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# C–H activation of 2,4,6-triphenylphosphinine: unprecedented formation of cyclometalated [(P^C)Ir(III)] and [(P^C)Rh(III)] complexes†‡

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**An unprecedented C–H activation of 2,4,6-triphenylphosphinine by Ir(III) and Rh(III) has been observed. Time-dependent $^{31}P\{^1H\}$ NMR spectroscopy gave insight into the cyclometalation reaction and the corresponding coordination compounds were characterized by means of X-ray crystallography. In contrast, 2,4,6-triphenylpyridine does not show any *ortho*-metalation, demonstrating a remarkable difference in reactivity between these two structurally related aromatic heterocycles.**

Cyclometalated transition metal complexes have attracted considerable interest for a wide variety of applications.[1] Especially the intramolecular C–H activation of 2-phenylpyridines by $d^6$-metals leads to functional coordination compounds, which find use as triplet-emitters in organic light emitting diodes (OLEDs) or as catalysts for the oxidation of water (type **A**, Fig. 1).[2,3]

The replacement of nitrogen by phosphorus in similar structures causes significantly diverse properties due to the electronic difference that exists between these heteroatoms. Phosphinines, for example, the homologs of pyridines, are particularly suitable for the stabilization of late transition metal centers in low oxidation states because of their pronounced π-accepting character.[4] In contrast, the preparation of phosphinine-complexes containing metal centers in higher oxidation states has virtually been neglected. Earlier attempts to prepare such compounds have shown that they are extremely sensitive towards nucleophilic attack, making their straightforward synthesis rather unattractive.[5] In fact, phosphinine-based coordination compounds containing transition metal centers in the formal oxidation state +2 are rare, while a stabilization of even higher oxidation states has not been reported in the literature to date.[6] Yet, the access to such compounds would open up new perspectives in the field of phosphorus containing molecular materials as well as homogeneous catalysis.

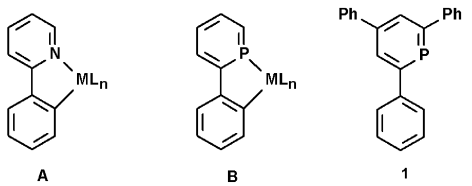


**Fig. 1** Cyclometalated coordination compounds and phosphinine **1**.

We could recently demonstrate that the aryl-groups in *ortho*-position of donor functionalized 2,4,6-triarylphosphinines along with the chelate effect contribute significantly to the formation and efficient kinetic stabilization of corresponding Pd(II) and Pt(II) complexes.[7] Motivated by these results we envisaged to use 2,4,6-triphenylphosphinine (**1**) as a phosphorus-derivative of 2-phenylpyridine and to study its potential reactivity towards cyclometalation reactions (type **B**, Fig. 1).[8,9] The metal precursors $[Cp^*MCl_2]_2$ (M = Ir, Rh) were chosen as they readily undergo C–H activation of 2-phenylpyridine in the presence of NaOAc, which assists as intramolecular base in the *ortho*-metalation reaction.[3,10,11]

Reaction of **1** with $[Cp^*IrCl_2]_2$ and NaOAc in the ratio 2 : 1 : 2 in $CD_2Cl_2$ quantitatively leads to species **2** that shows a broad signal at $\delta$ = 133.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum (Fig. 2, $t$ = 0) and a doublet ($^3J_{H-P}$ = 19.2 Hz) at $\delta$ = 8.03 ppm in the $^1H$ NMR spectrum, characteristic for the two peripheral protons of the phosphinine-core. The use of hydrated NaOAc was avoided in order to prevent potential reaction of $H_2O$ with the phosphinine–metal complex.[5] MALDI-TOF analysis of the reaction mixture reveals that **2** has the composition $C_{33}H_{32}Cl_2IrP$, which corresponds to the simple monomeric

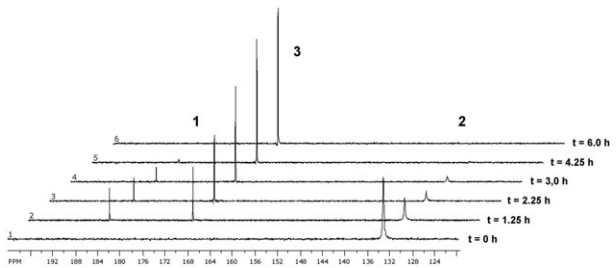


**Fig. 2** Time-dependent $^{31}P\{^1H\}$ NMR spectra for the reaction of **1** with $[Cp^*IrCl_2]_2$ in the presence of NaOAc at $T$ = 80 °C ($CD_2Cl_2$).

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‡ Electronic supplementary information (ESI) available: A detailed list of all experimental procedures, cif file and crystallographic data for compounds **3** and **5**. CCDC 798976 and 798977. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc04660d

P-coordinated neutral adduct [Cp*IrCl$_2$(**1**)] formed upon reaction of the Ir-dimer with the phosphinine. Any attempt to isolate and to further characterize **2** failed. X-Ray crystallographic investigations of the crystals formed after diffusion of Et$_2$O into the reaction mixture showed only the presence of regenerated [Cp*IrCl$_2$]$_2$ dimer. This is in line with earlier observations that monodentate phosphinines generally do not form stable coordination compounds with transition metal centers in higher oxidation states due to their weak σ-donor properties.[4]

Heating the reaction mixture to $T$ = 80 °C in a sealed NMR tube reveals, however, consumption of **2** and the appearance of a new phosphorus-containing compound (**3**) with a chemical shift of $\delta$ = 170.8 ppm in the $^{31}$P{$^1$H} NMR spectrum. Moreover, free phosphinine **1** ($\delta$ = 185.5 ppm) can be detected as an intermediate. Full conversion of **2** into **3** is finally achieved after 6 h at $T$ = 80 °C (Fig. 2). In the $^1$H NMR spectrum of **3** (CD$_2$Cl$_2$) two doublet of doublets ($^3J_{H-P}$ = 22.4, 21.6 Hz; $^4J_{H-H}$ = 1.6 Hz) at $\delta$ = 8.35 and 8.01 ppm are observed for the two peripheral protons of the phosphorus heterocycle. This pattern is characteristic for an asymmetrically substituted 2,4,6-triarylphosphinine.

Orange crystals suitable for X-ray diffraction were obtained by slow diffusion of Et$_2$O into a solution of **3** in CH$_2$Cl$_2$. The Ir-complex crystallizes enantiomerically pure in the non-centrosymmetric space group $P2_12_12_1$ (no. 19) and the molecular structure along with selected bond lengths and angles is shown in Fig. 3.

The X-ray crystal structure analysis of **3** unambiguously confirms the cyclometalation of 2,4,6-triphenylphosphinine by Ir(III) with elimination of HCl. The molecular structure of **3** shows the characteristic three-legged "piano-stool" arrangement around the iridium atom and represents the first crystallographic characterization of a phosphinine–M(III) complex reported in the literature. The chelate effect of the formally anionic bidentate ligand apparently contributes to the formation of such a coordination compound.

The presence of NaOAc turned out not to be essential for the C–H activation process. Heating a 2 : 1 mixture of **1** and [Cp*IrCl$_2$]$_2$ in CH$_2$Cl$_2$ to $T$ = 80 °C in a sealed NMR tube and monitoring it by means of $^{31}$P{$^1$H} NMR spectroscopy reveals consumption of **2** ($\delta$ = 133.0 ppm) and exclusive formation of **3** ($\delta$ = 170.8 ppm, see ESI‡). The reaction is considerably slower compared to the cyclometalation process in the presence of NaOAc and no free **1** is observed. Full conversion is not achieved and the maximum yield of **3** is 75% after 5 days. Interestingly, the C–H activation reaction is completely reversible. Cooling the sealed NMR tube to room temperature leads to the quantitative formation of the starting material **2** within 1 day. Pure **3** can thus be obtained by removing HCl during the cyclometalation reaction by means of vacuum.

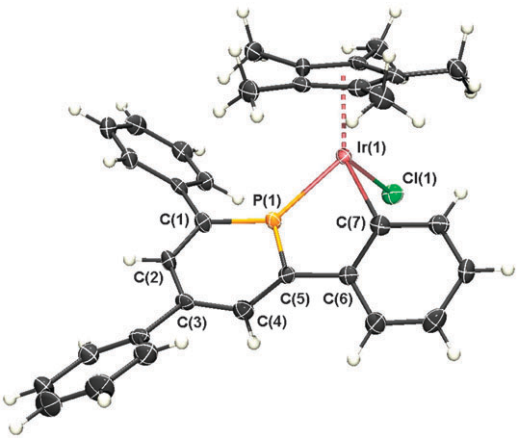
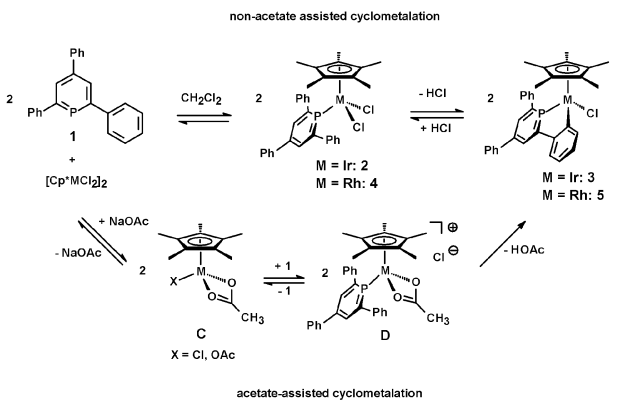



**Fig. 3** Molecular structure of **3** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–Ir(1): 2.2396(12); C(7)–Ir(1): 2.076(5); P(1)–C(1): 1.724(5); P(1)–C(5): 1.724(4); Ir(1)–Cp(cent.): 1.861(2); Ir(1)–Cl(1): 2.3902(12); C(1)–P(1)–C(5): 105.7(2); C(7)–Ir(1)–P(1): 78.72(14).

We assume that the formation of **3** proceeds by an acetate-assisted electrophilic C–H activation in analogy to the mechanism proposed for the reaction of [Cp*MCl$_2$]$_2$ with nitrogen-containing substrates.[10–12] The free phosphinine **1** observed during the course of the cyclometalation reaction in the presence of NaOAc might be the result of the reversible formation of **2** from **1** and [Cp*IrCl$_2$]$_2$ (*vide supra*).[11a] In the case of iridium, this equilibrium lies far to the product side. Transient Ir-dimer can, however, react reversibly with NaOAc under formation of Cp*Ir(III)-acetate and diacetate species of the type **C** (Scheme 1, lower pathway).[10,12] The phosphinine-containing cationic species **D** undergoes subsequently the acetate-assisted C–H activation and could not be detected by means of $^{31}$P NMR spectroscopy. The considerably slower cyclometalation reaction in the absence of NaOAc presumably proceeds by electrophilic substitution *via* a metal arenium (Wheland) intermediate after formation of a cationic Ir-complex (Scheme 1, upper pathway).

Similarly, the reaction of **1** with [Cp*RhCl$_2$]$_2$ and NaOAc in the ratio 2 : 1 : 2 in CH$_2$Cl$_2$ at $T$ = 80 °C gives the corresponding cyclometalated Rh-complex **5**. The reaction is slower and less selective than with iridium and **5** is obtained in 81% spectroscopic yield after 18 h. Moreover, the Rh-complex **4** could not be detected, which is probably due to a fast exchange process. The pure complex was isolated by slow diffusion of Et$_2$O into a solution of **5** in CH$_2$Cl$_2$ and shows a doublet at $\delta$ = 208.8 ppm in the $^{31}$P{$^1$H} NMR spectrum ($J_{P-Rh}$ = 187.8 Hz) and two doublets ($^3J_{H-P}$ = 21.2, 18.8 Hz) at $\delta$ = 8.34 and 8.03 ppm for the two peripheral protons of the phosphorus heterocycle in the $^1$H NMR spectrum. Red crystals of **5** suitable for X-ray diffraction were obtained by slow crystallization from CH$_2$Cl$_2$/Et$_2$O. The Rh-complex crystallizes in the centrosymmetric space group $P2_1/c$




**Scheme 1** Proposed reaction scheme for the cyclometalation of **1**.

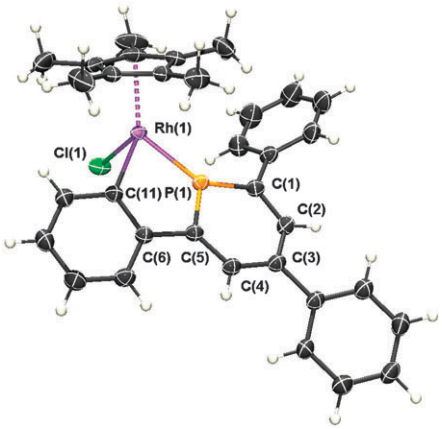


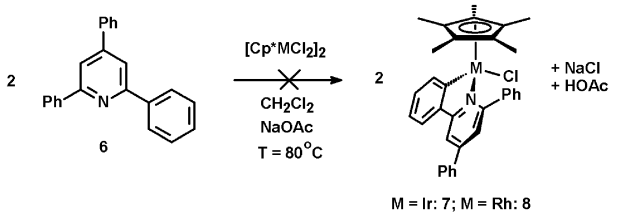

**Fig. 4** Molecular structure of **5** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–Rh(1): 2.2156(4); C(11)–Rh(1): 2.0687(15); P(1)–C(1): 1.7176(17); P(1)–C(5): 1.7160(15); Rh(1)–Cp(cent.): 1.8584(7); Rh(1)–Cl(1): 2.3931(4); C(1)–P(1)–C(5): 105.76(7); C(11)–Rh(1)–P(1): 78.26(4).

(no. 14) and the result of the X-ray crystal structure analysis along with selected bond lengths and angles is shown in Fig. 4. The molecular structure essentially resembles the one described for compound **3** and is the first structurally characterized phosphinine–Rh(III) complex.

Most strikingly, the here described results show that **3** and **5** are unexpectedly stable under the applied reaction conditions, as the P|C double bond generally becomes more reactive with increasing oxidation state of the metal center.[4,5] We assume that the additional phenyl-group in 2-position of the phosphorus heterocycle contributes significantly to a kinetic stabilization of the metal complex, as the P|C double bond is sterically more shielded for addition reactions in contrast to less substituted phosphinines.[7a]

In order to compare the reactivity of **1** with its pyridine-counterpart, we performed analogous experiments with 2,4,6-triphenylpyridine (**6**).[13] Interestingly, the reaction of **6** with either $[Cp^*IrCl_2]_2$ or $[Cp^*RhCl_2]_2$ in the presence of NaOAc or NaOAc·$3H_2O$ at $T$ = 80 °C does not lead to the corresponding cyclometalated products **7** and **8** (Scheme 2). In the $^1$H NMR spectrum of the reaction mixtures no traces of C–H activation in the aromatic region can be detected even after 8 days of heating. Only changes in the aliphatic region can be observed, which indicates reaction of the metal precursor with sodium acetate.[10]

Since the reaction of 2-phenylpyridine with $[Cp^*MCl_2]_2$ dimers is well known,[3,10–12] the here observed lack of reactivity can be attributed purely to steric factors. In fact, the phosphinine heterocycle is best described as distorted hexagon due to the larger P–C bond distances compared to the N–C bond




**Scheme 2** Attempted cyclometalation of 2,4,6-triphenylpyridine **6**.

lengths in pyridine. As a result, the phenyl groups in *ortho*-position of the phosphinine framework are bend away from the phosphorus atom, making the more diffuse and less directional phosphorus lone-pair even more accessible for σ-coordination to a metal center. The C–H activation can subsequently proceed. In contrast, the more localized nitrogen lone-pair in 2,4,6-triphenylpyridine is much better shielded by the phenyl groups in 2- and 6-position, reducing considerably its accessibility.

In summary we have achieved for the first time an unprecedented C–H activation of 2,4,6-triphenylphosphinine by Ir(III) and Rh(III) precursors. $^{31}P\{^1H\}$ NMR spectroscopic investigations gave insight in the cyclometalation reaction and the corresponding coordination compounds were characterized by means of X-ray crystallography. These compounds represent the first examples of isolated and crystallographically characterized phosphinine–M(III) complexes reported so far in the literature. The analogous reaction of 2,4,6-triphenylpyridine does not show any *ortho*-metalation, demonstrating a remarkable difference in reactivity between these two related heterocycles. This observed novel reactivity mode of phosphinines might open up new perspectives for future applications in phosphorus containing molecular materials and homogeneous catalysis. Corresponding studies are currently carried out in our laboratories.

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