Organometallic complexes of the platinum metals: Synthesis, structure, and catalytic applications

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Abstract. Reaction of a group of N-(aryl)picolinamides (**pic-R**) with $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$ in refluxing 2-methoxyethanol in the presence of a base affords hydrido complexes of two types (**1-R** and **2-R**), which are geometric isomers. Similar reaction with N-(naphthyl)picolinamide (**pic-nap**) yields an organoruthenium complex (**3**) via formation of a hydrido intermediate. Reaction of 2-(arylo)phenols (**ap-R**) with $[\text{Ir}(\text{PPh}_3)_3\text{Cl}]$ in refluxing ethanol affords a mono-hydrido intermediate (**4-R**), a di-hydrido intermediate (**5-R**) and an organoiridium complex (**6-R**) as the final product, where the azo-ligand is coordinated as CNO-donor. Reaction of **ap-R** ligands with $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ yields organorhodium complexes (**7-R**) analogous to **6-R**, but without any hydrido intermediate. N-(2'-hydroxyphenyl)benzaldimines (**hpbz-R**) react with $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ to yield a group of organorhodium complexes (**8-R**), where the **hpbz-R** ligands are coordinated in CNO-fashion. Upon interaction with $[\text{Ir}(\text{PPh}_3)_3\text{Cl}]$ 2-(2',6'-dimethylphenylazo)-4-methylphenol (**dmap**) undergoes a methyl C–H activation and affords organoiridium complex **9**, while 2-(2'-methylphenylazo)-4-methylphenol (**mmap**) undergoes a phenyl C–H activation and gives organoiridium complex **10**. Reaction of benzaldehyde thiosemicarbazones (**bztsc-R**) with $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, carried out with the expectation of inducing CNS-mode of coordination, actually has yielded complexes (**11-R**) where the **bztsc-R** is coordinated in an uncommon NS-mode forming a five-membered chelate ring associated with a restricted rotation around the imine (C=N) bond. These palladium complexes are found to catalyse C–C cross coupling reactions very efficiently. Crystal structures of selected complexes of each type have been determined by X-ray crystallography.

Keywords. Organometallic complexes; platinum metals; N-(aryl)picolinamides; 2-(arylo)-phenols; N-(2'-hydroxyphenyl)benzaldimines; benzaldehyde thiosemicarbazones; crystal structures; catalytic applications.

1. Introduction

The chemistry of organometallic complexes has always been receiving special attention, particularly owing to their application in promoting chemical transformation of organic molecules. Formation of a metal–carbon bond usually proceeds through a C–H, C–C or C–X (X = halogen atom) bond activation step. Choice of suitable organic ligands, as well as appropriate transition metal containing starting materials, is crucial for inducing such bond activation. We have been exploring the chemistry of organometallic complex of platinum metals for last several years, and here we report the summary of some of our selected studies.^{1–6} The primary objective of the present report is to highlight the initial reactions that hinted the possibility of synthesizing organometallic complexes, strategies formulated in order to induce C–H bond activation of organic ligands mediated by selected platinum metals, viz. ruthenium, rhodium, iridium and palladium, and finally the reactions which actually led to formation of new organometallic com-

plexes. The results of our attempts in this direction are described in this paper, with special reference to synthesis, structure and catalytic properties.

2. Experimental

All the experimental details, with regard to materials, synthesis of complexes, physical measurements and X-ray structure determination, catalytic reactions, are already reported in the literature.^{1–6}

3. Results and discussion

The present study was initiated with a simple reaction between ruthenium and a group of N-(aryl)picolinamide ligands (**pic-R**) derived from picolinic acid and *para*-substituted anilines. As the source of ruthenium, the $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$ complex was selected, particularly owing to its demonstrated ability to accommodate bidentate ligands through displacement of carbonyl and chloride. The selected amide ligands are known to bind to metal ions in various modes, viz. as mono-anionic NN-donor (**I**), as mono-anionic

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NO-donor (**II**) and also as neutral NO-donor (**III**). The primary objective of this part of the study was to examine the mode of binding to ruthenium. Reactions of the selected amides (**pic-R**) with $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$ proceed smoothly in refluxing 2-methoxyethanol in the presence of triethylamine, and from each of these reactions two complexes are obtained, viz. a golden yellow complex (**1-R**) and a yellow complex (**2-R**), in moderate yields. Preliminary characterizations on these complexes indicate presence of an amide ligand, two triphenylphosphines, a carbonyl, and a hydride in the coordination sphere. However, to find out the stereochemistry of these complexes and coordination mode of the picolinamide ligand in them, structure of one representative complex from each family, viz. **1-OCH₃** and **2-CH₃**, has been determined by X-ray crystallography. The structure of **1-OCH₃** (figure 1) shows that the amide ligand is coordinated to the metal centre, via dissociation of the N–H proton, as monoanionic NN-donor (**I**) and, two triphenylphosphines, a hydride and a carbonyl are also coordinated to ruthenium. The coordinated picolinamide, hydride and carbonyl constitute one equatorial plane with the metal at the centre, where the hydride is *trans* to the pyridine-nitrogen and the carbonyl is *trans* to the amide-nitrogen. The PPh_3 ligands have occupied the remaining two axial positions and hence they are mutually *trans*. The structure of **2-CH₃** (figure 2) shows that it is very similar to that of **1-OCH₃**, the only difference is in the disposition of coordinated carbonyl and hydride with respect to the coordinated picolinamide. The hydride is *trans* to the amide-nitrogen and the carbonyl is *trans* to the pyridine-nitrogen. Formation of the

Figure 2. View of the **2-CH₃** complex.

two stereoisomers (**1-R** and **2-R**) from the same reaction has been quite interesting, and some speculated steps, that seem probable, are shown in scheme 1. In the initial step, the amide ligand (**pic-R**) is believed to bind to the metal centre, via dissociation of the acidic N–H proton, as mono-anionic NN-donor, with simultaneous dissociation of a CO and a chloride from the ruthenium starting complex, to generate two stereoisomers (**A** and **B**) of an intermediate, probably via different kinetic routes. The ruthenium-bound chloride in these intermediates reacts with the solvent and thus leads to formation of a Ru–H fragment affording the **1-R** and **2-R** complexes, respectively.

Figure 1. View of the **1-OCH₃** complex.

Disposition of the Ru–H bond with respect to the pendent phenyl ring in **1-R** points to the possibility of a C–H activation of the aryl ring, which could not take place in the **1-R** complexes as the phenyl ring is not close enough to the Ru–H fragment. However, it was understood that in order to undergo C–H activation the aryl fragment should be so chosen that one of its C–H bonds can come in close proximity to the Ru–H bond. With this sim-

Scheme 1. Probable steps behind formation of the **1-R** and **2-R** complexes.

ple strategy in mind, N-(naphthyl)picolinamide (**pic-nap**) has been chosen as the modified amide ligand for the targeted C–H activation. Reaction of **pic-nap** with $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$, carried out similarly as before, has afforded an orange complex (**3**) containing an amide ligand, two triphenylphosphines and a carbonyl, but no hydride. Structure determination of complex **3** by X-ray crystallography (figure 3) shows that N-(naphthyl)picolinamide is indeed coordinated to ruthenium in the expected NNC-fashion (**IV**). The coordinated carbonyl is sharing the same equatorial plane with the amide ligand and the two PPh_3 ligands are *trans* as before. Probable sequences behind

formation of the cyclometalated complex **3** are illustrated in scheme 2. As before, an equilibrium mixture of two stereoisomers (**C** and **D**) of a hydride intermediate are formed initially, in both of which the amide ligand is coordinated in NN-fashion. Isomer **C** of the intermediate then undergoes the C–H activation at the 8-position of the naphthyl ring affording the cyclometalated species **3** via elimination of molecular hydrogen. As isomer **C** is irreversibly transformed into the cyclometalated species **3**, the equilibrium between the two isomers gradually shifts towards **C**, and thus the cyclometalated species **3** is obtained as the sole product from this reaction. This particular exercise thus demon-

Figure 3. View of the complex 3.

strates that Ru–H fragment can efficiently activate proximal aryl C–H bond.¹

pic-nap

IV

The success in C–H bond activation of N-(naphthyl)picolinamide (**pic-nap**), mediated by ruthenium, has encouraged us to explore similar activation reactions utilizing other platinum metals. In this perspective, we have studied the interaction between a group of 2-(aryloxy)phenols (**ap-R**) and iridium. As the source of iridium [Ir(PPh₃)₃Cl] has been selected,

Scheme 2. Probable steps behind formation of the complex 3.

particularly because of its ability to undergo oxidative insertion into acidic bonds. Reaction of the chosen **ap-R** ligands with $[\text{Ir}(\text{PPh}_3)_3\text{Cl}]$ in ethanol resulted in the formation of complexes of three different types with distinctly different colours, viz. purple (**4-R**), pink (**5-R**) and blue (**6-R**). Crystal structures of **4-Cl**, **5-Cl** and **6-Cl** have been determined (figures 4–6). The structures show that in the **4-R** complexes the **ap-R** ligand is coordinated as mono-anionic NO-donor (**V**) along with two PPh_3 ligands, a hydride and a chloride. The **5-R** complexes are similar to the corresponding **4-R** complexes, except that a hydride is coordinated to iridium in **5-R** instead of the chloride in **4-R**. In **6-R**, the **ap-R** ligand is coordinated as di-anionic CNO-donor (**VI**) along with two PPh_3 ligands and a hydride. It is believed that formation of these three types of complexes takes place sequentially, which is shown in scheme 3.

This speculation is backed up by the observation that any isolated purple **4-R** complex is gradually converted into the corresponding pink **5-R** complex upon standing in alcoholic medium in the presence of a base. Similarly, alcoholic solution of any isolated pink **5-R** complex gradually gets transformed into the corresponding blue **6-R** complex. It thus becomes quite apparent that

Figure 5. View of the **5-Cl** complex.

Ir–H bond can also successfully bring about activation of proximal aryl C–H bond.²

Prompted by the above observations, we have also carried out similar reaction of the same group of 2-(aryldiazenyl)phenols (**ap-R**) with $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$. The reactions proceed smoothly in refluxing toluene and afford the expected organorhodium complexes (**7-R**). However, no intermediate could be isolated from the reaction. Crystal structure of **7-NO₂** has been determined (figure 7), which shows that the **ap-R** ligand is coordi-

Figure 4. View of the **4-Cl** complex.

Figure 6. View of the **6-Cl** complex.

Scheme 3. Steps behind formation of complexes **4-R**, **5-R** and **6-R**.

nated to rhodium as di-anionic CNO-donor (**VI**) along with two PPh_3 ligands and a chloride. It is believed that a hydrido intermediate (analogous to the **4-R** complex in scheme 3) is generated initially, which is rapidly transformed into the cyclometallated species (**7-R**) via elimination of molecular hydrogen. This exercise thus indicates that the Rh-H bond, formed *in situ*, is very

reactive and it can also be utilized to activate aryl C-H bond leading to formation of interesting organorhodium complexes.³

Using the same strategy as before, reaction of a group of Schiff base ligands, viz. N-(2'-hydroxyphenyl)benzaldimines (**hpbz-R**), derived from 2-aminophenol and *para*-substituted benzaldehydes, has been carried out with $[\text{Rh(PPh}_3\text{)}_3\text{Cl}]$. These ligands have been chosen as they have skeletal similarity with the 2-(aryldiazo)phenols (**ap-R**). A group of organorhodium complexes (**8-R**) have been obtained from these reactions (scheme 4), as expected.⁴ Crystal structure of **8-OCH₃** complex has been solved (figure 8), which confirmed the CNO-mode of binding of the **apbz-R** ligand. The two triphenylphosphines are again mutually *trans* in this complex, and the coordinated chloride is found to share the equatorial plane with the CNO-coordinated ligand. Formation of these organorhodium **8-R** complexes is

Figure 7. View of the **7-NO₂** complex.

Scheme 4. Formation of **8-R** complexes.

Figure 8. View of the 8-OCH₃ complex.

Figure 10. View of the complex 10.

also believed to pass through the intermediacy of a hydrido-rhodium complex.

The observation, that the 2-(aryloxy)phenols (**ap-R**) can undergo facile orthometallation reactions affording interesting organometallic complexes, has encouraged us to examine the fate of similar ligands where both the *ortho* positions of the phenyl ring in the aryloxy fragment are blocked by alkyl groups. For this purpose, a modified 2-(aryloxy)phenol, viz. 2-(2',6'-dimethylphenylazo)-4-methylphenol (**dmap**), has been

selected. Reaction of this new azo-ligand (**dmap**) has been carried out with [Ir(PPh₃)₃Cl], which afforded a pink complex **9**. Structure determination of this complex **9** by X-ray crystallography (figure 9) shows that the **dmap** ligand has undergone a methyl C–H activation during the course of this reaction and is coordinated to iridium in ONC-mode (**VII**). To test the preference, if any, between methyl C–H activation and phenyl C–H activation, we have next chosen another azo-phenol ligand, viz. 2-(2'-methylphenylazo)-4-methylphenol (**mmap**), in which only one *ortho* position of the phenyl ring in the aryloxy fragment is blocked by a methyl group while the other *ortho* position is still unsubstituted. This

Figure 9. View of the complex 9.

Figure 11. View of the 11-CH₃ complex.

Figure 12. View of the 11-NO₂ complex.

mmap ligand, in principle, may show both the types of C–H bond activation (**VIII** and **IX**). Reaction of this **mmap** ligand, carried out with [Ir(PPh₃)₃Cl] in a similar fashion as before, has afforded a blue complex **10**. Structure determination of this complex **10** by X-ray crystallography (figure 10) shows that the **mmap** ligand has actually undergone a phenyl C–H activation during the course of this reaction and is coordinated to iridium in ONC-mode (**IX**). Hence, it is indicated that if option between methyl and phenyl C–H activations is available, the latter takes place preferentially. However, under unavoidable condition, as has been the case

with the **dmap** ligand, methyl C–H activation definitely takes place.⁵

Finally, we have scrutinized the possibility of C–H bond activation of a group of benzaldehyde thiosemicarbazones (**bztsc-R**) using palladium as the metal centre. In addition to their ability to serve as mono-anionic bidentate NS-donor, these ligands also have the potential to undergo orthometallation and display a CNS-mode of coordination (**X**). With an intention to achieve this CNS-mode of binding, reactions of the selected thiosemicarbazones have been carried out with [Pd(PPh₃)₂Cl₂], taken as the palladium starting material, which yielded a group of yellow complexes (**11-R**). However, structure determination of **11-CH₃** by X-ray crystallography (figure 11) shows that instead

Table 1. Suzuki cross coupling of aryl bromides with phenylboronic acid.^a

Entry	R ₁	Solvent	Temp, °C	Time (h)	Amt of cat., mol%	Conversion, ^b %	TON ^c
1	COCH ₃	Ethanol–toluene (1:1)	95	9	0.001	>99	100 000
2	CHO	Ethanol–toluene (1:1)	95	12	0.001	>99	100 000
3	CN	Ethanol–toluene (1:1)	95	12	0.001	>99	100 000
4	COCH ₃	Ethanol–toluene (1:1)	25	20	0.001	>99	100 000
5	COCH ₃	Water	100	12	1	>99	100

^aReaction conditions: aryl bromide (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (1.7 mmol), Pd catalyst, solvent (4 mL).

^bDetermined by ¹H NMR on the basis of residual aryl halide.

^cTON = turnover number ((mol of product)/(mol of catalyst))

of binding palladium in the expected CNS-mode, the thiosemicarbazone is actually coordinated to the metal centre in a rather uncommon NS-mode (**XI**) forming a five-membered chelate ring associated with a restricted rotation around the imine (C=N) bond.

To ensure that the same mode of binding of thiosemicarbazone is existing in all these **11-R** complexes, crystal structure of another member of this family, viz. **11-NO₂**, has also been solved, and the structure (figure 12) is found to be similar in every respect to that of the **11-CH₃** complex.

Due to the restricted rotation around the imine (C=N) bond, which has occurred during formation of the five-membered chelate ring in these **11-R** complexes, the phenyl group has moved away from the metal centre, and this vitiates the possibility of the expected cyclopalladation. Hence this exercise has been slightly disappointing. However, this disappointment has been partially compensated by the remarkable catalytic properties exhibited by these palladium complexes towards C–C cross coupling reactions of three different types, viz. Suzuki, Heck and Sonogashira coupling.⁶ For example, the **11-OCH₃** complex has been found to catalyse Suzuki coupling reaction between *para*-substituted phenyl bromides and phenylboronic acid with great efficiency (entries 1–3, table 1), with particular reference to relatively mild experimental condi-

tions, the absence of any external ligand, very low catalyst loading and high turnover numbers. Such coupling reactions are also found to be possible at room temperature (entry 4), as well as in aqueous medium (entry 5) with slight modification of the reaction parameters.

4. Conclusions

The present study shows that organometallic complexes of the platinum metals can be conveniently synthesized via C–H bond activation mediated by a M–H or M–Cl fragment (M = platinum metal). This study also demonstrates that aryl C–H bond activation is much more facile compared to alkyl C–H bond activation.

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