Porphyrinoids

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

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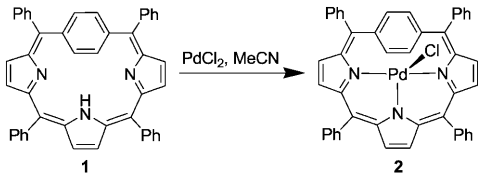
The contraction of benzene and its derivatives to form a cyclopentadiene ring has rarely been reported. Pioneering studies on the photooxidation of benzene led to the conclusion that cyclopentadienecarboxyaldehyde was formed in this reaction.[1] Since then, research on photoinduced reactions of hydroxy- 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-

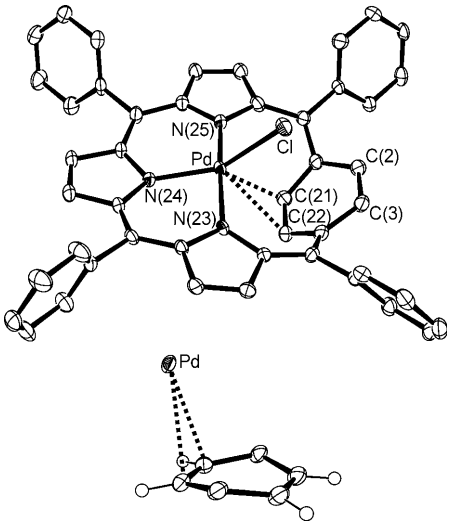


Figure 1. Crystal structure of **2** (top) and interaction geometry between the palladium(II) ion and the *p*-phenylene moiety (bottom). Thermal ellipsoids represent 50% probability. Selected bond lengths [Å]: Pd–N(23) 2.075(2), Pd–N(24) 2.035(2), Pd–N(25) 2.082(3).

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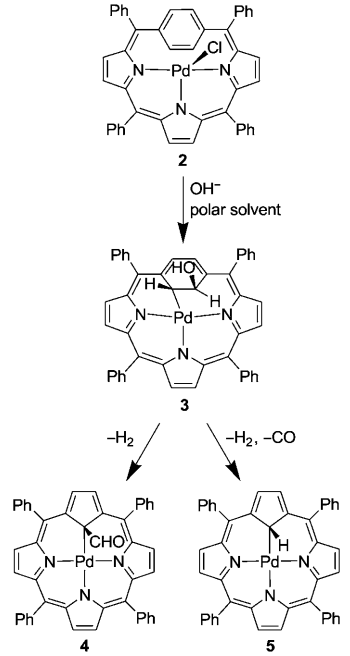
cyclic ligand, the size of the palladium(II) ion, and the predisposition of the palladium(II) for square-planar geometry.

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**.

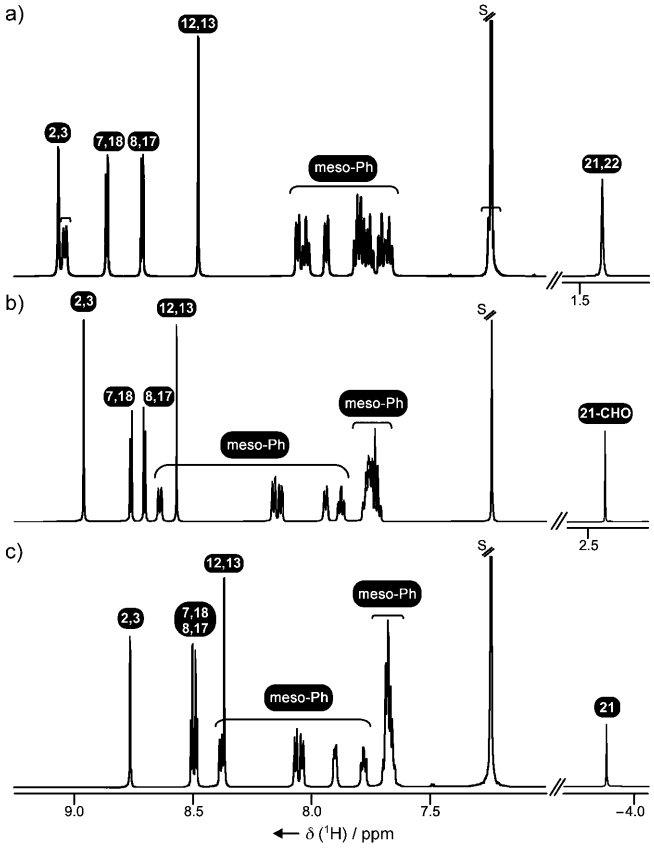


Figure 2. ^{1}H NMR spectra of a) **2** ($CDCl_3$, 215 K), b) **4** ($CDCl_3$, 280 K), and c) **5** ($CDCl_3$, 270 K). Resonance assignments follow the typical numbering of *p*-benziporphyrin (a) or N-confused porphyrins (b, c). S = solvent.

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-hydroxycyclohexadieneporphyrin **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),

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]

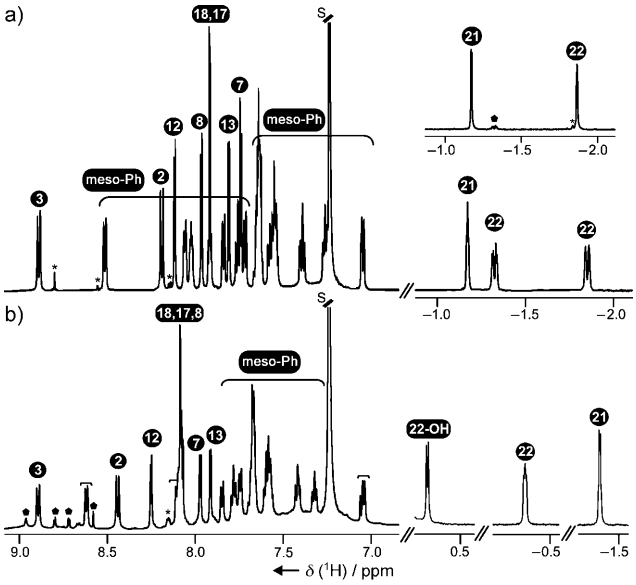
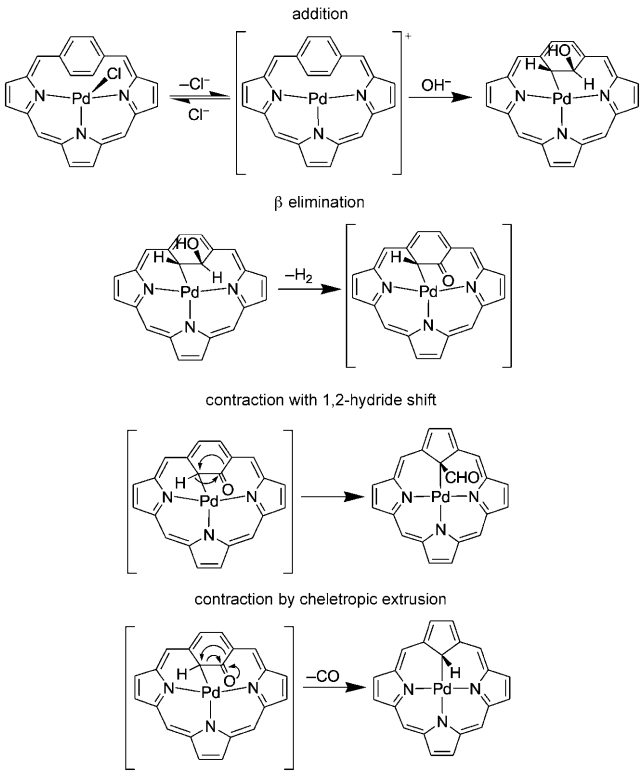


Figure 3. ^{1}H NMR spectra of a) **6**-H; b) **3** (both $CDCl_3$, 220 K). The inset shows the upfield part of the spectrum of **6**-D ($CDCl_3$, 220 K) as obtained in reaction of **2** with sodium borodeuteride in [D_4]methanol. The residual resonances of **4** in (b) and **6** (inset) are marked with 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 D_2O), 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.

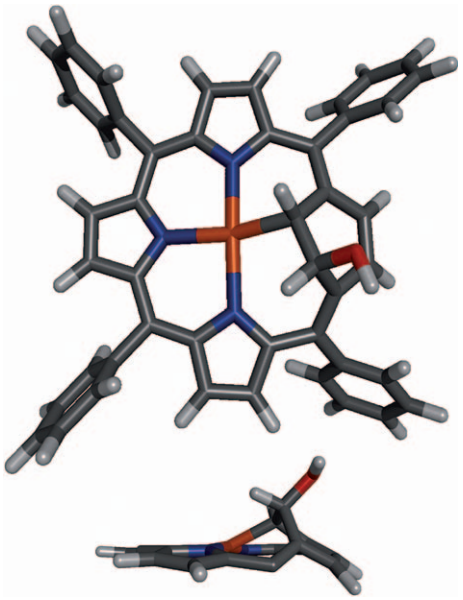


Figure 4. DFT-optimized structure of **3**. Selected bond lengths [Å] and angles [°]: Pd–C(21) 2.088, Pd–N(23) 2.173, Pd–N(24) 2.120, Pd–N(25) 2.063; N(23)-Pd-N(25) 172.0, N(25)-Pd-C(21) 161.0. C dark gray, H light gray, N blue, O red, Pd orange.

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]

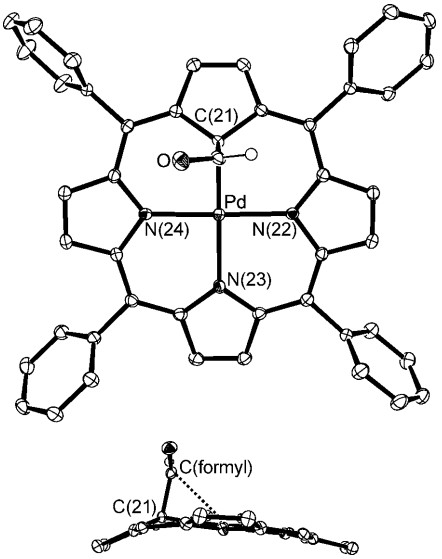
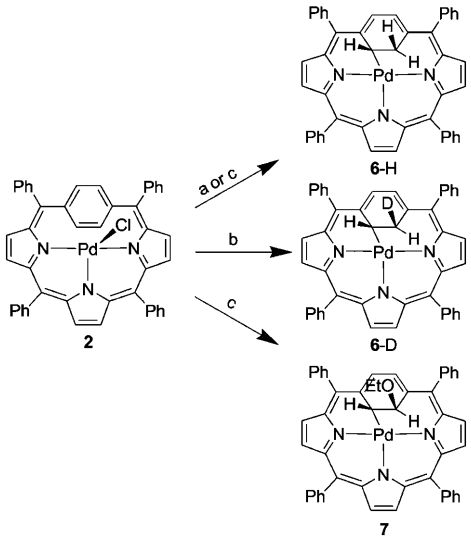


Figure 5. Crystal structure of **4** (top: perspective view, bottom: side view with phenyl groups omitted for clarity). Thermal ellipsoids represent 50% probability. Selected bond lengths [Å]: Pd–N(22) 2.012(2), Pd–N(23) 2.048(2), Pd–N(24) 2.023(2), Pd–C(21) 2.084(2). The side view shows the geometry 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 ^1H 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.

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[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.

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