Synthesis and Properties of (Phthalocyaninato)ruthenium(II) with Bisaxially Coordinated Azanaphthalenes

Michael Hanack* and Young-Goo Kang

Institut für Organische Chemie, Lehrstuhl für Organische Chemie II, Universität Tübingen, Auf der Morgenstelle 18, W-7400 Tübingen, F.R.G.

Received January 2, 1991

Key Words: Phthalocyanine / Ruthenium complexes / Azanaphthalenes

(Phthalocyaninato)ruthenium(II) (PcRu) reacts with different azanaphthalenes such as quinoxaline, 2-methylquinoxaline, quinazoline, phthalazine, quinoline, pyrido[2,3-*b*]pyrazine, pteridine, isoquinoline and 1,5-naphthyridine to form the corresponding bisaxially coordinated $PcRuL_2$ complexes **1**–**9**. The IR, ^{1}H-NMR, UV/Vis, TG/DTA, and FD-MS data are discussed in detail for all the complexes prepared.

Bisaxially coordinated macrocyclic transition-metal complexes $MacML_2$ and bridged systems $[MacM(L)]_n$ with phthalocyanine (Pc), tetrabenzoporphyrin (TBP), or 1,2- and 2,3-naphthalocyanine (1,2-, 2,3-Nc) as the macrocycle (Mac), transition metals, e.g. iron, ruthenium, and cobalt as the central metal atom (M), and ligands (L) like pyrazine (pyz), tetrazine (tz), diisocyanobenzene (dib), etc. have been systematically investigated by us regarding their semiconducting properties[1,2]. The semiconducting behavior of the bridged systems $[MacM(L)]_n$ as well as other properties, e.g. solubility of the monomers $MacML_2$ in organic solvents, do not only depend on the macrocycle Mac, but also on the nature of the ligands L[3].

For the synthesis of bisaxially coordinated transition-metal complexes $MacML_2$ and $[MacM(L)]_n$ till now only monocyclic ligands of the type mentioned above have been used. It is expected, that structually different ligands containing a more extended π system, could lead to different physical properties of the corresponding complexes, e.g. to higher solubilities in organic solvents or to lower oxidation potentials.

In this report, we describe for the first time the synthesis and properties of the azanaphthalene-coordinated (phthalocyaninato)ruthenium(II) complexes **1**–**9**.

Results and Discussion

Synthesis of (Phthalocyaninato)ruthenium(II) Complexes 1–9

The synthetic pathway to form the solid $PcRuL_2$ complexes **1**–**9** is given in Scheme 1. This route is basically similar to that which we used for the preparation of other $PcRuL_2$ complexes (L = e.g. pyz, dib)[3a,3b]. Except for $PcRu(ptd)_2$ (**7**) and $PcRu(npd)_2$ (**9**) where acetone was used as solvent, PcRu was treated under nitrogen with an excess of the molten or liquid ligand without solvent. This method avoids the formation of oligomers or crystalline solvent adducts. The complexes **1**–**9** were isolated as dark-blue to dark-violet powders or microcrystalline products. All complexes readily dissolve in chloroform, but not in acetone or methanol.

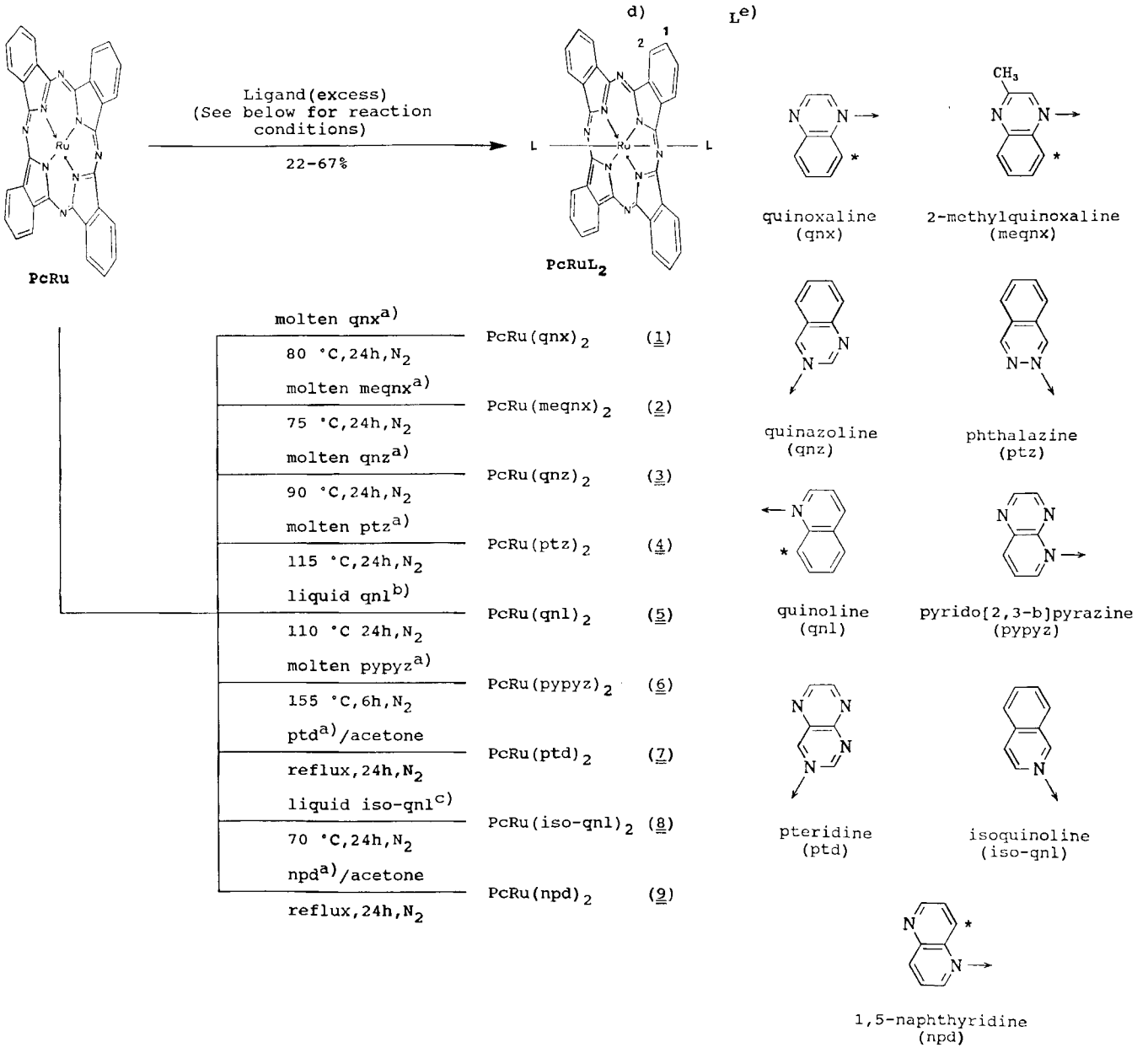
Characterization of Complexes 1–9

^{1}H-NMR Spectra: The ^{1}H-NMR spectra for the complexes $PcRu(qnz)_2$ (**3**), $PcRu(ptz)_2$ (**4**), $PcRu(ptd)_2$ (**7**), and $PcRu(iso\text{-}qnl)_2$ (**8**) with isoquinoline-like axial N-donor ligands were recorded in $CDCl_3$ solution. The chemical-shift data obtained are compiled in Table 1 together with the data of $PcRu(py)_2$[2e], $PcRu(pyz)_2$[3a] and the corresponding free ligands[4] for comparison.

The well-resolved ^{1}H-NMR spectra (Table 1) are almost free from impurities. They show diamagnetic ring-current shifts, which are found in other $PcRuL_2$ complexes such as $PcRu(py)_2$[2e] and $PcRu(pyz)_2$[3a]. The spectra show the usual two AA'BB' patterns (1-H: δ = 7.84–7.90; 2-H: δ = 9.15–9.20, in Pc, Scheme 1) at low field, while the axial ligands are considerably shielded by the Pc ring system[3]. All spectra clearly exhibit that the complexes have the PcRu/L stoichiometry 1:2, calculated by integration. In particular, the results of previous NMR investigations for $PcFe(n\text{-}BuNH_2)_2$[5] and $Eu(dpm)_3$/nitrogen-heterocyclic complexes[6] (dpm = dipivaloylmethanato) are useful for the following assignments. The two nonequivalent protons adjacent to the axially coordinated site in $PcRu(qnz)_2$ (**3**) and $PcRu(ptd)_2$ (**7**) complexes can be assigned in a manner similar to $Eu(dpm)_3$/qnz and $Eu(dpm)_3$/ptd[6]. The signals at δ = 3.26 and 3.08 in $PcRu(qnz)_2$ (**3**) are due to the corresponding protons H_a and H_b, respectively, the signals at δ = 3.65 and 3.22 in $PcRu(ptd)_2$ (**7**) correspond to H_a and H_b, respectively (Table 1). The remaining protons in these systems can be assigned as given in Table 1 on the basis of their spin multiplicities, H,H coupling constants, and the incremental shift calculations reported for $PcFe(n\text{BuNH}_2)_2$[5]. From these data (Table 1), it can be seen that in the complexes **3**, **4**, **7**, and **8** axial coordination to the central ruthenium atom takes place exclusively at the sterically less hindered isoquinoline-like N atom, as expected.

  0009–2940/91/0707–1607 $ 3.50+.25/0

Scheme 1



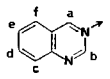
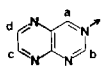
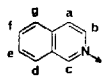
a) Molar ratio 1:20. — b) Molar ratio 1:40. — c) Molar ratio 1:30. — d) Numbers indicate corresponding hydrogen positions. — e) Abbreviations are given in parentheses for each ligand (L). The arrows indicate the coordination site of the ligands. Asterisk (*) denotes the corresponding hydrogen position (8-H).

In compounds **1**, **2**, **5**, **6**, and **9** with quinoline-like N-donor axial ligands, only the Pc protons can be assigned (see Experimental). The proton signals of the axial ligands are not assignable due to line broadening and signal weakening by the presence of paramagnetic PcRu and overlapping signals by dissociated free ligands ($PcRuL_2 \rightleftharpoons PcRu + 2L$). Also aggregation of $PcRuL_2$ molecules in $CDCl_3$ solution under the recording conditions is possible.

IR Spectra: The IR data obtained in this study (see Experimental) show a close correlation with those of PcRu(pyz)$_2$ [3a], PcRu($C_6H_5NH_2$)$_2$ [7], PcRu(4-pyCN)$_2$, PcRu(3-pyCN)$_2$ [8], and other similar PcM [9] (M = Fe, Co, Ni, Cu) and $PcML_2$ [10] (M = Fe, Co, L = py, pyz) systems, differing only in the absorptions which originate from Pc macrocyclic vibrations and additional new bands due to the different axial ligands.

In comparison with PcRu, the PcRu(pyz)$_2$ model system exhibits additional new bands at $\tilde{\nu}$ = 698 cm^{-1}, 807, 1227 and 1581 originating from the axial ligands [3a]. Moreover, other $PcRuL_2$ complexes like PcRu(bpyac)$_2$, PcRu(4-pyCN)$_2$

Table 1. ^{1}H-NMR spectral data (δ) of the $PcRuL_2$ complexes **3**, **4**, **7**, **8**, $PcRu(py)_2$, and $PcRu(pyz)_2$[a]

$PcRuL_2$	L		H_a	H_b	H_c	H_d	H_e	H_f	Pc[b] H^1	Pc[b] H^2
3			3.26(s,2H)	3.08(s,2H)	6.84(m,2H)	7.16(t,2H) ($^3J_{dc}$=7.5)	6.84(m,2H)	6.44(d,2H) ($^3J_{ef}$=8.4)	7.90(m,8H)	9.17(m,8H)
			[9.29][c]	[9.23]	[8.01]	[7.83]	[7.58]	[7.84]		
4			3.36(s,2H)	7.14(s,2H)	6.67(d,2H) ($^3J_{cd}$=7.9)	7.06(t,2H) ($^3J_{de}$=7.5, $^3J_{dc}$=7.9)	6.98(t,2H) ($^3J_{ed}$=7.5, $^3J_{ef}$=8.3)	6.37(d,2H) ($^3J_{fe}$=8.3)	7.84(m,8H)	9.16(m,8H)
			[9.44]	[9.44]	[7.93]	[7.85]	[7.85]	[7.93]		
7		d)	3.65(s,2H)	3.22(s,2H)	8.35(s,2H)	8.16(s,2H)			7.94(m,8H)	9.20(m,8H)
			[9.80]	[9.65]	[9.33]	[9.15]				
8		e)	5.56(d,2H) ($^3J_{ab}$=6.8)	2.35(d,2H) ($^3J_{ba}$=6.8)	3.10(s,2H)	6.43(d,2H) ($^3J_{de}$=8.4)	6.78(m,2H) ($^3J_{ef}$=7.7, $^3J_{ed}$=8.4)	6.93(m,2H) ($^3J_{fg}$=8.2)	7.86(m,8H)	9.15(m,8H)
			[7.50]	[8.45]	[9.15]	[7.87]	[7.50]	[7.57]		
		f)	2.35(m,4H)	6.43(m,4H)					7.90(m,8H)	9.20(m,8H)
			[8.63]	[8.63]						
		f)	2.43	5.21	6.02				7.87	9.13
			[8.60]	[7.25]	[7.64]					

[a] Measured at 400 MHz in $CDCl_3$ at ambient conditions; relative integrations for protons are consistent with the assignments; $CDCl_3$ (δ = 7.23) was used as reference. – [b] See Scheme 1. – [c] Chemical shifts given in brackets denote the corresponding free ligands[4]. – [d] Measured at 250 MHz in $CDCl_3$ under the same conditions. – [e] H_g: 6.64 (d, 2H) [7.71]. – [f] Ref.[2e,3a].

Table 2. UV/Vis data (λ_{max} [nm]) of $PcRuL_2$ complexes **1**–**9**[a]

Complex	*Q*			*B*		
$PcRu(qnx)_2$ (**1**)	645	594 sh	454			316
$PcRu(meqnx)_2$ (**2**)	646	595 sh	455			318
$PcRu(qnz)_2$ (**3**)	630	585 sh	475	365 sh		315
$PcRu(ptz)_2$ (**4**)	630	575 sh	465	385 sh	370 sh	325
$PcRu(qnl)_2$ (**5**)	633	578 sh	440 sh	383 sh		316
$PcRu(pypyz)_2$ (**6**)	635	575 sh	440 sh	380 sh		320
$PcRu(ptd)_2$ (**7**)	643	590 sh		383 sh		310
$PcRu(iso\text{-}qnl)_2$ (**8**)	630	575 sh	435	375		318
$PcRu(npd)_2$ (**9**)	634	580 sh	455	380 sh		315
$PcRu(py)_2$[b]	625	573		377		313
$PcRu(pyz)_2$[c]	641	587	442	376 sh		314
PcRu[d]	645	584				

[a] Measured in $CHCl_3$ solutions of approximate 1×10^{-5} to 5×10^{-6} mol/l. – [b] Ref.[2e]. – [c] Ref.[3a]. – [d] Ref.[7b].

and $PcRu(3\text{-}pyCN)_2$[8], and $PcML_2$ systems[1,10b] [M = Fe, Ru; L = py, tz, bpy (4,4′-bipyridine)] also show several new absorptions corresponding to the axial ligands. From this we can assign the newly observed bands as compared to those found for ligand absorptions[11] (see Experimental).

UV/Vis Spectra: The UV/Vis spectra of compounds **1**–**9** (Table 2) show a strong absorption in the *Q*-band region (λ_{max} = 630–646 nm) accompanied by a weaker shoulder at slightly higher energy (λ = 575–595 nm). Additional sharp and strong absorptions are observed in the Soret band region (λ = 310–325 nm) accompanied by weaker absorptions or shoulders at slightly lower energies (λ = 365 to 385 nm). Other additional weaker absorptions or shoulders at λ = 435–475 nm, which may be due to metal-ligand charge-transfer (ML CT) transitions are also observed between the *Q* and the Soret bands. Both the *Q* and the Soret bands show a similar pattern as compared to well-characterized other bisaxially coordinated $PcRuL_2$ complexes (L = py, pyz)[2e,3a], however, the different ligands in **1**–**9** lead to significant shifts of the *Q* bands.

The UV/Vis spectra obtained in this study are understood in terms of a porphyrinic four-orbital model with $\pi \rightarrow \pi^*$ *Q*-band and Soret-like transitions, and additional ML CT bands[12]. The *Q*-band shifts (Table 2) show a considerable variation due to annulation and coordinating site of the axial ligands. A comparison of the band at λ_{max} = 633 nm in $PcRu(qnl)_2$ (**5**) with that at λ_{max} = 625 nm in $PcRu(py)_2$[2e] shows a 8-nm red shift which may be attributed to the *b* fusion going from pyridine to quinoline. The data in Table 2 show that the annulation of a pyrazine ring with the pyridine ring in $PcRu(pypyz)_2$ (**6**) shifts the λ_{max} value by ca. 10 nm to the red. $PcRu(npd)_2$ (**9**) also shows a red shift of

about 9 nm due to the annulation of the pyridine ring. However, the *b* fusion going from pyrazine to quinoxaline does not affect the *Q* bands appreciably (λ_{max} = 641 vs 645 nm).

The *Q* band of PcRu(qnx)$_2$ (**1**) with a quinoline-like N-donor axial ligand appears at λ = 645 nm, unlike those of the isoquinoline-like systems such as PcRu(qnz)$_2$ (**3**) and PcRu(ptz)$_2$ (**4**) which appear at a higher energy (λ_{max} = 630 nm).

Thermogravimetric Analyses: The thermogravimetric (TG) and differential thermal analysis (DTA) data given in Table 3 clearly show from the mass losses that the complexes **1**–**9** have the stoichiometric ratio PcRu/L = 1:2. Except for PcRu(pypyz)$_2$ (**6**), the initial decomposition temperatures are lower in the complexes **1, 2, 5,** and **9** with quinoline-like N-donor axial ligands as compared to complexes with isoquinoline-like ligands (**3, 4, 8**), which is attributed to the closer contact between 8-H of the corresponding axial ligand (Scheme 1) and the Pc ring system in the former. The thermal stability of the PcRuL$_2$ complexes with quinoline-like N-donor axial ligands is also lower than that of the complexes with monocyclic ligands like PcRu(py)$_2$[13] and PcRu(pyz)$_2$[1b].

Table 3. TG/DTA data of PcRuL$_2$ complexes[a]

Complex	Decomposition temp. [°C]	DTA signal T_{max} [°C]	Mass loss (%) Calcd.[b]/Found
PcRu(qnx)$_2$ (**1**)	167–265	246	29.8/30.0
PcRu(meqnx)$_2$ (**2**)	160–215	204	32.0/29.6
	215–252	243	
PcRu(qnz)$_2$ (**3**)	271–380	366	29.8/26.4
PcRu(ptz)$_2$ (**4**)	268–417	394	29.8/27.0
PcRu(qnl)$_2$ (**5**)	198–374	242	29.6/27.6
PcRu(pypyz)$_2$ (**6**)	193–352	231, 275	29.9/27.8
PcRu(ptd)$_2$ (**7**)	200–415	237, 398	30.1/32.7
PcRu(iso-qnl)$_2$ (**8**)	270–401	384	29.6/27.9
PcRu(npd)$_2$ (**9**)	164–393	256	29.8/28.1
PcRu(py)$_2$[c]	250–390	374	20.5/20.3
PcRu(pyz)$_2$[d]	255–305	285	20.7/20.0
	330–560	540	

[a] Measured at a heating rate of 2 K/min under a nitrogen stream (25 ml/min). – [b] Calculated for loss of 2 equiv. of L. – [c] Ref.[13]. – [d] Ref.[1b].

Mass Spectra: Mass-spectral data could not be obtained for the complexes **1**–**9** by the normal method (200°C, 70 eV, direct inlet). However, FD mass spectra were obtained with chloroform as solvent. In all cases, except for PcRu(pypyz)$_2$ (**6**) (*m/z* = 614 [PcRu$^+$]) and PcRu(ptz)$_2$ (**4**) (*m/z* = 614 [PcRu$^+$], 1228 [(PcRu)$_2^+$]), they all show only the [(PcRu)$_2^+$] dimer peaks at *m/z* = 1228. These peaks were also found for other PcRuL$_2$ complexes such as PcRu(me$_2$PhNC)$_2$ and PcRu(Cl$_4$PhNC)$_2$[3b]. Dimerization is attributed to a direct metal bonding between two PcRu units by ionization during the FD-MS measurements. Similar structures have also been proposed for Ru(Porp)[14] [Porp = octaethylporphyrin (OEP), tetraphenylporphyrin (TPP)].

Quinoline, quinoxaline, and 2-methylquinoxaline were also treated with phthalocyaninatoiron (PcFe). In contrast to PcRu no complex formation could be observed with PcFe using these donor molecules. This is in accordance with the known lower stability of PcFeL$_2$ complexes in comparison to PcRuL$_2$ compounds[1,2].

The steric hindrance of the second ring in quinoxaline also prevents the formation of a bridged polymer [PcRu(qnx)]$_n$. In contrast, the corresponding system [PcRu(pyz)]$_n$ can be easily obtained[3a]. Only in the case of pteridine (ptd) a mixture of PcRu(ptd)$_2$ and [PcRu(ptd)]$_n$ can be obtained. However, attempts to separate these compounds have been unsuccessful.

The described experimental data demonstrate that not only monocyclic N-donor molecules like pyridine or pyrazine are able to form bisaxially coordinated phthalocyaninatoruthenium complexes[1,2] but also that bicyclic N-donor molecules are able to coordinate bisaxially with PcRu to form comparatively stable compounds. Compared to PcRuL$_2$ in which L is a monocyclic N-donor molecule like pyridine or pyrazine the PcRuL$_2$ complexes **1, 2, 5,** and **9** show a lower thermal stability, due to the steric reasons explained above (cf. Table 3).

In general, the solubility of **1**–**9** in aprotic solvents like chloroform or dichloromethane is much higher in comparison to the corresponding complexes PcRuL$_2$ (L = pyridine, pyrazine[1b,3a]).

Experimental

FT IR: Bruker IFS 48 spectrophotometer, bands denoted with an asterisk (*) correspond to coordinated ligands, bands due to pure ligands are given in parentheses for comparison[11]. Abbreviations: skel. st = skeletal stretching; o.p. bend = out-of-plane bending; i.p. bend = in-plane bending. – ^{1}H NMR: Bruker WM 400 (400 MHz), Bruker AC 250 (250 MHz). – UV/Vis: Shimadzu 365. – MS: Varian MAT 711. – TG/DTA: Netzsch Simultan STA 409. – Micro elemental analysis: Carlo-Erba Elemental Analyzer 1104, 1106.

PcRu was prepared according to the literature method[3a]. Since the IR spectrum of PcRu has not been reported in detail[3a], the values are given here. IR (nujol): $\tilde{\nu}$ = 1610 cm^{-1} w, 1586 w, 1496 s, 1416 s, 1329 s, 1289 s, 1197 vw br, 1165 s, 1120 vs, 1099 s, 1070 s, 1001 w, 969 vw, 938 w, 908 m, 864 w, 805 w, 771 s, 755 s, 725 vs, 643 vw. – Quinoxaline (Merck), 2-methylquinoxaline (Aldrich), quinoline (Fluka), and isoquinoline (Fluka) were vacuum-distilled before use. Phthalazine (Aldrich), quinazoline (Aldrich), and pyrido[2,3-*b*]pyrazine (Aldrich) were sublimed before use. Pteridine and 1,5-naphthyridine were synthesized according to known methods[15].

PcRu(qnx)$_2$ (**1**), *PcRu(qnz)$_2$* (**3**), *PcRu(ptz)$_2$* (**4**), *and PcRu(pypyz)$_2$* (**6**): In a tap-top sealed septum bottle with a Teflon-faced cap, a mixture of PcRu (153 mg, 0.25 mmol) and the corresponding ligand (5.00 mmol) was heated under nitrogen at 80°C (**1**), 90°C (**3**), 115°C (**4**), and 155°C (**6**), respectively, for 24 h (**1, 3, 4**) and 6 h (**6**) with stirring, and then cooled to 0°C (**1**) and room temperature (**3, 4, 6**). After pulverization, the product mixture was washed with a small amount of cold methanol, and then **6** was sublimed at 110°C to remove excess ligand. The resulting solid was vacuum-dried at 95°C (**1, 3**) and 110°C (**4**), respectively. Yields: 53–63%.

(Phthalocyaninato)bis(quinoxaline)ruthenium(II), PcRu(qnx)$_2$ (**1**): 138 mg (63%) of blue-violet powder. – IR (nujol): $\tilde{\nu}$ = 1607 cm^{-1}, 1580, 1570* (1575, skel. st), 1502* (1499, skel. st), 1482, 1412, 1352* (1354, skel. st), 1324, 1288, 1209, 1198, 1170, 1122, 1067,

1024* (1025, skel. st), 1005, 964* (955, C–H o.p. bend), 950, 912, 867, 852, 828*, 806, 779, 756, 739, 720, 643, 619*. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.93 (m, 8H, Pc, 1-H), 9.21 (m, 8H, Pc, 2-H).

$C_{48}H_{28}N_{12}Ru$ (873.91)
Calcd. C 65.97 H 3.23 N 19.23
Found C 66.52 H 3.23 N 18.83

(Phthalocyaninato)bis(quinazoline)ruthenium(II), PcRu(qnz)$_2$ (**3**): 116 mg (53%) of dark-violet powder. – IR (nujol): $\tilde{\nu}$ = 1617* cm^{-1} (1622, skel. st), 1583, 1573* (1569, skel. st), 1491, 1415, 1326, 1310* (1303, C–H i.p. bend), 1289, 1213*, 1171, 1153* (1150, C–H i.p. bend), 1123, 1067, 1006, 968, 952, 913, 869, 808, 789* (794, C–H o.p. bend), 778, 755, 734, 701, 645, 633*. – ^{1}H NMR: see Table 1.

$C_{48}H_{28}N_{12}Ru$ (873.91)
Calcd. C 65.97 H 3.23 N 19.23
Found C 66.12 H 3.47 N 18.24

Bis(phthalazine)(phthalocyaninato)ruthenium(II), PcRu(ptz)$_2$ (**4**): 129 mg (59%) of dark-blue violet powder. – IR (nujol): $\tilde{\nu}$ = 1617* cm^{-1} (1619, skel. st), 1576* (1577, skel. st), 1559* (1568, skel. st), 1493, 1415, 1326, 1289, 1276* (1278), 1241* (1246), 1168, 1123, 1066, 1006, 980* (975, C–H vib), 966, 945, 927, 914, 905*, 869, 833*, 808, 798, 773, 756* (767, C–H bend), 749*, 733, 723* (720, C–H bend), 654*, 644. – ^{1}H NMR: see Table 1.

$C_{48}H_{28}N_{12}Ru$ (873.91)
Calcd. C 65.97 H 3.23 N 19.23
Found C 65.17 H 3.21 N 18.56

(Phthalocyaninato)bis(pyrido[2,3-b]pyrazine)ruthenium(II), PcRu(pypyz)$_2$ (**6**): 136 mg (62%) of blue-violet powder. – IR (nujol): $\tilde{\nu}$ = 1599 cm^{-1}, 1581, 1556* (1564, skel. st), 1540*, 1487, 1414, 1326, 1288, 1279* (1289, C–H i.p. bend), 1266* (1271, C–H i.p. bend), 1204* (1205), 1187, 1170, 1123, 1067, 1018* (1015, skel. st), 1006, 956, 947* (949), 913, 879* (879, C–H o.p. bend), 862, 836, 807, 794, 787* (782, C–H o.p. bend), 778, 766* (757, skel. st), 755, 738, 719, 644, 616*, 609*. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.85 (m, 8H, Pc, 1-H), 9.28 (m, 8H, Pc, 2-H).

$C_{46}H_{26}N_{14}Ru$ (875.88)
Calcd. C 63.08 H 2.99 N 22.39
Found C 63.63 H 3.10 N 22.66

PcRu(meqnx)$_2$ (**2**) *and PcRu(qnl)$_2$* (**5**): In a tap-top sealed septum bottle with a Teflon-faced cap, a 0.25-mmol sample of PcRu (153 mg) was suspended in 2-methylquinoxaline (5.00 mmol, 721 mg) and quinoline (10.0 mmol, 1292 mg), respectively. The mixture was heated for 24 h at 75°C (**2**) and 110°C (**5**) under nitrogen with stirring. The reaction mixture was then dispersed in hexane, filtered, and the residue was washed with a small amount of cold methanol to remove excess ligand. The remaining residue was vacuum-dried at 90°C (**2**) and 95°C (**5**), respectively. Yields: 51–67%.

Bis(2-methylquinoxaline)(phthalocyaninato)ruthenium(II), PcRu(meqnx)$_2$ (**2**): 151 mg (67%) of dark-blue powder. – IR (nujol): $\tilde{\nu}$ = 1609 cm^{-1}, 1574* (1578, skel. st), 1558* (1560, skel. st), 1488, 1413, 1325, 1289, 1200* (1200, β-CH vib), 1169, 1124, 1066, 1034* (1034, β-CH vib), 1006, 948, 912, 870, 807, 776, 755, 736, 722, 701, 643, 621* (609). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.91 (m, Pc, 1-H), 9.17 (m, Pc, 2-H).

$C_{50}H_{32}N_{12}Ru$ (901.96)
Calcd. C 66.59 H 3.58 N 18.64
Found C 66.22 H 3.45 N 18.21

(Phthalocyaninato)bis(quinoline)ruthenium(II), PcRu(qnl)$_2$ (**5**): 111 mg (51%) of dark-violet powder. – IR (nujol): $\tilde{\nu}$ = 1609 cm^{-1}, 1582, 1511*, 1489, 1413, 1325, 1288, 1200, 1168, 1122, 1067, 1006, 952, 945, 913, 864, 825* (804, C–H o.p. bend), 807, 776, 754, 736, 731*, 700, 639*. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.87 (m, 8H, Pc, 1-H), 9.15 (m, 8H, Pc, 2-H).

$C_{50}H_{30}N_{10}Ru$ (871.93)
Calcd. C 68.88 H 3.47 N 16.06
Found C 69.37 H 3.44 N 15.43

PcRu(iso-qnl)$_2$ (**8**): In a tap-top sealed septum bottle with a Teflon-faced cap, a mixture of PcRu (153 mg, 0.25 mmol) and isoquinoline (969 mg, 7.5 mmol) was heated under nitrogen at 70°C for 24 h with stirring. The reaction mixture was dispersed in hexane immediately without cooling. The reaction slurry was filtered, washed with a small amount of cold methanol and then chromatographed on silica gel using dichloromethane as eluent. The solvent was evaporated and the resulting solid vacuum-dried at 90°C.

Bis(isoquinoline)(phthalocyaninato)ruthenium(II), PcRu(iso-qnl)$_2$ (**8**): 70 mg (32%) of violet microcrystalline compound. – IR (nujol): $\tilde{\nu}$ = 1609 cm^{-1}, 1582, 1491, 1415, 1326, 1288, 1215*, 1192, 1179, 1169, 1150, 1123, 1105, 1068, 1007, 968*, 940, 914, 871, 860, 830* (825, C–H o.p. bend), 807, 773, 755, 733, 726*, 642, 639*. – ^{1}H NMR: see Table 1.

$C_{50}H_{30}N_{10}Ru$ (871.93)
Calcd. C 68.88 H 3.47 N 16.06
Found C 68.12 H 3.46 N 15.39

PcRu(ptd)$_2$ (**7**) *and PcRu(npd)$_2$* (**9**): In a tap-top sealed septum bottle with a Teflon-faced cap, a suspension of PcRu (153 mg, 0.25 mmol) and the corresponding ligand (5.00 mmol) in acetone (25 ml) was heated at reflux under nitrogen with stirring for 24 h. After cooling, the volume of the reaction mixture was reduced to 1/3 by concentration in vacuo, and the residue was dispersed in hexane. The resulting slurry was filtered, washed with a small amount of cold methanol, and then **9** was chromatographed on silica gel with chloroform/ethanol (98:2). The resulting solid **7** and **9** was vacuum-dried at 70°C. Yields: 22–49%.

(Phthalocyaninato)bis(pteridine)ruthenium(II), PcRu(ptd)$_2$ (**7**): 108 mg (49%) of dark-blue powder. – IR (nujol): $\tilde{\nu}$ = 1596 cm^{-1}, 1582, 1555* (1558, skel. st), 1490, 1443, 1415, 1327, 1288, 1202* (1197), 1170, 1126, 1109, 1067, 1009* (1015, skel. st), 949, 927, 913, 887, 863, 821, 807, 784* (777, C–H o.p. bend), 777, 755, 740, 656*, 615*. – ^{1}H NMR: see Table 1.

$C_{44}H_{24}N_{16}Ru$ (877.86)
Calcd. C 60.20 H 2.76 N 25.53
Found C 58.72 H 2.81 N 24.93

Bis(1,5-naphthyridine)(phthalocyaninato)ruthenium(II), PcRu(npd)$_2$ (**9**): 48 mg (22%) of dark-violet microcrystalline compound. – IR (nujol): $\tilde{\nu}$ = 1600 cm^{-1}, 1582* (1588, skel. st), 1490, 1414, 1325, 1306* (1301, C–H i.p. bend), 1289, 1216, 1169, 1124, 1067, 1007, 946, 912, 875, 870, 816*, 807, 777, 755, 736, 644. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (s, 8H, Pc, 1-H), 9.12 (s, 8H, Pc, 2-H).

$C_{48}H_{28}N_{12}Ru$ (873.91)
Calcd. C 65.97 H 3.23 N 19.23
Found C 65.76 H 3.39 N 19.03

CAS Registry Numbers

1: 132673-09-7 / **2**: 132673-10-0 / **3**: 132673-11-1 / **4**: 132673-12-2 / **5**: 132673-13-3 / **6**: 132673-14-4 / 7: 132673-15-5 / **8**: 132673-16-6 / **9**: 132673-17-7 / PcRu: 27636-56-2

[1] [1a] M. Hanack, A. Datz, R. Fay, K. Fischer, U. Keppeler, J. Koch, J. Metz, M. Mezger, O. Schneider, H.-J. Schulze in *Handbook of Conducting Polymers* (T. Skotheim Ed.), p. 133, Marcel Dekker,

New York 1986. – [1b] M. Hanack, S. Deger, A. Lange, *Coord. Chem. Rev.* **83** (1988) 115.
[2] [2a] M. Hanack, R. Thies, *Chem. Ber.* **121** (1988) 1225. – [2b] M. Hanack, G. Renz, J. Strähle, S. Schmid, *Chem. Ber.* **121** (1988) 1479. – [2c] M. Hanack, R. Großhans, *Chem. Ber.* **122** (1989) 1665. – [2d] M. Hanack, A. Lange, M. Rein, R. Behnisch, G. Renz, A. Leverenz, *Synth. Met.* **29** (1989) F1. – [2e] M. Hanack, P. Vermehren, *Inorg. Chem.* **29** (1990) 134.
[3] [3a] W. Kobel, M. Hanack, *Inorg. Chem.* **25** (1986) 103. – [3b] U. Keppeler, W. Kobel, H.-U. Siehl, M. Hanack, *Chem. Ber.* **118** (1985) 2095. – [3c] U. Keppeler, M. Hanack, *Chem. Ber.* **119** (1986) 3363.
[4] [4a] S. Matsuura, T. Goto, *J. Chem. Soc.* **1963**, 1773. – [4b] E. Pretsch, J. Seibel, W. Simon, T. Clerc, *Strukturaufklärung Organischer Verbindungen*, Springer-Verlag, Berlin, Heidelberg 1986.
[5] J. E. Maskasky, J. R. Mooney, M. E. Kenney, *J. Am. Chem. Soc.* **94** (1972) 2132.
[6] W. L. F. Armarego, T. J. Batterham, J. R. Kershaw, *Org. Magn. Reson.* **3** (1971) 575.
[7] [7a] I. M. Keen, B. W. Malerbi, *J. Inorg. Nucl. Chem.* **27** (1965) 1311. – [7b] P. C. Krueger, M. E. Kenney, *J. Inorg. Nucl. Chem.* **25** (1963) 303.
[8] H.-J. Schulze, *Dissertation*, Universität Tübingen, 1985.
[9] [9a] A. N. Sidorov, I. P. Kotlyar, *Optika i Spektroskopiya* **11** (1961) 175 [*Chem. Abstr.* **55** (1961) 25467]. – [9b] H. F. Shurvell, L. Pinzuti, *Can. J. Chem.* **44** (1966) 125. – [9c] T. Kobayashi, F. Kurogawa, N. Uyeda, *Spectrochim. Acta, Part A*, **26** (1970) 1305. – [9d] B. Stymne, F. X. Sauvage, G. Wettermark, *Spectrochim. Acta, Part A*, **35** (1979) 1195.
[10] [10a] B. Stymne, F. X. Sauvage, G. Wettermark, *Spectrochim. Acta, Part A*, **36** (1980) 397. – [10b] J. Metz, O. Schneider, M. Hanack, *Spectrochim. Acta, Part A*, **38** (1982) 1265.
[11] [11a] S. F. Mason, *J. Chem. Soc.* **1955**, 2336. – [11b] A. R. Katritzky, R. A. Jones, *J. Chem. Soc.* **1960**, 2942. – [11c] For comparison of the IR spectral data of meqnx obtained in this work, see: G. W. E. Cheeseman, A. R. Katritzky, B. J. Ridgewell, *J. Chem. Soc.* **1963**, 3764. – [11d] W. L. F. Armarego, G. B. Barlin, E. Spinner, *Spectrochim. Acta* **22** (1966) 117. – [11e] S. C. Wait, Jr., J. C. McNerney, *J. Mol. Spectrosc.* **34** (1970) 56. – [11f] R. W. Mitchell, R. W. Glass, J. A. Merritt, *J. Mol. Spectrosc.* **36** (1970) 310.
[12] [12a] A. Antipas, J. W. Buchler, M. Gouterman, P. D. Smith, *J. Am. Chem. Soc.* **100** (1978) 3015. – [12b] A. B. P. Lever, S. R. Pickens, P. C. Minor, S. Licoccia, B. S. Ramaswamy, K. Magnell, *J. Am. Chem. Soc.* **103** (1981) 6800. – [12c] P. C. Minor, M. Gouterman, A. B. P. Lever, *Inorg. Chem.* **24** (1985) 1894.
[13] P. Vermehren, *Dissertation*, Universität Tübingen, 1989.
[14] J. P. Collman, C. E. Barnes, P. N. Swepston, J. A. Ibers, *J. Am. Chem. Soc.* **106** (1984) 3500.
[15] [15a] A. Albert, *J. Chem. Soc.* **1960**, 1790. – [15b] A. Albert, H. Yamamoto, *J. Chem. Soc. C*, **1968**, 2289. – [15c] Y. Hamada, I. Takeuchi, *Chem. Pharm. Bull.* **19** (1971) 1857.

[3/91]