

# *N*-Acetyl-*N,N*-dipyrid-2-yl (cyclooctadiene) rhodium (I) and iridium (I) complexes: Synthesis, X-ray structures, their use in hydroformylation and carbonyl hydrosilylation reactions and in the polymerization of diazocompounds

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Received 30 April 2007; received in revised form 6 August 2007; accepted 9 August 2007

Available online 16 August 2007

## Abstract

The synthesis of novel *N*-acetyl-*N,N*-dipyrid-2-yl complexes of Rh<sup>I</sup> and Ir<sup>I</sup>, i.e. [RhCl(CH<sub>3</sub>CONPy<sub>2</sub>)(COD)] (**1**) and [IrCl(CH<sub>3</sub>CONPy<sub>2</sub>)(COD)] (**2**), respectively, is described. Upon prolonged treatment in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, complex **1** is transformed into a cationic Rh-complex, i.e. [Rh(CH<sub>3</sub>CONPy<sub>2</sub>)(COD)<sup>+</sup>RhCl<sub>2</sub>(COD)<sup>-</sup>] (**1a**). Compound **1a** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*, complex **2** crystallizes in the triclinic space group *P* $\bar{1}$ . Compound **1** was investigated for its catalytic activity in the hydroformylation of cyclooctene as well as of 1-octene. In addition, **1** was used in various carbonyl hydrosilylation reactions of both aldehydes and ketones. There, turn-over numbers up to 50000 and yields in the range of 85–100% were observed. Finally, compound **1** was successfully used for the polymerization of N<sub>2</sub>CHCOOEt yielding highly stereoregular poly(ethoxycarbonylcarbene) with *M*<sub>w</sub> = 67000 g/mol and a polydispersity index (PDI) of 2.59. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Rhodium; Iridium; Hydroformylation; Carbonyl hydrosilylation; Polymerization; Diazo compounds

## 1. Introduction

In contrast to their P-analogues, N-based ligands are usually less strong electron donating ligands, however, possess the great advantage of being entirely stable towards oxygen even at higher temperatures. Some time ago, we reported on various dipyridylamide ligands, the corresponding Pd complexes, their immobilization on both organic and inorganic supports and their use in C–C coupling reactions such as Heck-, Suzuki and Sonogashira-Hagihara-type reactions [1–4]. Particularly Pd(II) complexes of *N*-acyl-*N,N*-dipyrid-2-yl amine allowed for

the highly effective coupling of aryl iodides, aryl bromides as well as activated aryl chlorides. Due to the high affinity of the ligand versus Pd, metal bleeding was low, allowing for the multiple use of particularly supported systems [1]. Later, non-acylated versions of dipyrid-2-ylamine were used by other groups [5–7]. In extension to our work, we report here on the synthesis of the corresponding Rh<sup>I</sup> and Ir<sup>I</sup> complexes of *N,N*-dipyrid-2-ylacetamide and their use in various catalytic reactions.

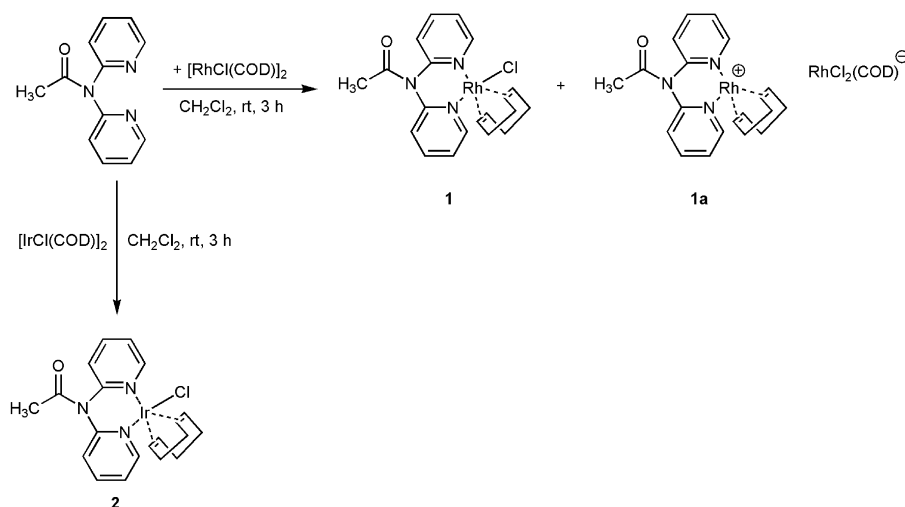
## 2. Results and discussion

### 2.1. Synthesis of Rh- and Ir-complexes of *N,N*-dipyrid-2-ylacetamide

Compound **1** was synthesized from [RhCl(COD)]<sub>2</sub> and *N,N*-dipyrid-2-ylacetamide in 95% yield (Scheme 1). Inter-

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Scheme 1. Synthesis of compounds **1**, **1a** and **2**.

estingly, prolonged treatment with methylene chloride gave rise to a further transformation that resulted in the formation of a cationic complex  $[\text{Rh}(\text{CH}_3\text{CONPy}_2)^+\text{RhCl}_2(\text{COD})^-]$  (**1a**). Compound **1a** crystallizes in the monoclinic space group  $P2_1/c$  (No. 14) with  $a = 1069.22(2)$  pm,  $b = 1268.89(2)$  pm,  $c = 2260.67(3)$  pm,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 95.928(1)^\circ$ ,  $Z = 4$  (Fig. 1a). Selected bond distances are also summarized in Fig. 1a. As can be deduced therefrom, the Rh(1)–N(1) and Rh(1)–N(2) distances were basically identical, i.e. 213.01(2) and 213.03(2) pm, the angle N(1)–Rh(1)–N(2) was  $83.58(7)^\circ$ .

Compound **2** was prepared in a similar manner from  $[\text{IrCl}(\text{COD})]_2$  and *N,N*-dipyridyl-2-ylacetamide in 90% yield (Scheme 1). Compound **2** crystallizes in the triclinic space group  $P\bar{1}$  (No. 2) with  $a = 1113.34(5)$  pm,  $b = 1304.17(7)$  pm,  $c = 1430.73(6)$  pm,  $\alpha = 96.321(2)^\circ$ ,  $\beta = 92.704(3)^\circ$  and  $\gamma = 105.319(2)^\circ$ ,  $Z = 4$  (Fig. 1b). Selected bond distances are also summarized in Fig. 1b. Surpris-

ingly, the distances Ir–N(2) and Ir–N(3) were comparable to those found in **1a**, i.e. 212.6(6) and 213.4(6) pm, respectively. The same accounts for the angle N(2)–Ir(1)–N(3), which was  $83.7(2)^\circ$ . This is remarkable, since the larger atom diameter of Ir would let expect both longer bonds and a larger angle. Since the Rh-complexes are in general more reactive than the corresponding Ir-analogues, complex **1** was used for all further investigations.

## 2.2. Hydroformylation reactions

Hydroformylation reactions are among the most important industrial processes with a world wide production of several million tons. Starting from readily available alkenes, dihydrogen and carbon monoxide, highly valuable *n*-aldehydes as well as the corresponding regioisomers are available [8–12]. Numerous transition metals such as Rh, Pt, Co and Ru may be used for these purposes, however,

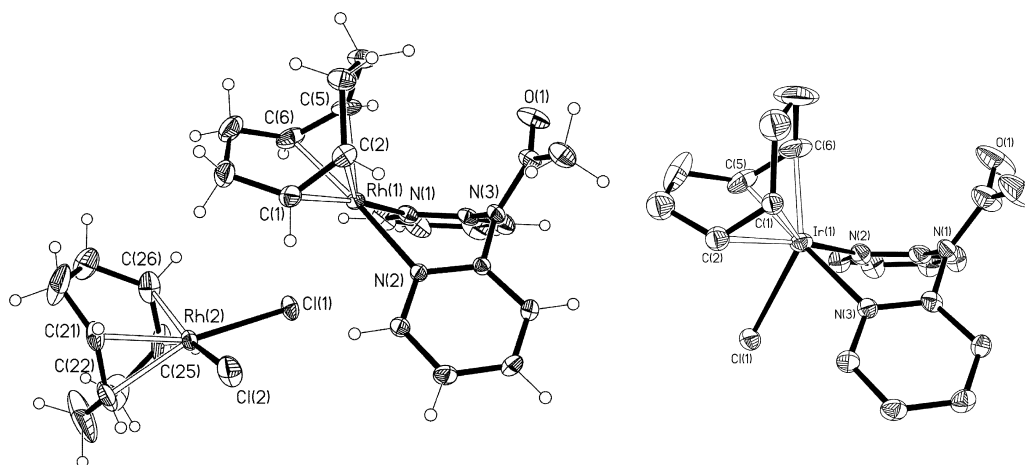


Fig. 1. X-ray structures of **1a** (left) Rh(1)–C(5) 210.1(2) pm, Rh(1)–C(6) 211.5(2) pm, Rh(1)–C(1) 212.5(2) pm, Rh(1)–N(2) 213.01(2) pm, Rh(1)–N(1) 213.05(2) pm, Rh(1)–C(2) 213.8(2) pm, Rh(2)–C(26) 208.9(3) pm, Rh(2)–C(25) 209.4(3) pm, Rh(2)–C(21) 209.9(2) pm, Rh(2)–C(22) 209.9(3) pm, N(2)–Rh(1)–N(1)  $83.58(7)^\circ$  and **2** (right) Ir(1)–C(5) 207.0(8) pm, Ir(1)–C(6) 209.2(9) pm, Ir(1)–N(2) 212.6(6) pm, Ir(1)–N(3) 213.4(6) pm, Ir(1)–C(1) 214.4(2) pm, Ir(1)–C(2) 218.3(2) pm, Ir(1)–Cl(1) 253.91(2) pm, N(2)–Ir(1)–N(3)  $83.7(2)^\circ$ .

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