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Helical Structures

Single Helicates of Dipalladium(II) Hexapyrroles: Helicity Induction and Redox Tuning of Chiroptical Properties**

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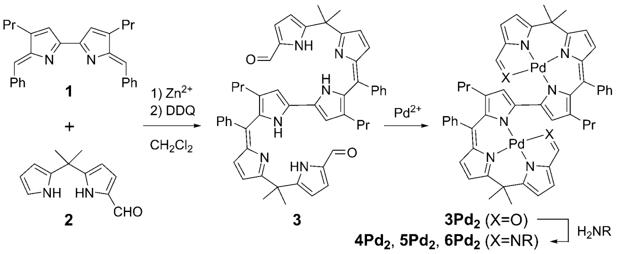
Single helicates have some flexibility in their structures, in contrast to double and triple helicates.[1] That is, their metal sites can be exposed externally and their twist angle and helical handedness can be changed under certain conditions.[2–5] Such a dynamic structural feature of single helicates constitutes a basis for unique molecular functions relevant to chirality. In this context, metal complexes of open chain oligopyrroles have been of great interest in view of their porphyrin-like nature. A number of mononuclear complexes of tetrapyrroles with helical structures have been reported,[6] and a few examples of multinuclear tetrapyrroles are also known.[7] However, control of their helical handedness is difficult, and successful examples have been limited.[8–10]

Induction of a unidirectional helical screw and increasing the chain length are the logical expansion in the chemistry of oligopyrrolic helicates. Open-chain oligopyrroles with more than five pyrrole units,[11] especially of their metal complexes, are rare.[8c,d,10,12] A racemic mixture of dicopper(II) octapyrrole has been reported recently as an exceptional example of the multinuclear single helicate of long oligopyroles.[13] But, these examples are short of structural diversity including control of helicity. Development of longer-chain oligopyrroles is necessary for new multinuclear single helicates. In particular, molecular design for the straightforward introduction of a unidirectional helical screw with high stability against racemization is very important. Herein, we describe hexapyrrole-α,ω-dialdehyde with eight donor atoms for metal coordination and the terminal aldehyde groups for introduction of chirality, leading to a large excess of unidirectional helical screw and the redox driven change of the chiroptical properties in the dipalladium(II) single helicate.



Scheme 1. Synthesis of hexapyrrole **3** and the dipalladium(II) complexes **3 Pd$_2$**, **4 Pd$_2$** (R = benzyl), **5 Pd$_2$** (R = (*S*)-(−)-1-phenylethyl), and **6 Pd$_2$** (R = (*R*)-(−)-1-cyclohexylethyl).

The reaction of 6,6′-diphenyl-4,4′-dipropyl-2,2′-bis(azafulvene) **1**[14] and 5-formyl-*gem*-dimethyl-2,2′-dipyrrylmethane **2**[15] in CH_2Cl_2 was promoted by zinc *p-tert*-butylbenzoate to give hexapyrrole-α,ω-dialdehyde **3**[16] in 73 % yield after oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (Scheme 1). As not only the dipyrrin unit but also the 2,2′-bipyrrole unit and the 2-formylpyrrole unit are regarded as potential bidentate ligands, various metal coordination modes are expected for **3**. When $[PdCl_2(MeCN)_2]$ was reacted with **3** in a mixture of CH_2Cl_2/MeOH for 12 h, a dinuclear palladium(II) complex **3Pd$_2$** was obtained in 57 % yield (Scheme 1). X-ray crystallography of **3Pd$_2$**[16] showed a single helicate composed of a pair of square-planar palladium coordination units with the Pd–Pd distance of 3.166 Å, which is shorter than twice the van der Waals radius of palladium (3.26 Å)[17] (Figure 1). The angle between the two pyrrole mean planes in the 2,2′-bipyrrole unit, the dipyrrylmethane unit, and the dipyrrin unit is 37.4°, 10.7°, and 11.3°, respectively. As a result, each palladium coordination plane is helically distorted and the twist in the central 2,2′-bipyrrole unit generates a primary helical chirality.

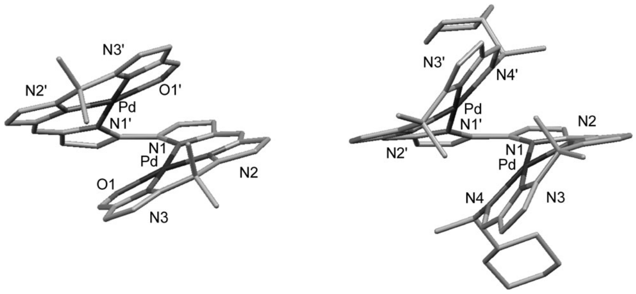


Figure 1. X ray structures of **3 Pd$_2$** (left) and **6 Pd$_2$** (right) with an atom numbering scheme. Propyl and phenyl groups are omitted for clarity. Pd–Pd distances [Å]: 3.1662(5) (left) and 3.4704(5) (right).

The variable-temperature (VT) ^{1}H NMR spectra of **3Pd$_2$** in $CDCl_3$ showed that a broad singlet at 1.25 ppm owing to the *gem*-dimethylmethylene bridge at 40 °C split into a pair of signals at 1.7 and 0.7 ppm at −60 °C (Figure 2). One is similar to the corresponding shift of **3** (1.80 ppm), while the other is considered to reflect the magnetic circumstance inside the cleft between two palladium coordination planes. This observation suggests that the closed helical form of **3Pd$_2$** is

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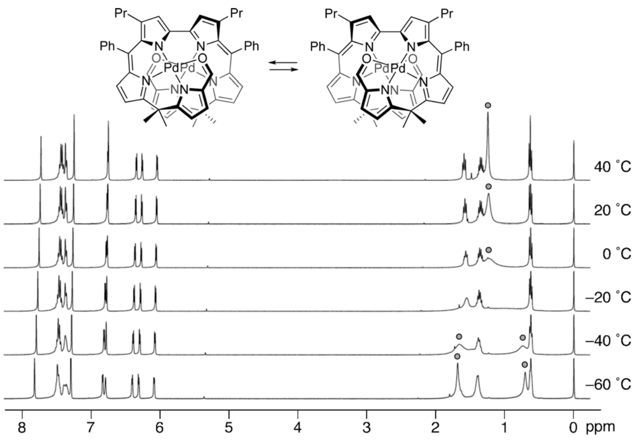
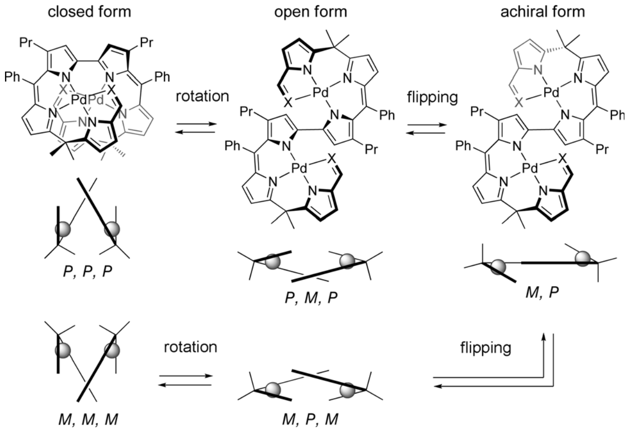


Figure 2. VT ^{1}H NMR spectra of **3 Pd$_2$** in CDCl$_3$. Marked signals are due to the methyl protons of the *gem*-dimethylmethylene bridge.

favored in solution as well as in the crystal and the helicity change is fast on the NMR timescale at room temperature. The energy barrier ($\Delta G^{\neq}_{253} \approx 47\,\mathrm{kJ\,mol^{-1}}$) was estimated on the basis of the coalescence temperature (−20 °C) and the chemical shift difference at −60 °C.[18] A recent study argues for the presence of a weak d^8–d^8 bonding interaction in the dipalladium(II) complexes with a short metal–metal distance.[19] It might contribute to stabilize a closed form of **3 Pd$_2$** in comparison with other conformational isomers.

The oxygen atoms of the terminal formyl groups of **3 Pd$_2$** come close to the 3,3′-hydrogen atoms of the 2,2′-bipyrrole unit when the 2,2′-bipyrrole unit takes an *s*-trans conformation in the course of interchanging helical chirality. Therefore, transformation of the formyl group to a bulkier alkylimine group would affect not only the dynamic behavior of the conformational change but also the helical handedness if the imine group is derived from an optically active alkylamine. When **3 Pd$_2$** was reacted with benzylamine, (*S*)-(−)-1-phenylethylamine, and (*R*)-(−)-1-cyclohexylethylamine in CHCl$_3$ at reflux, the hexapyrrole-α,ω-diimine dipalladium(II) complexes, **4 Pd$_2$**, **5 Pd$_2$**, and **6 Pd$_2$**, were obtained in 85 %, 59 %, and 80 % yield, respectively. As expected, a conformational change of **4 Pd$_2$** was so slow that three sets of signals owing to the conformational isomers were observed separately in the ^{1}H NMR. The molar ratio of 8:18:74 was determined on the basis of the singlets owing to the formimidoyl proton at 8.78, 8.52, and 7.03 ppm, respectively. A remarkable low-frequency shift of the latter signal can be explained in terms of the magnetic shielding effect of the closely situated Pd coordination plane in the closed form. The major isomer showed a pair of singlets owing to the *gem*-dimethylmethylene bridge at 1.64 and 0.85 ppm (Supporting Information, Figures S2, S3). As these chemical shifts are very similar to those observed for **3 Pd$_2$** at −60 °C, the major isomer of **4 Pd$_2$** is associated with the closed form, which was verified by the X-ray crystallography of **4 Pd$_2$**[16] after recrystallization. Three small singlets owing to the methyl protons of the *gem*-dimethylmethylene bridge of the other two isomers, an open form of the C_2 point group and an achiral form of the C_i point group, were observed at 1.85, 1.78, and 1.74 ppm with almost equal intensity (Scheme 2). This is probably because a pair of methyl singlets owing to the isomer of the least amount are overlapped. These three isomers are in equilibrium as seen by the change in their molar ratio from 4:10:86 at 20 °C to 7:13:80 at 90 °C in the ^{1}H NMR in [D$_8$]toluene (Supporting Information, Figure S4). The stereochemical feature of the closed form is described as (*P,P,P*) or (*M,M,M*) on the basis of three components of the local helicity (Scheme 2). Rotation around the bipyrrole 2,2′ bond of the (*P,P,P*) closed form leads to the (*P,M,P*) open form that goes to the achiral form through the flipping of the terminal formimidoylpyrrole moiety.



Scheme 2. Conformational change between closed forms (*P,P,P and M,M,M*), open forms (*P,M,P and M,P,M*), and an achiral form (*M,P*) of **4 Pd$_2$** (X = N-benzyl). The models are seen along the direction of the bipyrrole 2,2′-bond.

As the complexes **5 Pd$_2$** and **6 Pd$_2$** have a stereogenic center at the imine substituent, five diastereomers are distinguishable. In fact, the ^{1}H NMR analysis of **5 Pd$_2$** and **6 Pd$_2$** showed five and four sets of signals with the ratio of 4:1:1:1:1 and 16:1:1:1, respectively. For example, five quartets and four quintets owing to the methine proton at the stereogenic center of **5 Pd$_2$** and **6 Pd$_2$**, respectively, are seen (Figure 3 a,b). The major isomer showed a pair of singlets owing to the *gem*-dimethylmethylene bridge at 1.62 and 0.86 ppm for **5 Pd$_2$** and at 1.64 and 0.87 ppm for **6 Pd$_2$** that are characteristic of the closed form (Supporting Information, Figure S3). Repeated recrystallization of **6 Pd$_2$** from CH$_2$Cl$_2$/

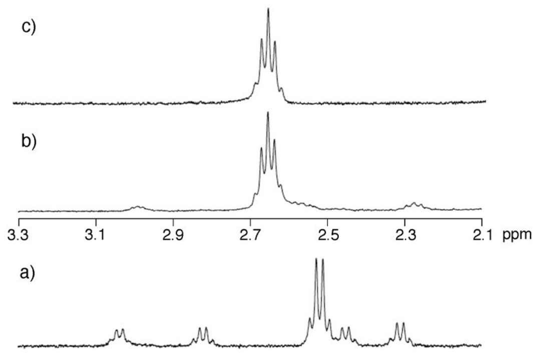


Figure 3. ^{1}H NMR signals in CDCl$_3$ due to the methine proton at the stereogenic center of a) **5 Pd$_2$**, b) **6 Pd$_2$**, and c) a (*P,P,P*) isomer of **6 Pd$_2$**.

MeOH gave the major diastereisomer in a pure form as evidenced by the ^{1}H NMR analysis, which also showed that racemization was negligible at ambient temperature for a couple of days in $CDCl_3$ (Figure 3c; Supporting Information, Figure S5). The (*P,P,P*) helicity was determined by X-ray crystallography (Figure 1).[16]

The relationship between the chiroptical property and the helical handedness in the 2,2′-bisdipyrrin and biliverdin derivatives has been known.[20] In accord with this, the (*P,P,P*) helical form of **6 Pd$_2$** showed a positive CD signal at 699 nm, while a mirror-image CD spectrum was observed for the enantiomer **6′Pd$_2$** prepared from **3 Pd$_2$** and (*S*)-(+)-1-cyclohexylethylamine (Figure 4). **5 Pd$_2$** which has an (*S*)-stereogenic center at the imine auxiliary, showed a weak CD signal of a negative sign at 689 nm. As **5 Pd$_2$** is an equilibrium mixture of the five diastereomers with a 4:1:1:1:1 ratio, the contributions of the minor diastereomers to the whole CD spectrum would be cancelled out. Thus, the observed CD spectrum of **5 Pd$_2$** is considered to reflect a CD profile of the major isomer with the (*M,M,M*) helical conformation.

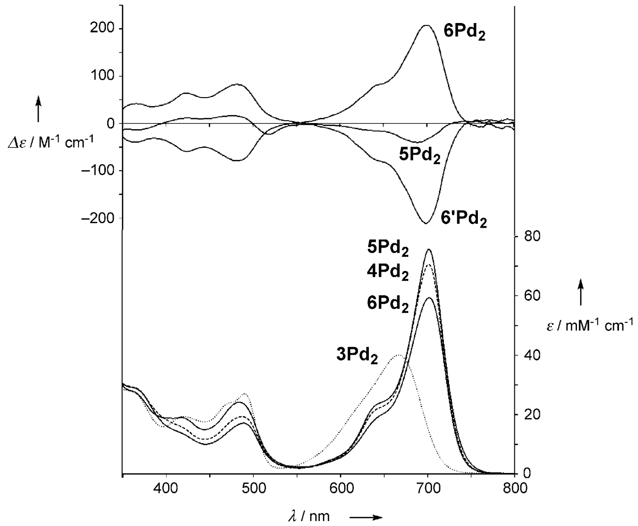


Figure 4. UV/Vis spectra of **3 Pd$_2$**, **4 Pd$_2$**, **5 Pd$_2$**, and **6 Pd$_2$** (bottom), and CD spectra of **5 Pd$_2$**, **6 Pd$_2$**, and **6′Pd$_2$** (top) in CH_2Cl_2.

In view of the recent progress in the chiroptical molecular switch,[21] the redox chemistry of the hexapyrrole dipalladium(II) complexes is of great interest. Cyclic voltammetry of **3 Pd$_2$** showed two redox couples at +0.21 and +0.60 V vs ferrocene/ferrocenium (Fc/Fc$^+$) standard in CH_2Cl_2 (Supporting Information, Figure S12). These values are similar to the potentials for the ligand centered oxidation of the 2,2′-bisdipyrrin metal complexes.[20a,22] Chemical oxidation of **3 Pd$_2$** in CH_2Cl_2 with $AgClO_4$ proceeded to cause a red shift of the major absorption band at 667 nm to 767 nm and appearance of an intense ESR signal at $g = 2.001$ with a linewidth of 5.0 G at room temperature (Supporting Information, Figures S13, S6). This is indicative of the formation of a π cation radical delocalized over the 2,2′-bisdipyrrin chromophore. Although the hyperfine splitting was not seen in the ESR signal, the nature of the oxidized species was inferred from the selective disappearance of the ^{1}H NMR signals owing to the 2,2′-bisdipyrrin part of **3 Pd$_2$** when 0.1 molar equiv of $AgClO_4$ was added (Figure 5). Signals for the protons far apart from the 2,2′-bisdipyrrin part did not disappear. This observation is rationalized in terms of rapid electron hopping between **3 Pd$_2$** and its π cation radical at the 2,2′-bisdipyrrin part.

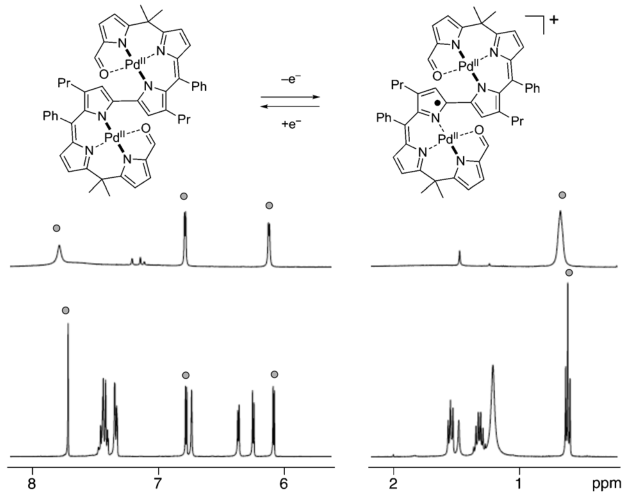


Figure 5. ^{1}H NMR spectra of **3 Pd$_2$** (8.9 mM) in CD_2Cl_2 (bottom) and after adding 0.1 molar equiv of $AgClO_4$ (59 mM) in [D$_8$]toluene (top). The marked signals are due to the formylpyrrole protons and the propyl γ-methyl protons.

One-electron oxidation of the (*P,P,P*) helical form of **6 Pd$_2$** occurred at by 0.07 V more negative potential than that of **3 Pd$_2$** (Supporting Information, Figure S12). The chemical oxidation of **6 Pd$_2$** with $AgClO_4$ completed at one molar equiv of $AgClO_4$. In the meanwhile, both the absorption band and the CD Cotton effect of **6 Pd$_2$** at 699 nm shifted to 741 nm, with isosbestic points at 428, 455, 522, 604, and 720 nm in the UV/Vis and at 406, 556, and 723 nm in the CD (Figure 6). An intense ESR signal at $g = 2.001$ with a linewidth of 6.0 G was observed at room temperature (Supporting Information, Figure S6). This one-electron oxidized species of **6 Pd$_2$** was reduced cleanly by $[Cu^I(MeCN)_4]ClO_4$ to regenerate the original UV/Vis and CD spectrum of **6 Pd$_2$**. It is remarkable that the helical chirality of **6 Pd$_2$** is maintained in this redox cycle with the great change in the CD intensity, that is, $\Delta(\Delta\varepsilon) = -150$ and $+117\,\mathrm{L\,mol^{-1}cm^{-1}}$, in the longer wavelength region at 699 and 741 nm, respectively, upon oxidation at the not so positive potential corresponding to the +0.14 V redox couple versus Fc/Fc$^+$.

In conclusion, the unique dynamic structure of the single helicate of dipalladium(II) hexapyrroles was elucidated. The rate of the conformational change was significantly slowed down by the conversion of the terminal formyl group into the imine group. The closed form was generally preferred in these helicates and the diastereoselectivity and helical handedness were markedly influenced by the point chirality at the imine substituent. As a matter of fact, the (*P,P,P*) helical isomer formed with as high as 85 % diastereoselectivity by using (*R*)-(−)-1-cyclohexylethylamine and it was readily isolated in

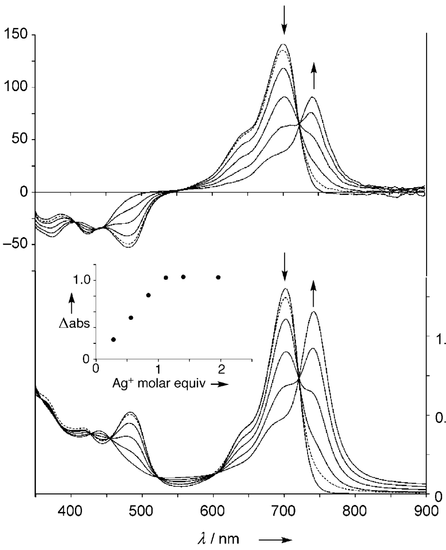


Figure 6. UV/Vis (bottom) and CD (top) titration of **6 Pd$_2$** (23.6 μM) in CH_2Cl_2 with $AgClO_4$ (3.45 mM) in toluene. The dotted line is after adding 8.7 equiv of $[Cu(MeCN)_4]ClO_4$ to the oxidized solution of **6 Pd$_2$** with $AgClO_4$ (2.0 equiv). Inset: a plot of the change of absorption Δabs of the 741 nm band with the added molar equiv of $AgClO_4$.

about 50% yield by recrystallization. The combined application of helical chirality and redox activity in the dinuclear single helicate of hexapyrroles is quite promising in the development of multifunctional materials.

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[16] Experimental procedures, details on the X-ray diffraction, and analytical data of all compounds are provided in the Supporting Information. CCDC 898174 (**3**), 898175 (**3 Pd$_2$**), 898176 (**4 Pd$_2$**), and 898177 (**6 Pd$_2$**) 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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