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2-(2′-Pyridyl)-4,6-diphenylphosphinine versus 2-(2′-Pyridyl)-4,6-diphenylpyridine: Synthesis, Characterization, and Reactivity of Cationic Rh^{III} and Ir^{III} Complexes Based on Aromatic Phosphorus Heterocycles

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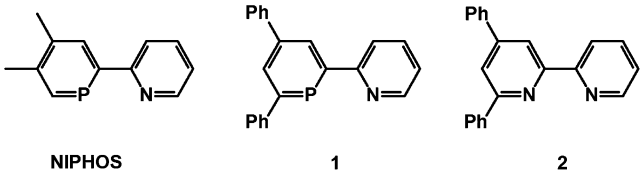
Abstract: The bidentate P,N hybrid ligand **1** allows access for the first time to novel cationic phosphinine-based Rh^{III} and Ir^{III} complexes, broadening significantly the scope of low-coordinate aromatic phosphorus heterocycles for potential applications. The coordination chemistry of **1** towards Rh^{III} and Ir^{III} was investigated and compared with the analogous 2,2′-bipyridine derivative, 2-(2′-pyridyl)-4,6-diphenylpyridine (**2**), which showed significant differences. The molecular structures of [RhCl(Cp*)(**1**)]Cl and [IrCl(Cp*)(**1**)]Cl (Cp* = pentamethylcyclopentadienyl) were determined by means of X-ray diffraction and confirm the mononuclear nature of the λ^3-phosphinine–Rh^{III} and Ir^{III} complexes. In contrast, a different reactivity and coordination behavior was found for the nitrogen analogue **2**, especially towards Rh^{III} as a bimetallic ion pair $[RhCl(Cp^*)(\mathbf{2})]^+$ $[RhCl_3(Cp^*)]^-$ is formed rather than a mononuclear coordination compound. [RhCl(Cp*)(**1**)]Cl and [IrCl(Cp*)(**1**)]Cl react with water regio- and diastereoselectively at the external P=C double bond, leading exclusively to the *anti*-addition products [MCl(Cp*)-(**1**H·OH)]Cl as confirmed by X-ray crystal-structure determination.

Keywords: chelates · coordination chemistry · heterocycles · N,P ligands · phosphorus

Introduction

2,2′-Bipyridine (bpy) and its derivatives are well studied nitrogen ligands and their rich coordination chemistry has often been exploited for the development of molecular devices, homogeneous catalytic systems or modern materials with interesting photophysical properties.[1] The replacement of a pyridine unit by a π-accepting λ^3-phosphinine entity[2,3] leads to 2-(2′-pyridyl)phosphinine, a semi-equivalent of bpy containing a low-coordinate "soft" phosphorus and a "hard" nitrogen heteroatom. Such chelates are intriguing bidentate P,N hybrid ligands, which have first been described by Mathey et al. in 1982 with the synthesis of 2-(2′-pyridyl)-4,5-dimethylphosphinine (NIPHOS).[4,5]



NIPHOS 1 2

However, replacing nitrogen by phosphorus in similar structures causes significant diverse properties due to the electronic difference that exists between these heteroatoms. Phosphinines are particularly suitable for the stabilization of late-transition-metal centers in low oxidation states because of their pronounced π-accepting character.[3] In contrast, the preparation of phosphinine complexes containing metal centers in medium-to-high oxidation states is rather challenging.[6] Especially for metal centers in higher oxidation states and with reduced π-back-donation capability, the aromaticity of the phosphinine heterocycle is significantly disrupted upon coordination. As a result, the phosphinine core behaves like a cyclophosphahexatriene containing a highly reactive P=C double bond. Earlier attempts to prepare such compounds have shown that they are extremely sensitive towards nucleophilic attack, making their straightforward synthesis, handling, characterization, and potential application rather unattractive.[7] Yet access to such species would open up new perspectives in the field of phosphorus-containing molecular materials, as well as in homogeneous catalysis.

We have recently started to investigate the synthesis and coordination chemistry of functionalized 2,4,6-triaryl-substituted phosphinines, which are generally accessible through

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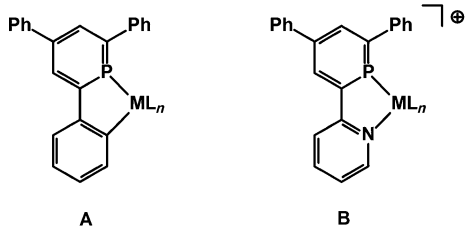
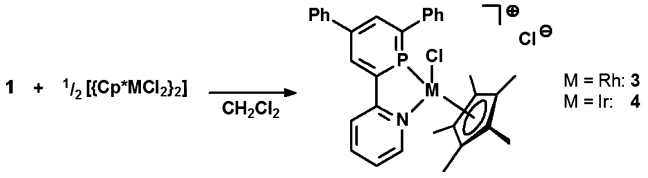
the modular pyrylium-salt route reported by Märkl and coworkers.[2a,8–10] It turned out that 2-(2′-pyridyl)-4,6-diphenylphosphinine (**1**) is readily available from the corresponding pyridyl-functionalized pyrylium salt.[11] Interestingly, this route also allowed us to prepare the 2,2′-bipyridine derivative 2-(2′-pyridyl)-4,6-diphenylpyridine (**2**) with an identical substitution pattern, which consequently made for the first time the direct structural comparison of these heterocycles and the corresponding transition-metal complexes possible.[12] We further demonstrated that the neutral complexes [$Pd^{II}Cl_2$(**1**)] and [$Pt^{II}Cl_2$(**1**)] could easily be prepared and isolated.[13] Moreover, we also achieved an unprecedented C–H activation of 2,4,6-triphenylphosphinine by Ir^{III} and Rh^{III} precursors.[14] The cyclometalated compounds of type **A** represent the first examples of isolated and structurally characterized neutral phosphinine-M^{III} coordination compounds reported so far.



Both the chelate effect of the bidentate P,N ligand and the phenyl-group in the 6-position of the heterocyclic framework of **1** are anticipated to contribute significantly to the formation and stabilization of such complexes. Because the formally anionic ligand (PC) in complex **A** is isoelectronic with the neutral P,N ligand **1**, we anticipated that cationic coordination compounds of type **B**, containing the same metal fragment should be accessible as well. We report herein on our first results concerning the synthesis, characterization, and reactivity of such novel cationic phosphinine–M^{III} (M = Rh, Ir) complexes.

Results and Discussion

Reaction of **1** with [{$RhCl_2$(Cp*)}$_2$] (Cp* = pentamethylcyclopentadiene) in the ratio of 2:1 in CD_2Cl_2 leads instantaneously to a dark-red solution. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows a single doublet at δ = 186.0 ppm and a coordination shift of $\Delta\delta(^{31}P) = -3.0$ ppm, which is in the expected region for phosphinine–metal complexes with an η^1-coordination mode of the phosphorus heterocycle. In the ^1H NMR spectrum two doublets ($^3J_{H-P}$ = 20.8 Hz) at δ = 8.44 and 8.82 ppm are observed for the two peripheral protons of the phosphorus heterocycle. Likewise, reaction of **1** with 0.5 equivalents of [{$IrCl_2$(Cp*)}$_2$] in CD_2Cl_2 leads exclusively to one single species according to NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture reveals a signal at δ = 158.0 ppm and a chemical shift difference upon coordination of $\Delta\delta(^{31}P) = -31.0$ ppm. The ^1H NMR spectrum shows two sets of doublet of doublets ($^3J_{H-P}$ = 25.1, $^3J_{H-P}$ = 19.2, $^4J_{H-H}$ = 1.4 Hz) at δ = 8.37 and 8.77 ppm for the two peripheral protons of the phosphorus heterocycle. From the NMR spectra we conclude that quantitative formation of the Rh and Ir complexes **3** and **4** has occurred according to Scheme 1.



Scheme 1. Synthesis of Rh^{III} and Ir^{III} complexes of **1**.

Orange crystals of **3** and **4** suitable for X-ray diffraction were isolated in 91 and 72% yield by slow diffusion of Et_2O into a diluted solution of **1** and [{$RhCl_2$(Cp*)}$_2$] and [{$IrCl_2$(Cp*)}$_2$] in CH_2Cl_2, respectively. Complexes **3** and **4** have the same crystal packing and are thus isomorphous with very similar unit-cell parameters. They crystallize enantiomerically purely in the noncentrosymmetric space group $P2_12_12_1$ with one metal complex in the asymmetric unit. Because both enantiomers were formed during the synthesis, it can be assumed that crystals of both enantiomers are present as a racemic conglomerate. Plots of the molecular structures in the crystal are given in Figure 1 and selected bonding geometries are compared in Table 1. For a comparison of bond angles, torsion angles, and interplanar angles in the molecular structures reported herein, see the Supporting Information.

Table 1. Selected distances [Å] and angles [°] in **3** and **4**.

Compound	**3** (Rh)	**4** (Ir)
M(1)–centroid	1.8078(11)	1.819(3)
M(1)–Cl(1)	2.3843(7)	2.3858(19)
P(1)–M(1)	2.2659(6)	2.2428(16)
N(1)–M(1)	2.136(2)	2.127(6)
C(5)–C(6)	1.475(3)	1.488(9)
P(1)–C(1)	1.720(2)	1.717(7)
P(1)–C(5)	1.720(2)	1.710(6)
C(1)–C(2)	1.400(3)	1.386(9)
C(2)–C(3)	1.406(3)	1.405(9)
C(3)–C(4)	1.394(3)	1.382(9)
C(4)–C(5)	1.389(3)	1.384(9)
N(1)–C(6)	1.347(3)	1.364(8)
C(1)-P(1)-C(5)	106.64(12)	106.7(3)
P(1)-M(1)-N(1)	77.93(5)	78.00(15)

The X-ray crystal structures of **3** and **4** in Figure 1 confirm the observed NMR spectroscopic data and reveal the mononuclear nature of the coordination compounds with the metal centers displaying the characteristic three-legged "piano-stool" arrangement. Figure 1 nicely shows the difference between the aromatic pyridine moiety and the aromatic phosphinine ring, which is best described as a distorted

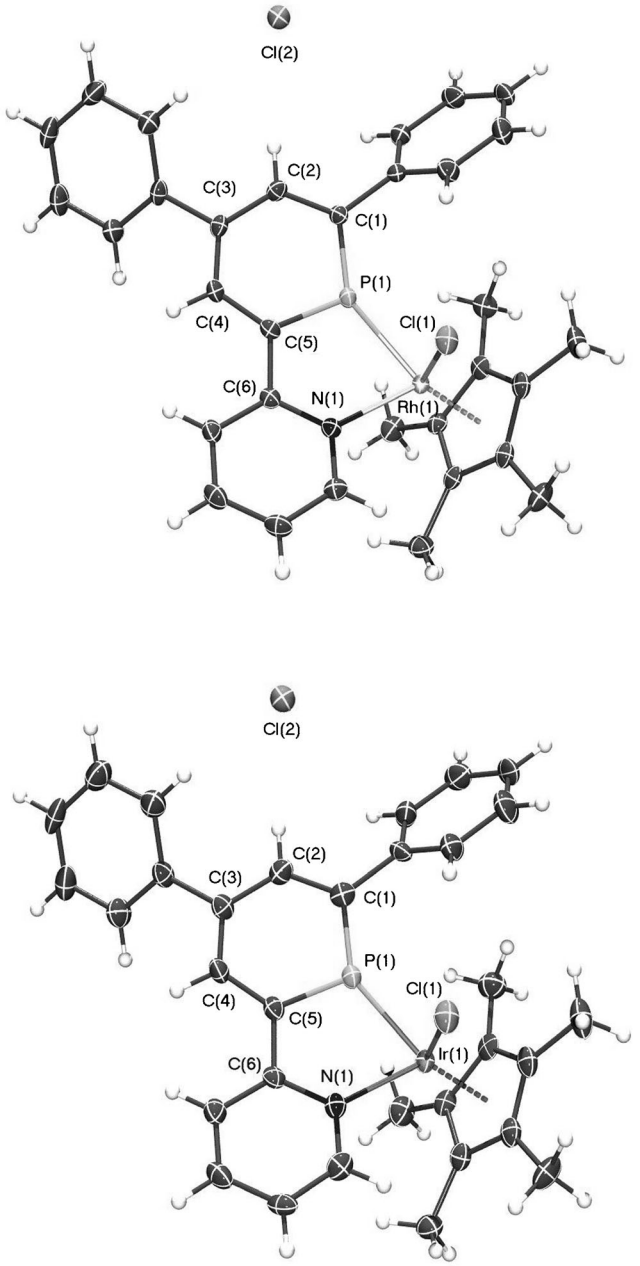


Figure 1. Molecular structures of **3** (top) and **4** (bottom) in the crystal. Displacement ellipsoids are shown at the 50% probability level. Only one enantiomer is shown. The absolute structure of **3** has been inverted in the drawing with respect to the X-ray crystal structure for reasons of clarity.

hexagon due to the larger P–C bond length in comparison to the N–C bond length. The two heterocyclic rings in **3** and **4** are essentially coplanar with respect to one another with an intercyclic C–C bond length of 1.475(3) in **3** and 1.488(9) Å in **4**. The P–C(1) and P–C(5) bond lengths of 1.720(2)/1.710(2) (**3**) and 1.717(7)/1.710(6) Å (**4**) are somewhat shorter than in free 2,4,6-triarylphosphinines (1.74–1.76 Å),[15] whereas the carbon–carbon bond lengths in the aromatic phosphinine subunit are in the usual range (1.389(3)–1.406(3) in **3** and 1.382(9)–1.405(9) Å in **4**) observed for both free and coordinated phosphinine ligands. The M(1)–P(1) bond lengths are 2.2659(6) in **3** and 2.2428(16) Å in **4**, and thus are very similar to those in the corresponding neutral complexes [RhCl(Cp*)(PC)Cl] and [IrCl(Cp*)(PC)] of type **A** (2.2156(4) and 2.2397(11) Å, respectively). The Ir(1)–N(1) distance of 2.127(6) Å is slightly larger than in the related 2,2′-bipyridine complex [Ir(bpy)Cl(Cp*)]Cl (Ir(1)–N(1) = 2.076(8), Ir(1)–N(2) = 2.090(2) Å).[16] The bite angles P(1)-M(1)-N(1) are very similar for the two coordination compounds with 77.93(5) (**3**) and 78.00(15)° (**4**) and slightly larger than in [Ir(bpy)Cl(Cp*)]Cl (76.2(3)°) due to the presence of two different heteroatoms. Most strikingly, the metal centers are not located in the ideal axis of the phosphorus lone pair but clearly shifted towards the nitrogen atom (C(5)-P(1)-Rh(1) = 108.23(9), C(1)-P(1)-Rh(1) = 145.10(8), C(5)-P(1)-Ir(1) = 108.8(2), C(1)-P(1)-Ir(1) = 144.4(2)°). Clearly, this effect is necessary for an efficient complexation of the metal atom by the chelating P,N ligand and facilitated by the more diffuse and less directional lone pair of the low-coordinate phosphorus atom relative to the sp^2-hybridized nitrogen atom in pyridines. Consequently, it is not observed for the M(1)–N(1) interactions (C(6)-N(1)-Rh(1) = 123.41(15), C(10)-N(1)-Rh(1) = 117.17(16), C(6)-N(1)-Ir(1) = 123.6(4), C(10)-N(1)-Ir(1) = 117.7(5)°). As observed by us before, the phenyl substituents in the α-position of the P-heterocycle are shifted away from the coordination site and are additionally rotated out of the plane of the P-heterocycle (torsion angles P(1)-C(1)-C(11)-C(12) = 42.8(3)° (**3**) and −43.3(9)° (**4**)). In this way, the P-ligating ability of such 2,4,6-triaryl-substituted phosphinines is apparently not influenced as dramatically as observed for $-SiMe_3$-substituted ones, which show a preference for η^6-coordination through the aromatic ring, rather than for η^1-coordination through the phosphorus lone pair.[17]

Complexes **3** and **4** are the first reported crystallographic characterizations of cationic phosphinine–Rh^{III} and Ir^{III} complexes. To form a strong bond with a Lewis acidic metal center the lone pair at the phosphorus atom, containing a high s character in the free ligand, must gain considerable p character upon coordination. This leads to an opening of the internal ∢C-P-C angle, which is approximately 100° in a free phosphinine. Because this phenomenon can thus be correlated with the electron-accepting character of a metal-fragment, it appears interesting to compare the ∢C-P-C angles in **3** and **4** with selected literature data.[18] In the Cr^0 complex $[Cr(CO)_4(tmbp)]$ (tmbp = tetramethylbisphosphinine),[19] the ∢C-P-C angle is 104.3°. As a matter of fact, this compound is highly stable towards nucleophilic attack. In the Rh^I complex $[Rh(cod)(\mathbf{1})][BF_4]$ (cod = 1,5-cyclooctadiene), the corresponding value is 105.25°, whereas in the Ru^{II} complex *cis*-$[RuCl_2(dmso)(tmbp)]$, it is 106.08°.[12a,20] The latter compound, however, is much less stable towards nucleophilic attack, which indicates the disruption of aromaticity upon coordination to a more electrophilic metal center. For compounds **3** and **4**, we find values of 106.64(12) and 106.7(3)°, respectively. Despite the fact that the large opening of this ∢C-P-C angle reflects significant disruption

of the aromaticity and consequently a high reactivity of the P=C double bond is expected (see below), both compounds can easily be isolated, handled, and characterized and seem to be considerably more stable than, for example, the NIPHOS-containing cationic Pd^{II} and Pt^{II} complexes described by Venanzi et al.[7,18] As mentioned above, we assume that the additional aryl substituents at the 2- and 6-positions of the heterocyclic framework might indeed contribute to a steric protection of the P=C double bond as we have observed before for neutral $[PdCl_2(\mathbf{1})]$ and $[PtCl_2(\mathbf{1})]$ complexes, as well as for the neutral phosphinine–Rh^{III} and Ir^{III} complexes $[MCl(Cp^*)(\widehat{PC})]$, containing a cyclometalated 2,4,6-triphenylphosphinine ligand.

To compare the coordination behavior of **1** with the analogous 2,2′-bipyridine derivative **2**, we reacted ligand **2** with $[\{RhCl_2(Cp^*)\}_2]$ in a ratio of 2:1 in CD_2Cl_2 under identical conditions to those described above. In the ^1H NMR spectrum of the reaction mixture the immediate formation of a new species was observed, which shows two different Cp* units. Moreover, one equivalent of unreacted ligand **2** was still present in solution and this ratio did not change upon heating the reaction mixture either. However, in the case of reacting **2** with $[\{IrCl_2(Cp^*)\}_2]$ in a ratio of 2:1 in CD_2Cl_2, the formation of only one single species was observed by ^1H NMR spectroscopy. Based on the NMR spectra we, therefore, propose the formation of the bimetallic ion pair $[RhCl(Cp^*)(\mathbf{2})]^+[RhCl_3(Cp^*)]^-$ (**5**), whereas a monomeric species is expected for compound **6** (Scheme 2).

By slow diffusion of Et_2O into a diluted solution of **5** and **6** in CD_2Cl_2, yellow and orange crystals, respectively, suitable for X-ray diffraction were isolated in 82 (based on Rh) and 89% yield. Compound **5** crystallizes enantiopurely in the orthorhombic space group $P2_12_12_1$ and the asymmetric unit consists of one metal complex molecule. The Ir complex **6** crystallizes as a racemate in the monoclinic space group $P2_1/n$ with one metal complex molecule in the asymmetric unit. Plots of the molecular structures of one enantiomer in the crystal are given in Figure 2 and selected bonding geometries are compared in Table 2.

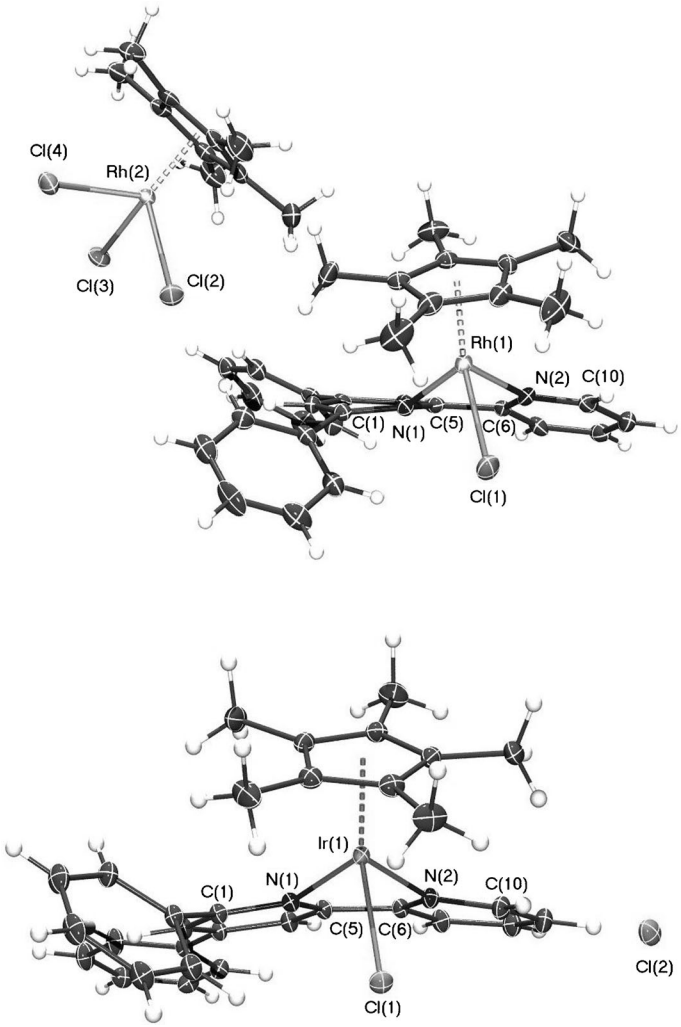
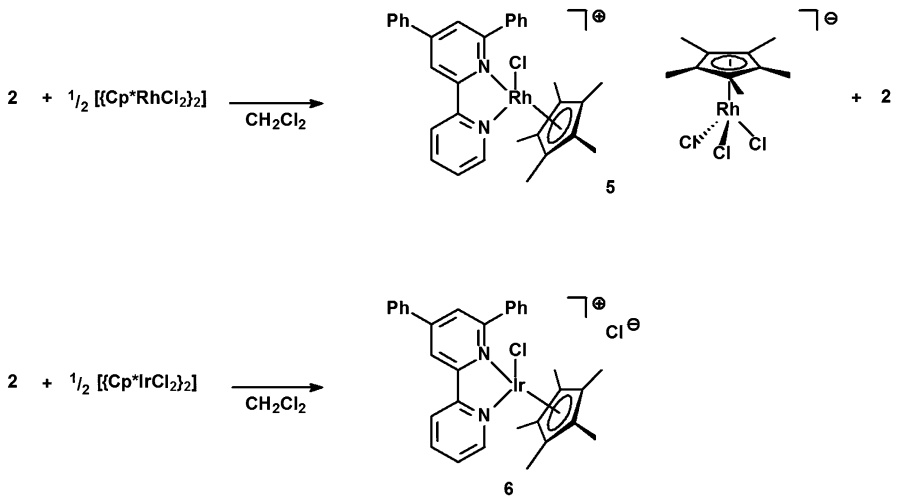


Figure 2. Molecular structures of **5** (top) and **6** (bottom) in the crystal. Displacement ellipsoids are shown at the 50% probability level. In the drawing of **6**, the asymmetric unit chosen is different from that in the Supporting Information for reasons of clarity.



Scheme 2. Synthesis of Rh^{III} and Ir^{III} complexes of **2**.

Indeed, the molecular structure of **5** in the crystal reveals the presence of the bimetallic ion pair $[RhCl(Cp^*)(\mathbf{2})]^+$ $[RhCl_3(Cp^*)]^-$, whereas **6** is present as a monomeric species, as observed in solution. It appears that complete dissociation of the metal precursor dimer, $[\{RhCl_2(Cp^*)\}_2]$, to form monomeric species cannot be achieved by the bidentate bipyridine derivative. This has been observed before for related sp^2-N donor ligands, although the

Table 2. Selected distances [Å] and angles [°] in **5** and **6**.

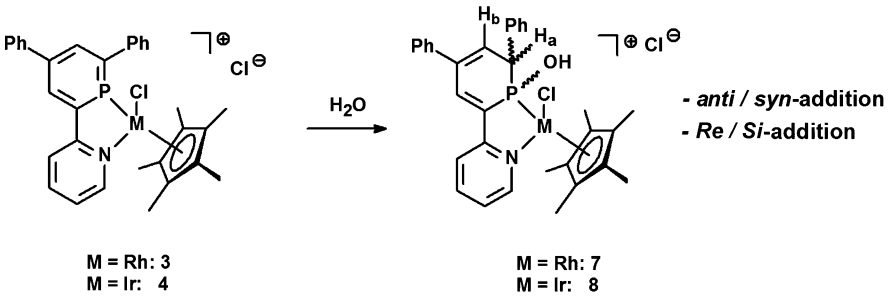
Compound	**5** (Rh)	**6** (Ir)
M(1)–centroid	1.7862(18)	1.794
M(2)–centroid	1.7578(18)	–
M(1)–Cl(1)	2.4003(11)	2.4110(4)
N(1)–M(1)	2.178(3)	2.1447(14)
N(2)–M(1)	2.071(3)	2.0784(14)
C(5)–C(6)	1.491(6)	1.471(2)
N(1)–C(1)	1.360(5)	1.362(2)
N(1)–(C5)	1.366(5)	1.371(2)
N(2)–C(6)	1.341(5)	1.352(2)
N(2)–C(10)	1.342(5)	1.342(2)
N(1)-M(1)-N(2)	76.47(13)	76.39(5)

different behavior of the Rh and Ir dimer is not clear at the moment.[21] Nevertheless, a clear difference concerning the reactivity and coordination behavior between the two ligand systems **1** and **2** is apparent.

In contrast to coordination compounds **3** and **4**, containing the P,N hybrid ligand, the molecular structure of the bipyridine-based complex **5** reveals a strong distortion, as the two pyridine rings are notably twisted (torsion angle N1-C5-C6-N2 = −15.9(5)°, interplanar angle between the least-square planes = 19.97(18)°). In contrast, the two pyridine rings are essentially coplanar in complex **6**, but bent towards one another (torsion angle N1-C5-C6-N2 = 1.6(2)°, interplanar angle between the least-square planes = 13.54(8)°). The intercyclic C(5)–C(6) bond length is 1.491(6) in **5** and 1.471(2) Å in **6**. Thus, in **5**, it is identical to that in the free 2,2′-bipyridine (1.490(3) Å)[22], and slightly shorter in **6**. The N(1)–C(5) bonds are 1.366(5) (**5**) and 1.371(2) Å (**6**), that is, slightly longer than the corresponding bond in 2,2′-bipyridine (1.346(2) Å). The bite angles N(1)-M(1)-N(2) are 76.47(13) in **5** and 76.39(5)° in **6**. The iridium compound **6** can be compared with the crystallographic data of [Ir(bpy)Cl(Cp*)]Cl. In the latter complex, the mean Ir–Cp* distance is 1.786 Å, whereas the N(1)–Ir(1) and N(2)–Ir(1) distances are very similar to **6** with 2.076(8) and 2.090(9) Å, respectively. The C(5)–C(6) bond length in [Ir(bpy)Cl(Cp*)]Cl is 1.49(1) Å and thus slightly longer than in **6**, while the bite angles N(1)-Ir-N(2) are equal within standard deviations. In contrast to compound **6**, the two pyridine rings in [Ir(bpy)Cl(Cp*)]Cl are perfectly coplanar and only slightly bent towards one another. It appears that ligand **2** does not behave like a typical 2,2′-bipyridine ligand. The observed differences in the coordination geometries are most likely due to the fact that the additional phenyl substituent at the α-position of the N(1)-pyridine ring of **2** is much closer to the coordination site relative to the situation in the corresponding pyridine–phosphinine ligand **1**. The steric interaction between the α-phenyl group and the remaining ligands around the metal center might consequently cause a distortion, which is essentially absent in [Ir(bpy)Cl(Cp*)]Cl, although it has been observed before in the complex [Rh(cod)(**2**)][BF_4].[12a]

Despite the fact that the additional aryl substituents at the 2- and 6-positions of the heterocyclic framework contribute significantly to a kinetic stabilization of the metal complexes **3** and **4** as they can easily be isolated, handled, and characterized, the larger opening of the ∢C-P-C angle in comparison to a free phosphinine reflects significant disruption of the aromaticity.[18] Consequently, a considerable reactivity of the P=C double bond in **3** and **4** towards H_2O is still anticipated as observed before by us for neutral and cationic Pd^{II} and Pt^{II} complexes as well. As a matter of fact, adding a drop of H_2O to a solution of **3** and **4** in CD_2Cl_2 leads to quantitative formation of the new species **7** and **8** and is accompanied by a color change from orange to yellow.

The addition of H_2O and alcohols to NIPHOS-containing cationic complexes $[PtCl(L)(NIPHOS)]^+$ and $[PdCl(L)(NIPHOS)]^+$ under formation of $[PtCl(L)(NIPHOSH{\cdot}OH)]^+$ and $[PdCl(L)(NIPHOSH{\cdot}OH)]^+$ has been described by Venanzi et al. before.[7] In contrast to these compounds, the addition of H_2O to the external P=C double bond of the chiral complexes **3** and **4** would lead principally to a mixture of diastereomers because not only a stereogenic C_α atom is generated due to the additional phenyl group at the 6-position of the heterocycle, but also to a stereogenic phosphorus atom. The addition of the H_2O molecule could occur in a *syn* or *anti* fashion and, furthermore, also through the *Re* or the *Si* site of the P=C double bond (Scheme 3).



Scheme 3. Reaction of **3** and **4** with H_2O.

The $^{31}P\{^1H\}$ NMR spectra of [RhCl(Cp*)(**1**H·OH)]Cl (**7**) and [IrCl(Cp*)(**1**H·OH)]Cl (**8**) show, however, only a single resonance at $\delta = 86.0$ and 58.0 ppm, respectively (CD_2Cl_2). This excludes the formation of diastereomeric product mixtures generated by either a random addition of the H_2O molecule to the *Re* or *Si* site of the P=C double bond or a random transfer of the proton to the C_α atom. Accordingly, the ^1H NMR spectra of **7** and **8** show only one set of signals, with characteristic resonances for the protons H_a and H_b at $\delta = 4.78$ (dd, $^3J_{H-H} = 2.8$, $^2J_{H-P} = 12.0$ Hz) and 6.53 ppm (dd, $^3J_{H-H} = 2.4$, $^3J_{H-P} = 8.0$ Hz; **7**), as well as at $\delta = 4.61$ (dd,

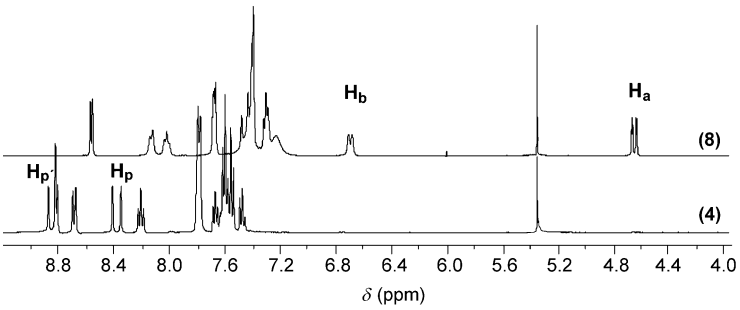


Figure 3. ^1H NMR spectra (CD_2C_2, 400 MHz) of **4** and **8**. $H_{p/p'}$ = peripheral H atoms at the P heterocycle with $^3J_{(H,P)}$ coupling.

$^3J_{H-H} = 2.8$, $^2J_{H-P} = 12.4$ Hz) and 6.66 ppm (br d, $^3J_{H-P} = 9.6$ Hz) for species **8**. Figure 3 illustrates the ^1H NMR spectra of the Ir complex **4** (H_p = peripheral hydrogen atoms of the heterocycle) and of the product **8** after the addition of H_2O. As expected, the bipyridine-containing complexes **5** and **6** do not show any reactivity towards H_2O under the same conditions as described for **3** and **4**, although Gillard et al. have found that [Pt(bpy)$(CN)_2$] also adds H_2O regioselectively, whereas the OH group adds to the C_α-atom due to the different charge distribution in pyridine and phosphinine.[23]

From these observations, we can conclude that the addition of H_2O to the external P=C double bond proceeds diastereoselectively and not randomly. Interestingly, due to the phenyl substituent at the 6-position of the P-heterocycle, an investigation of **7** and **8** by means of X-ray crystal-structure determinations would allow the differentiation between *anti*- and *syn*-addition, as well as between addition through the *Re* or *Si* site of the P=C double bond. Crystals of **7** and **8** suitable for X-ray diffraction were obtained in 85 and 96% isolated yield, respectively, by slow diffusion of Et_2O into a diluted solution of **7** and **8** in CD_2Cl_2. The compounds crystallize as racemates in the orthorhombic space group *Pbca* (**7**) and in the triclinic space group $P\bar{1}$ (**8**) with one metal complex molecule in the asymmetric unit. The molecular structures of one enantiomer each are depicted in Figure 4 and selected bonding geometries are compared in Table 3.

The molecular structures of **7** and **8** in the crystal unambiguously show that the H_2O molecule has been added in an *anti* fashion to the P(1)=C(1) double bond, rather than in a *syn* fashion. Moreover, the H_2O molecule has been added selectively to only one side of the heterocycle in such a way that the OH group is pointing away from the Cl ligand. Additionally, hydrogen bonding between the OH group and the Cl counteranion occurs. The phosphorus atom shows a distorted tetrahedral structure with a P(1)–C(1) bond length of 1.836(3) Å and a P(1)–C(5) distance of 1.811(3) in **7** and of 1.827(2) and 1.803(2) Å, respectively, in **8**, reflecting the sp^3 hybridization of C(1) and the sp^2 hybridization of C(5). Moreover, the C(1)–C(2) bond in **7** corresponds to a single bond (1.508(4) Å), whereas the remaining C–C bond lengths in the phosphorus heterocycle are in agreement with a diene structure, which shows the expected values of C(2)–C(3) = 1.350(5), C(3)–C(4) = 1.464(4), and C(4)–C(5) = 1.351(4) Å. In compound **8**, values of C(1)–C(2) = 1.505(3), C(2)–C(3) = 1.340(3), C(3)–C(4) = 1.471(3), and C(4)–C(5) = 1.344(3) Å were found. The bite angles N(1)-M(1)-P(1) are 82.27(7)° in **7** and 80.22(6) in **8**, and thus are larger than in the starting materials **3** and **4**.

Interestingly and in contrast to the *anti* addition of H_2O to the P=C double bond in **3** and **4**, we have recently observed that the reaction of the neutral complexes

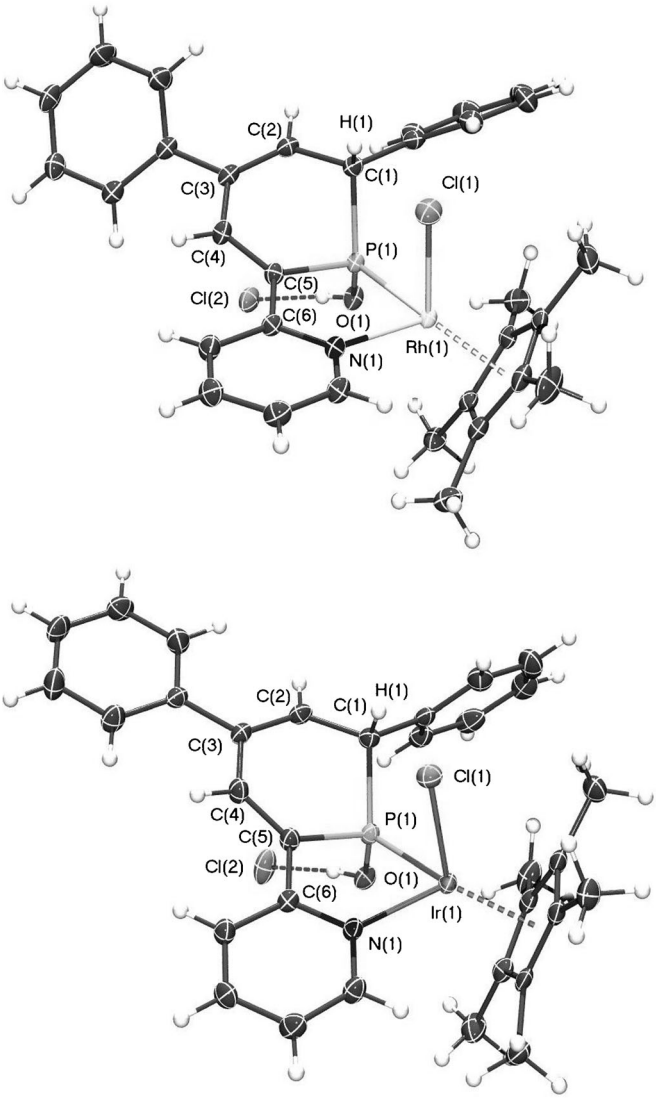


Figure 4. Molecular structures of **7** (top, two CH_2Cl_2 solvent molecules are omitted for clarity) and **8** (bottom) in the crystal. Displacement ellipsoids are shown at the 50% probability level. In the drawing of **8**, the asymmetric unit chosen is different from that in the Supporting Information for reasons of clarity.

[$PdCl_2$(**1**)] and [$PtCl_2$(**1**)] with methanol leads quantitatively and selectively to a *syn* addition of CH_3OH to the external P=C double bonds as demonstrated by single-crystal X-ray

Table 3. Selected distances [Å] and angles [°] in **7** and **8**.

Compound	**7** (Rh)	**8** (Ir)
M(1)–centroid	1.8324(14)	1.8453(12)
M(1)–Cl(1)	2.4012(8)	2.3972(6)
P(1)–M(1)	2.2552(8)	2.2548(6)
N(1)–M(1)	2.116(3)	2.1284(19)
C(5)–C(6)	1.468(4)	1.467(3)
P(1)–C(1)	1.836(3)	1.827(2)
P(1)–C(5)	1.811(3)	1.803(2)
C(1)–C(2)	1.508(4)	1.505(3)
C(2)–C(3)	1.350(5)	1.340(3)
C(3)–C(4)	1.464(4)	1.471(3)
C(4)–C(5)	1.351(4)	1.344(3)
N(1)–C(6)	1.354(4)	1.362(3)
P(1)–O(1)	1.578(2)	1.5745(18)
C(1)-P(1)-C(5)	98.52(14)	98.74(11)
P(1)-M(1)-N(1)	82.27(7)	80.22(6)

diffraction of the product $[PdCl_2(\mathbf{1}H{\cdot}OCH_3)]$ (Figure 5). The regioselective addition of methanol exclusively to the P(1)=C(1) double bond was attributed to the somewhat higher nucleophilicity of C(1) due to the electron-withdrawing character of the pyridine ring connected to C(5), leading to a preferred addition of a proton to C(1). However, the cause of the difference in *anti* and *syn* addition between these two systems remains speculative at the moment and needs further investigations.

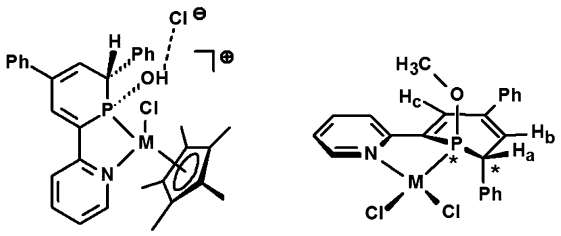


Figure 5. Water and methanol addition products of metal complexes containing ligand **1**.

Conclusion

We have demonstrated for the first time that the cationic mononuclear complexes [MCl(Cp*)(**1**)]Cl (M = Rh, Ir) containing the chelating P,N hybrid ligand 2-(2′-pyridyl)phosphinine (**1**) can easily be prepared and isolated by starting from the corresponding $[MCl_2(Cp^*)]_2$ metal precursors. The molecular structures of both compounds were determined by means of X-ray crystallography and represent the first structurally characterized cationic λ^3-phosphinine complexes of Rh^{III} and Ir^{III}. Both the chelate effect of the bidentate ligand and the aryl groups at the 2- and 6-positions of the heterocyclic framework are anticipated to contribute significantly to the formation and stabilization of such complexes. Due to the presence of electronically and sterically rather different phosphorus and nitrogen centers within the same structure, significant differences in the coordination behavior of the P,N ligand towards Rh^{III} and Ir^{III} were observed, compared to the structurally related N,N ligand (**2**). The N,N ligand not only causes a distortion of the corresponding Rh^{III} and Ir^{III} complex, due to steric interactions between the ligand framework and the coordinated {MCl(Cp*)} fragment but also leads to the formation of the bimetallic ion pair $[RhCl(Cp^*)(\mathbf{2})]^+[RhCl_3(Cp^*)]^-$. This repulsion is much less pronounced in the related phosphinine–pyridine ligand, mainly as a result of the larger phosphorus atom. The reaction with water leads quantitatively and regio- and diastereoselectively to an *anti* addition of H_2O to the external P=C double bonds as unambiguously demonstrated by X-ray crystal-structure determination of the products [MCl(Cp*)(**1**H·OH)]Cl (M = Rh, Ir). The results described herein demonstrate that the bidentate P,N hybrid ligand, 2-(2′-pyridyl)-4,6-diphenylphosphinine (**1**), allows for access for the first time to novel cationic Rh^{III} and Ir^{III} complexes, broadening significantly the scope of low-coordinate aromatic phosphorus heterocycles for potential applications.

Experimental Section

General remarks: All reactions were performed under argon by using Schlenk techniques or in an MBraun dry box unless stated otherwise. All glassware was dried prior to use. All common solvents and chemicals were commercially available. $[IrCl_2(Cp^*)]_2$ and $[RhCl_2(Cp^*)]_2$ were purchased from STREM and used without further purification. 2-(2′-Pyridyl)-4,6-diphenylphosphinine (**1**) and 2-(2′-pyridyl)-4,6-diphenylpyridine (**2**) were prepared according to literature procedures.[11,12a] The dry solvents were prepared by using custom-made solvent purification columns filled with Al_2O_3. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr (Germany). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 200 or 400 MHz spectrometer and all chemical shifts are reported relative to residual proton resonance of the deuterated solvents.

[RhCl(Cp*)(1)]Cl (3): A mixture of $[RhCl_2(Cp^*)]_2$ (19 mg, 0.03 mmol, 1.0 equiv) and **1** (20 mg, 0.06 mmol, 2.0 equiv) was suspended in CD_2Cl_2 (0.5 mL) and transferred to a Young NMR-Tube in a dry box. The reaction was completed after 4 h at room temperature. Crystals were obtained by slow diffusion of diethyl ether into the reaction mixture. Yield: 91% (after crystallization); ^1H NMR (CD_2Cl_2, 400 MHz): $\delta = 1.58$ (15H, d, $^3J_{(H,H)} = 5.6$ Hz; Me from Cp*), 7.48–7.63 (6H, m; H_{arom}), 7.70 (1H, t, $^3J = 6.6$ Hz; H_{arom}), 7.77 (2H, d, $^3J_{(H,H)} = 7.6$ Hz; H_{arom}), 7.82 (2H, d, $^3J_{(H,H)} = 7.2$ Hz; H_{arom}), 8.23 (1H, t, $^3J = 8.0$ Hz; H_{arom}), 8.44 (1H, d, $^3J_{(P,H)} = 20.8$ Hz; H_p), 8.54 (1H, d, $^3J_{(H,H)} = 4.0$ Hz; H_{arom}), 8.82 (1H, d, $^3J_{(P,H)} = 20.8$ Hz; $H_{p'}$), 8.83 ppm (1H, s; H_{arom}); ^{31}P NMR (CD_2Cl_2, 162 MHz): $\delta = 186.0$ ppm (d, $^1J_{(Rh,P)} = 130$ Hz); ^{13}C NMR (CD_2Cl_2 100.63 MHz): $\delta = 10.0$ (CH_3 from Cp*), 103.7 (C_q from Cp*), 122.1 (CH), 122.2 (CH), 127.5 (CH), 128.1 (CH), 128.2 (d, $^4J_{(C,P)} = 3.2$ Hz; CH), 128.6 (d, $^2J_{(C,P)} = 11.5$ Hz; CH), 129.3 (CH), 129.4 (CH), 129.7 (CH), 130.3 (CH), 130.5 (CH), 133.2 ($^2J_{(C,P)} = 14.7$ Hz, CH), 138.4 (C_q), 138.5 (C_q), 139.8 (d, $^2J_{(C,P)}$ 14.6 Hz; CH), 140.5 (C_q), 140.6 (C_q) 141.1 (CH), 143.5 (C_q), 155.9 (CH), 157.5 ppm (C_q); elemental analysis calcd (%) for $C_{32}H_{31}NPCl_2Rh{\cdot}0.5\,CH_2Cl_2$ (676.89 g mol^{-1}): C 57.67, H 4.76%, N 2.07; found: C 57.60, H 4.68, N 2.20.

[IrCl(Cp*)(1)]Cl (4): A mixture of $[IrCl_2(Cp^*)]_2$ (24 mg, 0.03 mmol, 1.0 equiv) and **1** (20 mg, 0.06 mmol, 2.0 equiv) was suspended in CD_2Cl_2 (0.5 mL) and transferred to a Young NMR-Tube in a dry box. The reaction was completed after 1 h at room temperature. Crystals were obtained by slow diffusion of diethyl ether into the reaction mixture. Yield: 72% (after crystallization); ^1H NMR (CD_2Cl_2, 400 MHz): $\delta = 1.62$ (15H,

d, $^4J_{(H,P)}=3.6$ Hz; Me), 7.47 (1H, m; H_{arom}), 7.53–7.66 (6H, m; H_{arom}), 7.75–7.79 (4H, m; H_{arom}), 8.17–8.20 (1H, m; H_{arom}), 8.37 (1H, dd, $^3J_{(H,P)}=25.1$, $^4J_{(H,H)}=1.4$ Hz; H_p), 8.62 (1H, d, $^3J_{(H,H)}=8.4$ Hz; H_{arom}), 8.77 (1H, dd, $^3J_{(H,P)}=19.2$, $^4J_{(H,H)}=1.4$ Hz; $H_{p'}$), 8.78 ppm (1H, d, $^3J_{(H,H)}=5.6$ Hz; H_{arom}); ^{31}P NMR (CD_2Cl_2, 162 MHz): $\delta=158.0$ ppm; ^{13}C NMR (CD_2Cl_2 100.63 MHz): $\delta=9.3$ (C_5Me_5), 97.3 (d, $^4J_{(C,P)}=2.6$ Hz; C_5Me_5), 121.5, 121.6, 127.27, 127.30, 127.9, 128.0, 128.6, 128.7, 128.9, 129.5, 130.1, 133.5 (d, $^2J_{(C,P)}=13.3$ Hz), 138.1 (d, $^2J_{(C,P)}=12.5$ Hz), 140.3 (d, $^2J_{(C,P)}=11.4$ Hz), 140.5 (d, $^3J_{(C,P)}=5.5$ Hz), 141.2, 141.4, 149.9 (d, $^1J_{(C,P)}=40.7$ Hz), 150.6 (d, $^1J_{(C,P)}=37.4$ Hz; C_α), 156.7, 158.7 ppm (d, $^2J_{(C,P)}=16.1$ Hz); elemental analysis calcd (%) for $C_{32}H_{31}NPCl_2Ir\cdot0.5\,CH_2Cl_2$ (766.20 g mol^{-1}): C 50.95, H 4.21, N 1.83; found: C 51.02, H 4.25, N 2.05.

[RhCl(Cp*)(2)][RhCl$_3$(Cp*)] (5): A mixture of $[RhCl_2(Cp^*)]_2$ (20 mg, 0.033 mmol, 1.0 equiv) and **2** (20 mg, 0.065 mmol, 2.0 equiv) was suspended in CD_2Cl_2 (0.5 mL) and transferred to a Young NMR-Tube in a dry box. The reaction was completed after 1 h at room temperature. Crystals were obtained by slow diffusion of diethyl ether into the reaction mixture. Yield: 82% (after crystallization, based on Rh); ^{1}H NMR (CD_2Cl_2, 400 MHz): 1.16 (15H, s; Me from Cp*), 1.54 (15H, s; Me from Cp*), 7.61 (6H, m; H_{arom}), 7.81 (1H, t, $^3J=6.2$ Hz; H_{arom}), 7.94 (2H, d, $^2J_{(H,H)}=7.2$ Hz; H_{arom}), 8.12 (1H, s; H_{arom}), 8.26 (1H, t, $^3J=7.8$ Hz; H_{arom}), 8.42 (2H, s; H_{arom}), 8.49 (1H, d, $^2J_{(H,H)}=8.4$ Hz; H_{arom}), 8.59 (1H, s; H_{arom}), 8.81 ppm (1H, d, $^3J_{(H,H)}=8.2$ Hz; H_{arom}); ^{13}C NMR (CD_2Cl_2 100.37 MHz): $\delta=8.8$ (CH_3 from C_5Me_5), 9.4 (CH_3 from C_5Me_5), 97.3 (C_q, C_5Me_5), 97.4 (C_q, C_5Me_5), 120.9 (CH), 126.0 (CH), 127.1 (CH), 127.3 (CH), 127.5 (CH), 128.1 (CH), 128.4 (CH), 129.0 (CH), 129.3 (CH), 129.4 (CH), 129.9 (CH), 131.1 (CH), 131.35 (CH), 131.43 (CH), 135.2 (C_q), 139.5 (C_q), 141.7 (CH), 152.2 (CH), 152.7 (C_q), 155.7 (C_q), 157.2 (C_q), 164.7 ppm (C_q); elemental analysis calcd (%) for $C_{42}H_{46}N_2Cl_4Rh_2\cdot5\,CH_2Cl_2$ (1351.56 g mol^{-1}): C 41.76, H 4.18, N 1.04; found: C 42.26, H 4.78, N 1.19.

[IrCl(Cp*)(2)]Cl (6): A mixture of $[IrCl_2(Cp^*)]_2$ (26 mg, 0.033 mmol, 1.0 equiv) and **2** (20 mg, 0.065 mmol, 2.0 equiv) was suspended in CD_2Cl_2 (0.5 mL) and transferred to a Young NMR-Tube in a dry box. The reaction was completed after 4 h at room temperature. Crystals were obtained by slow diffusion of diethyl ether into the reaction mixture. Yield: 89% (after crystallization). ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta=1.15$ (15H, s; Me), 7.59 (6H, m; H_{arom}), 7.80 (1H, t, $^3J=6.6$ Hz; H_{arom}), 7.84 (2H, d, $^2J_{(H,H)}=6.8$ Hz; H_{arom}), 8.07 (1H, s; H_{arom}), 8.24 (1H, t, $^3J=7.4$ Hz; H_{arom}), 8.36 (2H, s; H_{arom}), 8.60 (1H, d, $^2J_{(H,H)}=7.6$ Hz; H_{arom}), 8.63 (1H, d, $^4J_{(H,H)}=2.0$ Hz; H_{arom}), 8.76 ppm (1H, d, $^2J_{(H,H)}=5.6$ Hz; H_{arom}); ^{13}C NMR (CD_2Cl_2 100.37 MHz): $\delta=8.5$ (CH_3 from C_5Me_5), 89.6 (Cq, C_5Me_5), 120.9 (CH), 126.1 (CH), 127.9 (CH), 128.2 (CH), 128.7 (CH), 129.2 (CH), 129.8 (CH), 130.9 (CH), 131.5 (CH), 131.8 (CH), 134.8 (C_q), 140.1 (C_q), 141.7 (CH), 151.6 (CH), 152.4 (C_q), 156.5 (C_q), 158.2 (C_q), 164.7 ppm (C_q); elemental analysis calcd (%) for $C_{32}H_{31}N_2Cl_2Ir\cdot CH_2Cl_2$ (791.72 g mol^{-1}): C 50.06, H 4.20, N 3.55; found: C 50.69, H 4.49, N 3.81.

[RhCl(Cp*)(1H·OH)]Cl (7): Compound **3** (19 mg, 0.03 mmol, 1.0 equiv) was suspended in CD_2Cl_2 (0.5 mL) and transferred to a Young NMR-Tube under argon. An excess of water (22 mg, 1.20 mmol, 40.0 equiv) was added to the mixture and **7** was formed instantaneously. Crystals were obtained by slow diffusion of diethyl ether into the reaction mixture. Yield: 85% (after crystallization). ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta=1.30$ (15H, d, $^4J_{(H,P)}=3.2$ Hz; CH_3 from Cp*), 4.78 (1H, dd, $^2J_{(H,P)}=12.0$, $^3J_{(H,H)}=2.8$ Hz; H_a), 6.53 (1H, dd, $^3J_{(H,P)}=8.0$, $^3J_{(H,H)}=2.4$ Hz; H_b), 7.06 (2H, s; H_{arom}), 7.22 (3H, m; H_{arom}), 7.32 (1H, d, $^3J_{(H,P)}=17.6$ Hz; H_{arom}), 7.38 (4H, m; H_{arom}), 7.66 (2H, dd, $^3J_{(H,H)}=4.0$, $^2J_{(H,H)}=1.8$ Hz; H_{arom}), 8.03 (1H, t, $^3J=7.6$ Hz; H_{arom}), 8.12 (1H, d, $^3J_{(H,P)}=8.0$ Hz; H_{arom}), 8.60 ppm (1H, d, $^3J_{(H,H)}=5.6$ Hz; H_{arom}); ^{31}P NMR (CD_2Cl_2, 162 MHz): $\delta=86.0$ (d, $^1J_{(Rh,P)}=133$ Hz); ^{13}C NMR (CD_2Cl_2, 100.37 MHz): $\delta=9.0$ (CH_3 from Cp*), 51.3 (CH), 51.6 (CH), 101.6 (C_q from Cp*), 121.3 (d, $^2J_{(C,P)}=7.6$ Hz; CH), 125.3 (CH), 127.1 (CH), 127.9 (d, $^4J_{(C,P)}=2.8$ Hz; CH), 128.1 (CH), 128.8 (CH), 128.9 (d, $^4J_{(C,P)}=2.3$ Hz; CH), 130.9 (d, $^3J_{(C,P)}=5.4$ Hz; CH), 136.2 (CH), 137.2 (d, $^2J_{(P,C)}=10.1$ Hz; C_q), 138.0 (C_q), 138.9 (CH), 139.0 (CH), 139.1 (CH), 140.5 (d, $^3J_{(C,P)}=2.9$ Hz; C_q), 154.7 (CH), 159.3 (C_q), 159.5 ppm (C_q); elemental analysis calcd (%) for $C_{32}H_{33}NPOCl_2Rh\cdot CH_2Cl_2$ (791.73 g mol^{-1}): C 53.77, H 4.79, N 1.90; found: C 53.86, H 4.85, N 1.89.

[IrCl(Cp*)(1H·OH)]Cl (8): Compound **4** (22 mg, 0.03 mmol, 1.0 equiv) was suspended in CD_2Cl_2 (0.5 mL) and transferred to a Young NMR-Tube under argon. An excess of water (22 mg, 1.20 mmol, 40.0 equiv) was added to the mixture and **8** was formed instantaneously. Crystals were obtained by slow diffusion of diethyl ether into the reaction mixture. Yield: 96% (after crystallization); ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta=1.42$ (15H, s; Cp* CH_3), 4.61 (1H, dd, $^2J_{(H,P)}=12.4$, $^3J_{(H,H)}=2.8$ Hz; H_a), 6.66 (1H, br d, $^3J_{(H,P)}=9.6$ Hz; H_b), 7.19 (1H, s; H_{arom}), 7.28 (3H, m; H_{arom}), 7.38 (5H, m; H_{arom}), 7.45 (1H, s; H_{arom}), 7.66 (2H, m; H_{arom}), 7.99 (1H, t, $^3J=7.4$ Hz; H_{arom}), 8.12 (1H, d, $^3J_{(H,P)}=6.8$ Hz; H_{arom}), 8.55 ppm (1H, d, $^3J_{(H,H)}=5.6$ Hz; H_{arom}); ^{31}P NMR (CD_2Cl_2, 162 MHz): $\delta=58.0$ ppm; ^{13}C NMR (CD_2Cl_2, 100.37 MHz): $\delta=8.8$ (CH_3 from Cp*), 47.1 (CH), 47.5 (CH), 95.8 (C_q from Cp*), 121.4 (d, $^3J_{(C,P)}=7.6$ Hz; CH), 126.0 (CH), 127.3 (CH), 128.1 (d, $^4J_{(C,P)}=3.0$ Hz; CH), 128.2 (CH), 128.8 (CH), 129.0 (d, $^4J_{(C,P)}=2.5$ Hz; CH), 130.8 (d, $^3J_{(C,P)}=5.3$ Hz; CH), 138.1 (d, $^2J_{(C,P)}=11.4$ Hz; C_q), 139.3 (CH), 140.8 (d, $^3J_{(C,P)}=2.5$ Hz; C_q), 155.6 (CH), 159.8 (d, $^2J_{(C,P)}=18.1$ Hz; C_q); elemental analysis calcd (%) for $C_{32}H_{33}NPOCl_2Ir\cdot0.5\,CH_2Cl_2$ (741.13 g mol^{-1}): C 49.81, H 4.37, N 1.79; found: C 49.01, H 4.58, N 1.67.

Acknowledgements

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