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[1]Pyridine and phosphine functionalised *N*-heterocyclic carbene complexes of rhodium and iridium

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Abstract

The pyridine functionalised *N*-heterocyclic carbene complexes $[M(\kappa^2\text{-}NC^{DIPP})(COD)]^+A^-$, NC^{DIPP} = 3-(2, 6-$Pr^i_2C_6H_3$)-1-[2-(3-picolyl)]-imidazol-2-ylidene, $A^- = [Ar^F_4B]^-$, $[\{3,5\text{-}(CF_3)_2C_6H_2\}_4B]^-$, M = Rh, **1b**, Ir, **4**, have been prepared in two steps by reaction of the $[M(COD)Cl]_2$ with the isolated NC^{DIPP} to $[Rh(\kappa^1\text{-}NC^{DIPP})(COD)Cl]$, **2**, and $[Ir(\kappa^2\text{-}NC^{DIPP})(COD)Cl]$, **3**, followed by anion exchange with Na^+A^-. The phosphine functionalised *N*-heterocyclic carbene complex $[Rh(PCH_2C^{mes})_2]Br$, **6**, PCH_2C^{mes} = 1-(diphenylphosphino-methyl)-3-(2,4,6-$Me_3C_6H_2$)-imidazol-2-ylidene, was prepared by the reaction of the $[Rh(COD)Cl]_2$ with the corresponding *N*-heterocyclic carbene generated in situ. Monomeric $[Rh(PCH_2CH_2C^{DIPP})(acac)]$, **7** was prepared by an analogous reactions from $[Rh(COE)_2(acac)]$. In contrast, phosphine functionalised *N*-heterocyclic carbene complexes of iridium (I) were not easily accessible. However, the reaction of [Ir(COD)(μ-Cl)2(μ-H)]2 with $PCH_2CH_2C^{mes}$ gave complex $[Ir(COD)(PCH_2CH_2C^{mes}\cdot)Br]$, **8**, in which the carbene is coordinated to the metal in an 'abnormal' mode.

Keywords: Arduengo carbene; Iridium; Rhodium; Functionalised heterocyclic carbene; Pyridine; Crystal structure

1. Introduction

In recent years functionalised *N*-heterocyclic carbenes (NHC) have been used as ligands for the tuning of the coordination sphere of catalytic platinum group metals [1]. They can give rise to unusual bidentate or polydentate complexes with potential hemilability, electronic discrimination of coordination sites and chirality. In this area, we studied various bidentate pyridine and phosphine functionalised NHC complexes of Pd and 'pincer' tridentate pyridine di-carbenes of metals from across the periodic table [2]. The electronic similarity between the trialkylphophines and the NHCs points to a potential resemblance of the pyridine–NHC and PR_3–NHC donor systems to the pyridine–PR_3 and P_AR_3–P_BR_3, which are found in numerous catalysts, like Crabtree's hydrogenation catalyst, palladium polymerisation and carbonylation catalysts, etc. [3]. Our efforts to prepare rhodium and iridium complexes with the ligands shown in Scheme 1 led us to the observation that the C-3 of the pyridine is susceptible to facile metallation by iridium (I), while in the rhodium case a persistent C3–H agostic interaction was present in solution and the solid state [4].

This interaction was absent in analogous picoline-functionalised rhodium complexes (structure B), while we were unable to prepare well-defined iridium complexes with the latter ligand. C–H activation of other aliphatic and aromatic substituents of NHC ligands has recently been reviewed [5]. We reasoned that a

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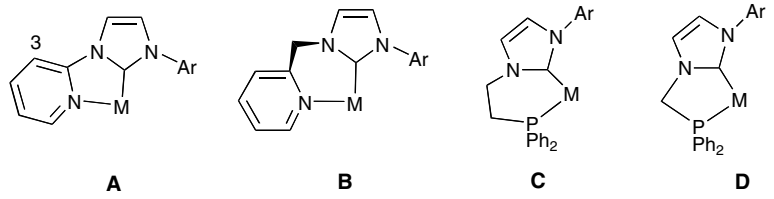
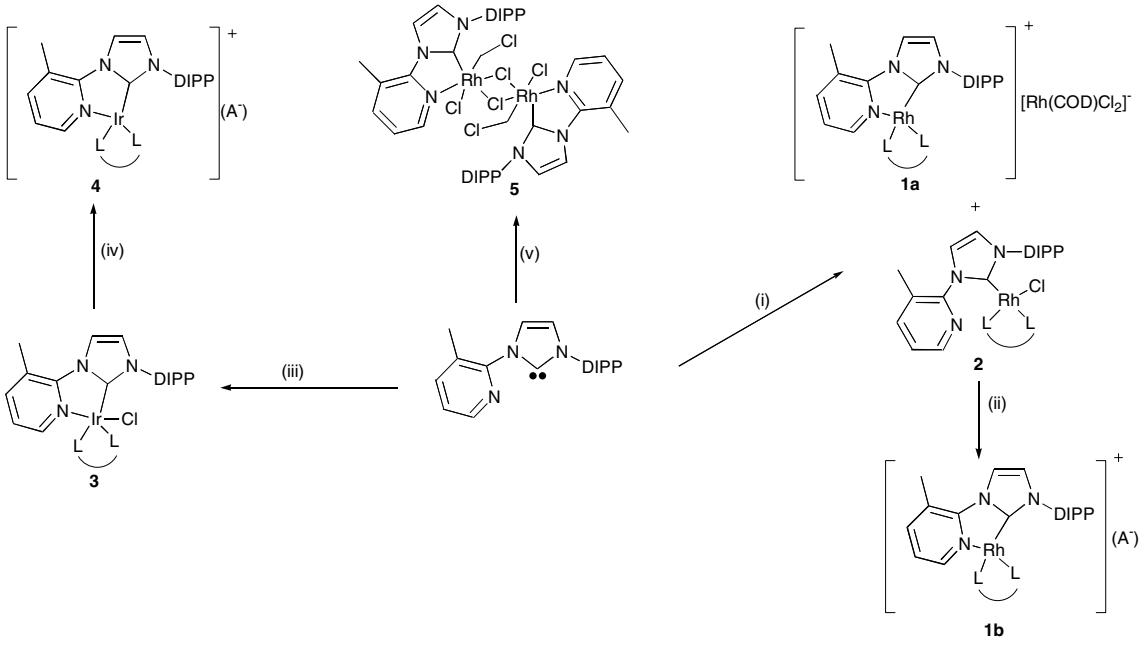
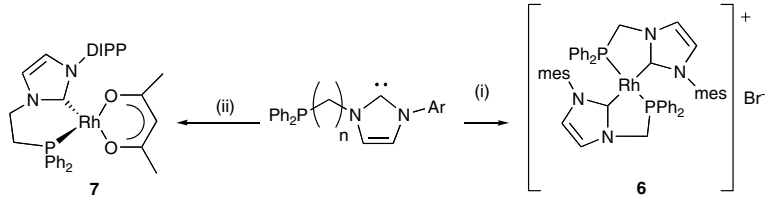


Scheme 1. Schematic representation of the pyridine and phosphine functionalised NHC ligands.



Scheme 2. (i) $[Rh(COD)Cl]_2$, thf, −78 °C; (ii) $Na[Ar^F_4B]$, ether; (iii) $[Ir(COD)Cl]_2$, thf, −78 °C; (iv) $Na[Ar^F_4B]$, ether; (v) $[Rh(COD)Cl]_2$, thf, −78 °C followed by CH_2Cl_2. L–L = 1,5-cyclooctadiene.



Scheme 3. (i) 0.5eq. $[Rh(COD)(\mu\text{-}OMe)]_2$ followed by 1eq. $KN(SiMe_3)_2$, thf; (ii) $KN(SiMe_3)_2$, 1eq. $[Rh(COE)_2(acac)]$.

reactivity of this type may cause problems in catalysis where M(I)/M(III) cycles are operating, especially in view of the stability of Ir–C(aryl) bonds. In this paper, we show that methyl substitution at the C3 of the pyridine ring in ligand systems of type A (Scheme 1) allowed the isolation of stable low oxidation state rhodium and iridium complexes in various coordination geometries. In addition, we describe extension of the synthesis of phosphine functionalised NHC complexes to rhodium and iridium. The new pyridine–NHC and phosphine–NHC complexes are summarised in Schemes 2 and 3, respectively.

2. Experimental

2.1. General methods

Elemental analyses were carried out by the University College, London, microanalytical laboratory. All manipulations were performed under nitrogen in a Braun glove-box or using standard Schlenck techniques, unless stated otherwise. Solvents were dried using standard methods and distilled under nitrogen prior use. The light petroleum used throughout had a b.p. 40–60 °C.

The starting materials $[Rh(COD)(\mu\text{-}Cl)]_2$ [6] [Rh-(COE)2(μ-Cl)]$_2$ [7], $[Rh(COD)(\mu\text{-}OMe)]_2$ [8], $[Rh(COE)_2$-acac] [9], and $[Ir(COD)(\mu\text{-}H)(\mu\text{-}Cl)_2]_2$ [10] as well as the phosphine imidazolium bromides $(PCH_2CH_2C^{mes}H)$-Br and $(PCH_2CH_2C^{DIPP}H)Br$ [2c] $(PCH_2C^{mes})Br$, $(PCH_2C^{DIPP})Br$ [11] and the pyridine functionalised NHC NC^{DIPP} [12] were prepared according to the literature procedures.

NMR data were recorded on Bruker AMX-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^1H), respectively. The spectra were referenced internally using the signal from the residual protio-solvent (^1H) or the signals of the solvent (^{13}C). $^{31}P\{^1H\}$ were recorded on Bruker AC-300, at 121.44 MHz and referenced externally relative to 85% H_3PO_4 in D_2O.

Mass spectra (ES^+) were run from acetonitrile solutions on a VG Biotec platform. The *m/z* of the ions with the highest abundance isotope are only given, however, the observed isotopic envelopes agreed well with those calculated.

2.2. {(Cyclooct-1,5-diene)-κ^2-1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-ylidene rhodium} {rhodium(cyclooctadiene)dichloride} (**1a**)

$[Rh(cod)Cl]_2$ (0.050 g, 0.10 mmol) was suspended in thf at −78 °C. To this was added a solution of 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazole-2-ylidene (0.032 g, 0.10 mmol) in thf (10 cm^3) at −78 °C. The mixture was allowed to warm to r.t. and was stirred for 2 h. After evaporation of the solvent under reduced pressure the resulting red solid was crystallised by layering a benzene solution with petroleum.

NMR (CD_2Cl_2), ^1H: δ 8.35 (1H, d, *o*-H of pyridyl), 8.20 (1H, d, *p*-H of pyridyl), 7.90 and 7.15 (2 × 1H, d, backbone imidazol-2-ylidene H), 7.60 (2H, m, *m*-H of pyridyl and *p*-H aromatic), 7.35 (2H, m, *m*-H aromatic), 5.10, 4.15 and 3.90 (2 × 2H and 1 × 4H, m, olefinic H of two cod ligands), 2.85 (3H, s, pyridyl CH_3), 2.60 (2H, septet, 2 $CH(CH_3)_2$), 2.10 (12H, m, aliphatic H of COD ligands), 1.35 (6H, d, $CH(CH_3)_2$), 1.10 (6H, d, $CH(CH_3)_2$). $^{13}C\{^1H\}$: 145.90, 144.36, 130.54, 125.37, 123.73, 123.16 and 118.88 (aromatic carbons), 98.80 (olefinic C of cod), 77.50 (olefinic C of cod), 30.37 (aliphatic C of cod), 27.78 (aliphatic C of cod), 27.42 ($CH(CH_3)_2$), 24.85 ($CH(CH_3)_2$), 21.59 ($CH(CH_3)_2$), 20.65 (pyridyl CH_3) ppm. MS (ES^+) *m/z* (%): 530 $(M + H)^+$. Calculated for $C_{37}H_{49}Cl_2N_3Rh_2$: C, 54.69; H, 6.07; N, 5.15. Found: C, 54.25; H, 5.52; N, 5.0%.

2.3. {(Cyclooct-1,5-diene)-κ^2-1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-ylidene rhodium}{tetrakis-[3,5-bis(trifluoromethylphenyl)]borate} (**1b**)

$[Rh(cod)Cl]_2$ (0.12 g, 0.24 mmol) was suspended in thf at −78 °C. To this was added a solution of 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazole-2-ylidene (0.154 g, 0.48 mmol) in thf at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 2 h. After evaporation of the solvent under reduced pressure, the resulting solid, was suspended in ether and to this was added a solution of Na[{3,5-$(CF_3)_2C_6H_2$}$_4$B] (0.42 g, 0.48 mmol) in ether. The resulting dark red suspension was filtered and evaporated to dryness giving a red solid residue which was crystallised by dissolving in benzene and layering the solution with petroleum. Yield: 0.28 g (0.20 mmol), 83%. NMR (CD_2Cl_2), ^1H: δ 8.10 (1H, d, *o*-H of pyridyl), 8.00 (1H, m, *p*-H of pyridyl), 7.80 (8H, s, *o*-H of $[Ar^F_4B]^-$), 7.75 (2H, m, *m*-H of pyridyl and aromatic *p*-H), 7.70 (4H, s, *p*-H of $[Ar^F_4B]$), 7.50 (2H, d, imidazol-2ylidene H), 7.40 (2H, m, *m*-H aromatic), 5.15 and 4.15 (2 × 2H, m, olefinic H of C_8H_{12}), 2.80 (3H, s, pyridyl CH_3) 2.70 (2H, septet, 2 $CH(CH_3)_2$), 2.45, 2.40 and 2.20 (8H, m, aliphatic H of C_8H_{12}), 1.60 (6H, d, $CH(CH_3)_2$), 1.30 (6H, d, $CH(CH_3)_2$). $^{13}C\{^1H\}$: δ 161.41, 160.42, 145.40, 145.14, 143.82, 132.01, 130.78, 124.85, 123.68, 122.15, 117.00, 116.44 (aromatic carbons), 133.76 (B–C–CH–CCF_3), 122.50 (CF_3C–CH–CCF_3), 98.92 (olefinic C of C_8H_{12}), 78.30 (olefinic C of C_8H_{12}), 30.87 (aliphatic C of C_8H_{12}), 27.55 (aliphatic C of C_8H_{12}), 27.02 ($CH(CH_3)_2$), 24.63 ($CH(CH_3)_2$), 21.37 ($CH(CH_3)_2$), 19.75 (pyridyl CH_3). MS (ES^+) *m/z* (%): 530, $[M + H]^+$. Calculated for $C_{61}H_{49}BF_{24}N_3Rh$: C, 52.56; H, 3.55; N, 3.01. Found: C, 52.25; H, 3.41; N, 2.82%.

2.4. Reaction of [Rh(COD)Cl]$_2$ with excess NC^{DIPP}. Formation of {(Cyclooct-1,5-diene)-κ^1-1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-ylidene rhodium} chloride (**2**)

$[Rh(cod)Cl]_2$ (0.10 g, 0.20 mmol) was suspended in thf at −78 °C. To this was added a solution of 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazole-2-ylidene (0.128 g, 0.40 mmol) in thf at −78 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. After evaporation of the solvent under reduced pressure the resulting orange solid was dissolved in benzene and crystallised by layering with petroleum. The products that crystallised were **2** (major component, yellow) and **1a** (minor component, red). Further attempts to isolate **2** by repeated recrystallisations or by performing the reactions under various conditions were not successful. The characterisation data outlined below were obtained from a sample containing ca 20% of **1a**. NMR (C_6D_6), ^1H: δ 8.40 (1H, d, *o*-H of pyridyl), 7.25 (1H, m, *m*-H of pyridyl), 7.15 (3H, m, backbone imidazol H and *p*-H of pyridyl), 6.80 (1H, m, *p*-H aromatic of DIPP), 6.45 (2H, d, *m*-H aromatic of DIPP), 5.00, 3.85 and 3.20 (4H, m, olefinic H of cod), 2.40 (3H, s, pyridyl methyl H), 2.00 and 1.70 (2 × 4H, m, aliphatic H cod), 1.45 (6H, d,

$CH(CH_3)_2$), 1.05 (6H, d, $CH(CH_3)_2$). $^{13}C\{^1H\}$: 145.90, 144.36, 130.54, 125.37, 123.73, 123.16 and 118.88 (aromatic carbons), 98.80 (olefinic C of cod), 77.50 (olefinic C of cod), 30.37 (aliphatic C of cod), 27.78 (aliphatic C of cod), 27.42 ($CH(CH_3)_2$), 24.85 ($CH(CH_3)_2$), 21.59 ($CH(CH_3)_2$), 20.65 (pyridyl CH_3) ppm.

2.5. [(Cycloocta-1,5-diene)-κ^2-1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-ylidene iridium chloride (3)

$[Ir(cod)Cl]_2$ (0.10 g, 0.15 mmol) was suspended in thf at −78 °C. To this was added a solution of 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene (0.096 g, 0.30 mmol) in thf at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 2 h. Evaporation of the solvent under reduced pressure gave a dark orange solid which was crystallised by layering a benzene solution with petroleum. Yield: 0.163 g, 83%. NMR (C_6D_6), ^1H: δ 8.10 (1H, d, *o*-H of pyridyl), 7.20 (3H, m, aromatic H), 6.90 and 6.30 ($2\times1H$, imidazol H), 6.80 (1H, d, *p*-H of pyridyl), 6.45 (1H, m, *m*-H of pyridyl), 4.00 and 3.40 ($2\times2H$, m, olefinic HC_8H_{12}), 2.35 (4H, m, 4 aliphatic H of C_8H_{12}), 1.90 (3H, s, pyridyl methyl H), 1.80 (2H, septet, $2CH(CH_3)_2$), 1.50 (6H, d, $CH(CH_3)_2$), 1.05 (6H, d, $CH(CH_3)_2$). $^{13}C\{^1H\}$: 175.70 (carbene –N–*C*–N–), 145.46 (pyridyl CCH_3), 133.89 (pyridyl N–*C*H), 129.62, 127.53, 125.04, 122.98, 121.95, 121.25 and 116.38 (aromatic carbons), 31.01 (aliphatic C of cod), 27.50 ($CH(CH_3)_2$), 24.98 ($CH(CH_3)_2$), 21.58 ($CH(CH_3)_2$), 20.63 (pyridyl CH_3) ppm. MS (ES^+) *m*/*z* (%): 618 $[M+H]^+$. Calculated for $C_{47}H_{55}ClIrN_3$: C, 63.45; H, 6.23; N, 4.47. Found: C, 62.83; H, 6.01; N, 4.15%.

2.6. {κ^2-1-[2-(3-Picolyl)]-3-(2,6-diisopropylphenyl) imidazol-2-ylidene 1,5-cyclooctadiene iridium}{tetrakis-[3,5-bis(trifluoromethylphenyl)]borate} (4)

Complex **3** (0.025 g, 0.038 mmol) was suspended in ether and to this was added a solution of $Na^+[Ar_4^FB]^-$ (0.033 g, 0.037 mmol) in ether. The solution turned dark green and was filtered in order to remove inorganic salts. The green solid that was collected after evaporation, was crystallised by layering a benzene solution with petroleum. Yield: 0.049 g, 90%. NMR (CD_2Cl_2), ^1H: δ 8.05 (3H, d, aromatic H of pyridyl), 7.75 (8H, s, *o*-H of Ar_4^FB), 7.55 (4H, s, *p*-H of Ar_4^FB), 7.40 (3H, m, aromatic H), 7.05 (2H, d, imidazol H), 4.90 and 3.70 ($2\times2H$, m, olefinic H of C_8H_{12}), 2.85 (3H, s, pyridyl CH_3), 2.64 (2H, septet, $CH(CH_3)_2$), 2.10 (8H, m, 8H of C_8H_{12}), 1.40 (6H, d, $CH(CH_3)_2$), 1.13 (6H, d, $CH(CH_3)_2$). $^{13}C\{^1H\}$: δ 147.55, 135.20, 145.25, 132.10, 127.12, 125.10, 124.50 and 119.00, 117.84 (aromatic carbons), 88.95 (olefinic C of C_8H_{12}), 66.77 (olefinic C of C_8H_{12}), 33.58 (aliphatic C of C_8H_{12}), 29.20 (aliphatic C of C_8H_{12}), 28.98 ($CH(CH_3)_2$), 25.82 ($CH(CH_3)_2$), 22.53 ($CH(CH_3)_2$), 21.12 (pyridyl CH_3). Calculated for $C_{143}H_{119}B_2F_{48}Ir_2N_6$: C, 53.05; H, 3.70; N, 2.59. Found: C, 52.83; H, 3.52; N, 2.43%.

2.7. Bis-{κ^2-1-[2-(3-picolyl)]-3-[(2,6-diisopropyl-phenyl)-imidazol-2-ylidene]}-chloromethyl-(di-μ-chloro)-dirhodium (5)

$[Rh(cod)Cl]_2$ (0.10 g, 0.20 mmol) was suspended in thf at −78 °C. To this, a solution of 1-[2-(3-methyl)-pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazole-2-ylidene (0.128 g, 0.40 mmol) in thf at −78 °C was added. The mixture was allowed to warm to room temperature and was stirred for 2 h. After evaporation of the solvent the resulting orange solid was dissolved in dichloromethane and layered with petroleum to yield light orange crystals. Yield: 0.146 g, 72%. No spectroscopic data could be collected, since the complex was insoluble in all common deuterated solvents.

2.8. Bis-{κ^2-1-(diphenylphosphino-methyl)-3-[(2,4,6-$Me_3C_6H_2$)-imidazol-2-ylidene]}-rhodiumbromide (6)

In the glove-box, a Shlenck tube was charged with 60 mg (0.12 mmol) of $[Rh(COD)(\mu\text{-}OMe)]_2$ and 155 mg (0.25 mmol) of $(PCH_2C^{mes}H)Br$. A second Shlenck was charged with 48 mg (0.12 mmol) of $KN(SiMe_3)_2$. To the solids was added thf (10 cm^3) and the cooled solution of the base was added dropwise to the suspension of the imidazolium salt at −78 °C. Upon addition the colour of the suspension changed from yellow to orange and eventually a homogeneous orange solution was obtained which was stirred at room temperature for 6 h. After evaporation of the volatiles under reduced pressure the remaining residue was dissolved in CH_2Cl_2 and filtered through a Celite pad. Removal of the solvent under reduced pressure and washing of the solid residue with ether afford the title compound. Yield: 70 mg (58%). Crystals were grown by layering a CH_2Cl_2 solution of the compound with Et_2O. NMR (CD_2Cl_2): ^1H: δ 1.05 (6H, s, CH_3), 2.00 (6H, s, CH_3), 2.33 (6H, s, CH_3), 4.42 (2H, broad s, $[Rh(PPh_2CH_2\text{-ylid})_2]^+$), 4.71 (2H, broad s, $[Rh(PPh_2CH_2\text{-ylid})^2]^+$), 6.66 (4H, broad s, aromatic), 6.73 (8H, m, aromatic), 7.33 (16H, m, aromatic); $^{13}C\{^1H\}$: δ 18.8, 19.1, 20.5 (s, CH_3), 52.8 (d, $^1J_{PC}=23.7$ Hz, $[Rh(PPh_2CH_2\text{-ylid})_2]^+$), 117.8 (s, ylidene backbone), 119.2 (s, ylidene backbone), 121.9 (s, aromatic), 124.4 (s, aromatic), 125.1 (d, $J_{PC}=7.1$ Hz), 125.9 (s, aromatic), 128.6 (d, $J_{PC}=11.8$ Hz, aromatic), 131.3 (s, aromatic), 137.5 (d, $J_{PC}=2.2$ Hz), 147.1 (s, aromatic), 179.9 (d, $^1J_{RhC}=48.9$ Hz, N*C*N); $^{31}P\{^1H\}$: δ 53.2 (d, $^1J_{RhP}=167.7$ Hz, $[Rh(PPh_2CH_2\text{-ylid})_2]^+$); ES^+: 903 $[M+MeOH]^+$. Calculated for $C_{50}H_{50}BrN_4P_2Rh\cdot6CH_2Cl_2$: C, 46.03; H, 4.28; N, 3.83. Found: C, 46.47; H, 4.07; N, 3.93%.

2.9. {κ²-1-(β-Diphenylphosphino-ethyl)-3-[(2,6-$Pr^i_2C_6H_3$)-imidazol-2-ylidene]}-rhodium acetylacetonate (7)

This was prepared by a method similar to the one used for **6** starting from 100 mg (0.22 mmol) of $Rh(COE)_2$-acac, 115 mg (1 equiv.) of ($PCH_2CH_2C^{DIPP}H$)Br and 48 mg of $KN(SiMe_3)_2$. After completion of the reaction, the volatiles were removed under reduced pressure and the yellow solid residue was extracted with petroleum ether 60–80 ($4 \times 25\ cm^3$) and filtered through a Celite pad. The Celite pad was washed with more warm petroleum ether (3×10 mL) and the volume of the combined petroleum washings was reduced to about 15 mL. Cooling of the solution at −30 °C gave the title compound. Yield: 43 mg (30%). NMR (C_6D_6), ^{1}H: δ 1.10 (6H, d, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 1.38 (3H, s, (O)C(CH_3)-CHC(CH_3)(O)), 1.42 (6H, d, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 1.65 (3H, s, (O)C(CH_3)CHC(CH_3)(O)), 1.78 (2H, broad m, [$PPh_2CH_2CH_2$-ylidene]Rh(acac)), 3.60 (4H, m, $CH(CH_3)_2$ and [$PPh_2CH_2CH_2$-ylidene]Rh(acac)), 5.17 (1H, s, C(O)C(CH_3)CHC(CH_3)C(O)), 6.12 (1H, d, $^3J_{HH} =$ 1.5 Hz, ylidene backbone), 6.27 (1H, d, $^3J_{HH} = 1.5$ Hz, ylidene backbone), 7.19 (9H, m, aromatics), 8.05 (4H, m, aromatics); ^{13}C{^{1}H}: δ 22.7 (s, (O)C(CH_3)-CHC(CH_3)(O)), 24.0 (s, $CH(CH_3)_2$), 24.8 (s, $CH(CH_3)_2$), 26.6 (d, $^1J_{PC} = 25.1$ Hz, [$PPh_2CH_2CH_2$-ylidene]Rh(acac)), 27.5 (s, (O)C(CH_3)CHC(CH_3)(O)), 29.0 (s, $CH(CH_3)_2$), 45.8 (s, [$PPh_2CH_2CH_2$-ylidene]Rh(acac)), 98.1 (s, (O)C(CH_3)CHC(CH_3)(O)), 118.9 (s, ylidene backbone), 122.8 (s, ylidene backbone), 123.7 (s, aromatic), 127.6 (d, $J_{PC} = 2.2$ Hz, aromatic), 128.2 (s, aromatic), 128.6 (s, aromatic), 129.1 (s, aromatic), 133.6 (d, $J_{PC} = 9.8$ Hz, aromatic), 137.8 (d, $J_{PC} = 15.7$ Hz, aromatic), 144.9 (s, aromatic), 180.1 (d, $^2J_{RhC} =$ 22.5 Hz, (O)C (CH_3)CHC(CH_3)(O)), 181.5 (d, $^2J_{RhC} =$ 18.9 Hz, (O)C(CH_3)CHC(CH_3)(O)), 183.4 (d, $^1J_{RhC} = 50.8$ Hz, NCN); ^{31}P{^{1}H}: δ 46.9 (d, $^1J_{RhP} =$ 205.7 Hz, [PPh_2-CH_2CH_2-ylidene]Rh(acac)).

2.10. Complex 8

In the glove-box, Schlenck tubes were charged with 50 mg (0.07 mmol) of $[Ir(COD)(\mu\text{-}H)(\mu\text{-}Cl)_2]_2$ and 67 mg (2 equiv.) of ($PCH_2CH_2C^{mes}H$)Br. A third Shlenck tube was charged with 31 mg (1.1 equiv. to imidazolium salt) of $KN(SiMe_3)_2$. To the solids was added thf (10 cm^3) and the cooled solution of the base was added dropwise to the suspension of the imidazolium salt at −78 °C. The carbene generated in this way was added to the suspension of the iridium complex in thf at −78 °C and the reaction was allowed to reach room temperature and stirred overnight. After removal of the solvent under vacuum, the solid was dissolved in CH_2Cl_2 and filtered though Celite. The volatiles were removed again and the remaining solid was washed with ether (10 cm^3) and petrol (10 cm^3) and dried under vacuum. The red residue was crystallised by layering CH_2Cl_2 solutions with ether at −30 °C to yield orange crystals of the title compound. NMR (CD_2Cl_2), ^{1}H: δ 1.4 (4H, broad s, COD–CH_2), 1.6 (4H, broad s, COD–CH_2), 1.9 (6H, s, *o*-CH_3), 2.4 (3H, s, *p*-CH_3), 2.8 (2H, broad s, olefinic COD–CH), 3.4 (2H, broad s, olefinic COD–CHs), 4.8 [2H, broad s, ($Ph_2PCH_2CH_2$imidazolium), 4.9 and 5.0 [1H each, distorted t, $^3J_{HH} = 5.85$ Hz, ($Ph_2PCH_2CH_2$-imidazolium)Ir(COD)Br], 6.6 (1H, s, imidazolium backbone), 6.9 (2H, s, $C_6H_2Me_3$ aromatics), 7.4 [5H, m, $P(C_6H_5)_2$ aromatics], 7.6 [5H, m, $P(C_6H_5)_2$ aromatics], 9.8 (1H, s, imidazolium proton); ^{31}P{^{1}H}: δ 23.2 [s, ($Ph_2PCH_2CH_2$-imidazolium) Ir(COD)Br].

3. X-ray crystallography

A summary of the crystal data, collection and refinement for compounds **1a**, **1b**, **2**, **3**, **4**, **5**, **6**, **7** and **8** are given in Table 1. All data sets were collected on an Bruker Nonius Kappa CCD area detector diffractometer with rotating anode FR591 and an Oxford Cryosystems low-temperature device operating in omega scanning mode with ϕ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack and Denzo [24]. The crystals were mounted on a glass fibre with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WINGX package [25] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters and hydrogens were added using a riding model.

4. Results and discussion

4.1. Pyridine functionalised NHC complexes

These were conveniently prepared by the reaction of $[M(COD)Cl]_2$, M = Rh, Ir with the free ligand NC^{DIPP} in thf. When M = Rh the nature of the products is dependent on the reactant ratio; pure salt of the type $(NC^{DIPP})Rh(COD)]^+[Rh(COD)Cl_2]$ (**1a**) was only obtained by using deficiency of ligand. With higher ligand to metal ratios the materials isolated after crystallisation were mixtures of **1a** and **2**. We were unable to isolate $[(NC^{DIPP})Rh(COD)]Cl$ (**2**) free from **1a**. The salt $[(NC^{DIPP})Rh(COD)]^+[Ar^F_4B]^-$ (**1b**) can be conveniently prepared in good yields in one pot by reacting **1a** or mixtures of **1a** and **2** with $Na^+[Ar^F_4B]^-$. When M = Ir the five coordinate $[(NC^{DIPP})Ir(COD)]Cl$ **3** was isolated which reacted further with $Na^+[Ar^F_4B]^-$ to the salt $[(NC^{DIPP})Ir(COD)]^+[Ar^F_4B]^-$ **4**. It is interesting to note that reactions of $[M(COD)Cl]_2$, M = Rh, Ir with silver carbene complexes $Ag(NC^{DIPP})Cl$ [13] in various solvents were very slow (as judged by the rate of AgCl

Table 1
Crystal data for complexes **1a**–**8**

	1a	1b	2	3	4	5	6	7	8
Chemical formula	$C_{37}H_{49}Cl_2N_3Rh_2$	$C_{61}H_{49}BF_{24}N_3Rh$	$C_{32}H_{40}ClN_3Rh$	$C_{47}H_{55}ClIrN_3$	$C_{143}H_{119}B_2F_{48}Ir_2N_6$	$C_{46}H_{58}Cl_{10}N_6Rh_2$	$C_{52}H_{54}BrCl_4N_4P_2Rh$	$C_{34}H_{40}N_2O_2PRh$	$C_{35}H_{41}BrCl_2IrN_2P$
Formula weight	812.51	1393.75	605.03	889.59	3239.46	1255.30	1121.55	642.56	863.68
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	10.4157(3)	14.5133(10)	26.1907(12)	20.4441(17)	13.5427(9)	14.5761(6)	16.6386(8)	17.762(4)	10.7061(3)
b (Å)	12.1013(4)	15.1913(11)	17.6313(8)	9.9961(8)	22.4946(13)	14.5909(7)	13.1204(5)	23.507(5)	12.0453(2)
c (Å)	14.5159(5)	16.4013(12)	15.2056(6)	22.0442(17)	23.7447(15)	16.0317(7)	24.8390(12)	17.809(4)	14.7376(4)
α (°)	100.9250(10)	109.726(2)	90	90	109.195(2)	65.572(2)	90.00	90.00	66.472(2)
β (°)	94.963(2)	111.909(2)	123.0630(10)	115.409(3)	97.935(2)	82.870(2)	105.4980(10)	98.77(3)	89.2960(10)
γ (°)	106.202(2)	100.915(2)	90	90	92.466(2)	63.152(2)	90.00	90.00	73.5670(10)
V (Å^3)	1706.17(10)	2945.1(4)	5884.6(4)	4069.2(6)	6735.7(7)	2761.5(2)	5225.3(4)	7349(3)	1660.37(7)
Z	2	2	8	4	2	2	4	8	2
T (K)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
μ (mm^{-1})	1.155	0.409	0.696	3.383	2.094	1.118	1.396	0.536	5.461
Number of data collected	26,728	38,618	29,454	26,296	96,527	46,957	54,316	27,877	23,917
Number of unique data	7792	11,763	6738	7326	24,998	12,653	11,909	13,688	7431
R_{int}	0.0585	0.0493	0.0470	0.1326	0.1646	0.1165	0.1188	0.1184	0.1912
Final $R(\|F\|)$ for $F_o > 2\sigma(F_o)$	0.0338	0.0422	0.0263	0.0769	0.0861	0.0569	0.0830	0.0843	0.0658
Final $R(F^2)$ for all data	0.0578	0.0649	0.0397	0.1413	0.1306	0.0978	0.1162	0.1602	0.0996

precipitation) and usually gave intractable mixtures. This behaviour is to be contrasted by the facile formation of [Rh(COD)(N^C^{mes})]Cl and [Rh(COD)-(N^C^{mes})]$^+$[Ar$_4^F$B]$^-$N^C^{mes} = 3-(2,4,6-Me$_3$C$_6$H$_2$)-1-[2-(α-picolyl)]- imidazol-2-ylidene (structure B in Scheme 1, M = Rh) by transmetallation from the corresponding silver carbene followed by salt metathesis, respectively [14]. Transmetallation was also used in the synthesis of (COD)M(carbene)Cl, where carbene is monodentate unsaturated NHC [15]. All complexes **1**–**4** are air stable crystalline materials, which are soluble in thf and aromatic hydrocarbons. They react after prolonged exposure (>2 h) with dichloromethane giving rise to the products of the oxidative addition of $ClCH_2$–Cl bond as described below. All NC^{DIPP} complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy. A common feature of the ^{1}H NMR spectra of **1a**, **1b** and **4** is the presence of two doublets in the range 1.30–1.70 ppm assignable to two groups of diastereotopic methyls on the *o*-isopropyl groups of the aromatic rings. This is in agreement with the presence of a plane of symmetry which coincides with the coordination plane. The two ends of the COD ligand are also inequivalent, being *trans* to electronically different donor atoms. Interestingly, the complexes **2** and **3**, which have lower molecular symmetry, exhibit the same pattern in the methyl region of their ^{1}H NMR spectra possibly due to accidental coincidence. The carbene C was observed by ^{13}C NMR spectroscopy only in **3**. The limited stability of all complexes in chlorinated solvents precluded acquisition with long pulse delays which may have facilitated the observation of the slow relaxing carbene C.

The structures of **1a**, **1b**, **2**, **3** and **4** have been determined by single crystal X-ray diffraction; ORTEP diagrams of the cation in **1b**, the molecules in **2** and **3** and the cation in **4** are given in Figs. 1–4, respectively.

The cations in **1a**, **1b** and **4** feature a square planar metal centre with chelating NC^{DIPP} and COD ligands. The bite angle of NC^{DIPP} is within 77–78° range, while the aromatic carbene and pyridine rings of the backbone and the chelate ring are virtually coplanar. The angle between the DIPP and the carbene rings is in the range 87–102°. The M–carbene bond lengths are comparable with those reported in the literature (for Rh) or shorter (for Ir) [4,15–19]. The distance between the metal and the double bond of the COD ligand (defined as the distance between the metal and a centroid located in the middle of the C=C bond) which is *trans* to the NHC is longer than the one *trans* to the pyridine (for **1b** 2.104 and 2.026 Å, respectively, for **4** 2.096 and 2.027 Å, respectively), however, the C=C bond length *trans* to the carbene is shorter than the one *trans* to the pyridine.

The metal geometry in **2** is square planar with chelating COD, monodentate NC^{DIPP} and dangling pyridine groups. Here, the angle between the coordination plane

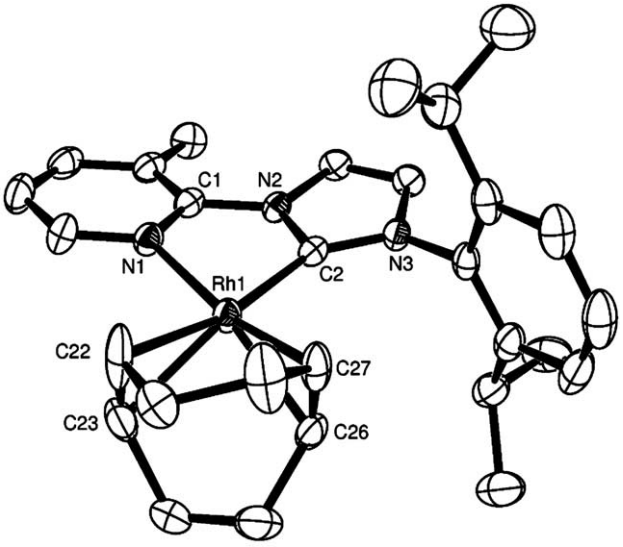


Fig. 1. ORTEP representation of the cation in **1b** (50% probability ellipsoids). Important bond lengths (Å) and angles (°): Rh(1)–C(2) = 2.012(3), Rh(1)–N(1) = 2.107(2), Rh(1)–C(22) = 2.214(3), Rh(1)–C(23) = 2.207(3), Rh(1)–C(26) = 2.141(3), C(22)–C(23) = 1.357(4), C(26)–C(27) = 1.389(4), Rh(1)–C(27) = 2.142(3); C(2)–Rh(1)–N(1) = 77.66(9); the metric data of the same cation in **1a** are very similar.

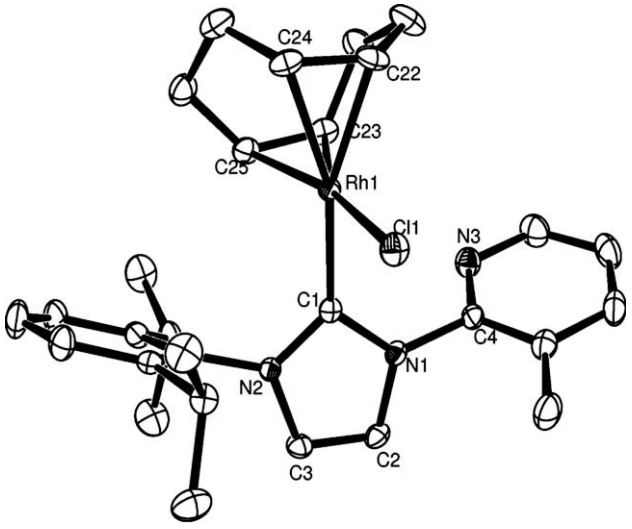


Fig. 2. ORTEP representation of the cation in **2** (50% probability ellipsoids); hydrogen atoms and one molecule of solvent benzene are omitted. Important bond lengths (Å) and angles (°): Cl(1)–Rh(1) = 2.3769(5), C(1)–Rh(1) = 2.0347(17); C(1)–Rh(1)–Cl(1) = 87.43(5), C(1)–Rh(1)–C(25) = 91.94(7), C(1)–Rh(1)–C(23) = 95.58(7), C(25)–Rh(1)–C(24) = 81.07(7), C(23)–Rh(1)–C(24) = 89.35(7).

and the NHC plane is 79.6°. The Rh–carbene bond is slightly longer than in **1a** and **1b**.

The metal geometry in **3** is best described as distorted square pyramidal with apical chloride; the COD and the bidentate NC^{DIPP} occupy the basal sites. The Ir–carbene bond is one of the shortest reported, even shorter than the corresponding bond in **4**. The M–C bond length of

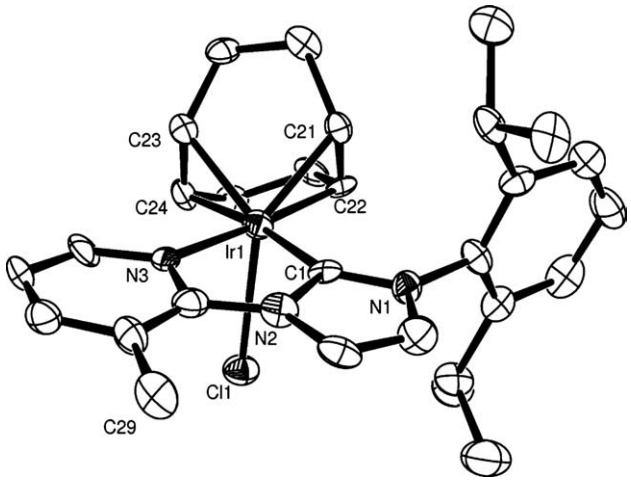


Fig. 3. ORTEP representation of **3** (50% probability ellipsoids). Hydrogen atoms and three solvent benzene molecules are omitted. Important bond lengths (Å) and angles (°): C(1)–Ir(1) = 1.994(10), C(21)–Ir(1) = 2.102(9), C(22)–Ir(1) = 2.061(10), C(23)–Ir(1) = 2.164(10), C(24)–Ir(1) = 2.188(10), N(3)–Ir(1) = 2.104(8), Cl(1)–Ir(1) = 2.546(3), C(21)–C(22) = 1.423(14), C(23)–C(24) = 1.404; C(1)–Ir(1)–N(3) = 77.7(4), N(3)–Ir(1)–Cl(1) = 83.4(2), C(1)–Ir(1)–Cl(1) = 87.1(3).

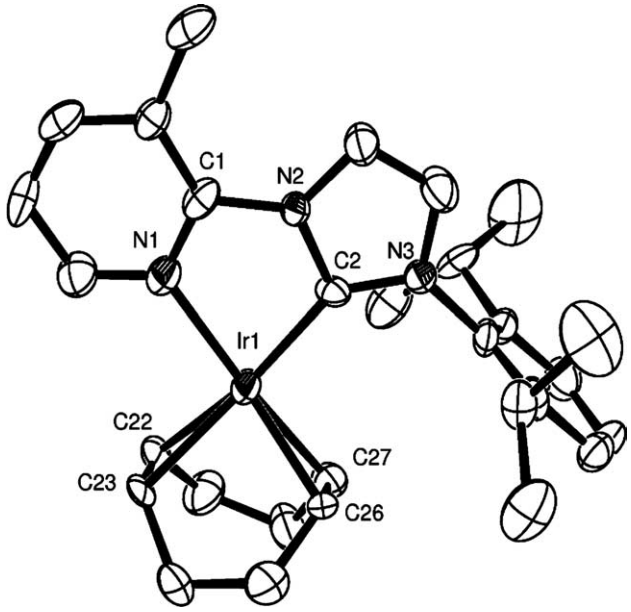


Fig. 4. ORTEP representation of the cation in **4** (50% probability ellipsoids). Hydrogen atoms and benzene molecules are omitted. Important bond lengths (Å) and angles (°): C(2)–Ir(1) = 2.015(9), C(22)–Ir(1) = 2.182(9), C(23)–Ir(1) = 2.227(10), C(26)–Ir(1) = 2.143(9), C(27)–Ir(1) = 2.153(9), C(22)–C(23) = 1.362(15), C(26)–C(27) = 1.417(14); C(2)–Ir(1)–N(1) = 78.0(4), C(2)–Ir(1)–C(26) = 97.9(4), C(2)–Ir(1)–C(27) = 100.6(4), N(1)–Ir(1)–C(22) = 95.9(4), N(1)–Ir(1)–C(23) = 96.2(4).

the double bond of the COD ligand (defined as above) which is *trans* to the NHC is longer (2.188 Å) than the one *trans* to the pyridine (2.062 Å), and the C=C bond length *trans* to the carbene and the one *trans* to the pyridine are equal within the observed e.s.d.s.

The structural data described above support strong metal–NHC bonds and higher *trans*-influence of the NHC relative to the pyridine. The observation of the dangling pyridine points to a kinetic barrier for the formation of the metal–pyridine bond in the Rh complex **2**. Abstraction of the Cl^- leads to facile pyridine coordination and concomitant formation of the square planar complexes **1a** and **1b**. The higher coordination numbers that are possible for the iridium account for the formation of the five coordinate **3**. When C–H bond is present in the C-3 position of the pyridine ring of the NC ligand, it is situated in close proximity to the metal and interacts with it to form either an agostic bond (Rh) or oxidative addition products (Ir) [4].

Attempts to crystallise **1a** or **2** from CH_2Cl_2 resulted in the isolation of product **5**, which originates from the oxidative addition of Cl–CH_2Cl to the metal centre. The complex is very insoluble in organic solvents, which hampered the collection of any NMR data. However, when the crystallisation was carried out by slow diffusion of petroleum into the dichloromethane X-ray quality crystals were obtained which allowed structural characterisation of $[(NC^{DIPP})RhCl(CH_2Cl)Cl]_2$ (**5**).

The diagram of the molecule is shown in Fig. 5. The complex is a centrosymmetric dimer with two octahedral rhodium centres bridged by two chloride ligands. The coordination sphere of each rhodium comprises, in addition to the chlorides, one bidentate NC^{DIPP} ligand, one terminal chloride and one CH_2Cl moiety. The metrical data for **5** are not unusual and do not need any further comment. The ease of the observed oxidative addition reaction may be due to the increased nucleophilicity of the Rh(I) centre after the coordination of the carbene ligand. However, we cannot distinguish whether there is higher reactivity towards the oxidative addition in a complex of type **1a** or **2**.

4.2. Phosphine functionalised NHC complexes of rhodium

The nature of the complexes isolated is strongly dependent on the type of the rhodium starting material that was used and the metal to ligand ratio. The complexes were isolated in moderate yields and characterised by spectroscopic and diffraction methods. The reaction of $[Rh(COD)(\mu\text{-}OMe)]_2$ with the imidazolium salt $(PCH_2CH^{mes})Br$ (metal/ligand = 1:2), in the presence of base gave rise to $[(PCH_2CH^{mes})_2Rh]Br$ **6**. Similar reaction with $(PCH_2CH^{DIPP})Br$ failed. The presence of the external base is necessary possibly due to the sensitivity of **6** to methanol. The new complex was identified by spectroscopic (NMR, MS) and diffraction methods. The presence of two ligands around the metal is supported by ES^+ MS data, while the geometry with carbene and phosphine donors *trans* to each other is established by a combination of $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopies. The phosphorus spectrum gives rise to a doublet ($^1J_{P-Rh} = 167.7$ Hz) and the carbene carbons appears as a single doublet at 179.9 ppm ($^1J_{Rh-C} = 48.9$ Hz). The structure of **6** was determined by single crystal X-ray diffraction; an ORTEP diagram of the cation is shown in Fig. 6.

The geometry around the metal centre is square planar with the NHC and phosphine functional groups disposed *trans* to each other. The Rh–carbene bond lengths

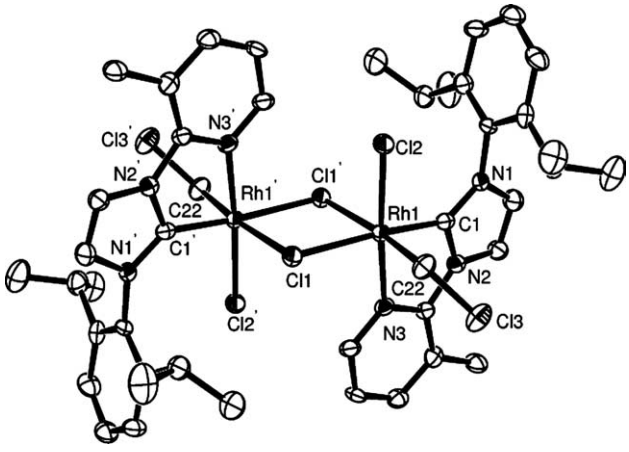


Fig. 5. ORTEP representation of the cation in **5** (50% probability ellipsoids). Hydrogen atoms and dichloromethane solvent molecules are omitted. Important bond lengths (Å) and angles (°): Rh(1)–C(1) = 1.949(5), Rh(1)–Cl(2) = 2.3379(11), Rh(1)–C(22) = 2.031(5), Rh(1)–N(3) = 2.051(3), Rh(1)–Cl(1) = 2.4712(12); C(22)–Rh(1)–N(3) = 91.71(17), C(1)–Rh(1)–N(3) = 79.48(16), C(1)–Rh(1)–C(22) 93.05(19).

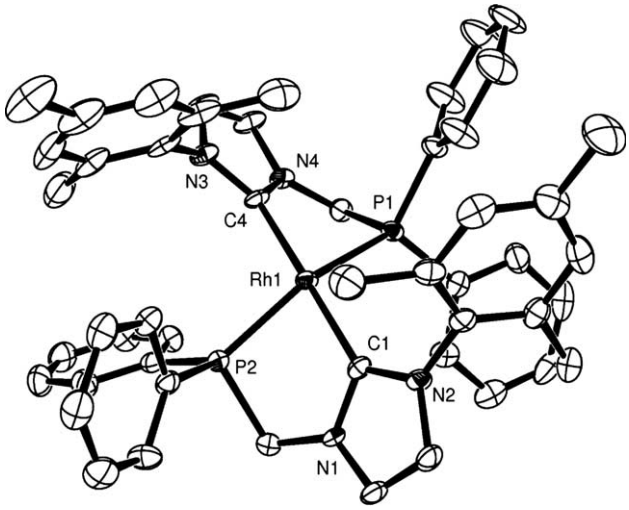


Fig. 6. ORTEP representation of the cation in **6** (50% probability ellipsoids); the bromide anion, two molecules of solvent (CH_2Cl_2) and H atoms are omitted. Selected bond lengths (Å) and angles (°): C(1)–Rh(1) = 2.044(6), C(4)–P(1)–Rh(1) = 2.2693(16), P(2)–Rh(1) = 2.2539(16); C(1)–Rh(1)–C(4) = 176.8(2), C(1)–Rh(1)–P(2) = 79.09(17), C(4)–Rh(1)–P(2) = 100.41(18), C(1)–Rh(1)–P(1) = 100.27(17), C(4)–Rh(1)–P(1) = 78.64(18), P(2)–Rh(1)–P(1) = 151.60(6).

are not unusual and equal within the observed e.s.d.s. The bite angle of the two ligands is 79.09(17)° and 78.64(18)°.

Complex **7** [$(PCH_2CH_2C^{DIPP})$Rh(acac)] was prepared by substitution of the labile cyclooctene in $Rh(COE)_2$-acac by the $PCH_2CH_2C^{DIPP}$, generated in situ from the corresponding imidazolium salt and base. In the ^{1}H NMR, the two acac ends are inequivalent and the diastereotopic methyls of the *o*-isopropyl groups appear as two doublets. The carbene carbon is easily observed as doublet at 183.4 ppm. The structure of **7** was established by single crystal X-ray diffraction and is shown in Fig. 7.

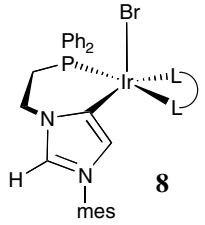
The geometry around the metal centre is square planar; the bite angle of the ligand is 91.5(2)°. The two Rh–O bond lengths are equal within the observed e.s.d.s, which is unexpected in view of the stronger *trans*-influence of the NHC relative to the phosphine functional groups. The Rh–C(carbene) and the Rh–P bond lengths are not uncommon and within the range previously reported.

4.3. Phosphine functionalised NHC complexes of iridium

Attempts to prepare phosphine functionalised iridium complexes were of limited success. For example, interaction of $[Ir(COD)Cl]_2$ with the phosphine functionalised NHCs generated in situ gave intractable solids, while reaction of the $(PCH_2CH_2CH^{DIPP})$Br with $[Ir(COD)Cl]_2$ gave the imidazolium functionalised phosphine complex of iridium [Ir(COD)(Br)($PCH_2CH_2CH^{DIPP}$)]. However, interaction of [Ir(COD)(μ-H)-(μ-Cl)$_2$]$_2$ with the $(PCH_2CH_2C^{mes})$ generated in situ gave after work up orange crystalline [$(PCH_2CH_2C^{mes})$Ir-(COD)]Br (**8**) (Scheme 4). The structure of **8** was determined by X-ray crystallography and is shown in Fig. 8.

This unusual complex incorporates an 'abnormal' carbene functionalised by the β-diphenylphosphinoethyl group. 'Abnormal' carbenes were first observed by Crabtree in pyridine functionalised iridium complexes, but more recently examples have been seen with tripodal and pincer carbene ligands [20–22].

The geometry around the metal centre in **8** is best described as square pyramidal with the basal positions occupied by the COD, the 'abnormal' carbene and the phosphine groups. The apical position is occupied by a



Scheme 4. Schematic representation of **8**; L–L is 1,5-COD.

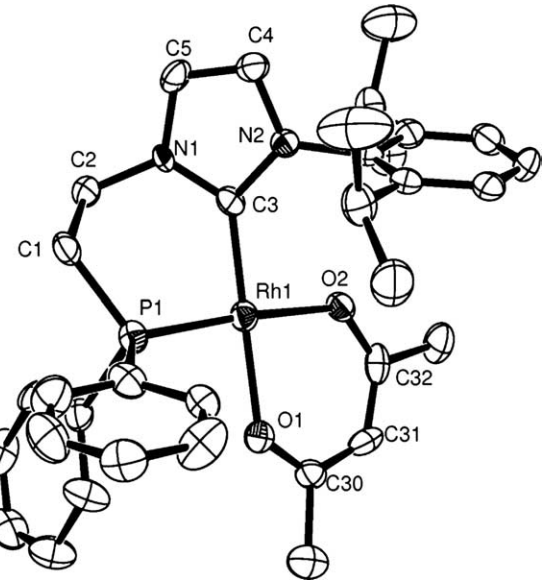


Fig. 7. ORTEP representation of **7** showing 50% probability ellipsoids. H atoms are omitted for clarity. The asymmetric unit consists of two molecules with similar metric data. Selected bond lengths (Å) and angles (°): C(3)–Rh(1) = 1.951(7), O(1)–Rh(1) = 2.058(5), O(2)–Rh(1) = 2.097(5), P(1)–Rh(1) = 2.160(2); C(3)–Rh(1)–O(1) = 175.2(3), C(3)–Rh(1)–O(2) = 93.2(3), O(1)–Rh(1)–O(2) = 89.0(2), C(3)–P(1) = 91.5(2), O(1)–Rh(1)–P(1) = 86.68(16), O(2)–Rh(1)–P(1) = 172.40(14).

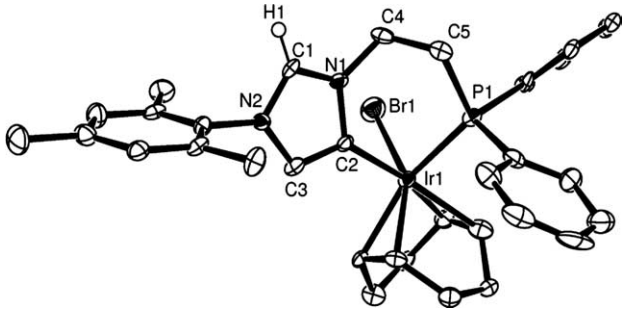


Fig. 8. ORTEP representation of **8** showing 50% probability ellipsoids. H atoms (except for the imidazolium proton H1) and one molecule of solvent (CH_2Cl_2) have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(2)–Ir(1) = 2.018(9), C(27)–Ir(1) = 2.089(8), C(28)–Ir(1) = 2.139(9), C(31)–Ir(1) = 2.217(9), C(32)–Ir(1) = 2.235(10), P(1)–Ir(1) = 2.283(2), Ir(1)–Br(1) = 2.6865(11); C(2)–Ir(1)–C(27) = 87.9(4), C(2)–Ir(1)–C(28) = 89.5(4), C(27)–Ir(1)–C(28) = 39.5(3), C(2)–Ir(1)–C(31) = 158.6(4), C(27)–Ir(1)–C(31) = 95.4(4), C(28)–Ir(1)–C(31) = 79.9(4), C(2)–Ir(1)–C(32) = 162.5(3), C(27)–Ir(1)–C(32) = 79.2(4), C(28)–Ir(1)–C(32) = 87.9(4), C(31)–Ir(1)–C(32) = 36.6(3), C(2)–Ir(1)–P(1) = 88.9(3), C(27)–Ir(1)–P(1) = 112.6(3), C(28)–Ir(1)–P(1) = 152.1(2), C(31)–Ir(1)–P(1) = 109.0(3), C(32)–Ir(1)–P(1) = 85.3(3), C(2)–Ir(1)–Br(1) = 86.6(2), C(27)–Ir(1)–Br(1) = 148.8(3), C(28)–Ir(1)–Br(1) = 109.7(2), C(31)–Ir(1)–Br(1) = 79.7(3), C(32)–Ir(1)–Br(1) = 110.5(2), P(1)–Ir(1)–Br(1) = 97.93(6).

bromide. The Ir–carbene bond distance is shorter than the one reported for the first 'abnormal' Ir(III) pyridine functionalised NHC complex [23].

^{1}H NMR data support the structure established crystallographically. Of high diagnostic value is the chemical shift of the C2–*H* at 9.8 ppm. The ^{13}C NMR spectrum could not be obtained due to sample decomposition.

5. Conclusions

In summary, we have synthesised new, C–H activation stabilised, pyridine functionalised *N*-heterocyclic carbene complexes of Rh(I) and Ir(I). Preliminary data show that the cationic iridium (I) complex **4** is active as transfer hydrogenation catalyst for carbonyl compounds. Attempts to prepare phosphine functionalised –NHC complexes of rhodium and iridium gave well-defined species only in a few cases.

6. Supplementary materials

The crystallographic data for this paper have been predeposited as follows: **1a** (CCDC 272980), **1b** (CCDC 272983), **2** (CCDC 272981), **3** (CCDC 272978), **4** (CCDC 272982), **5** (CCDC 272979), **6** (CCDC 272984), **7** (CCDC 272985), **8** (CCDC 272977). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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