

Small-Bandgap Porphyrins

Facile Oxidative Rearrangement of Dispiro-Porphodimethenes to Nonplanar and Sheetlike Porphyrins with Intense Absorptions in the Near-IR Region**

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The spectroscopy, redox potentials, spin states, and axial coordination chemistry of metalloporphyrins, chlorins, and related compounds can be modulated through distortions in planarity or the presence of exocyclic ring systems fused to the periphery of the macrocycle. In biological systems, the reactivity and properties of tetrapyrrolic macrocycles are often tuned through subtle combinations of these two factors.^[1] To help elucidate the origins resulting from modifications to the porphyrin frame, nonplanar porphyrins with

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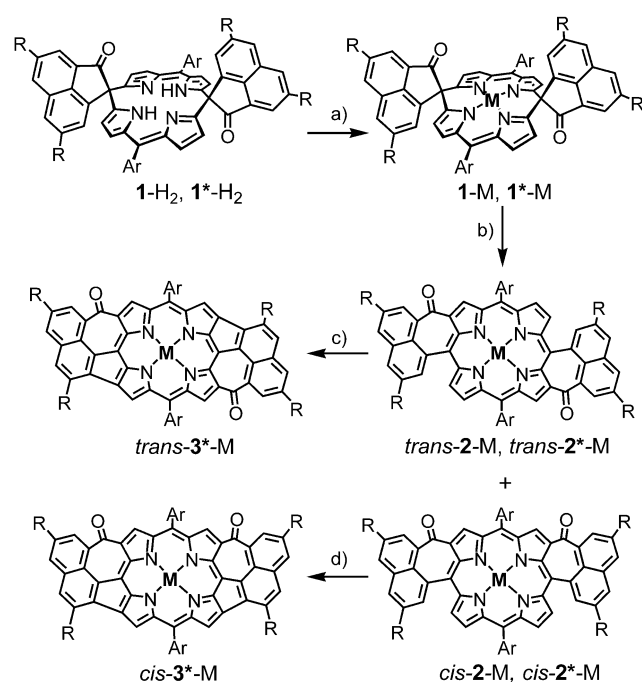
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unusual symmetries, as well as porphyrins exhibiting π -electron delocalization with extremely low-energy electronic transitions and multiple interacting ring systems, continue to be desirable synthetic targets.^[2] Along with providing theoretical insight into these biologically relevant but still poorly understood phenomena,^[3] synthetic porphyrins with small bandgaps may find practical utility as novel optical, electronic, or therapeutic materials,^[4] while nonplanar porphyrins with engineered deformations exhibit enhanced properties for a variety of applications in catalysis^[5] and host–guest chemistry.^[6] Herein, we present a straightforward oxidative-rearrangement method for the conversion of metalloporphodimethenes to intrinsically nonplanar porphyrins with two exocyclic naphthocycloheptanone ring systems. Further oxidative dehydrogenation generates exceedingly large, almost perfectly planar porphyrins, bearing bis(naphthoazulenone) ring systems, in high yield, and to the best of our knowledge, these compounds exhibit the longest absorption wavelength reported for monomeric metalloporphyrins.

Presumably due to their predisposition to form the fully aromatic porphyrin, the porphodimethene macrocycle, a two-electron reduced form of the porphyrin macrocycle with sp^3 carbons at two *trans meso* positions, has yet to be found in nature. Until only very recently,^[7] porphodimethenes such as **1-H₂** (Scheme 1) have been difficult to prepare in the laboratory.^[8,9] Reasoning that the conversion from porphodimethenes to porphyrins is a 2e, 2H⁺ process, and given the considerable driving force for forming the aromatic macrocycle, we undertook electrochemical investigations of **1-H₂**



Scheme 1. Synthetic methodology: a) for M = Cu: Cu(OAc)₂, CHCl₃/MeOH, Δ , 1 h; for M = Pd: [(C₆H₅CN)₂PdCl₂], THF, Δ , 2.5 h; b) $h\nu$, DDQ (2 \times 1.2 equiv), CH₂Cl₂, RT, 25–120 min; c) DDQ (7.2 equiv), FeCl₃·6 H₂O (20 equiv), CH₂Cl₂, Δ , 5–6 h; d) DDQ (4.8 equiv), FeCl₃·6 H₂O (10 equiv), CH₂Cl₂, Δ , 15 min. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, RT = room temperature. *Implies R = *t*Bu, otherwise, R = H.

and several of the metalated derivatives. In these experiments, irreversible oxidations were observed, with the free ligands having higher oxidation potentials than the metalated derivatives by 0.5 ± 0.2 V.^[10] Treatment of **1-H₂** under various oxidative conditions resulted in either no reaction or complex mixtures of often insoluble products. Reactions of **1-Cu** and **1-Pd** under the same sets of conditions led to green products and/or sparingly soluble dark red products. By using light and an excess of DDQ under anhydrous conditions, we optimized the conversions of **1-Cu** and **1-Pd** to the *cis* and *trans* isomer pairs of **2-Cu** and **2-Pd** to produce high combined yields of the two isomers (Scheme 1). Photolysis experiments with UV/Vis monitoring and initial photophysical measurements indicate photolytic cleavage, likely a Norrish Type I process, for the initiation of the reaction, but a donor–acceptor adduct with the oxidant may be the initial step in this pathway.^[11] The use of excess DDQ to rapidly drive the oxidative processes, as well as the rigorous exclusion of water and alcohols, was necessary to avoid competitive reactions.^[12]

The Soret bands in the UV/Vis spectra of these unusual porphyrins appear at lower energy than those of tetraphenylporphyrin and range from 466 nm (*trans-2-Pd*) to 490 nm (*cis-2*-Cu*). The low-energy electronic transitions for these porphyrins are also quite red-shifted (652 nm for *cis-2-Pd*; 705 nm for *trans-2*-Cu*) as well as broad and intense ($\lg \epsilon = 4.6$) in comparison to the Q bands found for typical metalloporphyrins. In the solid-state (Figure 1),^[13] the *trans* nonplanar porphyrin, *trans-2-Pd*, adopts an *anti* configuration with respect to the carbonyl groups of the cycloheptanone moieties. Steric clash of naphthyl (at C22, C33) and pyrrolic hydrogens (at C7, C17) induces a distortion in the macrocycle, resulting in a mean deviation of 0.32 Å for the 20 carbon atoms in the porphyrin core from the average plane defined by the four nitrogen atoms. The macrocycle exhibits a ruffled *B_{1u}* deformation with the *meso*-carbon atoms displaced alternately above and below this N-normal plane. Both the nonplanar distortion and the delocalization of electron density through the fused naphthocycloheptanone ring systems likely contribute to the bathochromic shifts observed for porphyrins of the type **2-M** and **2*-M**.

In addition to multiple reductive currents and one reversible oxidative wave, cyclic voltammograms of *cis-2-Cu* and *trans-2-Cu* exhibit irreversible oxidations at 1.36 and 1.30 V vs Ag/AgCl, respectively. Chemical treatment of these porphyrins with oxidants produces poorly soluble products similar to those obtained from the treatment of **1-Cu** and **1-Pd** with strong oxidants. In order to enhance the solubility of the products, *t*Bu groups were introduced at the 4- and 7-positions of the acenaphthenequinone precursor, and **1*-H₂** was prepared in the same way as **1-H₂** and other dispiroporphodimethenes.^[9] Although both the *syn*- and *anti*-porphodimethenes react analogously, the *anti* isomer was used exclusively for all reactions reported herein, because **1*-H₂** is easy to isolate.

Metalation of **1*-H₂** with Cu or Pd and oxidation to the corresponding nonplanar butylated cycloheptanone porphyrins proceed as expected. Chromatographic separation of the isomers for both palladium and copper results in the *cis* and *trans* porphyrins in an approximately 2:1 ratio, as observed for

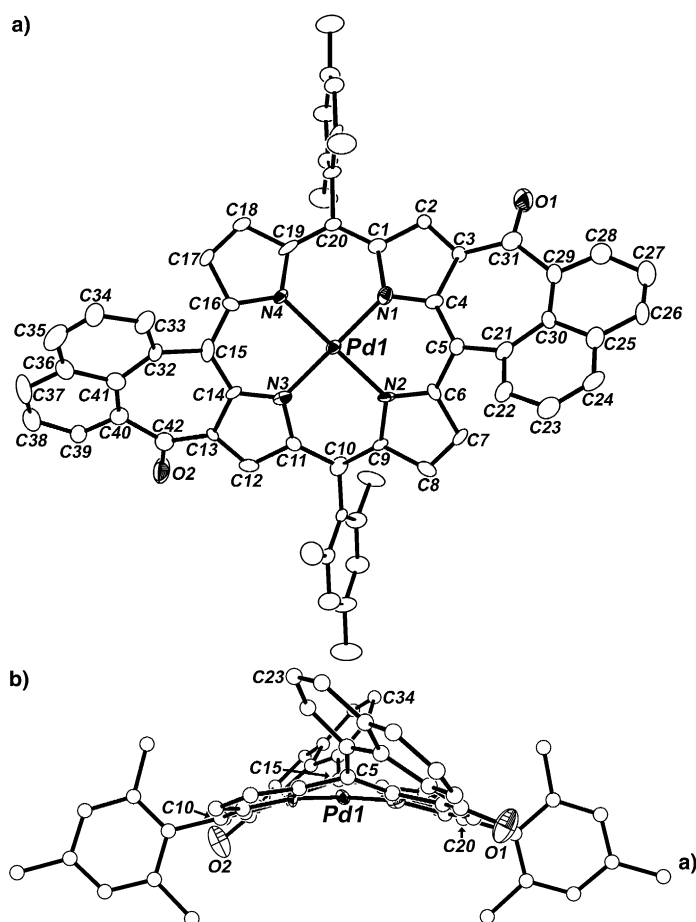


Figure 1. a) X-ray structure of *trans*-2-Pd (ellipsoids at 30% probability). Hydrogen atoms have been omitted for clarity. Only one of the two symmetry-inequivalent porphyrins found in the asymmetric unit is depicted. Selected bond lengths [Å] and angles [°]: Pd1-N1 1.990(6), Pd1-N2 1.986(7), Pd1-N3 2.005(7), Pd1-N4 2.002(6), N1-Pd1-N2 88.4(2), N1-Pd1-N3 175.7(2), N1-Pd1-N4 91.2(2). b) Side view of *trans*-2-Pd (arbitrary radii for carbon atoms) illustrating the ruffled deformation of the macrocycle.

the conversion of **1-M** to *cis*- and *trans*-2-M porphyrins. Reaction of *cis*-2*-M with an excess of both DDQ and FeCl₃·6H₂O in refluxing CH₂Cl₂, followed by aqueous workup and filtration over silica produces the *cis*-bisanaphthoazuleneone porphyrins, *cis*-3*-M. The flat *trans* isomer, *trans*-3*-M, can be generated similarly from *trans*-2*-M. Compared to the conversion of the *cis* isomers, however, reaction times are longer,^[14] and the procedure requires additional equivalents of oxidants and a reductive aqueous workup. The two oxidative processes can be performed in one pot, generating a mixture of *cis*- and *trans*-3*-M directly from **1***-M, but chromatographic resolution of the isomer pairs is considerably easier for the 2*-M porphyrins than for the 3*-M compounds. While oxidative biaryl-coupling reactions utilizing FeCl₃ or DDQ as an oxidant are common, it seems the only report of their use in combination involved the deprotection of methoxy phenyl methyl esters using catalytic amounts of DDQ with excess FeCl₃. In this system, Fe^{III} regenerates the active oxidant from its reduced form (H₂DDQ).^[15] DDQ in conjunction

with other metals such as Sc(OTf)₃ will induce the oxidative coupling of triarylporphyrins to generate coplanar diporphyrins,^[16] and although the Sc(OTf)₃/DDQ procedure was not attempted for the oxidation of 2*-M to 3*-M, numerous other reagents and conditions were tested. None of these trials produced the desired products in yields as high as those achieved with the FeCl₃/DDQ procedures described herein, and the isolation of the porphyrins was often more problematic.

Slow diffusion of diethyl ether into a saturated CH₂Cl₂ solution of *cis*-3*-Cu produced single crystals as purple plates with a green metallic luster. Structure analysis by X-ray diffraction reveals a relatively planar porphyrin interior, with a mean deviation of only 0.08(6) Å for the 20 carbon atoms in the porphyrin core from the average plane defined by the four nitrogens (Figure 2). The naphthyl moieties at the periphery of the ring system deviate slightly from this nitrogen plane with a mean deviation of 0.27(16) Å for the 22 carbon atoms in the two naphthyl groups (max. deviation 0.53 Å for C26). These minor deviations are likely induced by packing forces in the solid state. Interestingly, the largest displacement (0.78 Å) from the N₄ plane in the macrocyclic core is found at one of the carbonyl oxygens, O2. Many unusual bond angles are found in this ring system, which, discounting *t*Bu and mesityl aryl groups, contains 49 non-hydrogen nuclei arranged as eight six-, six five-, and two seven-membered

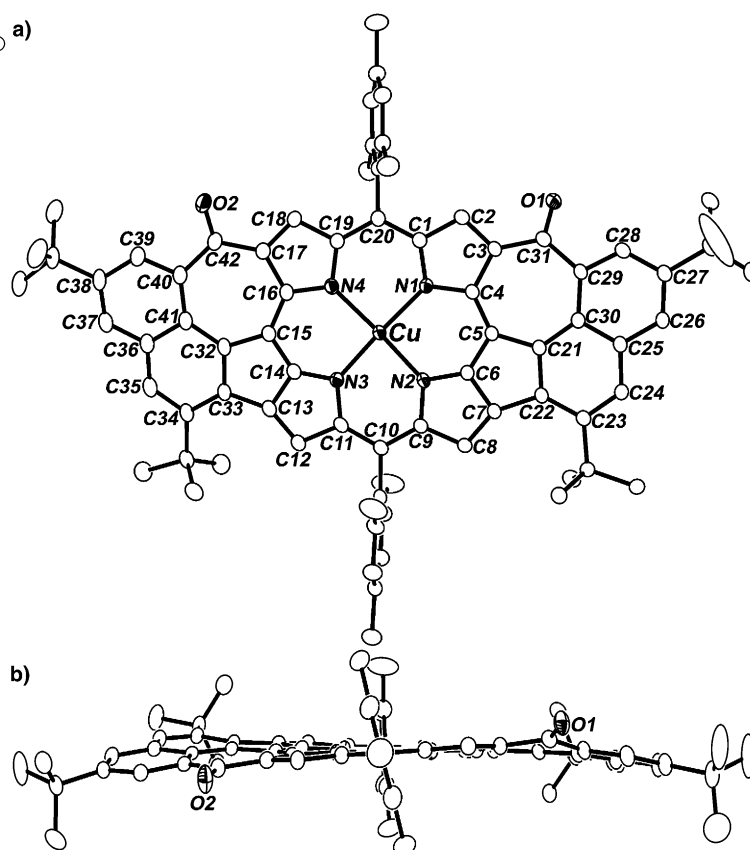


Figure 2. a) Top view and b) side view of the X-ray structure of *cis*-3*-Cu (30% ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu-N1 2.002(2), Cu-N2 1.952(2), Cu-N3 1.949(2), Cu-N4 1.997(2), N1-Cu-N2 92.33(8), N1-Cu-N3 176.86(9).

rings, interlocked in a highly delocalized π system, with two carbonyls in the plane of hybridization. Among the 42 sp^2 carbons in the porphyrin plane, 17 have a bond angle of 110° or less, and 9 have a bond angle of 130° or more, with extremes represented at the C7 and C13 vertices (C8-C7-C6: $104.5^\circ(2)$; C8-C7-C22: $149.8^\circ(2)$). The distance between the two furthest separated sp^2 carbon atoms (C27, C38) in the sheetlike macrocycle is 1.69 nm.

The UV/Vis/NIR spectra of these porphyrins display numerous exceptional features, including low-energy (Q-type) absorptions with dramatic bathochromic shifts relative to the absorptions of typical Cu and Pd porphyrins (Figure 3).

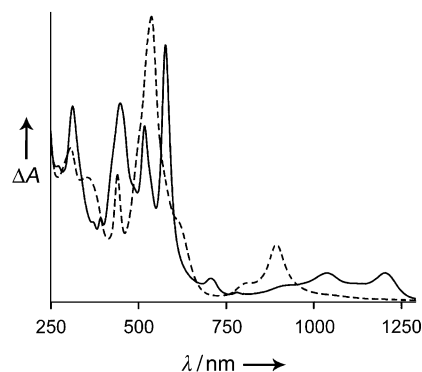


Figure 3. UV-Vis/NIR spectra of the sheetlike copper porphyrins *trans*-3*-Cu (—) and *cis*-3*-Cu (---).

All porphyrins of the type 3*-M have a band at ≈ 450 nm; the location of the other transitions is metal dependant, with copper species having spectra further red-shifted than those of their palladium analogues. Otherwise, the shapes of the spectra are very similar for each isomer, regardless of the metal incorporated. For both the *cis* and *trans* isomers, the most intense absorption band ($\lg \epsilon = 4.9$) occurs in the visible region ($\lambda = 540\text{--}579$ nm), and these bands approach the record low-energy Soret absorption of $\lambda = 625$ nm noted by Lash and co-workers.^[17] In addition to the aforementioned high-energy bands, the *cis* isomers exhibit a rather intense ($\lg \epsilon = 4.2$), Q-like band at $\lambda = 850$ nm for *cis*-3*-Pd and at $\lambda = 894$ nm for *cis*-3*-Cu. While the *trans* isomers have visible spectra that are only slightly red-shifted relative to the spectra of their *cis* counterparts, their Q-like bands exhibit extreme bathochromic shifts and are split into two less intense transitions in the near-IR region. For *trans*-3*-Pd these low-energy bands are found at $\lambda = 994$ nm and 1145 nm, and for *trans*-3*-Cu they are found at $\lambda = 1038$ nm and 1204 nm. Although the absorptions of triply fused, multiporphyrin tapes have been shown to reach further into the IR region,^[16b,18] the extremely red-shifted transitions observed for *trans*-3*-Cu are, to the best of our knowledge, the lowest energy electronic transitions ever observed for a monomeric porphyrin species.

In light of the spectral features in the NIR region indicating very small band-gaps, cyclic voltammetric studies of compounds *cis*-3*-Cu and *trans*-3*-Cu were carried out in benzonitrile. As expected based upon their spectrophotometry, the first oxidation potential was less positive and the first

reduction potential less negative for *trans*-3*-Cu ($ox_1 = 0.73$ V, $red_1 = -0.44$ V) than for *cis*-3*-Cu ($ox_1 = 0.87$ V, $red_1 = -0.46$ V). Special attention was paid to the difference in the first 1e oxidation and 1e reduction potentials for the macrocycles in comparison to the potentials for simple porphyrins such as Cu^{II} tetramesitylporphyrin (CuTMP). Relative to CuTMP ($ox_1 = 1.18$ V, $red_1 = -1.36$ V), the separation between the first reduction and oxidation potentials are quite small for both *cis*-3*-Cu and *trans*-3*-Cu (Figure 4). Even the second reversible 1e reductions for both *trans*-3*-Cu (-0.85 V) and *cis*-3*-Cu (-0.89 V) occur at potentials far less negative than the first 1e reduction for CuTMP.

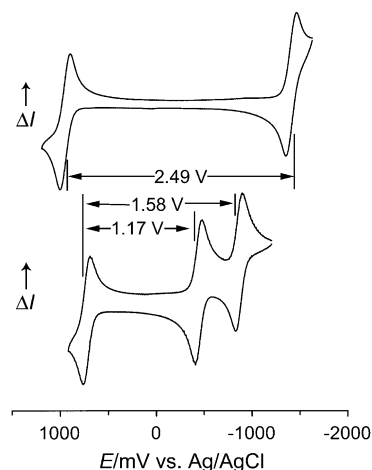


Figure 4. Cyclic voltammogram of *trans*-3*-Cu (bottom) compared to that of CuTMP (top).

With their tendency to form fully aromatic porphyrins, dispiro-porphodimethene macrocycles are excellent synthons for the preparation of distorted porphyrins bearing two naphthocycloheptanones fused to the macrocycle core as well as 1.69-nm wide, planar porphyrins with two naphthoazulen-8-one moieties. These unusual, soluble macrocycles can be isolated in high yields in one- or two-pot procedures from metallocporphodimethenes, allowing for the preparation of large quantities of material. Detailed investigations into the reactivity and photochemistry of the macrocycles, as well as the extension of the rearrangement and coupling procedures to other dispiro-porphodimethenes and biaryl systems, respectively, are underway.

Experimental Section

Complete experimental details including MS, NMR, and elemental data for all compounds are available in the Supporting Information. General procedure for the preparation of bis(naphthocycloheptanone) porphyrins **2-M** and **2*-M**: Metallocporphodimethenes **1-M** or **1*-M** were treated under an inert atmosphere, with excess DDQ in anhydrous, degassed CH_2Cl_2 . The solution was irradiated from a distance of 10 cm with a 20-W halogen light source fitted with a UV filter. Reaction times varied from 25 min (**2-Cu**) to 2 h (**2*-Pd**). Reaction mixtures were subsequently diluted with CH_2Cl_2 , washed with water, and dried over Na_2SO_4 , and the solvents removed. In the separation by silica gel column chromatography the *trans* isomers

eluted as the first major green bands. *trans*-2-Cu: 36% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 470 (5.2), 700 (4.5) nm. *cis*-2-Cu: 59% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 488 (5.2), 678 (4.5) nm. *trans*-2*-Cu: 32% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 473 (5.3), 705 (4.6) nm. *cis*-2*-Cu: 57% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 490 (5.3), 681 (4.6) nm; *trans*-2-Pd: 37% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 466 (5.3), 674 (4.6) nm; *cis*-2-Pd: 59% yield (88 mg); UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 483 (5.4), 652 (4.6) nm. *trans*-2*-Pd: 32% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 470 (5.4), 678 (4.7) nm. *cis*-2*-Pd: 62% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 486 (5.4), 656 (4.6) nm.

General procedures for the preparation of bis(naphthoazole-none) porphyrins 3*-M: *trans* Isomers: A solution of *trans*-2*-M in CH₂Cl₂ was treated with an excess of both DDQ and FeCl₃·6H₂O. The mixture was heated at reflux for 6 h, allowed to cool to room temperature, and decanted. Freshly prepared aqueous NaBH₄ was added to the solution, and the resulting biphasic mixture was stirred. After dilution with CH₂Cl₂ and water, the organic phase was separated, washed with water, dried over Na₂SO₄, and filtered over silica (4 × 4-cm, CHCl₃). The solvents were removed, and the residue was redissolved in *o*-C₆H₄Cl₂. Addition of hexanes to this solution causes the precipitation of *trans*-3*-M as a metallic, red-gray powder. *cis* Isomers: The *cis* isomers, *cis*-2*-M, were treated in analogy to the *trans* isomers, but the reaction times were considerably shorter (15–20 min) and less of the oxidant mixture was required. Filtration over silica (6 × 4-cm, CH₂Cl₂/hexanes 1:1) and slow removal of the solvents afforded *cis*-3*-M as purple-green microcrystalline solids. Normally, for convenience sake, the reactions were run on scales to produce the products in approximately 50-mg quantities, but the synthetic procedures allow for the isolation of the materials in amounts over a gram. *trans*-3*-Cu: 90% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 314 (4.8), 449 (4.8), 519 (4.7), 579 (4.9), 706 (3.8), 1038 (3.9), 1204 (3.9) nm. *cis*-3*-Cu: 98% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 308 (4.6), 441 (4.6), 540 (4.9), 894 (4.2) nm. *trans*-3*-Pd: 92% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 307 (4.6), 445 (4.7), 502 (4.5), 522 (4.5), 567 (4.9), 682 (3.8), 994 (3.8), 1145 (3.8) nm. *cis*-3*-Pd: 96% yield; UV/Vis (CH₂Cl₂): λ_{max} (lg ϵ) = 285 (4.6), 445 (4.8), 553 (4.9), 850 (4.2) nm.

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- [12] Details of some of these competitive reactions will be published in an upcoming paper.
- [13] Crystal structure data for *trans*-2-Pd·2CHCl₃·¹/₄C₃H₁₂: monoclinic, space group *P*₂₁/*c*, *a* = 12.085(3), *b* = 31.100(8), *c* = 28.596(7) Å, β = 98.472(4)°, *V* = 10630(4) Å³, *T* = 193 K, *Z* = 8, ρ_{calc} = 1.555 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 0.702 mm⁻¹, 50631 reflections collected, 16688 unique, of which 8508 with *I* > 2 σ were used in the refinement. *R*₁ = 0.0700 [*I* > 2 σ (*I*)], *wR*₂ = 0.1543, GOF = 0.902 for 1307 parameters. Crystal structure data for *cis*-3*-Cu·2CH₂Cl₂·¹/₂Et₂O: monoclinic, space group *C*2/*c*, *a* = 29.5740(14), *b* = 12.4738(6), *c* = 41.109(2) Å, β = 100.309(1)°, *V* = 14920.3(12) Å³, *T* = 193 K, *Z* = 8, ρ_{calc} = 1.193 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 0.484 mm⁻¹, 45023 reflections collected, 14679

unique, of which 10048 with $I > 2\sigma$ were used in the refinement. $R_1 = 0.0558$ [$I > 2\sigma(I)$], $wR_2 = 0.1550$, GOF = 1.098 for 811 parameters. CCDC-218523 (*trans*-2-Pd) and CCDC-218524 (*cis*-3*-Cu) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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