107. Complexes of Rhodium(III) with Two Chelating C^N Ligands and One Diimine Ligand

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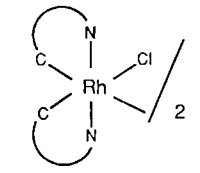
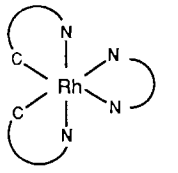
The synthesis of two series of cyclometalated Rh^{III} compounds is described, namely of 5 dinuclear chloro-bridged species $[\{Rh(C^\wedge N)_2\}(\mu\text{-}Cl)_2]$ **A** and of 15 mononuclear complexes $[Rh(C^\wedge N)_2(N^\wedge N)]^+$ **B**; C^N stands for five different cyclometalating ligands, *i.e.* deprotonated phenylpyridine, deprotonated 2-(thienyl)pyridine, and three deprotonated 1-aryl-1*H*-pyrazoles, and N^N for six diimine ligands such as 2,2-bipyridine, 2,2′-bi-1*H*-imidazole, and 2,2′-bipyrimidine. For (2,2′-bipyridine)bis[2-(thien-2-yl)pyridinato-$N,C^{3'}$]rhodium(III) chloride, an X-ray structure determination was carried out. In the other cases, ^{1}H-NMR spectra established the configuration of the complexes. All mononuclear and dinuclear complexes show a C,C *cis*-configuration. The UV/VIS-absorption bands at longest wavelength are most likely due to metal-to-ligand charge-transfer (MLCT) transitions, depending on the nature of the cyclometalating ligand C^N and on the diimine ligand N^N. The receptor orbital is in some cases on the cyclometalating ligand, in others on the diimine. All monomer complexes exhibit at least one reversible reduction wave in the cyclovoltammogram in dimethylformamide solutions, attributable to a ligand-centered reduction. It is, therefore, concluded that the LUMO in $[Rh(C^\wedge N)_2(N^\wedge N)]^+$ is of L(π^*) character, as opposed to $[Rh(bpy)_3]^{3+}$, where it is a metal d-orbital. The crystal system of (2,2′-bipyridine)bis[2-(thien-2-yl)pyridinato-$N,C^{3'}$]rhodium(III) chloride–water (1/2.125) is tetragonal (space group P^4; $R = 0.036$, $R_w = 0.040$). The Rh-atom has slightly distorted octahedral environment; the average distances are Rh–N/thienyl–pyridine) = 2.060 (3), Rh–C = 1.9885 (3), and Rh–N(bipyridine) = 2.1415 (3) Å. Of the three ligands the 2,2′-bipyridine is the most planar.

Introduction. – Complexes of transition metals comprising purely aromatic chelating ligands C^N recently found widespread interest as subjects of photochemical investigations [1–4]. The strong ligand-field influence of the C-donor, combined with the possibility of π-back donation into the metallocycle, yields generally high-lying d–d excited states. Charge-transfer states, particularly interesting in photochemistry, become therewith often the lowest excited states.

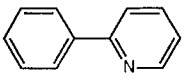
With the aim of tuning excited-state properties, in a way similar to the now well known case of tris(diimine)ruthenium(II) complexes [5], we prepared a series of $4d^6$ complexes with Rh^{III} as the central metal, having the general formula $[Rh(C^\wedge N)_2(N^\wedge N)]^+$. *Watts* and coworkers [6] described some complexes of related structures. Two structural characterizations of Rh^{III} complexes, one with a single metallocycle [7], the other a dinuclear species with two metallocycles on each center [8], were recently reported. In the present paper, we describe the synthesis and give a complete characterization, including the configuration of the bis(cyclometalated) Rh^{III} complexes **B**, which contain the chelating ligands derived from **1**–**5** and the diimine ligands **6**–**11**, and of some dimeric precursors **A**.



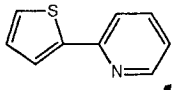
A $[\{Rh(C\hat{}N)_2\}_2(\mu\text{-}Cl)_2]$



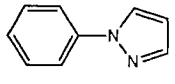
B $[Rh(C\hat{}N)_2(N\hat{}N)]^+$



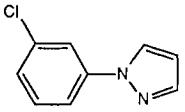
1 Hppy



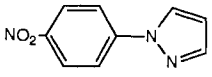
2 H(2-thpy)



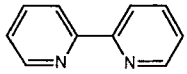
3 Hppz



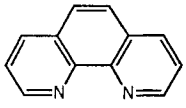
4 H(3-Clppz)



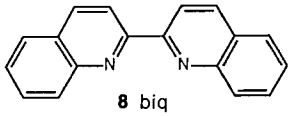
5 H(4-NO_2ppz)



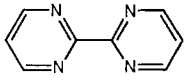
6 bpy



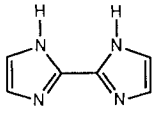
7 phen



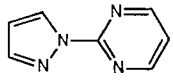
8 biq



9 bpym



10 H_2biim



11 pzpym

Experimental. – 1. *General.* Unless noted, all chemicals were purchased from *Fluka, Aldrich,* or *Alfa.* Solvents were dried prior to use by standard techniques. The 1-phenyl-1*H*-pyrazole [9] (**3**), 2,2′-bi-1*H*-imidazole [10] (**10**), 1-(4-nitrophenyl)-1*H*-pyrazole [9] (**5**), $[\{Rh(ppy)_2\}_2(\mu\text{-}Cl)_2]$ [11], and $[\{Rh(ppz)_2\}_2(\mu\text{-}Cl)_2]$ [12] (for abbreviations of ligands, see *Formulae*) were prepared by published procedures. Reactions were carried out under N_2 using *Schlenk*-tube techniques [13] [14]. UV/VIS Spectra: *Perkin-Elmer-555* or *Lambda-5* spectrometer; λ_{max} in nm, ε in $M^{-1}cm^{-1}$. ^{1}H-NMR Spectra: *Bruker-AM-360* spectrometer; δ in ppm rel. to the internal standard TMS, J in Hz. IR Spectra: *Perkin-Elmer-683* spectrometer; absorptions in cm^{-1}. Electrochemical measurements were carried out with a *Metrohm E 506 Polarecord,* a *Metrohm-E-612-VA* scanner, and a *Hewlett-Packard-7044-X-Y* recorder. Cyclic voltammograms were obtained in dimethylformamide (DMF) soln. under Ar by using a stationary Pt-disk working electrode, a Pt counter electrode, and an Ag/0.01M $Ag/AgNO_3$ reference electrode with $(Bu_4N)_3PO_4$ as supporting electrolyte. The scanning rate was 100 mV/s. The potentials of $[Ru(bpy)_3]^{2+}$ under the same experimental conditions were used as a secondary reference for the new complexes [15] (potential + 1.26 V *vs.* NHE).

2. *Syntheses.* The chloro-bridged dimers **A** were prepared according to procedure *2.2*, which is a modification of the method employed by *Nonoyama* [16]. The mixed-ligand monomers **B** were prepared by reactions of the appropriate dichloro-bridged dimers **A**. The synthetic procedure used was a modification of the method employed by *Nonoyama* [17] for the preparation of $[Rh(bzq)_2(ppy)]Cl$; details are given below. The preparation of $[Rh(ppy)_2(bpy)]PF_6$ is already described [18]. Errors in elemental analysis of the complexes are sometimes exceeding the generally accepted standards for simple org. compounds. This is most probably due to 'non-stoichiometric' inclusion of solvent molecules into the solids. Spectroscopic characterization is much more relevant in such cases.

2.1. *1-(3-Chlorophenyl)-1H-pyrazole* (**4**) was prepared according to [9]: A mixture of 1-(3-chlorophenyl)hydrazine hydrochloride (7.16 g, 0.04 mol) and 1,1,3,3 tetraethoxypropane (8.8 g, 0.04 mol) was refluxed in 95% EtOH for 30 min and then worked up according to [9]: 4.77 g (69%) of **4**. White needles. M.p. 32°. Anal. calc. for $C_9H_7N_2$: C 60.50, H. 3.92, N 15.68; found: C 60.41, H 4.01, N 15.70.

2.2. *Di-μ-chlorobis{bis[2-(thien-2'-yl)pyridinato-N,C^3']rhodium}* ($[\{Rh(2\text{-}thpy)_2\}_2(\mu\text{-}Cl)_2]$). $RhCl_3 \cdot 3H_2O$ (264 mg, 1 mmol) and 2-(thien-2'-yl)pyridine (**2**; 483 mg, 3 mmol) were suspended in 20 ml of 2-methoxyethanol, and the resulting yellow-red suspension was dispersed in an ultrasonic bath and then refluxed for 4 h (yellow → red-brown). After cooling, the solid by-products were removed by filtration. The orange soln. was concentrated and the precipitate filtered off, dissolved in 100 ml of CH_2Cl_2, and reprecipitated with Et_2O. The solid was collected on a glass-filter frit and dried *in vacuo*: 420 mg (91.7%) of $[\{Rh(2\text{-}thpy)_2\}_2(\mu\text{-}Cl)_2]$. UV/VIS ($CH_2Cl_2$): 408 (12800), 331 (sh, 23300), 289 (41700). IR (CsI): 3450*m*, 3100*w*, 3062*w*, 2970*w*, 1605*s*, 1557*w*, 1478*s*, 1440*m*, 1400*m*, 1360*s*, 1285*m*, 1245*w*, 1160*m*, 1140*w*, 870*m*, 765*m*, 750*m*, 720*m*, 710*m*, 640*m*, 630*m*, 440*w*, 320*w*. ^{1}H-NMR ($CDCl_3$): 8.98 (*ddd*, J = 5.9, 1.3, 0.9, H–C(6)); 7.72 (*ddd*, J = 7.7, 1.3, H–C(4)); 7.46 (*d*, J = 7.9, H–C(3)); 7.06 (*d*, J = 4.8, H–C(5')); 6.63 (*ddd*, J = 7.2, 7.1, 1.3, H–C(5)); 5.96 (*d*, J = 4.8, H–C(4')). Anal. calc. for $C_{36}H_{24}Cl_2N_4Rh_2S_4$: C 45.96, H 2.61, N 6.10; found: C 46.6, H 2.66, N 6.05.

2.3. *Di-μ-chlorobis{bis[1-(3'-chlorophenyl)-1H-pyrazolato-N,C^5']rhodium}* ($[\{Rh(3\text{-}Clppz)_2\}_2(\mu\text{-}Cl)_2]$). Precipitation from CH_2Cl_2/Et_2O gave 72% of a white/brown powder. UV/VIS (CH_2Cl_2): 344 (sh, 5000), 309 (20300), 247 (103300). IR (CsI): 3473*m*, 3417*m*, 3135*m*, 2929*w*, 2854*w*, 1737*m*, 1681*w*, 1613*m*, 1581*m*, 1563*m*, 1511*m*, 1483*s*, 1434*s*, 1418*s*, 1342*m*, 1267*m*, 1136*m*, 1112*m*, 1091*s*, 1068*s*, 1051*s*, 1024*s*, 974*m*, 843*m*, 808*m*, 777*s*, 745*s*, 713*s*, 610*m*, 553*w*, 437*w*, 382*w*, 286*w*. ^{1}H-NMR ($CDCl_3$): 8.14 (*d*, J = 2.6, H–C(5)); 7.84 (*d*, J = 2.1, H–C(3)); 7.14 (*d*, J = 2.2, H–C(2')); 6.6 (*dd*, J = 8.24, 2.1, H–C(4')); 6.57 (*dd*, J = 2.5, 2.3, H–C(4)); 5.86 (*dd*, J = 8.2, J (H, Rh) = 1.4, H–C(5')). Anal. calc. for $C_{36}H_{24}Cl_6N_8Rh_2$: C 43.77, H 2.44, N 11.37; found: C 42.92, H 2.47, N 11.26.

2.4. *Di-μ-chlorobis{bis[1-(4'-nitrophenyl)-1H-pyrazolato-N,C^2']rhodium}* ($[\{Rh(4\text{-}NO_2ppz)_2\}_2(\mu\text{-}Cl)_2]$). Precipitation from CH_2Cl_2/Et_2O gave 63% of a brown-yellow powder. UV/VIS (CH_2Cl_2): 367 (16300), 310 (49300), 256 (sh, 48000). IR (CsI): 3526*m*, 3139*m*, 3103*m*, 2904*w*, 2847*w*, 1620*m*, 1602*m*, 1569*m*, 1523*s*, 1511*s*, 1485*s*, 1407*s*, 1343*s*, 1336*s*, 1284*s*, 1246*w*, 1112*s*, 1070*s*, 1050*m*, 1024*m*, 965*m*, 893*m*, 868*m*, 820*m*, 747*s*, 714*w*, 704*w*, 665*w*, 606*w*, 533*w*, 453*w*, 348*w*. ^{1}H-NMR ((D$_6$)acetone): 9.08 (*d*, J = 2.7, H–C(5)); 7.99 (*d*, J = 2.1, H–C(3)); 7.86 (*dd*, J = 8.7, 2.3, H–C(5')); 7.8 (*d*, J = 8.7, H–C(6')); 7.03 (*dd*, J = 2.8, 2.2, H–C(4)); 6.80 (*dd*, J = 2.2, J (H, Rh) = 1.6, H–C(3')). Anal. calc. for $C_{36}H_{24}N_{12}O_8Rh_2$: C 41.99, H 2.33, N 16.33; found: C 40.16, H 2.26, N 15.81.

2.5. *(1,10-Phenanthroline)bis[2-phenylpyridinato-N,C^2']rhodium(III) Hexafluorophosphate* $[Rh(ppy)_2(phen)]PF_6$. A soln. of $[\{Rh(ppy)_2\}_2(\mu\text{-}Cl)_2]$ (83 mg, 0.1 mmol) and 1,10-phenanthroline (36 mg, 0.2 mmol) in 25 ml of CH_2Cl_2 was refluxed for 30 min. Upon addition of Et_2O and cooling, yellow crystals of $[Rh(ppy)_2(phen)]Cl$ were obtained. They were dissolved in 5 ml of MeOH, and 2 ml of 10% aq. NH_4PF_6 soln. was added. Addition of Et_2O resulted in formation of small yellow needles which were collected on a glass-filter frit and dried under vacuum: 80 mg (54%) of $[Rh(ppy)_2(phen)]PF_6$. UV/VIS (CH_2Cl_2): 454 (sh, 10), 372 (sh, 6460), 356 (7400), 312 (sh, 17800), 272 (sh, 48900), 266 (52800), 229 (56000). IR (CsI): 3046*w*, 2929*w*, 2854*w*, 1629*w*, 1610*s*, 1582*m*, 1568*w*, 1516*w*, 1484*s*, 1440*m*, 1428*s*, 1361*m*, 1345*m*, 1319*m*, 1273*w*, 1229*w*, 1149*w*, 1127*w*, 1108*w*, 1065*w*, 1027*w*, 897*m*, 844*s*, 758*s*, 740*m*, 726*s*, 644*w*, 630*w*, 560*s*, 420*w*, 374*w*. ^{1}H-NMR (CD_2Cl_2): 8.74 (*dd*, J = 8.2, 1.5, H–C(4), phen); 8.37 (*dd*, J = 4,9, 1.2, H–C(2), phen); 8.26 (*s*, H–C(5), phen); 8.0 (*d*, J = 8.0, H–C(3)); 7.89 (*dd*, J = 8.2, 4.9, H–C((3), phen); 7.85 (*ddd*, J = 7.8, 7.5, 1.5, H–C(4)); 7.82 (*dd*, J = 7.6, 1.3, H–C(6')); 7.30 (J = 5.1, H–C(6)); 7.16 (*ddd*, J = 7.7, 7.5, 1.2, H–C(5')); 7.04 (*ddd*, J = 7.5, 7.5, 1.4, H–C(4')); 6.93 (*ddd*, J = 7.5, 5.2, 1.4, H–C(5)); 6.41 (*d*, J = 7.7, H–C(3)). Anal. calc. for $C_{34}H_{24}F_6N_4PRh$: C 55.45, H 3.26, N 7.61; found: C 55.22, H 3.40, N 7.68.

2.6. *(2,2'-Biquinoline)bis[2-phenylpyridinato-N,C^2']rhodium(III) Hexafluorophosphate* $[Rh(ppy)_2(biq)]PF_6$. A soln. of $[\{Rh(ppy)_2\}_2(\mu\text{-}Cl)_2]$ (83 mg, 0.1 mmol) and 2.2'-biquinoline (102.4 mg, 0.2 mmol) in 25 ml of CH_2Cl_2 was refluxed for 4 h. After cooling, a 10% NH_4PF_6 soln. in MeOH was added and the mixture kept at *ca.* 0° overnight. The white precipitate (NH_4PF_6) was filtered off and the remaining yellow soln. reduced to ½ of his original volume. Addition of Et_2O resulted in formation of a yellow/orange precipitate which was recrystallized from CH_2Cl_2/Et_2O: 94 mg (58%) of yellow crystals of $[Rh(ppy)_2(biq)]PF_6$. UV/VIS (CH_2Cl_2): 444 (670), 359

(27700), 304 (sh, 24900), 271 (86300), 229 (51100). IR (CsI): 3153*w*, 3119*w*, 3058*w*, 2926*w*, 1621*m*, 1606*s*, 1484*s*, 1568*m*, 1555*m*, 1511*s*, 1482*s*, 1460*w*, 1434*s*, 1420*m*, 1379*m*, 1360*s*, 1320*w*,1272*m*, 1214*w*, 1166*m*, 1145*m*, 1096*m*, 1024*m*, 842*s*, 815*s*, 763*s*, 742*s*, 629*w*, 560*s*, 487*w*, 422*w*. ^{1}H-NMR ($CDCl_3$): 8.72 (*d*, *J* = 8.7, H–C(4), biq); 8.66 (*d*, *J* = 8.7, H–C(3), biq); 7.92 (*d*, *J* = 8.9, H–C(8), biq); 7.89 (*dd*, *J* = 8.2, 1.2, H–C(5), biq); 7.85 (*d*, *J* = 5.6, H–C(6)); 7.78 (br. *d*, *J* = 6.7, H–C(3)); 7.75 (*ddd*, *J* = 8.2, 6.8, 1.5, H–C(4)); 7.59 (*dd*, *J* = 7.8, 1.4, H–C(2′)); 7.47 (*ddd*, *J* = 7.9, 6.8, 1, H–C(6), biq); 7.15 (*ddd*, *J* = 8.7, 6.9, 1.5, H–C(7), biq); 7.05 (*ddd*, *J* = 7.7, 7.4, 1.1, H–C(5′)); 6.97 (*dd*, *J* = 5.6, 1.9, H–C(5)); 6.94 (*ddd*, *J* = 7.7, 7.3, 1.3, H–C(4′)); 6.31 (*d*, *J* = 7.7, H–C(3′)). Anal. calc. for $C_{40}H_{28}F_6N_4PRh$: C 59.12, H 3.45, N 6.89; found: C 58.98, H 3.48, N 7.00.

2.7. *(2,2′-Bipyridine)bis[2-(thien-2′-yl)pyridinato-*N,C$^{3'}$*]rhodium(III) Hexafluorophosphate* ([Rh(2-thpy)$_2$(bpy)]PF_6). A soln. of [{Rh(2-thpy)$_2$}$_2$(μ-Cl)$_2$] (91.6 mg, 0.1 mmol) and 2,2′-bipyridine (31.6 mg, 0.2 mmol) in 20 ml CH_2Cl_2 was refluxed for 1 h. After cooling, addition of 2 ml of 10% NH_4PF_6 soln. in MeOH resulted in formation of a white precipitate (NH_4PF_6) which was filtered off. Addition of Et_2O to the filtrate gave 113 mg (78%) of the orange [Rh(2-thpy)$_2$(bpy)]PF_6. UV/VIS (CH_2Cl_2): 505 (sh, 10), 383 (10300), 332 (sh, 12360), 306 (sh, 30500), 295 (34100), 265 (29100). ^{1}H-NMR (CD_2Cl_2): 9.26 (*d*, *J* = 8.2, H–C(3), bpy); 8.26 (*ddd*, *J* = 8.2, 7.7, 1.7, H–C(4), bpy); 7.96 (*ddd*, *J* = 5.3, 1.6, 0.9, H–C(6), bpy); 7.74 (*ddd*, *J* = 7.6, 6.3, 1.5, H–C(4)); 7.55 (*dd*, *J* = 6.9, 1.1, H–C(3)); 7.50 (*ddd*, *J* = 7.6, 5.3, 1.2, H–C(5), bpy); 7.46 (*d*, *J* = 4.8, H–C(5′)); 7.38 (*d*, *J* = 5.7, H–C(6)); 6.85 (*ddd*, *J* = 7.3, 5.7, 1.4, H–C(5)); 6.36 (*dd*, *J* = 4.8, *J* (H, Rh) = 0.4, H–C(4′)). Anal. calc. for $C_{28}H_{20}F_6N_4PRhS_2$: C 46.41, H 2.76, N 7.73; found: C 46.14, H 2.80, N 7.57.

2.8. *(1,10-Phenanthroline)bis[2-(thien-2′-yl)pyridinato-*N,C$^{3'}$*]rhodium(III) Hexafluorophosphate* ([Rh(2-thpy)$_2$(phen)]PF_6). [{Rh(2-thpy)$_2$}$_2$(μ-Cl)$_2$] (91.6 mg, 0.1 mmol) and 1,10-phenanthroline (36 mg, 0.2 mmol) were refluxed for 1 h in CH_2Cl_2. The mixture was then reduced to ½ of its original volume. After cooling, addition of Et_2O yielded a brownish-yellow precipitate. The crude product was purified by glass-permeation chromatography on a column (0.5 × 30 cm) of *Glyceril G 6-75-200* (*Sigma Chemical*) using MeOH for elution and Et_2O to give [Rh(2-thpy)$_2$(phen)]Cl. This was then converted to the PF_6^- salt as described in *2.7*. Yellow-orange crystals of [Rh(2-thpy)$_2$(phen)PF_6 (45%). UV/VIS (CH_2Cl_2): 500 (sh, 110), 383 (10470), 334 (sh, 11848), 296 (sh, 31900), 274 (49500), 229 (41100). IR (CsI): 3066*w*, 2927*w*, 2857*w*, 1624*m*, 1607*s*, 158*w*, 1480*s*, 1437*m*, 1430*m*, 1398*w*, 1360*m*, 1287*w*, 1161*m*, 1149*m*, 1107*w*, 878*s*, 840*s*, 772*m*, 725*m*, 646*w*, 630*w*, 560*s*, 511*w*, 450*w*, 380. ^{1}H-NMR (CD_3OD): 8.79 (*dd*, *J* = 8.3, 1.5, H–C(4), phen); 8.36 (*dd*, *J* = 4.8, 1.5, H–C(2), phen); 8.27 (*s*, H–C(5), phen): 7.93 (*dd*, *J* = 8.3, 4.8, H–C(3), phen); 7.77 (*ddd*, *J* = 8.0, 7.5, 1.4, H–C(4)); 7.64 (*dd*, *J* = 8.0, 1.4, H–C(3)); 7.55 (*d*, *J* = 4.8, H–C(5′)); 7.34 (*d*, *J* = 5.8, H–C(6)); 6.78 (*ddd*, *J* = 7.3, 5.8, 1.4, H–C(5)); 6.40 (*dd*, *J* = 4.8, *J* (H, Rh) = 0.4, H–C(4′)). Anal. calc. for $C_{30}H_{20}F_6N_4PRhS_2$: C 47.89, H 2.56, N 7.26; found: C 48.14, H 2.69, N 7.49.

2.9. *(2,2′-Biquinoline)bis[2-(thien-2′-yl)pyridinato-*N,C$^{3'}$*]rhodium(III) Hexafluorophosphate* [Rh(2-thpy)$_2$(biq)]PF_6. [{Rh(2-thpy)$_2$}$_2$(μ-Cl)$_2$] (91.6 mg, 0.1 mmol) and 2,2′-biquinoline (136 mg, 0.53 mmol) were treated as described in *2.7*: 280 mg (80.5%) of orange crystalline [Rh(2-thpy)$_2$(biq)]PF_6. UV/VIS (CH_2Cl_2): 464 (sh, 500), 380 (sh, 15000), 363 (29400), 304 (30900), 296 (sh, 34900), 272 (77600), 228 (47700). IR (CsI): 3523*w*, 3117*w*, 3062*w*, 2976*w*, 2925*w*, 2860*w*, 1606*s*, 1556*w*, 1512*s*, 1479*s*, 1437*m*, 1400*m*, 1362*m*, 1287*w*, 1249*w*, 1215*w*, 1160*m*, 1146*m*, 1098*w*, 874*s*, 844*s*, 777*m*, 769*m*, 751*m*, 736*m*, 719*m*, 561*s*, 496*w*, 452*w*. ^{1}H-NMR ((D$_6$)acetone): 8.93 (*s*, H–C(3), H–C(4), biq); 8.13 (*dd*, *J* = 8.5, 1.4, H–C(5), biq); 8.06 (*d*, *J* = 8.8, H–C(8), biq); 8.00 (*s*, *J* = 5.8, H–C(6)); 7.86 (*ddd*, *J* = 7.9, 7.5, 1.5, H–C(4)); 7.68 (*ddd*, *J* = 8.0, 6.8, H–C(6), biq); 7.63 (br. *d*, *J* = 8, H–C(3)); 7.60 (*d*, *J* = 4.8, H–C(5′)); 7.43 (*ddd*, *J* = 8.5, 6.9, 1.5, H–C(7), biq); 6.93 (*ddd*, *J* = 7.3, 5.8, 1.4, H–C(5)); 6.37 (*d*, *J* = 4.8, H–C(4′)). Anal. calc. for $C_{36}H_{24}F_6N_4PRhS_2$: C 51.00, H 3.06, N 6.57; found: C 52.43, H 2.91, N 6.79.

2.10. *(2,2′-Bipyrimidine)bis[2-(thien-2′-yl)pyridinato-*N,C$^{3'}$*]rhodium(III) Hexafluorophosphate* [Rh(2-thpy)$_2$(bpym)]PF_6. A soln. of [{Rh(2-thpy)$_2$}(μ-Cl)$_2$] (183.2 mg, 0.2 mmol) and 2,2′-bipyrimidine (94.8 mg, 0.6 mmol) in 30 ml of CH_2Cl_2 was refluxed for 30 min and then treated as described in *2.6*. The dark yellow precipitate was recrystallized from CH_2Cl_2/Et_2O: 250 mg (86%) [Rh(2-thpy)$_2$(bpym)]PF_6. UV/VIS (CH_2Cl_2): 382 (10800), 332 (sh, 11000), 290 (26300), 251 (31000). IR (CsI): 3450*w*, 3060*w*, 1605*s*, 1595*m*, 1570*s*, 1555*m*, 1480*s*, 1440*m*, 1400*s*, 1360*s*, 1290*m*, 1240*m*, 1160*m*, 870*s*, 840*s*, 770*m*, 750*m*, 710*m*. ^{1}H-NMR (CD_2Cl_2): 9.23 (*dd*, *J* = 4.8, 2.2, H–C(4), bpym); 8.23 (*ddd*, *J* = 5.4, 2.2, *J* (H, Rh) = 0.4, H–C(6), bpym); 7.8 (*ddd*, *J* = 8.0, 7.6, 1.5, H–C(4)); 7.70 (*dd*, *J* = 5.3, 4.9, H–C(5), bpym); 7.58 (*ddd*, *J* = 8.0, 1.5,1, H–C(3)); 7.48 (*dd*, *J* = 5.8, 1.6, H–C(6)); 7.48 (*d*, *J* = 4.8, H–C(5′)); 6.93 (*dd*, *J* = 7.6, 5.8, H–C(5)); 6.36 (*dd*, *J* = 4.8, *J* (H, Rh) = 0.9, H–C(4′)). Anal. calc. for $C_{26}H_{18}F_6N_6PRhS_2$: C 42.99, H 2.50, N 11.57; found: C 42.55, H 2.50, N 11.27.

2.11. *(2,2′-Bi-1*H*-imidazole)bis[2-(thien-2′-yl)pyridinato-*N,C$^{3'}$*]rhodium(III) Hexafluorophosphate* [Rh(2-thpy)$_2$(H$_2$biim)]PF_6. A soln. of [{Rh(2-thpy)$_2$}(μ-Cl)$_2$] (91.6 mg, 0.1 mmol) and 2,2′-bi-1*H*-imidazole (40.2 mg, 0.3 mmol) in 20 ml of CH_2Cl_2/EtOH 1:1 was refluxed for 2 h. A yellow precipitate was observed on evaporation of the CH_2Cl_2. Dissolution in 20 ml of CH_2Cl_2 and addition of 10% aq. NH_4PF_6 soln. (4 ml) gave a crystalline product which was washed with cold H_2O and EtOH. Recrystallization from CH_2Cl_2/MeOH and Et_2O yielded 79 mg

(67%) of yellow-orange [Rh(2-thpy)$_2$(H$_2$biim)]PF$_6$. UV/VIS (CH_2Cl_2): 389 (11100), 374 (sh, 9100), 334 (sh, 10230), 308 (sh, 23160), 293 (31000), 287 (sh, 29900). IR (CsI): 3450*m*, 3170*m*, 3130*m*, 1610*s*, 1530*w*, 1480*s*, 1420*m*, 1400*w*, 1285*w*, 1180*w*, 1160*w*, 1080*w*, 870*s*, 840*s*, 770*s*. ^{1}H-NMR (CD_2Cl_2): 14.2 (*s*, NH); 7.69 (*ddd*, J = 8.0, 7.5, 1.5, H–C(4)); 7.63 (*d*, J = 5.6, H–C(6)); 7.47 (*d*, J = 8.0, H–C(3)); 7.35 (*d*, J = 4.8, H–C(5′)); 7.14 (*d*, J = 1.4, H–C(4), H$_2$biim); 6.85 (*ddd*, J = 7.3, 5.6, 1.4, H–C(5)); 6.55 (*d*, J = 1.4, H–C(5), H$_2$biim); 6.37 (*dd*, J = 4.8, J(H, Rh) = 0.4, H–C(4′)). Anal. calc. for $C_{24}H_{18}F_6N_4PRhS_2$: C 41.06, H 2.56, N 11.98; found: C 42.10, H 2.55, N 12.11.

2.12. *[2-(1*H*-Pyrazol-1-yl)pyrimidine]bis[2-(thien-2′-yl)pyridinato-*N,C$^{3'}$*]rhodium(III) Hexafluorophosphate* [Rh(2-thpy)$_2$(pzpym)]PF$_6$. A soln. of [{Rh(2-thpy)$_2$}$_2$(μ-Cl)$_2$] (183 mg, 0.2 mmol) and 2-(1*H*-pyrazol-1-yl)pyrimidine (94.6 mg, 0.6 mmol) in 20 ml of CH_2Cl_2 was refluxed for 5 h and then treated as described in *2.7*: [Rh(2-thpy)$_2$(pzpym)]PF$_6$ (226 mg, 79%). UV/VIS (CH_2Cl_2): 385 (9150), 335 (sh, 9300), 288 (28100), 260 (31150). IR (CsI): 3450*w*, 3060*w*, 1610*s*, 1570*s*, 1530*m*, 1480*s*, 1455*s*, 1450*s*, 1440*m*, 1410*w*, 1360*s*, 1275*m*, 1240*m*, 1160*m*, 840*s*, 770*s*, 730*s*, 710*s*. ^{1}H-NMR (CD_2Cl_2): 8.97 (*dd*, J = 4.8, 2.1, H–C(6), pym); 8.81 (*dd*, J = 3.0, 0.6, H–C(5), pz); 8.05 (*dd*, J = 5.4, 2.3, H–C(3), pym); 7.79 (*ddd*, J = 7.9,7.7,1.5, H–C(4)); 7.65 (*dd*, J = 5.8, 0.6, H–C(6)); 7.56 (*d*, J = 2.7, H–C(3), pz); 7.55 (*dd*, J = 8.1, H–C(3)); 7.57–7.47 (*dd*, J = 4.9, 4.9, H–C(4), pym); 7.44 (*d*, J = 4.8, H–C(5′)); 6.98 (*ddd*, J = 7.7, 5.8, 1.4, H–C(5)); 6.77 (*dd*, J = 2.9, H–C(4), pz); 6.33 (*dd*, J = 4.8, H–C(4′)). Anal. calc. for $C_{25}H_{18}F_6N_4PRhS_2$: C 42.03, H 2.54, N 11.76; found: C 42.14, H 2.40, N 11.81.

2.13. *(2,2′-Bipyridine)bis[1-phenyl-1*H*-pyrazolato-*N,C$^{2'}$*]rhodium(III) Hexafluorophosphate* [Rh(ppz)$_2$(bpy)]PF$_6$. A soln. of [{Rh(ppz)$_2$}$_2$(μ-Cl)$_2$] (84.7 mg, 0.1 mmol) and bpy (31.6 mg, 0.2 mmol) in 20 ml of CH_2Cl_2 was refluxed for 1 h and then treated as described in *2.7*: 107 mg (78%) of white-brown [Rh(ppz)$_2$(bpy)]PF$_6$. UV/VIS (CH_2Cl_2): 320 (sh, 8830), 308 (20700), 298 (18540), 260 (sh, 30850). IR (CsI): 3148*w*, 3037*w*, 1603*m*, 1600*m*, 1515*w*, 1483*s*, 1448*s*, 1412*s*, 1361*s*, 1341*m*, 1315*w*, 1282*w*, 1251*w*, 1161*w*, 1111*w*, 1074*m*, 1056*m*, 1029*m*, 838*s*, 759*s*, 701*w*, 652*w*, 561*w*, 457*w*, 441*w*, 423*w*. ^{1}H-NMR ((D$_6$)acetone): 8.81 (*d*, J = 8.1, H–C(3), bpy); 8.76 (*d*, J = 2.8, H–C(5)); 8.33 (*ddd*, J = 8.0, 7.7, 1.6, H–C(4), pby); 8.27 (*d*, J = 5.3, H–C(6), bpy); 7.72 (*ddd*, J = 7.6, 5.3, 1.2, H–C(5), bpy); 7.65 (*dd*, J = 7.9, 1.2, H–C(6′)); 7.25 (*d*, J = 2.36, H–C(3)); 7.12 (*ddd*, J = 7.9, 7.4, 1.2, H–C(5′)); 6.94 (*ddd*, J = 7.4, 7.4, 1.2, H–C(4′)); 6.66 (*dd*, J = 2.7, 2.5, H–C(4)); 6.32 (*d*, J = 7.6, H–C(3′)). Anal. calc. for $C_{28}H_{22}F_6N_6PRh$: C 48.70, H 3.18, N 12.17; found: C 48.10, H 3.30, N 12.53.

2.14. *(2,2′-Biquinoline)bis[1-phenyl-1*H*-pyrazolato-*N,C$^{2'}$*]rhodium(III) Hexafluorophosphate* ([Rh(ppz)$_2$(biq)]PF$_6$). [{Rh(ppz)$_2$}$_2$(μ-Cl)$_2$] (84.7 mg, 0.1 mmol) and biq (51.2 mg, 0.2 mmol) in 20 ml of CH_2Cl_2 were refluxed for 5 h and then treated as described in *2.7*: 115 mg (73%) of pale yellow [Rh(ppz)$_2$(biq)]PF$_6$. UV/VIS (CH_2Cl_2): 414 (2340), 372 (22100), 306 (sh, 15850), 275 (43040), 255 (35860), 228 (61570). IR (CsI): 3493*m*, 3443*m*, 3062*m*, 2924*w*, 2855*w*, 1620*m*, 1599*s*, 1512*s*, 1484*s*, 1448*m*, 1434*s*, 1411*s*, 1361*s*, 1340*m*, 1282*w*, 1215*w*, 1146*w*, 1098*w*, 1075*m*, 1057*m*, 1028*m*, 845*s*, 783*m*, 748*s*, 561*s*, 500*w*. ^{1}H-NMR ((D$_6$)acetone): 9.01 (*d*, J = 8.8, H–C(4), biq); 8.95 (*d*, J = 8.8, H–C(3), biq); 8.76 (*d*, J = 2.8, H–C(5)); 8.18 (*d*, J = 8.9, H–C(8), biq); 8.15 (*dd*, J = 8.2, 1.5, H–C(5), biq); 7.66 (*ddd*, J = 8.2, 5.8, 1.1, H–C(6), biq); 7.59 (*dd*, J = 8.0, 1.3, H–C(6′)); 7.37 (*ddd*, J = 8.6, 5.8, 1.5, H–C(7), biq); 7.25 (*d*, J = 2.2, H–C(3)); 7.08 (*ddd*, J = 8.0, 7.5, 1.2, H–C(5′)); 6.87 (*ddd*, J = 7.6, 7.5, 1.3, H–C(4′)); 6.65 (*dd*, J = 2.7, 2.3, H–C(4)); 6.15 (*dd*, J = 7.6, 1.3, H–C(3′)). Anal. calc. for $C_{36}H_{26}F_6N_6PRh$: C 54.69, H 3.29, N 10.63; found: C 54.03, H 3.40, N 10.58.

2.15. *(2,2′-Bipyridine)bis[1-(3′-chlorophenyl)-1*H*-pyrazolato-*N,C$^{5'}$*]rhodium(III) Hexafluorophosphate* [Rh(3-Clppz)$_2$(bpy)]PF$_6$. [{Rh(3-Clppz)$_2$}(μ-Cl)$_2$] (98.7 mg, 0.1 mmol) and bpy (31.6 mg, 0.2 mmol) in 20 ml of CH_2Cl_2 were refluxed for 3 h and then treated as described in *2.7*: 108 mg (71%) of white [Rh(3-Clppz)$_2$(bpy)]PF$_6$. UV/VIS (CH_2Cl_2): 326 (6710), 308 (16480), 298 (14740), 260 (sh, 25000), 238 (43800), 227 (sh, 32400). IR (CsI): 3499*m*, 3159*m*, 1602*m*, 1580*w*, 1482*s*, 1447*m*, 1423*s*, 1411*s*, 1361*m*, 1342*m*, 1317*w*, 1139*w*, 1093*m*, 1075*m*, 1057*m*, 1028*m*, 978*w*, 836*s*, 814*m*, 775*m*, 752*m*, 611*w*, 561*s*, 455*w*, 443*w*. ^{1}H-NMR ((D$_6$)acetone): 8.87 (*d*, J = 2.9, H–C(5)); 8.82 (*dd*, J = 8.1, 1, H–C(3), bpy); 8.35 (*ddd*, J = 8.2, 7.6, 1.6, H–C(4), bpy); 8.32 (*d*, J = 5.3, H–C(6), bpy); 7.78 (*d*, J = 2.1, H–C(2′)); 7.75 (*ddd*, J = 7.6, 5.3, 1.2, H–C(5), bpy); 7.32 (*d*, J = 2.3, H–C(3)); 6.98 (*dd*, J = 8.1, 2.1, H–C(4′)); 6.71 (*dd*, J = 2.8, 2.3, H–C(4)); 6.32 (*dd*, J = 8.0, J(H, Rh) = 1, H–C(5′)). Anal. calc. for $C_{28}H_{20}Cl_2F_6N_6PRh$: C 44.29, H 2.66, N 11.07; found: C 43.00, H 2.70, N 10.85.

2.16. *(2,2′-Biquinoline)bis[1-(3′-Chlorophenyl)-1*H*-pyrazolato-*N,C$^{5'}$*]rhodium(III) Hexafluorophosphate* [Rh(3-Clppz)$_2$(biq)]PF$_6$. The complex was prepared in the same manner as described in *2.15* but with biq (51.2 mg, 0.2 mmol) instead of bpy: [Rh(3-Clppz)$_2$(biq)]PF$_6$ as a powdery yellow solid (103 mg, 60%). UV/VIS (CH_2Cl_2): 373 (24780), 355 (sh, 18220), 303 (sh, 17560), 275 (53480), 229 (79400). IR (CsI): 3442*w*, 3149*w*, 2922*w*, 2852*w*, 1621*w*, 1598*m*, 1512*s*, 1483*s*, 1435*m*, 1418*m*, 1340*w*, 1216*w*, 1147*m*, 1094*m*, 1073*m*, 1055*m*, 1025*m*, 845*s*, 778*m*, 750*m*, 561*s*. ^{1}H-NMR ((D$_6$)acetone): 9.03 (*d*, J = 8.7, H–C(4), biq); 8.98 (*d*, J = 8.7, H–C(3), biq); 8.87 (*d*, J = 2.8, H–C(3)); 8.17 (*dd*, J = 8.2, 1.4, H–C(5), biq); 8.13 (*d*, J = 8.8, H–C(8), biq); 7.73 (*d*, J = 2.1, H–C(2′)); 7.70 (*ddd*, J = 8.1, 6.8, 1, H–C(6), biq); 7.47 (*ddd*, J = 8.7, 6.8, 1.5, H–C(7), biq); 7.34 (*d*, J = 2.3, H–C(5)); 6.93

(*dd*, J = 8.2, 2.1, H–C(4′)); 6.71 (*dd*, J = 2.8, 2.4, H–C(4)); 6.15 (*dd*, J = 8.2, J (H, Rh) = 1.2, H–C(5′)). Anal. calc. for $C_{36}H_{24}Cl_2F_6N_6PRh$ (858.8): C 50.30, H 2.79, N 9.78; found: C 50.47, H 2.99, N 9.66.

2.17. *(2,2′-Bipyridine)bis[1-(4′-nitrophenyl)-1*H*-pyrazolato-*N,$C^{2'}$*]rhodium(III) Hexafluorophosphate* $[Rh(4\text{-}NO_2ppz)_2(bpy)]PF_6$. A soln. of $[\{Rh(4\text{-}NO_2ppz)_2\}_2(\mu\text{-}Cl)_2]$ (102.9 mg, 0.1 mmol) and bpy (31.2 mg, 0.2 mmol) in 25 ml of CH_2Cl_2 was refluxed for 4 h. After cooling, a brown-white powder precipitated. The solid was filtered off, dissolved in MeCN and treated with 4 ml of 10% NH_4PF_6 soln. in MeOH. The powder that appeared was filtered and recrystallized from MeCN/MeOH and Et_2O: 60 mg (38%) of $[Rh(4\text{-}NO_2ppz)_2(bpy)]PF_6$. UV/VIS ($CH_2Cl_2$): 341 (9020), 308 (29850), 299 (29600), 250 (sh, 25900), 224 (26200). IR (CsI): 3153*m*, 3030*w*, 2973*w*, 2809*w*, 1605*m*, 1569*m*, 1525*s*, 1448*m*, 1410*s*, 1342*s*, 1318*m*, 1284*m*, 1113*m*, 1074*m*, 1054*m*, 867*s*, 836*s*, 763*m*, 748*m*, 561*s*. ^{1}H-NMR (CD_3CN): 8.68 (*d*, J = 3, H–C(5)); 8.59 (*dd*, J = 8.2, H–C(3), bpy); 8.23 (*ddd*, J = 8.2, 7.7, 1.6, H–C(4), bpy); 8.15 (*dd*, J = 5.3, 0.7, H–C(6), bpy); 8.06 (*dd*, J = 8.8, 2.5, H–C(5′)); 7.72 (*d*, J = 8.8, H–C(6′)); 7.60 (*dd*, J = 2.4, J (H, Rh) = 1.2, H–C(3′)); 7.55 (*ddd*, J = 7.6, 5.4, 1.2, H–C(5), bpy); 7.23 (*d*, J = 2.3, H–C(3)); 6.73 (*dd*, J = 2.9, 2.4, H–C(4)). Anal. calc. for $C_{28}H_{20}F_6N_8O_4PRh$: C 43.09, H 2.58, N 14.36; found: C 42.03, H 2.50, N 13.99.

2.18. *(2,2′-Biquinoline)bis[1-(4-nitrophenyl)-1*H*-pyrazolato-*N,$C^{2'}$*]rhodium(III) Hexafluorophosphate* $[Rh(4\text{-}NO_2ppz)_2(biq)]PF_6$. $[Rh(4\text{-}NO_2ppz)_2Cl]_2$ and biq (51.2 mg, 0.2 mmol) in 25 ml of CH_2Cl_2/MeOH 5:1 were refluxed for 1 h and then treated as described in *2.7*: 91 mg (52%) of yellow $[Rh(4\text{-}NO_2ppz)_2(biq)]PF_6$. UV/VIS ($CH_2Cl_2$): 370 (sh, 32700), 367 (34140), 356 (35350), 307 (sh, 35800), 294 (39700), 273 (86850), 228 (60700). IR (CsI): 3153*w*, 3119*w*, 3058*w*, 2926*w*, 1621*m*, 1606*s*, 1584*m*, 1568*w*, 1555*w*, 1511*s*, 1482*s*, 1460*w*, 1434*s*, 1420*m*, 1379*m*, 1360*m*, 1320*w*, 1272*w*, 1214*w*, 1166*w*, 1145*w*, 1096*w*, 1024*w*, 842*s*, 815*s*, 763*s*, 742*s*, 629*w*, 560*s*, 487*w*, 422*w*. ^{1}H-NMR ((D$_6$)acetone): 9.09 (*d*, J = 8.8, H–C(4), biq); 9.03 (*d*, J = 8.8, H–C(3),biq); 9.03 (*s*, H–C(3′)); 8.19 (*dd*, J = 8.2, 1.3, H–C(5), biq); 8.03 (*dd*, J = 8.7, 2.3, H–C(5′)); 7.99 (*dd*, J = 8.8, 0.5, H–C(8), biq); 7.92 (*d*, J = 8.8, H–C(6′)); 7.68 (*ddd*, J = 8.0, 6.9, 1, H–C(6), biq); 7.63 (*d*, J = 2.7, H–C(5)); 7.48 (*ddd*, J = 8.7, 6.9,1.5, H–C(7), biq); 6.98 (*dd*, J = 2.3, J (H, Rh) = 1.3, H–C(3)); 6.88 (*dd*, J = 2.7, 2.3, H–C(4)). Anal. calc. for $C_{36}H_{24}F_6N_8O_4PRh$: C 49.10, H 2.72, N 12.79; found: C 47.52, H 2.59, N 12.14.

3. *Crystal-Structure Determination.* Preliminar *Weissenberg* and precession photographs served to determine the space group. Intensity data were measured on a *Stoe-Siemens-AED2* diffractometer at r.t. Crystals were sealed in *Lindemann* glass capillarities. Two crystals were required due to the large variation in the intensity of the standard reflections. Accurate cell parameters were obtained from $+\omega$ values of 14 reflections in the 2θ range 20–30°. The SHELX-76 program system [19] was used for solving the structure by *Patterson* and *Fourier* methods and in further calculations. Complex neutral-atom scattering factors where taken from the literature [20]. The crystal data are given in *Table 1*. The H-atoms were included in idealized positions (C–H 1.008 Å, H–C–H 109.5°) with an overall refineable U_{iso} (final value 0.0869 Å [20]). A total of four H_2O molecule sites were located from final difference maps, three of which were distorted and only partially occupied. Their occupancy factors were refined at first and later fixed at the closest whole fraction values (O(W1) 1.0, O(W2) 0.75, O(W3) 0.25, and O(W4) 0.125). Observed and calculated structure factors final positional parameters are available as supplcmentary material and deposited at the *Cambridge Crystallographic Data Center*.

Results and Discussion. – The C^N ligands **1–5** were used for the syntheses of the chloro-bridged dimers **A** and the diimines **6–11** for the cleavage of **A** to the monomers **B**. The structures of the monomers **B** were derived by ^{1}H-NMR spectroscopy and in one case also by X-ray analysis (*vide infra*).

^{1}H-NMR Spectra. The detailed analysis of the 360-MHz ^{1}H-NMR spectra for $[Rh(ppy)_2(bpy)]PF_6$ is already published [18]. In a similar way, the ^{1}H-NMR spectra of all complexes reported herein were analyzed, and with the aid of several independent decoupling experiments, all assignments were made assuming a similar geometry to that found for $[Rh(ppy)_2(bpy)]PF_6$. In agreement with literature data the ligand protons *ortho* to the metalated C-atom experience the largest shielding of all ligand protons [21]. With the help of the typically smallest coupling constant for H–C(6) and H–C(6′) of bipyridine ($^3J_{(5,6)}$ = 5.8 Hz), all bipyridine signals could easily be attributed.

For the complexes containing phenylpyrazoles as cyclometalating ligands, we found an assignement different from that published by *Nonoyama* [12] and *Hiraki et al.* [22].

Table 1. *Crystal Data of (2,2'-Bipyridine)bis[2-(thien-2'-yl)pyridinato-N,C$^{3'}$]rhodium(III) Chloride–Water (1/2.125)*[a])

Formula	$C_{28}H_{20}N_4S_2ClRh \cdot 2\frac{1}{8}H_2O$
Formula weight	615.4
Crystal colour, habit	orange rods
Crystal system, space group	tetragonal, $P\bar{4}$
$a = b$ [Å]	20.875(2)
c [Å]	13.861(6)
V [Å^3]	6040.15
Z	8
d_{calc} [gcm^{-3}]	1.351
Crystal dimensions [mm]	0.38 × 0.19 × 0.15 (mean for 2 crystals)
Radiation	Mo$K\alpha$, $\lambda = 0.71073$ Å (graphite monochromated)
Absorption coeff. (μ_λ) [cm^{-1}]	7.4
Data collection	ω–θ scans
θ Limits [deg]	$2.5 < \theta < 25$
Index limits	$-24 < h < 24, 0 < k < 24, 0 < l < 16$
No. of unique reflexions	5231 ($R_{int.} = 0.062$)
No. of reflexions used	3840 ($F_o > 6\sigma(F_o)$)[b])
Refinement method	weighted anisotropic full-matrix least-squares
No. of reflexions /no. of parameters	10/8
Final R value	0.036
Weighted final R value	$\Sigma(\|F_o\| - \|F_c\|)\sqrt{w}/\Sigma\|F_o\|\sqrt{w} = 0.040$
w	$[\sigma(F_o) + 0.00465\|F_o\|^2]^{-1}$
Param. shift/esd in last cycle of refinement	0.47 (max); < 0.07 (mean)
Residual density in final difference map [eÅ^{-3}]	+1.05 (max); −0.50 (min)

[a]) Standard deviations of last significant figure in parentheses.
[b]) Eighteen reflections (probably suffering from extinction) removed.

The signal of H–C(5) of the pyrazole ring undergoes a large low-field shift caused by a long-range ring-current effect, and the perturbation of the electronic environment of the proton, due to CH···CH interactions with H–C(6') (H–C(2') in the case of **4**), which has an appreciable deshielding effect [23]. The ^{1}H-NMR spectrum of the free biquinoline was published by *Draake* and *Jones* [24], that of the complexed ligand shows quite different chemical shifts for some protons. At lowest field are the signals of H–C(4) and H–C(3) which can be distinguished with the help of NOE effects on H–C(5). H–C(5) and H–C(8), on the other hand, are identified on the basis of different coupling constants, as in the free ligand ($^3J_{(5,6)} > {}^3J_{(7,8)}$).

Crystal and Molecular Structure of (2,2'-Bipyridine)bis[2-(thien-2'-yl)pyridinato-N,C$^{3'}$]rhodium(III) Chloride–Water (1/2.125). The Rh-atom has a slightly distorted octahedral environment (*Fig. 1*). As expected, the largest distortions are found in the chelate-ring angles and those angles involving atoms C(16) and C(26) of the thienyl groups (see *Table 2*). Of the three ligands, the 2,2'-bipyridine is the most planar. The dihedral angle between the best planes through the pyridine rings is 2.8°. In the 2-(thienyl)pyridine ligands, the best planes through the thienyl groups are on average inclined to those through the pyridine rings by 4.6(2°). The Cl-anion is located at a distance of 3.1(1) Å from O(W1) and O(W2) of the H_2O molecules. There are no short intermolecular contacts between non-H-atoms in the cations of symmetry-related molecules.

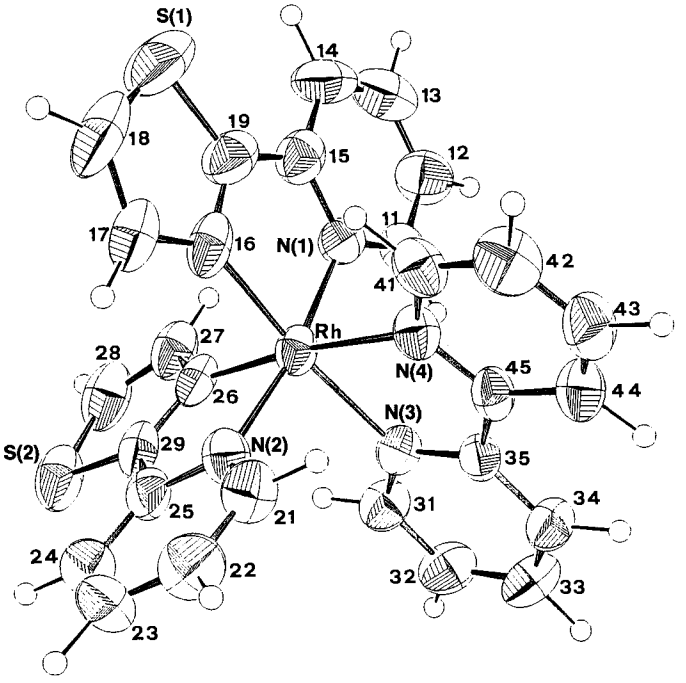


Fig. 1. *ORTEP-II* [30] *diagram of the cation (2,2'-bipyridine)bis[2-(thien-2-yl)pyridinato-*N,$C^{3'}$*]rhodium(III), showing the atomic-numbering* (arbitrary) *and the vibrational ellipsoids* (50% probability level)

Table 2. *Bond Distances* [Å] *and Angles* [°] *of (2,2'-Bipyridine)bis[2-(thien-2-yl)pyridinato-*N,$C^{3'}$*]rhodium(III)*

Rh–N(1)	2.055(4)	Rh–N(2)	2.065(4)
Rh–C(16)	1.984(4)	Rh–C(26)	1.993(5)
N(1)–C(11)	1.345(6)	N(2)–C(21)	1.322(6)
N(1)–C(15)	1.363(6)	N(2)–C(25)	1.350(6)
C(11)–C(12)	1.374(8)	C(21)–C(22)	1.389(7)
C(12)–C(13)	1.423(9)	C(22)–C(23)	1.387(8)
C(13)–C(14)	1.338(9)	C(23)–C(24)	1.328(9)
C(14)–C(15)	1.402(7)	C(24)–C(25)	1.435(8)
C(15)–C(19)	1.448(7)	C(24)–C(25)	1.435(8)
C(16)–C(19)	1.361(7)	C(26)–C(27)	1.401(7)
C(17)–C(18)	1.346(7)	C(27)–C(28)	1.413(9)
C(18)–S(1)	1.716(7)	C(28)–S(2)	1.641(10)
S(1)–C(19)	1.733(4)	S(2)–C(29)	1.708(5)
Rh–N(3)	2.145(3)	Rh–N(4)	2.138(4)
N(3)–C(31)	1.334(5)	N(4)–C(41)	1.350(5)
N(3)–C(35)	1.352(5)	N(4)–C(45)	1.338(5)
C(31)–C(32)	1.399(7)	C(41)–C(42)	1.367(7)
C(32)–C(33)	1.363(8)	C(42)–C(43)	1.395(7)
C(33)–C(34)	1.347(7)	C(43)–C(44)	1.387(7)
C(34)–C(35)	1.387(6)	C(44)–C(45)	1.414(6)
C(35)–C(45)	1.456(6)		
N(1)–Rh–N(2)	170.7(1)	N(2)–Rh–C(26)	80.7(2)
N(1)–Rh–N(3)	95.6(1)	N(3)–Rh–N(4)	76.7(1)

Table 2 (cont.)

N(1)–Rh–N(4)	90.8(1)	N(3)–Rh–C(16)	173.6(2)
N(1)–Rh–C(16)	81.1(2)	N(3)–Rh–C(26)	97.7(1)
N(1)–Rh–C(26)	92.6(2)	N(4)–Rh–C(16)	97.8(1)
N(2)–Rh–N(3)	91.7(1)	N(4)–Rh–C(26)	173.7(2)
N(2)–Rh–N(4)	96.5(1)	C(16)–Rh–C(26)	88.0(2)
N(2)–Rh–C(16)	92.2(2)		
Rh–N(1)–C(11)	125.7(3)	Rh–N(2)–C(21)	125.7(3)
Rh–N(1)–C(15)	114.4(3)	Rh–N(2)–C(25)	115.4(3)
C(11)–N(1)–C(15)	119.9(4)	C(21)–N(2)–C(25)	118.9(4)
N(1)–C(11)–C(12)	122.4(5)	N(2)–C(21)–C(22)	122.5(5)
C(11)–C(12)–C(13)	117.3(5)	C(21)–C(22)–C(23)	118.9(6)
C(12)–C(13)–C(14)	120.4(5)	C(22)–C(23)–C(24)	119.7(6)
C(13)–C(14)–C(15)	120.1(5)	C(23)–C(24)–C(25)	119.5(5)
N(1)–C(15)–C(14)	119.9(5)	N(2)–C(25)–C(24)	120.4(5)
N(1)–C(15)–C(19)	112.4(4)	N(2)–C(25)–C(29)	112.3(5)
C(14)–C(15)–C(19)	127.7(4)	C(24)–C(25)–C(29)	127.3(5)
Rh–C(16)–C(17)	136.0(4)	Rh–C(26)–C(27)	135.8(5)
Rh–C(16)–C(19)	113.3(3)	Rh–C(26)–C(29)	113.0(4)
C(17)–C(16)–C(19)	110.7(4)	C(27)–C(26)–C(29)	111.1(5)
C(16)–C(17)–C(18)	112.7(5)	C(26)–C(27)–C(28)	110.6(6)
C(17)–C(18)–S(1)	113.8(4)	C(27)–C(28)–S(2)	114.1(4)
C(18)–S(1)–C(19)	89.0(3)	C(28)–S(2)–C(29)	91.5(3)
S(1)–C(19)–C(15)	127.4(4)	S(2)–C(29)–C(25)	128.9(5)
S(1)–C(19)–C(16)	113.8(4)	S(2)–C(29)–C(26)	112.7(5)
C(15)–C(19)–C(16)	118.8(4)	C(25)–C(29)–C(26)	118.4(5)
Rh–N(3)–C(31)	124.8(3)	Rh–N(4)–C(41)	125.1(3)
Rh–N(3)–C(35)	114.8(3)	Rh–N(4)–C(45)	115.2(3)
C(31)–N(3)–C(35)	120.3(4)	C(41)–N(4)–C(45)	119.6(4)
N(3)–C(31)–C(32)	120.3(5)	N(4)–C(41)–C(42)	122.4(4)
C(31)–C(32)–C(33)	119.6(5)	C(41)–C(42)–C(43)	119.3(5)
C(32)–C(33)–C(34)	119.4(4)	C(42)–C(43)–C(44)	118.9(4)
C(33)–C(34)–C(35)	120.4(5)	C(43)–C(44)–C(45)	118.8(4)
N(3)–C(35)–C(34)	119.9(4)	N(4)–C(45)–C(44)	121.1(4)
N(3)–C(35)–C(45)	116.2(3)	N(4)–C(45)–C(35)	116.9(3)
C(34)–C(35)–C(45)	123.8(4)	C(44)–C(45)–C(35)	122.0(4)

Electronic Spectra. UV/VIS-Absoption spectra, emission spectra, and electrochemistry of $[Rh(ppy)_2(phen)]PF_6$, $[Rh(ppy)_2(biq)]PF_6$, $[Rh(2\text{-}thpy)_2(phen)]PH_6$, and $[Rh(2\text{-}thpy)_2(biq)]PF_6$ were discussed in detail elsewhere [25a]. The UV/VIS spectra of the synthesized complexes contain intense absorptions in the 200–*ca.* 320 nm region (*Table 3*; *Fig. 2*). Bands in this region were previously assigned to $\pi-\pi^*$ ligand transitions [25a]. Lower-energy absoptions which show a solvent dependence are, as previously discussed, not present in the spectra of the ligands. Thus, they must be attributed to metal-to-ligand charge-transfer (MLCT) transitions involving either the polypyridine or the cyclometalating ligand. For the complexes containing 2-thpy$^-$ as ligand, these absorptions are most probably due to a Rh → thpy$^-$ transition substantially unaffected by the nature of the polypyridine ligand. By analogy, the bands around 360 nm for the complexes containing ppy$^-$ as ligand can be due to a Rh → ppy$^-$ transition, although the situation is clear in this case (*Fig. 2*). A detailed investigation of the electronic spectra of $[Rh(ppy)_2(bpy)]^+$ under high-resolution conditions is reported elsewhere [25b].

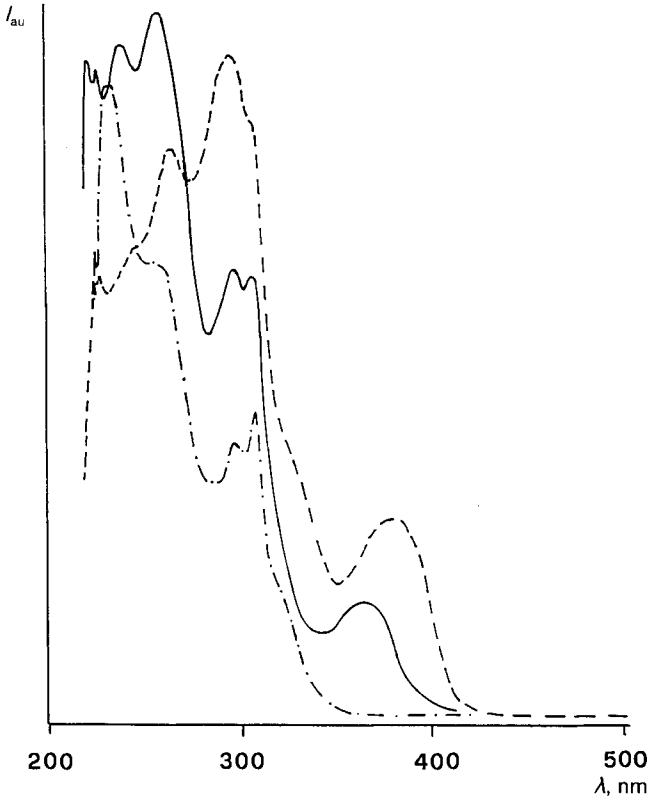


Fig. 2. *UV/VIS Spectra in CH_2Cl_2 of $[Rh(2\text{-}thpy)_2(bpy)]^+$ (– – –), $[Rh(ppy)_2(bpy)]^+$ (—), and $[Rh(ppz)_2(bpy)]^+$ (– · – · –)*

Table 3. *UV/VIS-Absorption Data for Rh(III) Complexes in Dichloromethane*

	λ [nm] ($\varepsilon \cdot 10^{-3}$[$M^{-1}cm^{-1}$])		
$[\{Rh(ppy)_2\}_2(\mu\text{-}Cl)_2]$	462 (sh, 0.05)	393 (7.7)	333 (sh, 15)
$[Rh(ppy)_2(bpy)]^+$	454 (sh, 0.01)	364 (7)	
$[Rh(ppy)_2(phen)]^+$	454 (sh, 0.01)	372 (sh, 6.5)	356 (7.4)
$[Rh(ppy)_2(biq)]^+$	444 (sh, 0.67)	359 (27.7)	
$[\{Rh(2\text{-}thpy)_2\}_2(\mu\text{-}Cl)_2]$	532 (sh, 0.004)	408 (12.80)	331 (sh, 23.3)
$[Rh(2\text{-}thpy)_2(bpy)]^+$	505 (sh, 0.01)	383 (10.3)	
$[Rh(2\text{-}thpy)_2(phen)]^+$	500 (sh, 0.11)	383 (10.5)	
$[Rh(2\text{-}thpy)_2(biq)]^+$	464 (sh, 0.5)	380 (sh, 15)	363 (29)
$[Rh(2\text{-}thpy)_2(bpym)]^+$	525 (sh, 0.005)	382 (10.8)	
$[Rh(2\text{-}thpy)_2(H_2biim)]^+$		389 (11.1)	
$[Rh(2\text{-}thpy)_2(pzpym)]^+$		385 (9.15)	
$[\{Rh(ppz)_2\}_2(\mu\text{-}Cl)_2]$			304 (26.2)
$[Rh(ppz)_2(bpy)]^+$		320 (sh, 8.8)	308 (20.7)
$[Rh(ppz)_2(biq)]^+$	418 (sh, 2.4)	372 (22.1)	
$[\{Rh(3\text{-}Clppz)_2\}_2(\mu\text{-}Cl)_2]$			309 (20.3)
$[Rh(3\text{-}Clppz)_2(bpy)]^+$		326 (sh, 6.7)	308 (16.5)
$[Rh(3\text{-}Clppz)_2(biq)]^+$	422 (sh, 2)	373 (24.8)	
$[\{Rh(4\text{-}NO_2ppz)_2\}_2(\mu\text{-}Cl)_2]$	367 (16.3)		310 (49.3)
$[Rh(4\text{-}NO_2ppz)_2(bpy)]^+$		340 (sh, 9)	308 (29.8)
$[Rh(4\text{-}NO_2ppz)_2(biq)]^+$		370 (sh, 32.7)	307 (35.8)

With the exception of $[Rh(2\text{-thpy})_2(H_2biim)]$ and $[Rh(2\text{-thpy})_2(pzpym)]$, the complexes containing ppy^- or 2-thpy^- as the cyclometalating ligand exhibit a weak shoulder at *ca.* 440–530 nm (ε 5–500) where the intensity is sensitive to the nature of the diimine ligand (highest values with biq). In accordance with emission spectroscopy data, these transitions can be attributed either to $d(Rh) \rightarrow {}^3MLCT$ or to $d(Rh) \rightarrow {}^3LC$ transitions [11] [25].

In the complexes $[Rh(ppz)_2(bpy)]PF_6$, $[Rh(ppz)_2(biq)]PF_6$, $[Rh(3\text{-Clppz})_2(bpy)]PF_6$, $[Rh(3\text{-Clppz})_2(biq)]PF_6$, however, the positions of the band maxima are related to the degree of π-delocalisation and, thus, to the π^*-levels of the diimine ligand. This is consistent with assigning these absoptions to the $d(Rh) \rightarrow \pi^*(bpy)$ or $d(Rh) \rightarrow \pi^*(biq)$ transition, respectively. The absence of a similar band in the chloro-bridged dimers $[\{Rh(ppz)_2\}_2(\mu\text{-Cl})_2]$ and $[\{Rh(3\text{-Clppz})_2\}_2(\mu\text{-Cl})_2]$ reinforces this assignment.

Electrochemistry. Protonated ligands and chloro-bridged dimers show no reversible reduction in the range of −2.0–0 V (*vs.* NHE). Oxidation of the metal centers is probably responsible for the irreversible peak in the dimeric species [26].

Monomeric complexes containing bpy or phen exhibit a reversible one-electron reduction in DMF solution at *ca.* −1.4 V (*Fig. 3*). Two waves appear at *ca.* −1.0 and −1.6 V with biq as diimine ligand. This behaviour contrasts sharply with that of $[Rh(bpy)_3]^{3+}$,

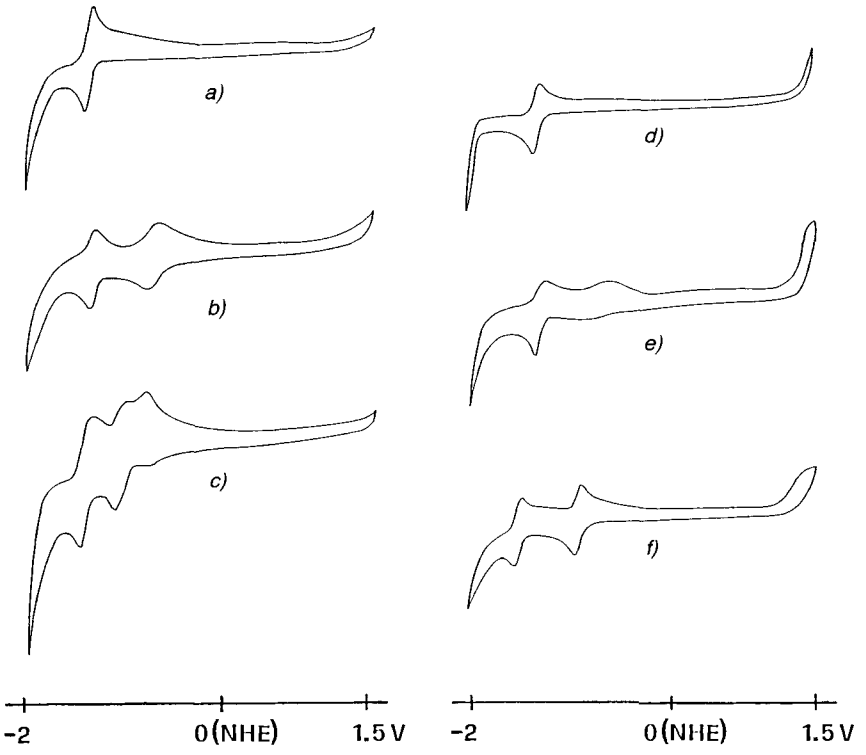


Fig. 3. *Cyclic voltammograms of* a) $[Rh(2\text{-thpy})_2(bpy)]^+$, b) $[Rh(2\text{-thpy})_2(phen)]^+$, c) $[Rh(2\text{-thpy})_2(biq)]^+$, d) $[Rh(ppz)_2(bpy)]^+$, e) $[Rh(3\text{-Clppz})_2(bpy)]^+$, *and* f) $[Rh(4\text{-}NO_2ppz)_2(bpy)]^+$

which undergoes [27] an irreversible two-electron reduction at *ca.* −0.8 V, leading to $[Rh(bpy)_2]^+$. This suggests that for the $[Rh(C^\wedge N)(N^\wedge N)]^+$ complexes, reduction is a ligand-centered process. The fact that a ligand-centered reduction occurs, as opposed to the metal-centered process in $[Rh(bpy)_3]^{3+}$, indicates an orbital diagram in which the empty d orbitals with σ^* character are above the π^* orbitals of the aromatic ligands due to the higher ligand-field strength of the cyclometalating ligands as compared to bpy. The strong variation of the first reduction in complexes with different diimine ligands (*Table 4*; increasingly negative potentials in the series biq < bpym < phen < bpy) suggests a

Table 4. *Potentials of Cyclic Voltammograms (E ≪ vs. NHE) for Rh(III) Complexes in DMF Solution*[a])

	E [V]					
$[\{Rh(ppy)_2\}_2(\mu\text{-}Cl)_2]$	1.25[b])		−0.42[b])			
$[Rh(ppy)_2(bpy)]^+$	1.46[b])					−1.48
$[Rh(ppy)_2(phen)]^+$			−0.59[b])			−1.42
$[Rh(ppy)_2(biq)]^+$				−1.06		−1.71
$[\{Rh(2\text{-}thpy)_2\}_2(\mu\text{-}Cl)_2]$	1.11[b])		−0.41[b])			
$[Rh(2\text{-}thpy)_2(bpy)]^+$						−1.42
$[Rh(2\text{-}thpy)_2(phen)]^+$			−0.64[b])			−1.38
$[Rh(2\text{-}thpy)_2(biq)]^+$				−1.02		−1.67
$[Rh(2\text{-}thpy)_2(bpym)]^+$				−1.09		−1.81
$[Rh(2\text{-}thpy)_2(H_2biim)]^+$			−0.78[b])	−1.15[b])		
$[Rh(2\text{-}thpy)_2(pzpym)]^+$						−1.53[b])
$[\{Rh(ppz)_2\}_2(\mu\text{-}Cl)_2]$	1.37[b])	1.09[b])	−0.37[b])			
$[Rh(ppz)_2(bpy)]^+$						−1.46
$[Rh(ppz)_2(biq)]^+$				−1.03		−1.69
$[\{Rh(3\text{-}Clppz)_2\}_2(\mu\text{-}Cl)_2]$	1.43[b])	1.09[b])	−0.41[b])			
$[Rh(3\text{-}Clppz)_2(bpy)]^+$			−0.79			−1.44
$[Rh(3\text{-}Clppz)_2(biq)]^+$			−0.99			−1.65
$[\{Rh(4\text{-}NO_2ppz)_2\}_2(\mu\text{-}Cl)_2]$	1.38[b])	1.12[b])		−1.25		
$[Rh(4\text{-}NO_2ppz)_2(bpy)]^+$			−0.88[b])	−1.16		−1.50
$[Rh(4\text{-}NO_2ppz)_2(biq)]^+$			−0.94	−1.18	−1.33	−1.85[b])

[a]) 0.1M $(Bu_4N)_3PO_4$; scan rate 0.1 mV/s; room temperature. [b]) Irreversible wave.

diimine-centered process, which is in agreement with the energetic orbital ordering observed in other complexes containing cyclometalating and diimine ligands [28] [29] (*Fig. 3*). The order of decreasing facility of reduction in the series with an identical diimine ligand, but different cyclometalating ligands is $4\text{-}NO_2ppz^- > 2\text{-}thpy^- = 3\text{-}Clppz^- > ppz^- > ppy^-$. These potential shifts suggest that electron density around the metal as well as on the diimine ligand may be controlled by a suitable choice of the cyclometalating ligand.

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