115. Cyclometallated Rhodium(III) Complexes with Diimine Ligands

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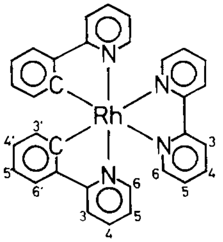
The synthesis of a mononuclear Rh(III) complex, as a representative example of a series of related species, containing two cyclometallating ligands ppy (2-phenylpyridine) and one diimine bpy (2,2′-bipyridine) from a binuclear Cl-bridged compound is described. The absorption spectrum shows a maximum at 364 nm ($\varepsilon = 7000$), with a very weak shoulder ($\varepsilon = 10$) at 454 nm. This band is tentatively assigned to a metal-to-ligand charge-transfer transition. A reversible, one-electron reduction appears in the cyclic voltammogram at $E_{1/2} = -1.41$ V (*vs.* NHE) and a irreversible oxydation at $E_p = +1.1$ V. A detailed NMR analysis including ^{13}C-NMR, NOE, SFORD as well as deuteration of the bpy ligand indicates the formation of only one isomer, having a C_2 axis, bisecting the bpy ligand, with the two carbon ligands in *cis*-position. ^{103}Rh,^{13}C and ^{103}Rh,H couplings are observed.

Introduction. – Complexes of the Pt group metals with diimine ligands have found in recent years widespread interest, especially for their photophysical and photochemical properties [1–3]. A long series of Ru(II) complexes (4d^6) was prepared [4] with the aim of tuning the energy of the states which are responsible for the photochemical and photophysical properties. Recently, we have shown that cyclometallated complexes of square planar Pt(II) have also interesting photophysical [5] [6] and photochemical [7] properties.

Here, we report on mixed ligand properties of complexes of another 4d^6 metal, namely Rh(III), containing aromatic, cyclometallating ligands besides bipyridine as a diimine ligand. The complex, described in detail is [Rh(ppy)$_2$(bpy)]$^+$ (**1**; ppy = 2-phenylpyridine, bpy = 2,2′-bipyridine).



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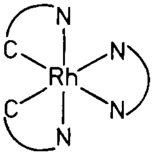
Experimental. – *General.* Chemicals were purchased from *Fluka* or *Aldrich.* UV: *Perkin-Elmer 555* spectrophotometer. Cyclic voltammetry: *Metrohm Polarecord E 506, VA* scanner *E 612*, X-Y Printer *HP 7044 A.* Electrodes: Pt disk, Pt auxiliary, Ag/AgNO$_3$. Supporting electrolyte: Bu$_4$NH$^+$ ClO$_4^-$. ^{1}H- and ^{13}C-NMR: ***Bruker** AM 360* spectrometer. Differential NOE experiments were carried out by substracting the interferograms of subsequent on- and off-resonance irradiations with 1.5-μW decoupler power during 2 s, until a sufficient signal-to-noise ratio was reached.

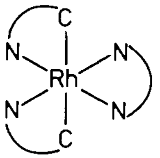
[Rh(ppy)$_2$(bpy)]$^+$. [Rh(ppy)$_2$Cl]$_2$ (200 mg) [8] is mixed with 800 mg of 2,2′-bipyridine and heated under N$_2$ to 140° (clear melt). The mass is dissolved, after cooling, in MeOH, and the complex salt precipitated with Et$_2$O. After two recrystallizations from MeOH/Et$_2$O, 220 mg of pale yellow needles of [Rh(ppy)$_2$(bpy)]Cl · Et$_2$O (m.p. 282–283°) are obtained. ^{1}H-NMR (360.13 MHz, CD$_2$Cl$_2$): *cf. Table 1.* ^{13}C-NMR (90.55 MHz, MeOD): 168.44 (*d*);

166.45; 155.97; 151.12; 149.91; 145.18; 141.00; 139.75; 133.97; 131.20; 128.78; 125.78; 125.24; 124.57; 124.46; 121.18. Elemental anal. was determined for the PF_6 salt. Anal. calc. for $C_{32}H_{24}F_6N_4PRh$ (712.44): C 53.94, H 3.37, N 7.86; found: C 53.86, H 3.40, N 7.95.

Results and Discussion. – *Stereochemistry and NMR Spectra.* The complex $[Rh(ppy)_2(bpy)]^+$ could give rise to 3 stereoisomers, each consisting of a pair of enantiomers. **A** and **B** have C_2 symmetry, whereas **C** has no symmetry elements. The ^{13}C- and the ^1H-NMR spectra clearly show the presence of a C_2 axis, excluding, therefore, isomer **C**. The ^{13}C-NMR spectrum shows 16 resonances. The line at lowest field is split by the ^{103}Rh nucleus (J(Rh,C) = 36 Hz), and, therefore, it can be attributed to the C(2')-atom of ppy, which is directly bound to RH(III).



A



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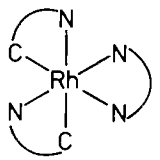

C

Furthermore, single-frequency off-resonance decoupling (SFORD) experiments yield 3 different kinds of C-atoms (C(1'), C(2) of ppy and C(2) of bpy) carrying no protons. This is again in agreement with a C_2 symmetry of the complex. In isomer **C**, all 6 C-atoms, which carry no proton, would be inequivalent.

The 360-MHz ^1H-NMR spectrum shows 12 multipletts in the region 6.3–8.7 ppm (*Table 1*). The splitting pattern and the number of signals indicate a system of 3 sets of 4 coupling spins. Decoupling and NOE experiments (*Table 2*) yield a definitive assignment of all protons.

Table 1. *^1H Chemical Shifts in $[Rh(ppy)_2(bpy)]^+$ in CH_2Cl_2* (TMS = 0)

ppy		bpy
H–C(3):	H–C(3'):	H–C(3):
8.135 (*ddd*, *J* = 8.3, 1.5, 1.1)	6.316 (*dddd*, *J* = 7.7, 1.2, 0.8, 0.5)	8.673 (*ddd*, *J* = 8.3, 1.2, 0.8)
H–C(4):	H–C(4'):	H–C(4):
7.929 (*ddd*, *J* = 8.3, 7.5, 1.5)	6.950 (*ddd*, *J* = 7.7, 7.3, 1.5)	8.190 (*ddd*, *J* = 8.3, 7.9, 1.7)
H–C(5):	H–C(5'):	H–C(5):
7.090 (*ddd*, *J* = 7.5, 5.8, 1.5)	7.098 (*ddd*, *J* = 7.8, 7.3, 1.2)	7.543 (*ddd*, *J* = 7.9, 5.4, 1.2)
H–C(6):	H–C(6'):	H–C(6):
7.598 (*dddd*, *J* = 5.8, 1.5, 1.1, 0.8)	7.875 (*ddd*, *J* = 7.8, 1.5, 0.8)	8.058 (*dddd*, *J* = 5.4, 1.7, 0.8, 0.5)

Table 2. *NOE Data* [%]

Irrad. on	NOE on				
	H–C(3)	H–C(3')	H–C(6)	H–C(6')	H–C(6) (bpy)
H–C(3)		0.8	–	17.9	–
H–C(3')	0.4		2.4	–	1.4
H–C(6)	–	2.8		–	2.8
H–C(6')	18.8	–	–		–
H–C(6) (bpy)	–	1.1	–	2.5	

The assignment of protons H–C(6) of bpy was confirmed by synthesis of a deuterated complex with [6,6'-D_2] bpy. The protons H–C(3) of bpy are strongly shifted by a change of solvent: 8.66 (MeOD) and 9.20 ppm (CD_2Cl_2). Under high resolution conditions, Rh, H couplings can be observed (J(Rh,H) ≈ 0.5 Hz).

The strong shift of protons H–C(3) of bpy, and H–C(3) and H–C(6') of ppy to low fields can be explained by an additional negative ring current due to the neighboring aromatic ring. On the other hand, the protons H–C(6) of ppy and H–C(6) of bpy are shifted to higher field compared to $[Rh(ppy)_2Cl]_2$[8] and $[Pt(ppy)_2]$ [7], because those protons experience a positiv ring current due to a neighboring ligand. In agreement with observations of other authors [9], the shifts of the most strongly shielded protons are in 3'-position of ppy. Differentiation between isomers **A** and **B** was achieved through the observation of a small mutual NOE enhancement between H–C(3) and H–C(3') of a second ligand which is only possible in isomer **A** *(Table 2)*.

UV/VIS Spectra. The UV/VIS spectrum of $[Rh(ppy)_2(bpy)]^+$ in CH_2Cl_2 shows a band at 364 nm ($\varepsilon = 7000$) with a weak shoulder at 454 nm ($\varepsilon = 10$). The properties are similar to MLCT (metal-to-ligand) transitions in Ru(II) complexes with diimine ligands [4]. It is, therefore, assigned to a Rh(III)→bpy charge transfer, in agreement with the electrochemical behavior *(vide infra)*.

Electrochemistry. $[Rh(ppy)_2(bpy)]^+$ shows a reversible reduction in the cyclic voltammogram (CV) at $E_{1/2} = -1.41$ V ($\Delta E = 70$ mV) in DMF. The oxydation at $E_P = +1.1$ V is completely irreversible. The behavior upon reduction is in sharp contrast to the one of $[Rh(bpy)_3]^{3+}$ [10], where one bpy ligands is eliminated in a 2e step, yielding the stable ($4d^8$) $[Rh(bpy)_2]^+$. It is most probable that in $[Rh(ppy)_2(bpy)]^+$ the first reduction is ligand-centered, in $[Rh(bpy)_3]^{3+}$ metal-centered. This difference must be due to the strongly electron-donating ppy ligands. This assignment corroborates with the interpretation of the UV/VIS spectra.

Conclusion. – As in the case of the Ru(II) complexes with three diimine ligands, the $4d^6$ Rh(III) complexes with two cyclometallated (C–N) ligands and one diimine show a behavior which is in agreement with the assumption of a ligand π^*LUMO. It might, therefore, be possible that, with this family of coordination compounds, similar fine tuning of the excited state will be possible, as it is the case for the Ru(II) complexes.

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