solid in 91% yield by following a method directly analogous to that for **1b-Cl**. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.15–7.38$ (m, 10H, $PPh_2$), 4.20–4.24 (m, 2H, $NCH_2$), 3.61 (s, 3H, $NCH_3$), 2.65 (s, 3H, $CH_3$), 2.46 (apparent t, $J = 7.2$ Hz, 2H, $PCH_2$), 2.08 (s, 3H, $CH_3$), 2.07 ppm (s, 3H, $CH_3$); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): $\delta = -21.9$ ppm (s, $PPh_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$): 142.6 (s, imidazole C2), 136.1 (d, $J_{P,C} = 11.5$ Hz, *ipso*-$PPh_2$), 132.6 (d, $J_{P,C} = 19.2$ Hz, $PPh_2$), 129.5 (s, $PPh_2$), 128.8 (d, $J_{P,C} = 7.7$ Hz, $PPh_2$), 126.1 (s, imidazole C4/5), 124.8 (s, imidazole C4/5), 43.4 (d, $J_{P,C} = 23.0$ Hz, $NCH_2$), 32.8 (s, $CH_3$), 28.8 (d, $J_{P,C} = 17.3$ Hz, $PCH_2$), 11.6 (s, $CH_3$), 10.1(s, $CH_3$), 8.9 ppm (s, $CH_3$). No satisfactory microanalysis could be obtained for ligand **1c-Cl** due to its hygroscopicity. The microanalysis of the $PF6^-$ salt gave satisfactory data (see **1c**).

**Compound 1c**: Compound **1c** was synthesized as a white solid in 95% yield by following a method directly analogous to that for **1b**. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.34–7.43$(m, 10H, CH of $PPh_2$), 4.04–4.11 (m, 2H, $NCH_2$), 3.45 (s, 3H, $NCH_3$), 2.47 (apparent t, $J = 7.9$ Hz, 2H, $PCH_2$), 2.39 (s, 3H, $CH_3$), 2.08 (s, 3H, $CH_3$), 2.07 ppm (s, 3H, $CH_3$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -22.1$ (s, $PPh_2$), $-144.1$ ppm (septet, $J_{P,F} = 708$ Hz, $PF_6$); $^{13}C$ NMR (75 MHz, $CDCl_3$): 141.9 (s, imidazole C2), 136.1 (d, $J_{P,C} = 11.2$ Hz, *ipso*-$PPh_2$), 132.5 (d, $J_{P,C} = 19.3$ Hz, $PPh_2$), 129.5 (s, $PPh_2$), 128.8 (d, $J_{P,C} = 7.1$ Hz, $PPh_2$), 126.2 (s, imidazole C4/5), 124.6 (s, imidazole C4/5), 42.8 (d, $J_{P,C} = 24.9$ Hz, $NCH_2$), 31.7 (s, $CH_3$), 28.4 (d, $J_{P,C} = 15.7$ Hz, $PCH_2$), 10.0 (s, $CH_3$), 10.1(s, $CH_3$) , 8.4 ppm (s, $CH_3$); elemental analysis (%) calcd for $C_{21}H_{26}F_6N_2P_2$ (482.4): C 52.29, H 5.43, C 5.81; found: C 52.41, H 5.48, C 5.94.

**Compound 5-oxide**: $Ph_2P(O)CH_2Br$ (1 g, 3.4 mmol) and 1-mesityl-2-methylimidazole (700 mg, 3.5 mmol) were charged into a vial, which was sealed and heated at 130°C for 3 d. The residue was dissolved in dichloromethane (1 mL), followed by addition of diethyl ether (10 mL) to afford a brown solid. Analytically pure **5-oxide** could be obtained by successive washing with diethyl ether. Yield: 77% (1.3 g, 2.6 mmol). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 8.22–8.24$ (m, 4H, $PPh_2$), 8.08 (s, 1H, imidazole H4/5), 7.55–7.59 (m, 6H, $PPh_2$), 7.03 (s, 2H, mesityl), 6.80 (s, 1H, imidazole H4/5), 6.08 (d, $J_{P,H} = 5.0$ Hz, 2H, $NCH_2$), 2.56 (s, 3H, $CH_3$), 2.36 (s, 3H, $CH_3$), 1.91 ppm (s, 6H, $2CH_3$); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): $\delta = 28.1$ ppm (s, $P(O)Ph_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 146.3$, 141.9, 134.6, 133.2 (d, $J_{P,C} = 1.9$ Hz, *p*-$PPh_2$), 131.7 (d, $J_{P,C} = 10.5$ Hz, $PPh_2$), 130.1, 129.9, 129.4 (d, $J_{P,C} = 12.4$ Hz, $PPh_2$), 128.4 (d, $J_{P,C} = 102.1$ Hz, *ipso*-$PPh_2$), 125.0, 120.6, 50.1 (d, $J_{P,C} = 65.8$ Hz, $NCH_2$), 21.2, 17.4, 10.9 ppm; HRMS ($ESI^+$): 415.1929; calcd for $[C_{26}H_{28}N_2OP^+]$ 415.1939.

**Compound 5**. A mixture of **5-oxide** (1.0 g, 2.0 mmol) and anhydrous chlorobenzene (15 mL) was placed in a glass pressure tube. Trichlorosilane (1.6 mL, 11.5 mmol) was added to the suspension at room temperature. The mixture was then sealed under nitrogen, heated to 120°C for 3 h, and cooled to room temperature. After addition of dichloromethane (30 mL), any excess of trichlorosilane was quenched by careful addition of degassed aqueous NaOH solution (10%) at 0°C. The organic phase was separated and the aqueous phase washed with dichloromethane. The dichloromethane layers were combined and dried with $Na_2SO_4$. Dichloromethane was then removed under vacuum and the residue was washed with diethyl ether to afford a white solid. This white solid was then dissolved in acetonitrile (10 mL), to which was added $KPF_6$ (2 g, 10.7 mmol). The mixture was stirred at room temperature for 10 h. Acetonitrile was then removed under vacuum and dichloromethane (15 mL) added to the residue. A clear solution was obtained after filtration. Removal of the solvent followed by addition of diethyl ether gave **5** as a white solid. Yield of these two steps: 48% (520 mg, 0.96 mmol). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.48–7.52$ (m, 4H, $PPh_2$), 7.43–7.45 (m, 6H, $PPh_2$), 7.27 (d, $J = 1.8$ Hz, 1H, imidazole H4/5), 7.03 (s, 2H, mesityl), 7.01 (d, $J = 1.9$ Hz, 1H, imidazole H4/5), 5.02 (d, $J_{P,H} = 5.9$ Hz, 2H, $NCH_2$), 2.36 (s, 3H), 2.02 (s, 3H, $CH_3$), 1.91 ppm (s, 6H, $2CH_3$); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): $\delta = -14.4$ (s, $PPh_2$), $-144.5$ ppm (septet, $J_{P,F} = 709$ Hz, $PF_6$); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 144.9$ (s), 141.6 (s), 134.8 (s), 133.2 (d, $J_{P,C} = 10.8$ Hz, *ipso*-$PPh_2$), 133.1 (d, $J_{P,C} = 19.4$ Hz, $PPh_2$), 130.5 (s), 130.1 (s), 129.9 (s), 129.3 ($J_{P,C} = 7.1$ Hz, $PPh_2$), 122.9 ($J_{P,C} = 3.6$ Hz, imidazole C4/5), 121.4 (s), 49.5 (d, $J_{P,C} = 18.7$ Hz, $NCH_2$), 21.1 (s), 17.1 (s), 9.85 ppm (s); elemental analysis (%) calcd for $C_{26}H_{28}F_6N_2P_2$ (544.5): C 57.36, H 5.18, C 5.15; found: C 57.19, H 5.31, C 5.47.




7-Cl 7

**Compound 7-Cl**: [2-(Chloromethyl)phenyl]diphenylphosphine (310 mg, 1 mmol) and 1,2,4,5-tetramethylimidazole (125 mg, 1 mmol) were dissolved in THF (5 mL), and the mixture heated to reflux under nitrogen for 24 h. THF was removed under vacuum and the residue washed with diethyl ether to give **7-Cl** as a white solid in 74% yield (322 mg, 0.74 mmol). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.30–7.40$ (m, 8H), 7.14–7.19 (m, 4H), 7.04–7.07 (m, 1H), 6.91–6.94 (m, 1H), 5.38 (s, 2H, $CH_2$),

3.71 (s, 3H, $NCH_3$), 2.62 (s, 3H, $CH_3$), 2.12 (s, 3H, $CH_3$), 2.03 ppm (s, 3H, $CH_3$);. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -15.5$ (s, $PPh_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 143.6$ (s, imidazole C2), 136.6 (d, $J_{P,C} = 23.4$ Hz, *ipso*-$PPh_2$), 135.3 (d, $J_{P,C} = 16.3$ Hz, $PPh_2$), 134.3 (s), 134.1 (d, $J_{P,C} = 7.8$ Hz, $PPh_2$), 133.8 (d, $J_{P,C} = 19.7$ Hz, $PPh_2$), 130.1 (s), 129.5 (s), 129.1 (s), 128.8 (d, $J_{P,C} = 7.3$ Hz, $PPh_2$), 127.6 (d, $J_{P,C} = 5.3$ Hz, $PPh_2$), 126.2 (s, imidazole C4/5), 125.6 (s, imidazole C4/5), 48.0 (d, $J_{P,C} = 25.5$ Hz, $CH_2$), 33.0(s, $NCH_3$), 11.7 (s, $CH_3$), 9.10 (s, $CH_3$), 8.92 ppm (s, $CH_3$). No satisfactory microanalysis could be obtained for ligand **7**-Cl due to its hygroscopicity. The microanalysis of the $PF_6^-$ analogue gave satisfactory data (see compound **7**).

**Compound 7**: Compound **7** was synthesized as a white solid in 94% yield by a method directly analogous to that for **1b**. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.30$–$7.46$ (m, 6H), 7.21–7.25 (m, 6H), 6.91–6.97 (m, 2H), 5.31 (s, 2H, $CH_2$), 3.54 (s, 3H, $NCH_3$), 2.37 (s, 3H, $CH_3$), 2.14 (s, 3H, $CH_3$), 2.02 ppm (s, 3H, $CH_3$); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): $\delta = -16.2$ (s, $PPh_2$), $-144.7$ ppm (septet, $J_{P,F} = 710$ Hz, $PF_6$); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 142.8$ (s, imidazole C2), 136.3 (d, $J_{P,C} = 23.3$ Hz, *ipso*-$PPh_2$), 135.1 (d, $J_{P,C} = 16.2$ Hz, $PPh_2$), 134.2 (s), 134.0 (d, $J_{P,C} = 6.2$ Hz, $PPh_2$), 133.8 (d, $J_{P,C} = 19.7$ Hz, $PPh_2$), 130.4 (s), 129.6 (s), 129.1 (s), 128.8 (d, $J_{P,C} = 7.3$ Hz, $PPh_2$), 127.0 (d, $J_{P,C} = 5.1$ Hz, $PPh_2$), 126.5 (s, imidazole C4/5), 125.6 (s, imidazole C4/5), 48.0 (d, $J_{P,C} = 25.5$ Hz, $CH_2$), 32.0 (s, $NCH_3$), 10.4 (s, $CH_3$), 8.86 (s, $CH_3$), 8.58 ppm (s, $CH_3$); elemental analysis (%) calcd for $C_{26}H_{28}F_6N_2P_2$ (544.5): C 57.36, H 5.18, C 5.15; found: C 57.29, H 5.11, C 5.09.

**General synthetic methods for 2-methyleneimidazoline complexes**: Method 1: Phosphine imidazolium ligand (0.2 mmol) was added to a solution of $[\{M(cod)Cl\}_2]$ (M = Rh, Ir; 0.1 mmol) or $[Pd(allyl)Cl]_2$ in THF (6 mL). The resulting solution was stirred at RT for 30 min. The solution was then cooled to −78 °C, and *t*BuOK (1 M THF solution, 0.21 mmol) was added. The mixture was stirred at −78 °C for 2 h and was slowly warmed to RT. All volatile substances were then removed under reduced pressure. $CH_2Cl_2$ (5 mL) was added to the residue, and the inorganic salt removed by filtration through Celite. The solution obtained was then concentrated to ca. 0.5 mL, followed by washing with pentane (2 × 5 mL) to give the final product.

Method 2: *t*BuOK (0.11 mL, 1 M in THF, 0.11 mmol) was slowly added to a solution of $[\{M(cod)Cl\}_2]$(M=Rh, Ir; 0.05 mmol) in THF (5 mL). The solution was stirred for 2 h followed by addition of a suspension of a phosphine imidazolium salt (0.1 mmol) in THF. The mixture was stirred at room temperature for another 6 h, followed by removal of all volatiles under reduced pressure. $CH_2Cl_2$ (5 mL) was added to the residue, and the inorganic salt removed by filtration through Celite to give a solution. The solvent was removed and the residue washed with pentane or $Et_2O$ (3 × 5 mL) to give the final products.

**Complex 2a**: Complex **2a** was synthesized as a red solid by following method 1 or 2. Yield: 91% (68.5 mg, 0.091 mmol, method 2). Single crystals of **2a** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether to a solution in $CH_2Cl_2$ after 7 days at −20 °C. $^1H$ NMR (300 MHz, [$D_6$]acetone): $\delta = 7.47$–$7.55$ (m, 10H, $PPh_2$), 6.81 (d, $J = 2.2$ Hz, 1H, imidazole H4/5), 6.38 (d, $J = 2.1$ Hz, 1H, imidazole H4/5), 4.83–4.86 (m, 2H, COD), 4.48–4.58 (m, 2H, $NCH_2$), 3.62 (s, 3H, $NCH_3$), 3.04–3.11 (m, 2H, $PCH_2$), 2.88 (d, $J = 1.6$ Hz, 2H, $CH_2Ir$), 2.81–2.83 (m, 2H, COD), 2.21–2.31 (m, 2H, COD), 1.95–2.15 (m, 4H, COD), 1.66–1.75 ppm (m, 2H, COD); $^{31}P\{^1H\}$ NMR (121 MHz, [$D_6$]acetone): $\delta = 15.4$ (s, $PPh_2$), $-143.6$ ppm (septet, $J_{P,F} = 703.8$ Hz, $PF_6$); $^{13}C$ NMR (100 MHz, [$D_6$]acetone): $\delta = 159.9$ (s, imidazole C2), 133.5 (d, $J_{P,C} = 13.0$ Hz, *o*- or *m*-$PPh_2$), 130.9 (d, $J_{P,C} = 2.0$ Hz, *p*-$PPh_2$), 130.3 (d, $J_{P,C} = 49.3$ Hz, *ipso*-$PPh_2$), 128.4 (d, $J_{P,C} = 10.0$ Hz, *o*- or *m*-$PPh_2$), 118.7 (s, imidazole C4/5), 117.4 (s, imidazole C4/5), 88.9 (d, $J_{P,C} = 10.0$ Hz, CH of COD), 63.7 (s, CH of COD), 42.8 (s, $NCH_2$), 33.5 (s, $NCH_3$), 31.7 (d, $J_{P,C} = 3.0$ Hz, $CH_2$ of COD), 30.4 (s, $CH_2$ of COD), 20.1 (d, $J_{P,C} = 29.4$ Hz, $PCH_2$), 13.9 ppm (d, $J_{P,C} = 5.0$ Hz, $IrCH_2$); elemental analysis (%) calcd for $C_{27}H_{33}F_6IrN_2P_2$ (753.7): C 43.03, H 4.41, C 3.72; found: C 43.39, H 4.53, C 3.91.

**Complex 2b**: Complex **2b** was synthesized as a red solid by following method 1 or 2. Yield: 88% (68.7 mg, 0.088 mmol, method 2). $^1H$ NMR (400 MHz, [$D_6$]acetone): $\delta = 7.48$–$7.58$ (m, 10H, $PPh_2$), 6.97 (d, $J = 2.0$ Hz, 1H, imidazole H4/5), 6.78 (d, $J = 2.0$ Hz, 1H, imidazole H4/5), 4.82 (br, 2H, COD), 4.52–4.58 (m, 2H, $NCH_2$), 3.64 (septet, $J = 6.6$ Hz, 1H, CH of *i*Pr), 3.08–3.12 (m, 2H, $PCH_2$), 2.96 (d, $J = 1.7$ Hz, 2H, $CH_2Ir$), 2.85 (br, 2H, COD), 2.11–2.29 (m, 2H, COD), 1.98–2.13 (m, 4H, COD), 1.71–1.80 (m, 2H, COD), 1.37 ppm (d, $J = 6.7$ Hz, 6H, $2CH_3$); $^{31}P\{^1H\}$ NMR (121 MHz, [$D_6$]acetone): $\delta = 13.2$ (s, $PPh_2$), $-144.7$ ppm (septet, $J_{P,F} = 705$ Hz, $PF_6$); $^{13}C$ NMR (75 MHz, [$D_6$]acetone): $\delta = 158.6$ (s, imidazole C2), 133.3 (d, $J_{P,C} = 10.9$ Hz, *o*- or *m*-$PPh_2$), 130.8 (d, $J_{P,C} = 2.1$ Hz, *p*-$PPh_2$), 130.4 (d, $J_{P,C} = 49.1$ Hz, *ipso*-$PPh_2$), 128.6 (d, $J_{P,C} = 9.9$ Hz, *o*- or *m*-$PPh_2$), 118.7 (s, C4/5), 113.8 (s, C4/5), 88.5 (d, $J_{P,C} = 13.2$ Hz, CH of COD), 64.1 (s, CH of COD), 49.1 (s, CH of *i*Pr), 42.7 (s, $NCH_2$), 31.6 (d, $J_{P,C} = 2.8$ Hz, $CH_2$ of COD), 30.5 (s, $CH_2$ of COD), 21.4 (s, $CH_3$), 19.5 (d, $J_{P,C} = 29.5$ Hz, $PCH_2$), 13.9 ppm (d, $J_{P,C} = 4.9$ Hz, $IrCH_2$); elemental analysis (%) calcd for $C_{29}H_{37}F_6IrN_2P_2$ (781.8): C 44.55, H 4.77, C 3.58; found: C 44.72, H 4.67, C 3.68.

**Complex 3a**. Complex **3a** was synthesized as a yellow solid by following method 1 or 2. Yield: 92% (61 mg, 0.0918 mmol, method 2). Single crystals of **3a** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether to a solution in THF after 2 d at room temperature. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta = 7.40$–$7.51$ (m, 10H, $PPh_2$), 6.46 (d, $J = 2.2$ Hz, 1H, imidazole H4/5), 6.03 (d, $J = 2.0$ Hz, 1H, imidazole H4/5), 5.16–5.18 (m, 2H, COD), 4.26–4.34 (m, 2H, $NCH_2$), 3.37–3.38 (m, 2H, COD), 3.35 (s, 3H, $NCH_3$), 2.60–2.67 (m, 2H, $PCH_2$), 2.43–2.49 (m, 2H, COD), 2.23–2.33 (m, 4H, COD), 2.08–2.09 (m, 2H. $RhCH_2$), 2.02–2.04 (m, 1H, COD), 1.83–1.87 ppm (m, 1H, COD); $^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$): $\delta = 24.5$ (d, $J_{Rh,P} = 164.9$ Hz, $PPh_2$), $-143.8$ (septet, $J_{P,F} = 708$ Hz, $PF_6$); $^{13}C$ NMR (75 MHz, $CD_2Cl_2$): $\delta = 159.2$ (s, imidazole C2), 133.1 (d, $J_{P,C} = 11.9$ Hz, *o*- or *m*-$PPh_2$), 130.9 (d, $J_{P,C} = 1.9$ Hz, *p*-$PPh_2$), 130.8 (d, $J_{P,C} = 40.3$ Hz, *ipso*-$PPh_2$), 128.5 (d, $J_{P,C} = 9.6$ Hz, *o*- or *m*-$PPh_2$), 118.2 (s, imidazole C4/5), 116.7 (s, imidazole C4/5), 100.5 (dd, $J_{P,C} = 10.8$ Hz, $J_{Rh,C} = 8.0$ Hz, CH of COD), 80.7 (d, $J_{Rh,C} = 9.2$ Hz, CH of COD), 42.9 (s, $NCH_2$), 34.0 (s, $CH_3$), 31.5 (d, $J_{P,C} = 2.3$ Hz, $CH_2$ of COD), 30.0 (s, $CH_2$ of COD), 21.1 (d, $J_{P,C} = 21.6$ Hz, $PCH_2$), 10.0 ppm (dd, $J_{P,C} = 8.0$ Hz, $J_{Rh,C} = 20.2$ Hz, $RhCH_2$); elemental analysis (%) calcd for $C_{27}H_{33}F_6N_2P_2Rh$ (664.4): C 48.81, H 5.01, C 4.22; found 48.69, H 5.14, C 4.09.

**Complex 3b**: Complex **3b** was synthesized as a yellow solid by following method 1 or 2. Yield: 91% (63 mg, 0.091 mmol, method 2). $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta = 7.40$–$7.53$ (m, 10H, $PPh_2$), 6.64 (d, $J = 2.3$ Hz, 1H, imidazole H4/5), 6.35 (d, $J = 2.3$ Hz, 1H, imidazole H4/5), 5.12 (br, 2H, COD), 4.27–4.34 (m, 2H, $NCH_2$), 4.21 (septet, $J = 6.7$ Hz, 1H, CH of *i*Pr), 3.40–3.41 (m, 2H, COD), 2.62–2.69 (m, 2H, $PCH_2$), 2.42–2.50 (m, 2H, COD), 2.26–2.30 (m, 4H, COD), 2.13 (apparent t, $J = 2.6$ Hz, 2H, $RhCH_2$), 1.99–2.11 (m, 1H, COD), 1.83–1.86 (m, 1H, COD), 1.38 ppm (d, $J = 6.7$ Hz, 6H, $CH_3$); $^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$): $\delta = 21.0$ (d, $J_{Rh,P} = 165.2$ Hz, $PPh_2$), $-143.8$ ppm (septet, $J_{P,F} = 708$ Hz, $PF_6$); $^{13}C$ NMR (75 MHz, $CD_2Cl_2$): $\delta = 157.9$ (s, imidazole C2), 133.1 (d, $J_{P,C} = 11.6$ Hz, *o*- or *m*-$PPh_2$), 131.0 (d, $J_{P,C} = 39.2$ Hz, *ipso*-$PPh_2$), 130.7 (d, $J_{P,C} = 2.0$ Hz, *p*-$PPh_2$), 128.7 (d, $J_{P,C} = 9.5$ Hz, *o*- or *m*-$PPh_2$), 118.0 (s, imidazole C4/5), 113.2 (s, imidazole C4/5), 99.9 (dd, $J_{P,C} = 10.8$ Hz, $J_{Rh,C} = 8.1$ Hz, CH of COD), 81.1 (d, $J_{Rh,C} = 9.1$ Hz, CH of COD), 49.1 (s, CH of *i*Pr), 42.7 (s, $NCH_2$), 31.4 (d, $J_{P,C} = 2.4$ Hz, $CH_2$ of COD), 30.5 (s, $CH_2$ of COD), 21.8 (s, $CH_3$), 20.8 (d, $J_{P,C} = 21.7$ Hz, $PCH_2$), 9.8 ppm (dd, $J_{P,C} = 8.2$ Hz, $J_{Rh,C} = 20.9$ Hz, $RhCH_2$); elemental analysis (%) calcd for $C_{29}H_{37}F_6N_2P_2Rh$ (692.5): C 50.30, H 5.39, C 4.05; found: C 50.42, H 5.28, C 4.17.

**Complex 3c**. Complex **3c** was synthesized as a yellow solid by following method 1 or 2. Yield: 94% (65.1 mg, 0.094 mmol, method 2). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 7.42$–$7.48$ (m, 10H, $PPh_2$), 5.17 (br, 2H, COD), 4.29–4.36 (m, 2H, $NCH_2$), 3.35 (br, 2H, COD), 3.19 (s, 3H, $CH_3$), 2.61–2.65 (m, 2H, $PCH_2$), 2.46–2.49 (m, 2H, COD), 2.24–2.31 (m, 4H, COD), 2.08 (m, 2H, $RhCH_2$), 2.03–2.06 (m, 1H, COD), 1.88 (s, 3H, $CH_3$), 1.84–1.87 (m, 1H, COD), 1.57 ppm (s, 3H, $CH_3$); $^{31}P\{^1H\}$ NMR (161 MHz, $CD_2Cl_2$): $\delta = 23.1$ (d, $J_{Rh,P} = 165.7$ Hz, $PPh_2$), $-144.5$ (septet, $J_{P,F} = 707$ Hz, $PF_6$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$): $\delta = 158.5$ (s, imidazole C2), 133.1 (d, $J_{P,C} = 11.9$ Hz, *o*- or *m*-$PPh_2$), 131.0 (d, $J_{P,C} = 40.3$ Hz, *ipso*-$PPh_2$), 130.8 (s, *p*-$PPh_2$), 128.4 (d, $J_{P,C} = 9.5$ Hz, *o*- or *m*-$PPh_2$), 121.2 (s, imidazole C4/5), 120.2 (s, imidazole C4/5), 100.7 (dd, $J_{P,C} = 10.7$ Hz, $J_{Rh,C} = 8.0$ Hz, CH of COD), 80.5 (d, $J_{Rh,C} = 9.0$ Hz, CH of COD), 39.7 (s, $NCH_2$), 31.5 (br, $CH_2$ of COD), 30.4 (s, $CH_3$), 30.4 (s, $CH_2$ of COD), 20.8 (d, $J_{P,C} = 22.0$ Hz, $PCH_2$), 10.9 (dd, $J_{P,C} = 7.9$ Hz, $J_{Rh,C} = 20.7$ Hz, $RhCH_2$), 7.6 (s, $CH_3$),

7.5 ppm (s, $CH_3$); elemental analysis (%) calcd for $C_{29}H_{37}F_6N_2P_2Rh$ (692.5): C 50.30, H 5.39, C 4.05; found: C 50.39, H 5.48, C 4.30.

**Complex 4**: Complex **4** was synthesized by following Method 1 starting from [{Pd(allyl)Cl}$_2$] and ligand **1b**. Yield: 81%. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 7.31–7.52 (m, 10H, $PPh_2$), 6.87 (d, $J$ = 2.5 Hz, 1H, imidazole H4/5), 6.62 (d, $J$ = 2.5 Hz, 1H, imidazole H4/5), 5.26–5.32 (m, 1H, allyl), 4.15–4.32 (m, 3H, $NCH_2$ and CH of *i*Pr), 3.18 (dd, $J$ = 2.3, 7.3 Hz, 1H, allyl), 2.92 (t, $J$ = 12.1 Hz, 1H, allyl), 2.75 (d, $J$ = 13.8 Hz, 2H, allyl), 2.48–2.66 (m, 2H, $PCH_2$), 1.37 (d, $J$ = 6.4 Hz, 3H, $CH_3$ of *i*Pr), 1.33 ppm (d, $J$ = 6.4 Hz, 3H, $CH_3$ of *i*Pr); $^{31}$P{$^1$H} NMR (121 MHz, $CD_2Cl_2$): $\delta$ = 11.9 (s, $PPh_2$), −143.8 ppm (septet, $J_{P,F}$ = 708 Hz, $PF_6^-$); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 156.3 (s, imidazole C2), 133.2 (d, $J_{P,C}$ = 60.6 Hz, *ipso*-$PPh_2$), 132.7 (d, $J_{P,C}$ = 13.4 Hz, *o*- or *m*-$PPh_2$), 132.3 (d, $J_{P,C}$ = 13.4 Hz, *o*- or *m*-$PPh_2$), 131.2 (s, *p*-$PPh_2$), 130.0 (s, *p*-$PPh_2$), 129.2 (d, $J_{P,C}$ = 10.5 Hz, *o*- or *m*-$PPh_2$), 129.1 (d, $J_{P,C}$ = 10.5 Hz, *o*- or *m*-$PPh_2$), 119.6 (d, $J_{P,C}$ = 4.8 Hz, CH of allyl), 118. 8 (s, imidazole C4/5), 113.6 (s, imidazole C4/5), 67.7 (s, $CH_2$ of allyl), 63.8 (d, $J_{P,C}$ = 33.4 Hz, $CH_2$ of allyl), 48.7 (s, CH of *i*Pr), 42.6 (s, $NCH_2$), 22.3 (d, $J_{P,C}$ = 21.9 Hz, $CH_2P$), 22.0 (s, $CH_3$ of *i*Pr), 21.9 (s, $CH_3$ of *i*Pr), −5.1 ppm (d, $J_{P,C}$ = 9.5 Hz, $PdCH_2$); elemental analysis (%) calcd for $C_{24}H_{30}N_2PPd$ (483.9): C 59.57, H 6.25, C 5.79; found: C 59.95, H 6.58, C 5.34.

**Complex 6**: Complex **6** was synthesized by following method 1, starting from [{Rh(cod)Cl}$_2$] (0.11 mmol), ligand **5** (0.22 mmol), and *t*BuOK (0.23 mmol). Yield: 93% (154 mg, 0.2 mmol). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 7.43–7.59 (m, 10H, $PPh_2$), 7.06 (s, 2H, mesityl), 6.73 (d, $J$ = 2.3 Hz, 1H, imidazole H4/5), 6.56 (d, $J$ = 1.8 Hz, 1H, imidazole H4/5), 4.77 (br, 2H, COD), 4.53 (d, $J$ = 1.4 Hz, 2H, $NCH_2$), 3.71 (br, 2H, COD), 2.34 (s, 3H, $CH_3$), 2.01–2.19 (m, 8H, COD), 2.09 (s, 6H, 2C$H_3$), 3.36 ppm (apparent t, $J$ = 2.7 Hz, 2H, $RhCH_2$); $^{31}$P{$^1$H} NMR (161 MHz, $CD_2Cl_2$): $\delta$ = 74.2 (d, $J_{Rh,P}$ = 187.3 Hz, $PPh_2$), −143.8 ppm (septet, $J_{P,F}$ = 714 Hz, $PF_6$); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): 157.5 (d, $J_{P,C}$ = 5.7 Hz, imidazole C2), 141.0, 135.4, 132.8 (d, $J_{P,C}$ = 12.5 Hz, *o*- or *m*-$PPh_2$), 131.8, 130.9, 129.9 (d, $J_{P,C}$ = 38.3 Hz, *ipso*-$PPh_2$), 129.7, 129.5 (d, $J_{P,C}$ = 9.6 Hz, *o*- or *m*-$PPh_2$), 118.7 (s, imidazole C4/5), 118.5 (s, imidazole C4/5), 102.3 (dd, $J_{P,C}$ = 10.5 Hz, $J_{Rh,C}$ = 7.8 Hz, CH of COD), 82.4 (d, $J_{Rh,C}$ = 8.6 Hz, CH of COD), 49.0 (d, $J_{P,C}$ = 20.1 Hz, $NCH_2$), 31.2 (s, $CH_2$ of COD), 30.1 (s, $CH_2$ of COD), 20.9 (s, $CH_3$), 17.8 (s, $CH_3$), 12.8 ppm (dd, $J_{P,C}$ = 5.3 Hz, $J_{Rh,C}$ = 18.7 Hz, $RhCH_2$); elemental analysis (%) calcd for $C_{34}H_{39}F_6N_2P_2Rh$ (754.5): C 54.12, H 5.21, C 3.71; found: C 54.33, H 5.51, C 3.69.

**Complex 8**: Complex **8** was synthesized as a yellow solid by following method 1. It was further washed with cold THF to get the analytically pure product. Yield: 65% (98 mg, 0.130 mmol). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.42–7.58 (m, 12H, $PPh_2$ and ArH), 7.31 (t, $J$ = 8.0 Hz, 1H, ArH), 7.20 (t, $J$ = 7.9 Hz, 1H, ArH), 6.08 (br, 2H, $NCH_2$), 4.69 (br, 2H, COD), 3.77 (br, 2H, COD), 3.26 (s, 3H, $NCH_3$), 2.28 (s, 3H, $CH_3$), 2.00–2.24 (m, 8H, COD), 2.05 (s, 3H, $CH_3$), 1.65 ppm (apparent t, $J$ = 4.0 Hz, 2H, $RhCH_2$); $^{31}$P{$^1$H} NMR (121 MHz, $CD_2Cl_2$): $\delta$ = 26.1(d, $J_{Rh,P}$ = 158.4 Hz, $PPh_2$), −143.9 ppm (septet, $J_{P,F}$ = 708 Hz, $PF_6$); $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 157.5 (d, $J_{P,C}$ = 5.7 Hz, imidazole C2), 138.8 (d, $J_{P,C}$ = 15.6 Hz, *ipso*-$PPh_2$), 134.7 (s), 139.9 (d, $J_{P,C}$ = 12.1 Hz, *o*- or *m*-$PPh_2$), 132.2 (s), 132.1 (d, $J_{P,C}$ = 2.1 Hz, *Ar*$PPh_2$), 131.6 (s), 131.3 (d, $J_{P,C}$ = 1.7 Hz, *p*-$PPh_2$), 129.8 (d, $J_{P,C}$ = 5.6 Hz, *Ar*$PPh_2$), 129.5 (d, $J_{P,C}$ = 20.6 Hz, *Ar*$PPh_2$), 129.4 (d, $J_{P,C}$ = 9.5 Hz, *o*- or *m*-$PPh_2$), 123.1 (s, imidazole C4/5), 122.7 (s, imidazole C4/5), 97.9 (apparent t, $J_{P,C}$ = $J_{Rh,C}$ = 8.9 Hz, CH of COD), 84.1 (d, $J_{Rh,C}$ = 8.6 Hz, CH of COD), 48.8 ($J_{P,C}$ = 17.2 Hz, $NCH_2$), 31.9 (s, $NCH_3$), 31.6 (d, $J_{P,C}$ = 2.1 Hz, $CH_2$ of COD), 31.1 (s, $CH_2$ of COD), 9.8 (s, $CH_3$), 9.2 (s, $CH_3$), 8.5 ppm (dd, $J_{P,C}$ = 8.2 Hz, $J_{Rh,C}$ = 23.3 Hz, $RhCH_2$); elemental analysis (%) calcd for $C_{34}H_{39}F_6N_2P_2Rh$ (754.5): C 54.12, H 5.21, C 3.71; found: C 54.31, H 5.29, C 3.60.

**Observation of a mixture 3a and 9**: *t*BuOK, NaOEt, or NaOMe (0.221 mmol, 2.05 equiv) was added to a stirred solution of [{Rh(cod)Cl}$_2$] (50 mg, 0.108 mmol) in THF (4 mL). The mixture was stirred for 4 h and then a suspension of ligand **1a** (2 equiv) in THF (3 mL) was added. The mixture was stirred at room temperature for a further 6 h, and a yellow solution was obtained after filtration. All volatile substances were then removed under vacuum and the residue washed with diethyl ether (2× 3 mL) to give **3a** or **3a**/**9** as a yellow powder. The ratio of **3a** and **9** was determined by $^1$H NMR spectroscopy. Selected NMR signals: $^1$H NMR (400 MHz, $CD_2Cl_2$) for **3a**: $\delta$ = 6.46 (d, $J$ = 2.1 Hz, imidazole H4/5), 6.03(d, $J$=2.1 Hz, imidazole H4/5), 5.17 (br, COD), 4.26–4.33 (m, $NCH_2$). $^1$H NMR (400 MHz, $CD_2Cl_2$) for **9**: $\delta$ = 6.55 (s, imidazole H4/5), 5.18 (br, COD), 4.50–4.57 ppm (m, $NCH_2$); $^{31}$P{$^1$H} NMR (121 MHz $CD_2Cl_2$): $\delta$ = 26.5 (d, $J_{Rh,P}$ = 121.1 Hz, **9**), 23.1 (d, $J_{Rh,P}$ = 122.7 Hz, **3a**), −144.4 ppm (septet, $J_{P,F}$ = 706 Hz, $PF_6^-$); $^{13}$C NMR (100 MHz $CD_2Cl_2$): $\delta$ = 10.1 (dd, $J$ = 8.8, 20.6 Hz, $RhCH_2$ of **3a**), 150.3 ppm (dd, $J$ = 13.9, 40.0 Hz, Rh-*C* of **9**).

**Conversion of 2a to 11**: Complex **2a** (15.0 mg, 0.02 mmol) and methanol (4 μL, 0.10 mmol) were dissolved in $CD_2Cl_2$ (0.6 mL), and the solution was loaded into a J. Young NMR tube. The NMR tube was heated at 45 °C. The reaction was monitored by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard, and 94% conversion was observed after two weeks. Complex **11** was obtained as a red solid after removal of all volatile substances, followed by washing with diethyl ether. Complex **11** could be alternatively synthesized by following a literature procedure.[12a] $^1$H NMR (400 MHz $CD_2Cl_2$): $\delta$ = 7.46–7.52 (m, 10H, $PPh_2$), 6.69 (s, 1H, imidazole H4/5), 4.92 (br, 2H, COD), 4.46–4.55 (m, 2H, $NCH_2$), 3.64 (s, 3H, $CH_3$), 3.30 (br, 2H, COD), 2.65–2.71 (m, 2H, $PCH_2$), 2.54 (s, 3H, $CH_3$), 2.04–2.30 (m, 8H of COD); $^{31}$P{$^1$H} NMR (121 MHz, $CD_2Cl_2$): $\delta$ = 11.21 (s, $PPh_2$), −144.4 ppm (septet, $J_{P,F}$ = 706 Hz, $PF_6^-$); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 149.6 (d, $J_{P,C}$ = 12.1 Hz, IrC), 141.7 (s, imidazole C2), 133.2 (d, $J_{P,C}$ = 11.1 Hz, *o*- or *m*-$PPh_2$), 132.7 (d, $J_{P,C}$ = 50.7 Hz, *ispo*-$PPh_2$), 130.9 (d, $J_{P,C}$ = 2.3 Hz, *p*-$PPh_2$), 128.7 (d, $J_{P,C}$ = 10.2 Hz, *o* or *m*-$PPh_2$), 125.8 (s, imidazole C4/5), 89.5 (d, $J_{P,C}$ = 12.3 Hz, CH of COD), 72.9 (s, CH of COD), 47.8 (d, $J_{P,C}$ = 2.4 Hz, $NCH_2$), 34.4 (s, $CH_3$), 31.6 (d, $J_{P,C}$ = 2.9 Hz, $CH_2$ of COD), 31.1 ($J_{P,C}$ = 1.9 Hz, $CH_2$ of COD), 26.8 (d, $J_{P,C}$ = 34.6 Hz, $CH_2P$), 9.67 ppm (s, $CH_3$); elemental analysis (%) calcd for $C_{27}H_{33}F_6IrN_2P_2$ (753.7): C 43.03, H 4.41, C 3.72; found: C 43.71, H 4.23, C 4.01.

**Complex 12**: A suspension of 3-[2-(diphenylphosphino)ethyl]-1-isopropyl-2-phenylimidazolium hexafluorophosphate (52 mg, 0.10 mmol) in THF (2 mL) was added to a solution of commercially available [{Ir(cod)(OMe)}$_2$] (33.4 mg, 0.05 mmol) in THF (2 mL). The mixture was stirred at room temperature for 6 h and a red solution formed. All volatiles were removed by vacuum and the residue was washed with diethyl ether (2 × 3 mL) to give a red solid. Yield: 96% (78.4 mg, 0.096 mmol). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.38–7.72 (m, 15H, $PPh_2$ and Ph), 6.93 (s, 1H, imidazole H4/5), 5.03–5.05 (m, 2H, COD), 4.34–4.45 (m, 2H, $NCH_2$), 3.59 (s, 3H, $CH_3$), 3.36–3.37 (m, 2H, COD), 2.56–2.63 (m, 2H, $PCH_2$), 2.04–2.30 ppm (m, 8H of COD); $^{31}$P{$^1$H} NMR (121 MHz, $CD_2Cl_2$): $\delta$ = 12.2 (s, $PPh_2$), −143.8 (septet, $J_{P,F}$ = 706 Hz, $PF_6^-$); $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 150.8 (d, $J_{P,C}$ = 11.9 Hz, IrC), 144.1 (s, imidazole C2), 133.2 (d, $J_{P,C}$ = 11.0 Hz, *o*- or *m*-$PPh_2$), 132.5 (d, $J_{P,C}$ = 50.8 Hz, *ispo*-$PPh_2$), 132.1 (s, *p*-Ph), 131.0 (d, $J_{P,C}$ = 2.3 Hz, *p*-$PPh_2$), 130.0 (s, *m* or *o*-Ph), 129.8 (s, *m* or *o*-Ph), 128.8 (d, $J_{P,C}$ = 10.1 Hz, *o* or *m*-$PPh_2$), 126.8 (s, imidazole C4/5), 122.4 (s, Ph), 89.8 (d, $J_{P,C}$ = 12.2 Hz, CH of COD), 73.6 (s, CH of COD), 48.4 (d, $J_{P,C}$ = 3.0 Hz, $NCH_2$), 35.0 (s, $CH_3$), 31.6 (d, $J_{P,C}$ = 3.0 Hz, $CH_2$ of COD), 31.1 ($J_{P,C}$ = 1.8 Hz, $CH_2$ of COD), 27.2 ppm (d, $J_{P,C}$ = 34.3 Hz, $CH_2P$); elemental analysis (%) calcd for $C_{32}H_{35}F_6IrN_2P_2$ (815.8): C 47.11, H 4.32, C 3.43; found: C 47.49, H 4.13, C 3.50.

**Crystallographic analysis**: X-ray quality single crystals of complexes **2a**, **3a**, and **6**·0.5$CH_2Cl_2$ were obtained by the slow diffusion of diethyl ether into solutions in dichloromethane. Crystal data were collected on a Bruker X8 Kappa CCD diffractometer at 173 K by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å). APEX2 Software Suite (Bruker, 2005) was used for data acquisition, structure solution, and refinement. Absorption corrections were applied with SADABS. The structure was solved by direct methods and refined by full-matrix least-squares methods on $F^2$ with Xshell. CCDC-698361 (**2a**), CCDC-698362 (**3a**) and CCDC-698363 (**6**·0.5$CH_2Cl_2$) 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.

## Acknowledgements

We thank the School of Physical and Mathematical Sciences, Nanyang Technological University for financial support and Johnson Matthey Co. for a loan of iridium and rhodium chlorides. Dr. Yongxin Li (NTU, Singapore) is gratefully acknowledged for the crystallographic studies. We thank Prof. Roy Periana for insightful discussions.

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Received: December 8, 2008
Published online: April 15, 2009

  