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Synthesis of the tris-cyclometalated complex fac-[Rh(ptpy)$_3$] and X-ray crystal structure of [Rh(acac)(ptpy)$_2$]

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ABSTRACT

New convenient syntheses of the cyclometalated complexes [Rh(acac)(ptpy)$_2$] (3, ptpy = 2-(p-tolyl) pyridinato) and *fac*-[Rh(ptpy)$_3$] (4) are described. The compounds were prepared in a kind of one-pot synthesis starting from *in situ* prepared [Rh(acac)(coe)$_2$] (2) (coe = *cis*-cyclooctene) followed by reaction with Hptpy in refluxing toluene. Under these conditions oxidative addition occurred and the new complex 3 was obtained in good yields. Compound 4 was prepared in good yields by reaction of 3 with Hptpy in excess. The complex 3 crystallized from dichloromethane/*iso*-hexane in the space group $P-1$ and its molecular structure was confirmed by a single-crystal X-ray diffraction study. The absorption and emission spectra exhibit the new compounds as red-emitting phosphorescent complexes.

Recently we described a new convenient synthesis of iridium(III) complexes bearing cyclometalated ligands like ppy (Hppy = 2-phenylpyridine) [1]. The method started from *in situ* prepared [Ir(acac)(coe)$_2$] (acac = acetylacetonato, coe = *cis*-cyclooctene) followed by oxidative addition of Hppy affording [Ir(acac)(ppy)$_2$] and [Ir(ppy)$_3$] (*mer* or *fac* isomer), respectively, in good yields. Little is known on the analogous rhodium compounds in the literature, presumably since the iridium species exhibit better photochemical and photophysical properties, e.g. in light of OLED applications [2]. Very recently, however, cyclometalated rhodium(III) complexes were investigated as luminescent biotinylation reagents beside their iridium analogues which have been used yet longer in this field [3]. [Rh(acac)(ppy)$_2$] [4] and *fac*-[Rh(ppy)$_3$] [5] are known from the literature, whereby the latter was prepared by a complicated procedure affording the compound in very moderate yield. Until now no further reports on the synthesis of this compound appeared. In the known preparative routes affording cyclometalated rhodium(III) complexes, [{Rh(μ-Cl)(ppy)$_2$}$_2$] [6] served as the usual starting complex. Our observation that 2-phenylpyridinato ligands can be introduced by oxidative addition of Hppy towards suitable iridium(I) compounds resulting in the corresponding Ir(III) species, prompted us to search for new convenient preparation methods to the analogous rhodium complexes. Thus we developed a synthesis of [Rh(acac)(ppy)$_2$] and *fac*-[Rh(ppy)$_3$], respectively, using [Rh(acac)(coe)$_2$] (2) [7] as the starting complex [8].

We describe here further results in this field supporting the general usefulness of our method for preparing cyclometalated rhodium(III) complexes bearing other derivatives of 2-phenylpyridine. Thus convenient syntheses of [Rh(acac)(ptpy)$_2$] (3, ptpy = 2-(p-tolyl)-pyridinato) and *fac*-[Rh(ptpy)$_3$] (4) as well as the structural characterization of the former by X-ray crystallography are reported.

Compound 3 was synthesized in good yields on the basis of our method [8] as used for [Rh(acac)(ppy)$_2$] and *fac*-[Rh(ppy)$_3$], respectively, namely by the *in situ* preparation of [Rh(acac)(coe)$_2$] (2) from [{Rh(μ-Cl)(coe)$_2$}$_2$] (1) [9] with Na(acac) in THF in the first step and subsequent oxidative addition of 2-(p-tolyl)pyridine, see Scheme 1 [10].

For the preparation of 3, we found that it is necessary to remove the sodium chloride by filtration [10]. Otherwise the formation of the compound [{Rh(μ-Cl)(ptpy)$_2$}$_2$] occurs to some extent in a side reaction. We explain this by the greater lability of the rhodium complexes with respect to ligand exchange processes in comparison with the analogous iridium species. As for iridium, we had no hints at related ligand substitutions during the development of the one-pot synthesis of [Ir(acac)(ppy)$_2$] and *fac*-[Ir(ppy)$_3$], respectively [1]. The inertness of the iridium analogues towards ligand exchange — generally of complexes of the 5d metals — is well documented in the literature.

Furthermore the tris-cyclometalated complex *fac*-[Rh(ptpy)$_3$] (4) was obtained in good yield by a similar one-pot procedure starting from 1 yielding 2 *in situ* followed by treatment with 2-(p-tolyl)pyridine without solvent under reflux for a short time [11]. (The excess of the ligand might be recovered by distillation.) These short reaction periods should be followed absolutely since decomposition with formation of rhodium metal occurs otherwise. The assignment of the *fac*- arrangement of the three cyclometalating ligands is based on its ^{1}H NMR spectrum, which

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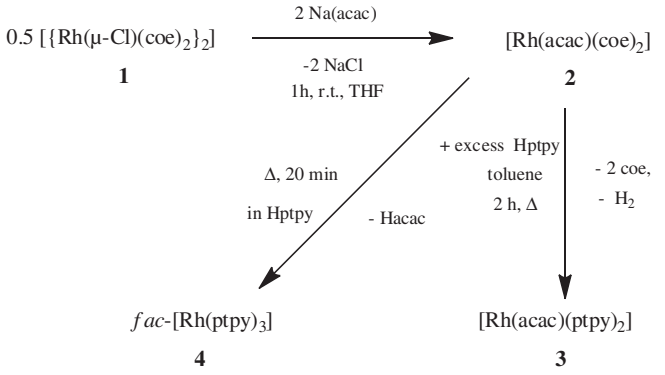

Scheme. 1. Syntheses of **2**, **3** and **4** from **1**.

shows only one singlet for the tolyl methyl protons, while for the *mer*-isomer three singlets would be expected [12].

The structure analysis on crystals of 3 [13] confirmed the molecular structure of [Rh(acac)(ptpy)$_2$]. Fig. 1 shows a selected ORTEP view of the molecule with important bond lengths and angles in the caption.

The rhodium complex exhibits the three chelating ligands in a pseudooctahedral coordination sphere at the metal center, with a trans arrangement of the pyridine nitrogen and a cis arrangement of the cyclometalated carbon atoms of the ptpy ligands. The Rh—N bond lengths with 2.038(2) and 2.0333(19) Å, respectively, are a little bit longer than in the complexes [Rh(acac)(ppy)$_2$] and [Rh(OAc)(ppy)$_2$], respectively, 2.026(2) Å in each case. Also the observed Rh—C bond lengths of 3 are slightly longer than in the latter two complexes, 1.973 (2) and 1.966(4) Å [4]. Furthermore, the C–C and C–N bond lengths

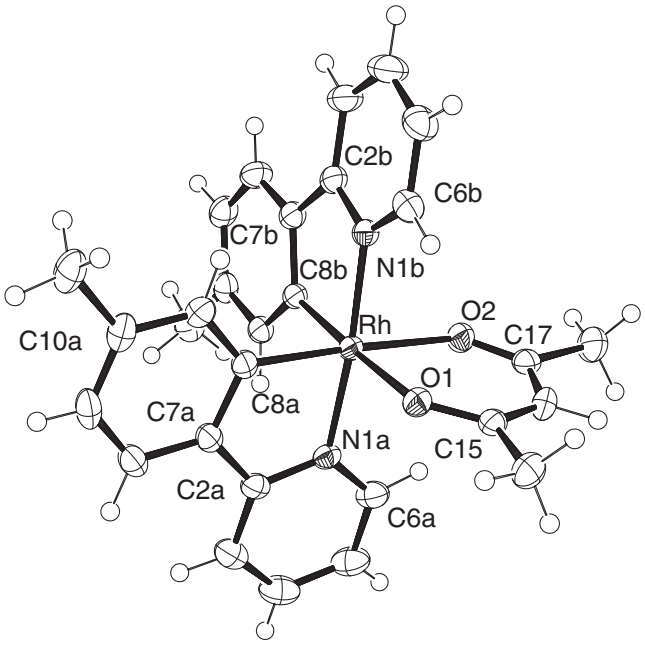

Fig. 1. ORTEP view of **3** with thermal ellipsoids are drawn at the 50% probability level. The solvate molecules (CH_2Cl_2) are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh–N(1a) 2.038(2), Rh–N(1b) 2.0333(19), Rh–O(1) 2.1690(17), Rh–O(2) 2.1626(16), Rh–C(8a) 1.983(2), Rh–C(8b) 1.981(2), O(1)-C(15) 1.271(3), O(2)-C(17) 1.260(3) Å; C(8b)-Rh-C(8a) 86.73(9), C(8b)-Rh-N(1b) 81.32(9), C(8a)-Rh-N(1b)95.85(9), C(8b)-Rh-N(1a) 93.62(9), C(8a)-Rh-N(1a) 81.17(9), N(1b)-Rh-N(1a) 174.31(8), C(8b)-Rh-O(2) 92.65(8), C(8a)-Rh-O(2) 176.22(8), N(1b)-Rh-O(2) 87.73(7), N(1a)-Rh-O(2) 95.15(7), C(8b)-Rh-O(1) 176.49(8), C(8a)-Rh-O(1) 93.14(8), N(1b)-RhO(1) 95.21(7), N(1a)-Rh-O(1) 89.82(7), O(2)-Rh-O(1) 87.71(6)°.

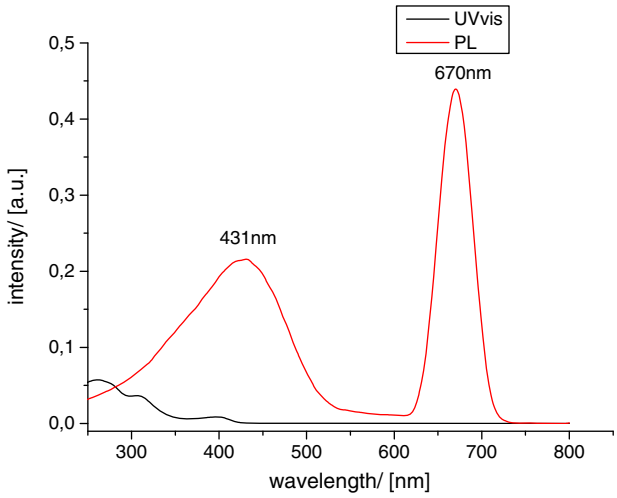

Fig. 2. Absorption and emission spectrum of **3** in CH_2Cl_2 at 298 K.

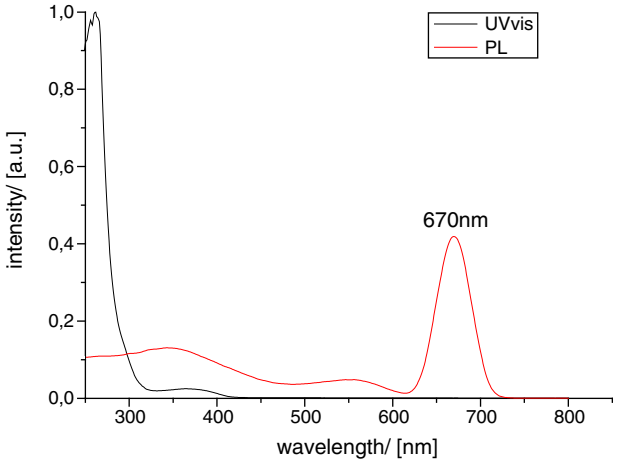

Fig. 3. Absorption and emission spectrum of **4** in CH_2Cl_2 at 298 K.

and angles are within normal ranges and are in accordance with the corresponding parameters described for other similar complexes.

The absorption and the emission spectra of 3 and 4 recorded in dichloromethane at room temperature are depicted in Figs. 2 and 3, respectively. In the UV/VIS-absorption spectrum of 3 bands at 261 and 306 nm were found, respectively, which can be assigned to spin-allowed (IL) ($\pi \rightarrow \pi^*$)(ptpy) transitions. The band at 398 nm corresponds to ^{1}MLCT [d_π(Rh) $\rightarrow \pi^*$(ptpy)] transitions. The emission spectrum of 3 shows a band maximum at 670 nm exhibiting the compound as a red-emitting complex. Generally it is likely that the emission in such cyclometalated complexes originates from a ^{3}IL($\pi \rightarrow \pi^*$) (ptpy) excited state, probably with mixing of some ^{3}MLCT [d_π(Rh) $\rightarrow \pi^*$(ptpy)] character. In the absorption spectrum of 4 a band at 262 nm was found which can be assigned as mentioned before. A second maximum at 365 nm corresponds to spin-allowed ^{1}MLCT (d_π(Rh) $\rightarrow \pi^*$(ptpy) transitions. The emission spectrum of 4 shows a band maximum at 670 nm exhibiting the compound even as a red-emitting complex. The emission spectra of the complex [Rh(acac)(ppy)$_2$] show a yellow-green emission described in [7]. These data correspond well with the observed ones of similar constituted complexes described in [3].

In conclusion, two new cyclometalated Rh(III) complexes were synthesized using oxidative addition reactions toward the Rh(I) species [Rh(acac)(coe)$_2$] in good yields and short reaction times. The compounds were characterized by means of spectroscopic methods as well as by X-ray single crystal diffraction.

Acknowledgments

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[10] Synthesis of [Rh(acac)(ptpy)$_2$] (**3**): To a solution of **1** (359 mg, 0.50 mmol) in 20 mL of THF solid Na(acac)·H_2O (140 mg, 1 mmol) was added. Immediately a clear deep orange solution resulted which was stirred for 1 h at room temperature. Then the solvent was removed in vacuo. The remaining residue was extracted with 30 mL of hexane and filtered to remove the NaCl. The solution was evaporated to dryness and the residue was dissolved in 20 mL of toluene. 2-(p-tolyl)pyridine (845 mg, 5 mmol) was added and the mixture refluxed with stirring for 2 h. After cooling to room temperature the solvent was evaporated to dryness, the residue was dissolved in a minimum of dichloromethane, and **3** precipitated by adding 30 mL of hexane. The yellow crystals were filtered off, washed three times with 10 mL portions of hexane and dried in vacuo. The crude product was chromatographed on alumina with dichloromethane as the eluent. Yield: 350 mg (65%). *Anal.* Calcd. for $C_{29}H_{27}N_2O_2Rh$: C, 64.69; H, 5.05; N, 5.20. Found: C, 64.61; H, 5.07; N, 5.15%. MS (FAB$^+$): $m/z = 538$ [M$^+$]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (m, 2H, ptpy), 7.86 (m, 4H, ptpy), 7.50 (d, $J = 7.68$ Hz, 2 H, ptpy), 7.18 (m, 2H, ptpy), 6.73 (d, $J = 7.68$ Hz, 2H, ptpy), 6.04 (s, 2H, ptpy), 5.29 (s, ^{1}H, C*H*-acac), 2.02 (s, 6 H, CH_3-ptpy), 1.83 (s, 6H, CH_3-acac). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.3 (*C*O-acac), 168.2 (d, $J_{Rh\text{-}C} = 35.5$ Hz, C metalated), 165.1, 148.9, 141.8, 138.8, 137.1, 134.6, 123.4, 123.1, 121.5, 118.5, 97.9 (*C*H-acac), 28.7 (ptpy-*C*H_3), 21.5 (*C*H_3-acac).
[11] Synthesis of [Rh(ptpy)$_3$] (**4**): To a solution of **1** (359 mg, 0.50 mmol) in 20 mL of THF solid Na(acac)·H_2O (140 mg, 1 mmol) was added and the mixture stirred for 1 h at room temperature. The solvent was removed in vacuo, the remaining residue dissolved in 5 mL of 2-(p-tolyl)pyridine and the mixture refluxed (268 °C) for 20 min. The solution was cooled to room temperature and the crude product precipitated by adding 30 mL of hexane. The slight yellow powder was filtered off and washed tree times with 10 mL portions of hexane and dried in vacuo. The product was purified by filtration on alumina with dichloromethane as the eluent. Yield: 321 mg (53%). *Anal.* Calc. for $C_{36}H_{30}N_3Rh$: C, 71.17; H, 4.89; N, 6.92. Found: C, 71.21; H, 4.84; N, 6.79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, m, 3H, ptpy), 7.66 (m, 3H, ptpy), 7.58 (d, $J = 8$ Hz, 3H, ptpy), 7.49 (m, 3H, ptpy), 6.88 (m, 3H, ptpy), 6.72 (m, 3H, ptpy), 6.65 (s, 3H, ptpy), 2.00 (s, 9H, CH_3). Due to solubility problems no ^{13}C-NMR spectra could be obtained, that showed all quaternary carbon atoms. MS (FAB$^+$): $m/z = 607$ [M$^+$].
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[13] Single crystals of **3** were obtained by slow diffusion of *iso*-hexane into a dichloromethane solution of the compound overnight. A suitable crystal was selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on an Oxford XCalibur diffractometer using Mo Kα radiation (λ = 0.71073 Å). The intensities were corrected for absorption by an empirical correction with SCALE3 ABSPACK [14]. The structure was solved by direct methods (SIR 97) [15] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [16]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. *Crystal data*: $C_{30}H_{29}Cl_2N_2O_2Rh$ (**3**·CH_2Cl_2) FW = 623.36, triclinic, space group *P*-1, a = 8.0821(2), $b = 12.3285(3)$, $c = 13.8138(3)$ Å, α = 85.7270(10)° β = 89.6400 (10)° γ = 79.2410(10)° $V = 1348.41(6)$ Å^3, Z = 2, $D_{calc} = 1.5535$ g cm^{-3}, T = 200(2) K, 13843 reflections were collected, of which 7250 ($R_{int} = 0.0392$ [$I > 2\sigma$ (I)] were unique.
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