Unexpected formation and structural characterisation of a novel rhodium B_{12} analogue

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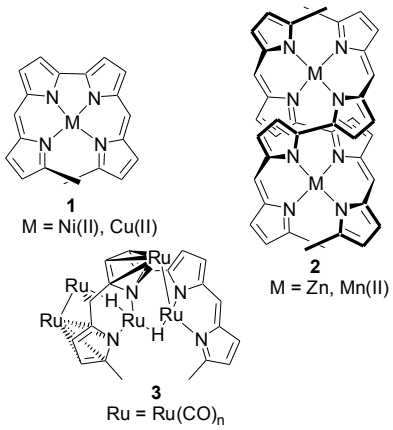
Dedicated to Prof. Dr. Dr. h.c. Helmut Werner for his contributions to inorganic chemistry.

The metalation reactions of 2,2'-bidipyrrin **4** with different rhodium(I) precursors yield the complexes **5** and **6** and the unusual corrinoid **7**, depending only on the type of visitor ligand employed.

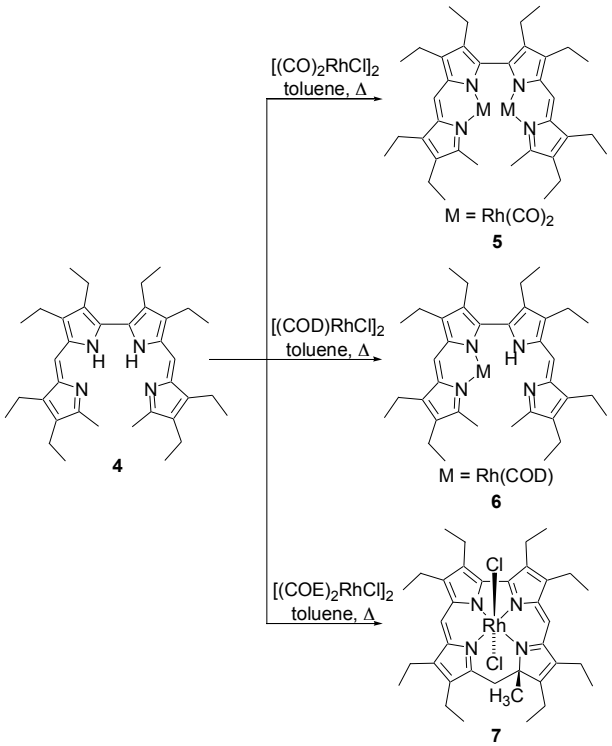
2,2'-Bidipyrrin,[1] an artificial open-chain tetrapyrrolic ligand related to the bile pigments[2] and the porphyrins,[3] has been shown in the past to establish two different binding modes with first row transition metals, i.e. the mononuclear and pseudoplanar mode **1**[4] and the dinuclear cooperative binding mode **2** (scheme 1).[5] For second and third row metals much less is known concerning their action on open-chain oligopyrroles. The available data, however, points towards a variety of unusual electronic and geometric features in these complexes, of which radical ligands[6] and tetra-[7] or pentanuclear cluster complexes as **3**[8] are most noteworthy.



Scheme 1 Known coordination modes of the 2,2'-bidipyrrin ligand.

Upon exploring the chemistry of rhodium-2,2'-bidipyrrins we found, that the nature of the precursor complex, and especially the visitor ligand employed, has a profound impact on the type of product formed. The use of the standard reagents $[(CO)_2RhCl]_2$ and potassium carbonate results, as expected, in the formation of the dinuclear species **5** as dark, green rhombohedra in 95% yield.[9] With $[(COD)RhCl]_2$ as the reagent the metalation stops at the stage of the turquoise mononuclear species **6** (scheme 2). An investigation of molecular models revealed, that the steric influence of the peripheral

ethyl groups of the tetrapyrrole enforces quasimacrocyclic conformations in both, the mono- and the dinuclear species. Therefore, the varying reactivities of $[(CO)_2RhCl]_2$ and $[(COD)RhCl]_2$ with bidipyrrin **4** are most likely caused by the differences in size and steric influence of the carbonyl and cyclooctadiene coligands. Other than the stable **5**, the mononuclear **6** undergoes quick hydrolytic cleavage, probably catalysed by the free NH···N function adjacent to the Rh(COD) moiety, and could be identified by mass spectroscopy only.



Scheme 2 Reactivity of 2,2'-bidipyrrin **4** against different Rh(I) precursors.

The reaction takes an entirely unexpected course, when the sterically even more demanding bis(cyclooctene) precursor $[(COE)_2RhCl]_2$ is used. After chromatographic work-up and recrystallisation, black needles of the novel rhodalamine analogue **7** (red in solution) can be isolated in 30% yield.[10] **7** was unambigously characterized by 1D and

2D nmr techniques. The fate of the former methyl termini of **4** upon cyclisation to **7** can favourably be monitored by the appearance of a singlett at 1.68 ppm [protons at C(36)] and an AB system for the protons at C(19) at 3.63 and 2.46 ppm, respectively, in the ^{1}H nmr, as well as by ^{13}C signals at 81.4 [C(18)], 37.3 [C(19)] and 28.6 ppm [C(36)]. Combustion analysis and EI mass spectra further support the postulated composition of **7**, which appears as a rare example of a rhodium analogue of vitamin B_{12}.[11]

Single crystals of **7** were grown by slow evaporation from a dichloromethane/pentane solution at room temperature. The x-ray structural analysis disclosed a dichloromethane solvate, in which the new macrocyclic complex as well as the solvent molecules are heavily disordered. For this reason, the structure refinement gave rather high deviations for the bond lengths and angles in the tetrapyrrolic ligand. Figure 1 represents an Ortep-plot of the molecule in the higher occupied position.[12]

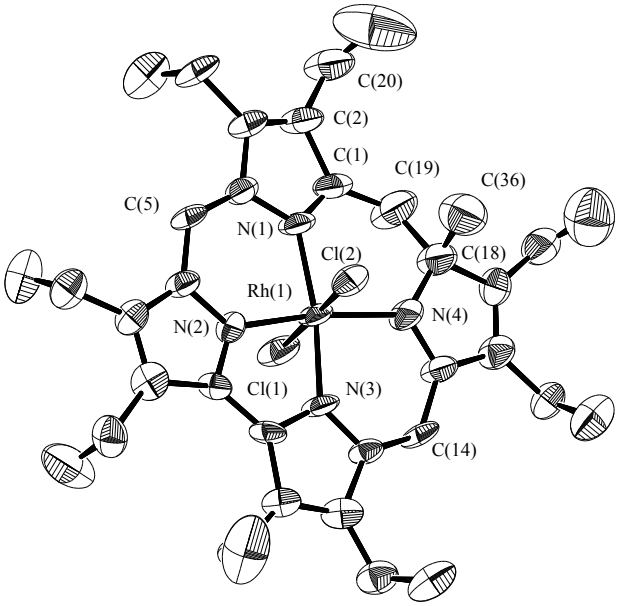
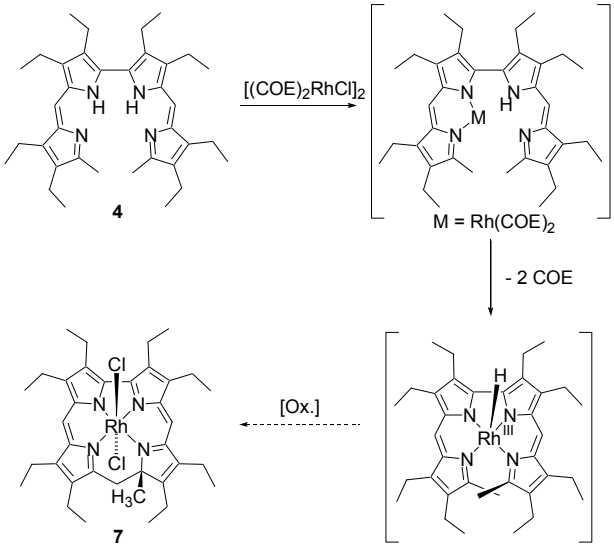


Fig. 1 Ortep plot of the molecular structure of **7**. Selected bond lengths (Å) and bond angles (°): Rh(1)-Cl(1) 2.348(3), Rh(1)-Cl(2) 2.359(3), Rh(1)-N(1) 1.992(7), Rh(1)-

N(2) 1.933(6), Rh(1)-N(3) 1.940(6), Rh(1)-N(4) 1.998(7), Cl(1)-Rh(1)-Cl(2) 178.17(10).

Although the quality of the obtained data does not allow a detailed structural discussion in depth, the x-ray analysis clearly proofs the nmr structural assignments as correct and allows a first glimpse into the molecular arrangement of **7**. Despite the fact, that the sp^3 carbon centres C(18) and C(19) do not allow a flat arrangement of the monoanionic macrocyclic ligand, the central RhN_4-unit is essentielly planar with a mean deviation from planarity of only 0.018 Å. In order to minimise the distortions of the octahedral coordination of the rhodium(III) ion, the tetrapyrrole adopts a weakly ruffled conformation with the largest torsion at the C_4N ring at N(4), which is found tilted at 16.1° with respect to the RhN_4 mean plane. This ligand flexibility also arranges the four N donors in distances of 1.933-1.998 Å from the Rh(III) atom, which are typical for porphyrinoid Rh(III) complexes.



Schema 3 Mechanistic proposal for the early steps in the transformation of **4** to **7**.

Mechanistically we believe, that due to the size of the COE coligands in a first step a mononuclear complex similar to **6** is produced. This Rh(I) complex than looses the COE ligands with concommitant oxidative addition into the adjacent NH-bond (scheme 3). The fate of a so produced Rh(III) hydride complex is not clear, and the formation of a Rh(II) species as a reactive intermediate on the way to **7** can not be ruled out so far.[13] However, as a stoichiometric argument it should be possible to produce **7** also from the reaction of $RhCl_3(H_2O)_3$, 2,2'-bidipyrrin **4** and two equivalents of an oxidant. In fact, with AgOAc as the oxidising agent the formation of **7** proceeds smoothly and in a comparable yield. This experiment strongly points to a mechanism employing a late Rh(III) templated radical ring closure step.

Given the lately published variety of different starting 2,2'-bidipyrrins[1] this new reaction will provide a broad functional entry into the almost unnoticed field of rhodalamin analogues. We are actually exploring these opportunities.

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9 *Spectroscopic data* for **5**: mp. 162°C (decomp.); ^{1}H nmr (400 MHz, CD_2Cl_2): δ = 7.07 (s, 2H), 2.75 (s, 6H), 2.76-2.40 (m, 16H), 1.23, 1.18, 1.14, 0.95 (4×t, 24H); ^{13}C nmr (100.6 MHz, CD_2Cl_2): δ = 186.5, 182.1, 163.3, 152.1, 145.2, 142.2, 134.7, 132.4, 131.6, 131.3, 121.1, 18.7, 18.6, 17.6, 17.5, 16.5, 16.3, 14.5, 14.1; MS (FAB): *m*/*z* 854, M^+; calc. for $C_{40}H_{48}N_4O_4Rh_2$: C 56.21, H 5.66, N 6.55; found: C 56.33, H 5.62, N 6.29%.

10 *Spectroscopic data* for **7**: mp. 109°C (decomp.); ^{1}H nmr (400 MHz, C_6D_6): δ = 7.18 (s, 1H), 6.38 (s, 1H), 3.63, 2.46 (AB, 2H), 2.74-2.00 (m, 16H), 1.68 (s, 3H), 1.24, 1.22, 1.15, 1.14, 1.12, 1.11, 0.98, 0.82 (8×t, 24H); ^{13}C nmr (100.6 MHz,

C_6D_6): δ = 170.8, 170.3, 168.0, 167.7, 150.4, 149.2, 148.9, 144.3, 143.5, 141.8, 141.7, 139.3, 138.7, 138.5, 136.9, 121.5, 107.3, 81.4, 37.3, 28.6, 18.5, 18.4, 18.2, 17.1, 16.9, 16.8, 16.6, 16.4, 16.1, 15.5, 15.2, 14.9, 14.3, 13.6, 13.4, 12.4; MS (FAB): *m*/*z* 708, M^+; calc. for $C_{36}H_{47}N_4Cl_2Rh$: C 60.94, H 6.67, N 7.89; found: C 61.32, H 6.34, N 7.68%.

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12 *Crystal data* for $C_{36}H_{47}N_4Cl_2Rh$ **7** × 2 CH_2Cl_2: black needles, M = 879.44, monoclinic, space group $P\,2_1/n$, a = 14.4846(11), b = 20.5801(15), c = 15.9102(11) Å, β = 115.9660(10)°, U = 4264.0(5) Å^3, Z = 4, D_c = 1.370 g cm^{-3}, μ = 0.807 mm^{-1}, F(000) = 1816, 50221 reflections collected ($1.59 < \theta < 25.35°$) at 173(2) K, 7810 independent (R_{int} = 0.0439), 6449 used in the structure refinement; R_1 = 0.0959 [$I > 2\sigma(I)$], wR_2 = 0.2427 (all data), GOF = 1.160 for 886 parameters and 382 restraints, largest difference peak, hole = 1.618, -0.969 e Å^{-3}.

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