Ruthenium(II) Octaphenylporphyrazine Complexes with Mixed Axial Ligands: Peculiarities of Their Formation and Spectral Properties

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Keywords: Isocyanide ligands / N ligands / NMR spectroscopy / Porphyrinoids / Ruthenium / Self-assembly

A series of new axially bis-coordinated (octaphenylporphyrazinato)ruthenium(II) complexes {[(Ph_8Pz)RuL_2], L = cyclohexyl isocyanide, CyNC, (**1b**); 4,4′-bipyridine, bpy, (**2c**); *N*-methylimidazole, CH_3Im, (**3a**)} was prepared and characterized. The reaction of the bis-isocyanide adducts [(Ph_8Pz)Ru(*t*-BuNC)$_2$] (**1a**) or [(Ph_8Pz)Ru(CyNC)$_2$] (**1b**) with monodentate N-heterocycles gave, under certain conditions, the mixed-ligand complexes [(Ph_8Pz)Ru(Py)(*t*BuNC)] (**4a**), [(Ph_8Pz)Ru(Py)-(CyNC)] (**4b**) and [(Ph_8Pz)Ru(CH_3Im)(CyNC)] (**3b**). The reaction of **1a** or **1b** with an excess of bidentate 4,4′-bipyridine under the same conditions resulted in the formation of the corresponding dimeric species [(Ph_8Pz)Ru(*t*BuNC)]$_2$(μ-bpy) (**2a**) and [(Ph_8Pz)Ru(CyNC)]$_2$(μ-bpy) (**2b**) in high yield. The structures of all the complexes were unambiguously proved by ^{1}H NMR spectroscopy, and the possibility of their self-assembly is discussed. All mixed-ligand compounds were also characterized by UV/Vis and IR spectroscopy, as well as elemental analysis. The ^{1}H NMR spectra of these compounds are discussed in detail.

Introduction

The high interest in complexes of porphyrins (Por), and their analogues, with transition metals such as Co, Fe, Ru, Os, etc. has arisen, especially in recent years, due to their possible application in materials science and industry. Many peculiar properties of these compounds appear to be a consequence of their ability to bind additional axial ligands, as well as to change the oxidation state of the central metal relatively easily. In particular, a high catalytic activity in different processes — decarbonylation of aldehydes,[1a] isomerization of epoxides,[1b] oxidation of different organic substrates,[1c,1d] etc. — has been observed for transition-metal complexes with porphyrin-type macrocycles, including phthalocyanines (Pc).[1e] Polymeric axially linked complexes of iron, cobalt and ruthenium with phthalocyanines and naphthalocyanines (Nc) possess semiconducting properties in the solid state.[2] Porphyrin complexes of ruthenium and osmium have also been used to construct different self-organized multimacrocyclic assemblies through axial coordination,[3] in which energy- or electron-transfer effects can appear due to the special intramolecular interaction between face-to-face or side-to-face oriented macrocycles, leading to the possibility of light harvesting and efficient photocurrent generation by these systems.[4] Additionally, the important role played by porphyrin-like complexes with different transition metals, especially iron and cobalt, in many biological processes has led to a vast amount of research on analogous model compounds, including phthalocyanines. This research was aimed mainly at the investigation of the axial-ligand-exchange rules and mechanisms in macrocyclic systems.[5]

Complexes of alkyl- and aryl-substituted porphyrazines (Pz), which have an intermediate structure between porphyrins and phthalocyanines, have been less-well investigated and only a few studies on the synthesis and properties of these compounds are available. We have previously prepared and characterized a series of monomeric and oligomeric iron and ruthenium complexes with octaphenylporphyrazine (Ph_8Pz), containing different axial ligands,[6] and investigated the axial-ligand-exchange processes in [(Ph_8Pz)Fe(L)(L′)], where L and L′ are isocyanides or N-heterocycles.[7] Here we continue the study of axially coordinated complexes of octaphenylporphyrazine with iron subgroup metals. We have reported previously that "crude" [(Ph_8Pz)Ru], which can be prepared by template condensation of diphenylfumaronitrile and [$Ru(NH_3)_5(N_2)$]Cl_2,[6e] is a very convenient starting material for the synthesis of hexacoordinate (octaphenylporphyrazinato)ruthenium(II) complexes [(Ph_8Pz)RuL_2], where L is one of various N-heterocycles or isocyanides. Thus, refluxing crude [(Ph_8Pz)Ru]

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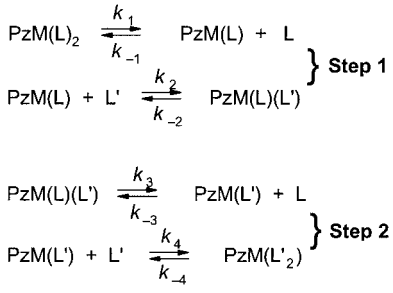
in pyridine for 24 h gave the corresponding bis-pyridine adduct [(Ph_8Pz)Ru($Py)_2$] (**4c**) and heating [(Ph_8Pz)Ru] with *tert*-butyl isocyanide resulted in the formation of [(Ph_8Pz)-Ru(tBuNC)$_2$] (**1a**).[6c] A similar route was chosen in the present work to prepare bis adducts of (octaphenylporphyrazinato)ruthenium(II) with cyclohexyl isocyanide {[(Ph_8Pz)Ru-(CyNC)$_2$] (**1b**)}, 4,4′-bipyridine {[(Ph_8Pz)Ru(bpy)$_2$] (**2c**)} and *N*-methylimidazole {[(Ph_8Pz)Ru($CH_3Im)_2$] (**3a**)}. The bis-isocyanide complexes **1a** and **1b** were utilized to prepare the mixed axial ligand complexes [(Ph_8Pz)Ru(Py)(tBuNC)] (**4a**), [(Ph_8Pz)Ru(Py)(CyNC)] (**4b**), [(Ph_8Pz)Ru(CH_3Im)-(CyNC)] (**3b**), [(Ph_8Pz)Ru(tBuNC)$_2$(bpy) (**2a**) and [(Ph_8Pz)Ru(CyNC)]$_2$(bpy) (**2b**) shown in Scheme 1. The structure of these compounds was verified by means of UV/Vis, IR and NMR spectroscopy (see discussion below), as well as by elemental analysis. Mass spectrometry was found not to give enough information on the structure of axially coordinated ruthenium octaphenylporphyrazines due to a complete loss of axial ligands even under the relatively soft conditions of the FD technique.[6c] Therefore, we did not apply this method of analysis for the compounds reported here.

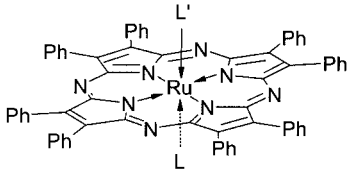
Results and Discussion

Ruthenium complexes of porphyrins or phthalocyanines are, in general, more stable towards the loss of axial ligands than their iron analogues.[5e,10] This is also true for octaphenylporphyrazine systems. For example, the complete substitution of axially coordinated isocyanides by pyridine, or vice versa, in iron complexes proceeds with rather high rates ($\tau_{1/2} \approx 1-10$ min) even at room temperature.[7] On the other hand bis-isocyanide adducts [(Ph_8Pz)Ru($RNC)_2$] with ruthenium as a central metal remain unchanged in pyridine solution at room temperature at least for several hours. Early investigations on axial-ligand-exchange in iron or ruthenium phthalocyanines allowed the proposal of a dissociative mechanism for these processes.[5] Additionally, in complexes with axial ligands that exhibit a strong *trans* effect, substitution usually proceeds in two well-separated steps, as shown in Scheme 2, where Pz is a porphyrazine-type macrocycle and M is iron or ruthenium. We have also observed this mechanism for the substitution of axially coordinated isocyanides by N-heterocycles in (octaphenylporphyrazinato)iron complexes.[7]

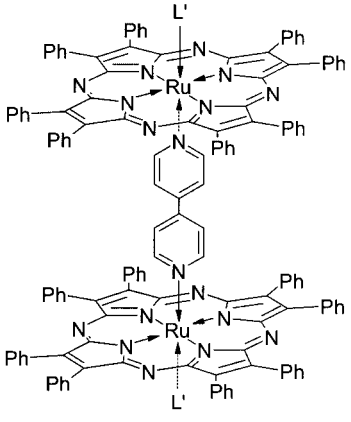
In this work we studied the substitution behavior of axially coordinated isocyanides in (octaphenylporphyrazinato)-ruthenium(II) complexes. Although these compounds remain spectroscopically unchanged at room temperature in pyridine solution for a relatively long time, as pointed out above, heating them to elevated temperatures (but below 100 °C) results in modest changes in their UV/Vis spectra (see **a** in Figure 1, dotted line), although the resulting spectra do not correspond to that of the bis-pyridine adduct **4c**. The spectra were, however, found to be similar to the spec-



Scheme 2



1a, 1b, 2c, 3a, 3b, 4c, 4a, 4b



2a, 2b

L =	tBuNC	CyNC	bpy	CH_3Im	CH_3Im	Py	Py	Py	---	---
L' =	*t*BuNC	CyNC	bpy	CH_3Im	CyNC	Py	*t*BuNC	CyNC	*t*BuNC	CyNC
Nr.	**1a**	**1b**	**2c**	**3a**	**3b**	**4c**	**4a**	**4b**	**2a**	**2b**

Scheme 1. Structure and numbering of the prepared complexes

tra of solutions of (octaphenylporphyrazinato)iron(II) complexes [(Ph_8Pz)Fe(L)(L′)] with two different axial ligands — one isocyanide and one nitrogen heterocycle, such as pyridine. These spectra were observed in our titration experiments on [(Ph_8Pz)Fe($RNC)_2$] with nitrogen heterocycles, in which we were not able to isolate the mixed-ligand compounds in the solid state due to their high lability.[7] Additionally, the formation of [(Ph_8Pz)Fe(L)(L′)] adducts from [(Ph_8Pz)Fe($RNC)_2$] was found to be so fast that we were not able to study the kinetics of this process by common spectroscopic techniques. In contrast, the reaction of [(Ph_8Pz)Ru(tBuNC)$_2$] with pyridine could be followed easily. The reaction was found to be first order in ruthenium complex {a linear dependence of ln(C^o/C) on reaction time was observed, where C^o and C are the starting and current concentrations of [(Ph_8Pz)Ru(tBuNC)$_2$] respectively} and zero order in pyridine (see Figure 2). This, and the observed spectral changes, allowed us to assume that under these reaction conditions only the first step shown in Scheme 2 {formation of the mixed-ligand complex [(Ph_8Pz)Ru(Py)(tBuNC)] (**4a**)} takes place. The activation energy of this process is rather high (see Table 1), which explains the observed high kinetic stability of ruthenium complexes **1a** and **1b** at room temperature. However, a comparison of the kinetic parameters of the described reaction with those of analogous reactions of [PcRu($BzNC)_2$] (Bz = benzyl) reveals a higher lability of the porphyrazine complex.[10] A similar trend was observed in our studies on (octaphenylporphyrazinato)iron complexes.[7]

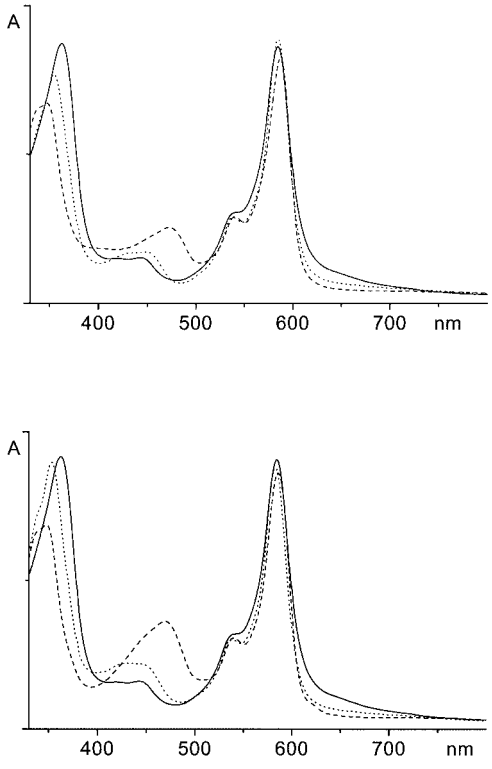


Figure 1. Comparison of the UV/Vis spectra in dichloromethane: a) [(Ph_8Pz)Ru(tBuNC)$_2$] (**1a**, solid line), [(Ph_8Pz)Ru(Py)$_2$] (**4c**, dashed line) and [(Ph_8Pz)Ru(Py)(tBuNC)] (**4a**, dotted line); b) [(Ph_8Pz)Ru(tBuNC)$_2$] (**1a**, solid line), [(Ph_8Pz)Ru(bpy)$_2$] (**2c**, dashed line) and [(Ph_8Pz)Ru(tBuNC)]$_2$(μ-bpy) (**2a**, dotted line)

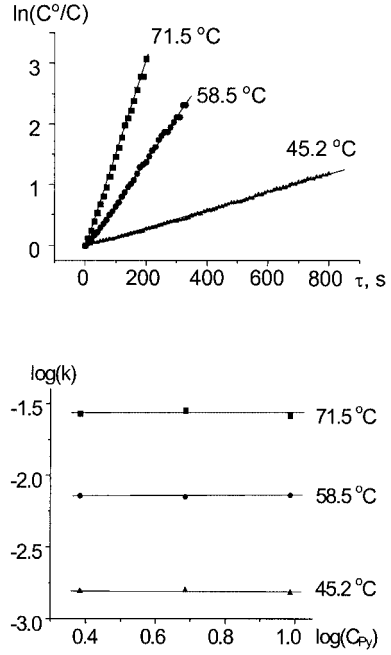


Figure 2. Kinetics results for the reaction of [(Ph_8Pz)Ru(tBuNC)$_2$] (**1a**) with pyridine in toluene; top: the dependence of ln(C^o/C) on reaction time; bottom: the dependence of the rate constant on the concentration of pyridine

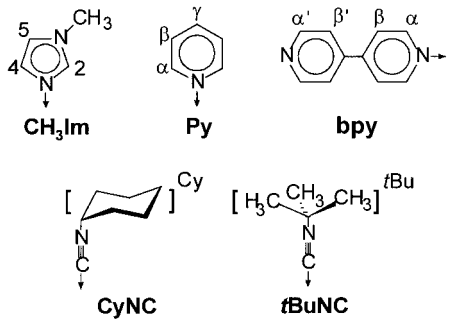
Table 1. Kinetic parameters of reaction of [(Ph_8Pz)Ru(tBuNC)$_2$] (**1a**) with pyridine in toluene

Concentration of pyridine (mol/L)	Temperature (K)	$k_1 \times 100$ (s^{-1})	E^o_a (kJ/mol)
9.68	344.7	2.60 ± 0.03	99 ± 3
	331.7	0.729 ± 0.006	
	318.4	0.151 ± 0.001	
4.84	344.7	2.82 ± 0.05	
	331.7	0.713 ± 0.006	
	318.4	0.158 ± 0.001	
2.42	344.7	2.69 ± 0.04	
	331.7	0.722 ± 0.005	
	318.4	0.155 ± 0.001	

[(Ph_8Pz)Ru(Py)(tBuNC)] (**4a**) was isolated and its IR and NMR spectra were recorded. The obtained spectroscopic data proved the mixed-ligand nature of the compound. The analogous complexes of iron or ruthenium phthalocyanine or porphyrins have been described previously.[10] Several other compounds, such as CO, nitroso derivatives and phosphites,[10–12] can also be utilized as strong-field axial ligands to build similar mixed-ligand complexes. Here (octaphenylporphyrazinato)ruthenium mixed-ligand complexes with axially coordinated isocyanides and nitrogen heterocycles have been isolated and characterized for the first time.

It is remarkable that upon heating the reaction mixture above 100 °C in the presence of an excess of the nitrogen heterocycle the second step in Scheme 2 can also take place to yield the bis adduct of the corresponding heterocycle, which does not happen under milder conditions with the same concentration of heterocycle. Therefore, and in contrast to iron complexes, in the case of porphyrazinatoruthenium isocyanides the kinetic control of the substitution reaction becomes obvious. This allowed us to prepare and isolate mixed-ligand complexes of (octaphenylporphyrazinato)ruthenium(II) with axially coordinated alkyl isocyanides and nitrogen heterocycles, namely [(Ph_8Pz)Ru(Py)(CyNC)] (**4b**) and [(Ph_8Pz)Ru(CH_3Im)(CyNC)] (**3b**). Interestingly, the reaction of [(Ph_8Pz)Ru(RNC)$_2$] even with a large excess of 4,4′-bipyridine (see Exp. Sect.) under mild conditions results in an almost quantitative yield of the dimeric bipyridine-bridged complexes **2a** or **2b** with no monomeric mixed-ligand species. The structure of these self-assembled dimers was determined from their ^{1}H NMR spectra.

The position of the ^{1}H NMR resonances of the axial ligands depends strongly on the distance of the protons from the coordinating metal because of the different shielding effect of the porphyrazine macrocycle ring current. This allows, for example, to use iron and ruthenium phthalocyanines as shift reagents in NMR spectroscopy for some coordination compounds.[13a,13b] The protons closest to the center of the macrocycle undergo the strongest shielding ring-current effect, which can be as much as 9 ppm, as was observed, for example, for the α-protons in dioctylgermanium phthalocyanine.[13c] Dependence of the ring-current shielding effect on the position of the proton about phthalocyanines or naphthalocyanines was also calculated.[13d,13e] Accordingly, the observed ^{1}H NMR signals of coordinated axial ligands in different complexes of (octaphenylporphyrazinato)ruthenium(II) can be assigned as shown in Table 2. The signals of coordinated pyridine appear as three multiplets, which have slightly different positions for the bis-pyridine adduct **4c** and the mixed-ligand species **4a** and **4b**. The position of the α-proton signals was found to be the most sensitive to the nature of the *trans* ligand (see Table 2 and Scheme 3). The resonance of the α-proton in **4a**, for example, is shifted upfield by 0.28 ppm relative to **4c**. Therefore, taking into account also the integration, it can clearly be seen that the mixed-ligand complexes **4a** and **4b** do not contain any admixture of bis-pyridine adduct **4c** or of starting material **1a** or **1b** (see also **a** in Figure 3).



Scheme 3. Designation of protons in axially coordinated molecules used for ^{1}H NMR signals' assignment

Similarly, the proton signals of the coordinated *N*-methylimidazole undergo a noticeable upfield shift when going from the bis(*N*-methylimidazole) adduct **3a** to the mixed-ligand complex **3b** (see Table 2). Their shifts are even stronger than for the pyridine adducts. In contrast, the signals of coordinated alkyl isocyanides do not depend as strongly on the nature of the *trans* ligand. Thus, the difference in position of the singlet of coordinated *t*BuNC in **1a** and **4a** is only 0.04 ppm. The signals of coordinated CyNC appear as several broad multiplets in the region $\delta = -0.6$ to 0.9 ppm and their assignment is complicated because of

Table 2. ^{1}H NMR spectroscopic data of the prepared compounds; intervals are given for broad multiplets or groups of multiplets; middle position is given for narrow multiplets

Compound	Macrocycle resonances (ppm)[a]	N-Heterocycle signals (ppm); assignment and multiplicity	Resonances of alkyl isocyanide (ppm)	Solvent/frequency
[(Ph_8Pz)Ru(*t*BuNC)$_2$] (**1a**)[6c]	8.33 (*o*-Ph); 7.42−7.57 (*m*-, *p*-Ph)	−	−0.16 (*t*Bu), s	$CDCl_3$/250 MHz
[(Ph_8Pz)Ru(CyNC)$_2$] (**1b**)	8.31 (*o*-Ph); 7.44−7.53 (*m*-, *p*-Ph)	−	−0.38 − 0.86 (Cy), m	$CDCl_3$/250 MHz
[(Ph_8Pz)Ru(bpy)$_2$] (**2c**)	8.23 (*o*-Ph); 7.56 (*m*-Ph); 7.45 (*p*-Ph)	3.14 (α), m; 5.82 (β), m; 6.67 (β′), m; 8.28 (α′), m	−	CD_2Cl_2/400 MHz
[(Ph_8Pz)Ru(*t*BuNC)]$_2$(bpy) (**2a**)	8.17 (*o*-Ph); 7.35−7.50 (*m*-, *p*-Ph)	2.40 (α, α′), m; 4.95 (β, β′), m	−0.28 (*t*Bu), s	$CDCl_3$/250 MHz
[(Ph_8Pz)Ru(CyNC)]$_2$(bpy) (**2b**)	8.10 (*o*-Ph); 7.48 (*m*-Ph); 7.40 (*p*-Ph)	2.44 (α, α′), m; 4.94 (β, β′), m	−0.65 − 0.80 (Cy), m	CD_2Cl_2/400 MHz
[(Ph_8Pz)Ru(CH_3Im)$_2$] (**3a**)	8.18 (*o*-Ph); 7.53 (*m*-Ph); 7.41 (*p*-Ph)	2.42 (−C*H*$_3$), s; 2.69 (*4*), m; 3.11 (*2*), m; 5.09 (*5*), m	−	CD_2Cl_2/400 MHz
[(Ph_8Pz)Ru(CH_3Im)(CyNC)] (**3b**)	8.30 (*o*-Ph); 7.43−7.56 (*m*-, *p*-Ph)	2.35(−C*H*$_3$), s; 2.13 (*4*), m; 2.53 (*2*), m; 4.97 (*5*), m	−0.44 − 0.95 (Cy), m	$CDCl_3$/250 MHz
[(Ph_8Pz)Ru(Py)$_2$] (**4c**)[6c]	8.25 (*o*-Ph); 7.37−7.53 (*m*-, *p*-Ph)	3.03 (α), m; 5.56 (β), m; 6.30 (γ), m	−	$CDCl_3$/250 MHz
[(Ph_8Pz)Ru(Py)(*t*BuNC)] (**4a**)	8.33 (*o*-Ph); 7.43−7.58 (*m*-, *p*-Ph)	2.75 (α), m; 5.59 (β), m; 6.33 (γ), m	−0.20 (*t*Bu), s	$CDCl_3$/250 MHz
[(Ph_8Pz)Ru(Py)(CyNC)] (**4b**)	8.30 (*o*-Ph); 7.40−7.56 (*m*-, *p*-Ph)	2.77 (α), m; 5.61 (β), m; 6.34 (γ), m	−0.55 − 0.96 (Cy), m	$CDCl_3$/250 MHz

[a] Signals appear as multiplets.

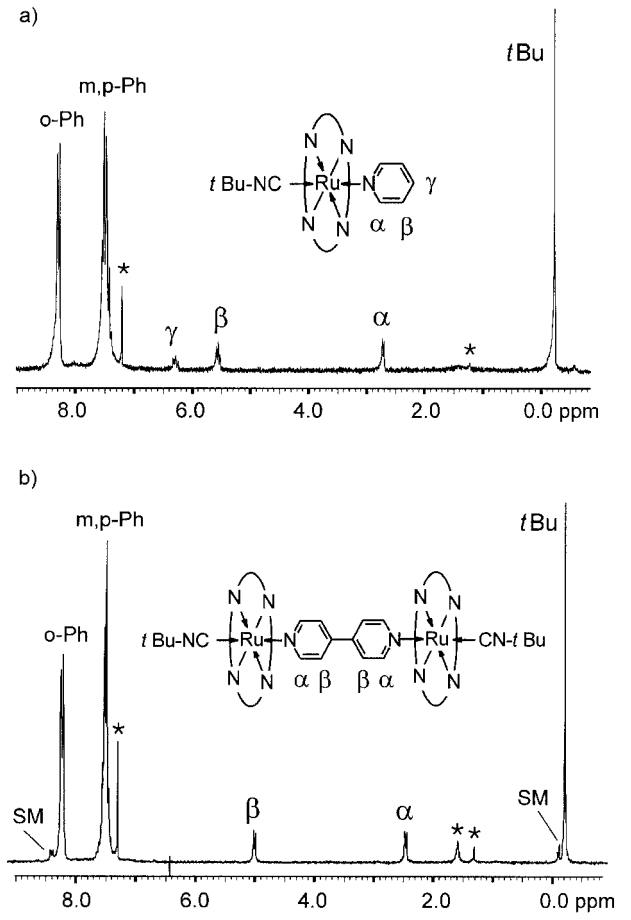


Figure 3. ^{1}H NMR spectra of [(Ph_8Pz)Ru(Py)(*t*BuNC)] (a) and [(Ph_8Pz)Ru(*t*BuNC)]$_2$(μ-bpy) (b) in $CDCl_3$ (250 MHz); signals of impurities ($CHCl_3$, H_2O etc.) are marked with an asterisk; signals of starting materials are denoted as SM

the different possible conformations of CyNC (axial and equatorial position of NC group, for example).

The upfield shift of the proton signals of nitrogen heterocycles upon *trans* substitution with isocyanide can be explained as an effect of the displacement of the central metal from the macrocycle plane towards a stronger coordinating axial ligand, which is an isocyanide in our case. The crystal-structure parameters summarized in ref.[10] clearly show, for example, a tendency of carbonyl coordinated *trans* to pyridine, THF or DMF in Fe, Ru or Os complexes to pull the metal out of the Por or Pc plane. In our case, the nitrogen heterocycle *trans* to the isocyanide ligand is closer to the macrocycle plane than in the bis-heterocycle adduct, and therefore is more strongly affected by the ring-current of the macrocycle. Additional effects of electron redistribution between axial ligands can also play a role. For example, the binding energy of isocyanide in these mixed-ligand complexes is higher than that in bis-isocyanide adducts due to the weaker *trans* effect of the nitrogen heterocycle, resulting in a stronger π-back bonding effect of isocyanide. Therefore, a shorter bond between the coordinating carbon of the isocyanide and the central metal should be expected. Indeed, an increase of the π-back bonding effect of the isocyanide in mixed-ligand complexes of (Ph_8Pz)Ru compared to the corresponding bis-isocyanide adducts can be observed as a lowering of the stretching vibration frequency of the NC group.[6c,14] Thus, ν_{NC} was found to be 2135 cm^{-1} and 2120 cm^{-1} for [(Ph_8Pz)Ru(*t*BuNC)$_2$] (**1a**) and [(Ph_8Pz)Ru(Py)(*t*BuNC)] (**4a**), respectively. Similarly, for cyclohexyl isocyanide-containing complexes **1b** and **4b** it is 2151 and 2128 cm^{-1}, respectively.

Products **2a** and **2b** from the reaction of 4,4′-bipyridine with bis-isocyanide adducts **1a** and **1b** exhibit an analogous decrease of the NC-group vibration frequency, indicating the substitution of one molecule of isocyanide. In their ^{1}H NMR spectra only two multiplets (doublets of doublets) belonging to the coordinated bipyridine were observed at approximately δ = 2.4 and 4.9 ppm, whereas in the ^{1}H NMR spectrum of the bis adduct **2c** with 4,4′-bipyridine four multiplets (doublets of doublets) of bipyridine were observed at δ = 3.14, 5.82, 6.67 and 8.28 ppm (α, β, β′ and α′ respectively, see Scheme 3). Additionally, integration of the signals in the ^{1}H NMR spectra of **2a** and **2b** shows that the ratio between the macrocycle and bipyridine in these compounds is 2:1. This allowed us to ascribe a dimeric structure to these compounds with bipyridine as bridging ligand (see **b** in Figure 3). For **2a** and **2b** the α and α′ protons become magnetically equivalent, as do the β and β′ protons, giving only two signals, α and β, for the coordinated bridging bipyridine. The shielding effect of two macrocycles towards the protons of the bridging ligand is almost additive, which can be seen as follows:

δ_d (β, β′) ≈ δ_m (β) − [δ_m (β′) − δ_m (β)], or 4.9 ≈ 5.82 − (6.67 − 5.82)

where δ_d is the chemical shift of the corresponding proton in the dimers **2a** and **2b** and δ_m is the chemical shift of the corresponding protons in the monomeric compound **2c**. This was also observed in our previous work on iron complexes of octaphenylporphyrazine with diisocyanodurole as axial ligand, where a mixture of corresponding linear oligomers was analyzed by means of ^{1}H NMR spectroscopy.[6d] In the present case, self-assembly of ruthenium porphyrazine complexes to give the dimeric structures **2a** or **2b** occurs, even in the presence of excess 4,4′-bipyridine, with practically no formation of monomeric mixed-ligand complexes, as was mentioned above and can also be seen from the ^{1}H NMR spectra of the products (see **b** in Figure 3 for example). This fact, to the best of our knowledge, has not been observed before for phthalocyanine complexes of ruthenium, although the preferential formation of a dimeric species upon interaction of *trans*-(ethanol)(carbonyl)(octaethylporphyrinato)ruthenium(II) with an excess of different diaza compounds has been reported previously.[15] In our case the self-assembly leading to the symmetric dimers **2a** or **2b** could be realized either during the reaction of bis-isocyanide adducts **1a** or **1b** with 4,4′-bipyridine (thermodynamically controlled possibility of error-correction towards more organized system[16]) or during purification of the reaction product, for example when removing the excess bipyridine and column chromatography (shifting the equilibrium towards dimeric species by removal of the excess of bridging ligand). However, for realization of the latter case it is

necessary that the corresponding monomeric mixed-ligand complexes [(Ph_8Pz)Ru(bpy)(RNC)] are labile enough towards splitting off the coordinated axial ligand (bipyridine) even at room temperature, which is not the case for the starting bis-isocyanide adducts **1a** and **1b**, as mentioned above. On the other hand, the additional forces leading to a stabilization of the dimeric structures **2a** and **2b** (e.g. van der Waals interaction of the macrocycles in the dimer) are required to shift the equilibrium from the monomeric towards the dimeric species.

The chemical shifts of the protons in the peripheral phenyl groups also depend on the structure of the complexes and the nature of the axial ligands. In general, in the spectra recorded at 250 MHz the phenyl protons appear as two multiplets: a downfield-shifted multiplet for the *ortho* protons, and a multiplet for the *meta* and *para* protons in the region $\delta = 7.4-7.6$ ppm. At 400 MHz these signals become better resolved giving three multiplets, which can be considered as a doublet (*ortho* protons) and two triplets (*meta* and *para* protons) showing an upfield shift of the same order. The chemical shift of the *ortho* protons appears to be the most sensitive to the nature of the axial ligands: axial ligands exhibiting stronger π-acceptor properties, such as isocyanides, lead to a slight downfield shift of the *ortho* proton signals. For example, their resonances in [(Ph_8Pz)Ru(*t*BuNC)$_2$] (**1a**), [(Ph_8Pz)Ru(Py)(*t*BuNC)] (**4a**), [(Ph_8Pz)Ru(Py)$_2$] (**4c**) and [(Ph_8Pz)Ru(CH_3Im)$_2$] (**3**) are observed at $\delta = 8.33$, 8.33, 8.25 and 8.18 ppm, respectively. In the dimeric species **2a** and **2b** they are shifted upfield because of the mutual shielding effect of the neighboring macrocycles and appear at $\delta = 8.17$ and 8.10 ppm, respectively (see Table 2).

No mutual co-facial electronic interaction of the neighboring macrocycles in the dimeric species **2a** and **2b** was observed in the UV/Vis spectra (no noticeable broadening or blue shift of the dimer's Q-band), probably due to the comparatively large distance between the macrocycles. The UV/Vis spectral pattern displayed by these compounds was found to be practically the same as that of the monomeric mixed-ligand complexes, such as [(Ph_8Pz)Ru(Py)(*t*BuNC)] (**4a**). The molar-absorption coefficients for the most intense bands are almost double those of the monomeric species.

The most noticeable changes in the UV/Vis spectra of all prepared compounds, caused by axial-ligand exchange, occur in the region of the B-band (350−360 nm) and charge-transfer (CT) band[6c] (400−500 nm). The Q-band experiences only a slight red shift if a strong π-accepting axial ligand is substituted by a weaker acceptor, whereas the B-band shifts noticeably to the blue if axially coordinated isocyanides are substituted by nitrogen heterocycles. The explanation for these observations is given in our previous work.[6c] The CT bands between 400 and 500 nm are perhaps the most sensitive to the nature of the axial ligands. Their intensity and bathochromic shift increase unambiguously with decreasing π-accepting properties of the axial ligands. However, even one coordinated molecule of isocyanide is enough to noticeably shift these CT-bands hypsochromically due to its pronounced π-accepting effect. Therefore, the position and intensity of the CT bands in mixed-ligand complexes is closer to those in bis-isocyanide adducts than in bis-heterocycle adducts (see Figure 1). The spectral changes shown in Figure 1 are typical for the whole series of adducts (bis-isocyanide → mixed-ligand → bis-heterocycle) and independent of the nature of the isocyanide or the heterocycle. This also allows us to see whether one or two isocyanide molecules are substituted by nitrogen heterocycles by UV/Vis spectroscopy. The obtained UV/Vis data for the prepared complexes are summarized in Table 3.

Experimental Section

The following equipment was used for the characterization of compounds: UV/Vis: Hitachi U-2000 and Specord M-40. IR: Specord M-80, Bruker IFS-48. ^1H and ^{13}C NMR: Bruker AC 250 and AC 400; elemental analysis: Carlo−Erba Elemental Analyzer 1104, 1106.

The kinetics of axial ligand substitution in [(Ph_8Pz)Ru(*t*BuNC)$_2$] was studied spectrophotometrically, registering the changes in optical density at the wavelength of the absorption maximum growth during the course of the reaction, using a computer-linked Hitachi U-2000 spectrophotometer with a thermostatted probe-holder. A series of experiments with constant concentrations of starting [(Ph_8Pz)Ru(*t*BuNC)$_2$] (approx. 2×10^{-5} M) in toluene and three different concentrations of pyridine in toluene were carried out at three different temperatures. Before mixing, the solutions of [(Ph_8Pz)Ru(*t*BuNC)$_2$] and pyridine were thermostatted separately. Toluene and pyridine for kinetic studies and for the syntheses were purified by standard procedures.[8] Other solvents were used without additional purification. Cyclohexyl isocyanide was prepared ac-

Table 3. UV/Vis data of the prepared compounds

Compound	Absorption maxima, nm (log ε)	Solvent
[(Ph_8Pz)Ru(*t*BuNC)$_2$] (**1a**)[6c]	276 (4.80); 364 (4.97); 421 (4.05); 443 (4.07); 540 (4.47); 585 (5.00)	CH_2Cl_2
[(Ph_8Pz)Ru(CyNC)$_2$] (**1b**)	365; 421; 445; 542; 588	$CHCl_3$
[(Ph_8Pz)Ru(bpy)$_2$] (**2c**)	286 (4.76); 349 (4.79); 470 (4.50); 541 (4.41); 587 (4.91)	CH_2Cl_2
[(Ph_8Pz)Ru(*t*BuNC)]$_2$(bpy)] (**2a**)	276 (5.16); 353 (5.27); 431 (4.63); 538 (4.78); 583 (5.26)	CH_2Cl_2
[(Ph_8Pz)Ru(CyNC)]$_2$(bpy)] (**2b**)	357; 449; 541; 587	$CHCl_3$
[(Ph_8Pz)Ru(CH_3Im)$_2$] (**3a**)	301 (4.82); 349 (4.86); 503 (4.55); 546 (4.43); 594 (4.89)	CH_2Cl_2
[(Ph_8Pz)Ru(CH_3Im)(CyNC)] (**3b**)	359; 450; 542; 588	$CHCl_3$
[(Ph_8Pz)Ru(Py)$_2$] (**4c**)[6c]	288 (4.79); 349 (4.86); 407 (4.21); 473 (4.41); 541 (4.49); 588 (4.98)	CH_2Cl_2
[(Ph_8Pz)Ru(Py)(*t*BuNC)] (**4a**)	277 (4.79); 354 (4.93); 448 (4.25); 538 (4.50); 585 (5.02)	CH_2Cl_2
[(Ph_8Pz)Ru(Py)(CyNC)] (**4b**)	358 (4.91); 449 (4.25); 541 (4.48); 588 (5.01)	$CHCl_3$

cording to the literature procedure.[9] Other chemicals were acquired from commercial sources.

Synthesis of the starting material {"crude" [(Ph_8Pz)Ru]} for the preparation of the axially coordinated complexes [(Ph_8Pz)RuL_2], as well as the synthesis of [(Ph_8Pz)Ru(*t*BuNC)$_2$] (**1a**), have been described before.[6c] Other complexes were prepared as described below.

Bis(cyclohexyl isocyanide)(octaphenylporphyrazinato)ruthenium(II) [(Ph_8Pz)Ru(CyNC)$_2$] (1b): Crude [(Ph_8Pz)Ru] (65 mg) was refluxed in a mixture of cyclohexyl isocyanide (2 mL) and toluene (5 mL) for 24 h. After cooling, 100 mL of CH_2Cl_2 was added to the reaction mixture and stirred for 24 h to dissolve the product as completely as possible. The formed solution was filtered and chromatographed on Al_2O_3 with CH_2Cl_2 as eluent The blue-colored fraction was collected, the solvent was partially evaporated and methanol (ca. 100 mL) was added to precipitate the product, which was filtered off, washed with methanol and dried. Yield 37 mg (49%) of a dark-violet powder. IR (KBr): $\tilde{\nu}$ = 3048 w, 2936 m, 2856 w, 2152 vs, 1600 w, 1560 w, 1472 s, 1448 m, 1368 m, 1320 w, 1168 s, 1088 m, 992 s, 912 w, 888 w, 832 w, 768 w, 744 m, 696 s cm^{-1}. $C_{78}H_{62}N_{10}Ru$ (1240.5): calcd. C 75.52, H 5.04, N 11.29; found C 75.06, H 5.29, N 10.93.

Bis(4,4′-bipyridine)(octaphenylporphyrazinato)ruthenium(II) [(Ph_8Pz)Ru(bpy)$_2$] (2c): Crude [(Ph_8Pz)Ru] (150 mg) was stirred in molten 4,4′-dipyridine hydrate (4 g) at 130 °C for 10 h. After cooling, the reaction mixture was suspended in 200 mL of methanol. The insoluble residue was filtered off, washed thoroughly with methanol and chromatographed as described for [(Ph_8Pz)Ru(CyNC)$_2$]. Yield 120 mg (63%) of a dark-red powder. IR (KBr): $\tilde{\nu}$ = 3049 m, 1594 m, 1468 s, 1448 m, 1405 m, 1367 m, 1171 s, 1066 w, 1004 s, 991 s, 912 w, 887 w, 829 m, 808 m, 779 m, 770 m, 741 m, 693 s, 623 w, 608 m, 542 m cm^{-1}. $C_{84}H_{56}N_{12}Ru{\cdot}2H_2O$ (1334.5 + 36): calcd. C 73.61, H 4.41, N 12.26; found C 73.26, H 4.26, N 11.95.

Bis(*N*-methylimidazole)(octaphenylporphyrazinato)ruthenium(II) [(Ph_8Pz)Ru(CH_3Im)$_2$] (3a): Crude [(Ph_8Pz)Ru] (120 mg) and *N*-methylimidazole (1 mL) were refluxed in 15 mL of toluene for 24 h. After cooling, 25 mL of CH_2Cl_2 was added to the reaction mixture and the formed solution was chromatographed on Al_2O_3 with CH_2Cl_2 as eluent The first colored fraction was collected, diluted slightly with toluene and left to evaporate to dryness in the air at room temperature to give dark-violet rhombic crystals. Yield 45 mg (33%). IR (KBr): $\tilde{\nu}$ = 3129 w, 3047 w, 1601 m, 1575 w, 1534 w, 1495 w, 1468 s, 1448 m, 1420 w, 1368 m, 1287 w, 1241 w, 1174 s, 1107 m, 1094 m, 1066 w, 1028 w, 1004 s, 992 s, 911 w, 888 w, 829 m, 779 m, 768 m, 740 m, 693 s, 661 w, 616 w, 608 m, 542 m, 524 w, 467 w cm^{-1}. $C_{72}H_{52}N_{12}Ru{\cdot}2.5C_7H_8$ (toluene) (1186.4 + 230.4): calcd. C 75.88, H 5.12, N 11.86; found C 75.54, H 5.17, N 11.62.

***trans*-(*tert*-Butyl isocyanide)(octaphenylporphyrazinato)pyridineruthenium(II) [(Ph_8Pz)Ru(Py)(*t*BuNC)] (4a):** [(Ph_8Pz)Ru(*t*BuNC)$_2$] (**1a**; 64 mg, 54 μmol) in 15 mL of pyridine was heated at 80 °C for 8 h. After cooling, the pyridine was removed in vacuo and the residue was chromatographed as described for [(Ph_8Pz)Ru(CyNC)$_2$] (**1b**). Yield 53 mg (83%). IR (KBr): $\tilde{\nu}$ = 3048 w, 2120 s, 1600 m, 1576 w, 1472 s, 1368 s, 1168 s, 1064 w, 992 s, 912 m, 888 w, 832 m, 744 m, 692 s, 608 m, 544 s, 456 w cm^{-1}. $C_{74}H_{54}N_{10}Ru{\cdot}H_2O$ (1184.4 + 18): calcd. C 73.92, H 4.69, N 11.65; found C 74.18, H 4.61, N 11.58.

***trans*-(Cyclohexyl isocyanide)(octaphenylporphyrazinato)pyridineruthenium(II) [(Ph_8Pz)Ru(Py)(CyNC)] (4b):** [(Ph_8Pz)Ru(CyNC)$_2$] (**1b**; 50 mg, 40 μmol) was heated in 50 mL of pyridine at 100 °C for 5 h. After cooling, the reaction mixture was filtered and the product was isolated from solution as described for [(Ph_8Pz)Ru(Py)(*t*BuNC)] (**4a**). Yield 44 mg (88%). IR (KBr): $\tilde{\nu}$ = 3056 w, 2928 m, 2848 w, 2128 s, 1600 w, 1168 s, 992 s, 696 s cm^{-1}. $C_{76}H_{56}N_{10}Ru{\cdot}H_2O$ (1210.4 + 18): calcd. C 74.31, H 4.76, N 11.40; found C 73.93, H 4.70, N 11.71.

***trans*-(Cyclohexyl isocyanide)(*N*-methylimidazole)(octaphenylporphyrazinato)ruthenium(II) [(Ph_8Pz)Ru(CH_3Im)(CyNC)] (3b):** (Ph_8Pz)Ru(CyNC)$_2$ (**1b**; 25 mg, 20 μmol) and 1 mL of *N*-methylimidazole were heated in 50 mL of toluene at 80 °C for 10 h. The product was isolated as described for [(Ph_8Pz)Ru(Py)(CyNC)] (**4b**). Yield 15 mg (62%). $C_{75}H_{57}N_{11}Ru{\cdot}H_2O$ (1213.4 + 18): calcd. C 73.15, H 4.83, N 12.51; found C 73.51, H 5.25, N 12.88.

(μ-4,4′-Bipyridyl)bis[(*tert*-butyl isocyanide)(octaphenylporphyrazinato)ruthenium(II)] [(Ph_8Pz)Ru(*t*BuNC)]$_2$(μ-bpy) (2a): [(Ph_8Pz)Ru(*t*BuNC)$_2$] (**1a**; 100 mg, 84 μmol) and 4,4′-bipyridine (3 g) were heated in 30 mL of toluene at 90 °C for 16 h. The toluene was then removed under vacuum, and the excess of bipyridine was removed by washing with methanol. The residue was chromatographed (Al_2O_3, dichloromethane), precipitated with methanol and dried. Yield 80 mg (80%). $C_{148}H_{106}N_{20}Ru_2$ (2366.7): calcd. C 75.11, H 4.51, N 11.84; found C 74.79, H 4.90, N 12.02.

(μ-4,4′-Bipyridyl)bis[(cyclohexyl isocyanide)(octaphenylporphyrazinato)ruthenium(II)] [(Ph_8Pz)Ru(CyNC)]$_2$(μ-bpy) (2b): [(Ph_8Pz)Ru(CyNC)$_2$] (**1b**; 100 mg, 81 μmol) was used following the same procedure as described for **2a**. Yield 72 mg (73%). IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} w, 2931 m, 2853 w, 2135 s, 1602 m, 1470 s, 1448 m, 1365 m, 1168 s, 1004 s, 990 s, 829 m, 743 m, 692 s, 607 m, 543 m. $C_{152}H_{110}N_{20}Ru_2{\cdot}H_2O$ (2418.8 + 18): calcd. C 74.92, H 4.63, N 11.50; found C 75.08, H 5.03, N 11.25.

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Received January 15, 2004
Early View Article
Published Online May 13, 2004

