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Reactivity of Phosphane–Imidazolium Salts Towards $[Ir(COD)Cl]_2$: Preparation of New Hydridoiridium(III) Complexes Bearing Abnormal Carbenes

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Dedicated to Prof. W. A. Herrmann on the occasion of his 60th birthday

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The unusual reactivity of chelating phosphane–imidazolium salts $MesImEtPPh_2^+Br^-$, $DIPP\text{-}ImEtPPh_2^+Br^-$, and $MesImEtPPh_2^+BF_4^-$ towards the low-oxidation-state iridium complex $[Ir(COD)(\mu\text{-}Cl)]_2$ was studied. In the absence of a base, the C–H insertion at the C5 position of the imidazolium ring was the only reaction that occurred, with no normal NHC observed, leading to hydridoiridium(III) complexes. This reactivity was independent of the nature of the imidazolium counteranion and of the substitution pattern of the aryl group.

Introduction

N-Heterocyclic carbene (NHC) complexes are now widely used for catalytic applications.[1] This interest is particularly due to the production of more robust catalysts by coordination of NHCs to transition metals such as palladium, nickel, rhodium, ruthenium, and iridium.[2] Over the last fifteen years, a number of bidentate as well as polydentate ligands incorporating NHCs[3] and other coordinating atoms,[4–8] have been developed and used successfully in catalysis.

A different binding mode for NHCs was described by Crabtree and coworkers;[9] instead of the normal C2 coordination, the metal atom can bind to the C4 or C5 atom of an imidazolium salt. Since this discovery, only a few examples of "abnormal" carbenes have been described, for example with iridium,[10–12] ruthenium,[13] osmium,[14] and several other transition metals.[15] In the case of Crabtree's work with the iridium precursor $IrH_5(PPh_3)_2$, it was shown that the formation of classical or abnormal NHCs was anion-dependent; imidazolium salts bearing a halogen anion led preferentially to classical NHCs, whereas noncoordinating anions BF_4^- or PF_6^- gave mostly abnormal NHCs.[12] Monodentate ligands were then used instead of bidentate NHCs, with similar results, showing no chelate effect.[11] Recently, the group of Li reported hydridoiridium(III) complexes bearing chelating phosphane–(abnormal)NHC ligands.[16] They did not observe any influence of the counteranion on the product selectivity.

We are interested in the preparation of bifunctional imidazolium salts containing a coordinating heteroatom such as phosphorus or sulfur, and their use as ligands or ligand precursors for transition metals.[4–6] More particularly, we recently described the use of phosphane–imidazolium salts to prepare zwitterionic Ni^{II} complexes and showed their excellent activities for Kumada–Tamao–Corriu cross-coupling reactions.[4] We now report the unusual reactivity of these salts with $[Ir(COD)Cl]_2$. These results were obtained during attempts to synthesise new Ir^I precatalysts, according to the same procedure that allowed us to access Ni^{II} and Pd^{II} analogues.[4,5]

Results and Discussion

The phosphane–imidazolium salts were prepared according to previously reported procedures (Scheme 1).[4] The reaction of 1-[2-(diphenylphosphanyl)ethyl]-3-(2,4,6-trimethylphenyl)imidazolium bromide salt $MesImC_2H_4PPh_2^+Br^-$ (**1**) with $[Ir(COD)(\mu\text{-}Cl)]_2$ yielded a mixture of two hydrido complexes (**4a** and **4b**) in a 1:1 ratio (Scheme 2). The two complexes exhibit two almost equivalent ^{31}P NMR signals at δ = –1.1 and –2.4 ppm and two equivalent ^1H NMR hydride doublet resonances at δ = –15.22 and –14.55 ppm (see Figure 1a).

We attribute this behavior to halogen exchange induced by the bromide anion of **1**. This hypothesis is confirmed by the observation that using $MesImC_2H_4PPh_2^+BF_4^-$ (**3**) in

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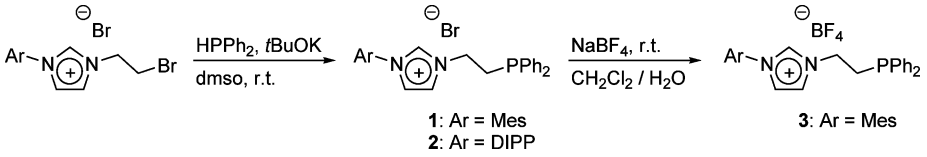
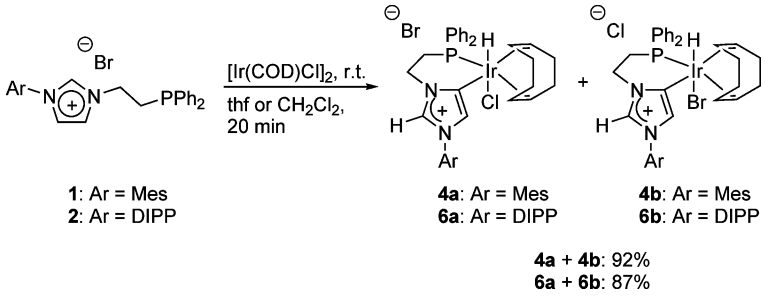


Scheme 1. Synthesis of phosphane–imidazolium salts. Mes = mesityl or 2,4,6-trimethylphenyl; DIPP = 2,6-diisopropylphenyl.



Scheme 2. Mixture of isomers **4a**+**4b** from the reaction of ligand **1**, or isomers **6a**+**6b** from the reaction of ligand **2**, with $[Ir(COD)(\mu\text{-}Cl)]_2$.

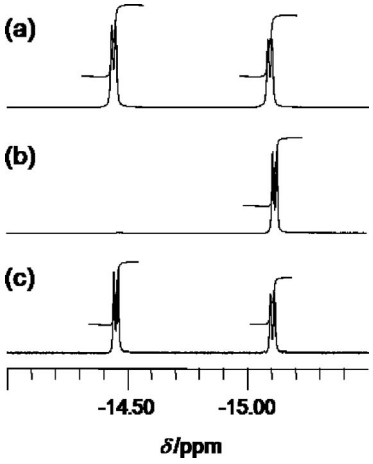
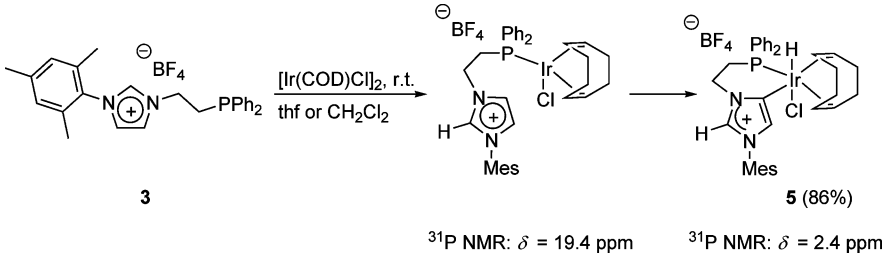


Figure 1. ^{1}H NMR spectra (500 MHz, 20 °C) of complexes (a) **4a**/**4b** ($CDCl_3$), (b) **5** (CD_2Cl_2), (c) **6a**/**6b** (CD_2Cl_2) (hydride resonances).

place of **1** led to a single product **5**, whose ^{31}P and ^{1}H (hydride) NMR resonances match with those of **4a** (Scheme 3, Figure 1b). Thus, both products **4a** and **5** contain a chlorido ligand and a different counterion (Br^- for **4a** and BF_4^- for **5**), whereas the chloride and bromide ions are exchanged in **4b**.

The ^{1}H NMR spectrum of the **4a**/**4b** mixture indicates C_1 symmetry and reveals three signals corresponding to the imidazole ring protons at δ = 9.74, 6.24, and 6.18 ppm, with integration values of 1:0.5:0.5, whereas that of compound **5** exhibits two 1:1 resonances at δ = 8.45 and 6.40 ppm (see Figure 2). Whereas the upfield imidazole ring ^{1}H NMR resonances of **5** approximately match with those of **4a**, the downfield one is quite anion-dependent. Furthermore, 1:1 ^{13}C NMR resonances for quaternary carbon atoms are observed at δ = 119.9 and 121.1 ppm, which is a typical region for aryl substituents and not for NHC ligands. These results indicate that the products are Ir^{III} complexes coordinated by a bidentate phosphane–(abnormal)carbene ligand (Scheme 2). The shift of the downfield ^{1}H NMR resonance is attributed to differences in hydrogen bonding between the acidic imidazolium proton and the different counterion. Related hydridoiridium(III) complexes, also featuring an abnormal carbene coordination, were recently reported by Li et al. and show similar NMR spectroscopic features (complex **A**, Figure 3).[16] Danopoulos et al. also obtained and crystallographically characterised a similar complex, $[Ir(COD)(Br)\{\kappa^2\text{:}P,C5\text{-}Ph_2PCH_2CH_2(N_2C_3HMes)\}]$ (**B** in Figure 3), from the reaction of **1** with $[Ir(COD)(HCl)(\mu\text{-}Cl)_2]_2$. It is related to **4b** by elimination of HCl.[8]

Complex **5** was also characterised by X-ray crystallography (Figure 4, Table 2). The Ir1–C2 distance [2.068(5) Å] and the Ir1–Cl1 distance are in agreement with the data given by Li et al. for **A** (Table 1).[16] The Ir1–P1 distance, however, appears much shorter than that in Li's compound,



Scheme 3. Synthesis of complex **5** via an iridium(I) intermediate.

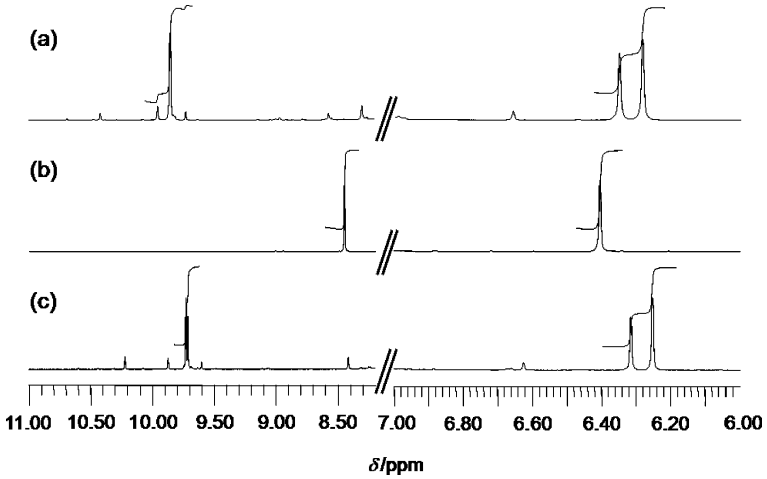


Figure 2. ^{1}H NMR spectra (500 MHz, 20 °C) of complexes (a) **4a/4b** ($CDCl_3$), (b) **5** (CD_2Cl_2), (c) **6a/6b** (CD_2Cl_2) (imidazolium resonances).

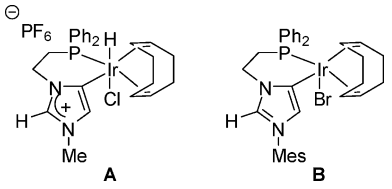


Figure 3. Related iridium complexes reported by Li et al. (**A**)[16] and Danopoulos et al. (**B**).[8]

but is very close to the distance measured in Danopoulos' compound **B**[8] where the N2 atom is also substituted with a bulky aryl group. The C2–Ir1–P1 bite angle is also very close to that of Li's complex, with a large value of 92.70(13)°. The structure confirms the binding of the imidazole moiety through C5 (labeled as C2 in the structure). It also shows the presence of a hydrido ligand *trans* to the chlorido ligand, with an Ir1–H100 bond length of

Table 1. Comparison of the main structural parameters of **5** and of the iridium complexes described by Li et al. (**A**)[16] and Danopoulos et al. (**B**).[8]

	5	**A**	**B**
Bond lengths/Å			
Ir1–C2[a]	2.068(5)	2.065(6)	2.018(9)
Ir1–P1	2.2972(16)	2.585(1)	2.283(2)
Ir1–Cl1	2.4845(15)	2.5097(9)	–
Ir1–Br1	–	–	2.6865(11)
Ir1–H100	1.586(19)	–	–
Bond angles/°			
C2–Ir1–P1	92.70(13)	92.24(16)	88.9(3)
C2–Ir1–Cl1	82.75(15)	85.50(16)	–
P1–Ir1–Cl1	86.81(5)	90.83(5)	–
C2–Ir1–H100	82(2)	–	–
P1–Ir1–H100	92(2)	–	–
Cl1–Ir1–H100	164(2)	–	–

[a] Labeled as C9 in Li's complex **A**.[16]

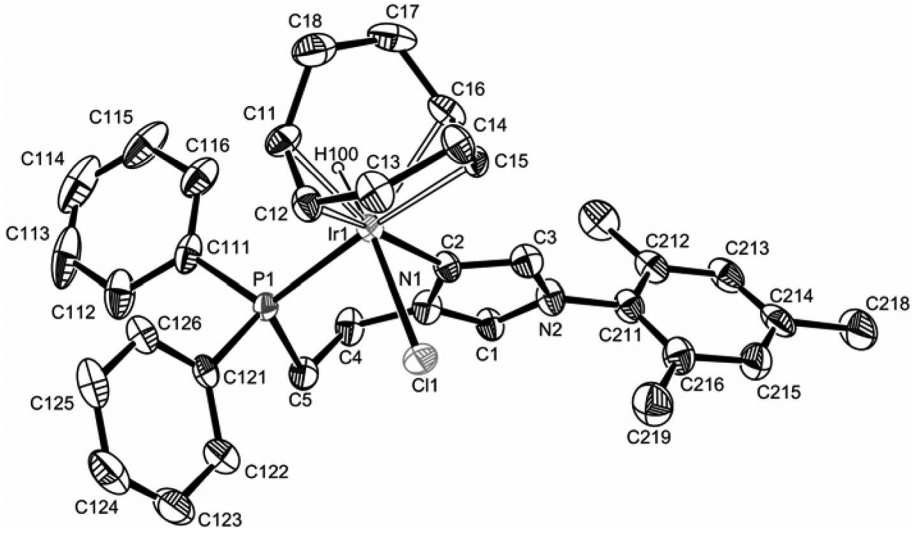


Figure 4. ORTEP view of compound **5**. Ellipsoids are represented at the 30% probability level. Hydrogen atoms (except H100), cocrystallised solvent molecules, and BF_4^- are omitted for clarity.

1.586(19) Å and a relative angle to the Cl atom of 164(2)°. The coordination is distorted octahedrally at the iridium(III) center. All other characterisations (elemental analysis and mass spectrometry) confirmed the nature of these products.

A ^{31}P NMR spectroscopic monitoring of the [Ir(COD)(μ-Cl)]$_2$/**3** reaction at room temperature revealed additional features. After 5 min, the ligand was completely consumed and two products were visible: the final product with signal at δ = 1.1 ppm and an intermediate compound with signal at δ = 19.4 ppm which quickly disappeared (Scheme 3). Our hypothesis is that, in a first step, the phosphane coordinates to the iridium center, splitting the dimer. Subsequently, the C–H insertion occurs at the C5 position of the imidazolium ring, possibly assisted by a chelating effect. This hypothesis is supported by the recent results obtained by Li et al.[16]

However, our observed reactivity differs from the results described by Danopoulos with a similar ligand, where the mesityl substituent is replaced by DIPP (2,6-diisopropylphenyl; compound **2**).[8] That contribution indicated that the interaction of [Ir(COD)(μ-Cl)]$_2$ with **2**, under unspecified reaction conditions, afforded the simple addition product where the chlorido ligand had been replaced by a bromide ion, [Ir(COD)(Br)(PPh$_2$CH$_2$CH$_2$Im^{DIPP})], similar to the proposed intermediate of our reaction leading to **5**. In the interest of checking whether a simple change of aryl group would enforce such a significant reactivity change, we decided to repeat the same reaction under conditions similar to those leading to **4a/4b**. The reactions were carried out in two different solvents (CH_2Cl_2 or thf), which always led to complete conversion at room temperature in 20 min and led to an iridium complex bearing an abnormal carbene (mixture of isomers, **6a**+**6b**, Scheme 2). These compounds were fully characterised by NMR spectroscopy and mass spectrometry, leaving no doubt about their nature. Indeed, the NMR spectra present many similar features to those of complexes **4a** and **4b**; the ^1H NMR spectrum shows four signals corresponding to the imidazole ring protons at δ = 9.73, 9.71, 6.35, and 6.28 ppm, with integration values of 0.5 each, for the mixture of **6a** and **6b**. We also observe two equivalent ^1H NMR hydride doublets at δ = –15.07 and –14.41 ppm (Figure 1c) and two signals at δ = –2.04 and –3.08 ppm in the ^{31}P NMR spectrum, corresponding to the two isomers. Moreover, the mass spectrum clearly shows two peaks at *m*/*z* = 777.9 and 821.8, assigned to cations **6a**$^+$ and **6b**$^+$, respectively.

Conclusions

We have described an unusual reactivity of chelating phosphane–imidazolium salts towards low-oxidation-state iridium complexes. In the absence of a base, we have shown that the C–H insertion at the C5 position of the imidazolium ring is the only occurring reaction, with no normal NHC observed. Contrary to related iridium chemistry previously reported by the Crabtree group,[12] this reactivity is independent of the nature of the imidazolium counteranion. It is also independent of the substitution pattern of the aryl group. In fact, the recent paper by Li et al.[16] shows identical chemistry for ligands bearing alkyl substituents (Me, *i*Pr) on the N3 atom of the imidazolium ring. Thus, this reactivity pattern appears to be quite general.

Experimental Section

General: All reactions were carried out under dry argon using Schlenk glassware and vacuum-line techniques. Solvents for syntheses were dried and degassed by standard methods before use. Elemental analyses were carried out by the analytical service of the "Laboratoire de Chimie de Coordination" in Toulouse. ^1H NMR spectroscopic data were recorded with a Bruker AV-500 spectrometer, operating at 500 MHz. $^{13}C\{H,P\}$ and $^{31}P\{H\}$ NMR spectroscopic data were recorded with a Bruker AV-500 instrument, operating at 125.8 and 202.5 MHz, respectively. ^{19}F NMR spectroscopic data were recorded with a Bruker AC-200 instrument, operating at 188 MHz. The spectra were referenced internally using the signal of the residual protio solvent (^1H) or the solvent signals (^{13}C), the signal of CF_3CO_2H (10%) in C_6D_6 (^{19}F) and externally using 85% H_3PO_4 for ^{31}P. Mass spectra were obtained from acetonitrile or methanol solutions with a ThermoElectron TSQ7000 instrument (electrospray ionisation), and from dmso or dmf solutions with a Nermag R10-10 instrument (FAB). [Ir(COD)(μ-Cl)]$_2$ was obtained from Strem and used as received. MesImEtPPh$_2^+$Br$^-$ (**1**), DIPP-ImEtPPh$_2^+$Br$^-$ (**2**), and MesImEtPPh$_2^+$BF$_4^-$ (**3**) were prepared as described previously.[4]

General Procedure for the Synthesis of Ir^{III} Complexes: In a Schlenk tube, CH_2Cl_2 was added to a phosphane–imidazolium salt and [Ir(COD)(μ-Cl)]$_2$ mixture, and the mixture was stirred at room temp. for 30 min. The solvent was removed under vacuum, the residue washed with diethyl ether until the ethereal phase remained colorless, and then dried under vacuum. These reactions were also performed in thf without any change in the results.

(Chlorido)(1,5-cyclooctadiene){1-[2-(diphenylphosphanyl)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-5-ylidene}iridium Bromide and (Bromido)(1,5-cyclooctadiene){1-[2-(diphenylphosphanyl)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-5-ylidene}iridium Chloride (4a+4b): CH_2Cl_2 (3 mL), MesImEtPPh$_2^+$Br$^-$ (**1**) (60 mg, 125.4 μmol), and [Ir(COD)(μ-Cl)]$_2$ (46 mg, 68.5 μmol). A pale-yellow, air-sensitive product was obtained. Yield: 94 mg (92%). $C_{34}H_{40}BrClIrN_2P\cdot CHCl_3$ (934.66): calcd. C 44.98, H 4.42, N 3.00; found C 45.01, H 4.35, N 2.80. MS (FAB, mNBA matrix): *m*/*z* (%) = 627 (100) [$C_{26}H_{28}ClIrN_2P^+$], 671 (92) [$C_{26}H_{26}BrIrN_2P^+$], 735 (34) [$C_{34}H_{40}ClIrN_2P^+$], 779 (36) [$C_{34}H_{40}BrN_2IrP^+$]. **First Isomer:** ^1H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 9.74 (s, 1 H, NC*H*N), 7.88–7.98 [m, 2 H, *o*-C*H*(Ph^2)], 7.54–7.64 [m, 3 H, *m*,*p*-C*H*(Ph^2)], 7.32–7.51 [m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)], 6.92 [br. s, 2 H, C*H*(Mes)], 6.18 (d, ^3J = 1.4 Hz, 1 H, MesNC*H*=), 5.74–5.83 (m, 1 H, NCH_2), 5.29–5.33 [m, 1 H, C*H*(COD)], 5.17–5.23 [m, 1 H, C*H*(COD)], 4.61–4.69 [m, 1 H, C*H*(COD)], 3.83–3.91 (m, 1 H, NCH_2), 3.73–3.81 [m, 1 H, C*H*(COD)], 3.37–3.55 (m, 1 H, CH_2P), 3.01–3.12 [m, 1 H, CH_2(COD)], 2.65–2.80 [m, 4 H, CH_2(COD); CH_2P], 2.40–2.60 [m, 2 H, CH_2(COD)], 2.25–2.40 [m + s, 4 H, CH_2(COD); *p*-CH_3], 1.90–2.12 [m + s, 7 H, CH_2(COD); *o*-CH_3], –14.55 (d, $^2J_{P,H}$ = 8.1 Hz, 1 H, Ir*H*) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C): δ = 140.2 [s, *p*-*C*(Mes)], 137.1 (s, N*C*HN), 135.0, 134.1 [s, *o*-*C*(Mes)], 134.5 [d, $^2J_{C,P}$ = 10.4 Hz, *o*-*C*H(Ph^2)], 132.9 [d, $^2J_{C,P}$ = 7.8 Hz, *o*-*C*H(Ph^1)], 132.6 [d, $^4J_{C,P}$ = 2 Hz, *p*-*C*H(Ph^2)], 131.7 [d, $^4J_{C,P}$ = 2 Hz, *p*-*C*H(Ph^1)], 131.5 [s, N*C*(Mes)], 129.5 [d, $^3J_{C,P}$ = 15 Hz, *m*-*C*H(Ph^2)],

129.4, 129.3 [s, *C*H(Mes)], 128.6 [d, *i*-*C*(Ph^2)], 128.1 [d, $^3J_{C,P}$ = 10.6 Hz, *m*-*C*H(Ph^1)], 128.0 [d, *i*-*C*(Ph^1)], 123.8 (s, MesN*C*H=), 119.9 (d, $^2J_{C,P}$ = 7.9 Hz, Ir*C*), 96.7 [d, $^2J_{C,P}$ = 16 Hz, *C*H(COD)], 93.3 [d, $^2J_{C,P}$ = 9.5 Hz, *C*H(COD)], 91.7, 82.4 [s, *C*H(COD)], 45.3 (s, N*C*H$_2$), 34.1 [d, $^3J_{C,P}$ = 2 Hz, *C*H$_2$(COD)], 31.6, 30.0 [s, *C*H$_2$(COD)], 29.7 [d, $^3J_{C,P}$ = 2 Hz, *C*H$_2$(COD)], 25.0 (d, $^1J_{C,P}$ = 40.1 Hz, *C*H$_2$P), 21.1 [s, *p*-*C*H$_3$(Mes)], 17.9, 17.7 [s, *o*-*C*H$_3$(Mes)] ppm. ^{31}P NMR (202.5 MHz, $CDCl_3$, 20 °C): δ = –2.39 (s, *P*Ph$_2$) ppm. **Second Isomer:** ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 9.74 (s, 1 H, NC*H*N), 7.88–7.98 [m, 2 H, *o*-C*H*(Ph^2)], 7.54–7.64 [m, 3 H, *m*,*p*-C*H*(Ph^2)], 7.32–7.51 [m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)], 6.94 [br. s, 2 H, C*H*(Mes)], 6.24 (d, ^3J = 1.4 Hz, 1 H, MesNC*H*=), 5.74–5.83 (m, 1 H, NC*H*$_2$), 5.35–5.41 [m, 1 H, C*H*(COD)], 5.06–5.11 [m, 1 H, C*H*(COD)], 4.61–4.69 [m, 1 H, C*H*(COD)], 4.07–4.17 (m, 1 H, NC*H*$_2$), 3.63–3.69 [m, 1 H, C*H*(COD)], 3.37–3.55 (m, 1 H, C*H*$_2$P), 3.01–3.12 [m, 1 H, C*H*$_2$(COD)], 2.65–2.80 [m, 4 H, C*H*$_2$(COD); C*H*$_2$P], 2.40–2.60 [m, 2 H, C*H*$_2$(COD)], 2.25–2.40 [m + s, 4 H, C*H*$_2$(COD); *p*-C*H*$_3$], 1.90–2.12 [m + s, 7 H, C*H*$_2$(COD); *o*-C*H*$_3$], –15.22 (d, $^2J_{P,H}$ = 8.3 Hz, 1 H, Ir*H*) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C): δ = 140.2 [s, *p*-*C*(Mes)], 137.4 (s, N*C*HN), 134.8, 134.2 [s, *o*-*C*(Mes)], 134.4 [d, $^2J_{C,P}$ = 10.4 Hz, *o*-*C*H(Ph^2)], 132.8 [d, $^2J_{C,P}$ = 7.9 Hz, *o*-*C*H(Ph^1)], 133.3 [d, $^4J_{C,P}$ = 11 Hz, *p*-*C*H(Ph^2)], 131.6 [d, $^4J_{C,P}$ = 2 Hz, *p*-*C*H(Ph^1)], 131.5 [s, N*C*(Mes)], 129.6 [d, $^3J_{C,P}$ = 15 Hz, *m*-*C*H(Ph^2)], 129.4, 129.3 [s, *C*H(Mes)], 128.6 [d, *i*-*C*(Ph^2)], 128.2 [d, $^3J_{C,P}$ = 10.4 Hz, *m*-*C*H(Ph^1)], 128.0 [d, *i*-*C*(Ph^1)], 123.5 (s, MesN*C*H=), 121.1 (d, $^2J_{C,P}$ = 8.1 Hz, Ir*C*), 98.6 [d, $^2J_{C,P}$ = 16.2 Hz, *C*H(COD)], 93.8 [d, $^2J_{C,P}$ = 9.1 Hz, *C*H(COD)], 93.9, 83.7 [s, *C*H(COD)], 45.6 (s, N*C*H$_2$), 35.5, 31.0 [s, *C*H$_2$(COD)], 29.6 [d, $^3J_{C,P}$ = 2 Hz, *C*H$_2$(COD)], 28.2 [d, $^3J_{C,P}$ = 2 Hz, *C*H$_2$(COD)], 24.9 (d, $^1J_{C,P}$ = 39.5 Hz, *C*H$_2$P), 21.1 [s, *p*-*C*H$_3$(Mes)], 17.8, 17.6 [s, *o*-*C*H$_3$(Mes)] ppm. ^{31}P NMR (202.5 MHz, $CDCl_3$, 20 °C): δ = –1.14 (s, *P*Ph$_2$) ppm.

(Chlorido)(1,5-cyclooctadiene){1-[2-(diphenylphosphanyl)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-5-ylidene}iridium Tetrafluoroborate (5): CH_2Cl_2 (3 mL), MesImEtPPh$_2^+$BF$_4^-$ (**3**) (60 mg, 123 μmol), and [Ir(COD)(μ-Cl)]$_2$ (43 mg, 63 μmol). A cream-white, air-sensitive product was obtained. Yield: 87 mg (86%). Suitable X-ray crystals were obtained by layer diffusion of pentane into a CH_2Cl_2 solution at –20 °C. $C_{34}H_{40}BClF_4IrN_2P{\cdot}0.5CH_2Cl_2$ (864.66): calcd. C 47.93, H 4.78, N 3.24; found C 47.53, H 4.90, N 3.36. ESI-MS (positive mode): *m*/*z* (%) = 627.1 (10) [$C_{26}H_{28}ClIrN_2P^+$], 735.1 (100) [$C_{34}H_{40}ClIrN_2P^+$]. ESI-MS (negative mode): *m*/*z* (%) = 87 (100) [BF_4^-]. ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ = 8.45 (s, 1 H, NC*H*N), 7.99 [dd, ^3J = 7 Hz; $^3J_{P,H}$ = 11.5 Hz, 2 H, *o*-C*H*(Ph^2)], 7.63–7.72 [m, 3 H, *m*,*p*-C*H*(Ph^2)], 7.43–7.57 [m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)], 7.04 [br. s, 2 H, C*H*(Mes)], 6.40 (d, ^4J = 1 Hz, 1 H, MesNC*H*=), 5.47–5.54 [m, 1 H, C*H*(COD)], 5.14 (dddd, $^{2,3}J$ = 2.3, 7.6, 14.3 Hz; $^3J_{P,H}$ = 27.4 Hz, 1 H, NC*H*$_2$), 5.05–5.12 [m, 1 H, C*H*(COD)], 4.73–4.77 [m, 1 H, C*H*(COD)], 4.12 (ddd, $^{2,3}J$ = 11, 12 Hz; $^3J_{P,H}$ = 19.6 Hz, 1 H, NC*H*$_2$), 3.62–3.69 [m, 1 H, C*H*(COD)], 3.49–3.58 (m, 1 H, C*H*$_2$P), 3.02–3.12 [m, 1 H, C*H*$_2$(COD)], 2.92–3.00 [m, 1 H, C*H*$_2$(COD)], 2.66–2.82 [m, 3 H, C*H*$_2$(COD); C*H*$_2$P], 2.47–2.58 [m, 2 H, C*H*$_2$(COD)], 2.32–2.42 [m + s, 4 H, C*H*$_2$(COD); *p*-C*H*$_3$], 2.00–2.15 [m + s, 7 H, C*H*$_2$(COD); *o*-C*H*$_3$], –15.12 (d, $^2J_{P,H}$ = 8.3 Hz, 1 H, Ir*H*) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2, 20 °C): δ = 140.6 [s, *p*-*C*(Mes)], 135.9 (s, N*C*HN), 134.8, 134.4 [s, *o*-*C*(Mes)], 134.3 [d, $^2J_{C,P}$ = 7.3 Hz, *o*-*C*H(Ph^2)], 132.8 [d, $^2J_{C,P}$ = 8 Hz, *o*-*C*H(Ph^1)], 132.6 [d, $^4J_{C,P}$ = 2.3 Hz, *p*-*C*H(Ph^2)], 131.4 [d, $^4J_{C,P}$ = 2.6 Hz, *p*-*C*H(Ph^1)], 131.3 [s, N*C*(Mes)], 129.5 [d, $^3J_{C,P}$ = 10.6 Hz, *m*-*C*H(Ph^2)], 129.4 [br. s, *C*H(Mes)], 128.8 [d, $^1J_{C,P}$ = 58.7 Hz, *i*-*C*(Ph^1)], 128.6 [d, $^1J_{C,P}$ = 58.7 Hz, *i*-*C*(Ph^2)], 128.1 [d, $^3J_{C,P}$ = 10.5 Hz, *m*-*C*H(Ph^1)], 124.5 (s, MesN*C*H=), 121.4 (d, $^2J_{C,P}$ = 9.2 Hz, Ir*C*), 98.7 [d, $^2J_{C,P}$ = 15.6 Hz, *C*H(COD)], 94.6 [d, $^3J_{C,P}$ = 9.4 Hz, *C*H(COD)], 94.1, 84.4 [s, *C*H(COD)], 45.7 (s, N*C*H$_2$), 35.6, 30.7 [s, *C*H$_2$(COD)], 29.6 [d, $^3J_{C,P}$ = 2.1 Hz, *C*H$_2$(COD)], 28.0 [d, $^3J_{C,P}$ = 3.8 Hz, *C*H$_2$(COD)], 25.1 (d, $^1J_{C,P}$ = 39.7 Hz, *C*H$_2$P), 20.8 [s, *p*-*C*H$_3$(Mes)], 17.1, 17.0 [s, *o*-*C*H$_3$(Mes)] ppm. ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20 °C): δ = 2.42 (s, *P*Ph$_2$) ppm. ^{19}F NMR (188 MHz, CD_2Cl_2, 20 °C): δ = –76.2 (s, B*F*$_4$) ppm.

(Chlorido)(1,5-cyclooctadiene){1-[2-(diphenylphosphanyl)ethyl]-3-(2,6-diisopropylphenyl)imidazol-5-ylidene}iridium Bromide (6a+6b): CH_2Cl_2 (3 mL), DIPP-ImEtPPh$_2^+$Br$^-$ (**2**) (82 mg, 157 μmol), and [Ir(COD)(μ-Cl)]$_2$ (53 mg, 79 μmol). A pale-yellow, air-sensitive product was obtained. Yield: 118 mg (87%). $C_{37}H_{46}BrClIrN_2P{\cdot}CH_2Cl_2$ (942.30): calcd. C 48.44, H 5.13, N 2.97; found C 48.41, H 5.13, N 2.92. ESI-MS (positive mode): *m*/*z* (%) = 777.9 (100) [$C_{37}H_{46}ClIrN_2P^+$], 821.8 (33) [$C_{37}H_{46}BrIrN_2P^+$]. **First Isomer:** ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ = 9.73 (d, ^4J = 1.1 Hz, 1 H, NC*H*N), 8.02–8.05 [m, 2 H, *o*-C*H*(Ph^2)], 7.63–7.69 [m, 3 H, *m*,*p*-C*H*(Ph^2)], 7.39–7.55 [m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)], 7.32 [d, ^3J = 6.5 Hz, 1 H, *m*-C*H*(DIPP)], 7.31 [d, ^3J = 6.6 Hz, 1 H, *m*-C*H*(DIPP)], 6.28 [d, ^3J = 1.6 Hz, 1 H, (DIPP)NC*H*=], 5.70–5.78 (m, 1 H, NC*H*$_2$), 5.31–5.36 [m, 1 H, C*H*(COD)], 5.16–5.20 [m, 1 H, C*H*(COD)], 4.67–4.75 [m, 1 H, C*H*(COD)], 3.89–3.97 (m, 1 H, NC*H*$_2$), 3.66–3.74 [m, 1 H, C*H*(COD)], 3.54–3.61 (m, 1 H, C*H*$_2$P), 3.00–3.09 [m, 1 H, C*H*$_2$(COD)], 2.66–2.91 [m, 3 H, C*H*$_2$(COD); C*H*$_2$P], 2.54–2.63 [m, 1 H, C*H*$_2$(COD)], 2.32–2.52 [m, 4 H, C*H*$_2$(COD); C*H*(CH$_3$)$_2$], 1.90–2.12 [m, 1 H, C*H*$_2$(COD)], 1.16–1.26 [m, 12 H, CH(C*H*$_3$)$_2$], –14.41 (d, $^2J_{P,H}$ = 8.2 Hz, 1 H, Ir*H*) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2, 20 °C): δ = 146.0, 145.3 [s, *o*-*C*(DIPP)], 137.4 (s, N*C*HN), 134.6 [d, $^2J_{P,C}$ = 10.5 Hz, *o*-*C*H(PPh$_2$)], 133.0 [s, $^2J_{P,C}$ = 6.7 Hz, *o*-*C*H(PPh$_2$)], 132.5 [d, $^4J_{P,C}$ = 2.6 Hz, *p*-*C*H(PPh$_2$)], 131.4 [d, $^4J_{P,C}$ = 2.7 Hz, *p*-*C*H(PPh$_2$)], 131.2 [s, N*C*(Mes)], 131.0 [s, *p*-*C*H(DIPP)], 129.4 [d, $^3J_{P,C}$ = 10.5 Hz, *m*-*C*H(PPh$_2$)], 127.9 [d, $^3J_{P,C}$ = 10.5 Hz, *m*-*C*H(PPh$_2$)], 125.5 [d, $^3J_{C,P}$ = 8.5 Hz, (DIPP)N*C*H=], 124.3, 124.1 [s, *m*-*C*H(DIPP)], 120.1 (d, $^2J_{C,P}$ = 8.4 Hz, Ir*C*), 96.8 [d, $^2J_{P,C}$ = 16.2 Hz, *C*H(COD)], 93.8 [d, $^2J_{P,C}$ = 9.0 Hz, *C*H(COD)], 91.7, 82.7 [s, *C*H(COD)], 45.4 (s, N*C*H$_2$), 33.7 [d, $^3J_{P,C}$ = 2.1 Hz, *C*H$_2$(COD)], 31.9 [s, *C*H$_2$(COD)], 29.9 [d, $^3J_{P,C}$ = 4.3 Hz, *C*H$_2$(COD)], 29.7 [d, $^3J_{P,C}$ = 2.2 Hz, *C*H$_2$(COD)], 28.5, 28.4 [s, *C*H(CH$_3$)$_2$], 25.0 (d, $^1J_{C,P}$ = 40.3 Hz, *C*H$_2$P), 24.3, 24.2, 24.1, 24.0 [s, CH (*C*H$_3$)$_2$] ppm. ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20 °C): δ = –3.08 (s, *P*Ph$_2$) ppm. **Second Isomer:** ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ = 9.71 (d, ^4J = 1.2 Hz, 1 H, NC*H*N), 7.98–8.01 [m, 2 H, *o*-C*H*(Ph^2)], 7.63–7.69 [m, 3 H, *m*,*p*-C*H*(Ph^2)], 7.39–7.55 [m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)], 7.36 [d, ^3J = 7.9 Hz, 1 H, *m*-C*H*(DIPP)], 7.35 [d, ^3J = 7.9 Hz, 1 H, *m*-C*H*(DIPP)], 6.35 [d, ^3J = 1.5 Hz, 1 H, (DIPP)NC*H*=], 5.70–5.78 (m, 1 H, NC*H*$_2$), 5.37–5.43 [m, 1 H, C*H*(COD)], 5.10–5.17 [m, 1 H, C*H*(COD)], 4.67–4.75 [m, 1 H, C*H*(COD)], 4.20–4.27 (m, 1 H, NC*H*$_2$), 3.76–3.83 [m, 1 H, C*H*(COD)], 3.38–3.43 (m, 1 H, C*H*$_2$P), 3.00–3.09 [m, 1 H, C*H*$_2$(COD)], 2.66–2.91 [m, 3 H, C*H*$_2$(COD); C*H*$_2$P], 2.54–2.63 [m, 1 H, C*H*$_2$(COD)], 2.32–2.52 [m, 4 H, C*H*$_2$(COD); C*H*(CH$_3$)$_2$], 1.90–2.12 [m, 1 H, C*H*$_2$(COD)], 1.16–1.26 [m, 12 H, CH(C*H*$_3$)$_2$], –15.07 (d, $^2J_{P,H}$ = 8.1 Hz, 1 H, Ir*H*) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2, 20 °C): δ = 145.9, 145.4 [s, *o*-*C*(DIPP)], 137.6 (s, N*C*HN), 134.4 [d, $^2J_{P,C}$ = 10.5 Hz, *o*-*C*H(PPh$_2$)], 132.9 [s, $^2J_{P,C}$ = 8.0 Hz, *o*-*C*H(PPh$_2$)], 132.5 [d, $^4J_{P,C}$ = 2.4 Hz, *p*-*C*H(PPh$_2$)], 131.4 [d, $^4J_{P,C}$ = 2.5 Hz, *p*-*C*H(PPh$_2$)], 131.1 [s, N*C*(Mes)], 131.0 [s, *p*-*C*H(DIPP)], 129.4 [d, $^3J_{P,C}$ = 10.5 Hz, *m*-*C*H(PPh$_2$)], 128.1 [d, $^3J_{P,C}$ = 10.6 Hz, *m*-*C*H(PPh$_2$)], 125.3 [d, $^3J_{C,P}$ = 8.5 Hz, (DIPP)N*C*H=], 124.3, 124.2 [s, *m*-*C*H(DIPP)], 120.2 (d, $^2J_{C,P}$ = 8.6 Hz, Ir*C*), 98.7 [d, $^2J_{P,C}$ = 15.7 Hz, *C*H(COD)], 94.2 [d, $^2J_{P,C}$ = 9.3 Hz, *C*H(COD)], 93.9, 84.2 [s, *C*H(COD)], 45.8 (s, N*C*H$_2$), 35.2 [d, $^3J_{P,C}$ = 2.1 Hz, *C*H$_2$(COD)], 32.2 [s, *C*H$_2$(COD)], 29.4 [d, $^3J_{P,C}$ = 2.1 Hz, *C*H$_2$(COD)], 28.6, 28.5 [s, *C*H(CH$_3$)$_2$], 28.3

[d, $^3J_{P,C}$ = 3.9 Hz, CH_2(COD)], 25.1 (d, $^1J_{C,P}$ = 39.6 Hz, CH_2P), 24.3, 24.2, 24.1, 24.0 [s, $CH(CH_3)_2$] ppm. ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20 °C): δ = –2.04 (s, PPh_2) ppm.

Crystallographic Data: A single crystal was mounted under inert perfluoropolyether on the tip of a glass fiber and cooled in the cryostream of a Bruker APEX2 diffractometer. Data were collected using the monochromatic Mo-K_α radiation (λ = 0.71073). The final unit-cell parameters were obtained by the least-squares refinement of a large number of selected reflections (Table 2). The structures were solved by direct methods (SIR97[17]) and refined by least-squares procedures on F^2 with the SHELXL-97 program[18] using the integrated system WINGX(1.63).[19] Hydrogen atoms attached to carbon atoms were introduced at calculated positions and treated as riding on their parent atoms [d(CH) = 0.96–0.98 Å] with a displacement parameter equal to 1.2× (C_6H_5, CH_2) or 1.5× (CH_3) that of the parent atom. The hydride atom was located in difference Fourier syntheses, and its coordinates were refined using an Ir–H restraint of 1.60(2) Å. The BF_4 anion was partially disordered by rotation around one B–F axis; this disorder was treated using the tools available in SHELX-97.[17] Some residual electron densities were difficult to model and therefore, the SQUEEZE function of PLATON[20] was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. There are two cavities of 127 Å^3 per unit cell. PLATON estimated that each cavity contains 62 electrons which may correspond to a mixture of dichloromethane and pentane solvent molecules. The molecular views were realised with the help of ORTEP-III.[21,22] CCDC-681170 contains 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/datarequest/cif.

Table 2. Crystallographic data for compound **5**.

	5
Empirical formula	$C_{36}H_{44}BCl_5F_4IrN_2P$
Formula mass	991.96
Temperature/K	180(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	10.071(5)
b/Å	15.126(5)
c/Å	15.988(5)
α/°	68.528(5)
β/°	74.532(5)
γ/°	78.030(5)
V/Å^3	2168.0(15)
Z	2
Density	1.520
μ/mm^{-1}	3.468
F(000)	984
Range for data collection θ/°	$30.5 > \theta > 1.4$
Reflections collected	57426
Independent reflections	13227 [R(int) = 0.0612]
Goodness-of-fit on F^2	1.087
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0481, wR_2 = 0.1217
R indices for all data	R_1 = 0.0628, wR_2 = 0.1267

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