pated in the chemistry of these ligands. The remarkable facility with which the ruthenaboratrane forms may presumably be traced to both the lability of $HB(mt)_3$ chelation and the increased ring size of the chelates, which allows the scorpion's sting to more closely approach the metal center.

Experimental Section

$Na[HB(mt)_3]$: Finely and intimately ground $Na[BH_4]$ (2.08 g, 60 mmol) and 1-methylimidazole-2-thiol (Hmt, 25.0 g, 220 mmol) were suspended in xylene (30 mL) and heated under reflux for 2 h. The crude product was filtered off, washed with hot toluene and hexane, and dried in vacuo. Yield 19.17 g (94 %).

4: A mixture of $[Ru(CH{=}CHCPh_2OH)Cl(CO)(PPh_3)_2]$ (0.36 g, 0.40 mmol) and $Na[HB(mt)_3]$ (0.15 g, 0.40 mmol) in dichloromethane (50 mL) was stirred for 30 min and then filtered through diatomaceous earth and freed of volatiles. The residue was crystallized from a mixture of dichloromethane and hexane to provide yellow crystals. Yield 0.24 g (81 %). IR (Nujol): $\tilde{\nu} = 1888\ \mathrm{cm^{-1}}$ (vs; CO); IR (CH_2Cl_2): $\tilde{\nu} = 1894\ \mathrm{cm^{-1}}$ (vs; CO); ^1H NMR (270 MHz, $CDCl_3$, 25 °C)**:** $\delta = 3.43$ (s, 6H; NCH_3), 3.60 (s, 3H; NCH_3), 6.39, 6.70 (AB, $^3J_{AB} = 2.1$ Hz, 2H; CH=CH), 6.98 and 7.35 ($(AB)_2$, $^3J_{AB} = 2.0$ Hz, 4H; CH=CH), 7.25–7.35 and 7.55–7.61 (m × 2, 15H; C_6H_5); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C)**:** $\delta = 206.5$ (RuCO), 170.5, 170.4 (CS), 138.5 (d, $^1J_{PC} = 21.8$ Hz; C1 (C_6H_5)), 133.6 (d, $^2J_{PC} = 13.4$ Hz; C2, C6 (C_6H_5)), 128.4 (C4 (C_6H_5)), 127.8 (d, $^3J_{PC} = 8.9$ Hz; C3, C5 (C_6H_5)), 122.0 (2C), 119.2 (1C), 116.3 (2C), 113.7 (1C; CH=CH), 34.2 (1C; NCH_3), 33.7 (2C; NCH_3); ^{11}B NMR ($CDCl_3$, 25 °C, BF_3OEt_2)**:** $\delta = 17.1$; $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$, 25 °C, 85 % H_3PO_4)**:** $\delta = 26.6$ (br s); FAB-MS: m/z (%): 743 (4) $[M^+]$, 714 (3) $[M^+ - CO]$, 452 (19) $[M^+ - COPPh_3]$. The complex crystallized from chloroform as a bis-solvate and was also characterized crystallographically.[7]

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[1] S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943.
[2] H. C. Brown, E. A. Fletcher, *J. Am. Chem. Soc.* **1951**, *73*, 2808.
[3] A. F. Hill, *J. Organomet. Chem.* **1990**, *395*, C35; N. W. Alcock, A. F. Hill, R. P. Melling, *Organometallics* **1991**, *10*, 3898.
[4] J. C. Cannadine, A. L. Hector, A. F. Hill, *Organometallics* **1992**, *11*, 2323; J. C. Cannadine, A. F. Hill, A. J. P. White, D. J. Williams, J. D. E. T. Wilton-Ely, *Organometallics* **1996**, *15*, 5409.
[5] M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer, A. R. Kennedy, *Chem. Commun.* **1996**, 1975.
[6] K. J. Harlow, A. F. Hill, T. Welton, A. J. P. White, D. J. Williams, *Organometallics* **1998**, *17*, 1916.
[7] Crystal data for **4**: $C_{31}H_{30}N_6OBPS_3Ru \cdot 2\,CHCl_3$, $M_r = 980.4$, yellow blocks, $0.93 \times 0.77 \times 0.53$ mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.932(1)$, $b = 13.329(3)$, $c = 14.484(2)$ Å, $\alpha = 68.75(1)$, $\beta = 74.55(1)$, $\gamma = 81.67(1)°$, $V = 2066.3(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.576\ \mathrm{g\,cm^{-3}}$, $\mu(Mo_{K\alpha}) = 9.94\ \mathrm{cm^{-1}}$, $F(000) = 988$, $T = 293$ K; Siemens P4/PC diffractometer, graphite-monochromated $Mo_{K\alpha}$ radiation, ω-scans, 7128 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms of the complex, and the major occupancy non-hydrogen atoms of the disordered chloroform solvent molecules, were refined anisotropically (the others isotropically) with full matrix least-squares based on F^2 to give $R_1 = 0.049$, $wR_2 = 0.113$ for 5475 independent observed reflections $[|F_o| > 4\sigma(|F_o|), 2\theta \leq 50°]$ and 453 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116432. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[8] G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685.
[9] G. J. Irvine, W. R. Roper, L. J. Wright, *Organometallics* **1997**, *16*, 2291; G. R. Clark, G. J. Irvine, W. R. Roper, L. J. Wright, *Organometallics* **1997**, *16*, 5499; C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Organometallics* **1998**, *17*, 4869.
[10] H. Braunschweig, M. Koster, R. Wang, *Inorg. Chem.* **1999**, *38*, 415.
[11] J. M. Burlitch, J. H. Burk, M. E. Leonowicz, R. E. Hughes, *Inorg. Chem.* **1979**, *18*, 1702.
[12] I. D. Burns, A. F. Hill, A. J. P. White, D. J. Williams, J. D. E. T. Wilton-Ely, *Organometallics* **1998**, *17*, 1552.

Tetrapyrroles as π Donors: A Pd_2^{2+} Unit Sandwiched between Two Helical Bilindione–Palladium Moieties**

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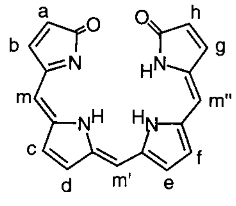
The linear tetrapyrroles of the bilindione family **1**[1] are metabolites of heme degradation which show biological activity (antioxidant[2] and antiviral activity[3]) that is poorly understood at the molecular level. Like porphyrins bilindiones form four-coordinate metal complexes that undergo a variety of changes in redox state, electronic structure, and axial ligation.[4–6] The general mode of coordination of both the bilindiones and porphyrins involves bonding of the four nitrogen atoms to a central metal ion. With the bilindione ligand, the four nitrogen atoms cannot be coplanar when bonded to a relatively small first-row transition metal ion. Consequently, helical complexes result. Here we report on the formation of complexes that involve a larger second-row transition metal ion and in which the metalation of the linear tetrapyrrole results in an unusual sandwich structure.



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Treatment of octaethylbilindione H_3OEB (**1**, a–h = Et) with palladium(II) acetate in chloroform/ethanol followed by chromatography on silica gave dark green crystals of $[Pd_4(OEB)_2]$ in 66 % yield. The electronic spectrum of the complex which displays bands at 831 nm ($\varepsilon = 2.2 \times 10^4$), 358 nm ($\varepsilon = 4.6 \times 10^4$), and 284 nm ($\varepsilon = 3.7 \times 10^4$), resembles that of $[Zn^{II}(OEBOMe)]$[7] rather those of other complexes in which the tetrapyrrole is coordinated to the metal center simply through four M–N bonds, such as $[Co(OEB)]$[4] and

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[Ni(OEB)].[5] Consequently, an additional bond to one of the oxygen atoms of the OEB ligand was expected.

The structure of $[\mathrm{Pd_4(OEB)_2}]\cdot$THF, as determined by a single-crystal X-ray diffraction study, is shown in Figure 1. The complex, which has no crystallographically imposed symmetry, consists of two helical Pd$^{\mathrm{II}}$(OEB) units that are joined through a $(\mathrm{Pd}^{\mathrm{I}}_{2})^{2+}$ unit. Remarkably, each OEB ligand donates seven pairs of electrons to the two palladium atoms to which it is bound. While the coordination geometry within the two Pd$^{\mathrm{II}}$(OEB) portions of the tetranuclear complex is similar to those of a number of mononuclear complexes of the OEB ligand, the mode of interaction with the central $\mathrm{Pd_2}^{2+}$ portion is not.

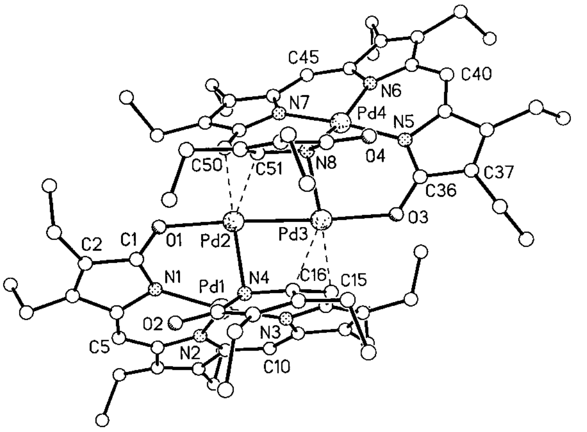

Figure 1. Perspective view of $[\mathrm{Pd_4(OEB)_2}]$. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.051(8), Pd1–N2 2.011(9), Pd1–N3 2.017(8), Pd1–N4 2.082(9), Pd3–N8 2.091(8), Pd4–N5 2.007(10), Pd4–N6 2.017(9), Pd4–N7 2.036(10), Pd4–N8 2.094(8), Pd2–N4 2.107(8), Pd2–C50 2.183(10), Pd2–C51 2.223(11), Pd3–C15 2.185(9), Pd3–C16 2.202(9), Pd2–O1 2.108(7), Pd3–O(3) 2.126(7), Pd2–N3 2.4725(11); N2-Pd1-N1 89.3(3), N2-Pd1-N3 90.4(3), N3-Pd1-N4 88.8(3), N1-Pd1-N4 93.4(3), N3-Pd1-N1 171.0(3), N2-Pd1-N4 167.5(3), N5-Pd4-N6 88.1(4), N6-Pd4-N7 89.8(4), N7-Pd4-N8 91.3(4), N5-Pd4-N8 93.1(4), N5-Pd4-N7 170.0(4), N6-Pd4-N8 165.8(3), O1-Pd2-Pd3 172.12(19), N4-Pd2-O1 94.6(3), N4-Pd2-Pd3 81.8(2), N8-Pd3-O3 94.6(3), N8-Pd3-Pd2 80.5(3).

The coordination environment of the central $(\mathrm{Pd}^{\mathrm{I}}_{2})^{2+}$ moiety, which is suspended between the two Pd(OEB) units, has several novel features. Each palladium atom of the $(\mathrm{Pd}^{\mathrm{I}}_{2})^{2+}$ unit is coordinated to an olefinic bond of one of the two Pd(OEB) units. Such η^2 coordination of a transition metal center to the π system at one of the *meso* carbon atoms of the OEB ligand is unprecedented in the chemistry of linear tetrapyrroles and porphyrins.[8] Coordination of transition and alkali metal ions to individual pyrrole rings of porphyrins[9, 10] and porphyrinogens[11, 12] (which are nonconjugated) has been observed, but in the present example, the coordination is to a π bond that is exocyclic to the adjacent pyrrole ring. Two of the nitrogen atoms (N4 and N8), that is, one from each tetrapyrrole ring, are also coordinated to the central $(\mathrm{Pd}^{\mathrm{I}}_{2})^{2+}$ unit. These nitrogen atoms act as direct bridging links between Pd1 and Pd2 and between Pd3 and Pd4. The Pd–N distances that involve the bridging nitrogen atoms (Pd1–N4 2.082(9), Pd2–N4 2.107(8) Pd3–N8 2.091(8), Pd4–N8 2.094(8) Å) are longer than the strictly terminal Pd–N distances (2.007(10)–2.051(8) Å). Such bridging by pyrrole nitrogen atoms in transition metal complexes of porphyrins and related tetrapyrroles is uncommon. However, bridging pyrrole nitrogen atoms were observed in the tetraphenylporphyrin ($\mathrm{H_2tpp}$) complexes $[\mathrm{(tpp)\{Re(CO)_3\}_2}]$ and $[\mathrm{(tpp)\{Re(CO)_3\}\{Re(CO)_3Cl\}][SbCl_6]}$.[13, 14] In these complexes the two rhenium atoms are bound to opposite sides of the the porphyrin by coordination to three pyrrole nitrogen atoms, and two of the four pyrrole nitrogen atoms bridge the two rhenium centers. In these rhenium complexes, the Re–N distances are also longer for the bridging nitrogen atoms than for the terminal nitrogen atoms. Finally, one of the oxygen atoms of each Pd$^{\mathrm{II}}$(OEB) unit is coordinated to the $(\mathrm{Pd}^{\mathrm{I}}_{2})^{2+}$ moiety.

The overall structure at the center of $[\mathrm{Pd_4(OEB)_2}]$ conforms to that seen in other dinuclear Pd$^{\mathrm{I}}$ complexes. These dinuclear complexes generally involve six donor centers that are arranged about the Pd–Pd bond to give planar coordination at each metal atom. In the $(\mathrm{Pd}^{\mathrm{I}}_{2})^{2+}$ unit the Pd–Pd distance of 2.4725(11) Å is indicative of a Pd–Pd single bond. In comparison, the lengths of the unsupported Pd–Pd single bonds in $[\mathrm{Pd}^{\mathrm{I}}_{2}\mathrm{(CNMe)_6}]^{2+}$ and $[\mathrm{Pd}^{\mathrm{I}}_{2}\mathrm{(CNMe)_4I_2}]$ are 2.5310(9)[15] and 2.533(1) Å, respectively.[16] Other Pd–Pd single bonds have bond lengths in the range 2.5–2.7 Å.[17] The remaining Pd···Pd separations (Pd1···Pd2 3.1298(11), Pd3···Pd4 3.1224(11) Å) are much longer and are inconsistent with any direct bonding between them. The diamagnetism of $[\mathrm{Pd_4(OEB)_2}]$ is readily explained: two diamagnetic $(\mathrm{OEB})^{3-}$ ligands chelate two diamagnetic Pd$^{\mathrm{II}}$ centers (Pd1 and Pd4), and the d^9 Pd$^{\mathrm{I}}$ centers (Pd2 and Pd3) are spin-coupled through the direct Pd–Pd bond, as in many dinuclear Pd$^{\mathrm{I}}$ complexes.

Each Pd(OEB) unit in $[\mathrm{Pd_4(OEB)_2}]$ is chiral and has a *p*-helical configuration. Thus, each individual tetranuclear complex is chiral. However, the space group $P\bar{1}$ is centrosymmetric, and consequently crystals of $[\mathrm{Pd_4(OEB)_2}]$ contain a racemate of the two enantiomeric helices.

Treatment of $[\mathrm{Pd_4(OEB)_2}]$ with pyridine/ethanol leads to the precipitation of black crystals of the odd-electron complex [Pd(OEB)], which shows an intense EPR spectrum with $g = 2.003$ in toluene at 23 °C and no NMR spectrum. The structure of this complex, as determined by X-ray diffraction, is shown in Figure 2. The complex has the helical geometry that is typical of other [M(OEB)] complexes and similar to that of

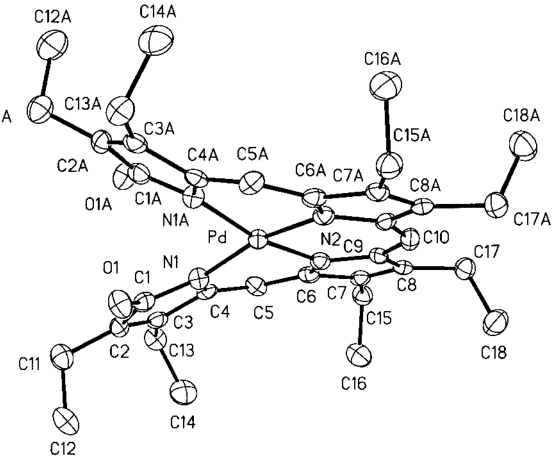

Figure 2. Perspective view of [Pd(OEB)]. Selected bond lengths [Å] and angles [°]: Pd–N1 2.012(4), Pd–N2 2.011(4); N1-Pd-N2 89.42(14), N1-Pd-N1A 93.5(2), N1-Pd-N2A 167.03(16), N2-Pd-N2A 90.6(2).

the two end units of [$Pd_4(OEB)_2$]. The formation of [Pd(OEB)] from the pyridine/ethanol solution is governed by the ability of pyridine to coordinate to the central Pd_2 unit and thus to facilitate its dissociation from [$Pd_4(OEB)_2$].

The η^2 coordination of the bilindione by a palladium center not only produces the novel structure shown in Figure 1, but also alters the chemical reactivity of the ligand. We will describe the rearrangement of the ligand core in [$Pd_4(OEB)_2$] elsewhere.[18]

Experimental Section

[$Pd_4(OEB)_2$]: Under a dinitrogen atmosphere, a solution of palladium(II) acetate (115 mg, 0.512 mmol) in chloroform (5 mL) was added to a solution of octaethylbiliverdin (30 mg, 0.054 mmol) in ethanol (25 mL). (Ethanol is critical for the success of the reaction and serves as reductant.) After the mixture was heated to 65 °C for 5 min and stirred for 1.5 h at 25 °C, the solvent was evaporated. The residue was subjected to chromatography on silica with chloroform as the eluant. The first dark green fraction was collected and evaporated to dryness (yield: 27.5 mg, 66.5 %). Crystals suitable for X-ray crystallography were grown by slow diffusion of water into a solution of the complex in THF. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 6.759 (s, *meso*-CH), 6.007 (s, *meso*-CH), 5.156 (s, *meso*-CH), 2.575 – 1.892 (m, CH_2), 1.340 – 0.863 (m, CH_3). UV/Vis: λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 831 (2.2×10^4), 358 (4.6×10^4), 284 (3.7×10^4). MALDI MS (positive ion): parent cluster at 1527.00 amu.

Crystal data for [$Pd_4(OEB)_2$]·THF: Dark green plate, dimensions $0.22 \times 0.16 \times 0.02$ mm, triclinic, space group $P\bar{1}$, $a = 14.7685(15)$, $b = 14.935(2)$, $c = 16.328(2)$ Å, $\alpha = 87.407(9)$, $\beta = 83.278(8)$, $\gamma = 76.132(8)°$, $V = 3472.0(6)$ Å^3, $\lambda = 1.54178$ Å, $Z = 2$, $\rho_{calcd} = 1.532$ Mg m^{-3}; $\mu(Cu_{K\alpha}) = 8.665$ mm^{-1}; Siemens P4 diffractometer, rotating anode; $2\Theta - \omega$ scans, $2\Theta_{max} = 113$; $T = 130$ K; 9187 reflections collected; 9187 independent reflections; min./max. transmission 0.2516/0.8458; solution by direct methods (SHELXS-97, G. M. Sheldrick, **1990**); refinement by full-matrix least-squares methods on F^2 (SHELXL-97; G. M. Sheldrick, **1997**); 806 parameters, $R1 = 0.0893$, $wR2 = 0.1772$ for all data; $R1 = 0.0649$ for 6915 observed data ($I > 2\sigma(I)$). An empirical absorption correction was applied.[19]

Crystal data for [Pd(OEB)]: Black needle, dimensions $0.44 \times 0.08 \times 0.08$ mm, monoclinic, space group $I2/a$, $a = 13.274(3)$, $b = 18.655(4)$, $c = 14.144(3)$ Å, $\beta = 116.00(3)°$, $V = 3141.3(11)$ Å^3, $\lambda = 0.71073$ Å, $Z = 4$, $\rho_{calcd} = 1.392$ Mg m^{-3}; $\mu(Mo_{K\alpha}) = 0.628$ mm^{-1}; Siemens R3m/V diffractometer; $2\Theta - \omega$ scans, $2\Theta_{max} = 45$; $T = 140(2)$ K; 2198 reflections collected; 2030 independent relections; min./max. transmission 0.770/0.952; solution by direct methods (SHELXS-97, G. M. Sheldrick, **1990**); refinement by full-matrix least-squares methods on F^2 (SHELXL-97; G. M. Sheldrick, **1997**); 195 parameters, $R1 = 0.055$, $wR2 = 0.0900$ for all data; $R1 = 0.042$ for 1715 observed data ($I > 2\sigma(I)$). An empirical absorption correction was applied. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-113559 and CCDC-114918. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] H. Falk, *The Chemistry of Linear Oligopyrroles and Bile Pigments*, Springer, Vienna, **1989**.

[2] R. Stocker, Y. Yamamoto, A. F. McDonagh, A. N. Glazer, B. N. Ames, *Science* **1987**, *235*, 1043.

[3] T. Nakagami, S. Taji, M. Takahashi, K. Yamanishi, *Microbiol. Immunol.* **1992**, *36*, 381; H. Mori, T. Otake, M. Morimoto, N. Ueba, N. Kunita, T. Nakagami, N. Yamasaki, S. Taji, *Jpn. J. Cancer Res.* **1991**, *82*, 755.

[4] A. L. Balch, M. Mazzanti, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1994**, *116*, 9114.

[5] J. V. Bonfiglio, R. Bonnett, D. G. Buckley, D. Hamzetash, K. M. Hursthouse, K. M. A. Malik, A. F. McDonagh, J. Trotter, *Tetrahedron* **1983**, *39*, 1865.

[6] a) A. L. Balch, M. Mazzanti, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1993**, *115*, 12206; b) S. Attar, A. L. Balch, P. M. Van Calcar, K. Winkler, *J. Am. Chem. Soc.* **1997**, *119*, 3317; c) S. Attar, A. Ozarowski, P. M. Van Calcar, K. Winkler, A. L. Balch, *Chem. Commun.* **1997**, 1115; d) A. L. Balch, L. Latos-Grażyński, B. C. Noll, M. M. Olmstead, N. Safari, *J. Am. Chem. Soc.* **1993**, *115*, 9056.

[7] a) L. Latos-Grażyński, J. A. Johnson, S. Attar, M. M. Olmstead, A. L. Balch, *Inorg. Chem.* **1998**, *37*, 4493; b) R. Koerner, L. Latos-Grażyński, A. L. Balch, *J. Am. Chem. Soc.* **1998**, *120*, 9246.

[8] A compound in which two lithium ions are sandwiched between two anionic porphyrins has been structurally characterized: C. S. Alexander, S. J. Retig, B. R. James, *Organometallics* **1994**, *13*, 2542.

[9] K. K. Dailey, G. P. A. Yap, A. L. Rheingold, T. B. Rauchfuss, *Angew. Chem.* **1996**, *108*, 1985; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1833.

[10] M. Senge, *Angew. Chem.* **1996**, *108*, 2051; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1923.

[11] C. Floriani, E. Solari, G. Solari, A. Chiesi-Villa, C. Rizzoli, *Angew. Chem.* **1998**, *110*, 2367; *Angew. Chem. Int. Ed.* **1998**, *37*, 2245.

[12] C. Floriani, *Chem. Commun.* **1996**. 1257.

[13] D. Cullen, E. Meyer, T. S. Srivstava, M. Tsutsui, *J. Am. Chem. Soc.* **1972**, *94*, 7603.

[14] S. Kato, M. Tsutsui, D. Cullen, E. Meyer, Jr., *J. Am. Chem. Soc.* **1977**, *99*, 620.

[15] D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg, J. S. Miller, *J. Am. Chem. Soc.* **1975**, *97*, 1961.

[16] N. M. Rutherford, M. M. Olmstead, A. L. Balch, *Inorg.Chem.* **1984**, 23, 2833.

[17] A. L. Balch, *Comments Inorg. Chem.* **1984**, *3*, 51.

[18] P. Lord, M. M. Olmstead, A. L. Balch, unpublished results.

[19] S. Parkin, B. Moezzi, H. Hope, *J. Appl. Crystalogr.* **1995**, *28*, 53.

The Concept of Docking/Protecting Groups in Biohydroxylation**

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The application of enzymes and microorganisms in organic synthesis has become a valuable and indispensable tool of synthetic chemistry within the last ten to fifteen years.[1] Since, in general, nonnatural substrates are transformed, it is not surprising that these compounds are not always well accepted by the biocatalysts in question. With regard to biohydroxylation, it was recognized at an early stage that the presence of

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