Synthesis and Properties of (Tetra-*tert*-butylphthalocyaninato)ruthenium(II) and (Tetra-*tert*-butyl-2,3-naphthalocyaninato)ruthenium(II)

Michael Hanack*, Siegfried Knecht, and Rainer Polley

Institut für Organische Chemie, Lehrstuhl für Organische Chemie II, der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Received April 20, 1995

Key Words: (Phthalocyaninato)ruthenium, soluble *tert*-butyl-substituted / (2,3-Naphthalocyaninato)ruthenium, *tert*-butyl-substituted / Ruthenium complexes / Phthalocyaninato complexes

The first synthesis of pure *tert*-butyl-substituted (phthalocyaninato)- and (2,3-naphthalocyaninato)ruthenium [(tBu)$_4$MacRu] by thermal decomposition of (tBu)$_4$MacRu(L)$_2$ (L = 3-chloropyridine, ammonia) is described. The compounds were characterized by UV/Vis, IR, and NMR measurements.

Some years ago, we reported on the synthesis of pure (phthalocyaninato)ruthenium(II) (PcRu) by thermal decomposition of PcRu(DMSO)$_2$ · 2 DMSO[1]. Later, we developed a more convenient method for the preparation of pure PcRu via the corresponding bisisoquinoline complex PcRu(iqnl)$_2$[2], which is readily available and can be thermally decomposed at 250°C with formation of pure PcRu[3]. Recently, we also prepared (2,3-naphthalocyaninato)ruthenium(II) (2,3-NcRu) by thermal decomposition of the monomeric complex 2,3-NcRu(L)$_2$ [L = 3-chloropyridine and (2-ethylhexyl)amine][4].

Ruthenium complexes of the type MacRu(L)$_2$ and [MacRu(L)]$_n$ [Mac = Pc, 2,3-Nc; L = e.g. pyrazine (pyz), tetrazine (tz), or 1,4-diisocyanobenzene (dib)] are more stable than the well-studied iron complexes toward oxidation of the central metal atom [M(II) → M(III)][5]. They show an increased stability due to the larger radius of the ruthenium ion.

By peripheral attachment of bulky (e.g. *tert*-butyl) or long-chain groups (e.g. alkyl or alkoxy) to the macrocycles, transition metal phthalocyanine complexes R$_x$PcM(L)$_2$ and their bridged systems [R$_x$PcM(L)]$_n$ can be made soluble in common organic solvents, e.g. chloroform or toluene[6,7]. The *tert*-butyl group is especially suitable to increase the solubility of phthalocyanines in organic solvents[6]. Several attempts to prepare (tetra-*tert*-butylphthalocyaninato)ruthenium(II) (tBu)$_4$PcRu (**1**) have only led to impure (tBu)$_4$PcRu(L)$_x$[8]. However, the crude compound can be used for the preparation of defined bisaxially coordinated monomers (tBu)$_4$PcRu(L)$_2$ (L = e.g. pyridine, *tert*-butyl isocyanide)[9] and oligomers [(tBu)$_4$PcRu(L)]$_n$ (L = dib and me$_4$dib)[8]. For the coordination of weak bases such as pyrazine (pyz) or tetrazine (tz), which are important bridging ligands for e.g. intrinsic semiconductors[6], pure and non-coordinated (tBu)$_4$PcRu (**1**) is necessary because the ligands pyz and tz are not able to remove coordinated impurities in the process of preparation of [(tBu)$_4$PcRu(L)]$_n$, L = pyz, tz, etc.

In this paper we report on the synthesis and properties of pure (tBu)$_4$PcRu (**1**) and (tBu)$_4$-2,3-NcRu (**2**) which are potential precursors of soluble organic semiconductors.

Results and Discussion

For the synthesis of (tBu)$_4$PcRu (**1**) and (tBu)$_4$-2,3-NcRu (**2**) by thermal decomposition of the corresponding bisaxially coordinated monomeric complexes (tBu)$_4$Mac(L)$_2$ attention must be paid to the fact that only the axial ligands and not the peripheral tBu substituents are split off. To attain a low decomposition temperature of the complexes (tBu)$_4$MacRu(L)$_2$ (Mac = Pc, 2,3-Nc) some effects of the ligands L must be taken into consideration, e.g. electronic effects, which led us to use 3-chloropyridine (3-Clpy) because the chlorine atom in the 3-position should lower the coordination strength of the ligand[4]. On the other hand, a back-bonding effect from ruthenium to a π system of the ligand should be excluded. For this reason ammonia which could meet this requirement was selected.

The monomeric complexes (tBu)$_4$PcRu(3-Clpy)$_2$ (**3**) and (tBu)$_4$-2,3-NcRu(3-Clpy)$_2$ (**4**) were prepared by reaction of stoichiometric amounts of 4-*tert*-butylphthalonitrile and 6-*tert*-butyl-2,3-dicyanonapthalene[10], respectively, with RuCl$_3$ · 3 H$_2$O in 2-ethoxyethanol in the presence of an excess of 3-chloropyridine and catalytic amounts of DBU. The bisammonia complex (tBu)$_4$PcRu(NH$_3$)$_2$ (**5**) was obtained by refluxing a mixture of stoichiometric amounts of 5-*tert*-butyl-1,3-dihydro-1,3-diiminoisoindole and RuCl$_3$ · 3 H$_2$O in 2-ethoxyethanol which was saturated with NH$_3$. During the reaction ammonia was bubbled through the solution from time to time.

The monomeric complexes **3**–**5** were characterized by NMR, UV/Vis, IR, and MS as well as by elemental analyses. These complexes are sufficiently soluble in CHCl$_3$ or toluene to record ^{1}H-NMR spectra. The ^{1}H-NMR spectra of phthalocyanines[11] and napthalocyanines[12] are known to show large diamagnetic ring-current shifts. The spectra of the complexes **3**–**5** are in agreement with the proposed

  0009–2940/95/0909–0929 $ 10.00+.25/0

structures. The signals of the macrocyclic protons appear at low field, while the axial ligands are considerably shielded. The shorter the distance between the protons of the axial ligand and the centre of the macrocycle, the larger the shift of the ^1H resonances to higher field. The protons of the axial ligands of (tBu)$_4$-2,3-NcRu(3-Clpy)$_2$ (**4**) are lesser shifted to higher field than those of (tBu)$_4$PcRu(3-Clpy)$_2$ (**3**). This observation is in accordance with other experimental results[12].

In general, tetrasubstituted phthalocyanines are formed as a mixture of four constitutional isomers[13]. In the ^1H-NMR spectra of **3** and **5** the signals of the macrocyclic protons are only weakly split because the protons of the eight non-equivalent isoindole units with regard to their neighbors formed by the synthesis exhibit only slightly different chemical shifts. In (tBu)$_4$-2,3-NcRu(3-Clpy)$_2$ (**4**) the interactions between the *tert*-butyl groups are even weaker, and hence no splitting of the ^1H resonances caused by the existence of a mixture of isomers is observed. The high solubility of (tBu)$_4$PcRu(3-Clpy)$_2$ (**3**) and (tBu)$_4$PcRu(NH$_3$)$_2$ (**5**) made even a ^{13}C-NMR measurement possible. The signals of the quaternary C atoms were separated from those of the tertiary CH atoms by a spin-echo experiment. The resonances of the 3-chloropyridine ligand were assigned by comparison with the ^{13}C-NMR spectrum of the free ligand.

The UV/Vis spectra of **3**–**5** show the typical pattern of a phthalocyanine or a naphthalocyanine, respectively, mainly the π-π^* transitions within the heteroaromatic π system. The absorption maxima recorded in chloroform are given in Table 1. Attachment of the electron-donating *tert*-butyl group to a macrocycle gives rise to a weak bathochromic shift of the Q band in comparison with the corresponding unsubstituted compounds. An increase of the π system on going from complex **3** to **4** leads to a shift of the electronic absorption maxima to longer wavelengths.

Table 1. Electronic absorption maxima [nm] of MacRu(L)$_2$ in chloroform

Compound	Q band			B band		
PcRu(3-Clpy)$_2$ [9]	626	573 sh		402	363	321
(tBu)$_4$PcRu(3-Clpy)$_2$ (**3**)	633	585 sh		410	364	313
(tBu)$_4$PcRu(py)$_2$ [9]	631	580 sh			376	315
2,3-NcRu(3-Clpy)$_2$ [4]	718	688 sh	643			318
(tBu)$_4$-2,3-NcRu(3-Clpy)$_2$ (**4**)	720	692 sh	644	421	365	321
PcRu(NH$_3$)$_2$ [14]	631	579 sh			378	315
(tBu)$_4$PcRu(NH$_3$)$_2$ (**5**)	635	580 sh			382	316
(tBu)$_4$PcRu(tBuNC)$_2$ (**6**) [9]	648	586 sh				314
2,3-NcRu(tBuNC)$_2$ [4]	714	684 sh	641			325
(tBu)$_4$-2,3-NcRu(tBuNC)$_2$ (**7**)	716	688 sh	642			330

The suitability of the bisaxially coordinated complexes **3**–**5** to form pure (tBu)$_4$PcRu (**1**) and (tBu)$_4$-2,3-NcRu (**2**), respectively, after thermal treatment under vacuum was tested by thermogravimetric measurements under nitrogen. Although it is known that the thermal decomposition temperature decreases under vacuum, TG is an easy procedure to get information on the thermal stability of a complex MacM(L)$_2$. The results of the measurements are given in Table 2. The *tert*-butyl substituents start to split off at about

Table 2. Thermal analysis of bisaxially coordinated complexes MacM(L)$_2$ (**3**–**5**)

Compound	Dissociation range [°C]	mass loss (%) calcd./found	T_{max} [°C] (endothermic)
(tBu)$_4$PcRu(3-Clpy)$_2$ (**3**)	160-390	21.3/21.5	297
(tBu)$_4$-2,3-NcRu(3-Clpy)$_2$ (**4**)	250-380	17.9/17.9	370
(tBu)$_4$PcRu(NH$_3$)$_2$ (**5**)	150-375	3.9/4.0	280

400 °C in the case of **3** and **5** and at 430 °C in the case of **4**.

Thermal decomposition experiments under vacuum at 250 °C with complexes **3** and **5** and at 280 °C with complex **4** afforded pure (tBu)$_4$PcRu (**1**) and (tBu)$_4$-2,3-NcRu (**2**), respectively, in quantitative yield by elimination of the ligands. To secure that only the axial ligands and none of the *tert*-butyl groups are split off at the thermal decomposition of the monomers **3**–**5** the obtained **1** and **2** were treated with *tert*-butyl isocyanide to afford (tBu)$_4$PcRu(tBuNC)$_2$ (**6**) and (tBu)$_4$-2,3-NcRu(tBuNC)$_2$ (**7**), respectively. The complexes **6** and **7** were characterized by spectroscopic methods. The number and the integration of the resonances in the ^1H-NMR spectra of **6** and **7** confirmed that no *tert*-butyl substituents are split off during thermal decomposition under vacuum of **3**–**5**. Complex **6** is described in ref.[9], the spectroscopic data of **7** are given in the experimental section.

(tBu)$_4$PcRu (**1**) and (tBu)$_4$-2,3-NcRu (**2**) are black powders which are stable toward air. Compound **1** is soluble in common organic solvents (e.g. benzene, chloroform, acetone) whereas the four *tert*-butyl groups in **2** are not sufficient to increase its solubility in these solvents. The stoichiometry of **1** and **2** was confirmed by elemental analyses. The ^{13}C-CP/MAS-NMR spectra of **1** and **2** and the ^1H-NMR spectrum of **1** recorded in $CDCl_3$ show broad and poorly resolved signals because of the expected paramagnetism of the non-coordinated square-planar ruthenium(II) complexes.

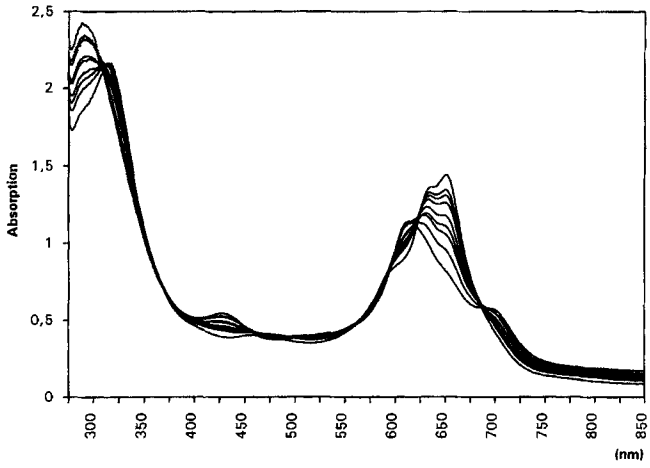
Due to its solubility in organic solvents, we concentrate only on the magnetic and spectroscopic properties of (tBu)$_4$PcRu (**1**). The temperature-dependent measurements of the magnetic susceptibility show **1** to exhibit a paramagnetic behavior with a strong coupling. The magnetic moment increases from 0.63 μ_B (T = 20 K) to 1.68 μ_B (T = 300 K), i.e. it approximates asymptotically the spin-only value of one unpaired electron (1.73 μ_B). Complex **1** therefore has only one spin per ruthenium(II) ion, although for a d^6 transition metal in a square-planar ligand field two unpaired electrons are expected. This points to the fact that **1** exists as a dimeric structure with a ruthenium-ruthenium double bond as reported for (octaethylporphyrinato)ruthenium(II)[15] and recently also for unsubstituted (phthalocyaninato)ruthenium(II), PcRu[16]. For homometallic met-

alloporphyrin dimers a molecular orbital diagram was developed[17] which proposes that only d electrons participate in metal-metal bonding. In addition, the reasonable assumption was made that the dimers have D_{4h} (eclipsed) or D_{4d} (staggered) symmetry. The σ bonds to the porphyrinic nitrogen atoms involve the metal $d_{x^2-y^2}$ levels, and these high-energy σ* orbitals may be ignored for metal-metal bonding[17]. The remaining d orbitals (d_{xz}, d_{yz}, d_{z^2}, and d_{xy}) are available for the metal-metal bonding along the *z* axis. Dimeric ruthenium(II) porphyrins as well as phthalocyanines possess 12 d electrons. The resulting electronic configuration, $\sigma^2\pi^4\delta^{nb4}\pi^{*2}$, produces a formal Ru–Ru double bond with two unpaired electrons (one per macrocycle).

The UV/Vis spectrum of (*t*Bu)$_4$PcRu (**1**) recorded in dried and oxygen-free chloroform under protected conditions shows a broad Q band at λ = 614 nm which is shifted hypsochromically in comparison with bisaxially coordinated complexes (*t*Bu)$_4$PcRu(L)$_2$ (e.g. **3**: 633 nm). The Soret or B band is also shifted to shorter wavelength in comparison with the precursor complex **5**. Furthermore, an absorption at λ = 700 nm is observed. A similar spectrum was also obtained for unsubstituted (phthalocyaninato)ruthenium(II), PcRu[16,18]. The hypsochromic shifts may be caused by particles in the solution, but they can also be due to a dimeric structure of **1**. A comparison of the UV/Vis spectrum of the monomer PcSi(OR)$_2$ with that of the dimer RO–Si(Pc)–O–Si–(Pc)–OR reveals a hypsochromic shift of the Q and the B band[19]. This blue shift is caused by exciton interactions[20] which is evidence of a structure with coplanarly arranged phthalocyanine rings. A red-shifted transition like the observed transition at λ = 700 nm in the UV/Vis spectra of (*t*Bu)$_4$PcRu (**1**) is also observed in the spectra of octaalkoxy-substituted phthalocyaninatodisiloxanes but not in the spectra of unsubstituted phthalocyaninatodisiloxanes[21]. In the case of the phthalocyaninatosilicon compounds this effect was explained by the non-planarity of the substituted macrocycle. From the X-ray powder spectra of dimeric (phthalocyaninato)ruthenium(II), [(PcRu)$_2$], it was concluded that the macrocycles are also not planar[16]. The assumption of a dimeric structure for **1** requires also a strong non-planarity of the phthalocyanine ring system. A dimeric structure may also be responsible for the insolubility of (*t*Bu)$_4$-2,3-NcRu, whereas *tert*-butyl-substituted transition metal 2,3-naphthalocyanines are usually well soluble in common organic solvents[6].

Dissolution of (*t*Bu)$_4$PcRu (**1**) in chloroform in the presence of atomospheric oxygen is accompanied by a rapid color change of the solution from bluish-green to blue. Correspondingly, the UV/Vis absorption spectrum of the solution changes. Initially, the spectrum shows an intense maximum at λ = 289 nm (B band), visible absorption of lower intensity at λ = 426 and 700 nm and the intensive Q band absorption at λ = 614 nm as described above. By recording an UV/Vis spectrum of the solution every five minutes, characteristic spectral changes are observed which go to completion within ca. one hour. With a decrease of the extinction the B band shifts to λ = 318 nm. The Q band also shifts bathochromically from λ = 614 to 654 nm with an increase of extinction. Simultaneously, a shoulder at 596 nm appears whereas the absorptions at 426 and 700 nm disappear. After the reaction, absorptions at λ = 318, 596, and 654 nm are observed in the UV/Vis spectrum (see Figure 1). The UV/Vis reaction spectrum shows isosbestic points at λ = 311, 392, 461, 560, and 685 nm which clearly excludes the formation of spectrally detectable intermediates in going from the first to the final spectrum. The phenomena described here are reproducible and were similarly observed for PcRu[16], where they were assigned to interaction of PcRu with atmospheric oxygen. The dioxygen activation of PcRu was applied to the oxidation of 1-octene with O_2 in THF in the presence of $(C_6H_5CN)_2PdCl_2$ as the olefin activator with selective formation of 2-octanone[16].

Figure 1. UV/Vis spectra of a solution of (*t*Bu)$_4$PcRu (**1**) in the presence of atmospheric oxygen



For (*t*Bu)$_4$PcRu (**1**) and (*t*Bu)$_4$-2,3-NcRu (**2**) an electrical conductivity $\sigma_{RT} = 3.4 \cdot 10^{-7}$ and $1.2 \cdot 10^{-5}$ S · cm^{-1}, respectively, was measured. These conductivities are significantly higher than those observed for monomeric and generally non-conducting metallophthalocyanines and -naphthalocyanines. The high conductivities found for **1** and **2** and also for PcRu ($\sigma_{RT} = 2.0 \cdot 10^{-5}$ S · cm^{-1}[1]) and 2,3-NcRu ($\sigma_{RT} = 3.3 \cdot 10^{-4}$ S · cm^{-1}[4]) may also be caused by the dimeric structure in the solid state[16].

In summary we reported for the first time on the successful synthesis of pure (*t*Bu)$_4$PcRu (**1**) and (*t*Bu)$_4$-2,3-NcRu (**2**). Compound **1** is highly soluble in common organic solvents whereas the influence of the *tert*-butyl group in **2** is insufficient to obtain a noticeable solubility. The magnetic and spectroscopic properties found for **1** are very similar to those observed for PcRu. These results led us to the conclusion that **1** like PcRu forms a dimeric structure in the solid state. The magnetic and spectroscopic behavior of 2,3-NcRu[4] also points to a dimeric structure. Hence we assume that (*t*Bu)$_4$-2,3-NcRu (**2**) also forms a dimer. The ruthenium complexes **1** and **2** were used for the preparation of axially bridged oligomers [MacRu(L)]$_n$ with e.g., L = pyz, tz, bpy which are further investigated with respect to their electrical properties[22]. Using **1** as starting complex we obtained soluble oligomers with chain lengths up to 25 units which were fully characterized in solution[14].

Experimental

6-*tert*-Butylphthalonitrile[7,23,24], 5-*tert*-butyl-1,3-dihydro-1,3-diiminoisoindole[24], and 6-*tert*-butyl-2,3-dicyanonapthalene[10] were prepared according to methods described in the literature. – All reactions involving organometallics were carried out under nitrogen. – Microelemental analyses: Carlo-Erba Elemental Analyzer 1104, 1106. – NMR. Bruker AC 250 (^{1}H, 250 MHz; 13C, 62.9 MHz). – ^{13}C-CP/MAS NMR: Bruker MLS 200 [50.325 MHz, non-quaternary suppression (NQS)]. – FT-IR: Bruker IFS 48. – UV/Vis: Shimdazu UV 2102/3102 Pc. – MS: Finnigan MAT ISQ 70. – TG/DTA: Netzsch Simultan STA 409. – Squid magnetometer: MPMS system, Quantum Design, San Diego, CA.

Bis(3-chloropyridine)(tetra-tert-butylphthalocyaninato)-ruthenium(II) and -(2,3-naphthalocyaninato)ruthenium(II) (**3**, **4**): A mixture of $RuCl_3 \cdot 3\ H_2O$ (1.0 g, 3.8 mmol), 6-*tert*-butylphthalonitrile (2.75 g, 14.91 mmol) or 6-*tert*-butyl-2,3-dicyanonaphthalene (3.43 g, 14.91 mmol), respectively, 3 ml of 3-chloropyridine, 1.5 ml of DBU, and 40 ml of 2-ethoxyethanol was refluxed for 24 h. The cooled solution was poured into methanol/water (1:1), and the precipitate was centrifuged and dried. After purification by column chromatography (silica gel; chloroform) the compounds **3** and **4** were dried at 60 °C in vacuo. – $(t\text{Bu})_4$PcRu(3-Clpy)$_2$ (**3**): Yield: 1.82 g (45%), purple powder. – $C_{58}H_{56}Cl_2N_{10}Ru$ (1065.1): calcd. C 65.43, H 5.30, Cl 6.66, N 13.15; found C 65.79, H 5.49, Cl 7.03, N 12.51. – ^{1}H NMR ($CDCl_3$): δ = 9.20 (m, 4H, Pc), 9.1 (m, 4H, Pc), 7.96 (m, 4H, Pc), 6.00 (d, 2H, Clpy), 5.14 (dd, 2H, Clpy), 2.35 (s, 2H, Clpy), 2.24 (d, 2H, Clpy), 1.72 (s, 36H, *t*Bu). – ^{13}C NMR ($CDCl_3$): δ = 151.70 (–, Pc), 148.80 (+, Clpy), 148.09 (+, Clpy), 143.79 (–, Pc), 143.55 (–, Pc), 140.60 (–, Pc), 138.21 (–, Pc), 133.15 (+, Clpy), 129.94 (–, Clpy), 125.70 (+, Pc), 122.54 (+, Clpy), 121.20 (+, Pc), 118.05 (+, Pc), 35.63 (–, *t*Bu), 32.05 (+, *t*Bu). – IR (KBr): $\tilde{\nu}$ = 3099 cm^{-1} w, 3076 w, 2959 vs, 2903 m, 2866 m, 1614 m, 1590 w, 1555 w, 1491 s, 1466 m, 1394 m, 1364 m, 1317 m, 1281 m, 1256 s, 1191 m, 1151 s, 1128 s, 1115 m, 1091 m, 1051 m, 941 w, 895 w, 829 w, 791 w, 766 m, 758 m, 743 w, 692 w, 669 w. – UV/Vis ($CHCl_3$): λ_{max} = 634, 585 sh, 414, 364, 313 nm. – $(t\text{Bu})_4$-2,3-NcRu(3-Clpy)$_2$ (**4**): Yield: 1.20 g (38%), green powder. – $C_{74}H_{64}Cl_2N_{10}Ru$ (1265.4): calcd. C 70.24, H 5.10, Cl 5.60, N 11.07; found C 70.62, H 5.66, Cl 5.83, N 10.83. – ^{1}H NMR ($CDCl_3$): δ = 9.70 (s, 4H, Nc), 9.66 (s, 4H, Nc), 8.43 (d, 4H, Nc), 8.40 (s, 4H, Nc), 7.87 (d, 4H, J = 8.7 Hz, Nc), 6.07 (d, J = 9.2 Hz, 2H, Clpy), 5.23 (m, 2H, Clpy), 2.69 (d, J = 2.2 Hz, 2H, Clpy), 2.61 (d, J = 4.8 Hz, 2H, Clpy), 1.57 (s, 18H, *t*Bu). – IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} vw, 2959 s, 2905 w, 2868 vw, 1501 m, 1466 m, 1367 s, 1358 vs, 1271 w, 1259 w, 1188 vw, 1163 w, 1144 m, 1113 vs, 1042 w, 949 w, 903 m, 810 w, 754 w, 721 w. – UV/Vis ($CHCl_3$): λ_{max} = 720, 692 sh, 644, 421, 365, 321 nm. – MS (FAB), *m/z*: 1083 [M^+ – 2 · 3-Clpy].

Bis(ammin)(tetra-tert-butylphthalocyaninato)ruthenium(II) (**5**): A mixture of 5-*tert*-butyl-1,3-dihydro-1,3-diiminoisoindol (1.5 g, 7.45 mmol), $RuCl_3 \cdot 3\ H_2O$ (500 mg, 1.9 mmol), and 50 ml of 2-ethoxyethanol was saturated with ammonia and refluxed for 24 h. During the reaction ammonia was bubled through the solution from time to time. The solution was poured into methanol/water (3:1), and the precipitate was centrifuged and dried. Purification was carried out by column chromatography (neutral alumina, chloroform and silica gel, chloroform). After drying (50 °C, 0.01 Torr) pure **5** was obtained; yield: 381 mg (23%), purple powder. – $C_{48}H_{54}N_{10}Ru$ (872.1): calcd. C 66.11, H 6.24, N 16.06; found C 64.31, H 6.26, N 14.20. – ^{1}H NMR ($CDCl_3$): δ = 8.90 (m, 4H, Pc), 8.76 (m, 4H, Pc), 7.84 (m, 4H, Pc), 1.69 (s, 36H, *t*Bu), –5.96 (NH_3). – ^{13}C NMR ($CDCl_3$): δ = 151.34 (–, Pc), 144.04 (–, Pc), 140.95 (–, Pc), 138.15 (–, Pc), 125.32 (+, Pc), 120.78 (+, Pc), 117.46 (+, Pc), 35.52 (–, *t*Bu), 32.04 (+, *t*Bu). – IR (KBr): $\tilde{\nu}$ = 3330 cm^{-1} w, 3264 w, 3080 w, 2957 vs, 2903 s, 2864 m, 1614 m, 1491 s, 1394 m, 1364 m, 1316 m, 1281 m, 1256 s, 1192 m, 1152 s, 1127 s, 1115 m, 1092 m, 1056 m, 944 w, 896 w, 823 m, 766 m, 756 m, 692 w, 669 w. – UV/Vis ($CHCl_3$): λ_{max} = 635, 580 sh, 382, 316 nm. – MS (FD), *m/z*: 837.8 [M^+ – 2 NH_3], 1675.6 [2 · (M^+ – 2 NH_3)].

(Tetra-tert-butylphthalocyaninato)ruthenium(II) (**1**) *and -(2,3-naphthalocyaninato)ruthenium(II)* (**2**): $(t\text{Bu})_4$PcRu(3-Clpy)$_2$ (**3**) (200 mg, 0.19 mmol) or $(t\text{Bu})_4$PcRu$(NH_3)_2$ (**5**) (166 mg, 0.19 mmol) and $(t\text{Bu})_4$-2,3-NcRu(3-Clpy)$_2$ (**4**) (300 mg, 0.24 mmol), respectively, were heated slowly (5 °C/min) in vacuo (0.01 Torr) to a final temperature of 250 or 280 °C, respectively, which was maintained for 8 h to afford pure $(t\text{Bu})_4$PcRu (**1**) and $(t\text{Bu})_4$-2,3-NcRu (**2**), respectively, as black powders in quantitative yield. – **1**: Yield: 159 mg (100%). – $C_{48}H_{48}N_8Ru$ (838.0): calcd. C 68.80, H 5.77, N 13.37; found C 68.01, H 5.99, N 13.01. – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1} w, 2957 vs, 2903 s, 2868 s, 1612 m, 1572 w, 1483 s, 1466 s, 1394 s, 1364 s, 1321 s, 1281 m, 1256 s, 1200 m, 1153 m, 1113 m, 1094 m, 1051 m, 939 m, 890 w, 827 m, 766 w, 752 w, 689 w, 668 w. – UV/Vis ($CHCl_3$): λ_{max} = 700, 614, 426, 289 nm. – **2**: Yield: 246 mg (100%). – $C_{64}H_{56}N_8Ru$ (1038.3): calcd. C 74.04, H 5.44, N 10.79; found C 73.56, H 5.60, N 10.47. – ^{13}C-CP/MAS-NMR (ref. glycine, δ_{COOH} = 176.03): Flip: δ = 147.5, 143.6, 129.3, 123.7, 31.7, NQS: δ = 147.5, 143.6, 131.6, 124.4, 31.6. – IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} w, 2957 vs, 2905 m, 2868 m, 1612 m, 1502 s, 1460 vs, 1393 w, 1364 m, 1323 m, 1312 m, 1271 m, 1258 m, 1161 w, 1148 w, 1109 m, 1096 m, 1042 w, 949 m, 903 s, 810 s, 756 s. – UV/Vis (Uvasol): λ_{max} = 1052, 621, 534, 396, 304 nm. – MS (FAB), *m/z*: 1037 [M^+].

Bis(tert-butyl isocyanide)(tetra-tert-butyl-2,3-naphthalocyaninato)ruthenium(II) (**7**): $(t\text{Bu})_4$-2,3-NcRu (100 mg, 96 mmol) was stirred in a mixture of 1 ml of *tert*-butyl isocyanide and 3 ml of chloroform for 24 h at 50 °C in a tap-top-sealed septum bottle with a teflon-faced cap. The solvent and the excess of ligand were evaporated, and the residue was purified by column chromatography (silica gel, chloroform) and dried (60 °C/0.01 Torr) to afford **7** as a green powder. Yield: 95 mg (82%). – $C_{74}H_{74}N_{10}Ru$ (1204.5): calcd. C 73.79, H 6.19, N 11.63; found C 74.77, H 7.44, N 10.72. – ^{1}H NMR ($CDCl_3$): δ = 9.73 (s, 4H, Nc), 9.70 (s, 4H, Nc), 8.46 (d, 4H, Nc), 8.43 (s, 4H, Nc), 7.89 (d, J = 8.7 Hz, 4H, Nc), 1.63 (s, 36H, *t*Bu), –0.40 (s, 18H, *t*BuNC). – IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} w, 2955 s, 2905 w, 2868 w, 2131 vs, 1616 m, 1501 s, 1369 s, 1356 vs, 1271 m, 1204 m, 1188 m, 1142 s, 1111 vs, 1042 m, 901 s, 889 m, 808 m, 721 s. – UV/Vis ($CHCl_3$): λ_{max} = 716, 688, 642, 330 nm. – MS (FAB), *m/z*: 1121 [M^+ – *t*BuNC], 1038 [M^+ – 2 *t*BuNC].

[1] W. Kobel, M. Hanack, *Inorg. Chem.* **1986**, *25*, 103.
[2] R. Polley, M. Hanack, *Synthesis*, in preparation.
[3] M. Hanack, J. Osio-Barcina, E. Witke, J. Pohmer, *Synthesis* **1992**, 211.
[4] M. Hanack, R. Polley, *Inorg. Chem.* **1994**, *33*, 3201.
[5] T. Nyokong, *Polyhedron* **1993**, *12*, 375.
[6] For reviews: [6a] H. Schulz, H. Lehmann, M. Rein, M. Hanack, *Struct. Bonding (Berlin)* **1990**, *74*, 41. – [6b] M. Hanack, M. Lang, *Adv. Mater.* **1994**, *6*, 819.
[7] [7a] S. A. Mikhalenko, S. V. Barkanova, O. L. Lebedev, E. A. Luk'yanets, *J. Gen. Chem. USSR* **1971**, *41*, 2770. – [7b] T. J. Marks, D. R. Stojakovic, *J. Am. Chem. Soc.* **1978**, *100*, 1695. – [7c] E. A. Cuellar, T. J. Marks, *J. Inorg. Chem.* **1981**, *20*, 3766. – [7d] C. C. Leznoff, S. M. Marcuccio, S. Greenberg, A. B. P. Lever, K. B. Tomer, *Can. J. Chem.* **1985**, *63*, 623. – [7e] M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown, A. J. Thomson, *J. Chem. Soc., Chem. Commun.* **1987**, 1086. – [7f] D. Masurel, C. Sirlin, J. Simon, *New J. Chem.* **1987**, *11*, 455. –

[7g] M. Hanack, A. Gül, A. Hirsch, B. K. Mandal, L. R. Subramanian, E. Witke, *Mol. Cryst. Liq. Cryst.* **1990**, *187*, 365. – [7h] M. Hanack, A. Hirsch, H. Lehmann, *Angew. Chem.* **1990**, *102*, 1499; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1467.

[8] M. Hanack, P. Vermehren, *Synth. Met.* **1989**, *32*, 257.

[9] M. Hanack, P. Vermehren, *Chem. Ber.* **1991**, *124*, 1733.

[10] E. I. Kovshev, V. A. Puchnova, E. A. Luk'yanets, *Z. Org. Chim.* **1971**, *7*, 369.

[11] [11a] C. K. Choy, J. R. Mooney, M. E. Kenney, *J. Magn. Reson.* **1979**, *35*, 1. – [11b] U. Keppeler, W. Kobel, H.-U. Siehl, M. Hanack, *Chem. Ber.* **1985**, *118*, 2095.

[12] B. L. Wheeler, G. Nagasubramanian, A. J. Bard, L. A. Schectman, D. R. Dininny, M. E. Kenney, *J. Am. Chem. Soc.* **1984**, *106*, 7404.

[13] M. Hanack, G. Schmid, M. Sommerauer, *Angew. Chem.* **1993**, *105*, 1540; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1422.

[14] S. Knecht, Ph. D. Thesis, Universität Tübingen, **1994**.

[15] [15a] J. P. Collman, C. E. Barnes, P. N. Swepston, J. A. Ibers, *J. Am. Chem. Soc.* **1984**, *106*, 3500. – [15b] J. P. Collman, H. J. Arnold, *Acc. Chem. Res.* **1993**, *26*, 586.

[16] A. Capobianchi, A. M. Paoletti, G. Pennesi, G. Rossi, R. Caminiti, C. Ercolani, *Inorg. Chem.* **1994**, *33*, 4635.

[17] [17a] F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, J. S. Wood, *Science* **1964**, *145*, 1305. – [17b] F. A. Cotton, *Inorg. Chem.* **1965**, *4*, 334.

[18] J. Pohmer, Ph. D. Thesis, Universität Tübingen, **1994**.

[19] E. Ciliberto, K. A. Doris, W. J. Pietro, G. M. Reisner, D. E. Ellis, I. Fragala, F. H. Herbstein, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1984**, *106*, 7748.

[20] A. S. Davydov, *Theory of Molecular Excitons*, McGraw-Hill, New York, **1962**; M. Kasha in *Spectroscopy of the Excited State* (Ed.: B. DiBartolo), Plenum Press, New York, **1976**, p. 337.

[21] M. K. Engel, Ph. D. Thesis, Universität Tübingen, **1992**.

[22] S. Knecht, R. Polley, M. Hanack, *Appl. Organomet. Chem.*, in press.

[23] J. Metz, O. Schneider, M. Hanack, *Inorg. Chem.* **1984**, *23*, 1065.

[24] M. Hanack, J. Metz, G. Pawlowski, *Chem. Ber.* **1982**, *115*, 2836.

[95053]