Cluster stabilization by an open-chain tetrapyrrolic ligand: first evidence for NH activation as an initial step in tetrapyrrole metalation processes

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Bisdipyrrin 1 reacts with $Ru_3(CO)_{12}$ to yield the pentanuclear cluster 2; the X-ray structure of 2 sheds new light on the metalation processes of oligopyrrolic ligands.

The coordination chemisty of bile pigments and related ligands,[1] an emerging branch of porphyrin research, has been developed mainly in the last decade.[2] Most of the structurally characterized complexes of this class were found to exhibit metalloporphyrin-like structures with the metal ion bound to the four central nitrogen atoms of the ligand. The higher flexibility of the open-chain tetrapyrroles with respect to the porphyrins, however, also allows other coordination modes, and some examples of M_2L_2 arrangements[3] as well as complexes coordinated through donor atoms of the ligand periphery[4] were obtained. In our efforts to explore the coordination chemistry of open-chain oligopyrroles and to apply helical chiral chelates in catalytic processes, ruthenium complexes have become a major goal. This communication reports the unprecedented coordination of ruthenium to the bile pigment analogue bisdipyrrin 1[5] and provides the first example for the role of NH activation in tetrapyrrole metalation processes.

The method most widely used to introduce a ruthenium ion into a porphyrin is the reaction of the ligand with an excess of $Ru_3(CO)_{12}$ in a high boiling solvent.[6] When applying these conditions (Scheme 1) to the bisdipyrrin 1 (twofold molar excess of ruthenium carrier, toluene, 130 °C), a single defined product was observed by TLC and could subsequently be isolated using radial chromatography (13% yield). Upon slow evaporation from hexane–CH_2Cl_2, dark red crystals suitable for

X-ray diffraction were obtained. As the structural analysis[7] revealed, the product was not the anticipated (carbonyl)ruthenium bisdipyrrin, but the pentanuclear cluster 2.[8]

The complicated arrangement of the Ru_5H_2 cluster core found in 2 can best be understood as composed from three subunits. Two Ru_2 moieties are located above and below the tetrapyrrolic ligand. While one of these is bound through a normal dipyrrin N_2 chelate and a η^5-coordinated pyrrole [Ru(2)–Ru(5)], the other is found to bind to the *meso*-carbon atom C(34) of the second dipyrrolic half of the bisdipyrrin, supported by another η^5 coordination [Ru(3)–Ru(4)].[9] Finally, the fifth ruthenium center Ru(1) is situated in between the two remaining nitrogen atoms N(3) and N(4) and acts as a central unit, connecting the two Ru_2 fragments *via* μ-hydrido bridges to Ru(2) and Ru(3), respectively. Fig. 1 demonstrates the action of the flexible and severely twisted bisdipyrrin ligand on the Ru_2–H–Ru–H–Ru_2 moiety. In addition, eleven surrounding CO ligands serve to saturate the coordination spheres of the ruthenium centers of cluster 2, allowing octahedral geometries for all five metal atoms (Fig. 2). The cluster core and the tetrapyrrolic ligand thus both adopt conformations optimized for the stabilization of the uncommon structure. This synergysm accounts for the surprising fact that 2 shows enhanced resistance against thermal cluster degradation and decomposition.

Since the assignment of hydride ligands bound to heavy metal atoms through X-ray diffraction is generally problematic, a ^{1}H NMR spectroscopic investigation of 2 was undertaken which showed signals at −15.30 and −18.40 corresponding to the two hydrido ligands in 2 (Fig. 3). The coupling (4 Hz) between these hydrides is in accord with them both being bound to the same ruthenium center. In addition, the signal at δ −18.40 shows a coupling of 1 Hz with the resonance of the *meso* proton
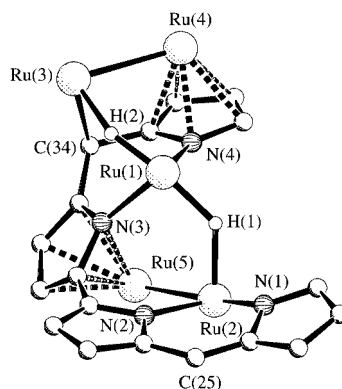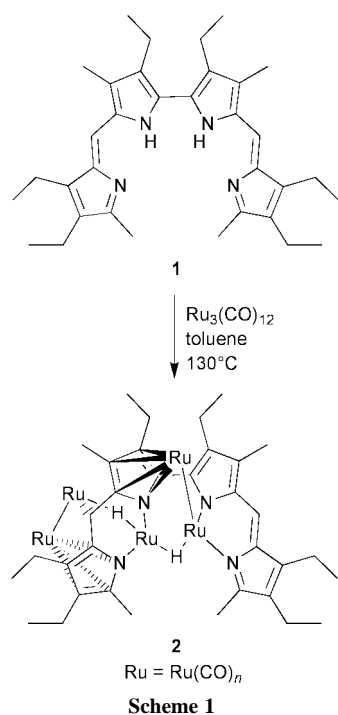
Ru = Ru(CO)$_n$

Scheme 1

Fig. 1 Schakal plot of the molecular structure of **2** (alkyl groups and CO ligands omitted for clarity). Selected bond lengths (Å) and bond angles (°): Ru(1)–Ru(2) 3.26, Ru(1)–Ru(3) 3.27, Ru(3)–Ru(4) 2.778(13), Ru(2)–Ru(5) 2.793(12), Ru(3)–C(34) 2.209(10), Ru(1)–N(3) 2.086(7), Ru(1)–N(4) 2.205(8), Ru(2)–N(1) 2.149(7), Ru(2)–N(2) 2.119(8), C(33)–C(34) 1.482(13), C(34)–C(35) 1.470(13), C(24)–C(25) 1.361(15), C(25)–C(26) 1.415(14); Ru(1)–H(1)–Ru(2) 130.7, Ru(1)–H(2)–Ru(3) 154.7, N(1)–Ru(2)–N(2) 84.3(3), N(3)–Ru(1)–N(4) 89.0(3).
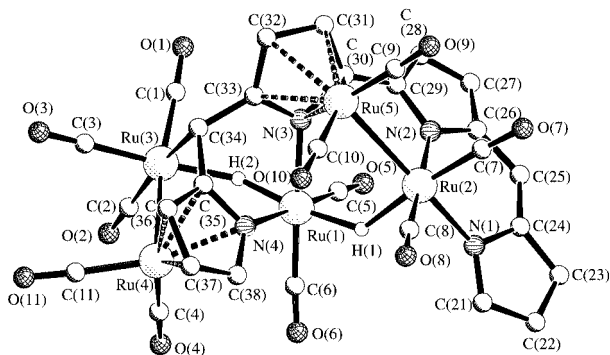
Fig. 2 View of the octahedral coordination geometries of the five ruthenium metal centers in **2** (alkyl groups omitted for clarity).
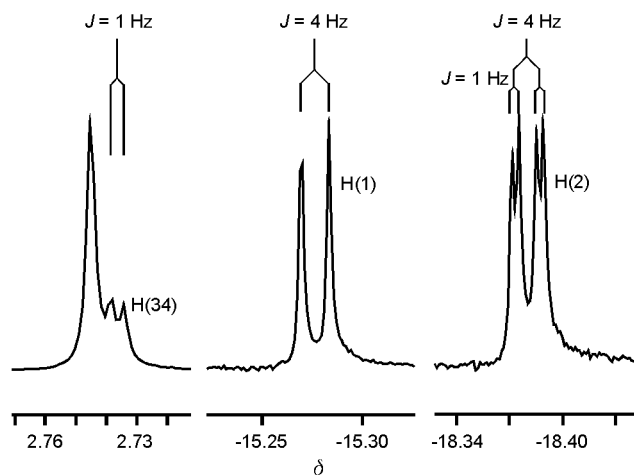

Fig. 3 Details of the ^{1}H NMR spectrum of **2** (300 MHz, benzene-d$_6$).

H(34), indicative of the close vicinity of H(2) and H(34), so strongly supporting the structural findings.

The bridging hydrides originate from the NH functionalities of the bisdipyrrin ligand and indicates that the well-established mechanism for tetrapyrrole metalation, deformation of the macrocycle, subsequent binding of a metal ion to two nitrogen donors, and insertion into the porphyrin cavity with concomitant deprotonation,[10] is not the only plausible mechanistic pathway. Obviously, a route involving the oxidative addition of an NH moiety on an appropriate metal carrier constitutes a suitable alternative, especially if carriers with metal centers in low oxidation states are employed.[11] For porphyrins, the initial structures formed during metalation processes using metal carbonyls probably resemble cluster fragment complexes similar to that found for bisdipyrrin **2**; owing to the rigid macrocyclic character of porphyrins, however, cluster degradation should be fast and inevitably result in the well-known N$_4$-coordinated metal porphyrins.[12]

Notes and references

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7 *Crystal data* for C$_{45}$H$_{46}$N$_4$O$_{11}$Ru$_5$ **2**: red prisms, M = 1324.21, monoclinic, space group $P2_1/c$, a = 19.633(4), b = 15.226(3), c = 17.809(4) Å, β = 89.76(3)°, U = 5323.7(18) Å^3, Z = 4, D_c = 1.652 g cm^{-3}, μ = 1.441 mm^{-1}, $F(000)$ = 2608, 54724 reflections collected (2.47 < θ < 25.10°) at 173(2) K, 9374 independent (R_{int} = 0.1057), 4350 used in the structure refinement; R_1 = 0.0542 [$I > 2\sigma(I)$], wR_2 = 0.1526 (all data), GOF = 0.815 for 623 parameters and 12 restraints, largest difference peak, hole = 0.434, −0.074 e Å^{-3}. CCDC 182/1687. See http://www.rsc.org/suppdata/cc/b0/b003815f/ for crystallographic files in .cif format.

8 *Spectroscopic data* for **2**: mp 132 °C (decomp.); MS(DCI, isobutane): m/z 1325.8, [M + H]$^+$; $\delta_H$benzene-d$_6$): 7.08 [s, 1H, H(25)], 2.72 (s, 3H, CH$_3$), 2.71 [d, J (HH) 1 Hz, 1H, H(34)], 2.62–2.11 (m, 10H, 5 × C*H*$_2$CH$_3$), 2.57, 2.20 (2 × s, 6H, 2 × CH$_3$), 1.97–1.88 (m, 2H, CH$_2$CH$_3$), 1.89 (s, 3H, CH$_3$), 1.17–0.81 (m, 18H, 6 × CH$_3$), −15.30 [d, J(HH) 4 Hz, 1H, H(1)], −18.40 [dd, 1H, H(2)]; $\delta_C$benzene-d$_6$): 208.2, 208.1, 206.6, 199.8, 198.11, 198.10, 196.0, 193.1, 192.4, 191.8, 191.0 (11 × CO); 164.9, 147.2, 144.9, 141.2, 138.4, 137.1, 134.2, 134.0, 133.6, 120.8, 117.1, 117.0, 115.5, 108.8, 105.9, 96.3 (16 × C$_{quat}$); 123.8 [C(25)]; 19.9, 19.7, 19.6, 19.1, 18.8, 18.4 (6 × CH$_2$CH$_3$); 19.3, 18.5, 17.6, 16.4, 16.3, 15.9, 15.8, 15.6, 11.0, 10.4 (10 × CH$_3$); 3.5 [C(34)]; IR (KBr): v/cm^{-1} 2969, 2933, 2873 (s, v_{C-H}); 2072, 2053 (sh), 2045, 2024, 2003 (sh), 1997, 1971, 1953, 1927, 1920 (sh) (s, $v_{C≡O}$); 1607 (s, $v_{C=C}$) (Calc. for C$_{45}$H$_{46}$N$_4$O$_{11}$Ru$_5$: C, 40.82; H, 3.50; N, 4.23. Found: C 39.81, H 3.40, N 3.95%).

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12 For an interesting exception, see: Y.-W. Chan, F. E. Wood, M. W. Renner, H. Hope and A. L. Balch, *J. Am. Chem. Soc.*, 1984, **106**, 3380; A. L. Balch, Y.-W. Chan, M. M. Olmstead, M. W. Renner and F. E. Wood, *J. Am. Chem. Soc.*, 1988, **110**, 3897.