Heteroporphyrins

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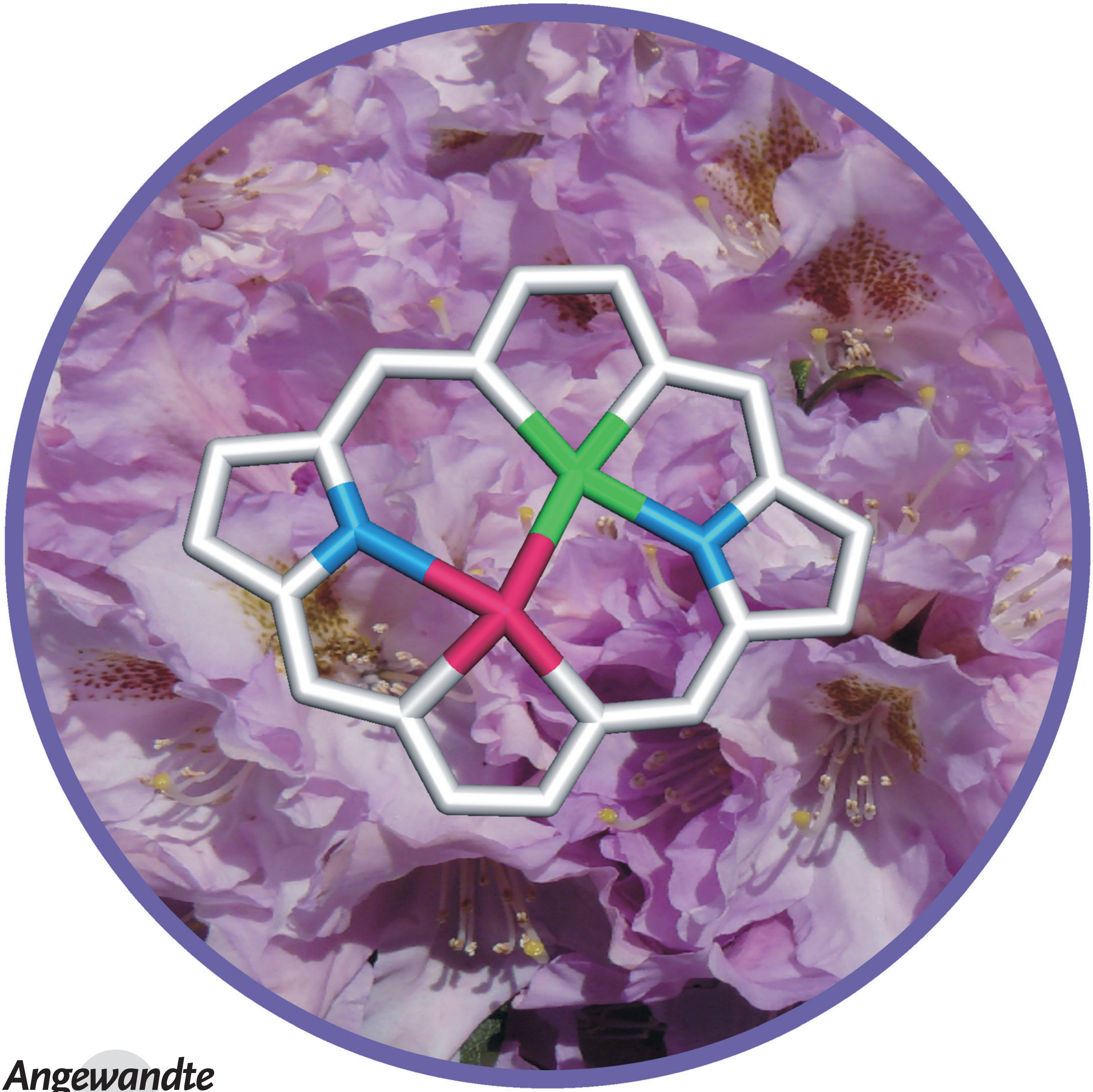
A Porphyrin Skeleton Containing a Palladacyclopentadiene**

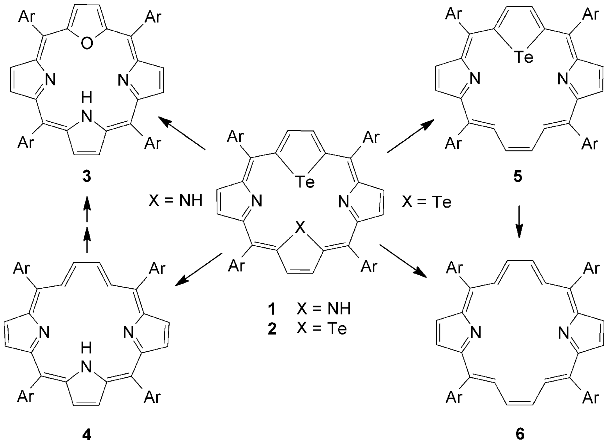
Ewa Pacholska-Dudziak, Michał Szczepaniak, Aleksandra Książek, and Lechosław Latos-Grażyński**



In concept, heteroporphyrins are constructed by the replacement of one or more pyrrole nitrogen atom of a porphyrin with other atoms with preservation of the porphyrin scaffold. Up to now only a limited range of alternative heteroatoms, mostly group 16 elements (O, S, Se, Te), have been incorporated; recently, phosphorus has been built in to form a phosphaporphyrin.[1–8] The analogous modification of the porphyrin core by introduction of CH unit(s) affords the intensively explored carbaporphyrinoids.[9–12] A silicon atom has also been incorporated, albeit only to form the nonaromatic 21-silaphlorin.[13] The entrapment of metal ions in the coordination core of heteroporphyrins allows for the stabilization of extremely rare, virtually unknown oxidation/electronic states of metal ions.[14,15]

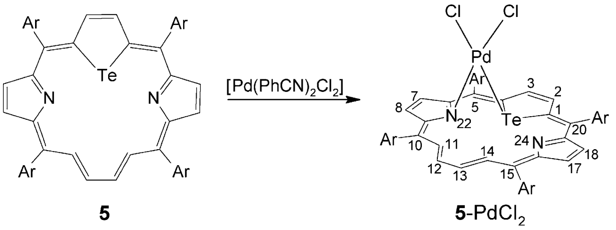
A key step in the synthesis of heteroporphyrinoids is the construction of a suitable synthon for the introduction of the heterocyclic ring into the porphyrin skeleton.[15–17] Rational methods based on [3+1] or [2+2] approaches are widely used; alternatively, stochastic condensations of mixtures of smaller units are, under certain conditions, convenient.[1,3,6] Another approach to core-heteroatom substitution for predefined macrocycles, is represented by the transformation of tetraoxaporphyrinogen into tetrathia- and tetraselenaporphyrinogens with H_2S and H_2Se, respectively, and subsequent oxidation to tetrathia- and tetraselenaporphyrin dications.[18] In a related method the annulation reaction of 1,3-butadiyne-bridged cyclic carbazole dimer with sodium sulfide produced a porphyrinoid containing thiophene and carbazole moieties.[19]

Telluraporphyrins have unique features, as the inner tellurium atom can be removed from the parent 21-telluraporphyrin, **1**, without changing the integrity of the porphyrin skeleton (Scheme 1). Extrusion of a tellurium atom from **1** under oxidative conditions afforded 21-oxaporphyrin **3**,[20] whereas in a strongly acidic solution vacataporphyrin **4** was formed.[21,22] A vacataporphyrin has a vacant space in place of a bridging heteroatom(s) and two hydrogen atoms substituting for one tellurium atom. Remarkably iron(II) vacataporphyrin **4**-Fe, reacts with dioxygen to form iron(II) 21-oxaporphyrin **3**-Fe.[23] 21-Tellura-23-vacataporphyrin **5**, and 21,23-divacataporphyrin **6**, have been formed from 5,10,15,20-tetraaryl-21,23-ditelluraporphyrin **2** by applying the above replacement strategy.[24] In this study on the coordination properties of tellurophene embedded in porphyrinoid frames, we examined the metal binding abilities of 21,23-ditelluraporphyrin **2**[4] and 21-tellura-23-vacataporphyrin[24] **5**, and discovered palladium(II) was the metal of choice. We describe the substitution of one tellurium atom by a palladium atom to afford a unique metallaporphyrin, that is, 21-pallada-23-telluraporphyrin **7** (see Scheme 3), thus extending the scope of this replacement strategy. This molecular hybrid combines features characteristic of a regular porphyrin frame with properties inherent for organopalladium compounds.



Scheme 1. Transformations of telluraporphyrins.

5,10,15,20-Tetraphenyl-21-tellura-23-vacataporphyrin, **5**, reacted with $[Pd(PhCN)_2Cl_2]$ in dichloromethane at room temperature, to give a brown-red-colored complex **5**-$PdCl_2$ in high yield (Scheme 2). The X-ray molecular structure of **5**-$PdCl_2$ shows the side-on coordination of palladium to the porphyrin and the tellurophene ring (Figure 1).[25] The metal is bound to two neighboring porphyrin heteroatoms, tellurium and nitrogen, and to two chlorides in a *cis* arrangement in a square planar geometry. The plane defined by the palladium center bound to these four donors is almost at a right angle to the plane of the tellurophene ring (91.2(1)°).



Scheme 2. Reaction of palladium(II) with 21-tellura-23-vacata-porphyrin, **5**. Ar = phenyl.

The coordination environment of the palladium center is distorted from a regular square owing to the short Te⋯N distance in the porphyrin, this short distance is also reflected by the small Te-Pd-N22 angle (78.8(2)°). The coordination induced a slight nonplanarity of the macrocycle and caused asymmetry of the porphyrin skeleton, as revealed by differences between the Te⋯N22 (2.957(5) Å) and Te⋯N24 (2.662(6) Å) distances.

Notably, on examination of literature only two examples of metal–η^1-tellurophene coordination were found; these examples were of rhodium(III) bound to dibenzotelluro-

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[*] Dr. E. Pacholska-Dudziak, M. Szczepaniak, A. Książek, Prof. L. Latos-Grażyński
Department of Chemistry, University of Wrocław
ul. F. Joliot-Curie 14, 50-383 Wrocław (Poland)
E-mail: ewa.dudziak@chem.uni.wroc.pl
lechoslaw.latos-grazynski@chem.uni.wroc.pl
Homepage: http://llg.chem.uni.wroc.pl/

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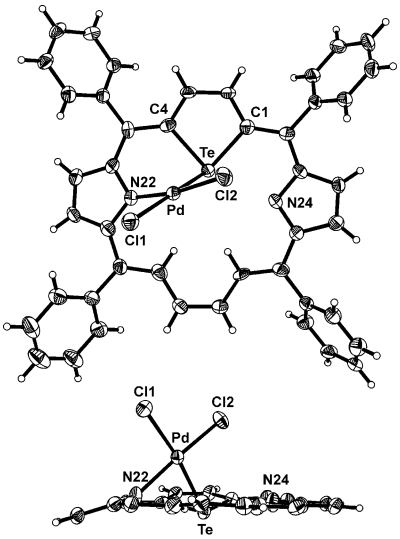


Figure 1. Molecular structure of **5**-PdCl$_2$ (top: perspective view, vibrational ellipsoids set at 50% probability; bottom: side view, aryl groups omitted for clarity). The structure displays disorder in the location of the Te, Pd, and Cl atoms; only the major form is shown. Selected bond lengths (in Å) Pd–Te: 2.523(1); Pd–N22: 2.110(6); Te–C1: 2.090(7); Te–C4: 2.153(7).

phene and the sum of angles around tellurium were 297° and 305,° compared to 276° for **5**-PdCl$_2$.[26]

The ^{1}H NMR spectrum of **5**-PdCl$_2$ (Figure 2) is fully consistent with the solid-state structure of this complex, in terms of the number of resonances, which indicate non-equivalency of all hydrogen atoms. The side-on coordination of palladium causes differentiation of signals of meso-phenyl substituents, observed below 280 K. The proton chemical shifts that are characteristic of porphyrins and the characteristic pattern of the UV/Vis electronic spectrum, which contains an intense Soret-like band at 442 and 493 nm, (Figure 3) are consistent with **5**-PdCl$_2$ having macrocyclic aromaticity.

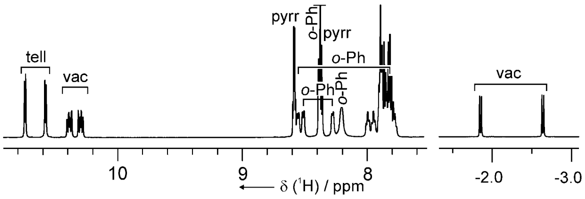


Figure 2. ^{1}H NMR spectrum of **5**-PdCl$_2$ (CD$_2$Cl$_2$, 270 K).

5,10,15,20-Tetraaryl-21,23-ditelluraporphyrin **2**, has an unusual conformation with one tellurophene ring strongly tilted out of the porphyrin plane with a tellurium atom pointing outwards and thus not in the coordination core (Scheme 3 and Scheme 4).[4] The products of the reaction of 5,10,15,20-tetraaryl-21,23-ditelluraporphyrins, with palladium(II) salts, depend strongly on the reaction conditions and the palladium source. The ligand reacts with palladium(II) acetate in the presence of triethylamine in dichloromethane heated to reflux, to give exclusively the pink-red-colored 5,10,15,20-tetraaryl-21-pallada-23-telluraporphyrin **7** (Scheme 3), in which one tellurium atom is replaced by a palladium atom, or in an alternative description, an inverted tellurophene ring is replaced by a "regular" palladacyclopentadiene (palladole) ring.

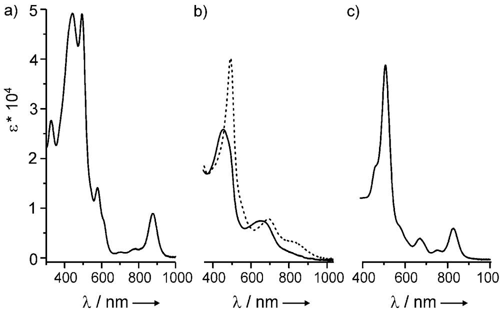
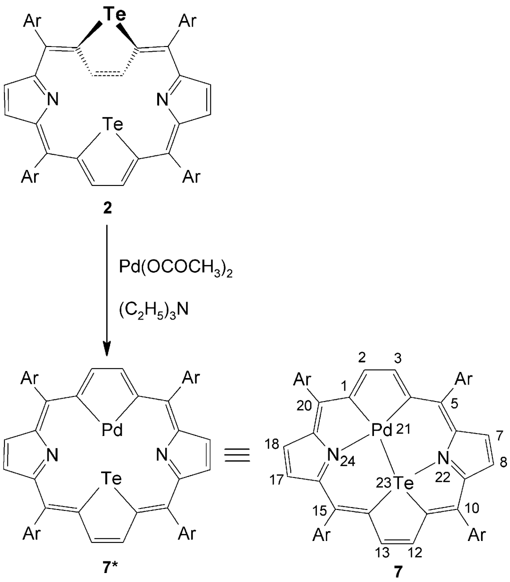


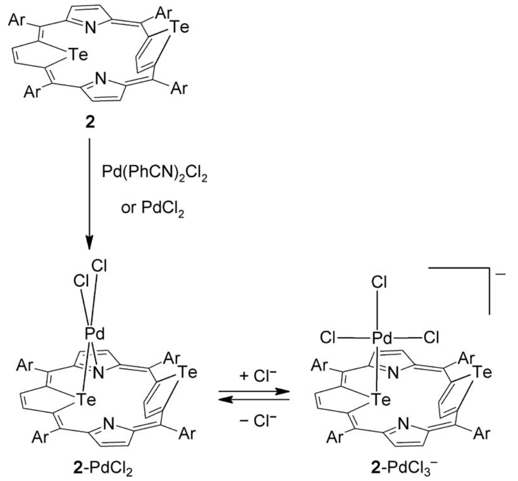
Figure 3. Electronic absorption spectra (in CH$_2$Cl$_2$) of a) **5**-PdCl$_2$; b) **2**-PdCl$_2$ (dotted line) and **2**-PdCl$_3^-$ (solid line); and c) **7**.



Scheme 3. Formation of **7**. Ar = 4-methoxyphenyl.

Insight into the pathway of this unexpected and unprecedented reaction was obtained by studying the reaction of **2** with PdCl$_2$ in dichloromethane/acetonitrile solution, where a brown complex, **2**-PdCl$_2$, a direct precursor to **7**, was obtained nearly quantitatively (Scheme 4). Addition of an excess of chloride anions (as NaCl/D$_2$O or (C$_2$H$_5$)$_4$NCl) to the solution of **2**-PdCl$_2$ yielded another species with spectroscopic (UV/Vis and ^{1}H NMR spectroscopy) data similar to that of **2**, and which we believe to be **2**-PdCl$_3^-$.

The products were characterized in solution by ^{1}H NMR and UV/Vis spectroscopy, and this characterization was supported by HRMS (see the Supporting Information). Both complexes ionize in electrospray conditions to **2**-PdCl$^+$ cations, whereas in ^{1}H NMR spectroscopy, in the investigated temperature range (180–300 K), they exhibit spectroscopic features of side-on complexes of different symmetry: C_s for **2**-PdCl$_3^-$ and C_1 for **2**-PdCl$_2$ (Figure 4). The side-on coordina-



Scheme 4. Formation of palladium(II) 21,23-ditelluraporphyrins.

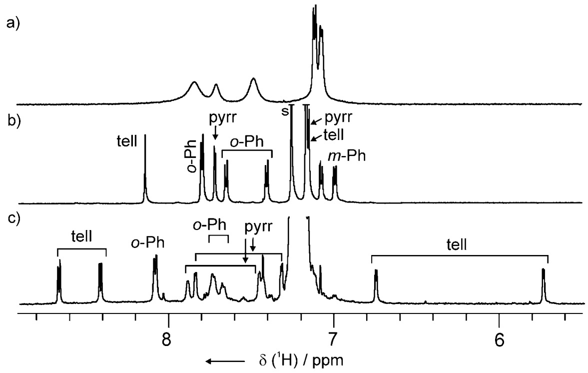


Figure 4. ^{1}H NMR spectra of a) the equilibrium mixture of **2**-PdCl$_2$ and **2**-PdCl$_3$$^-$ (300 K, CD$_2$Cl$_2$); b) **2**-PdCl$_3$$^-$ (220 K, CDCl$_3$); and c) **2**-PdCl$_2$ (240 K, CDCl$_3$).

tion through the N and Te donors of **2**-PdCl$_2$ resembles the coordination mode of **5**-PdCl$_2$. The ROESY experiment carried out at 250 K, on a solution that contained both **2**-PdCl$_3$$^-$ and **2**-PdCl$_2$, revealed the EXSY correlation peaks owing to the **2**-PdCl$_3$$^-$$\rightleftarrows$**2**-PdCl$_2$ exchange processes (Scheme 4). Exchange between two enantiomeric structures of **2**-PdCl$_2$ was documented.

In the presence of triethylamine, both complexes, **2**-PdCl$_2$ and **2**-PdCl$_3$$^-$ convert slowly into 21-pallada-23-telluraporphyrin **7**, albeit in low yield. An analogous side-on acetate complex, is believed to transform much more easily and efficiently, thus impeding its isolation and characterization.

21-Pallada-23-telluraporphyrin **7** is unexpectedly very porphyrin-like with regard to its pink-red color and aromaticity. The electronic spectrum of **7** contains a distinct Soret band and well defined Q-bands, feature that are typical in the spectra of aromatic porphyrins and heteroporphyrins (Figure 3). The previously reported the red-shift observed for the Soret and Q$_1$ band when the number of core heteroatoms is increased and with progression down the periodic table, was confirmed by **7**.[14] Thus, in the spectrum for 21-pallada-23-telluraporphyrin the Soret band is at 453 nm and Q$_1$ at 813 nm.

The geometric relationship between the tellurophene ring and palladium atom in **7** (Figure 5) is apparently different than that in **5**-PdCl$_2$, in which there is a side-on coordination of the palladium(II) center to the tellurophene plane.[25] For **7** there is an atypical, nearly in-plane coordination mode, as reflected by the sum of bond angles around the tellurium atom, 347° for **7** and 276° for **5**-PdCl$_2$. The macrocycle is distorted from planarity (mean dev. for the 24-atom skeleton is 0.11 Å) with dihedral angles between the C$_{4\mathrm{meso}}$ plane and heterocyclic rings equal: 15.3(2)° for palladacyclopentadiene, 2.6(3)° for tellurophene, 11.4(2)° and 5.4(3)° for the N24 and N22 pyrroles, respectively. Another structural feature of **7** is the in-plane distortion of the porphyrin skeleton from the rectangular geometry. The meso carbon atoms are located at vertices of a rhomboid as demonstrated by the angle values, C20-C5-C10 = 99° and C5-C10-C15 = 81°, which are clearly distinct from right angle. The geometry around the palladium(II) center reveals pyramidal distortion from the common square planar structure (the sum of angles around the palladium center equal 341°).

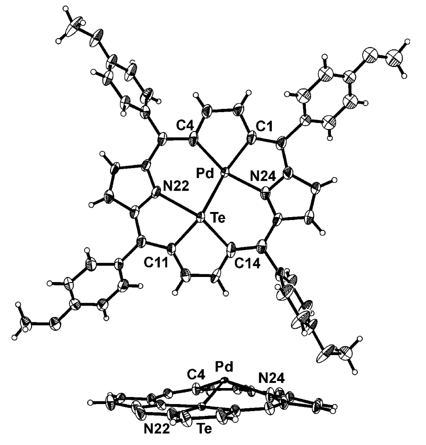


Figure 5. Molecular structure of **7** (top: perspective view, vibrational ellipsoids set at 35% probability; bottom: side view, aryl groups omitted for clarity). The structure displays disorder in the location of the Te and Pd atoms; only the major form is shown. Selected bond lengths [Å] Pd–Te 2.599(1), Pd–N24 2.405(5), Te–N22 2.125(6), Te–C11 2.009(8), Te–C14 2.120(7), Pd–C1 2.046(7), Pd–C4 2.081(8).

The main features of the solid state structure are apparent in the ^{1}H NMR spectrum of **7** at 180 K (Figure 6c), which contains four AB patterns that can be assigned to tellurophene, palladacyclopentadiene, and the pyrrole rings. A gradual increase of temperature reveals exchange between two limiting enantiomeric structures **7A** and **7B** (Scheme 5), and at 300 K dynamic equivalence of pairs of protons is achieved, thus resulting in an ^{1}H NMR spectrum corresponding to an effective C_s symmetry (Figure 6a).

The mechanism of the dynamic exchange involves concerted palladium and tellurium hopping between two pyrrolic nitrogen atoms. Two carbon and one tellurium donors are conserved in the coordination environment of palladium atom, whereas the fourth apex is alternatively filled with N22 or N24. Presumably the transformation is achieved by

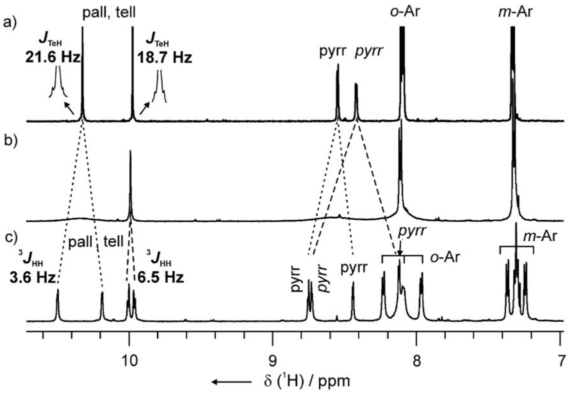
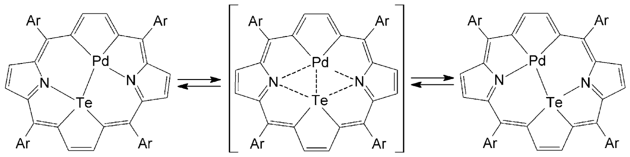


Figure 6. ¹H NMR spectra of **7** (CD_2Cl_2) at a) 300 K; b) 240 K; and c) 180 K.



7A **7#** **7B**

Scheme 5. Fluxional behavior of 21-pallada-23-telluraporphyrin **7**.

exchanging positions that are chemically nonequivalent in the stationary conformers, with the intermediacy of a symmetric transition state **7#**.

The process defined in Scheme 5 was studied by variable-temperature ¹H NMR spectroscopy in the 180–310 K temperature. The reaction activation enthalpy estimated from coalescence temperatures for β-tellurophene and β-palladacyclopentadiene resonances is $\Delta G^{\neq} = 11.0\ \text{kcal mol}^{-1}$ (240 K).

The spectroscopic pattern of **7** at 300 K, which contains a single pyrrolic AB system and two singlets assigned to the tellurophene and palladacyclopentadiene units, is deceptively consistent with the idealized structure **7*** (Scheme 3) and displays features seen for aromatic 21,23-diheteroporphyrins of two-fold symmetry.[3,27,28] The chemical shifts of β-pyrrole and β-tellurophene match values determined for other heteroporphyrins.[3,14,20,27,28] The tellurophene and palladacyclopentadiene singlets are flanked by ^{125}Te satellites, manifesting $^3J_{\text{Te-H}}$ and $^4J_{\text{Te-H}}$ couplings (Figure 6a).

In summary, the unique transformation of palladium(II) 21,23-ditelluraporphyrin resulted in the replacement of a tellurium atom by a palladium atom to give 21-pallada-23-telluraporphyrin. This core-modified porphyrin can be formally derived from 21-telluraporphyrin by replacement of one pyrrolic unit by palladacyclopentadiene[29,30] and its specific stabilization in the porphyrin-like environment. Alternatively **7** can be classified as a palladium(II) complex of 21-tellura-23-vacataporphyrin dianion $\mathbf{5}^{2-}$, deprotonated at two "α" carbons (C11 and C14) of the acyclic C_4 fragment, thus contributing to a library of nontrivial coordination modes of vacataporphyrins.[22,23] This approach is not merely theoretical, as the demetallation reaction **7**→**5** does proceed under acidic conditions (HCl) at room temperature. Noticeably two modes of η¹-tellurophene coordination, that is, side-on and in-plane, have been trapped in the porphyrinoid environment. 21-Pallada-23-telluraporphyrin links several, seemingly distant fields of exploration, broadening the concept of heteroporphyrins and adding more general perspective to metallacylopentadiene chemistry.[29–35]

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