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Singly and doubly β -to- β platinum-bridged porphyrin dimers and their reductive eliminations[†]

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2-Borylated porphyrins reacted with Pt(cod)Cl₂ to give β -to- β platinum-bridged porphyrin dimers, which were converted to β -to- β directly linked porphyrin dimers through triphenylphosphine-mediated reductive elimination. Similar reactions of 2,18-diborylated Ni(II)-porphyrin and Zn(II)-porphyrin gave the corresponding doubly β -to- β platinum-bridged porphyrin dimers. Treatment of the doubly β -to- β platinum-bridged Ni(II)-porphyrin dimer with triphenylphosphine caused a single reductive elimination to produce a Ni(II)-porphyrin dimer possessing a β -to- β platinum bridge and a β -to- β direct C-C bond.

Introduction

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In the past decade, porphyrins bearing a metal fragment directly at their peripheries have been actively explored in light of their characteristic optical and electronic properties and catalytic reactivity.¹⁻⁴ As an extension of these species, directly metal-bridged porphyrin dimers have also been developed, which display intriguing structural features and characteristic electronic interactions between the porphyrin units through the metal bridge.⁵ Representative examples are shown in Chart 1. The doubly 2,6-pyridylene-bridged Ni(II)-porphyrin dimer underwent smooth palladation to give dimer A, in which the two porphyrin units have meso-to-meso trans-coordination to the palladium metal, and the incorporated palladium metal increases both the electronic interaction and molecular curvature.4e meso-Diphenylphosphanyl Zn(II)-porphyrin facilitated palladation and platination at the adjacent β -position to produce dimer **B**, which shows β -to- β *trans*-coordination of the two porphyrins.^{2b,c} Platinum-bridged dimer C formed from complexation of β -(pyrid-2-yl)-substituted Ni(π)-porphyrin with (Bu₄N)₂PtCl₆ possesses meso-to-meso cis-coordination and shows intriguing conformational slippage upon two-electron reduction at the bridging platinum metal.4d

Recently, we reported the synthesis of cyclic 2,12-porphyrinylene nanorings by following Yamago's synthetic strategy.^{6,7} 2,12-Diborylated Ni(II)-porphyrins were transformed to platinum-bridged oligomeric porphyrin rings, which reacted with triphenylphosphine to induce reductive elimination.⁶ A key factor in the synthesis of such porphyrin nanorings is a preferred *cis*-geometry of the platinum-bridged nanoring intermediates, which causes molecular curvature, as a favorable structural feature for nanoring formation.^{7,8} In this paper, we examined the reactions of 2-borylporphyrins and 2,18diborylporphyrins with Pt(cod)Cl₂ to get information on the structural and electronic details of platinum-bridged porphyrin dimers. Actually, these reactions afforded singly and doubly β to- β platinum-bridged porphyrin dimers, both of which possess *cis*-coordination geometries (dimer **D**) and thus undergo reductive elimination upon treatment with triphenylphosphine.

Results and discussion

2-Borylated Ni(II) porphyrin **1Ni** was treated with 0.5 equiv. Pt(cod)Cl₂ in the presence of cesium fluoride and 1,5-cyclooctadiene (cod) in refluxing THF under an argon atmosphere to give β -to- β platinum-bridged porphyrin dimer **2Ni** in 84% yield as a stable solid (Scheme 1).⁹ Matrix-assisted laser desorption/



Chart 1 Examples of directly metal-bridged porphyrin dimers.

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[†] Electronic supplementary information (ESI) available: Experimental and computational details, as well as X-ray crystallographic data for **2H**, **2Zn**, **3Zn**, **5Ni** and **6Ni** are available. CCDC 1406329–1406332 and 1406343. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc02553b

ionization time-of-flight mass spectrometry (MALDI-TOF-MS) detected the parent ion peak at m/z = 1782.73 (calcd for C₁₀₄- $H_{114}N_8^{58}Ni_2^{192}Pt = 1782.75 [M]^+$). The ¹H NMR spectrum of 2Ni showed singlets due to the meso-protons at 10.66 ppm (H^a) and 9.67 ppm (H^b) and a singlet due to the β -proton (H^c) at 9.12 ppm. Under the same reaction conditions, 2-borylporphyrins 1H and 1Zn were dimerised to give 2H and 2Zn in 60 and 82% yields, respectively. In these reactions, 1,5-cyclooctadiene ligand was found to be crucial, since the reactions with platinum salts with other ligands such as 1,3-bis(diphenylphosphino)propane, ethylenediamine, 2,2'-bipyridine and 2,5-norbornadiene did not give platinum-bridged dimers. The structures of 2H and 2Zn have been unambiguously confirmed by X-ray diffraction analysis (Fig. 1 and ESI[†]). Both dimers 2H and 2Zn display cisarrangements of the two porphyrins at the platinum bridge with bite angles ($\angle C\beta$ -Pt-C β) of 88.18° and 86.33°, respectively. In addition, the two porphyrins in 2H and 2Zn take offset arrangements, as seen in their top views. The C₆-Pt bond lengths are 2.024 and 2.036 Å in 2H, and 2.002 and 2.032 Å in 2Zn, which are longer than the Cmeso-Pt bonds in meso-to-meso cis-Pt(II) bridged Ni(II) porphyrin dimer C (1.933 Å).4 Treatment of 2Ni, 2H and 2Zn with triphenylphosphine induced reductive elimination to yield directly β - β -linked porphyrin dimers 3Ni, 3H and 3Zn in 81, 76 and 78% yields, respectively. X-ray diffraction analysis of 3Zn has revealed a β-to-β direct C-C bond with a bond distance of 1.462 Å and a dihedral angle of the two porphyrins of 57.51°. The structures of 3Ni, 3H and 3Zn are fully consistent with their spectroscopic data (ESI⁺).¹⁰ It is worthy to mention that meso-platinum-bridged porphyrin dimers were not obtained from meso-borylporphyrins under similar conditions, probably due to serious steric hindrance at the mesoposition.

In the next step, we examined the reaction of 2,18-diborylated Ni(II)-porphyrin **4Ni** with an equimolar amount of Pt(cod) Cl₂ in 1,4-dioxane under similar conditions, which afforded doubly β -to- β platinum-bridged porphyrin dimer **5Ni** as a stable compound in 84% yield (Scheme 2). MALDI-TOF-MS showed the mass ion peak of **5Ni** at m/z = 2356.95 (calcd. for $C_{132}H_{152}N_8^{58}Ni_2^{192}Pt_2 = 2357.02$ [M-cod]⁺). The ¹H NMR

PPha

toluene

reflux

3M

Pt(cod)Cl₂

cod

CsF THF reflux

Boin

1M (M = Ni, 2H, Zn)

cod = 1,5-cyclooctadiene

Ar = 3,5-di-*tert*-butylphenyl

Bpin =

Scheme 1 Synthesis of 2M and 3M.



Fig. 1 X-ray crystal structures of 2H and 3Zn. *tert*-Butyl groups, solvent molecules including pyridines coordinated to Zn ions, and hydrogen atoms (except for inner NHs) are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Top view of 2H. (b) Side view of 2H. (c) Top view of 3Zn. (d) Side view of 3Zn.

spectrum of 5Ni exhibited a singlet at 11.86 ppm due to the *meso*-protons and a singlet at 8.76 ppm due to the β -protons adjacent to the platinum linkage. The doubly bridged structure of 5Ni has been confirmed by X-ray analysis, in which the two porphyrins take cis-coordination geometries with C_B-Pt bond lengths of 2.020, 2.044, 2.021 and 2.033 Å (Fig. 2). Therefore, the two porphyrins are held in an oblique arrangement with bite angles of 88.41° and 89.89° . In addition, the two Ni(II) porphyrins take on saddle confirmations with mean-plane deviations of 0.306 Å. This is the first example of doubly and directly metal-bridged porphyrin dimer. The reaction of 4Zn with Pt(cod)Cl₂ under the same conditions gave 5Zn in 70% yield. This complex was found to decompose slowly under ambient conditions but could be stored without serious deterioration under an inert atmosphere at low temperature. In contrast, the reactions of 4H with Pt(cod)Cl2 gave complicated mixtures under all conditions we tested.

Finally, the reductive elimination of **5Ni** was attempted by the reaction with triphenylphosphine in refluxing toluene, which gave rise to a single platinum elimination as well as a ligand replacement of 1,5-cyclooctadiene with two triphenylphosphines to provide dimer **6Ni** in 78% yield (Scheme 3). MALDI-TOF-MS showed the parent ion peak of **6Ni** at m/z =



Scheme 2 Synthesis of doubly platinum-bridged porphyrin dimer 5M.

2579.21 (calcd for $C_{160}H_{170}N_8^{58}Ni_2P_2^{192}Pt = 2579.14 \text{ }[M]^+$). The ¹H NMR spectrum of **6Ni** exhibited a singlet at 11.79 ppm due to the meso-protons and singlets at 9.00 and 8.01 ppm due to the β protons adjacent to the platinum bridge and the direct C-C linkage. The structure of 6Ni has been determined by X-ray analysis, and shows a β-to-β direct C-C bond with a bond distance of 1.486 Å. Owing to the structural constraint imposed by this direct β -to- β connection, the platinum bridge has now a trans coordination geometry with a large C_{β} -Pt- C_{β} angle of 159.04° and slightly longer C_{β} -Pt bond lengths of 2.059 and 2.084 Å as compared with those of 5Ni. The two porphyrins of 6Ni show slightly larger mean-plane deviations of 0.322 and 0.329 Å. Further reductive elimination of 6Ni was attempted under stronger reaction conditions but ended in failure. This failure may be ascribed to the trans-coordination of 6Ni and severe steric hindrance in the expected doubly β -to- β connected porphyrin dimer due to the closely located meso-hydrogen atoms. The reductive elimination of 5Zn was attempted but resulted in the production of a complicated mixture. These results suggest that the central metal in the porphyrin pocket plays a vital role in these reactions.

Fig. 3 shows the UV/vis absorption spectra of **2Ni**, **3Ni**, **5Ni** and **6Ni** in CH₂Cl₂. As compared with the sharp Soret band $(\lambda_{max} = 412 \text{ nm})$ of 5,15-diaryl Ni(π)-porphyrin,¹¹ the Soret band of **2Ni** becomes considerably broadened with a substantial blue shift to 400 nm, reflecting the exciton coupling and the influence of the platinum-bridge. The Soret band of **3Ni** is observed as a much broader band at 408 nm as a consequence of the increased exciton coupling as well as the through-bond electronic interactions. The UV/vis



Fig. 2 X-ray crystal structures of **5Ni** and **6Ni**. 3,5-Di-*tert*-butylphenyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Perspective view of **5Ni**. (b) Side view of **5Ni**. (c) Perspective view of **6Ni**. (d) Side view of **6Ni**.



Fig. 3 UV/vis absorption spectra of 2Ni, 3Ni, 5Ni and 6Ni in CH_2Cl_2 .

absorption spectrum of **5Ni** displays a split Soret band at 412 and 435 nm probably as a consequence of increased exciton coupling due to its fixed conformation by the double Pt bridges. Naturally, the absorption spectrum of **6Ni** exhibits a much broader Soret band at 421 nm and the most red-shifted Q-band at 604 nm.

The electrochemical properties of 2Ni, 3Ni, 5Ni and 6Ni have been investigated by cyclic voltammetry and differential pulse voltammetry in benzonitrile (Table 1). The reference Ni(II) porphyrin exhibits an oxidation potential at 0.53 V and a reduction potential at -1.76 V, which leads to the estimation of an electrochemical HOMO-LUMO gap ($\Delta E_{\rm HL}$) of 2.29 eV. The platinum-bridged dimers display negatively shifted oxidation and reduction potentials, at 0.36 and -1.87 V for 2Ni and 0.28 and -1.97 V for 5Ni. The DFT molecular orbital calculations have revealed that the presence of C-Pt bonds substantially raises the MO energy levels due to $d-\pi$ antibonding interactions.^{2c,4c} In other words, the platinum bridge works as an electron-donating substituent to Ni(II) porphyrin. In contrast, the direct C_{β} - C_{β} connection results in split frontier molecular orbitals due to interporphyrin π -orbital interaction. It is thus expected that the LUMO of 6Ni is stabilised by the electronic interaction between the two Ni(II)-porphyrins, but the HOMO is destabilised due to the electronic interaction between the two Ni(II)-porphyrins as well as the antibonding interaction with the platinum bridge. Consequently, the ΔE_{HL} value of 6Ni is smaller than those of 2Ni and 5Ni, in line with their UV/vis absorption spectral data.

Table 1 Summary of the electrochemical potentials ^a					
	$E_{\mathrm{ox2}}^{1/2}$	$E_{\rm ox1}^{1/2}$	$E_{\rm red1}^{1/2}$	$E_{\rm red2}^{1/2}$	$\Delta E_{\mathrm{HL}}^{\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $
Ni(1) porphyrin ^c 2Ni 3Ni 5Ni 6Ni	0.50	0.53^d 0.36^d 0.62^d 0.28^d 0.32	-1.76 -1.87 -1.69 -1.97 -1.87	-1.80 -2.07^{d}	2.29 2.23 2.31 2.25 2.19

^{*a*} Conditions; nBu_4NPF_6 electrolyte 0.1 M in PhCN, Ag/AgClO₄ reference electrode, Pt working electrode, Pt wire counter electrode, scan rate 0.05 V s⁻¹. All values were determined by differential pulse voltammetry (in V). ^{*b*} ΔE_{HL} = electrochemical HOMO-LUMO gap (= $E_{ox1}^{1/2} - E_{red1}^{1/2}$ [eV]). ^{*c*} 5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(π). ^{*d*} Irreversible peaks.



 $\label{eq:scheme 3} Scheme \ 3 \ Synthesis \ of \ 6Ni \ from \ 5Ni.$

Conclusions

2-Borylporphyrins reacted with $Pt(cod)Cl_2$ in the presence of cesium fluoride to produce β -to- β platinum-bridged porphyrin dimers, which were converted to β - β directly linked porphyrin dimers through triphenylphosphine-mediated reductive elimination. A similar reaction of 2,18-diborylated Ni(π)-porphyrin gave a doubly β -to- β platinum-bridged Ni(π)-porphyrin dimer, which was converted to a Ni(π)-porphyrin dimer bearing a β -to- β platinum-bridge and a β -to- β direct C–C bond *via* similar reductive eliminations. These platinum-bridged porphyrin dimers display characteristic electronic and optical properties. Further extension of this strategy to longer porphyrin arrays is now in progress in our laboratory.

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