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Note

Efficient synthesis of the cyclometalated complex *fac*-[Rh(ppy)$_3$] (ppy = 2-phenylpyridinato)

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ABSTRACT

A new convenient high-yield synthesis of the *tris*-cyclometalated complexes *fac*-[Rh(ppy)$_3$] (**4**; ppy = 2-phenylpyridinato) was developed. Complex **4** was prepared in a kind of one-pot synthesis starting from in situ prepared [Rh(acac)(coe)$_2$] (**2**) which was heated in refluxing 2-phenylpyridine for a short time. After purification by filtration over alumina, compound **4** was obtained in yields of 65%. Also [Rh(acac)(ppy)$_2$] (**3**) was prepared in a similar manner by oxidative addition of Hppy in refluxing toluene in high yields. In contrast to previous findings with the analogous iridium compounds, there was not any hint at the formation of the isomer *mer*-[Rh(ppy)$_3$] using similar reaction conditions as applied for iridium. Furthermore the compound [{Rh(μ-Cl)(ppy)$_2$}$_2$] (**5**) was prepared from [{Rh(μ-Cl)(coe)$_2$}$_2$] (**1**) and Hppy in refluxing toluene in nearly quantitative yield.

1. Introduction

Recently we described a new convenient synthetic pathway to iridium(III) complexes bearing cyclometalated ligands like ppy (Hppy = 2-phenylpyridine) [1]. The method started with the in situ preparation of [Ir(acac)(coe)$_2$], followed by oxidative addition of Hppy in different molar ratios affording [Ir(acac)(ppy)$_2$] and [Ir(ppy)$_3$] (*mer* or *fac* isomer), respectively, in good yields. The advantages of this synthesis compared to known procedures in this field are good yields in short reaction times, the need of no silver salts for chloride abstraction, and sufficient purity of the products so that usually a chromatographic workup is not necessary. In the literature little is known about the analogous rhodium compounds, presumably since the iridium species exhibit better photochemical and photophysical properties, e.g. in the field of OLED applications [2]. Recently, however, beside the well established cyclometalated iridium(III) complexes, also the analogous rhodium species were used as luminescent labels for biomolecules [3]. The complexes [Rh(acac)(ppy)$_2$] (**3**, acac = acetylacetonato) [4] and *fac*-[Rh(ppy)$_3$] (**4**) [5] are known from the literature. Compound **4** was obtained by a more complicated procedure in very moderate yields of 4% after twofold chromatographic workup. No further reports on the synthesis of the latter species appeared in the literature. Mononuclear cyclometalated rhodium complexes were generally prepared from [{Rh(μ-Cl)(ppy)$_2$}$_2$] (**5**) [6]. Our observation that 2-phenylpyridinato ligands can be introduced by oxidative addition of Hppy towards iridium(I) compounds resulting in the corresponding Ir(III) species [1], prompted us to search for a similar preparation method to the analogous rhodium complexes. Now we found a synthesis of **5** using [{Rh(μ-Cl)(coe)$_2$}$_2$] (**1**, coe = *cis*-cyclooctene) [7] as the starting complex, but we have still not published this method. Compound **3** was prepared from **5** and potassium acetylacetonate in good yield [4]. We describe here a slightly modified synthesis of [Rh(acac)(coe)$_2$] (**2**) [8] and its usefulness for an efficient one-pot synthesis of the cyclometalated rhodium(III) complexes **3** and **4**, respectively.

2. Experimental

2.1. General considerations

All manipulations were performed under an atmosphere of dry nitrogen using conventional Schlenk techniques. Solvents were dried with standard procedures and stored under nitrogen. [{Rh(μ-Cl)(coe)$_2$}$_2$] (**1**) was prepared according to the literature procedure [7]. THF was dried over sodium-benzophenone ketyl and freshly distilled under nitrogen prior to use. NMR spectra were measured using Jeol Eclipse 270 and 400 instruments operating at 270 and 400 (^{1}H), and 100 MHz (^{13}C), respectively. Chemical shifts

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are given in ppm relative to TMS. Mass spectra were recorded using a Jeol Mstation JMS 700. Elemental analyses (C, H, N and Cl) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

2.2. Synthesis of [Rh(acac)(ppy)$_2$] (**3**) from in situ prepared [Rh(acac)(coe)$_2$] (**2**)

To a solution of **1** (359 mg, 0.50 mmol) in 20 mL of THF solid Na(acac)·H$_2$O (140 mg, 1 mmol) was added. Immediately a clear deep orange solution resulted which was stirred for 30 min at room temperature. Then the solvent was removed in vacuo. At this point the residue contained only [Rh(acac)(coe)$_2$] (**2**) in nearly quantitative yield as checked by NMR spectroscopy. To remove the sodium chloride, the remaining residue was treated with 15 mL of cold hexane, the solution filtered and the solvent evaporated to dryness in vacuo. The residue was dissolved in 15 mL of toluene and 2-phenylpyridine (620 mg, 4 mmol) was added and the mixture was refluxed with stirring for 1 h. During this time a yellow powder precipitated from the solution. After cooling to room temperature the solid was filtered off, washed three times with 10 mL portions of hexane and dried in vacuo. Yield: 439 mg (86%). *Anal.* Calc. for $C_{27}H_{23}N_2O_2Rh$: C, 63.54; H, 4.54; N, 5.49. Found: C, 63.73; H, 4.51; N, 5.63%. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 187.4 (*C*O-acac), 168.3 (d, J_{Rh-C} = 35.5 Hz, *C*, metalated), 165.1, 149.0, 144.5, 137.3, 133.8, 128.7, 123.6, 122.1 (2 singlets overlapped), 118.9, 97.9 (*C*H-acac), 28.6 (*C*H$_3$-acac). The ^{1}H NMR data agreed with the reported ones [4].

2.3. Synthesis of fac-[Rh(ppy)$_3$] (**4**) from in situ prepared [Rh(acac)(coe)$_2$] (**2**)

To a solution of **1** (359 mg, 0.50 mmol) in 20 mL of THF solid Na(acac)·H$_2$O (140 mg, 1 mmol) was added and the mixture stirred at room temperature for 30 min. Then the solvent was removed in vacuo. The remaining residue was treated with 10 mL of cold hexane, the solution filtered and the solvent evaporated to dryness in vacuo. The residue was dissolved in 5 mL of 2-phenylpyridine and the mixture refluxed for 20 min. The solution was cooled to room temperature and the product precipitated by adding 30 mL of hexane. The powder was filtered off, washed three times with 10 mL portions of hexane and dried in vacuo. The raw product was purified by filtration over alumina using dichloromethane as the eluent. Yield: 360 mg (64%). *Anal.* Calc. for $C_{33}H_{24}N_3Rh$: C, 70.09; H, 4.28; N, 7.43. Found: C, 69.93; H, 4.41; N, 7.61%. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 178.9 (d, J_{Rh-C} = 38.4 Hz, *C*, metalated), 163.9, 147.4, 143.6, 137.2, 136.5, 129.0, 123.5, 121.8, 120.8, 118.7 MS (FAB$^+$): m/z = 565 [M$^+$]. The ^{1}H NMR data agreed well with the reported ones [5]. The excess of 2-phenylpyridine could be recovered by distillation and reused in further preparations.

2.4. Synthesis of [{Rh(μ-Cl)(ppy)$_2$}$_2$] (**5**) from [{Rh(μ-Cl)(coe)$_2$}$_2$] (**1**)

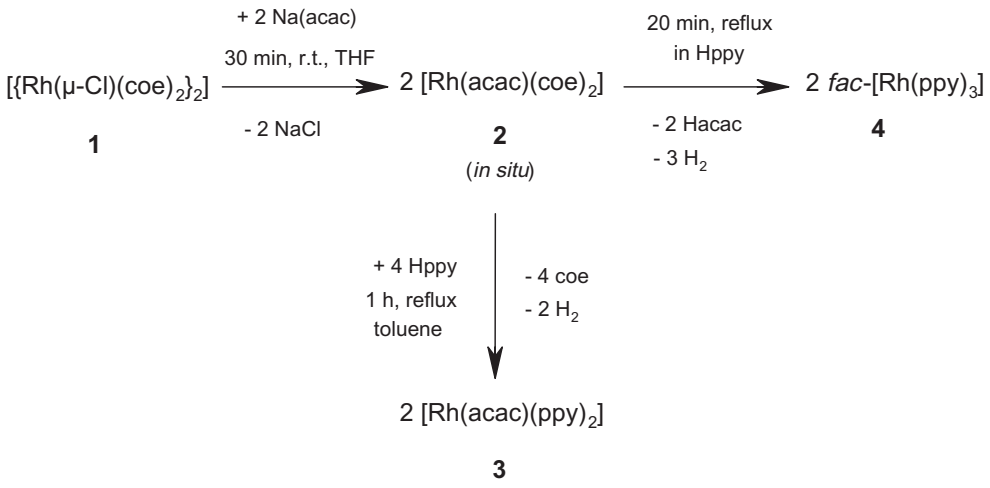
To a solution of **1** (359 mg, 0.50 mmol) in 25 mL of toluene 2-phenylpyridine (310 mg, 2 mmol) was added and the mixture stirred under reflux for 1 h. During this period the color of the solution changed from deep orange to pale yellow and a yellow powder precipitated from the solution. After cooling to room temperature the solvent was reduced in vacuo to 10 mL. The crystals were filtered off, washed three times with 10 mL portions of hexane and dried in vacuo. Yield: 438 mg (98%). *Anal.* Calc. for $C_{44}H_{32}Cl_2N_4Rh_2$: C, 59.15; H, 3.61; Cl, 7.94; N, 6.27. Found: C, 58.93; H, 3.41; Cl, 7.89; N, 6.42%. The NMR data (^{1}H and ^{13}C) agreed with the literature data [9].

3. Results and discussion

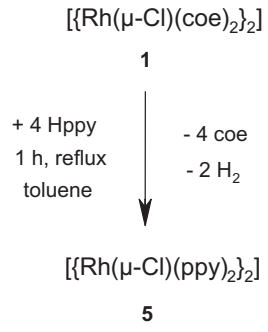
The compound [Rh(acac)(coe)$_2$] (**2**) was described in the literature [8] and prepared by the reaction of [{Rh(μ-Cl)(coe)$_2$}$_2$] (**1**) with Na(acac) in toluene at 40 °C during 3 h. We have slightly modified this procedure by using THF as the solvent. Thus a very short reaction time of about 20 min is only necessary. Recently we described an analogous synthesis for [Ir(acac)(coe)$_2$] [1]. Because of the successful use of the latter species in the preparation of iridium(III) complexes containing cyclometalated C^N ligands, we developed a similar procedure for the synthesis of the analogous rhodium(III) complexes (Scheme 1).

In accordance with the known higher stability of iridium(III) complexes in ligand substitution processes compared to the analogous rhodium species, we found that the synthesis of the rhodium compounds could be realized in shorter reaction times and under milder reaction conditions. Thus the treatment of **1** with two equivalents of hydrated Na(acac) in THF at room temperature resulted immediately in a clear orange solution. After a short reaction period, complex **2** was obtained after evaporation of the solvent in nearly quantitative yield as yellow powder. The purity of **2** was checked by NMR spectroscopy and the data agreed well with the reported ones [8]. As illustrated in Scheme 1, the *in situ* prepared complex **2** reacts with two equivalents of Hppy in refluxing toluene during 1 h under oxidative addition to [Rh(acac)(ppy)$_2$] (**3**) in high yield. The latter compound is known from the literature and was unambiguously identified by its known ^{1}H NMR data [4]. Additionally we collected the $^{13}C\{^1H\}$ NMR data of **3** (see Section 2).

Furthermore we examined the subsequent reaction pathway to the *tris*-cyclometalated complex [Rh(ppy)$_3$] by reacting **2** and **3**, respectively, with an excess of Hppy (reflux conditions). Recently we could show that the complex *mer*-[Ir(ppy)$_3$] can be prepared by reaction of [Ir(acac)(ppy)$_2$] with a slight excess of Hppy in refluxing ethoxyethanol during 3 h [1]. Adapting this method to the rhodium species **3** as the precursor to generate the complex *mer*-[Rh(ppy)$_3$] failed in numerous attempts. In all cases we were unable to detect signals belonging to *mer*-[Rh(ppy)$_3$] by ^{1}H NMR spectroscopy. A distinction between the fac and mer isomers in the ^{1}H NMR spectra is easy to realize. Because of the lower symmetry of the mer isomer in comparison with the fac configured species, more complex ^{1}H NMR spectra should be usually observed for the mer isomers. In comparison with an octahedral complex with facial arrangement of ligands, which exhibit a set of eight coupled protons due to the threefold symmetry of the molecule, in a meridional configuration of ligands the protons are magnetically inequivalent resulting in a set of 24 coupled protons. Thus the treatment of **3** with Hppy in excess under various reaction conditions, e.g. in ethoxyethanol (3 h, reflux) or treatment in an open vessel to remove the Hacac by distillation, or treatment in Hppy at 180 °C in an oil bath for 2 h, resulted not in the formation of *mer*-[Rh(ppy)$_3$]. By ^{1}H NMR spectroscopy only the unreacted precursor **3** could be detected in each case. This was somewhat surprising and frustrating because we were able to isolate the corresponding two iridium isomers [1]. Otherwise the synthesis of the isomer *fac*-[Rh(ppy)$_3$] (**4**) was possible in our hands by treatment of in situ prepared **2** which was dissolved in a small amount of 2-phenylpyridine and refluxed for 20 min at 260 °C (Scheme 1). It should be noted that a longer reaction time resulted in a markedly decomposition accompanied with separation of some rhodium metal from the solution. The crude product **4** was precipitated with hexane as a powder, which was filtered over alumina with dichloromethane as the solvent. Compound **4** was obtained as yellow crystals in yields of 65%. The NMR data agreed well with the reported ones [5] and showed that only the isomer *fac*-[Rh(ppy)$_3$]



Scheme 1.



Scheme 2.

was formed under these conditions. Unfortunately, despite of many efforts, we were unable to obtain suitable single crystals of **4** for an X-ray diffraction study. In the literature [5] however was reported that *fac*-[Rh(ppy)$_3$] and *fac*-[Ir(ppy)$_3$] crystallize in an isomorphous structure as confirmed by X-ray powder diffraction studies.

As mentioned above we found that the synthesis of **5** using **1** as the starting complex is possible by using the new oxidative addition pathway (Scheme 2). Thus complex **1** reacted with the fourfold amount of 2-phenylpyridine in refluxing toluene during 1 h yielding **5** in nearly quantitative yield. Compound **5** was unambiguously characterized by its known NMR data [9].

In conclusion, the advantages of the herein described synthetic procedures are that the complexes [Rh(acac)(ppy)$_2$] (**3**) and *fac*-[Rh(ppy)$_3$] (**4**) can be obtained in good yields by an efficient one-pot method starting from [{Rh(μ-Cl)(coe)$_2$}$_2$], which afforded [Rh(acac)(coe)$_2$] (**2**) as an intermediate in situ, followed by oxidative addition of 2-phenylpyridine. The described procedure demanding only short reaction times, afforded the cyclometalated rhodium(III) complexes in high yields and did not need the use of silver salts as chloride abstraction reagents. In comparison with the recently reported synthetic pathway to the analogous iridium complexes [1], we found that for preparing the rhodium complexes shorter reaction times and even milder reaction conditions were necessary. The general usefulness of the described procedures for the synthesis of closely related cyclometalated rhodium(III) complexes will be examined by us in the near future. First results in this field were currently achieved in the preparation of the new compounds [{Rh(μ-Cl)(ptpy)$_2$}$_2$] (ptpy = 2-(*p*-tolyl)pyridinato) [10], as well as [Rh(acac)(ptpy)$_2$] and *fac*-[Rh(ptpy)$_3$] [11].

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