number of compounds in high purity for potential applications in chemical biology and medicinal chemistry. Continuing efforts are aimed towards the development of additional carbonyl-based coupling strategies to extend the scope of this method into new structural classes.

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Novel Ruthenium Building Blocks for the Efficient Modular Construction of Heterobimetallic Molecular Squares of Porphyrins**

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The construction of structurally well defined, highly ordered supramolecular systems containing porphyrins and metalloporphyrins is of prime interest. By virtue of the

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inherent useful photochemical and redox properties of the porphyrin molecule, such arrays are being investigated for modeling the photosynthetic system[1] and for developing new photonic materials and light-harvesting devices.[2] The metal-mediated self-assembly approach, which exploits the formation of coordination bonds between peripheral basic site(s) on the porphyrins and metal centers, has provided many large discrete assemblies of porphyrins in good yields.[3]

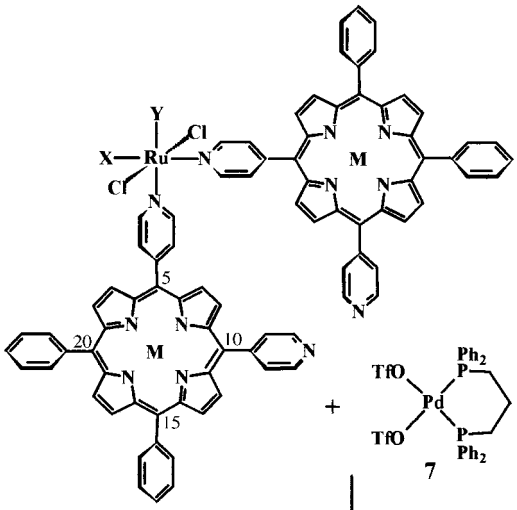
Among the various architectures reported for such porphyrin aggregates, there are only a few examples of molecular squares, and they are all homometallic.[4–7] Most were obtained by treatment of *meso*-di(4′-pyridyl)porphyrins, such as 5,10-bis(4′-pyridyl)-15,20-diphenylporphyrin (4′-*cis*DPyP) and 5,15-bis(4′-pyridyl)-10,20-diphenylporphyrin (4′-*trans*-DPyP), with suitable *cis* and *trans* square-planar Pd^{II} and Pt^{II} complexes, which are precursors for angular (90°, $\mathbf{A}_a$) or linear (180°, $\mathbf{L}_a$) acidic building blocks.[4, 5] There is current interest in the photophysical investigation of properly designed molecular squares of porphyrins which, unlike open-chain systems, may allow the locking of chromophores in a mutually coplanar geometry.[8]

We report here a flexible, stepwise approach that, through the design and synthesis of novel chelating bis-porphyrin ruthenium intermediates, leads efficiently to unprecedented heterobimetallic molecular squares of porphyrins featuring different diagonally opposed metal ions. In particular, [2+2] molecular squares are described in which two 4′-*cis*DPyP units are linked through an octahedral, neutral Ru^{II} center and a square-planar, charged Pd^{II} center (see Scheme 1).

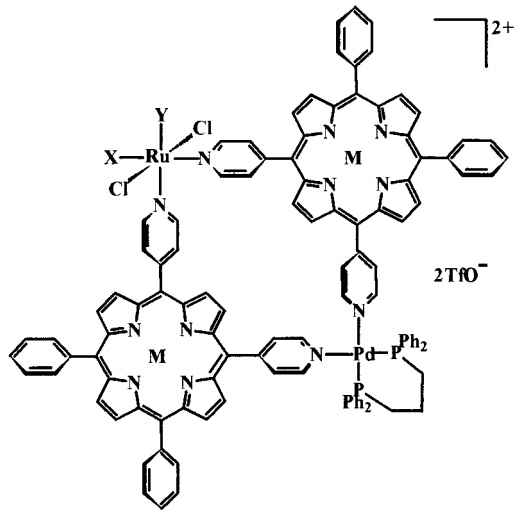
The Ru^{II}–sulfoxide complexes *trans*-$[RuCl_2(Me_2SO)_4]$ (**1**, Me_2SO bound through S), *trans*-$[RuCl_2(Me_2SO)_3(CO)]$ (**2**), and *trans*-$[RuCl_2(Me_2SO)_2(CO)_2]$ (**3**, Me_2SO bound through O) easily undergo replacement of two *cis* Me_2SO ligands and are thus suitable precursors for octahedral $\mathbf{A}_a$ building blocks. Treatment of **1**–**3** with excess 4′-*cis*DPyP under mild conditions led to the isolation of *trans*,*cis*,*cis*-$[RuCl_2(X)(Y)(4'\text{-}cis\text{DPyP})_2]$ compounds **4**–**6** in pure form (Scheme 1). The nature and geometry of the products were established by ^1H and ^{13}C NMR spectroscopy,[9] as described previously for the corresponding 5-(4′-pyridyl)-10,15,20-triphenylporphyrin (4′-MPyP) complexes.[10] Integration of the signals for **4** and **5** revealed the adduct stoichiometry, whereas COSY spectra allowed unambiguous assignment of the signals.

In general, coordination of 4′-*cis*DPyP to the central *trans*,*cis*-$RuCl_2(X)(Y)$ moiety (*t*Ru) induced downfield shifts for the H2,6 and H3,5 resonances of the 4′-N(py) ring (position 5, py = pyridyl) involved in the new bond. Conversely, the resonances of the six-membered rings at positions 10 and 20 experienced an upfield shift of about 0.2 ppm with respect to 4′-*cis*DPyP, which is characteristic of two mutually *cis* pyridylporphyrins displaying free rotation about the metal–pyridyl axis.[10] Compounds **4** and **6** have C_{2v} symmetry,[11] and thus the two porphyrins are equivalent. In **5** the two 4′-*cis*DPyP units are inequivalent; the resonances of the two *t*Ru-4′N(py) rings are well resolved, whereas the other signals overlap.[9]

Compounds **4**–**6**, in which the two *cis*-coordinated 4′-*cis*DPyP units have one residual unbound 4′-N(py) ring, are preprogrammed basic building blocks capable of chelating



4, X = Y = Me_2SO, M = 2H
5, X = Me_2SO, Y = CO, M = 2H
6, X = Y = CO, M = 2H
6Zn, X = Y = CO, M = Zn



8, X = Y = Me_2SO, M = 2H
9, X = Me_2SO, Y = CO, M = 2H
10, X = Y = CO, M = 2H
10Zn, X = Y = CO, M = Zn

Scheme 1. Synthesis of **8**–**10** and **10**Zn. For **4**, **5**, **8**, and **9** the Me_2SO molecule is bound through S.

suitable acidic modules displaying an angle of 90°. As an example, we investigated the reactivity of **4**–**6** towards $[Pd^{II}(dppp)(OTf)_2]$ (**7**; dppp = 1,3-bis(diphenylphosphanyl)-propane, OTf = trifluoromethanesulfonate = triflate), a widely used precursor for square-planar $\mathbf{A}_a$ units.[4]

^1H NMR spectroscopy established that titration of **7** into solutions of **4**–**6** in chloroform led readily to the quantitative formation of the corresponding heterobimetallic [2+2] molecular squares of formula [Pd(dppp){*trans*,*cis*,*cis*-$RuCl_2(X)(Y)(4'\text{-}cis\text{DPyP})_2$}]$(OTf)_2$ (**8**–**10**, Scheme 1). Chelation of the Pd–bis-phosphane fragment by **4**–**6** induced characteristic shifts both in the ^1H NMR spectrum (which concerned mainly the resonances of the previously unbound 4′-N(py) ring at position 10, Figure 1),[9] and in the proton-decoupled ^{31}P NMR spectrum (upfield shift $\Delta\delta \approx 10$ compared to **7**, as is

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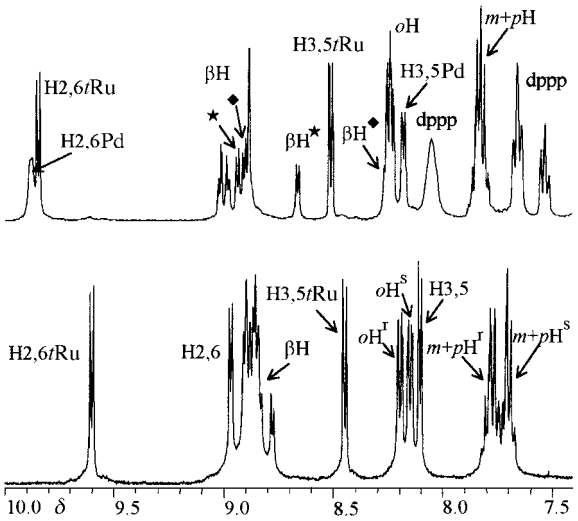

Figure 1. Bottom: Downfield region of the ^{1}H NMR spectrum of **6** in $CDCl_3$ (^{r}: position 15, ^{s}: position 20). Top: The same spectral region after addition of one equivalent of **7**, leading to the quantitative formation of molecular square **10** (pyrrole (β) resonances labeled with ⋆ and ◆ are coupled to each other in the COSY spectrum).

the case for $[Pd(dppp)(4'\text{-}cis\text{DPyP})]_2(OTf)_4$ (**11**)).[4] The macrocycles were not affected by an accidental excess of **7**, and no evidence of homometallic molecular squares was found.

In solution squares **8** and **10** maintain the C_{2v} symmetry of the corresponding Ru precursor,[12] and the two porphyrins at opposite corners are equivalent. The resonances of the Pd–4′N(py) rings are well resolved from those of the *t*Ru–4′N(py) rings. The most downfield H2,6 and the most upfield H3,5 signals (correlated in the COSY spectrum) are unaffected by the nature of X and Y, and were thus attributed to the Pd–4′N(py) rings. Two of the eight inequivalent pyrrole protons of **8** and **10** have remarkably upfield shifted resonances (one overlaps with *ortho*-H resonances) and are not correlated to each other in the COSY spectrum (Figure 1). We attributed these resonaces to βH8 and βH12, that is, the pyrrole protons closest to Pd (Scheme 1).[13] These assignments are also in good agreement with those reported by Stang et al. for **11**.[4]

Macrocycle **9** lacks an orthogonal mirror plane containing the two metal atoms; hence the two porphyrin units are inequivalent. In the ^{1}H NMR spectrum of **9** the resonances of the two *t*Ru–4′N(py) rings are well resolved, whereas those of the Pd–4′N(py) rings overlap.[9] The other porphyrin resonances, with the exception of those of the internal NH groups and of the pyrrole protons closest to Pd (upfield shifted signals), are not resolved. Also the ^{31}P{^{1}H} resonances for the two inequivalent phosphorous atoms of dppp overlap.

Some resonances in the ^{1}H NMR spectra of **8**–**10**—namely, H2,6 of Pd–4′N(py) rings as well as *ortho*-H and CH_2 moieties of the dppp ligand—are broadened. This is very likely due to conformational motion of the diphosphane bridge occurring at an intermediate rate on the NMR time scale at ambient temperature.

Treatment of **6** with excess zinc acetate led to the insertion of zinc into both porphyrin rings (**6**Zn); the ^{1}H NMR spectrum of **6**Zn in $CDCl_3$ is affected by the extensive intermolecular coordination of the pyridyl groups, not bound to Ru, to the Zn atoms. Titration of **7** into a solution of **6**Zn in $CDCl_3$ quantitatively yielded the corresponding molecular square **10**Zn (Scheme 1), which represents the first example of an heterotrimetallic molecular square of porphyrins.[15] The ^{1}H NMR spectrum of **10**Zn is very similar to that of **10**.[9, 15]

The structure of **10**, in which two 4′-*cis*DPyP units alternate with the Pd^{II} and Ru^{II} angular units, was established by X-ray single crystal analysis (Figure 2).[16] This represents the first case in which data on the solid-state structure of a molecular

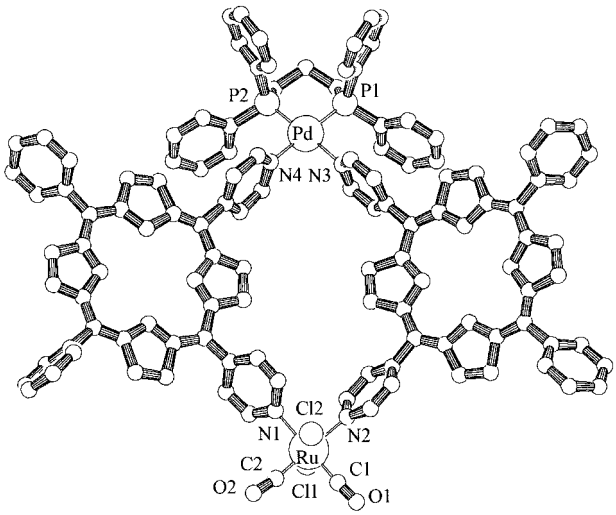

Figure 2. Molecular structure of the cation of molecular square **10**. Selected bond lengths [Å] and angles[°]: Pd-N4 2.117(12), Pd-N3 2.164(14), Pd-P2 2.255(6), Pd-P1 2.268(5), Ru-C2 1.85(2), Ru-C1 1.85(3), Ru-N2 2.132(13), Ru-N1 2.167(14), Ru-Cl1 2.379(7), Ru-Cl2 2.389(8); N3-Pd-P2 178.2(5), N4-Pd-P1 177.1(5), C2-Ru-N2 179.5(9), C1-Ru-N1 177.8(13), Cl1-Ru-Cl2 177.43(19).

square of porphyrins has become available.[18] The distances from the metals to the porphyrin centers are about 9.83 Å; the diagonal Pd ··· Ru distance of 14.015(3) Å is close to the value of 15 Å obtained from molecular modeling of similar square-shaped Pd^{II} adducts.[4] Interestingly, in the solid state the macrocycle exhibits an arrangement in which the least-squares planes of the porphyrins form a dihedral angle of 41.7(1)°, approximating C_s symmetry. The *meso* pyridine and phenyl rings are tilted from the normal to the corresponding porphyrin plane by 64.2(4)–79.2(6)° and 43.4(6)–60.6(4)°, respectively. The coordination bond lengths and angles are well in the range of values found in Ru^{II} and Pd^{II} compounds. An interesting feature is represented by the conformation of the diphosphane ligand, in which two phenyl rings display stacking interactions with the adjacent coordinating pyridines; the shortest distance between the *ipso*-C atom and the pyridine N atom is about 3.1 Å.

In future, this stepwise synthetic approach might be efficiently applied to the construction of novel homo- and heterobimetallic discrete assemblies of porphyrins bearing metal ions with programmed features (such as geometry, charge, functionalities of the ancillary ligands) at spatially well-defined positions.

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Experimental Section

Complexes **1**–**3** and **7** were prepared according to the literature procedures.[4, 10] The ^{1}H NMR signals were referenced to signals from residual $CHCl_3$ ($\delta = 7.26$), and assignments were made with the aid of 2D COSY experiments as detailed in the text. The UV/Vis spectra were obtained on a Jasco V-550 spectrophotometer. All reagents were analytical grade. Column chromatography was performed on mesh silica gel (40–63 μm; BDH Laboratory Supplies, UK).

4–**6**: Complexes **1**–**3** were treated at room temperature in $CHCl_3$ with a fourfold excess of 4′-*cis*DPyP (reaction time: 5 h (**4**), 24 h (**5**), 3 d (**6**)). Column chromatography of the reaction mixtures afforded pure products as noncrystalline purple solids which gave satisfactory elemental analyses. Pure **5** and **6** were obtained (third band) from columns eluted with $CHCl_3$/ethanol (99/1); pure **4** was obtained (fourth band) from a column eluted with $CHCl_3$/ethanol (99/1 →98/2). Yields of isolated products: ca. 40%. As for the corresponding 4′-MPyP compounds,[10] the electronic absorption spectra of **4**–**6** were very similar to that of the unbound porphyrin.

6Zn: Compound **6** (10 mg) dissolved in $CHCl_3$ (5 mL) was treated for 48 h with a fourfold excess of zinc acetate dissolved in methanol (2 mL). The product precipitated upon addition of *n*-hexane. It was washed throughly with water, methanol, and diethyl ether and then dried under vacuum (yield of isolated product: ca. 70%). The final product was purified by chromatography on a column eluted with $CHCl_3$ (first band).

Molecular squares **8**–**10** were obtained by addition of **7** (1 equiv) to solutions of the corresponding precursor in $CDCl_3$. The reactions were monitored by ^{1}H NMR spectroscopy, and the ratio of the reactants was adjusted accordingly. Formation of **8**–**10** also involved minor red shifts of the Soret and Q bands of **4**–**6** by about 4 nm (with clear isosbestic points), accompanied by a concomitant decrease in intensity (ca. 10%). Similar spectral variations were also observed in the formation of **11**.[4] Analytically pure crystalline samples of the purple-red macrocycles were obtained by addition of *n*-hexane into the solutions. Yield of isolated products: ca. 80%.

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[9] For the ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4**–**6**, **8**–**10**, and **10**Zn, see the Supporting Information.

[10] E. Alessio, M. Macchi, S. L. Heath, L. G. Marzilli, *Inorg. Chem.* **1997**, *36*, 5614–5623.

[11] A sharp singlet appears at $\delta = 3.66$ for the four equivalent Me_2SO methyl groups in the ^{1}H NMR spectrum of **4**. A singlet appears at $\delta = 195.0$ for the two equivalent CO groups in the ^{13}C NMR spectrum of **6** (100.1 MHz, $CDCl_3$).

[12] For **8** singlet appears at $\delta = 3.64$ for the four equivalent Me_2SO methyl groups in the ^{1}H NMR spectrum, and a singlet at $\delta = 5.8$ in the $^{31}P\{^1H\}$ NMR spectrum (161.9 MHz, $CDCl_3$, H_3PO_4). For **10** a singlet appears at $\delta = 194.9$ for the two equivalent CO groups in the ^{13}C NMR spectrum, and a singlet at $\delta = 5.7$ in the $^{31}P\{^1H\}$ NMR spectrum. For **10**Zn: A singlet at $\delta = 194.9$ for the two equivalent CO groups in the ^{13}C NMR spectrum, and a singlet at $\delta = 5.5$ in the $^{31}P\{^1H\}$ NMR spectrum.

[13] Interestingly, in **8**–**10** the H2,6 resonances of *t*Ru-4′N(py) and of Pd-4′N(py) are almost equally downfield shifted compared to 4′-*cis*DPyP ($\Delta\delta = 1.08/0.78$). In contrast, while the H3,5 resonance of *t*Ru-4′N(py) is shifted downfield ($\Delta\delta = 0.36/0.19$), that of Pd-4′N(py) is virtually unaffected by coordination. Thus the resonances of H3,5-Pd and of the pyrrole protons closest to Pd are anomalously upfield. A similar situation is found in the corresponding homometallic Pd square **11**[4] but not in the Ru squares.[14] Therefore this effect seems to be attributable to the dppp ligand rather than to the metal. Examination of the solid-state structure of **10** suggests that these protons might fall into the shielding cone of the phenyl rings of dppp, whose conformation is not frozen in solution.

[14] E. Iengo, E. Ciani, E. Zangrando, S. Geremia, E. Alessio, *Abstr. Pap. 7th Int. Conf.* "*The Chemistry of the Platinum Group Metals*" (Nottingham, UK) **1999**, p. 101.

[15] Insertion of Zn was not performed for **4** and **5** because the corresponding zincated squares are expected to give auto-aggregation processes in solution, due to interactions between Zn and the oxygen atom of the Me_2SO groups.[10]

[16] Crystals of **10** were obtained by slow diffusion of *n*-hexane into a solution in $CHCl_3$. The crystals, when redissolved in $CDCl_3$, yielded the same spectrum as the raw material. Crystal data for **10**·*n*-hexane·$CHCl_3$ ($C_{122}H_{97}Cl_5F_6N_{12}O_8P_2PdRuS_2$): $M_r = 2483.90$, monoclinic, space group $C2/c$ (no. 15), $a = 40.315(6)$, $b = 20.487(4)$ $c = 35.125(6)$ Å, $\beta = 104.70(2)^\circ$, $V = 28061.57$ Å^3, $Z = 8$, $\rho_{calcd} = 1.176$ g cm^{-3}, $F(000) = 10144$, $T = 100$ K, $\mu = 3.767$ mm^{-1}. Data collection performed at the X-ray diffraction beamline of Elettra Synchrotron, Trieste (Italy), on a 30 cm MAR2000 image plate, 32 frames collected with rotation of 3° about φ, fixed dose of radiation ($\lambda = 1.0527$ Å). Total reflections collected 14472 (resolution 1.2 Å), unique 9281 ($R_{int} = 0.0631$). Data reduction and cell refinement carried out using the program MOSFLM.[18] Two disordered $CHCl_3$ molecules (occupancy factor 0.5 each) and a molecule of *n*-hexane were detected on the ΔF map. Final $R1 = 0.1171$, $wR2 = 0.2847$, S (GOF) $= 1.252$ for 5149 observed reflections [$I > 2\sigma(I)$] and 764 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132681. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] W. Kabsch, *J. Appl. Crystallogr.* **1993**, *24*, 795–800.

[18] **Note added in proof** (February 2, 2000): During publication of this work a paper containing the X-ray structure of **11** appeared: M. Schmitz, S. Leininger, T. Fan, A. M. Arif, P. J. Stang, *Organometallics* **1999**, *18*, 4817–4824.

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