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Mononuclear rhodium and iridium compounds with pyridyl-pyrazole ligands

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Dedicated to Professor F. Gordon A. Stone on the occassion of his 80th birthday

Abstract

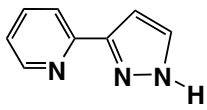
Neutral $[MCl(L_2)(Hpzpy)]$, $[M(L_2)(pzpy)]$ and cationic $[M(L_2)(Hpzpy)]CF_3SO_3$ rhodium(I) or iridium(I) complexes [M = Rh or Ir; L_2 = diolefin or $(CO)_2$; pzpy = 3-(2-pyridyl)pyrazolate] have been prepared; the pzpy and Hpzpy ligands coordinate to the metal as bidentate chelate groups through one pyrazole nitrogen and the pyridine nitrogen atom. The reactivity of these complexes towards oxidative addition reactions of halogens, methyl iodide or triflic acid and towards displacement reactions has been studied. The neutral and cationic iridium(I) complexes are modest catalysts for the hydrosilylation of phenylacetylene with triethylsilane at 60 °C. The complexes have been characterised by analytical and spectroscopic data; their configuration has been confirmed by COSY and NOESY experiments and the molecular structure of $[Rh(COD)(Mepzpy)(PPh_3)]CF_3SO_3$ has been established by an X-ray diffraction study.

Keywords: Rhodium; Iridium; Pyridyl-pyrazole ligand; Oxidative addition; X-ray crystallography

1. Introduction

Pyrazoles are known as both monodentate and exobidentate ligands and their nitrogen atoms coordinate to the metal centre as both anionic or neutral groups. Pyrazolate-bridged binuclear and polynuclear transition metal complexes have attracted special interest for many years [1–3].

An interesting situation arises when a five-membered heterocycle such as pyrazole and a six-membered heterocycle such as pyridine are directly linked in a single ligand system. In fact, the complexes of such ligands give rise to significantly different electronic properties [4,5]. The strong σ-donor properties of the pyrazole group, together with the π-accepting ability of the pyridyl ring, enhance the stability of the five-membered ring metal chelate. Among this type of ligands, the 3-(2-pyridyl)pyrazole provides a great potential to isolate mono- or polynuclear complexes. With this ligand, transition metal complexes as well as complexes containing principal group metals have been described [6–13].



3-(2-pyridyl)pyrazole (Hpzpy)

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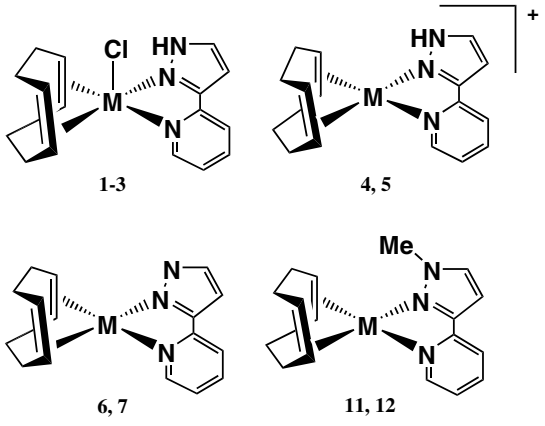
One of our research interests consists of the study of rhodium and iridium complexes, which are well known to show good performance in various catalytic reactions. Attention has been put in polynucleating ligands in order to synthesize homo or hetero polynuclear complexes [14–17], that could bring synergetic effects in their potential catalytic activity.

As a first step towards the synthesis of polynuclear species, in this paper, we wish to report the preparation and characterization of a new series of neutral and cationic mononuclear rhodium or iridium complexes with the 3-(2-pyridyl)pyrazole ligand. Their reactivity towards oxidative addition, displacement or hydrosilylation reactions is described. In these compounds the polydentate ligand coordinates to the metals through the pyridine nitrogen and one of the pyrazole or pyrazolate nitrogens.

2. Results and discussion

The coordination of the 3-(2-pyridyl)pyrazole ligand, acting as chelate to Rh or Ir, can be achieved from different starting products. The reaction of this ligand with the chloro-bridge rhodium or iridium diolefin dimers, $[\{M(\mu\text{-}Cl)(diolefin)\}_2]$, produces the cleavage of the chloro bridges and the formation of the mononuclear, pentacoordinated [MCl(Hpzpy)(diolefin)] [M = Rh, diolefin = 1,5-cyclooctadiene, COD, (**1**) or tetrafluorobenzobarrelene, TFB, (**2**); M = Ir, diolefin = COD, (**3**)] complexes in high yield (Fig. 1). These compounds were characterised on the basis of IR and multinuclear NMR spectroscopy, microanalysis and mass spectrometry.

The coordination of the chlorine atom to the metal can be inferred from the IR absorption bands at 297 (**1**), 275 (**2**) and 235 (**3**) cm^{-1}. In the ^1H NMR spectra the N–H signals appear at δ 15.2 (**1**), 15.9 (**2**) and 15.4 (**3**) ppm, downfield relative to the free ligand (δ 12.0 ppm). Most of the signals of the aromatic protons of the Hpzpy ligand are also shifted downfield with respect to the free ligand albeit the observed displacement is relatively small. However, the signal due to H2 proton, *ortho* to the pyridinic nitrogen (see Section 3), is shifted upfield and with larger displacement [$\Delta\delta$ 1.0, (**1**), 1.2 (**2**) and 0.7 (**3**)], showing that this proton increases its shielding when the ligand coordinates to the metals. This fact is probably due to the anisotropic effect caused by the olefinic carbon–carbon double bond [18], very close to the position of H2, and it has been observed in all complexes described in this paper. Each diolefin, COD or TFB, gives only a broad signal for the four =C*H* protons (from room temperature to −80 °C) at δ 4.7 (**1**), 4.5 (**2**) or 4.8 (**3**), which means that one or more dynamic processes make equivalent the four olefinic protons. The same behaviour has been observed for the four olefinic carbons. For complexes **1** and **3** signals in the $^{13}C\{^1H\}$ NMR spectra were assigned through ^1H-^{13}C correlation experiments. Complex **2** was not soluble enough to run its ^{13}C NMR spectrum. The signals of the carbon atoms of the ligand Hpzpy in complexes **1** and **3** appear downfield respect to the free ligand with the exception of C2 that moves upfield upon coordination. Compounds **1** and **3** only show one signal, at δ 83.8 (d, $^2J_{Rh-C}$ = 12.4 Hz, **1**) and 70.3 (s, **3**), for the four =*C*H groups, either at room or low temperature. This fluxional behaviour has only been observed in the pentacoordinated complexes prepared with this ligand, so the equilibrium in solution may be associated to the pentacoordination, like Berry's pseudorotation.



M = Rh or Ir; diolefin = COD or TFB

Fig. 1. Structures of various rhodium or iridium complexes in this study.

The reaction of the Hpzpy ligand with the solvated $[M(diolefin)(Me_2CO)_x]^+$ intermediates, prepared by the reaction of the chloro-bridged Rh or Ir dimers with silver salts and filtration of the silver chloride formed, causes the displacement of the solvent giving square-planar cationic mononuclear complexes $[M(Hpzpy)(COD)]^+$, crystallized with triflate as counterion, [M = Rh (**4**) or Ir (**5**)]. These products are solids of bright colours (yellow and red, respectively) stable to the air. In their IR spectra the absorption due to the triflato group, at around 1300 cm^{-1}, can be observed. Their conductivity measures show the complexes to be 1:1 electrolytes in acetone. The proton NMR spectra of these complexes consist of broad signals for the acidic protons of the pyrazole ligands at δ 13.6 (**4**) and 14.1 (**5**). The resonances of the remaining six protons of the ligand are observed between δ 6.7 and 8.1 all shifted downfield with the commented exception of H2 that appears upfield with respect to the free ligand. At higher fields the signals of the COD ligand are localized: the olefinic protons at δ 5.1 and 4.3 ppm for (**4**) and 5.0 and 4.0 (**5**) ppm (2 protons each) and the CH_2 hydrogens give two signals between δ 1.9 and 2.5 ppm. The

$^{13}C\{^1H\}$ NMR spectra show the signals due to the pyrazole ligand together with those of the COD group; however there is not signal detected for the triflate anion, probably due to the limited solubility of these compounds and to the difficulty of observing quaternary carbons with high multiplicity.

Neutral square-planar mononuclear complexes [M(pzpy)(COD)] [M = Rh (**6**) or Ir (**7**)], in which the pyrazole has lost its acidic proton, have also been prepared by reaction of the ligand with the methoxy-bridged rhodium or iridium dimers [{M(μ-OMe)(diolefin)}$_2$]. The presence of a nitrogen atom uncoordinated with a free electron pair makes these monomers potentially useful to prepare complexes of higher nuclearity. The ^1H NMR spectra were assigned on the basis of ^1H and ^1H-^{13}C correlation experiments. The absence of the acidic proton can be deduced from the proton NMR spectra: no signals above δ 8 ppm were detected. The integrals of the pzpy and COD signals are in 1:1 proportion. The olefinic protons of the COD give two signals of two protons each, at δ 5.0 and 4.1 ppm (**6**) and δ 4.9 and 3.7 ppm (**7**). The $^{13}C\{^1H\}$ NMR spectra show the signals of the 8 carbon atoms of the ligand as well as the resonances of the carbons of the COD (two for the olefinic protons, doublets with $^3J_{Rh-C}$ = 12.1 y 11.1 Hz for compound **6**, and two for the CH_2 protons) (see Section 3).

2.1. Oxidative addition reactions

Due to the great importance of the oxidative addition processes and the possibility of oxidation of complexes of Rh(I) or Ir(I) to Rh(III) and Ir(III) we have carried out a study of this type of reactions on the prepared complexes. An important factor to force the complexes to experiment this type of reactions is that the metal maintains a relatively high electron density. In our case, the metal is bonded to a diolefin and to the pyridinyl-pyrazole ligand. The bond of the diolefin to the metal has an important π back component but the N of the heterocycles has different behaviour according to the size of the ring: the pyridine (6 member ring) is π-acceptor while the pyrazole (5 member ring) is better π-donor. We have studied the reactions of the monomers with the following oxidative addition reagents: chlorine, iodine, triflic acid (HOtf), methyl iodide, and methyl triflate (MeOtf).

Reactions with halogens. The reactivity of complexes **1**–**7** with iodine has been checked. All of them react but only for complex **7** the isolation and characterization of the final product, as *trans*-[IrI_2(pzpy)(COD)] (**8**), has been possible. The ^1H NMR spectrum gives two multiplets for the =C*H* protons at δ 6.2 and 5.7. The $^{13}C\{^1H\}$ NMR spectrum shows two signals for the =*C*H at δ 87.6 and 85.9, and two for the *C*H_2 at δ 32.4 and 32.3. These values indicate the presence of a symmetry plane in the molecule that should be coincident with the coordination plane of the pzpy ligand, and corroborate the configuration of complex **8** as the *trans* isomer.

The reaction with chlorine of complexes **1**–**7** gives solids of low solubility and their NMR spectra indicate that mixtures of products are present. However the complex *cis*-[$IrCl_2$(pzpy)(COD)] (**9**) has been obtained by reaction of complex **7** with [AuCl(tht)] (tht = tetrahydrothiophene). The reaction was planned to prepare a dinuclear Ir–Au complex by coordination of the gold to the deprotonated nitrogen of the pzpy ligand. The dinuclear compound is probably formed but quickly evolves to give gold metal and the yellow compound **9**. The reaction is not a conventional oxidative addition reaction but a redox reaction involving the two metals. The iridium is oxidised from Ir(I) to Ir(III) and the gold is reduced from Au(I) to Au(0). The characterisation and the stereochemistry of complex **9** have been assigned by combining information from the ^1H and $^{13}C\{^1H\}$ NMR spectra and from NOE experiments. All data (see Section 3) are in agreement with the *cis* disposition of the chlorine atoms, being one of them *trans* to the *N*-pyrazole and the other *trans* to a C=C double bond.

Reactions with trifluoromethylsulfonic acid. The reactions of HOtf with CH_2Cl_2 solutions of complexes **1**, **4** or **5** gave mixtures of unidentified products. The reaction with complex **3** led to the oxidative addition of the reagent and to the preparation of a hydride Ir(III) complex of stoichiometry [Ir(H)Cl(Hpzpy)(COD)]Otf. However the product was a mixture of three isomers and, even doing the reaction at low temperature, none of them could be isolated. With complexes **6** and **7** the triflic acid produces the protonation of the pzpy ligand giving complexes **4** and **5**, respectively.

Reactions with methyl iodide. Rhodium complexes **1**, **4** or **6** did not give pure compounds under reaction with MeI. With complex **1** only a slow Cl/I exchange is detected. Complex **4** does not react with MeI and complex **6** gives mixtures of products. Iridium compounds **3**, **5** and **7** react with MeI but while the white reaction products of **3** and **5** where not completely identified, **7** reacted immediately giving an octahedral Ir(III) complex of stoichiometry [Ir(Me)I(pzpy)(COD)] (**10**). The analytical and mass spectroscopic data are in agreement with the proposed formulation. The ^1H and $^{13}C\{^1H\}$ NMR spectra show the lost of the symmetry plane of the molecule and NOE experiments show that a *trans* addition has taken place which suggest a SN2 mechanism for the oxidative addition reaction.

Trying to elucidate the mechanism of these reactions we did the reactions of complexes **1**–**7** with methyl triflate. With this reagent, the weakest oxidant used, only the neutral square-planar complexes reacted but the

reactions do not produce the expected oxidation products. Instead, N-methylation of the pyrazolate ligand takes place giving [M(Mepzpy)(COD)]Otf (M = Rh, **11**, or Ir, **12**)] cationic products. N-alkylation is one of the most important and most studied reactions of pyrazoles. Can be carried out using alkyl halides (usually iodides and bromides), diazomethane or alkyl salts [19]. Complex **12** is air, moisture and temperature sensitive in solution or in solid state. The analytical data are in agreement with the proposed formulation. Their conductivity measures show the complexes to be 1:1 electrolytes in acetone and in CH_2Cl_2. The mass spectra (FAB+) show the peaks for the species [M(Mepzpy)-(COD)]. These data support its formulation as ionic species with the Otf group out of the metal coordination sphere. The ^1H NMR spectra of **11** and **12** show only one signal for the four =C*H* protons (at δ 4.7, **11**, and 4.5, **12**); the methyl signals are at δ 3.8 and 3.9, respectively. In the $^{13}C\{^1H\}$ NMR spectrum of **12** the signal of the methyl group appears at δ 22.3.

Complexes **11** and **12** react with PPh_3 or $P(OMe)_3$ giving pentacoordinated cationic species [M(Mepzpy)-(COD)L]Otf [M = Rh, L = PPh_3, **13**, $P(OMe)_3$, **14**; M = Ir, L = PPh_3, **15**, $P(OMe)_3$, **16**] with the phosphorous ligand joined to the Rh or Ir atoms. Both Rh(I) complexes show thermal and air stability while the Ir(I) compounds have to be kept under argon atmosphere. Their corresponding analytical and spectroscopic data are shown in Section 3. They are 1:1 electrolytes in acetone solutions and, in $CDCl_3$, the pentacoordination around the metal atoms is maintained as it can be observed in the NMR spectra.

A single-crystal diffraction study of complex **13** was carried out to get an insight into its geometrical molecular parameters. A perspective view of the cationic metal complex, together with the atomic numbering scheme, is illustrated in Fig. 2; selected bond lengths and angles are listed in Table 1. The rhodium atom exhibits a saturated penta-coordinated environment, with bonds to the two nitrogens of the pyridylpyrazole and to the two olefinic moieties.

The metal coordination sphere is well described in terms of a slightly distorted trigonal-bipyramidal structure. The phosphine ligand and the C(14)–C(15) double bond of the cyclo-octadiene group occupy the axial positions; the three remaining coordinated moieties configure the equatorial plane (two nitrogens and the second olefinic double bond C(10)–(17)). The major terms of distortion come from the geometrical restrains introduced by the two quelating ligands: the pyridylpyrazole and the cyclo-octadiene groups. The goodness of the approximation could be inferred from L_{ax}–Rh–L_{eq} bond angles which are in the range 85.85(7)–100.01(6)° and from the sum of the inter-equatorial angles, 359.88(7)°, in spite of the narrow byte angle of the pyridyl-pyrazole chelate group (72.42(7)°).

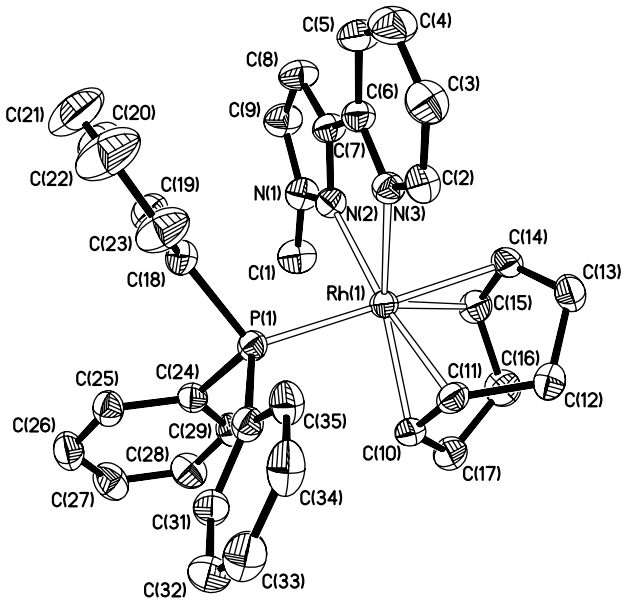


Fig. 2. Molecular structure of complex **13**. Hydrogens have been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for complex **13**

Rh(1)–P(1)	2.3147(6)	N(1)–N(2)	1.348(3)
Rh(1)–N(2)	2.1726(19)	N(1)–C(1)	1.439(3)
Rh(1)–N(3)	2.313(2)	N(1)–C(9)	1.353(3)
Rh(1)–M(1)[a]	1.9834(18)	N(2)–C(7)	1.344(3)
Rh(1)–C(10)	2.125(2)	N(3)–C(2)	1.344(3)
Rh(1)–C(11)	2.088(2)	N(3)–C(6)	1.345(3)
Rh(1)–M(2)[a]	2.1071(18)	C(10)–C(11)	1.421(4)
Rh(1)–C(14)	2.204(2)	C(14)–C(15)	1.374(4)
Rh(1)–C(15)	2.228(2)		
P(1)–Rh(1)–N(2)	90.15(5)	M(1)–Rh(1)–M(2)[a]	85.85(7)
P(1)–Rh(1)–N(3)	92.89(5)	N(2)–N(1)–C(1)	121.6(2)
P(1)–Rh(1)–M(1)[a]	90.81(5)	N(2)–N(1)–C(9)	110.9(2)
P(1)–Rh(1)–M(2)[a]	166.41(5)	C(1)–N(1)–C(9)	127.5(2)
N(2)–Rh(1)–N(3)	72.42(7)	Rh(1)–N(2)–N(1)	135.26(15)
N(2)–Rh(1)–M(1)[a]	164.77(7)	Rh(1)–N(2)–C(7)	118.92(16)
N(2)–Rh(1)–M(2)[a]	89.67(7)	Rh(1)–N(3)–C(2)	125.96(17)
N(3)–Rh(1)–M(1)[a]	122.69(7)	Rh(1)–N(3)–C(6)	115.49(15)
N(3)–Rh(1)–M(2)[a]	100.01(6)		

[a] M(1) and M(2) represent the midpoints of the olefinic bonds C(10)–C(11) and C(14)–C(15), respectively.

The most intriguing feature of the structure concerns the relative long Rh–N(3) bond distance, 2.313(2) Å. This distance is only comparable with values observed for pyridines as axial ligands in lantern complexes of the type $[Rh_2(\mu\text{-}RCO_2)_4(pyR')_2]$ (around 2.25 Å) when situated *trans* to the metal–metal bond [20,21] or in pentacoordinated Rh(I)-diolefin-pyridine complexes (range 2.273(4)–2.320(2) Å) containing tridentate pyridine-amine-pyridine ligands [22,23]. This parameter seems to reflect the relatively high electron density of the rhodium(I) atom in this coordinatively saturated complex

and its well known tendency to form square-planar environments.

The cyclo-octadiene molecule is linked to the metal through the two olefinic bonds showing its usual tub conformation; however the two double bonds exhibit very different bonding parameters with Rh–C mean distances of 2.097(2) Å (C(10) and C(11)) and 2.216(2) Å (C(14) and C(15)). The different metal-olefin interaction is also reflected in the C–C double bonds, which are 1.421(4) and 1.374(4) Å, respectively. This peculiar behaviour should be associated to the different π-character of the nearly *trans* ligands (P(1)–Rh–M(2) 166.41(5)°; N(2)–Rh–M(1) 164.77(7)°).

2.2. Displacement reactions

The diolefin ligand of complexes **1**–**7** can easily be displaced by bubbling carbon monoxide through their solutions. However, in many cases, the formed products are not soluble enough to run their NMR spectra, making difficult their identification. The low solubility along with the dark colours observed and the planarity of the species suggest the presence of electronic interactions due to the stacking in columns of these metal complexes. These compounds exhibit low stability both in deoxygenated solutions and in the solid state and consequently they have to be kept at low temperature and under inert atmosphere.

With the pentacoordinated complexes **1** or **3**, dark blue solids, of stoichiometry $[MCl(Hpzpy)(CO)_2]$ (M = Rh or Ir) with four IR *v*(CO) stretching bands in the terminal carbonyl region are formed. The products are not soluble enough to run their NMR spectra. They are probably mixtures of the pentacoordinated complexes and the ionic compounds with the chlorine atom out of the coordination sphere.

Cationic compounds **4** and **5** give, under carbonylation, pure bis-carbonyl complexes $[M(Hpzpy)(CO)_2]Otf$ (M = Rh, **17**; Ir, **18**) that can be isolated and characterised. They are not very soluble but, in acetone, it is possible to obtain their proton NMR spectra. They show six signals for the aromatic protons of the Hpzpy ligand and complex **17** also shows a wide signal at low field (δ 14.3) due to the N–H proton. Complex **18** is less soluble and the N–H signal was not observed.

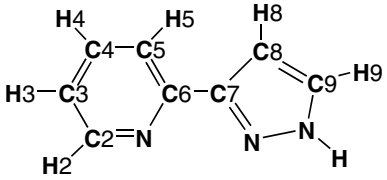
When the neutral complexes **6** or **7**, with the deprotonated pyrazole, are used their reaction with CO gives mixtures of dicarbonylated mononuclear products $[M(pzpy)(CO)_2]$ together with dinuclear complexes $[\{M(pzpy)(CO)\}_2]$ in which the pyrazole is coordinated as exo bidentate bridge. The solid obtained for M = Rh shows three IR *v*(CO) stretching bands at 2085, 2017 cm^{-1}, attributed to the mononuclear species, and at 1965 cm^{-1}, assigned to the dinuclear compound. For the Ir products only two IR *v*(CO) stretching bands are observed, those of the mononuclear complex. The iridium dinuclear compound is not soluble enough, so the *v*(CO) absorption could not be detected.

2.3. Hydrosilylation reactions

Catalytic hydrosilylation of alkynes is a relevant process generating important reagents for a number of organic transformations [24]. The neutral [Ir(pzpy)(COD)] complex is a modest catalyst for the hydrosilylation of phenylacetylene with triethylsilane in 1,2-dichloroethane at 60 °C. After 1420 min, the conversion is 58.5% and the products formed are *cis*-$PhCH{=}CH(SiEt_3)$ (42.5%), *trans*-$PhCH{=}CH(SiEt_3)$ (18.8%), $Ph(SiEt_3)C{=}CH_2$ (6.6%), $PhC{\equiv}CSiEt_3$ (19.3%), $PhCH{=}CH_2$ (9.8%) and $PhCH_2{-}CH_3$, (9.8%). The amount of $PhC{\equiv}CSiEt_3$ formed by the dehydrogenative silylation was similar to that of $PhCH{=}CH_2$ plus that of $PhCH_2{-}CH_3$. A normal hydrosilylation together with the dehydrogenative silylation of phenylacetylene and simultaneous formation of styrene has been previously observed and rationalized for the cationic $[Ir(iPr_2CH_2CH_2OMe)(COD)][BF_4]$ complex [25]. We have also studied the activity of the cationic $[Ir(Hpzpy)(COD)]^+$ complex that, although a little bit faster (66% conversion after 1420 min) produces along with the normal products of hydrosilylation significant amounts of ethylbenzene (39.4%).

3. Experimental

Reactions were routinely carried out by standard Schlenk-line techniques under an argon atmosphere, using dioxygen-free solvents unless noted otherwise. Elemental analyses (C, H, N and S) were carried out in a Perkin–Elmer 240 C microanalyser. Infrared spectra (4000–400 cm^{-1}) were recorded on a Nicolet 550 or on Perkin–Elmer 883 (4000–200 cm^{-1}) spectrophotometers using Nujol mulls between polyethylene sheets or in solution in NaCl cells. Conductivity measurements were performed, using a Phillips conductivity bridge, at 20 °C in ca. 5×10^{-4} M acetone solutions. FAB mass spectra (*m*-nitrobenzyl alcohol matrix) were recorded in a V.G. Autoespec double-focusing mass spectrometer operating in the positive mode; high-resolution mass spectra are in accordance with the simulated isotopic pattern distribution. NMR spectra were recorded on Varian Gemini 2000, Varian Unity 300 or Bruker ARX 300 spectrometers. Chemical shifts are reported in ppm and the solvents were used as internal reference. The atoms numbering of the ligand used for NMR descriptions is as follows:



The complexes [{Rh(μ-Cl)(COD)}$_2$] [26], [{Rh(μ-OMe)(COD)}$_2$] [27], [{Ir(μ-Cl)(COD)}$_2$] [28], [{Ir(μ-OMe)(COD)}$_2$] [29], [{Rh(μ-Cl)(TFB)}$_2$] [30], [IrCl(TFB)$_2$] [31] and [{Rh(μ-Cl)(CO)$_2$}$_2$] [32] and the ligand [3-(2-pyridinyl)pyrazole] [33,34] were prepared according to the reported methods.

3.1. Synthesis of [MCl(diolefin)(Hpzpy)] (M = Rh, diolefin = COD, 1; M = Rh, diolefin = TFB, 2; M = Ir, diolefin = COD, 3)

To dichloromethane solutions of [{M(μ-Cl)(diolefin)}$_2$] (0.40 mmol) Hpzpy (0.116 mg, 0.80 mmol) was added. The solutions were stirred for 1 h and the solvent was partially evaporated under reduced pressure. Upon addition of diethyl ether solids were formed, which were filtered, washed with diethyl ether and dried under reduced pressure. Data for **1**: yellow, yield 89%. *Anal*. Calc. for $C_{16}H_{19}ClN_3Rh$: C, 49.06; H, 4.89; N, 10.73. Found: C, 48.72; H, 5.31; N, 11.07%. MS (FAB) *m/e* 356 [(M–Cl)$^+$, 40]. IR (nujol, polyethylene sheets): *ν*(Rh–Cl) 297 cm^{-1}. ^{1}H NMR (CD_2Cl_2, −80 °C), *δ*, 15.2 (br, 1H, N–H), 8.0 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, H-4), 7.8 (2H, H-9 + H-5), 7.6 (d, $^3J_{H-H}$ = 5.3 Hz, 1H, H-2), 7.4 (t, $^3J_{H-H}$ = 6.4 Hz, 1H, H-3), 6.8 (d, $^3J_{H-H}$ = 2.6 Hz, 1H, H-8), 4.7 (br, 4H, =CH), 2.4 (br, 4H, CH_2), 2.0 (m, 4H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, −80 °C), *δ*, 148.1 (s, C-2), 140.4 (s, C-9), 134.0 (s, C-4), 125.0 (s, C-3), 121.6 (s, C-5), 103.5 (s, C-8), 83.8 (d, J_{C-Rh} = 12.4 Hz, =CH), 30.8 (s, CH_2). Data for **2**: yellow, 70% yield. *Anal*. Calc. for $C_{20}H_{13}ClF_4N_3Rh$: C, 47.13; H, 2.57; N, 8.24. Found: C, 46.59; H, 2.31; N, 8.04%. MS (FAB) *m/e* 474 [(M–Cl), 100]. ^{1}H NMR ($CDCl_3$), *δ*, 15.9 (br, 1H, N–H), 8.0 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, H-4), 7.7 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, H-5), 7.7 (br, 1H, H-9), 7.4 (d, $^3J_{H-H}$ = 5.1 Hz, 1H, H-2), 7.4 (t, $^3J_{H-H}$ = 6.6 Hz, 1H, H-3), 6.7 (d, $^3J_{H-H}$ = 2.4 Hz, 1H, H-8), 5.7 (br, 2H, TFB), 4.5 (br, 4H, TFB). ^{19}F NMR ($CDCl_3$), *δ*, −148.0 m, −160.1 m. Data for **3**: Red, yield 88%. *Anal*. Calc. for $C_{16}H_{19}ClIrN_3$: C, 39.95; H, 3.98; N, 8.74. Found: C, 39.76; H, 3.98; N, 8.74%. MS (FAB) *m/e* 480 (M, 15), 446 [(M–Cl), 100]. *ν*(Ir–Cl) 235 cm^{-1}. ^{1}H NMR (CD_2Cl_2), *δ*, 15.4 (br, 1H, N–H), 8.1 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, H-4), 7.9 (br, 1H, H-2), 7.9 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, H-5), 7.8 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, H-9), 7.5 (t, $^3J_{H-H}$ = 6.2 Hz, 1H, H-3), 6.8 (d, $^3J_{H-H}$ = 2.5 Hz, 1H, H-8), 4.8 (br, 4H, =CH), 2.3 (m, 4H, CH_2), 1.9 (m, 4H, CH_2). ^{13}C{^{1}H} RMN (CD_2Cl_2), *δ*, 156.4 (s, C-7), 150.0 (s, C-6), 143.1 (s, C-2), 137.2 (s, C-9), 127.2 (s, C-4), 123.2 (s, C-3), 121.9 (s, C-5), 105.6 (s, C-8), 70.3 (s, =CH), 33.1 (s, CH_2).

3.2. Synthesis of [M(COD)(Hpzpy)] (CF_3SO_3) (M = Rh, 4; M = Ir, 5)

To CH_2Cl_2/acetone solutions (10/5 ml) of [{M(μ-Cl)(COD)}$_2$] (0.51 mmol), $AgCF_3SO_3$ (260 mg, 1.01 mmol) was added. After 30 min at room temperature (r.t.), the white solid (AgCl) formed was filtered off, and the ligand, Hpzpy (148 mg, 1.02 mmol) was added to the solution. The mixtures were stirred for 15 min. Partial evaporation of the solvent and addition of diethylether led to the precipitation of compounds **4** and **5**, which were filtered off, washed with diethylether and vacuum dried. Data for **4**: Yellow, 82% yield. *Anal*. Calc. for $C_{17}H_{19}F_3N_3O_3RhS$: C, 40.41; H, 3.79; N, 8.32; S, 6.35. Found: C, 40.54; H, 3.99; N, 8.34; S, 6.22%. IR (nujol, polyethylene sheets): *ν*(N–H) 3100, br, cm^{-1}. MS (FAB) *m/e* 356 [M$^+$, 100]. Λ_M 99.5 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$), *δ*, 13.6 (br, 1H, N–H), 8.0 (td, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.4 Hz, 1H, H-4), 7.9 (d, $^3J_{H-H}$ = 2.5 Hz, 1H, H-9), 7.8 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, H-5), 7.7 (td, $^3J_{H-H}$ = 6.4 Hz, $^3J_{H-H}$ = 1.2 Hz, 1H, H-3), 7.6 (d, $^3J_{H-H}$ = 5.5 Hz, 1H, H-2) 6.7 (d, $^3J_{H-H}$ = 2.8 Hz, 1H, H-8), 5.1 (br, 2H, =CH), 4.3 (br, 2H, =CH), 2.5 (m, 4H, CH_2), 2.1 (m, 4H, CH_2). ^{19}F NMR ($CDCl_3$), *δ*, −80.6 s. ^{13}C{^{1}H} NMR ($CDCl_3$), *δ*, 152.6 (s, C-7), 152.3 (s, C-6), 147.7 (s, C-2), 140.5 (s, C-9), 134.4 (s, C-4), 125.1 (s, C-3), 121.5 (s, C-5), 103.4 (s, C-8), 84.7 (br, =CH), 82.4 (br, =CH), 30.6 (br, CH_2), 29.9 (br, CH_2). Data for **5**: Red, 84% yield. *Anal*. Calc. for $C_{17}H_{19}F_3IrN_3O_3S$: C, 34.34; H, 3.22; N, 7.07; S, 5.39. Found: C, 34.42; H, 3.37; N, 7.18; S, 5.25%. IR (nujol, polyethylene sheets): *ν*(N–H) 3150, br, cm^{-1}. MS (FAB) *m/e* 446 [M$^+$, 100]. Λ_M 93 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$), *δ*, 14.1 (br, 1H, N–H), 8.1 (td, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, H-4), 8.0 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-9) 7.9 (d, $^3J_{H-H}$ = 5.7 Hz, 1H, H-2), 7.8 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, H-5), 7.5 (td, $^3J_{H-H}$ = 6.5 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, H-3) 6.8 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-8), 5.0 (br, 2H, =CH), 4.0 (br, 2H, =CH), 2.3 (br, 4H, CH_2), 1.9 (m, 4H, CH_2). ^{19}F NMR ($CDCl_3$), *δ*, −80.5 s. ^{13}C{^{1}H}NMR ($CDCl_3$), *δ*, 148.2 (s, C-2), 141.3 (s, C-9), 135.8 (s, C-4), 125.8 (s, C-3), 121.5 (s, C-5), 104.0 (s, C-8), 71.0 (s, =CH), 67.2 (s, =CH), 31.5 (s, CH_2), 30.5 (s, CH_2).

3.3. Synthesis of [M(COD)(pzpy)] (M = Rh, 6; M = Ir, 7)

The ligand Hpzpy (107 mg, 0.74 mmol) was added to dichloromethane (15 ml) solutions of [{M(μ-OMe)(COD)}$_2$] (0.37 mmol). The solutions were stirred for

2 and then the solvent was partially evaporated under reduced pressure. Upon addition of diethyl ether solids were formed, which were filtered, washed with diethyl ether and dried under reduced pressure. Data for **6**: Yellow, 84% yield. *Anal*. Calc. for $C_{16}H_{18}N_3Rh$: C, 54.10; H, 5.11; N, 11.83. Found: C, 54.10; H, 5.04; N, 11.89%. MS (FAB) *m/e* 356 [MH^+, 100]. ^{1}H NMR ($CDCl_3$, −55 °C) δ, 7.7 (td, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, H-4), 7.6 (d, $^3J_{H-H}$ = 1.8 Hz, 1H, H-9), 7.5 (d, $^3J_{H-H}$ = 6.3 Hz, 1H, H-2), 7.5 (d, $^3J_{H-H}$ = 9.0 Hz, 1H, H-5), 7.0 (td, $^3J_{H-H}$ = 6.5 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, H-3), 6.4 (d, $^3J_{H-H}$ = 1.8 Hz, 1H, H-8), 5.0 (br, 2H, =CH), 4.1 (br, 2H, =CH), 2.5 (m, 4H, CH_2), 2.0 (br, 4H, CH_2). $^{13}C\{^1H\}$ RMN ($CDCl_3$, −55 °C), δ, 154.7 (s, C-7), 151.1 (s, C-6), 146.7 (s, C-2), 141.0 (br, C-9), 139.4 (s, C-4), 121.6 (s, C-3), 119.3 (s, C-5), 102.3 (s, C-8), 82.6 (d, J_{C-Rh} = 12.1 Hz, =CH), 80.8 (d, J_{C-Rh} = 11.1 Hz, =CH), 30.3 (s, CH_2). Data for **7**: Red, 93% yield. *Anal*. Calc. for $C_{16}H_{18}IrN_3$: C, 43.23; H, 4.08; N, 9.45. Found: C, 42.97; H, 4.17; N, 9.38%. MS (FAB) *m/e* 446 [MH^+, 100]. ^{1}H NMR ($CDCl_3$), δ, 7.8 (2H, H-2 + H-4), 7.6 (d, $^3J_{H-H}$ = 1.8 Hz, 1H, H-9), 7.5 (dd, $^3J_{H-H}$ = 8.7 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, H-5), 7.1 (td, $^3J_{H-H}$ = 6.6 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, H-3), 6.4 (d, $^3J_{H-H}$ = 1.8 Hz, 1H, H-8), 4.9 (br, 2H, =CH), 3.7 (br, 2H, =CH), 2.3 (m, 4H, CH_2), 1.8 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ, 157.1 (s, C-7), 153.7 (s, C-6), 147.0 (s, C-2), 142.3 (s, C-9), 140.1 (s, C-4), 121.8 (s, C-3), 118.9 (s, C-5), 103.0 (s, C-8), 68.0 (br, =CH), 63.7 (br, =CH), 31.1 (s, CH_2).

3.4. Synthesis of trans-[IrI_2(COD)(pzpy)] (**8**)

Iodine (45 mg, 0.18 mmol) was added to a dichloromethane solution of **7** (75 mg, 0.17 mmol) and the mixture was stirred for 4.5 h giving a red suspension. The solvent was evaporated under reduced pressure till a small volume. Upon addition of diethyl ether a red solid was formed, which was filtered, washed with diethyl ether and dried under reduced pressure. The product was recrystallised from dichloromethane-diethyl ether. Yield 60%. The data are for the *trans* isomer, which was obtained in a 98% proportion. *Anal*. Calc. for $C_{16}H_{18}I_2IrN_3$: C, 27.52; H, 2.60; N, 6.02. Found: C, 27.42; H, 2.63; N, 5.94%. ^{1}H NMR ($CDCl_3$), δ, 7.8 (dt, $^3J_{H-H}$ = 5.7 Hz, $^4J_{H-H}$ = 0.9 Hz, 1H, H-2), 7.8 (2H, H-4 + H-5), 7.6 (d, $^3J_{H-H}$ = 2.4 Hz, 1H, H-9), 7.1 (td, $^3J_{H-H}$ = 5.9 Hz, $^4J_{H-H}$ = 3.0 Hz, 1H, H-3), 6.8 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, H-8), 6.2 (m, 2H, =CH), 5.7 (m, 2H, =CH), 3.1 (m, 4H, CH_2), 3.0–2.8 (4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ, 156.8 (s, C-7), 149.6 (s, C-6), 148.2 (s, C-2), 142.0 (s, C-9), 140.1 (s, C-4), 122.3 (s, C-3), 121.0 (s, C-5), 105.8 (s, C-8), 87.6 (s, =CH), 85.9 (s, =CH), 32.4 (s, CH_2), 32.3 (s, CH_2).

3.5. Synthesis of cis-[$IrCl_2$(COD)(pzpy)] (**9**)

To a dichloromethane solution of **7** (100 mg, 0.22 mmol) [AuCl(tht)] (144 mg, 0.44 mmol) was added. After 20 min the solution darkened and a black solid (metallic gold) was deposited on the Schlenk walls. The suspension was kept stirring for two days and the black solid was filtered through kieselguhr giving a yellow solution. Most of the solvent was removed under reduced pressure and diethyl ether was added yielding a yellow solid, which was filtered, washed with diethyl ether and vacuum dried. Yield 62%. *Anal*. Calc. for $C_{16}H_{18}Cl_2IrN_3$: C, 37.28; H, 3.52; N, 8.15. Found: C, 37.33; H, 3.60; N, 8.10%. IR (nujol, polyethylene sheets): ν(Ir–Cl) 276 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ, 9.5 (d, $^3J_{H-H}$ = 6.2 Hz, 1H, H-2), 7.9–7.7 (3H, H-4 + H-5 + H-9), 7.2 (td, $^3J_{H-H}$ = 6.7 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, H-3), 6.8 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, H-8), 6.7 (m, 1H, =CH), 6.0 (m, 1H, =CH), 5.3 (m, 1H, =CH), 4.1 (m, 1H, =CH), 3.4–1.4 (8H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ, 154.3 (s, C-7), 147.7 (s, C-2), 146.1 (s, C-6), 141.9 (s, C-9), 139.7 (s, C-4), 121.4 (s, C-3), 119.9 (s, C-5), 105.8 (s, C-8), 103.7 (s, =CH), 102.1 (s, =CH), 97.7 (s, =CH), 97.3 (s, =CH), 32.3 (s, CH_2), 32.1 (s, CH_2), 29.0 (s, CH_2), 28.4 (s, CH_2).

3.6. Synthesis of [Ir(Me)I(COD)(pzpy)] (**10**)

The addition of iodomethane (0.5 μl, 8.0 mmol) to a red dichloromethane solution of **7** (50 mg, 0.11 mmol) gave a yellow-orange suspension, in 10 min. Half of the solvent was evaporated under reduced pressure. Upon addition of diethyl ether a yellow solid was formed, which was filtered, washed with diethyl ether and dried under reduced pressure. The product was recrystallised from dichloromethane-diethyl ether. Yield 58%. *Anal*. Calc. for $C_{17}H_{21}IIrN_3$: C, 34.82; H, 3.61; N, 7.58. Found: C, 35.09; H, 3.66; N, 7.16%. MS (FAB) *m/e* 588 [M, 100]. ^{1}H NMR ($CDCl_3$), δ, 7.8–7.7 (3H, H-2 + H-4 + H-5), 7.6 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, H-9), 7.1 (td, $^3J_{H-H}$ = 6.0 Hz, $^4J_{H-H}$ = 1.6 Hz, 1H, H-3), 6.7 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, H-8), 5.8 (t, $^3J_{H-H}$ = 7.1 Hz, 1H, =CH), 5.2 (t, $^3J_{H-H}$ = 7.1 Hz, 1H, =CH), 4.8 (m, 1H, =CH), 4.3 (m, 1H, =CH), 3.2–2.0 (8H, CH_2), 1.8 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ, 155.6 (s, C-7), 147.8 (s, C-6), 146.4 (s, C-2), 141.0 (s, C-9), 139.3 (s, C-4), 121.7 (s, C-3), 120.8 (s, C-5), 104.7 (s, C-8), 83.6 (s, =CH), 82.8 (s, =CH), 82.2 (s, =CH), 81.8 (s, =CH), 33.5 (s, CH_2), 32.9 (s, CH_2), 27.9 (s, CH_2), 27.5 (s, CH_2), 9.0 (s, Me).

3.7. Synthesis of [M(Mepzpy)(COD)](Otf) (M = Rh, 11; M = Ir, 12)

MeOtf (32 μl, 0.28 mmol) was added to dichloromethane (15 ml) solutions of [M(COD)(pzpy)] (**6** or **7**) (100 mg, 0.28 mmol for **6**, 127 mg, 0.28 mmol for **7**). The solutions were stirred for 2 h and 3/4 of the solvent was evaporated under reduced pressure. Upon addition of 15 ml of diethyl ether solids were formed, which were filtered, washed with diethyl ether and dried under reduced pressure. The products were recrystallised from dichloromethane/diethyl ether. They are no stable and have to be kept under argon atmosphere and at low temperature. Data for **11**: Yellow, 81% yield. *Anal*. Calc. for $C_{18}H_{21}F_3N_3O_3RhS$: C, 41.63; H, 4.08; N, 8.09; S, 6.17. Found: C, 41.70; H, 4.01; N, 7.85; S, 5.93%. MS (FAB) *m/e* 370 [M^+, 100]. Λ_M (acetone) 107 Ω^{-1} cm^2 mol^{-1}. Λ_M (dichloromethane) 47 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$), δ, 8.0 (td, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, H-4), 7.9 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, H-5), 7.9 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-9), 7.6 (d, $^3J_{H-H}$ = 5.7 Hz, 1H, H-2), 7.4 (td, $^3J_{H-H}$ = 6.5 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, H-3), 6.9 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-8), 4.7 (br, 4H, =CH), 3.8 (s, 3H, Me), 2.6 (m, 4H, CH_2), 2.0 (m, 4H, CH_2). Data for **12**: Red, 86% yield. *Anal*. Calc. for $C_{18}H_{21}F_3IrN_3O_3S$: C, 35.52; H, 3.48; N, 6.90; S, 5.27. Found: C, 35.52; H, 3.09; N, 6.81; S, 4.92%. MS (FAB) *m/e* 460 [M^+, 100]. Λ_M (acetone) 100 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$), δ, 8.1 (2H, H-4 + H-5), 8.0 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-9), 7.9 (d, $^3J_{H-H}$ = 5.7 Hz, 1H, H-2), 7.5 (td, $^3J_{H-H}$ = 6.0 Hz, $^4J_{H-H}$ = 2.7 Hz, 1H, H-3), 7.1 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-8), 4.5 (br, 4H, =CH), 3.9 (s, 3H, Me), 2.4 (m, 4H, CH_2), 1.8 (m, 4H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$), δ, 146.8 (s, C-2), 142.2 (s, C-9), 139.8 (s, C-4), 126.1 (s, C-3), 122.8 (s, C-5), 106.2 (s, C-8), 31.2 (s, CH_2), 22.3 (s, Me).

3.8. Synthesis of [M(Mepzpy)(PPh$_3$)(COD)](Otf) (M = Rh, 13; M = Ir, 14)

To dichloromethane solutions (15 ml) of **11** or **12** (0.20 mmol) PPh_3 (52.46 mg, 0.20 mmol) was added. The solutions were stirred for 15 min, the solvent was partially removed and the addition of hexane led to yellow solids, which were filtered, washed with hexane and vacuum dried. Complex **14** is not stable in solution and in the solid state has to be kept under argon at low temperature. Data for **13**: Yield 74%. *Anal*. Calc. for $C_{36}H_{36}F_3N_3O_3PRhS$: C, 55.32; H, 4.61; N, 5.38; S, 4.09. Found: C, 54.90; H, 4.31; N, 5.36; S, 3.80%. MS (FAB) *m/e* 524 [(Rh(Mepzpy)(PPh_3))$^+$, 15], 370 [(Rh(Mepzpy)(COD))$^+$, 100], 262 [Rh(Mepzpy)$^+$, 25]. Λ_M 84 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$), δ, 8.8 (d, $^3J_{H-H}$ = 5.1 Hz, 1H, H-2), 8.0 (d, $^3J_{H-H}$ = 2.5 Hz, 1H, H-9), 7.8 (td, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 1.3 Hz, 1H, H-4), 7.5 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, H-5), 7.3–7.1 (m, 15 H, PPh_3), 6.5 (d, $^3J_{H-H}$ = 2.5 Hz, 1H, H-8), 4.2 (s, 3 H, Me–N), 3.8 (br, 4H, =CH), 2.5 (m, 4H, CH_2), 1.9 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$), δ, 151.0 (s, C2), 150.1 (s, C6), 149.8 (s, C7), 138.4 (s, C9), 136.3 (s, C4), 133.2 (d, *o*-C, PPh_3, $^2J_{C-P}$ = 10 Hz), 130.4 (s, *p*-C, PPh_3), 129.7 (d, *ipso*-C, PPh_3, $^1J_{C-P}$ = 37.7 Hz), 128.4 (d, *m*-C, PPh_3, $^3J_{C-P}$ = 8.8 Hz), 124.7 (s, C3), 122.1 (s, C5), 105.4 (s, C8), 80.8 (s, =CH, COD), 40.3 (s, Me–N), 31.1 (s, CH_2, COD).^{31}P NMR (20 °C, $CDCl_3$), δ, 28.0 (br); (−60 °C, $CDCl_3$), δ, 32.7 (d, $^1J_{Rh-P}$ = 129.6 Hz). ^{19}F NMR ($CDCl_3$), δ, −80.0 (s, ^{19}F). Data for **14**: Yellow; yield 70%. *Anal*. Calc. for $C_{36}H_{36}F_3IrN_3O_3PS$: C, 49.64; H, 4.14; N, 4.82; S, 3.70. Found: C, 49.04; H, 3.99; N, 4.70; S, 3.68%. MS (FAB) *m/e* 721 [M^+, 15], 460 [(Ir(Mepzpy)(COD))$^+$, 100]. Λ_M 75 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$), δ, 9.0 (2H, H-4 + H-5), 8.0 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-9), 7.8 (td, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, H-3), 7.6 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, H-2), 7.2 (m, 15 H, PPh_3), 6.7 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-8), 4.2 (s, 3H, Me–N), 3.2 (br, 4H, =CH), 2.4 (m, 4H, CH_2), 1.8 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$), δ, 152.1 (s, C6), 151.7 (s, C2), 151.5 (s, C7), 138.6 (s, C9), 136.4 (s, C4), 133.1 (d, *o*-C, PPh_3, $^2J_{C-P}$ = 10.25 Hz), 130.6 (s, *p*-C, PPh_3), 128.9 (d, *ipso*-C, PPh_3, $^1J_{C-P}$ = 38.5 Hz), 128.4 (d, *m*-C, PPh_3, $^3J_{C-P}$ = 9.51 Hz), 125.1 (s, C3), 122.2 (s, C5), 105.9 (s, C8), 63.7 (s, =CH, COD), 40.5 (s, Me–N), 32.3 (s, CH_2, COD). ^{31}P NMR ($CDCl_3$), δ, 10.4 (s, ^{31}P). ^{19}F NMR ($CDCl_3$), δ, −80.0 (s, ^{19}F).

3.9. Synthesis of [M(Mepzpy)(P(OMe)$_3$)(COD)](Otf) (M = Rh, 15; M = Ir, 16)

To dichloromethane solutions (15 ml) of **11** or **12** (0.19 mmol) $P(OMe)_3$ (22.73 μl, 0.19 mmol) was added very slowly. The solutions were stirred (3 h for the rhodium complex and 3 min for the iridium complex), the solvent was partially removed and the addition of hexane or diethyl ether led to yellow solids, which were filtered, washed with hexane and vacuum dried. Complex **16** has to be kept under argon at low temperature. Data for **15**: Yellow, 72% yield. *Anal*. Calc. for $C_{21}H_{30}F_3N_3O_6PRhS$: C, 39.19; H, 4.66; N, 6.53; S, 4.97. Found: C, 38.84; H, 4.35; N, 6.20; S, 4.47%. Λ_M 91 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$), δ, 8.1 (td, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.3 Hz 1H, H-4), 7.9 (d, $^3J_{H-H}$ = 7.3 Hz, 1H, H-5), 7.8 (d, $^3J_{H-H}$ = 2.3 Hz, 1H, H-9), 7.6 (d, $^3J_{H-H}$ = 5.2 Hz, 1H, H-2), 7.4 (td, $^3J_{H-H}$ = 6.3 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, H-3), 6.9 (d, $^3J_{H-H}$ = 2.8 Hz, 1H, H-8), 5.0 (br, 4H, =CH), 4.1 (s, Me–N), 3.9 (d, $^3J_{H-P}$=12.4 Hz, 9-H, O–CH_3), 2.7 (m, 4H, CH_2), 2.2 (m, 4H, CH_2). ^{31}P NMR ($CDCl_3$), δ, 143.4 (d, $^1J_{P-Rh}$ = 275.4 Hz). ^{19}F NMR ($CDCl_3$), δ, −80.1 (s). Data for **16**: White-yellow, 70% yield. *Anal*. Calc. for $C_{21}H_{30}F_3IrN_3O_6PS$: C, 34.41; H, 4.09; N,

5.74; S, 4.37. Found: C, 34.04; H, 3.87; N, 5.60; S, 4.18%. MS (FAB) *m/e* 584 [M^+, 10], 460 [(Ir(Mepzpy)-(COD))$^+$, 100]. Λ_M 85 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$), δ, 9.2 (2H, H-4 + H-5), 8.0 (d, $^3J_{H-H}$ = 2.5 Hz, 1H, H-9), 7.9 (d, $^3J_{H-H}$ = 5.4 Hz, 1H, H-2), 7.5 (td, $^3J_{H-H}$ = 6.1 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, H-3), 7.0 (d, $^3J_{H-H}$ = 2.5 Hz, ^{1}H, H-8), 4.4 (br, 4H, =CH), 4.3 (s, Me–N), 3.4 (d, $^3J_{H-P}$ = 11.11 Hz, 9-H, O–CH_3), 2.4 (m, 4H, CH_2), 2.1 (m, 4H, CH_2). ^{31}P NMR ($CDCl_3$), δ, 86.9 (s). ^{19}F NMR ($CDCl_3$), δ, −80.11 (s).

3.10. Synthesis of [M(CO)$_2$(Hpzpy)](CF$_3$SO$_3$) (M = Rh, 17; M = Ir, 18)

Through acetone or dichloromethane solutions (10 ml) of **4** or **5** (0.20 mmol), respectively, CO (1 atm, r.t.) was bubbled for 50 min; complexes **17** and **18** were forming as orange and green solids. To complete the precipitation of the complexes diethyl ether was added to the solution. The solids were filtered off under argon atmosphere, washed with diethyl ether and vacuum dried. Both complexes are not stable to the air or to the temperature so they have to be kept under argon and in the fridge. Compound **18** is not soluble enough to run its ^{13}C NMR. Data for **17**: Orange; yield 65%. *Anal*. Calc. for $C_{11}H_7F_3N_3O_5RhS$: C, 26.51; H, 1.56; N, 9.27; S, 7.08. Found: C, 27.03; H, 1.70; N, 9.34; S, 7.18%. IR (nujol, polyethylene sheets, cm^{-1}): ν(N–H) 3120, br; ν(CO) 2105, 2046. IR (CH_2Cl_2): ν(CO) 2104, 2042. Λ_M 104 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (HDA), δ, 14.3 (br, 1H, N–H), 8.9 (d, $^3J_{H-H}$ = 5.1 Hz, 1H, H-2), 8.4 (2H, H-5 + H-4), 8.3 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-9), 7.8 (t, $^3J_{H-H}$ = 5.7, 1H, H-3), 7.4 (d, $^3J_{H-H}$ = 2.7, 1H, H-8). ^{19}F NMR (HDA), δ, −74.4 s. ^{13}C NMR (HDA), δ, 155.2 (s, C-2), 143.4 (s, C-9), 136.2 (s, C-4), 127.5 (s, C-3),123.5 (s, C-5), 105.7 (s, C-8). Data for **18**: Green, 72% yield. *Anal*. Calc. for $C_{11}H_7F_3IrN_3O_5S$: C, 22.14; H, 1.30; N, 7.75; S, 5.91. Found: C, 22.92; H, 1.56; N, 7.58; S, 5.41%. IR (nujol, polyethylene sheets, cm^{-1}): ν(CO) 2077, 2031. Λ_M 97.0 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (HDA), δ, 9.1 (d, $^3J_{H-H}$ = 5.1 Hz, 1H, H-2), 8.6–8.5 (2H, H-4 + H-5), 8.4 (d, $^3J_{H-H}$ = 3.0 Hz, 1H, H-9), 7.9 (td, $^3J_{H-H}$ = 6.5 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, H-3), 7.5 (d, $^3J_{H-H}$ = 2.7 Hz, 1H, H-8). ^{19}F NMR (HDA), δ, −76.0 s.

3.11. X-ray structural analysis of complex 13

A summary of crystal data and refinement parameters is reported in Table 2. Data for the complex were obtained at 150(1) K from a BrukerAXS SMART APEXII CCD diffractometer installed at station 9.8 of the SRS Daresbury laboratory. Radiation was monochromated with a silicon 111 crystal (λ = 0.69340 Å); data were collected using narrow frames (0.3° in ω). Cell parameters were refined from the observed setting angles and detector positions of a set of strong reflections (11088 ref.). During data collection instrument and crystal stability was evaluated from measurement of equivalent reflections at different measuring times; no important variations were observed. Intensities were integrated from several series of exposure frames covering the whole reciprocal space [35]. Data were corrected for Lorentz and polarisation effects, and a semi-empiricial absorption correction, based on repeated and symmetry-equivalent reflections, was also applied [36].

Table 2
Crystal data and structure refinement parameters for complex **13**

Empirical formula	$C_{36}H_{36}F_3N_3O_3PSRh \cdot CH_2Cl_2$
Formula weight	866.54
Crystal system	orthorhombic
Space group	*Pbcn*
a (Å)	35.0719(12)
b (Å)	11.8495(4)
c (Å)	18.4056(6)
V (Å^3)	7649.1(4)
Z	8
D_{calc} (g cm^{-3})	1.505
μ (mm^{-1})	0.737
Crystal size (mm)	0.09 × 0.06 × 0.02
θ_{max} (°)	2.07–27.51
Index ranges	$-46 \leqslant h \leqslant 46$, $-14 \leqslant k \leqslant 15$, $-24 \leqslant l \leqslant 24$
Reflections measured	60 020
Independent reflections	9450 [R_{int} = 0.0504]
Maximum and minimum transmission	0.9854 and 0.9366
Data/restraints/parameters	9450/0/594
Goodness-of-fit on F^2	1.043
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0358, wR_2 = 0.0899
R indices (all data)	R_1 = 0.0484, wR_2 = 0.0950
Largest peak and hole (e Å^{-3})	0.810 and −0.622

The structure was solved by direct methods and completed by successive difference Fourier syntheses. Anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were included from observed positions and refined as free isotropic atoms (except those of the methyl group, which were refined with riding positional and displacement parameters). A dichloromethane solvent molecule was also detected in the crystal structure; its carbon atom was observed disordered and split in two complementary positions. Refinements were carried out by full-matrix least-squares on F^2 for all data [37]. Final agreement factors are collected in Table 2. All the residual peaks in the final difference map were below 1 e Å^{-3}. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program [37].

4. Supplementary material

Crystallographic data has been deposited with the Cambridge Data Centre (Deposition no. CCDC 247480). Copies of the information can be obtained from the Director (E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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