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 $[Pd_4(OEB)_2] \cdot THF$: 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 diffractometrer; $2\Theta - \omega$ 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 CB2 1EZ, 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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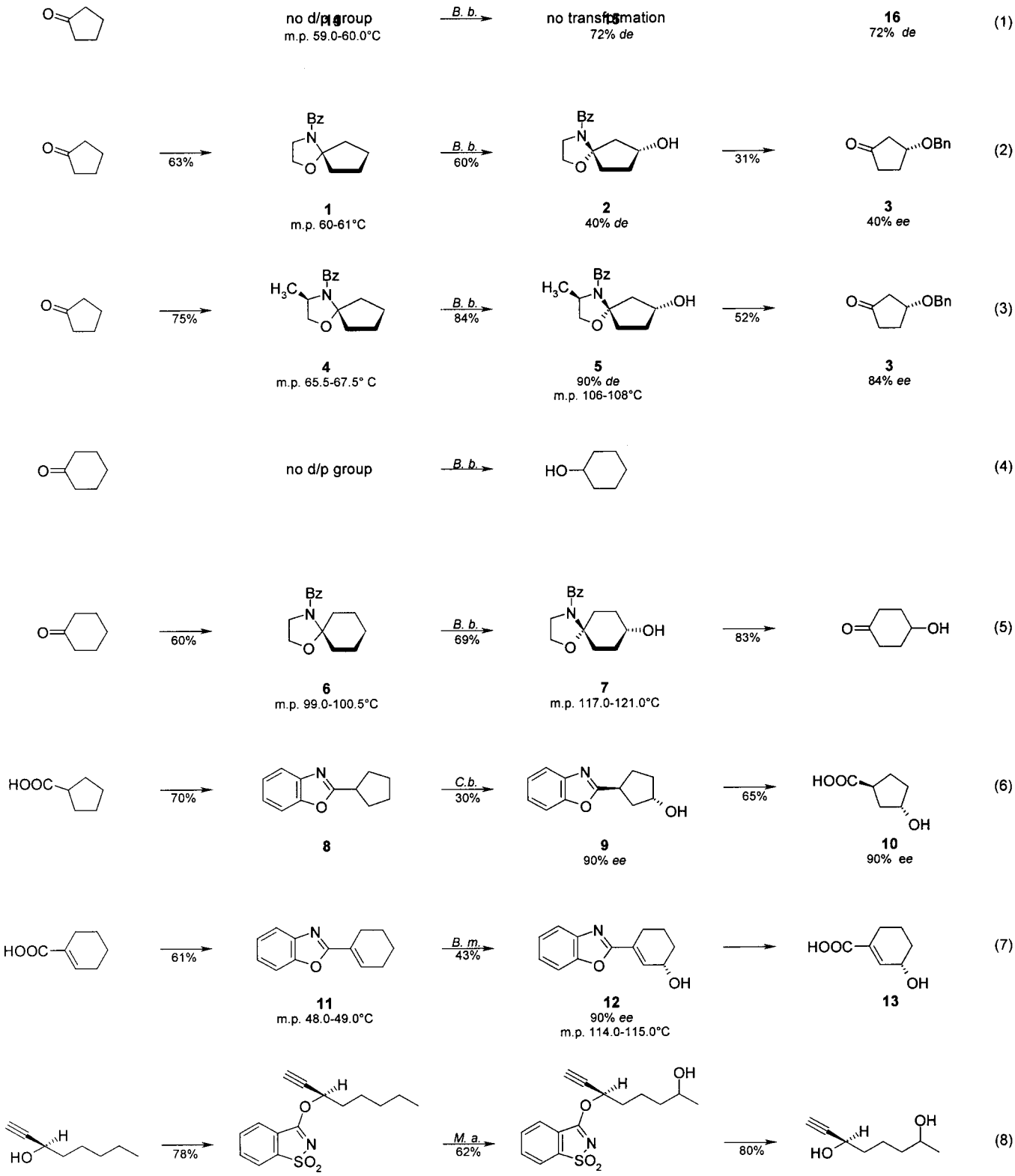
certain functional groups has a positive influence on substrate acceptance.[2] On the basis of this observation and extending a strategy first suggested by Furstoss et al. for the hydroxylation of compounds such as alcohols and alkenes,[3] we developed a general concept which can be successfully applied for biohydroxylation. Similar to the common practice of using protective groups in organic chemistry, a docking/protecting (d/p) group is first introduced, ideally under mild conditions and in high yield, and subsequently the biotransformation is performed. Under the conditions employed in this work, without the d/p group hydroxylation did not take place or side reactions occurred [Eq. (1) and (4)].[4] After the biotransfor-



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mation, the d/p group is removed. Besides promoting interaction of the substrate with the active site of the hydroxylating enzyme, the d/p group should be UV-active to facilitate detection (TLC, HPLC). In some cases, it would also be beneficial to reduce the volatility of the parent substance by the introduction of the d/p group to avoid substrate losses during the fermentation. In accordance with these criteria, a number of compounds were prepared and their suitability as d/p groups experimentally accessed. This was achieved by screening these substrates with a range of microorganisms which were known to hydroxylate similar organic compounds.

As can be seen from the selected entries presented (further examples will be published in a forthcoming paper), this concept could be successfully applied to a number of different substrate classes.

The fungus *Beauveria bassiana* ATCC 7159[5] (*B. b.*) is a microorganism with broad substrate acceptance.[6] In particular, the presence of a benzamide group proved to be beneficial for substrate acceptance.[2, 7] Taking this into account for the biohydroxylation of aldehydes and ketones, the transformation of these substrates into *N*-benzoyloxazolidines and *N*-benzoylspirooxazolidines, respectively, was carried out as an application of the d/p group concept. Unlike cyclopentanone which is not accepted by *B. b.* [Eq. (1)], after introduction of the d/p group (one-pot reaction: 1) $NH_2CH_2CH_2OH$ (1 equiv), K_2CO_3 (2 equiv), CH_2Cl_2, RT, 48 h; 2) BzCl (1 equiv), RT, 24 h) to give *N*-benzoylspirooxazolidine **1**, biohydroxylation took place and (5*R*,7*S*)-4-benzoyl-1-oxa-4-azaspiro[4.4]nonan-7-ol (**2**) was obtained in 60% yield and 40% *de*. This compound was then benzylated (BnBr, NaH, THF/DMF, 20 °C) prior to the last deprotection step (IR 120 (H^+), CH_3CN, 20 °C) to avoid elimination. Consequently, ketone **3** was afforded as the final product (40% *ee*). The optical purity and yield of the hydroxylated product improved dramatically when a chiral d/p group was used. This is illustrated with one of the chiral derivatives from this group of ketones, substrate **4** [Eq. (3)]. After fermentation, spirononanol **5** was isolated in 84% yield and 90% *de*. Since the benzyl derivative of **5** is crystalline it is possible to further raise the enantiopurity by recrystallization.

In a similar manner, cyclohexanone was also hydroxylated to give **7** [Eq. (5)]. The benefits of chiral derivatives, such as **4**, may not be restricted to the improvement of product optical purity and yield. These compounds may also be valuable as "active site" probes by changing the substitution on the d/p group. Such minor variations in substrate structure and the effect on the site of hydroxylation would give valuable information on substrate structure requirements. In this context, in an extension of work by Fonken et al,[8] Furstoss et al.,[9] and Haufe et al.,[10] we are currently carrying out molecular modeling investigations.

This d/p group concept has also been applied to the hydroxylation of cycloalkane carboxylic acids. Here, the parent acid is transformed into a benzoxazole.[11] As can be seen from Equation (6), benzoxazole **8** was hydroxylated by *Cunninghamella blakesleeana* DSM 1906[11] (*C. b.*) and deprotected (4N aq. HCl/EtOH (1:1, v/v), $ZnCl_2$ (2 equiv), reflux) to afford (1*S*,3*S*)-3-hydroxycyclopentanecarboxylic acid (**10**) in acceptable chemical yield and enantiopurity. In an analogous manner, cyclohexenecarboxylic acid derivative **11** [Eq. (7)], after treatment with *Bacillus megaterium* DSM 32 (*B. m.*),[11] furnished a mixture of alcohol **12** (43%, *ee* > 90%, absolute configuration was determined by X-ray structure analysis) and the corresponding ketone (28%). Suitable conditions to deprotect alcohol **12** and afford derivative **13** are currently under investigation.

The biohydroxylation of alcohols according to this concept was accomplished by the preparation of isosaccharine derivatives, as shown with Equation (8). Derivative **14**, obtained from (*R*)-3-octynol ($C_8H_{13}OH$ (1 equiv), C_5H_5N (2 equiv) 3-chloro-1,2-benzisothiazole-1,1-dioxide (2 equiv), CH_2Cl_2, RT, 24 h) was hydroxylated regioselectively by *Mortierella alpina* ATCC 8979[12] (*M. a.*) to give **15** (72% *de*) which was deprotected ($NaOCH_3$ (0.5 equiv), CH_3OH (absolute), RT, 3 h) to yield diol **16**. The absolute configuration of the second hydroxy group in the molecule is currently under investigation.

To date, biohydroxylation of nonactivated C–H bonds of alkyl or cycloalkyl moieties has been mainly applied in the area of steroids with considerable success regarding yield and regio- and enantioselectivity. In comparison, biohydroxylation of other substrates is far removed from being a method of general use in preparative organic chemistry. However, the use of the d/p group concept broadens the applicability of biohydroxylations in synthetic organic chemistry. Details of this work, experimental methods, and the assignment of the absolute configurations will be discussed in a forthcoming full paper.

Experimental Section

As a representative example of this d/p concept, the biohydroxylation of cyclopentanone is described [Eq. (3)].

By employing (*R*)-1-amino-2-propanol (Aldrich, 98% *ee*) as the d/p group, **4** was prepared in a manner similar to that given for **1**, the procedure being based on a procedure published by Saavedra.[13] Yield 75%; 98% *ee*; m.p. 65.5–67.5 °C; $[\alpha]_{20}^{D} = -79.8$ ($c = 2.1$ in CH_2Cl_2); ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.96$ (d, $J = 6.5$ Hz, 3H; Me), 1.64–1.98, 2.37–2.71 (2 × m, 6H, 2H; H6, 7, 8, 9), 3.60 (m, 1H; H2), 4.00 (m, 2H; H2,3), 7.40 (s, 5H; benzoyl); GC-MS: *m/z* (%): 245 (8) [M^+].

5: After exposure of **4** to *B. bassiana* ATCC 7159[5] and chromatographic isolation, the crystalline compound **5** was obtained as the major diastereoisomer in 84% yield and with 90% *de*; m.p. 106–108 °C; $[\alpha]_{20}^{D} = -78.4$ ($c = 0.9$ in CH_2Cl_2); ^1H NMR (200 MHz, $CDCl_3$, 25 °C, minor diastereoisomer given in italics; * implies that the assignment could be interchanged): $\delta = 0.93$ (d, $J = 5.7$ Hz, 3H; Me); 1.73–2.41 (m, 4H; H6, 8, 9*, 9), 2.57–2.69 (m, 2H; H8*, OH), 2.75, *2.94* (2 × dd; $J = 5.7$ Hz, $J' = 14.0$ Hz, 1H ratio: 20:*1*; H6), 3.63 (dd, $J = 5.1$ Hz, $J' = 11.3$ Hz, 1H; H2), 3.98 (m, 2H; H2, H3), 4.42 (br.s, 1H; H7), 7.37 (s, 5H, benzoyl); GC-MS: *m/z* (%): 261 (2) [M^+].

3: Benzylation of **5** under standard conditions[14] and d/p group removal afforded **3** as a syrup. Yield (over two steps) 52%; 84% *ee*; $[\alpha]_{20}^{D} = -43.0$ ($c = 1.0$ in CH_2Cl_2); NMR data in agreement with literature values.[15]

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[1] a) *Biotechnology: Biotransformations I*, *Vol. 8a* (Ed.: D. Kelly), Wiley-VCH, Weinheim, **1998**; b) K. Faber, *Biotransformations in Organic Chemistry*, 3rd ed., Springer, Berlin, **1997**; c) *Enzyme Catalysis in Organic Synthesis* (Eds.: K. Drauz, H. Waldmann), VCH, Weinheim, **1995**.
[2] G. S. Fonken, R. A. Johnson, *Chemical Oxidations with Microorganisms*, Marcel Dekker, New York, **1972**.
[3] R. Furstoss, A. Archelas, J. D. Fourneron, B. Vigne in *Organic Synthesis: an interdisciplinary challenge*, *IUPAC* (Eds.: J. Streith, H. Prinzbach, G. Schill), Blackwell, Oxford, **1985**, pp. 215–226.
[4] A. Kergomard, M. F. Renard, H. Veschambre, *J. Org. Chem.* **1982**, *47*, 792–798.
[5] In this work, *B. bassiana* ATTC 7159 was cultivated in a manner similar to that reported in reference [7c].
[6] H. L. Holland, *Organic Synthesis with Oxidative Enzymes*, VCH, New York, **1992**, pp. 72–76.
[7] For recent examples of the application of benzamide groups in biohydroxylation: a) R. A. Johnson, M. E. Herr, H. C. Murray, C. G. Chidester, F. Han, *J. Org. Chem.* **1992**, *57*, 7209–7212; b) C. R. Davis, R. A. Johnson, J. I. Cialdella, W. F. Liggett, S. A. Mizsak, F. Han, V. P. Marshall, *J. Org. Chem.* **1997**, *62*, 2252–2254; c) H. F. Olivo, M. S. Hemenway, M. H. Gezginci, *Tetrahedron Lett.* **1998**, *39*, 1309–1312.
[8] R. A. Johnson, M. E. Herr, H. C. Murray, G. S. Fonken, *J. Org. Chem.* **1968**, *33*, 3217–3221.
[9] R. Furstoss, A. Archelas, J. D. Fourneron, B. Vigne in *Enzymes as Catalysts in Organic Synthesis* (Ed.: M. P. Schneider), D. Reidel, **1986**, pp. 361–370.
[10] S. Peitz, D. Wolker, G. Haufe, *Tetrahedron* **1997**, *53*, 17067–17078.
[11] A. de Raadt, H. Griengl, M. Petsch, P. Plachota, N. Schoo, H. Weber, G. Braunegg, I. Kopper, M. Kreiner, A. Zeiser, K. Kieslich, *Tetrahedron: Asymmetry* **1996**, *7*, 467–496.
[12] *M. alpina* ATCC 8979 was cultured in the same manner as that described for *C. blakesleeana* DSM 1906, reference [11].
[13] J. E. Saavedra, *J. Org. Chem.* **1985**, *50*, 2379–2380.
[14] T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd ed., Wiley, New York, **1991**.
[15] T. H. Eberlein, F. G. West, R. W. Tester, *J. Org. Chem*, **1992**, *57*, 3479–3482.

The Mixed-Valent (μ-Nitrido)dimanganese Complex Anion $[(CN)_5Mn^{V}(\mu\text{-}N)Mn^{II}(CN)_5]^{6-}$**

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The synthesis and reactivity of complexes of the first-row transition metals with terminal and bridging nitrido ligands is a rapidly expanding area of research. Complexes with terminal nitrido ligands are known for V, Cr, and Mn,[1] whereas nitride-bridged complexes have been described for V, Cr, and Fe but not for Mn.[2] Interest in these systems derives from their unique molecular structures with very short covalent M–N bonds (1.50–1.60 Å), their electronic structures with strong axial ligand fields from the bound nitride, and from the ability of these systems to engage in N-atom transfer reactions. To date such reactions have been most thoroughly investigated for nitridomanganese(v) complexes containing tetrapyrrole or Schiff-base auxiliary ligands, where transfer of the nitrogen atom to olefins has been demonstrated.[3] N-transfer reactions between two metal ions, for example, from nitrido(porphyrinato)manganese(v) to porphyrinatochromium(iii) has been demonstrated by Bottomley and Neely.[4] The homometallic N-transfer reaction from a nitridomanganese(v) complex to a different manganese(iii) species has also been observed.[5] Thus, it is remarkable that no nitrido-bridged manganese complexes have been described to date. Here we report the synthesis and characterization of the (μ-nitrido)dimanganese complex $[Mn_2(\mu\text{-}N)(CN)_{10}]^{6-}$.

Treatment of solutions containing $[Mn^{V}(N)(salen)]$[3b] (H_2salen = bis(salicylidene)ethylenediamine) and KCN with reductants such as hydrazine or methanol produced intensely colored red-purple solutions from which the salt $K_5H[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 2H_2O$ (**1**) was isolated in low yield. The same compound was obtained in high yield from the reaction of an Mn^{II} salt with an aqueous KCN solution of $[NMe_4]_2Na[Mn^{V}(N)(CN)_5]\cdot H_2O$.[1b] The stability of aqueous solutions of **1** depends strongly on the cyanide concentration. With no added cyanide, the complex decomposes in seconds, whereas it is stable for more than 30 min in 1M NaCN. From such solutions the mixed sodium–rubidium salt $Na_2Rb_4[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 6H_2O$ (**2**) and $[Rh(tn)_3]_2[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 10H_2O$ (**3**) (tn = propane-1,3-diamine) were isolated by addition of RbCl or $[Rh(tn)_3]Cl_3$.

The structure of the anion in **2** is shown in Figure 1.[6] It consists of an eclipsed $[Mn_2(\mu\text{-}N)(CN)_{10}]^{6-}$ ion,[7] which possesses crystallographic 2/*m* symmetry; the center of the complex resides on an inversion center. Inspection of the thermal parameters of the atoms C(10) and N(1) (Figure 1a) reveals that these atoms are severely disordered. This disorder was successfully modeled by using a split-atom model for these atoms with isotropic thermal parameters (Figure 1b). The refinement converged smoothly to give two equally populated sites for each of these atoms. Thus, the anion in **2** is asymmetric with a short Mn≡N bond (1.58(1) Å) and a long Mn–N bond (1.84(1) Å). The shorter Mn≡N bond is only 0.05–0.08 Å longer than the Mn≡N bond in monomeric nitridocyanomanganates(v).[1b] The Mn–C bond *trans* to the short Mn≡N bond is then considered to be the long one (2.19(2) Å) due to a *trans* influence and the short Mn–C bond (1.95(2) Å) is *trans* to the longer Mn–N bond. Interestingly, the four equatorial Mn–C distances in $[Mn^{II}(CN)_6]^{4-}$ *and* $[Mn^{V}(N)(CN)_5]^{3-}$ (1.95(1) Å and 1.985(8)–2.001(8) Å,[8] respectively) are nearly equidistant despite the fact that these Mn ions differ in formal oxidation states by three.[9] In **2** the equatorial average Mn–C distance is 2.005(4) Å. This interpretation of the structure of **2** renders the anion $[Mn_2(\mu\text{-}N)(CN)_{10}]^{6-}$ a mixed-valent Mn^{V}–Mn^{II} species which is statistically disordered over two sites in the crystal.

The effective magnetic moment of solid **3** increases from 1.72 μ_B at 4 K to 2.03 μ_B at 300 K. The salts **1** and **2** also have magnetic moments in this range, but they are less temper-

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