



Controlled synthesis of ruthenium phthalocyanines and their use in the construction of supramolecular arrays

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Abstract—(Monocarbonyl) and bis(benzonitrile)ruthenium phthalocyanines, conveniently prepared from metal-free phthalocyanine precursors, are used as supramolecular building-blocks in the construction of phthalocyanine-porphyrin multi-chromophore arrays. © 2003 Elsevier Science Ltd. All rights reserved.

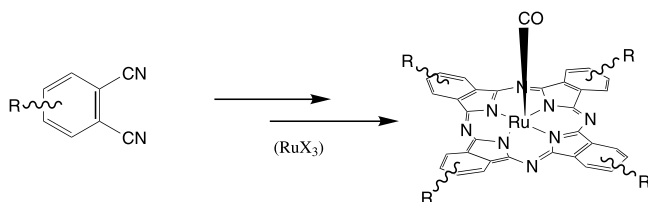
Ruthenated phthalocyanines are currently receiving much attention, not least due to their potential application as the photosensitising element of photoelectrochemical cells.^{1,2} In general, metallated phthalocyanines are prepared by one of two methods:³ (i) cyclotetramerisation of a phthalic acid derivative (such as phthalonitrile or diiminoisoindoline) in the presence of a metal salt, (ii) insertion of a metal into preformed metal-free phthalocyanine. In the case of ruthenium phthalocyanines (RuPc's), the favoured method is the former (Scheme 1).² Applications of the latter are few.^{4,5} We now report the synthesis of ruthenium phthalocyanines from a metal-free precursor⁶ (**1H₂**, Scheme 2) bearing sterically demanding substituents in the non-peripheral positions. Metallation can be easily achieved using Ru₃(CO)₁₂.⁵ Most importantly we have demonstrated that the experimental conditions can be suitably varied to yield ruthenium phthalocyanines bearing either a single CO ligand or two labile ligands. This provides potential access to a wide variety of

axially substituted RuPc's, examples of which are described in this letter.

In initial experiments, **1H₂** was treated with Ru₃(CO)₁₂ in refluxing benzonitrile. Ruthenium was successfully inserted but a mixture of two products was obtained. These were identified as **1Ru(Benz)₂** and **1Ru(CO)** (Scheme 2). Careful examination of experimental conditions permitted formation of either material exclusively. Prolonged heating in benzonitrile (under a stream of nitrogen) led to **1Ru(Benz)₂** (which was purified by flash chromatography and isolated in 96% yield by reprecipitation). Treatment of the initially formed mixture with carbon monoxide led to **1Ru(CO)** (similarly purified and isolated in 71% yield).

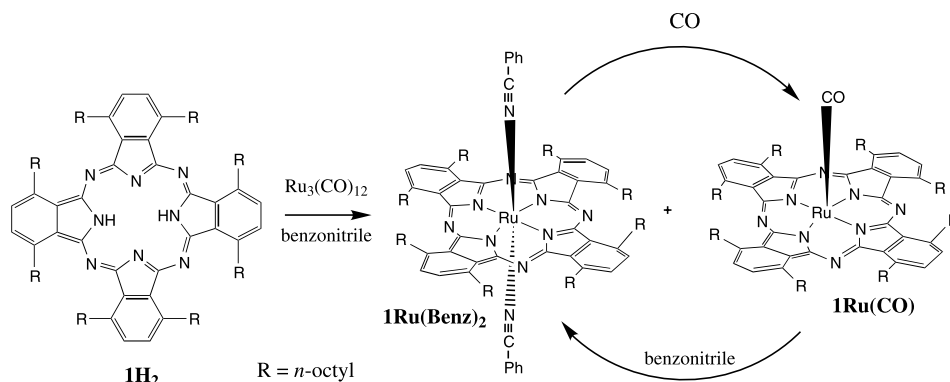
As expected, **1Ru(CO)** smoothly binds to 1 equiv. of another ligand (pyridine) and the resulting complex is stable to prolonged treatment with excess ligand. **1Ru(Benz)₂** reacts readily with 2 equiv. of ligand (pyridine). Interestingly, the product from a single substitution could never be detected [e.g. reaction with 1 equiv. of pyridine led to a 1:1 mixture of **1Ru(Benz)₂** and **1Ru(pyridine)₂**].

This synthetic control is particularly useful for the exploitation of ruthenium phthalocyanines as building blocks for the generation of supramolecular arrays. We are particularly interested in the construction of multi-chromophore arrays⁷ and representative examples have been synthesised from **1Ru(CO)** and **1Ru(Benz)₂** and pyridyl porphyrins. The 2:1 phthalocyanine-porphyrin array **3⁸** can be prepared by treatment of 2 equiv. of **1Ru(CO)** with dipyrindyl porphyrin **2** (Scheme 3). In a

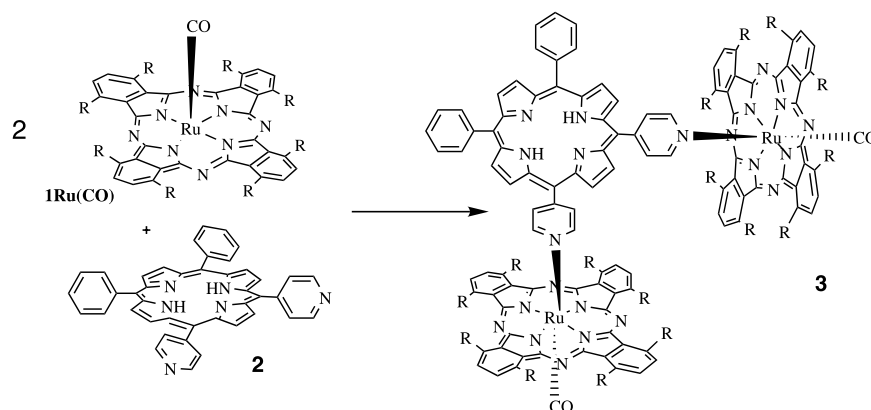


Scheme 1. Synthesis of ruthenium phthalocyanines from phthalonitriles (or derivatives).

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Scheme 2. The direct synthesis of non-peripherally substituted ruthenium phthalocyanines.



Scheme 3. Synthesis of 2:1 phthalocyanine–porphyrin array **3**.

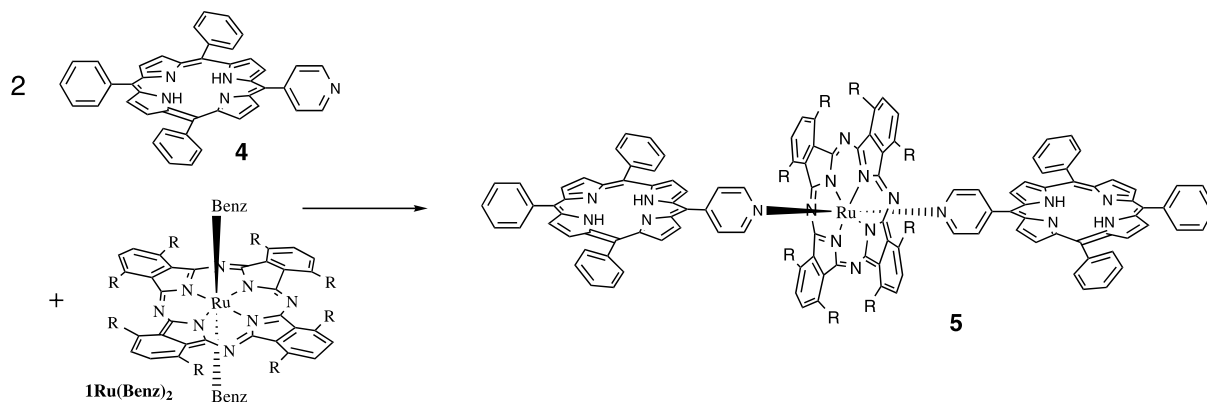
complementary fashion, the related 1:2 array **5**⁸ can be prepared by treatment of **1Ru(Benz)₂** with 2 equiv. of monopyridyl porphyrin **4** (Scheme 4). Arrays **3** (65%) and **5** (70%) were purified by flash chromatography and reprecipitation. More complex arrays and polymers can be envisaged.

Spectral data from the arrays indicate that (as expected) there is little ground state interaction between the chromophores, e.g. the absorption spectrum of **3** is essentially identical to the sum of the spectra obtained from **2** and $[2 \times \text{1Ru(CO)}]$. More detailed investigation of the

excited state interaction (energy transfer, etc.) is currently under investigation and will be reported in due course.

Acknowledgements

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Scheme 4. Synthesis of 1:2 phthalocyanine–porphyrin array **5**.

References

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8. *Selected data.* **3**: ^1H NMR (300 MHz, C_6D_6): δ = 8.46 (2H, s), 8.02 (2H, d, J = 5.0 Hz), 7.94 (8H, s), 7.63 (4H, d, J = 8.0 Hz), 7.34 (2H, t, J = 7.8 Hz), 7.24 (4H, t, J = 7.8 Hz), 6.66 (2H, d, J = 5.0 Hz), 6.29 (2H, s), 5.26 (4H, d, J = 6.4 Hz), 5.08 (16H, m), 4.84 (16H, m), 2.76 (4H, d, J = 6.4 Hz), 2.46 (32H, m), 1.87 (32H, m), 1.45–0.85 (128H, m), 0.65 (48H, t, J = 6.9 Hz), –1.40 (2H, br s); UV–vis (CH_2Cl_2) λ_{max} (log ϵ) = 356 (4.55), 421 (5.11), 517 (4.01), 542s (390), 606 (4.46), 671 (5.07). **5**: ^1H NMR (400 MHz, C_6D_6): δ = 8.74 (4H, d, J = 4.0 Hz), 8.70 (4H, d, J = 4.0 Hz), 8.27 (4H, d, J = 4.0 Hz), 7.95–7.87 (12H, m), 7.82 (8H, s), 7.47–7.32 (18H, m), 7.06 (4H, d, J = 4 Hz), 5.51 (4H, d, J = 5.2 Hz), 5.04 (16H, t, J = 6.8 Hz), 3.46 (4H, d, J = 5.2 Hz), 2.56 (16H, m), 1.92 (16H, m), 1.50–0.84 (64H, m), 0.56 (24H, t, J = 7.0 Hz), –2.85 (4H, br s); UV–vis (CH_2Cl_2) λ_{max} (log ϵ) = 366 (4.40), 419 (5.35), 515 (4.15), 554 (4.01), 591 (4.12), 646 (4.26), 662 (4.25).