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

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The metalation reactions of the 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 the ancillary 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** (Fig. 1).[5] For second and third row metals much less is known concerning their action on open-chain oligopyrroles. The available data, however, point towards a variety of unusual electronic and geometric features in these complexes, of which radical ligands[6] and tetra-[7] or pentanuclear cluster complexes like **3**[8] are most noteworthy.

Upon exploring the chemistry of rhodium-2,2′-bidipyrrins, we found that the nature of the precursor complex, and especially the ancillary 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 1). 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. The second metalation step should therefore be sterically disfavoured, and it occurs only if the ancillary ligands of the first $Rh(L)_n$ fragment are sufficiently π-acidic to increase the acidity of the second NH moiety through the tetrapyrrole π system. The varying reactivities of $[(CO)_2RhCl]_2$ and $[(COD)RhCl]_2$ with bidipyrrin **4** are thus caused by a combination of steric and electronic differences of the coligands. This interpretation is further supported by the finding that a dark green dinuclear complex is obtained from the reaction of the bidipyrrin **4** with the precursor $[(COD)Rh(\mu\text{-}OMe)]_2$, containing the strongly basic methoxo ligand, in a polar solvent like THF. Other than the stable **5**, the mononuclear **6** and its dinuclear pendant undergo quick hydrolytic cleavage, and could be identified by mass spectroscopy only.

The reaction takes an unexpected course when the sterically 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 unambiguously 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 singlet 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 FAB 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, with occupancies of the major

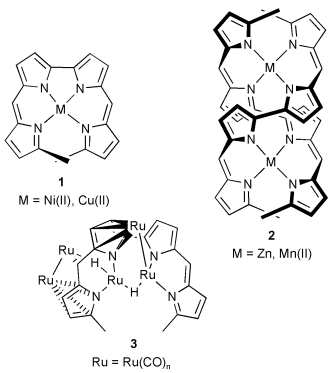
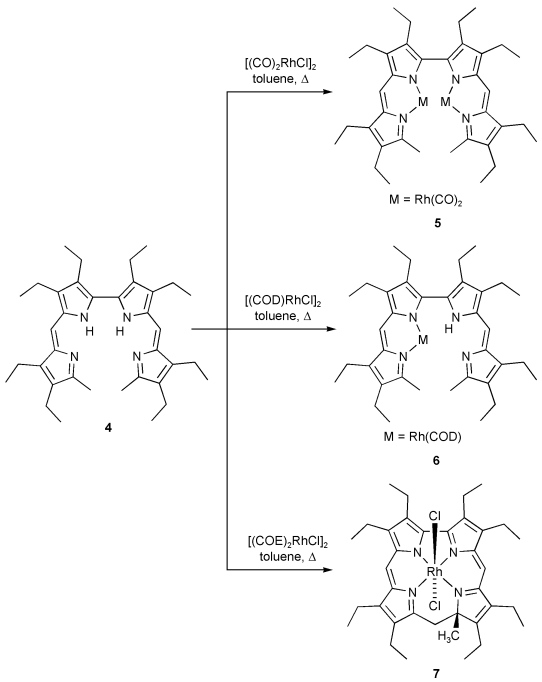


Fig. 1 Known coordination modes of the 2,2′-bidipyrrin ligand.



Scheme 1 Reactivity of the 2,2′-bidipyrrin **4** for different Rh(I) precursors.

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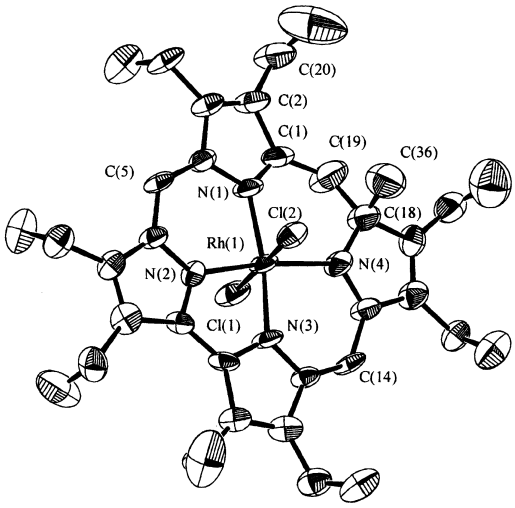
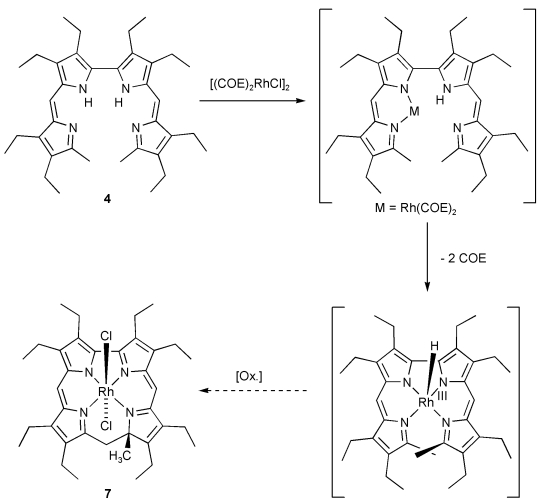


Fig. 2 Ortep plot of the molecular structure of **7**. Selected bond lengths (Å) and bond angles (°): Rh(1)–Cl(1) 2.348(3), Rh(1)–Cl(2) 2.360(3), Rh(1)–N(1) 1.991(7), Rh(1)–N(2) 1.935(6), Rh(1)–N(3) 1.941(6), Rh(1)–N(4) 2.002(7), Cl(1)–Rh(1)–Cl(2) 178.12(10).

and the minor form of 0.757(3) and 0.243(3), respectively. For this reason, the structure refinement gave rather high deviations for the bond lengths and angles in the tetrapyrrolic ligand. Fig. 2 represents an Ortep plot of the molecule in the higher occupied position.[12]

Although the quality of the obtained data does not allow a detailed structural discussion, the X-ray analysis clearly proves that the NMR structural assignments are 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 essentially 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.

Mechanistically we believe that due to the size and electronic influence of the COE coligands a mononuclear complex similar to **6** is produced in the first step. This Rh(I) complex then loses the rather labile COE ligands with concomitant oxidative addition of the adjacent N–H bond (Scheme 2). The fate of a so produced Rh(III) hydride complex is not clear, and the formation



Scheme 2 Mechanistic proposal for the early steps in the transformation of **4** to **7**.

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 also be possible to produce **7** from the reaction of $RhCl_3(OH_2)_3$, the 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 and supports the mechanistic proposal in Scheme 2.

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 rhodalamine 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 (2 × CH_2), 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**·$2CH_2Cl_2$: black needles, M = 879.44, monoclinic, space group $P2_1/n$, 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, 50208 reflections collected (1.59 < θ < 25.35°) at 173(2) K, 7808 independent (R_{int} = 0.0439), 6447 used in the structure refinement; R_1 = 0.0961 [$I > 2\sigma(I)$], wR_2 = 0.2402 (all data), GOF = 1.159 for 886 parameters and 403 restraints, largest difference peak, hole = 1.610, −0.971 e Å^{-3}. CCDC 193547. See http://www.rsc.org/suppdata/cc/b2/b208935c/ for crystallographic files in CIF or other electronic format.

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