A Facile Palladium-Mediated Contraction of Benzene to Cyclopentadiene: Transformations of Palladium(II) *p*-Benziporphyrin**

Bartosz Szyszko, Lechosław Latos-Grażyński,* and Ludmiła Szterenberg

The contraction of benzene and its derivatives to form a cyclopentadiene ring has rarely been reported. Pioneering studies on the photooxidation of benzene led to the conclusion that cyclopentadienecarboxyaldehyde was formed in this reaction.[1] Since then, research on photoinduced reactions of hydroxy- and dihydroxybenzene revealed interesting mechanistic features, including ring contraction from benzene to cyclopentadiene.[2] A similar structural motif was detected in the course of thermal decomposition of anisole or dihydroxybenzene.[3] The oxidation of phenol with dioxygen in the presence of metallic copper resulted in the aromatic ring contraction to afford substituted cyclopentenes.[4] Carbocycle contraction to benzvalene followed by opening of the ring to form benzene was postulated in theoretical studies on the high-temperature intramolecular topomerization of [1,2-$^{13}C_2$]benzene to [1,3-$^{13}C_2$]- and [1,4-$^{13}C_2$]benzene.[5] In more general terms, the benzene contraction belongs to an exclusive group of reactions where the cleavage of aromatic structures is of fundamental importance. Significantly, oxidative ring cleavage is a key metabolic step in the biodegradation of aromatic compounds by bacteria. The common metabolic pathway is a ring fission by catechol dioxygenases that contain a nonheme iron(II) center in the active site.[6] The representative examples where such a challenge has been chemically addressed include cleavage of the aromatic rings with formation of metallacyclopentadiene complexes according to a retro-alkyne cyclotrimerization mechanism,[7] a reductive silylation of silylsubstituted arenes,[8] or insertion of tungsten into unstrained aromatic rings.[9] Recently, an impressive room-temperature C−C bond fission of an arene by a metallacarborane was reported.[10]

Porphyrinoids (including carbaporphyrinoids) provide a unique macrocyclic platform that is suitable for exploring organometallic chemistry confined to a particular macrocyclic environment.[11–15] Often C−H or C−C bonds are held close to the metal center, thus enforcing an unusual coordination

geometry and unique reactivity. Herein we report the contraction of the benzene ring embedded in palladium(II) *p*-benziporphyrin **1**. This process affords palladium(II) 21-formyl-21-carbaporphyrin **4** and palladium(II) 21-carbaporphyrin **5**, and proceeds via palladium(II) 22-hydroxycyclohexadieneporphyrin **3** as a spectroscopically detectable intermediate.

Reaction of palladium(II) chloride with *p*-benziporphyrin **1** in acetonitrile results in the formation of the four-coordinate palladium(II) *p*-benziporphyrin **2** (Scheme 1). The geometry
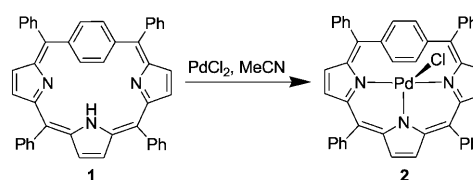
Scheme 1. Synthesis of **2**. Reaction conditions: palladium(II) chloride (3.3 equiv), acetonitrile, 293 K, 48 h, 72%.

of **2** as determined by X-ray crystallography[16] (Figure 1) resembles the structure of palladium(II) vacataporphyrin or nickel(II) and cadmium(II) *p*-benziporphyrins,[17–19] and reflects the balance between the constraints of the macro-
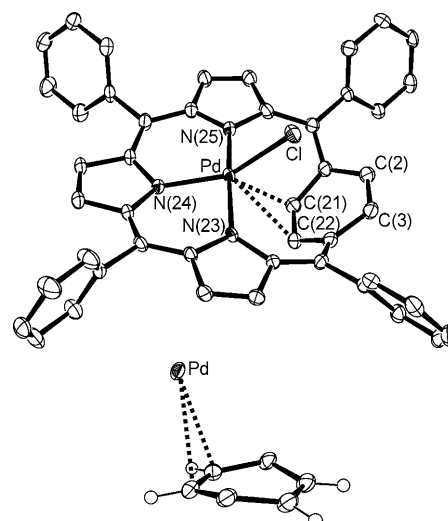
Figure 1. Crystal structure of **2** (top) and interaction geometry between the palladium(II) ion and the *p*-phenylene moiety (bottom). Thermal ellipsoids represent 50% probability. Selected bond lengths [Å]: Pd–N(23) 2.075(2), Pd–N(24) 2.035(2), Pd–N(25) 2.082(3).

[*] B. Szyszko, Prof. L. Latos-Grażyński, Dr. L. Szterenberg
Department of Chemistry, University of Wrocław
14 F. Joliot-Curie St., 50-383 Wrocław (Poland)
Fax: (+48) 71-328-2348
E-mail: llg@wchuwr.pl
Homepage: http://llg.chem.uni.wroc.pl

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cyclic ligand, the size of the palladium(II) ion, and the predisposition of the palladium(II) for square-planar geometry.

The distinct feature of the structure is the very pronounced bending of the chloride ligand toward the annulenic unit. Significantly, the N(23)-Pd-N(25) fragment (168.9(1)°) is slightly distorted from linearity, while N(24)-Pd-Cl is bent (150.0(1)°) as a consequence of strain induced by incorporation of a metal–chloride bond into a macrocyclic ring. In particular, the *p*-phenylene approaches palladium(II) at a distance much shorter (Pd···C(21) 2.83 Å, Pd···C(22) 2.85 Å) than the expected van der Waals contact (Pd···C 3.3 Å),[20] but still larger than commonly observed Pd–C bond lengths, as the typical values for palladium(II)–C(η^2) alkene complexes are in the order of 2.18 Å.[21,22] The palladium(II) ion interacts with the benzene ring in a η^2 fashion. The projection of the palladium(II) ion onto the C(2)C(3)C(21)C(22) plane (C^4 plane) lies close to the center of the C(21)–C(22) bond.

The coordination of palladium(II) constrains the libration of *p*-phenylene, and the ^{1}H NMR spectrum of **2** contains sharp *p*-phenylene signals ($\delta_{2,3} = 9.04$ ppm, $\delta_{21,22} = 1.40$ ppm) with no signs of conformational exchange at the 220 K–298 K range (Figure 2a). The palladium(II)···*p*-phenylene interaction in solution can be readily confirmed by analysis of the ^{13}C chemical shift difference of the C(21) resonances for **2** and **1** ($\Delta\delta = 25.5$ ppm). This interaction might be also be evidenced

by the ^{13}C chemical shift difference between C(2) and C(21) carbon atoms in **2** ($\Delta\delta = 33.1$ ppm).

A solution of palladium(II) *p*-benziporphyrin **2** in acetonitrile underwent a reaction over 12 h after addition of potassium carbonate at 293 K to form a heterogeneous mixture. Palladium(II) 21-formyl-21-carbaporphyrin **4** and palladium(II) 21-carbaporphyrin **5** were identified as the final products of this reaction (Scheme 2). These species are reproducibly formed in a 3.5:1 (**4/5**) molar ratio under the
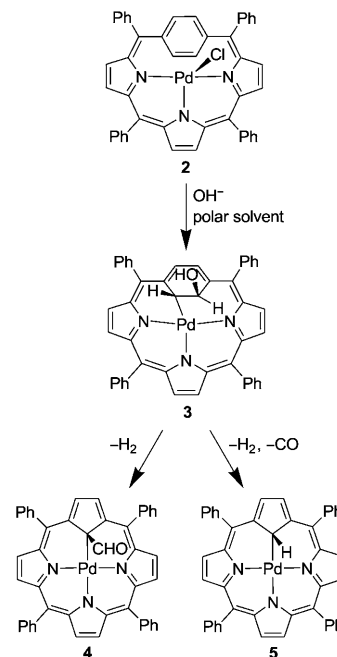
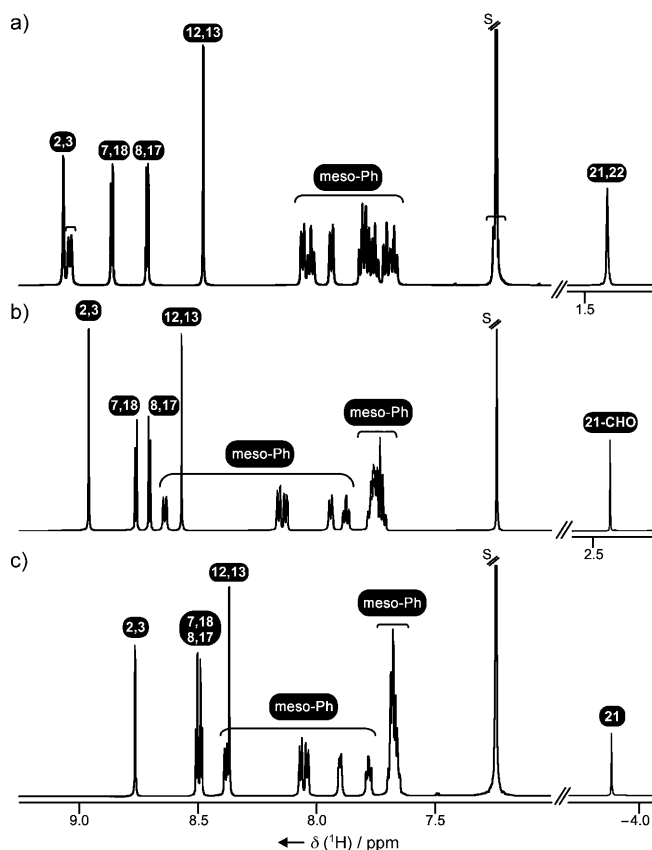***Scheme 2.*** Contraction of palladium(II) *p*-benziporphyrin **2**.

reaction conditions. Importantly, independent experiments have shown that the direct transformation of **4** into **5** has not been detected in acetonitrile solution in the presence of potassium carbonate. On the synthetic (16.5 mg) scale, **4** and **5** were obtained in 42% and 12% yields, respectively, after chromatographic workup. In fact, when the reaction was carried out in a variety of solvents, it was clear that the composition of contracted products is dependent on the choice of solvent. Compound **5** is preferentially formed in protic solvents (methanol and ethanol), whereas only **4** was detected in chloroform or dichloromethane solutions. A mixture of **4** and **5** was typically formed in polar aprotic solvents (DMSO, THF, acetonitrile).

The progress of the contraction from **2** to **4** was directly followed by ^{1}H NMR spectroscopy under conditions that allowed the best spectroscopic monitoring of the reaction (i.e., in CDCl$_3$ saturated with water in the presence of solid potassium carbonate). Initially an unstable intermediate, namely aromatic palladium(II) 22-hydroxycyclohexadiene-porphyrin **3**, was produced at 298 K and results from the stereoselective *anti*-addition of palladium(II) and a hydroxide ion across the C(21)–C(22) double bond. After 0.5 h (298 K),

Figure 2. ^{1}H NMR spectra of a) **2** (CDCl$_3$, 215 K), b) **4** (CDCl$_3$, 280 K), and c) **5** (CDCl$_3$, 270 K). Resonance assignments follow the typical numbering of *p*-benziporphyrin (a) or N-confused porphyrins (b,c). S = solvent.

the transient **3** converts into the aromatic **4**, which is the sole stable product of the reaction.

The ^{1}H NMR spectra of **3**, **4**, and **5** (Figures 2 and 3) show the basic features of aromatic carbaporphyrinoids.[12,15,21]
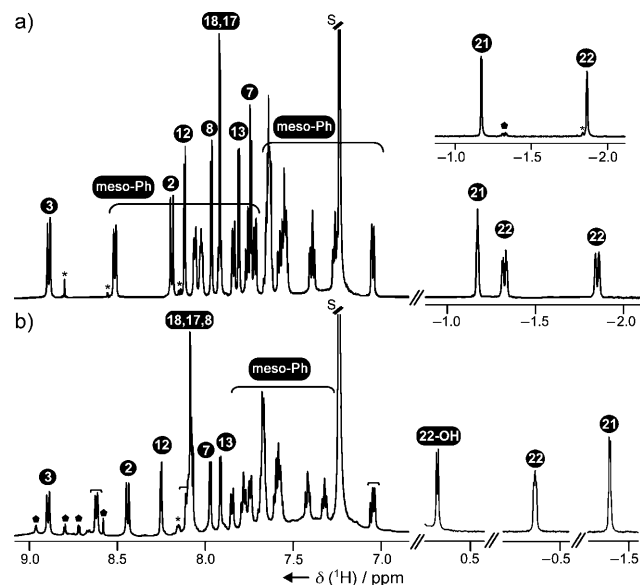

Figure 3. ^{1}H NMR spectra of a) **6**-H; b) **3** (both CDCl₃, 220 K). The inset shows the upfield part of the spectrum of **6**-D (CDCl₃, 220 K) as obtained in reaction of **2** with sodium borodeuteride in [D₄]methanol. The residual resonances of **4** in (b) and **6** (inset) are marked with asterisks. Resonance assignments follow the numbering of *p*-benziporphyrin. S = solvent.

Complete assignments of resonances have been made on the basis of relative intensities and through a combination of homonuclear (COSY, NOESY, ROESY) and heteronuclear (HMQC, HMBC) correlation techniques. The ^{1}H NMR spectrum of transient **3**, which was efficiently trapped at 220 K to prevent any further transformation (Figure 3b), shows an increased multiplicity of resonances compared to the spectra of C_s-symmetric **2**, **4**, and **5** (Figure 2). The spectra of **3** and palladium(II) cyclohexadieneporphyrin **6** (Scheme 4) show some similarities (Figure 3), as both species contain the cyclohexadiene moiety.

The most notable structural feature of **3** is the coordination of palladium(II) by the tetrahedrally hybridized C(21) center. A complete set of resonances that correspond to OH, ($\delta = 0.69$ ppm, readily exchangeable with deuterium after addition of D₂O), H(21) ($\delta = -1.40$ ppm), and H(22) ($\delta = -0.36$ ppm) serve as the fingerprint of the unprecedented 22-hydroxycyclohexadienyl moiety. The structural model of **3**, generated by DFT optimization (Figure 4), reflects the structural constraints determined by NOE measurements. In fact, the cyclohexadiene ring adopts the highly strained half-chair conformation. The palladium(II) and hydroxy units are located at the vicinal carbon atoms and occupy axial positions to result in an *anti* arrangement. The NOE correlations (Figure S3 in the Supporting Information), which result from through-space interactions OH···H(2), OH···H(3), OH···20-*o*-Ph, and H(21)···20-*o*-Ph, confirm unambiguously the axial
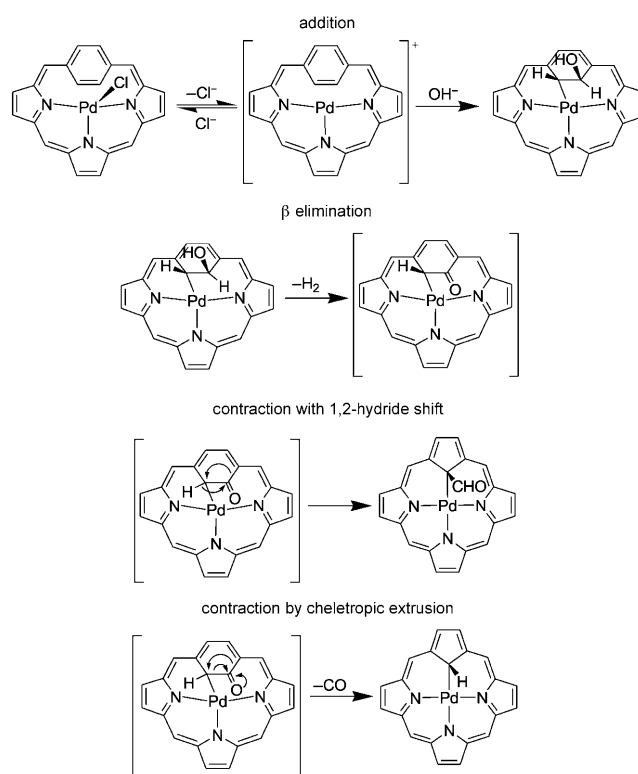
Scheme 3. Palladium(II)-mediated contraction mechanism.

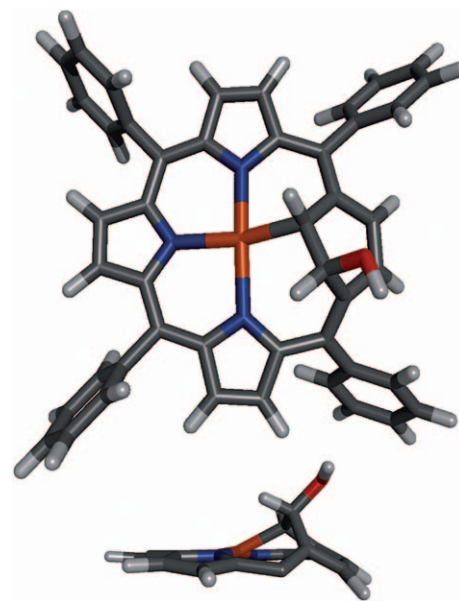**Figure 4.** DFT-optimized structure of **3**. Selected bond lengths [Å] and angles [°]: Pd–C(21) 2.088, Pd–N(23) 2.173, Pd–N(24) 2.120, Pd–N(25) 2.063; N(23)-Pd-N(25) 172.0, N(25)-Pd-C(21) 161.0. C dark gray, H light gray, N blue, O red, Pd orange.

position of the hydroxy group in the cyclohexadiene unit; this conformation results from the *anti*-addition of palladium(II) and a hydroxide ion to **2**.

The specific [1]H ($\delta = 2.43$ ppm) and [13]C ($\delta = 170.0$ ppm) resonances of the 21-formyl unit in **4** and H(21) ($\delta = -3.86$ ppm) in **5** readily confirmed the identity of these

complexes. Significantly, the ^{13}C chemical shifts determined for the C(21) atoms of **3** ($\delta = 22.3$ ppm), **4** ($\delta = 59.9$ ppm), **5** ($\delta = 34.0$ ppm), and **6** ($\delta = 14.2$ ppm) reflect the tetrahedral geometry around the coordinating carbon atom.

The coordination environment of the palladium(II) center corresponds to the conventional square-planar structure with the N(22), N(23), N(24), and C(21) atoms occupying equatorial positions. The macrocycle reveals the bond-length pattern expected for the aromatic 21-carbaporphyrin.[15] The specific localization of the 21-formyl substituent results in the relatively short Pd···C(formyl) distance (2.531(2) Å). Significantly, in spite of the intensive exploration of metallocarbaporphyrinoids, **4** (Figure 5) and **5** are the very first representatives of 21-carbaporphyrin complexes.[13,15,23–25]
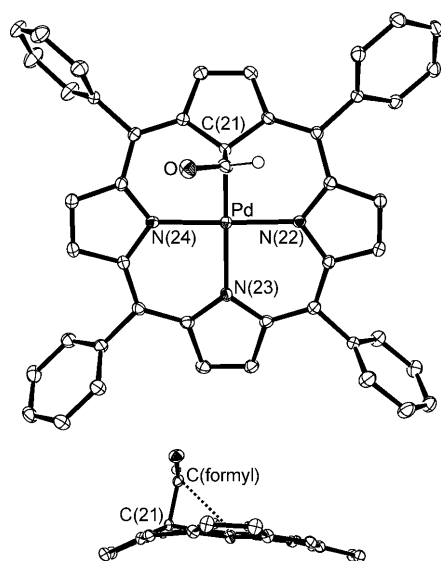

Figure 5. Crystal structure of **4** (top: perspective view, bottom: side view with phenyl groups omitted for clarity). Thermal ellipsoids represent 50% probability. Selected bond lengths [Å]: Pd–N(22) 2.012(2), Pd–N(23) 2.048(2), Pd–N(24) 2.023(2), Pd–C(21) 2.084(2). The side view shows the geometry of interaction between palladium(II) and the formyl substituent.

A feasible mechanism of contraction consistent with formation of **3**, **4**, and **5** is shown in Scheme 3 and comprise the following major steps: 1) addition of palladium(II) and a hydroxide ion to the C(21)–C(22) double bond,[26] 2) β elimination,[27] and 3) competing contractions by 1,2-hydride shift or cheletropic extrusion of carbon oxide. The contraction is accompanied by a relief of strain energy of the embedded conjugated 1,3-cyclohexadiene ring and finally by the formation of a new aromatic porphyrinoid system.

Activation of the *p*-phenylene moiety of **2** toward a combined addition of palladium(II) and a nucleophile of choice is of particular importance and has been proven to be a more general reactivity route. In fact, reaction of **2** with sodium borohydride (in methanol), sodium borodeuteride (in [D$_4$]methanol), and sodium ethoxide afforded **6**-H, **6**-D, and **7** respectively (Scheme 4). Significantly, **6** and **7** do not undergo further conversion, thus directly confirming the unique role of the hydroxy group in the contraction mechanism. The
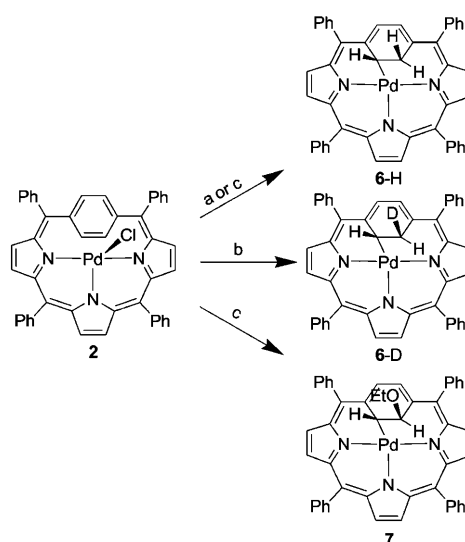
Scheme 4. Addition to **2**. Reaction conditions: a) sodium borohydride, methanol, b) sodium borodeuteride, [D$_4$]methanol, and c) sodium ethoxide in ethanol.

addition of alkoxides is reversible as **2** forms from **7** during column chromatography on silica gel. The addition of the ethoxide ion to form **7** competes with the reduction of **2** to form **6**-H. The ethoxide ion in ethanol acted as the reducing agent, as equimolar amounts of **6**-H and ethanal were detected by ^{1}H NMR spectroscopy in the reaction mixture (Figure S5).

In conclusion, palladium(II) *p*-benziporphyrin provides a unique environment to alter the fundamental reactivity of the benzene unit. The possibility of a metal···(carbon–carbon) interaction by encapsulating the specific donor center (CCNNN) in the porphyrinic core is of fundamental importance.[12,17,18] By taking advantage of the additional stabilization that arises from geometrical constraints of the porphyrin macrocycle, a cascade of intramolecular rearrangements has been efficiently promoted. Accordingly, the remarkable, facile palladium(II)-mediated contraction of *p*-phenylene to cyclopentadiene affords the first reported complex of 21-carbaporphyrin.

[1] a) M. Luria, G. Stein, *Chem. Commun.* **1970**, 1650–1651; b) L. Kaplan, L. A. Wendling, K. E. Wilzbach, *J. Am. Chem. Soc.* **1971**, *93*, 3819–3820.

[2] a) C. Guyon, P. Boule, J. Lemaire, *Tetrahedron Lett.* **1982**, *23*, 1581–1584; b) C. Guyon, P. Boule, J. Lemaire, *New J. Chem.* **1984**, *8*, 685–692; c) C. Richard, P. Krajnik, G. Grabner, *Phys. Chem. Chem. Phys.* **2010**, *12*, 14322–14329.

[3] a) A. M. Scheer, C. Mukarakate, D. J. Robichaud, G. B. Ellison, M. R. Nimlos, *J. Phys. Chem. A* **2010**, *114*, 9043–9056; b) C. A. Taatjes, D. L. Osborn, T. M. Selby, G. Meloni, A. J. Trevitt, E.

Epifanovsky, A. I. Krylov, B. Sirjean, E. Dames, H. Wang, *J. Phys. Chem. A* **2010**, *114*, 3355 – 3370; c) L. Khachatryan, J. Adounkpe, B. Dellinger, *J. Phys. Chem. A* **2008**, *112*, 481 – 487; d) S. Thomas, E. B. Ledesma, M. J. Wornat, *Fuel* **2007**, *86*, 2581 – 2595; e) M. Altarawneh, B. Z. Dlugogorski, E. M. Kennedy, J. C. Mackie, *J. Phys. Chem. A* **2010**, *114*, 1098 – 1108.

[4] M. Lanfranchi, L. Prati, M. Rossi, A. Tiripicchio, *J. Mol. Catal. A* **1995**, *101*, 75 – 80.

[5] H. F. Bettinger, P. R. Schreiner, H. F. Schaefer III, P. von R. Schleyer, *J. Am. Chem. Soc.* **1998**, *120*, 5741 – 5750.

[6] a) J. A. Field, R. Sierra-Alvarez, *Biodegradation* **2008**, *19*, 463 – 480; b) P. C. A. Bruijnincx, G. Van Koten, R. J. M. K. Gebbink, *Chem. Soc. Rev.* **2008**, *37*, 2716 – 2744; c) M. Costas, M. P. Mehn, M. P. Jensen, L. Que, *Chem. Rev.* **2004**, *104*, 939 – 986.

[7] R. M. Pope, S. L. VanOrden, B. T. Cooper, S. W. Buckner, *Organometallics* **1992**, *11*, 2001 – 2003.

[8] C. Krempner, H. Reinke, R. Wustrack, *Inorg. Chem. Commun.* **2007**, *10*, 239 – 242.

[9] A. Sattler, G. Parkin, *Nature* **2010**, *463*, 523 – 526.

[10] D. Ellis, D. McKay, S. A. Macgregor, G. M. Rosair, A. J. Welch, *Angew. Chem.* **2010**, *122*, 5063 – 5065; *Angew. Chem. Int. Ed.* **2010**, *49*, 4943 – 4945.

[11] J. D. Harvey, C. J. Ziegler, *Coord. Chem. Rev.* **2003**, *247*, 1 – 19.

[12] M. Stępień, L. Latos-Grażyński, *Acc. Chem. Res.* **2005**, *38*, 88 – 98.

[13] T. D. Lash, *Eur. J. Org. Chem.* **2007**, 5461 – 5481.

[14] M. Toganoh, H. Furuta, in *Handbook of Porphyrin Science: with Applications to Chemistry, Physics, Materials Science Engineering, Biology and Medicine, Vol. 2* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific Publishing, Singapore, **2010**, pp. 295 – 367.

[15] M. Pawlicki, L. Latos-Grażyński in *Handbook of Porphyrin Science with Applications to Chemistry, Physics, Materials Science Engineering, Biology and Medicine, Vol. 2* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific Publishing, Singapore **2010**, pp. 104 – 192.

[16] CCDC 818561 (**2**) and 818562 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] M. Stępień, L. Latos-Grażyński, *J. Am. Chem. Soc.* **2002**, *124*, 3838 – 3839.

[18] M. Stępień, L. Latos-Grażyński, L. Szterenberg, J. Panek, Z. Latajka, *J. Am. Chem. Soc.* **2004**, *126*, 4566 – 4580.

[19] E. Pacholska-Dudziak, J. Skonieczny, M. Pawlicki, L. Szterenberg, Z. Ciunik, L. Latos-Grażyński, *J. Am. Chem. Soc.* **2008**, *130*, 6182 – 6195.

[20] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441 – 451.

[21] B. Binotti, G. Bellachioma, G. Cardaci, A. Macchion, C. Zuccaccia, E. Foresti, P. Sabatino, *Organometallics* **2006**, *21*, 346 – 354.

[22] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, *J. Chem. Soc. Dalton Trans.* **1989**, S1 – S83.

[23] K. Berlin, *Angew. Chem.* **1996**, *108*, 1955 – 1957; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1820 – 1822.

[24] T. D. Lash, M. J. Hayes, *Angew. Chem.* **1997**, *109*, 868 – 870; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 840 – 842.

[25] J. Skonieczny, L. Latos-Grażyński, L. Szterenberg, *Chem. Eur. J.* **2008**, *14*, 4861 – 4874.

[26] J. A. Keith, P. M. Henry, *Angew. Chem.* **2009**, *121*, 9200 – 9212; *Angew. Chem. Int. Ed.* **2009**, *48*, 9038 – 9049.

[27] J. D. Zhang, B. B. Wayland, L. Yun, S. Li, X. F. Fu, *Dalton Trans.* **2010**, *39*, 477 – 483.