

Coordination compounds as building blocks: single-step synthesis of multi-ruthenium(II) complexes

Dimitrios Tzalis and Yitzhak Tor*†

Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0358, USA

Palladium-mediated cross-coupling reactions of [(bpy)₂Ru(3-bromo-1,10-phenanthroline)]²⁺(PF₆⁻)₂ with various aromatic acetylenes and of [(bpy)₂Ru(3-ethynyl-1,10-phenanthroline)]²⁺(PF₆⁻)₂ with aromatic iodides give mono-, di- and tri-nuclear complexes in high yields and under mild conditions.

Multimetallic assemblies of defined architectures are key design targets for the study of energy and electron transfer,¹ the construction of nanostructured materials² and the fabrication of molecular devices.³ Ruthenium complexes of polypyridine ligands play a central role in these systems due to their chemical stability, redox properties and favourable photophysical characteristics.⁴ Multinuclear Ru^{II} complexes have been predominantly constructed by a stepwise synthesis of multitopic ligands followed by metal complexation.^{1c-g,5} This approach, although productive, is elaborate and does not provide full control over the final structure and composition of the assembly.⁶ We report herein on a convergent and powerful approach for the construction of multimetallic Ru^{II} arrays, utilizing coordination complexes as synthetic building blocks.

Palladium-mediated cross-coupling methodology has become instrumental in constructing complex organic molecules.⁷ Recently it has been applied to the synthesis of acetylenic porphyrins and metalloporphyrins,⁸ and elegantly utilized for the fabrication of multiporphyrinic arrays.⁹ Here we demonstrate for the first time that coordination compounds such as tris-chelate Ru^{II} complexes are good substrates for this powerful carbon-carbon bond-forming methodology. Palladium mediated cross-coupling reactions of [(bpy)₂Ru(L)]²⁺(PF₆⁻)₂ complexes, where L is a functionalized 1,10-phenanthroline ligand, provide structurally sophisticated multinuclear complexes in a single synthetic step.

The complex [(bpy)₂Ru(3-bromo-1,10-phenanthroline)]²⁺(PF₆⁻)₂ **1** is an attractive building block for the synthesis of multimetallic Ru^{II} arrays using cross-coupling methodology. The 1,10-phenanthroline ligand is substituted at the 3-position which is sterically and geometrically favoured and provides electronic conjugation.¹⁰ The Ru^{II} complexed 3-bromo-1,10-phenanthroline is expected to be relatively electron-deficient and to therefore undergo facile oxidative addition reactions. Furthermore, the phenanthroline's nitrogens are 'masked', and complications due to complexation of the transition-metal catalysts are prevented.¹¹

Treating a DMF solution of **1**‡ with 4-ethynyltoluene at room temperature for 1 h in the presence of (Ph₃P)₂PdCl₂, CuI and Et₃N proceeds smoothly to afford **3** in excellent yield (Table 1).§ Similarly, reacting **1** with 1,4-diethynylbenzene, or 4,4'-diethynyl-1,1'-biphenyl affords the bimetallic complexes **4**

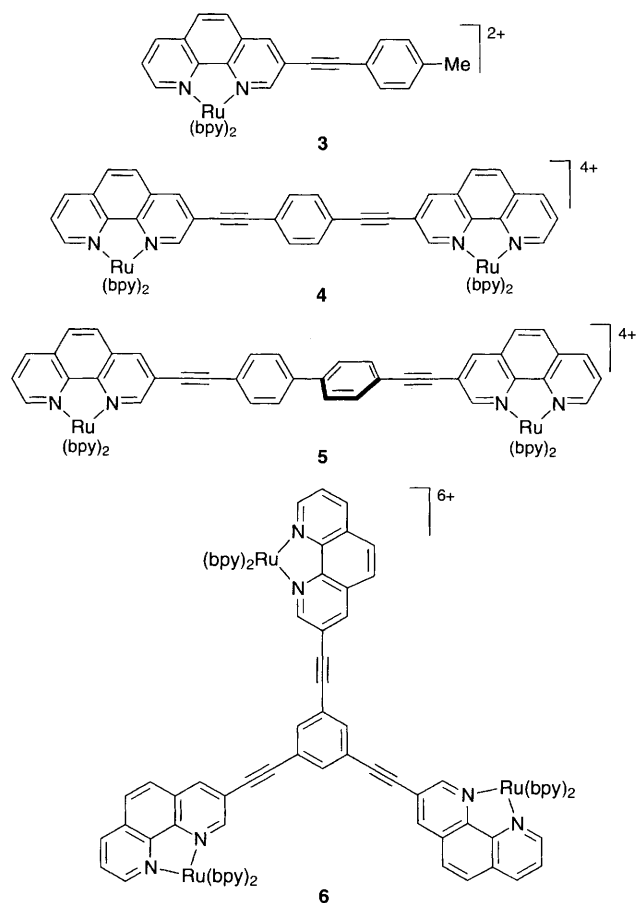
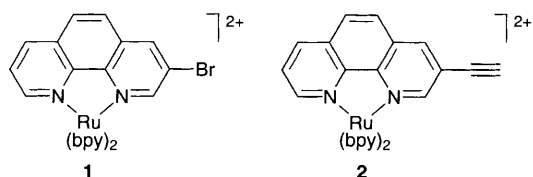


Table 1 Preparation and selected spectral data for Ru^{II} complexes

Complex	Yield (%) ^a	MS ^b	UV-VIS ^c
1	68	819.3 (M ⁺)	236 (4.2), 272 (6.6), 286 (6.5), 448 (1.5)
2	68	763 (M ⁺)	238 (4.2), 276 (6.3), 286 (6.1), 450 (1.2)
3	91	853.5 (M ⁺)	244 (4.2), 286 (7.6), 346 (3.0), 452 (1.3)
4	86	327 (M ⁴⁺)	238 (8.2), 286 (15.3), 362 (8.1), 440 (2.9)
5	73	347 (M ⁴⁺)	238 (7.6), 286 (13.8), 368 (8.4), 440 (2.6)
6	70	554 (M ⁴⁺)	244 (14.4), 286 (24.5), 338 (11.8), 440 (3.6)

^a Isolated yields of recrystallized complexes as their PF₆⁻ salts. The yields reported for complexes **3** through **6** represent the reaction yields of **1** with the corresponding acetylene (see text). ^b Electrospray Ionization Mass Spectrum. The observed peaks correspond to [M-nPF₆⁻]ⁿ⁺. ^c UV-VIS spectra were taken in acetonitrile. Absorption maxima are given in nm and 10⁻⁴ ε (in parenthesis) is given in dm³ mol⁻¹ cm⁻¹.

and **5**, respectively, in good yields. The same mild reaction conditions are applied for the coupling of 1,3,5-triethynylbenzene with 3 equiv. of **1** to afford the trinuclear complex **6** in 70% yield.[†] Cross-coupling reactions of the Ru^{II} complex containing the alkyne functionality with aromatic electrophiles have been found to proceed efficiently as well. Thus, treating [(bpy)₂Ru(3-ethynyl-1,10-phenanthroline)]²⁺(PF₆⁻)₂ **2** with 1,4-diiodobenzene or 4,4'-diiodobiphenyl under the same reaction conditions, affords the binuclear Ru^{II} complexes **4** and **5**, in 43 and 56% yield, respectively. In general, the reactions of **2** with aromatic iodides proceed slower than the reactions of **1** with aromatic acetylenes.

The compounds synthesized represent a novel family of multi Ru^{II} complexes of various structures and spectral properties (Table 1). The parent complex **1** exhibits two main absorption bands at 272 and 286 nm due to the overlapping π - π^* transitions of the bpy and phenanthroline ligands. Although the major band of the bpy appears to remain largely unchanged, extending the conjugation of the phenanthroline ligand results in the appearance of a lower energy band above 330 nm (Table 1).¹⁰ For example, in addition to a strong absorption at 286 nm, **3** shows a new band at 346 nm. This lower energy π - π^* transition is further red-shifted with increasing conjugation as is evidenced when comparing the spectrum of **3** to that of **4** (362 nm). The binuclear complex **5** shows similar behaviour to that of **4**, indicating a substantial electronic conjugation between the two phenanthroline ligands through the biphenyl ring. In contrast, the lower energy π - π^* transition of the phenanthroline ring in the trinuclear complex **6** appears at a much shorter wavelength (338 nm) as compared to **4** (362 nm) and **5** (368 nm), and is almost overlapping with that of the mononuclear complex **3** (346 nm). This indicates that each of the metal centres in **6** is electronically isolated and is not involved in π -conjugation. The visible metal to ligand charge transfer (MLCT) bands appear around 440 nm for all derivatives. This somewhat unexpected behaviour has been observed in other mono- and bi-nuclear Ru^{II} complexes.^{1,8,10} Nevertheless, the different nuclearity of the complexes **3,4 (5)** and **6** is beautifully evident from the approximate 1:2:3 ratio of the extinction coefficients of the major π - π^* as well as the MLCT bands.

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Footnotes

[†] E-mail: ytor@chem.ucsd.edu

[‡] **1** was prepared by refluxing a mixture of 3-bromo-1,10-phenanthroline¹² and (bpy)₂RuCl₂·2H₂O in ethanol for 12 h. Addition of aqueous KPF₆ precipitated the product. **2** was prepared in a similar fashion using 3-ethynyl-1,10-phenanthroline which was synthesized in two steps from 3-bromo-1,10-phenanthroline.

[§] Representative procedure for the palladium-mediated cross-coupling reactions between **1** and aromatic acetylenes: A mixture of **1** (50 mg, 0.052 mmol), (Ph₃P)₂PdCl₂ (4 mg, 0.0057 mmol) and CuI (0.5 mg, 0.0026 mmol) was treated with a degassed solution of 4-ethynyltoluene (11 μ l, 0.11 mmol) in DMF (5 ml) and triethylamine (3 ml) for 1 h at room temp. under Ar. The crude reaction mixture was evaporated to dryness and the product **3** was obtained in 91% yield as an orange-red powder after successive crystallizations from dichloromethane-ethanol. *Selected spectroscopic data for 3*: ¹H NMR (500 MHz, CD₃CN) δ 8.72 (d, 1 H, H-2_{phen}), 8.62 (d, 1 H, H-9_{phen}), 8.56–8.49 (m, 4 H, H₈_{bpy}), 8.27 (d, 1 H, H-5_{phen}), 8.22 (d, 1 H, H-6_{phen}), 8.19 (d, 1 H, H-4_{phen}), 8.12–8.07 (m, 3 H, H-7_{phen}, 2 H₉_{bpy}), 8.04–7.99 (m, 2 H, H₇_{bpy}), 7.86 (d, 1 H, H₄_{bpy}), 7.81 (d, 1 H, H₅_{bpy}), 7.74 (dd, 1 H, H-8_{phen}), 7.65 (d, 1 H, H₃_{bpy}), 7.52 (d, 1 H, H₆_{bpy}), 7.48–7.45 (m, 4 H, 2 H₈_{bpy}, 2 H_{phenyl}), 7.28–7.23 (m, 4 H, H₈_{bpy}, 2 H_{phenyl}) and 2.24 (s, 3 H, CH₃). IR (film, NaCl) ν_{\max} 2215 cm⁻¹ (C≡C).

[¶] All Ru^{II} complexes were synthesized as their PF₆⁻ salts and showed spectroscopic data (UV-VIS, IR, NMR and MS) consistent with the

assigned structure. EIMS has been found particularly useful in analyzing these complexes due to the characteristic formation of multiply charged species with typical isotopic distribution. Note that the binuclear and trinuclear complexes are formed as a mixture of stereoisomers. No attempt has been made to resolve these complexes at this point.

References

- (a) A. C. Benniston, V. Goulle, A. Harriman, J.-M. Lehn and B. Marczinke, *J. Phys. Chem.*, 1994, **98**, 7798; (b) J. L. Sessler, B. Wang and A. Harriman, *J. Am. Chem. Soc.*, 1995, **117**, 704; (c) A. Harriman, F. Odobel and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1995, **117**, 9461; (d) J.-P. Collin, A. Harriman, V. Heitz, F. Odobel and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 5679; (e) P. Belser, R. Dux, M. Baak, L. DeCola and V. Balzani, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 595; (f) V. Grossshenny, A. Harriman and R. Ziesel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1100; (g) J. Bolger, A. Gourdon, E. Ishow and J.-P. Launay, *J. Chem. Soc., Chem. Commun.*, 1995, 1799; (h) M. J. Crossley, P. L. Burn, S. J. Langford and J. K. Prashar, *J. Chem. Soc., Chem. Commun.*, 1995, 1921.
- S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto and V. Balzani, *Chem. Eur. J.*, 1995, **1**, 211.
- J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspective*, VCH: Weinheim, 1995; M. D. Ward, *Chem. Soc. Rev.*, 1995, 121; V. Balzani, A. Credi, and F. Scandola, *Transition Metals in Supramolecular Chemistry*, ed. L. Fabbri and A. Poggi, Kluwer, 1994, pp. 1–32.
- A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85; J.-P. Sauvage, J. P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
- E. C. Constable and A. M. W. Chargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1995, 1615; M. Hissler and R. Ziessel, *New J. Chem.*, 1995, **19**, 751; J.-P. Collin, P. Laine, J.-P. Launay, J.-P. Sauvage and A. Sour, *J. Chem. Soc., Chem. Commun.*, 1993, 434; F. M. Romero and R. Ziessel, *Tetrahedron Lett.*, 1994, **35**, 9203; V. Grossshenny and R. Ziesel, *J. Organomet. Chem.*, 1993, **453**, C19; M. Beley, S. Chodorowski, J.-P. Collin and J.-P. Sauvage, *Tetrahedron Lett.*, 1993, **34**, 2933; L. De Cola, F. Barigelletti, V. Balzani, P. Belser, A. von Zelewsky, C. Seel, M. Frank and F. Vögtle, in *Supramolecular Chemistry*, ed. V. Balzani and L. De Cola, Kluwer, 1992, pp. 157–180.
- Non-conjugated multinuclear complexes have been recently synthesized by nucleophilic displacement reactions on Ru^{II} complexes of 4'-substituted terpyridines; see E. C. Constable, A. M. W. Cargill Thompson, P. Harveson, L. Macko and M. Zehnder, *Chem. Eur. J.*, 1995, **1**, 360.
- K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467; for recent reviews, see: L. S. Hegeudis, in *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, CA 1994; pp. 65–127; R. Rossi, A. Carpita and F. Bellina, *Org. Prep. Proc. Int.*, 1995, **27**, 127; for recent examples of key steps in the total synthesis of natural products, see: K. C. Nicolaou, A. D. Piscopio, P. Bertinato, T. K. Chakraborty, N. Minowa and K. Koide, *Chem. Eur. J.*, 1995, **1**, 318; M. D. Shair, T. Yoon and S. J. Danishefsky, *J. Org. Chem.*, 1994, **59**, 3755; for recent examples in the synthesis of new materials, see: Z. Xu, M. Kahr, K. L. Walker, C. L. Wilkins and J. S. Moore, *J. Am. Chem. Soc.*, 1994, **116**, 4537; D. L. Pearson, J. S. Schumm and J. M. Tour, *Macromolecules*, 1994, **27**, 2348.
- S. G. DiMagno, V. S.-Y. Lin and M. J. Therien, *J. Org. Chem.*, 1993, **58**, 5983.
- S. Prathapan, T. E. Johnson and J. S. Lindsey, *J. Am. Chem. Soc.*, 1993, **115**, 7519; R. W. Wagner, T. E. Johnson, F. Li and J. S. Lindsey, *J. Org. Chem.*, 1995, **60**, 5266; J. Seth, V. Palaniappan, T. E. Johnson, S. Prathapan, J. S. Lindsey and D. F. Bocian, *J. Am. Chem. Soc.*, 1994, **116**, 10578; V. S.-Y. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105; H. L. Anderson and J. K. M. Sanders, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1400.
- D. Tzalis and Y. Tor, *Tetrahedron Lett.*, 1995, **36**, 6017.
- J. Suffert and R. Ziessel, *Tetrahedron Lett.*, 1991, **32**, 757.
- D. Tzalis, Y. Tor, S. Failla and J. S. Siegel, *Tetrahedron Lett.*, 1995, **36**, 3489.

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