

Synthesis of (2,3-Naphthalocyaninato)ruthenium(II) and Reactions with Bidentate Ligands

Michael Hanack* and Rainer Polley

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

Received January 4, 1994

During the course of our work on organic conductors, we have shown that bridged phthalocyaninato transition metal complexes ($[\text{PcM}(\text{L})]_n$ with $\text{M} = \text{Fe}, \text{Ru},$ and Os and $\text{L} = \text{e.g. pyrazine (pyz)}, \text{tetrazine (tz)},$ and p -diisocyanobenzene (dib)) show good to very good semiconducting properties with and without doping.¹ The next higher homolog of phthalocyanine, 2,3-naphthalocyanine (2,3-Nc), has only been used as a macrocycle in the case of 2,3-NcFe, leading to the corresponding bridged systems $[2,3\text{-NcFe}(\text{L})]_n$, $\text{L} = \text{pyz}, \text{tz},$ and dib , which exhibit even better semiconducting properties in comparison with the bridged (phthalocyaninato)iron compounds.¹ From the corresponding bridged (2,3-naphthalocyaninato)ruthenium coordination polymers $[2,3\text{-NcRu}(\text{L})]_n$ with $\text{L} = \text{pyz}$ or tz we expect the same electrical properties but higher complex stabilities.

Some years ago we reported on the synthesis of pure (phthalocyaninato)ruthenium(II), PcRu, by thermal decomposition of $\text{PcRu}(\text{dms})_2 \cdot 2\text{dms}$.² Also (phthalocyaninato)osmium(II) was prepared for the first time using this method.³

Ruthenium complexes of the type $\text{PcRu}(\text{L})_2$ and $[\text{PcRu}(\text{L})]_n$, $\text{L} = \text{e.g. pyz}, \text{dib},$ and tz ,² are more stable than the well-studied iron derivatives toward oxidation of the central metal atom.⁴ This, the higher complex stabilities, and the fact that the bridged (2,3-naphthalocyaninato)iron compounds $[2,3\text{-NcFe}(\text{L})]_n$, $\text{L} = \text{pyz}, \text{tz},$ and dib , have better conductivities on account of their lower HOMO–LUMO gap,⁵ prompted us to synthesize for the first time (2,3-naphthalocyaninato)ruthenium(II), 2,3-NcRu^{II}, and the bridged compounds $[2,3\text{-NcRu}(\text{L})]_n$, $\text{L} = \text{pyz}$ and tz .

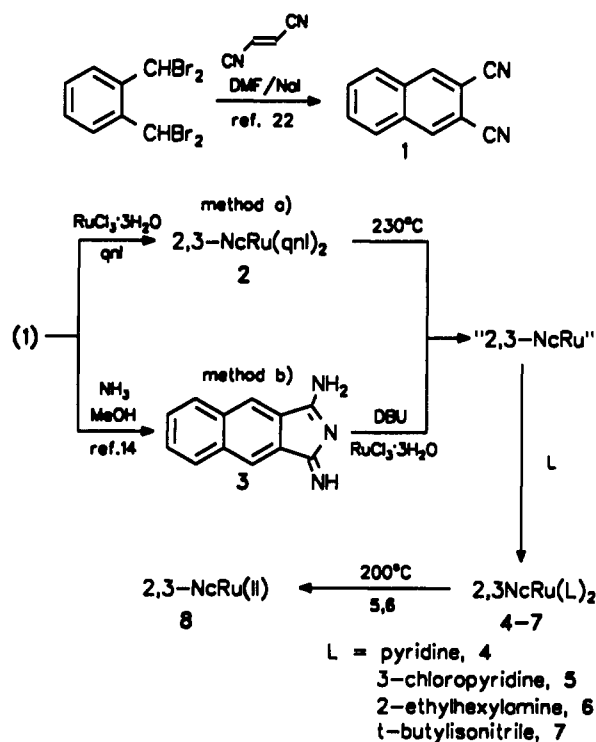
The synthesis of PcRu via the reported $\text{PcRu}(\text{dms})_2$ complex² has some disadvantages like the somewhat tedious reaction path for its preparation and the fact that DMSO is not able to remove coordinative impurities in the case of substituted phthalocyanines, e.g. $t\text{-Bu}_4\text{PcRu}$.⁶ This made the synthesis of soluble, peripherally substituted (phthalocyaninato)ruthenium(II) complexes difficult. Hence we developed a more easy method for the preparation of pure PcRu via the corresponding diquinoline complex $\text{PcRu}(\text{qnl})_2$.⁷ The easily available $\text{PcRu}(\text{qnl})_2$ was thermally decomposed already at 250 °C with formation of pure PcRu.⁷

This new synthesis route provided the basis for the preparation of (2,3-naphthalocyaninato)ruthenium(II) described in this paper.

Results and Discussion

2,3-NcRu(qnl)₂ (**2**) was prepared by refluxing a solution of RuCl_3 and 2,3-naphthalodinitrile (**1**) in quinoline for 4 h. First, the preparation of pure 2,3-NcRu^{II} (**8**) by thermal decomposition

Scheme 1



of the obtained 2,3-NcRu(qnl)₂ (**2**) under vacuum at 230 °C was attempted, but it proved that 2,3-NcRu^{II} (**8**) could not be obtained completely pure by this technique. The reason is the higher oxidative and thermal sensitivity of the 2,3-Nc-ring system.⁸ Therefore only a crude "2,3-NcRu^{II}" of about 80–90% purity was obtained. Crude "2,3-NcRu^{II}" was also obtained by reaction of 1-imino-1H-benz[*f*]-isindol-3-amine (**3**), RuCl_3 , and DBU in ethoxyethanol (Scheme 1). In this case the product contains only about 20% of 2,3-NcRu^{II} besides metal-free 2,3-NcH₂ and other byproducts.

For purification of the crude "2,3-NcRu^{II}" the soluble complexes 2,3-NcRu(L)₂ ($\text{L} = \text{pyridine (py)} (4), 3\text{-chloropyridine (3-Clpy)} (5),$ and 2-ethylhexylamine (2-eha) (**6**)) were synthesized and characterized. Beside these complexes, the more stable *tert*-butyl isocyanide complex, 2,3-NcRu(*t*-BuNC)₂ (**7**), was prepared to allow spectral comparison with the corresponding iron compound.

To reach a low decomposition temperature of the complexes 2,3-NcRu(L)₂ some effects of the ligands L must be taken into account: e.g. electronic effects, which led us to use 3-chloropyridine because the chlorine atom in the 3-position should lower the coordination strength of the ligand. On the other hand, a back-bonding effect from ruthenium to a π -system of the ligand should be excluded. For this reason a saturated ligand, e.g. 2-ethylhexylamine which could meet this requirement, was selected.

The bisaxially coordinated complexes 2,3-NcRu(qnl)₂ (**2**), 2,3-NcRu(py)₂ (**4**), 2,3-NcRu(3-Clpy)₂ (**5**), 2,3-NcRu(2-eha)₂ (**6**), and 2,3-NcRu(*t*-buNC)₂ (**7**) were characterized by UV/vis, IR, NMR, MS, and elemental analyses. The UV/vis spectra of the 2,3-NcRu compounds **2** and **4–7** show a blue shift of the Q-band in comparison with that of 2,3-NcFe(*t*-buNC)₂. The same is true for the Pc compounds listed in Table 1. The observed blue

(1) Schulz, H.; Lehmann, H.; Rein, M.; Hanack, M. *Structure and Bonding*; Buchler, J. W., Ed.; Springer-Verlag: Berlin-Heidelberg, 1990; Vol. 74. Hanack, M.; Datz, A.; Fay, R.; Fischer, K.; Keppeler, U.; Koch, J.; Metz, J.; Mezger, M.; Schneider, O.; Schulze, H.-J. *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. I, p 133. Hanack, M.; Lange, A. *Coord. Chem. Rev.* 1988, 83, 115.

(2) Kobel, W.; Hanack, M. *Inorg. Chem.* 1986, 25, 103.

(3) Hanack, M.; Vermehren, P. *Inorg. Chem.* 1990, 29, 134.

(4) Nyokong, T. *Polyhedron* 1993, 12, 375.

(5) Orti, E.; Piqueras, M. C.; Crespo, R.; Bredas, J. L. *Chem. Mater.* 1990, 2, 110.

(6) Hanack, M.; Vermehren, P. *Chem. Ber.* 1991, 124, 1733.

(7) Hanack, M.; Osio-Barcina, J.; Witke, E.; Pohmer J. *Synthesis* 1992, 211.

(8) Deger, S.; Hanack, M. *Isr. J. Chem.* 1986, 27, 347.

(9) Hudson, A.; Whitfield, J. J. *Inorg. Chem.* 1967, 6, 1120. Vermehren, P. P.Ph.D. Thesis, Universität Tübingen, 1989.

(10) Dolphin, D. H.; James, B. R.; Murray, A. J.; Thornback, J. R. *Can. J. Chem.* 1980, 58, 1125.

(11) Deger, S. P.Ph.D. Thesis, Universität Tübingen, 1986.

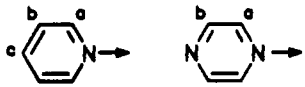
Table 1. Electronic Absorption Maxima (nm) of MacM(L)₂ in Chloroform

compd	Q band		soret band	
PcFe(4-pic) ₂ ⁹	656	594	410	328
PcRu(py) ₂ ¹⁰	625	573	377	313
2,3-NcFe(<i>t</i> -buNC) ₂ ¹¹	750	717 sh	670	359
2,3-NcRu(qln) ₂ (2)	717	688 sh	642	313
2,3-NcRu(py) ₂ (4)	717	688 sh	643	316
2,3-NcRu(3-Clpy) ₂ (5)	718	688 sh	643	318
2,3-NcRu(2-eha) ₂ (6)	722	690 sh	644	315
2,3-NcRu(<i>t</i> -buNC) ₂ (7)	714	684 sh	641	325
2,3-NcRu(py) ₂ (9)	721	690 sh	646	322
[2,3-NcRu(py) ₂] _n (10)	740	670 sh	330	
[2,3-NcRu(tz)] _n (11)	740	665 sh	330	

Table 2. NC Valence Frequencies of MacM(*t*-BuNC)₂

compd.	ν_{NC} , cm ⁻¹	compd.	ν_{NC} , cm ⁻¹
PcFe(<i>t</i> -BuNC) ₂ ¹²	2150	2,3-NcFe(<i>t</i> -buNC) ₂ ¹¹	2147
PcRu(<i>t</i> -buNC) ₂ ¹²	2142	2,3-NcRu(<i>t</i> -buNC) ₂ (7)	2139

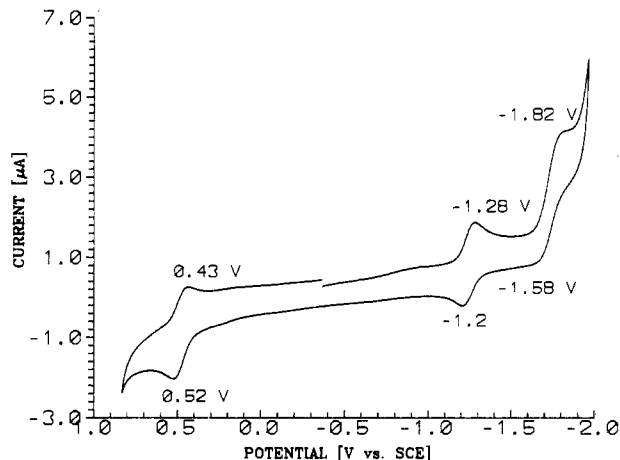
Table 3. ¹H-NMR Data for MacRu(L)₂

compd			
	H ^a	H ^b	H ^c
PcRu(py) ₂ ^{2,15}	2.43	5.21	6.02
2,3-NcRu(py) ₂ (4)	2.75	5.30	6.10
PcRu(py) ₂ ²	2.35	6.43	
2,3-NcRu(py) ₂ (9)	2.78	6.55	

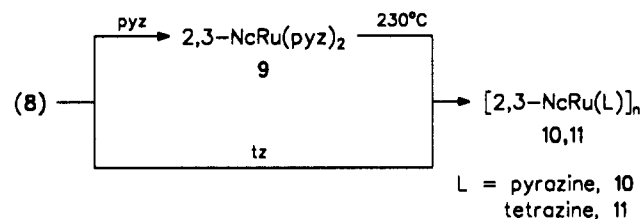
shift can be correlated to the d_π-donor ability of the central metal atom. In the IR spectrum of 7 the CN valence frequency is shifted 8 cm⁻¹ to lower values in comparison with that of 2,3-NcFe(*t*-buNC)₂. The same shift is observed for the corresponding phthalocyanines (Table 2). This is also due to the increase of the π-donor ability of the central metal atom.

The solubility of the bisaxially coordinated complexes 2,3-NcRu(L)₂ in chloroform is sufficient to measure ¹H-NMR spectra. The NMR spectra of phthalocyanines¹³ and naphthalocyanines¹⁴ are known to show large ring current effects. The H^a, H^b, and H^c protons of the axially coordinated ligands in 4 and 9 appear at lower field in comparison with PcRu(L)₂ (Table 3). The high solubility of 2,3-NcRu(2-eha)₂ (6) made even a ¹³C-NMR measurement possible. A spin-echo experiment showed the expected three quartenary C atoms of the macrocycle at 143.6, 137.5, and 133.4 ppm and the CH carbons at 129.7, 126.4, and 120.0 ppm. The secondary C atoms of 2-eha appear at 42.1, 28.5, 27.2, 22.0, and 21.7 ppm. The CH₃ and CH carbons are assigned to signals at 37.7, 13.2, and 9.1 ppm, respectively.

Cyclic voltammetry of 2,3-NcRu(py)₂ (4) was measured in pyridine. The cyclic voltammogram (Figure 1) show one oxidation at 0.48 V and two reductions at -1.24 and -1.70 V. The energy difference (1.72 eV) between the oxidation and the first reduction has the same value as found for the Q-band (717 nm = 1.73 eV) in the UV/vis spectrum. Hence the peaks at 0.48 and -1.24 V can be assigned to an oxidation and reduction of the macrocycle and not of the central metal atom. In the case of the corresponding iron compound 2,3-NcFe(py)₂ the energy difference between the first oxidation and the first reduction step is 1.48 eV with a Q-band at 750 nm (=1.65 eV), indicating that the central iron must be involved in the oxidation or the reduction. This is in accordance with the known examples of iron phthalocyanines;¹⁶ however,

**Figure 1.** Cyclic voltammogram of 2,3-NcRu(py)₂ (4) in pyridine. Scan rate: 20 mV/s, 10 mA.**Table 4.** Thermal Analysis of Bisaxially Coordinated (2,3-Naphthalocyaninato)ruthenium(II) Compounds 2,3-NcRu(L)₂

compd	dissociation range, °C	mass loss (%): calc/found	T _{max} , °C (endothermic)
2,3-NcRu(qln) ₂ (2)	280–410	24.1/25.3	395
2,3-NcRu(py) ₂ (4)	290–380	16.3/18.8	370
2,3-NcRu(3-Clpy) ₂ (5)	270–340	21.8/19.1	327
2,3-NcRu(2-eha) ₂ (6)	230–320	24.1/23.8	312
2,3-NcRu(py) ₂ (9)	180–270	8.2/7.4	239
	290–500	8.2/8.4	451

Scheme 2

ruthenium phthalocyanines in the oxidation state III have not been reported.⁴

The suitability of the bisaxially coordinated complexes 2,3-NcRu(L)₂ to form pure 2,3-NcRu^{II} (8), after thermal treatment under vacuum, was tested with 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 suitability of various 2,3-NcRu₂ complexes to form pure 2,3-NcRu^{II} (8). The results of the measurements are given in Table 4.

Thermal decomposition experiments under vacuum were carried out with complexes 2 and 4–6. Under these conditions compounds 2 and 4 did not afford pure 2,3-NcRu^{II} (8) by scission of the ligand.

An analytically pure 2,3-NcRu^{II} (8) was obtained, however, by thermal decomposition of 2,3-NcRu(3-Clpy)₂ (5) and 2,3-NcRu(2-eha)₂ (6), respectively. The temperature of the decomposition in vacuum was about 200 °C in both cases.

Starting from pure 2,3-NcRu^{II} (8), the bridged systems [2,3-NcRu(py)₂]_n (10) and [2,3-NcRu(tz)]_n (11) were prepared (Scheme 2). For [2,3-NcRu(py)₂]_n (10) an excess of pyrazine was reacted with 2,3-NcRu^{II} (8) leading to 2,3-NcRu(py)₂ (9). The thermogravimetric data show that in the case of 9 the thermal scission of the ligands takes place in two separate steps. At first, the polymer [2,3-NcRu(py)₂]_n (10) is formed, which then decomposes completely to 2,3-NcRu^{II} (8) in the second step. A

(12) Keppeler, U.; Kobel, W.; Siehl, H.-U.; Hanack, M. *Chem. Ber.* **1985**, *118*, 2095.

(13) Choy, C. K.; Mooney, J. R.; Kenney, M. E. *J. Magn. Reson.* **1979**, *35*, 1.

(14) Wheeler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schectman, L. A.; Dininny, D. R.; Kenney, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7404.

(15) Farrell, N. P.; Murray, A. J.; Thornback, J. R.; Dolphin, D. H.; James, B. R. *Inorg. Chim. Acta* **1978**, *28*, L144.

(16) Lever, A. B. P.; Milaeva, E. R.; Speier, G. *Phthalocyanines Properties and Applications*; Leznoff, C. C.; Lever, A. B. P., Eds.; VCH: New York, 1993; Vol. 3.

Table 5. Powder Conductivities of MacM, MacM(py_z)_n, and MacM(tz)_n

compd	σ_{RT} , S/cm	compd	σ_{RT} , S/cm
β -PcFe ²⁰	4×10^{-11}	[2,3-NcFe(py _z) _n] ¹¹	5×10^{-5}
PcRu ²	2×10^{-5}	[2,3-NcRu(py _z) _n] _n (10)	7×10^{-3}
2,3-NcFe ⁸	5×10^{-5}	[PcFe(tz)] _n ¹⁸	2×10^{-2}
2,3-NcRu (8)	3×10^{-4}	[PcRu(tz)] _n ¹⁸	1×10^{-2}
[PcFe(py _z) _n] ²¹	1×10^{-6}	[2,3-NcFe(tz)] _n ¹⁸	3×10^{-1}
[PcRu(py _z) _n] ²	1×10^{-7}	[2,3-NcRu(tz)] _n (11)	4×10^{-2}

similar procedure has been found to occur in the case of PcRu(py_z)₂, affording at first [PcRu(py_z)_n] and then PcRu^{11,2}. Thus the 2,3-NcRu(py_z)₂ complex was decomposed in a nitrogen stream at 230 °C to form [2,3-NcRu(py_z)_n] (10). The tetrazine-bridged [2,3-NcRu(tz)]_n (11) was directly obtained by reacting 2,3-NcRu¹¹ (8) with tetrazine in CHCl₃ at 60 °C.

The characterization of 2,3-NcRu¹¹ (8), [2,3-NcRu(py_z)_n] (10), and [2,3-NcRu(tz)]_n (11) which are practically insoluble in organic solvents was carried out by IR, UV/vis, elemental analyses, ¹³C-CP/MAS-NMR, and FAB-MS. In the FAB-MS of 2,3-NcRu¹¹ (8), the M⁺ peak was found to be the basic peak. The ¹³C-CP/MAS-NMR spectrum of 8 shows only one very wide peak between 113 and 147 ppm with a maximum at 129.5 ppm. The poor resolution is due to the paramagnetism of the axial uncoordinated complex. 2,3-NcRu¹¹ (8) has a magnetic moment of 1.58 μ_B at room temperature. This value corresponds to only one spin per ruthenium. For a d₆-transition metal in a quadratic ligand field we expect two unpaired electrons. The spin of only one electron may be due to weak metal-metal bonds, which are also reported for ruthenium porphyrins.¹⁷ We were not able to obtain a UV/vis spectrum of the deep black 2,3-NcRu (8) in reflection. The UV/vis spectrum of 8 could, however, be measured in H₂SO₄ showing the Q-band at 853 nm.

The ¹³C-CP/MAS-NMR spectra of the diamagnetic 10 and 11 are much better resolved than the spectra of 2,3-NcRu¹¹ (8). Especially the spectrum of the [2,3-NcRu(py_z)_n] (10) corresponds very well to a spectrum of soluble 2,3-NcRu(2-eha)₂ (6) taken in solution. The UV spectra of [2,3-NcRu(tz)]_n (11) show between 1650 and 950 nm a charge-transfer band which is typical for tz-bridged phthalocyanine transition metal coordination polymers.¹⁸ Comparison of the IR spectra of 2,3-NcRu(py_z)₂ (9) and the product left from thermal decomposition confirms the oligomerization and formation of bridged [2,3-NcRu(py_z)_n] (10). The characteristic absorption of the monodentate pyrazine molecule at 1583 cm⁻¹ in 2,3-NcRu(py_z)₂ (9), which is assigned to the centrosymmetric vibrational mode of the axially coordinated pyrazine, appears only as a very weak band after oligomerization.¹⁹ The weak absorption is attributed to the end groups of the oligomer [2,3-NcRu(py_z)_n] (10).¹⁹

The powder conductivities of 2,3-NcRu (8), [2,3-NcRu(py_z)_n] (10), and [2,3-NcRu(tz)]_n (11) were measured by the 4-probe technique to be $\sigma_{RT} = 3 \times 10^{-4}$, 7×10^{-3} , and 4×10^{-2} S/cm, respectively. In comparison with the corresponding iron compounds, the ruthenium compounds 8 and 10 show a 10 times higher conductivity. However, the tetrazine derivative 11 exhibits some decrease in conductivity in comparison with the corresponding iron compound (Table 5).

In summary, we have described for the first time the successful preparation of pure 2,3-NcRu¹¹ (8) and of the coordination polymers [2,3-NcRu(py_z)_n] (10) and [2,3-NcRu(tz)]_n (11).

- (17) Collman, J. P.; Arnold, H. J. *Acc. Chem. Res.* 1993, 26, 586.
 (18) Hanack, M.; Hayashida, S.; Grosshans, R. *Mol. Cryst. Liq. Cryst.* 1992, 217, 197. Keppeler, U.; Deger, S.; Lange, A.; Hanack, M. *Angew. Chem.* 1987, 99, 349. Hayashida, S.; Hanack, M. *Synth. Met.* 1992, 52, 241. Hanack, M.; Lange, A.; Grosshans, R. *Synth. Met.* 1991, 45, 59. Hanack, M.; Gül, A.; Subramanian, L. R. *Inorg. Chem.* 1992, 31, 1542.
 (19) Metz, J.; Schneider, O.; Hanack, M. *Spectrochim. Acta* 1982, 38A, 1265.
 (20) Schneider, O. Ph.D. Thesis, Universität Tübingen, 1983.
 (21) Schneider, O.; Hanack, M. *Angew. Chem.* 1980, 92, 391.

Experimental Section

2,3-Dicyanonaphthalene (1)^{8,22} and 1-imino-1*H*-benz[*f*]-isoindol-3-amine (3)¹⁴ were prepared according to the methods given in the literature. All reactions involving organometallics were carried out under N₂ atmosphere.

Instrumentation. FT-IR: Bruker IFS 48. NMR: Bruker AC 250 (¹H, 250 MHz; ¹³C, 62.9 MHz). ¹³C-CP/MAS-NMR: Bruker MLS 200 (50.325 MHz, nonquaternary suppression (NQS)). UV/vis: Schimadzu 365. MS: Finnigan TSQ 70. TG/DTA: Netzsch Simultan STA 409. Micro elemental analyses: Carlo Erba Elemental Analyser 1104, 1106. Squid magnetometer: MPMS system, Quantum Design, San Diego, CA. Cyclic voltammetry: PAR-273 (Fa. EG & G). Working electrode: Pt-disk. Counterelectrode: Pt-sheet. Reference electrode: Ag-wire. Internal reference: ferrocene.

Bis(quinoline)(2,3-naphthalocyaninato)ruthenium(II) (2). A mixture of RuCl₃·3H₂O (500 mg, 1.9 mmol), 2,3-dicyanonaphthalene (1) (6 g, 33 mmol), and freshly distilled quinoline (20 mL) was refluxed for 4 h. After cooling, the excess of quinoline was removed under reduced pressure. The residue was purified by column chromatography (silica gel/CHCl₃) and dried (100 °C, 0.01 Torr) to afford 2. Yield: 1.10 g (54%). Anal. Calc for C₆₆H₃₈N₁₀Ru (*M_r* = 1072.2): C, 73.9; H, 3.6; N, 13.0. Found: C, 71.7; H, 3.8; N, 12.0. IR (KBr): $\nu = 3051$ w, 1493 s, 1371 vs, 1354 s, 1340 s, 1261 w, 1200 w, 1165 s, 1130 s, 1107 vs, 1037 w, 1016 w, 887 w, 760 s, 739 m, 714 w cm⁻¹. UV/vis (CHCl₃): $\lambda_{max} = 717, 688$ sh, 642, 430, 313 nm. ¹H-NMR (CDCl₃, 250 MHz): $\delta = 9.70$ (s, 8H), 8.47 (m, 8H), 7.75 (m, 8H), 6.93 (m, 2H), 6.75 (m, 2H), 6.65 (m, 2H), 6.45 (d, *J* = 8.3, 2H), 5.64 (d, *J* = 6.9, 2H), 3.43 (s, 2H), 2.66 (d, *J* = 6.7, 2H). MS (FD, CHCl₃): *m/z* = 1073 (M⁺), 1628 [2 × (M⁺ - 2qnl)].

Bis(pyridine)-, Bis(3-chloropyridine)-, Bis(2-ethylhexylamine)-, and Bis(*tert*-butyl isocyanide)(2,3-naphthalocyaninato)ruthenium(II) (4-7). **Method a.** A 1-g amount of 2,3-NcRu(qnl)₂ (2) was heated under vacuum to 250 °C for 8 h. After cooling, the product was extracted with CHCl₃. The residue was dried and stirred in the respective nitrogen base for 1 h at 80 °C. Excess of the solvent was removed at reduced pressure, and the crude 2,3-NcRu(L)₂ was purified by column chromatography (silica gel, CHCl₃) and dried (100 °C, 0.01 Torr).

Method b. A mixture of 1.5 g of the isoindolenine 3, 500 mg of RuCl₃·3H₂O, 1 mL of DBU, and 30 mL of ethoxyethanol was refluxed for 24 h. After cooling, the mixture was poured into methanol and the precipitate was filtered out, dried, and washed with *n*-hexane. The residue was stirred in the respective nitrogen base for 1 h at 100 °C. Excess of the solvent was removed at reduced pressure, and the crude 2,3-NcRu(L)₂ was purified by column chromatography (silica gel, CHCl₃) and dried (100 °C, 0.01 Torr).

Analytical Data for 2,3-NcRu(py_z)₂ (4). Yield (method a): 610 mg (67%). Anal. Calc for C₅₈H₃₄N₁₀Ru (*M_r* = 972.1): C, 71.6; H, 3.5; N, 14.4. Found: C, 70.3; H, 4.2; N, 13.3. IR (KBr): $\nu = 3049$ w, 1493 m, 1447 w, 1371 s, 1354 s, 1340 m, 1261 w, 1200 w, 1163 s, 1130 s, 1107 vs, 1036 m, 1016 m, 951 vw, 885 m, 806 w, 760 s, 739 w, 714 m, 690 w cm⁻¹. UV/vis (CHCl₃): $\lambda_{max} = 717, 688$ sh, 643, 429, 316 nm. ¹H-NMR (CDCl₃, 250 MHz): $\delta = 9.67$ (s, 8H), 8.45 (m, 8H), 7.75 (m, 8H), 6.10 (m, 2H), 5.30 (m, 4H), 2.75 (d, *J* = 5.2 Hz, 4H). MS (FD, CHCl₃): *m/z* = 972 (M⁺), 814 (M⁺ - 2py), 1628 [2 × (M⁺ - 2py)].

Analytical Data for 2,3-NcRu(3-Clpy)₂ (5). Yield (method b): 220 mg (11%). Anal. Calc for C₅₈H₃₂N₁₀Cl₂ (*M_r* = 1040.9): C, 66.9; H, 3.3; N, 13.5; Cl, 6.7. Found: C, 65.5; H, 3.8; N, 12.2; Cl, 7.3. IR (KBr): $\nu = 3049$ w, 1556 vw, 1493 m, 1445 w, 1418 vw, 1371 vw, 1354 s, 1340 m, 1263 vw, 1200 w, 1163 s, 1130 s, 1107 vs, 1036 w, 1016 w, 951 vw, 891 w, 872 vw, 806 vw, 760 m, 740 w, 713 w, 690 vw cm⁻¹. UV/vis (CHCl₃): $\lambda_{max} = 718, 688$ sh, 643, 423, 318 nm. ¹H-NMR (CDCl₃, 250 MHz): $\delta = 9.74$ (s, 8H), 8.48 (m, 8H), 7.76 (m, 8H), 6.10 (m, 2H), 5.26 (m, 2H), 2.70 (s, 2H), 2.62 (d, *J* = 5.8 Hz, 2H). MS (FD, CHCl₃): *m/z* = 813 (M⁺ - 2·3-Clpy), 1631 [2 × (M⁺ - 2·3-Clpy)].

Analytical Data for 2,3-NcRu(2-eha)₂ (6). Yield (method b): 260 mg (13%). Anal. Calc for C₆₄H₅₈N₁₀Ru (*M_r* = 1068.3): C, 71.7; H, 5.8; N, 13.1. Found: C, 71.9; H, 5.8; N, 12.7. IR (KBr): $\nu = 3049$ w, 2955 m, 2924 m, 2856 w, 1493 s, 1462 m, 1371 vs, 1354 s, 1340 s, 1261 w, 1200 m, 1163 s, 1130 vs, 1105 vs, 1036 w, 1014 w, 887 m, 762 s, 714 m cm⁻¹. UV/vis (CHCl₃): $\lambda_{max} = 722, 690$ sh, 644, 439, 315 nm. ¹H-NMR (CDCl₃, 250 MHz): $\delta = 9.69$ (s, 8H), 8.48 (m, 8H), 7.76 (m, 8H), 0.27 (m, 4H), 0.17 (m, 6H), -0.29 (m, 4H), -0.55 (m, 10H), -0.8 (m, 4H), -1.28 (m, 2H), -2.20 (m, 4H), -5.26 (m, 4H). ¹³C-NMR (CDCl₃,

- (22) Luk'yanets, E. A.; Mikhaleiko, S. A. *Zh. Obshch. Khim.* 1969, 39, 2554; *J. Gen. Chem. USSR* 1969, 39, 2449.

250 MHz): $\delta = 143.6, 137.5, 133.4, 129.7, 126.4, 120.0, 42.6, 37.7, 28.5, 27.2, 22.0, 21.7, 13.2, 9.1$. MS (FD, CHCl_3): $m/z = 813$ ($M^+ - 2$ 2-cha), 1629 [$2 \times (M^+ - 2$ 2-cha)].

Analytical Data for 2,3-NcRu(*t*-BuNC)₂ (7). Yield (method a): 540 mg (59%). Anal. Calc for $\text{C}_{58}\text{H}_{42}\text{N}_{10}\text{Ru}$ ($M_r = 980.2$): C, 71.1; H, 4.2; N, 14.3. Found: C, 70.8; H, 4.3; N, 12.9. IR (KBr): $\nu = 3051$ w, 2977 w, 2138 vs, 1492 s, 1371 vs, 1352 s, 1338 s, 1259 w, 1234 w, 1200 m, 1159 s, 1128 s, 1103 vs, 1016 m, 885 m, 758 s, 737 m, 714 cm^{-1} . UV/vis (CHCl_3): $\lambda_{\text{max}} = 714, 684$ sh, 641, 325 nm. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): $\delta = 9.73$ (s, 8H), 8.53 (m, 8H), 7.81 (m, 8H), -0.39 (s, 18H). MS (FD, CHCl_3): $m/z = 813$ ($M^+ - 2t$ -BuNC), 1628 [$2 \times (M^+ - 2t$ -BuNC)].

(2,3-Naphthalocyaninato)ruthenium(II) (8). 2,3-NcRu(3-Clpy)₂ (5) (200 mg, 0.19 mmol) and 2,3-NcRu(2-cha)₂ (6) (200 mg, 0.19 mmol) respectively was heated under vacuum (0.01 Torr) at 200 °C for 6 h. After cooling, the product was extracted with CHCl_3 in a Soxhlet apparatus until the solvent was colorless. The residue was dried (100 °C, 0.01 Torr) to afford pure 2,3-NcRu(II). Yield: 110 mg (71%). Anal. Calc for $\text{C}_{48}\text{H}_{24}\text{N}_8\text{Ru}$ ($M_r = 813.9$): C, 70.8; H, 3.0; N, 13.7. Found: C, 69.0; H, 3.1; N, 13.5. IR (KBr): $\nu = 3053$ w, 1627 m, 1609 m, 1591 m, 1508 s, 1466 s, 1447 vs, 1371 s, 1340 vs, 1315 vs, 1277 m, 1161 m, 1144 m, 1130 s, 1107 s, 1038 m, 1016 m, 949 w, 889 m, 762 vs, 716 cm^{-1} . UV/vis (H_2SO_4): $\lambda_{\text{max}} = 853, 305, 235$ nm. $^{13}\text{C-CP/MAS-NMR}$ (reference glycine, $\delta_{\text{COOH}} = 176.03$ ppm): $\delta = 129.5$; NQS 131.9, 122.2 ppm. MS (FAB): $m/z = 814, M^+$.

Bis(pyrazine)(2,3-naphthalocyaninato)ruthenium(II) (9). 2,3-NcRu^{II} was dissolved in a mixture of pyrazine (1 g) of 10 mL of chloroform at 50 °C. After 4 h, the chloroform was distilled off and the excess ligand was removed by extraction with *n*-hexane in a Soxhlet apparatus over 2 d. NcRu(py₂)₂ was purified by column chromatography (silica gel/ CHCl_3) and dried (80 °C, 0.01 Torr). Yield: 158 mg (54%). Anal. Calc for $\text{C}_{56}\text{H}_{32}\text{N}_{12}\text{Ru}$ ($M_r = 974.0$): C, 69.1, H, 3.3; N, 17.3. Found: C, 69.4; H, 4.0; N, 15.6. IR (KBr): $\nu = 3049$ w, 1538 m, 1504 m, 1493

s, 1416 m, 1371 vs, 1354 vs, 1339 s, 1261 w, 1200 m, 1163 s, 1130 vs, 1107 vs, 1036 m, 1016 m, 953 vw, 889 m, 871 m, 806 w, 760 s, 739 m, 714 cm^{-1} . UV/vis (CHCl_3): $\lambda_{\text{max}} = 721, 690$ sh, 646, 416, 322 nm. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): $\delta = 9.74$ (s, 8H), 8.48 (m, 8H), 7.77 (m, 8H), 6.55 (d, $J = 4.4$ Hz, 4H), 2.78 (d, $J = 4.4$ Hz, 4H). MS (FD, CHCl_3): $m/z = 813$ ($M^+ - 2\text{pyz}$), 1630 [$2 \times (M^+ - 2\text{pyz})$].

(μ -Pyrazine)(naphthalocyaninato)ruthenium(II) (10). 2,3-NcRu-(py₂)₂ (9) (100 mg, 0.1 mmol) was heated under a nitrogen stream slowly to 230 °C. The temperature was kept for 2 h. After cooling, the residue was washed with CHCl_3 and dried (80 °C, 0.01 Torr). Yield: 67 mg (73%). Anal. Calc for $\text{C}_{52}\text{H}_{28}\text{N}_{10}\text{Ru}$: C, 69.9; H, 3.1; N, 15.7. Found: C, 67.4; H, 2.9; N, 14.5. IR (KBr): $\nu = 3049$ w, 1582 w, 1504 w, 1489 m, 1441 w, 1416 w, 1371 s, 1330 vs, 1261 w, 1200 w, 1161 m, 1130 s, 1107 vs, 1036 m, 1016 m, 950 w, 887 m, 869 m, 806 w, 758 s, 736 w, 714 cm^{-1} . UV/vis (flourolube): $\lambda_{\text{max}} = 740, 670$ sh, 420, 330 nm. $^{13}\text{C-CP/MAS-NMR}$ (reference glycine, $\delta_{\text{COOH}} = 176.03$ ppm): $\delta = 143.1, 130.3, 125.9$ sh, 120.1; NQS 142.6, 132.8 ppm. MS (FAB): $m/z = 814, M^+ - \text{pyz}$.

(μ -Tetrazine)(naphthalocyaninato)ruthenium(II) (11). 2,3-NcRu^{II} (8) (162 mg, 0.2 mmol) and tetrazine (18 mg, 0.22 mmol) were stirred in 3 mL of CHCl_3 for 1 d. The product was filtered off, extracted with CHCl_3 , and dried (80 °C, 0.01 Torr). Yield: 150 mg (84%). Anal. Calc for $\text{C}_{50}\text{H}_{26}\text{N}_{12}\text{Ru}$: C, 67.0; H, 2.9; N, 18.8. Found: C, 65.0, H, 3.4; N, 17.0. IR (KBr): $\nu = 3051$ w, 1593 w, 1493 m, 1429 w, 1371 s, 1337 vs, 1263 w, 1200 w, 1161 m, 1130 s, 1105 vs, 1038 m, 1016 w, 953 w, 889 m, 758 s, 735 m, 714 cm^{-1} . UV/vis (flourolube): $\lambda_{\text{max}} = 1650$ – $950, 740, 665$ sh, 400 sh, 330 nm. $^{13}\text{C-CP/MAS-NMR}$ (reference glycine, $\delta_{\text{COOH}} = 176.03$ ppm): $\delta = 147, 128.9$; NQS 132.9, 142.0 ppm. MS (FAB): $m/z = 814, M^+ - \text{tz}$.

Acknowledgment. We thank Dr. L. R. Subramanian for his help with the manuscript, U. Schlick for the cyclic voltammetry, and S. Fiedler for the $^{13}\text{C-CP/MAS-NMR}$ measurements.

Additions and Corrections

1994, Volume 33

M. H. Chisholm,* Ivan P. Parkin, William E. Streib, and O. Eisenstein[†]: Tungsten(6+) Tris(pinacolate): Structure and Comments on the Preference for an Octahedral Geometry Relative to Trigonal Prismatic (D_{3h}) for a d^0 Complex in the Presence of Strong π -Donor Ligands.

Pages 812–815. It has been brought to our attention that the title compound had been previously reported¹ as the ultimate product of the reaction between $(\eta^2\text{-C}_2\text{Ph}_2)\text{W}(\text{O-}i\text{-Bu})_4$ and pinacol. Furthermore, in this communication the authors inferred from spectroscopic data that the compound was chiral and did not racemize on the ^1H NMR time scale. The molybdenum analogue has also been prepared and the crystal and molecular structure of the glycolate $\text{Mo}(\text{OCH}_2\text{CH}_2\text{O})_3$ reported.²

(1) Theopold, K. H.; Holmes, S. J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 1010.

(2) Bath, S.; Wocadlo, S.; Neumüller, B.; Weller, F.; Dehnicke, K. Z. *Naturforsch.* 1992, 47B, 706.