Notiz / Note

Soluble (Phthalocyaninato)ruthenium(II) Phosphane Complexes

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Received June 30, 1993

Key Words: Phthalocyaninato complexes / Ruthenium complexes / Phosphanes

Hitherto unknown ruthenium phthalocyanine complexes with phosphane ligands – $PcRu(PEt_2Ph)_2$ (**1**) and $PcRu(PPh_3)_2$ (**2**) – soluble in common organic solvents were prepared. Two methods were used for their synthesis: 1) Reaction of phthalonitrile with $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in *n*-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 2) reaction of PcRu with the corresponding phosphanes. The products **1** and **2** were characterized by their IR, UV/Vis, FD-MS, and ^{1}H-NMR data.

Transition metal phthalocyanines (PcM), their bisaxially coordinated complexes $PcML_2$, and bridged systems $[PcM(L)]_n$ were investigated intensively by us with respect to their electrical, nonlinear optical or liquid-crystalline properties[1]. A variety of ligands, e.g., acetylenes[2], nitrogen-containing ligands such as pyrazine[1], tetrazine[3], isonitriles such as diisocyanobenzene[1], tetramethyldiisocyanobenzene[4], and cyanide[5], were successfully used to prepare the axially coordinated bridged complexes $[PcM(L)]_n$. We envisaged that structurally distinct ligands with different heteroatoms, e.g., phosphorus, could change the physical properties of the corresponding complexes, especially their solubility in nonpolar solvents. Accordingly, we report in this paper on the phosphane-coordinated ruthenium phthalocyanines $PcRu(PEt_2Ph)_2$ (**1**) and $PcRu(PPh_3)_2$ (**2**). To our knowledge only very few examples of metallophthalocyanines with axial phosphanes were prepared[6–8].

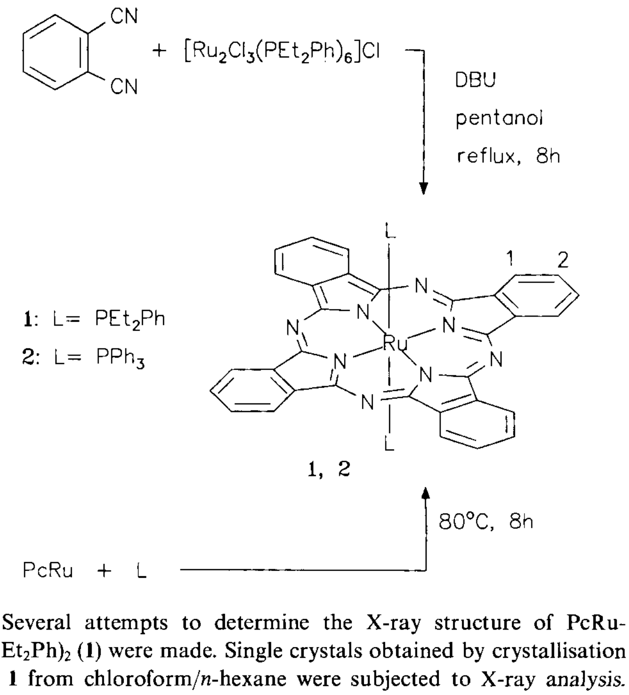
Ruthenium was chosen as the central metal because complexes of the type $PcRuL_2$ and $[PcRu(L)]_n$ are more stable toward oxidation[1,9] of the central metal atom [M(II) → M(III)] in comparison with the well-investigated iron derivatives and show an increased complex stability due to the stronger covalent bonding of the ruthenium ion.

The phosphane complex $PcRu(PEt_2Ph)_2$ (**1**) was prepared by refluxing a solution of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$[10] with phthalonitrile in *n*-pentanol in the presence of DBU (Scheme 1) according to the procedure used for the preparation of some metallophthalocyanines[11]. Complex **1** was also synthesized by stirring PcRu[12,13] with PEt_2Ph at 80°C for 8 hours (Scheme 1). $PcRu(PPh_3)_2$ (**2**) was prepared by stirring PcRu in a melt of PPh_3 for 8 hours at 80°C. Both **1** and **2** are blue powders soluble in common organic solvents, e.g. $CHCl_3$, THF.

The UV/Vis spectra of **1** and **2** in $CHCl_3$ show the typical pattern of a phthalocyanine, mainly the π-π* transition within the heteroaromatic 18-π electron system. The Q bands at $\lambda = 637$ (**1**) and 641 nm (**2**) are accompanied by the characteristic weak satellite bands. The Soret or B bands appear at $\lambda = 303$ (**1**) and 319 nm (**2**).

The ^{1}H-NMR spectra of **1** and **2** show diamagnetic ring-current shifts such as found in other $PcRuL_2$ complexes[14]. The spectra consist of the usual two AA′XX′ patterns (1-H: $\delta = 8.93$ for **1** and 8.83 for **2**; 2-H: $\delta = 7.82$ for **1** and 7.72 for **2** in Pc) at low field, while the axial ligands are considerably shielded by the Pc ring system. The shorter the distance between the protons of the ligand and the centre of the metallophthalocyanine, the larger the shift of the resonances to higher field. For **1** the phenyl protons of the ligand appear at $\delta = 4.34$, 6.28, and 6.71. The signal of the methyl protons of the ethyl groups is observed at $\delta = -1.10$ whereas the signals of the two non-equivalent methylene protons are revealed at $\delta = -1.58$ and -2.00. For **2** the phenyl protons of the triphenylphosphane ligand appear at $\delta = 4.43$, 6.21, and 6.62.

Scheme 1



Several attempts to determine the X-ray structure of $PcRu(PEt_2Ph)_2$ (**1**) were made. Single crystals obtained by crystallisation of **1** from chloroform/*n*-hexane were subjected to X-ray analysis. However, the quality of the crystals was insufficient to solve the structure. Compound **1** crystallizes triclinic, space group $P\bar{1}$ with unit cell dimensions of $a = 1389.8(6)$, $b = 1444.3(7)$, $c = 1450.4(5)$ pm, $\alpha = 67.52(4)$, $\beta = 84.77(3)$, $\gamma = 79.11(3)°$, $V = 2641.1 \cdot 10^6$ pm^3, $Z = 2$.

Chem. Ber. **1993**, *126*, 2565–2566 © VCH Verlagsgesellschaft mbH, D-69451 Weinheim, 1993 0009–2940/93/1111–2565 $ 10.00+.25/0

We are grateful to Dr. *C. Maichle*, Institut für Anorganische Chemie, Universität Tübingen, for performing the X-ray diffraction study.

Experimental

IR: Bruker IFS 48. – UV/Vis: Shimadzu 365. – MS: Varian MAT 711. – ^{1}H NMR: Bruker AC 250. – Elemental analyses: Carlo Erba Elemental Analyzer 1104, 1106. – $[Ru_2Cl_3(PEt_2Ph)_6]Cl$[10] and PcRu[12,13] were prepared according to literature methods.

Bis(diethylphenylphosphane)(phthalocyaninato)ruthenium(II), $PcRu(PEt_2Ph)_2$ (**1**)

Method 1: A mixture of phthalonitrile (1.28 g, 10 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (1.52 g, 10 mmol), and $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ (1.68 g, 1.25 mmol) was heated under nitrogen in 30 ml of *n*-pentanol for 8 h under reflux. The cooled dark blue solution was poured into methanol (50 ml), and the precipitate formed was centrifuged, washed with *n*-hexane and dried. Further purification was performed by column chromatography (alumina neutral/chloroform). The blue fraction was collected and the solvent evaporated, yielding 141.9 mg (12%) of **1** as a blue powder.

Method 2: In a tap-top-sealed septum bottle with a Teflon-faced cap, a suspension of PcRu (153 mg, 0.25 mmol) and PEt_2Ph (831 mg, 5 mmol) was stirred under nitrogen at 80°C for 8 h. The excess of ligand was evaporated, the residue washed with *n*-hexane and then chromatographed as described above on alumina neutral by using chloroform as the eluent. Yield: 113.5 mg (48%). – IR (KBr): $\tilde{\nu} = 3053$ w cm^{-1}, 2970 w, 2937 w, 2808 w, 1558 w, 1539 w, 1489 s, 1458 w, 1435 w, 1414 m, 1325 m, 1288 m, 1169 s, 1123 s, 1065 m, 1041 w, 1028 w, 1007 w, 943 w, 912 w, 841 w, 775 m, 754 s, 735 s, 712 m, 692 m. – UV/Vis ($CHCl_3$): $\lambda_{max} = 637$ nm, 576 (sh), 432, 303. – ^{1}H NMR ($CDCl_3$): $\delta = -2.00$ (m, 4H, CH_2), -1.58 (m, 4H, CH_2), -1.10 (m, 12H, CH_3), 4.34 (m, 4H, Ph), 6.28 (m, 4H, Ph), 6.71 (m, 2H, Ph), 7.82 (m, 8H, Pc, 2-H), 8.93 (m, 8H, Pc, 1-H). – FD-MS ($CHCl_3$), *m/z* (%): 946.8 ($[PcRu(PEt_2Ph)_2]^+$), 780.1 ($[PcRu(PEt_2Ph)]^+$). – $C_{52}H_{46}N_8P_2Ru$ (946.0): calcd. C 66.02, H 4.90, N 11.84; found C 65.11, H 4.91, N 11.51.

(Phthalocyaninato)bis(triphenylphosphane)ruthenium(II), $PcRu(PPh_3)_2$ (**2**): In a tap-top-sealed septum bottle with a Teflon-faced cap, PcRu (153 mg, 0.25 mmol) was stirred in a melt of PPh_3 (1.31 g, 5 mmol) for 8 h at 80°C under nitrogen and then cooled to room temp. After pulverization the blue product mixture was thoroughly washed with *n*-hexane to remove excess ligand and then chromatographed on alumina neutral by using chloroform as the eluent. The blue fraction was collected, and the solvent was evaporated to yield 190.6 mg (67%) of **2** as a blue powder. – IR (KBr): $\tilde{\nu} = 3053$ m cm^{-1}, 2953 w, 2924 w, 1489 s, 1433 m, 1412 m, 1325 m, 1288 m, 1169 s, 1123 s, 1090 m, 1077 s, 1028 w, 1005 w, 974 w, 943 w, 912 w, 775 m, 754 m, 735 s, 696 s. – UV/Vis ($CHCl_3$): $\lambda_{max} = 641$ nm, 582 (sh), 319. – ^{1}H NMR ($CDCl_3$): $\delta = 4.43$ (m, 12H, Ph), 6.21 (m, 12H, Ph), 6.62 (m, 6H, Ph), 7.72 (m, 8H, Pc, 2-H), 8.83 (m, 8H, Pc, 1-H). – FD-MS ($CHCl_3$), *m/z* (%): 875.2 ($[PcRu(PPh_3)]^+$). – $C_{68}H_{46}N_8P_2Ru$ (1138.2): calcd. C 71.76, H 4.07, N 9.84; found C 71.90, H 4.20, N 9.35.

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[206/93]

Heft 11 wurde am 2. November 1993 ausgegeben / Issue 11 was distributed on November 2, 1993

Verantwortlich für den Inhalt: Prof. Dr. Heinrich Nöth, München (Teil A), Prof. Dr. Henning Hopf, Braunschweig (Teil B). Redaktion: Dr. Robert Temme, Weinheim.

VCH Verlagsgesellschaft mbH (Geschäftsführer: Hans Dirk Köhler, Dr. Karlheinz Köpfer), Pappelallee 3, Postfach 101161, D-69451 Weinheim.

Anzeigenleitung: R. J. Roth, Weinheim.

In der Zeitschrift werden keine Rezensionen veröffentlicht; zur Besprechung eingehende Bücher werden nicht zurückgesandt.
Satz und Druck: Krebs-Gehlen Druckerei, Hemsbach/Bergstraße.
Printed on chlorine- and acid-free paper / Gedruckt auf säurefreiem und chlorfrei gebleichtem Papier