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Conformational flexibility of 1,4-naphthiporphyrin promotes a palladium-mediated contraction of naphthalene to isoindene.

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The carbaporphyrinoids 5,10,15,20-tetraphenyl-1,4-naphthiporphyrin and 5,20-diphenyl-10,15-ditolyl-24-thia-1,4-naphthiporphyrin, which contain a naphthalene ring embedded in the macrocyclic framework, were obtained in a modification of the “3 + 1” approach using the naphthalene analogue of tripyrrane. The 1,4-naphthiporphyrin and 24-thia-1,4-naphthiporphyrin are planar except for the tilt of the naphthalene moiety toward the center of the macrocycle, as determined by X-ray crystallography. Extensive NMR studies demonstrated that the diprotonation of 1,4-naphthiporphyrin forced a remarkable conformational change due to flipping of the naphthalene moiety, which afforded the extended macrocyclic structure. The reaction of palladium(II) chloride with 1,4-naphthiporphyrin in acetonitrile yielded palladium(II) 1,4-naphthiporphyrin, which preserved the folded conformation of the free base. The remarkable, facile palladium(II)-stimulated contraction of naphthalene to isoindene produced the first complex of metal(II) benzocarbaporphyrin which acquires a unique tetrahedral carbon coordination mode.

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