



S0040-4039(96)00474-1

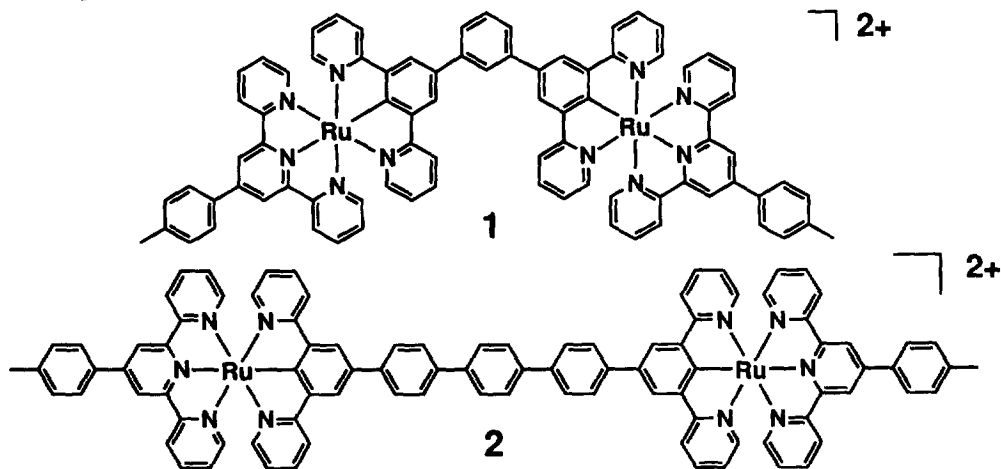
Construction of Multicomponent Systems by Utilizing Functionalized Transition Metal Complexes as Building Blocks

Sandrine Chodorowski-Kimmes, Marc Beley, Jean-Paul Collin* and Jean-Pierre Sauvage

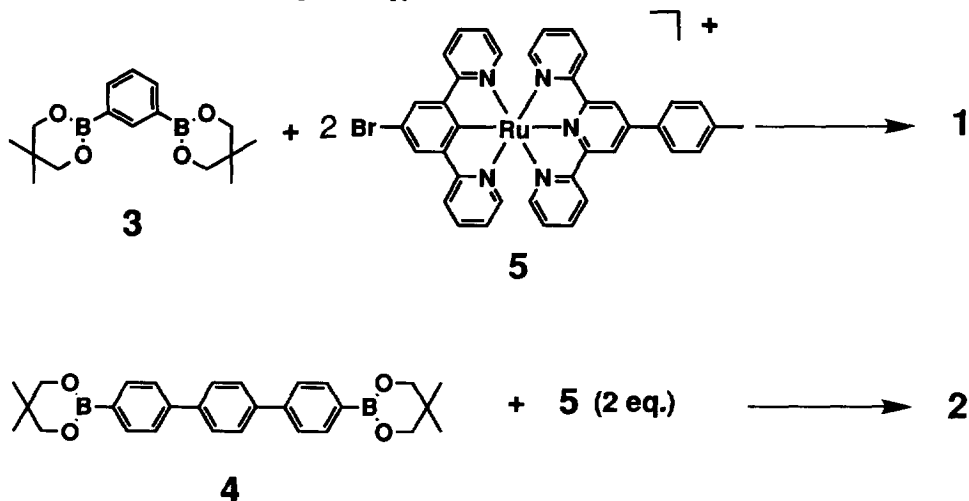
Laboratoire de Chimie Organo-Minérale, associé au CNRS, Faculté de Chimie, Université Louis Pasteur
4, rue Blaise Pascal, 67008 Strasbourg, France

Abstract. Two dinuclear ruthenium complexes have been prepared using functionalized mononuclear complexes as building block in a classical aromatic cross coupling reaction (Suzuki's procedure) with a difunctionalized aromatic spacer. Copyright © 1996 Published by Elsevier Science Ltd

The synthesis of multicomponent systems incorporating kinetically inert metal complexes linked by various bridges is an essential aspect in the field of electro- and photochemical molecular devices¹. Different strategies, including the formation of covalent linkages^{2,3}, hydrogen bonds^{4,5}, cation chelation⁶, etc... have been used to elaborate such multinuclear systems. The main synthetic approaches employ transition metals as assembling species⁷, transition metal complexes as building blocks⁸ or a combination of these two possibilities⁹. Two examples, in which ruthenium(II) complexes react in an oxidative or reductive coupling reaction affording homo-dinuclear species have been recently published^{7,8}. We now describe a more general procedure, leading to the synthesis of two homo-dinuclear ruthenium(II) complexes (**1** and **2**) related to optical electron transfer in mixed-valence complexes.



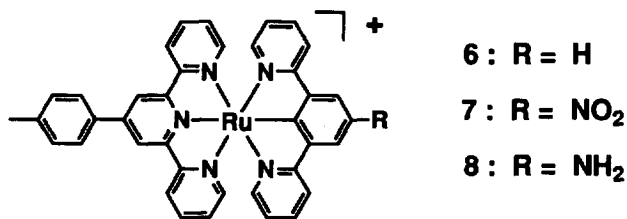
Aromatic cross-coupling reaction (Suzuki's procedure¹⁰) between the diboronic derivatives of the bridge (**3** or **4**) and the brominated ruthenium complex **5** (Scheme 1) leads to the expected compounds in moderate yields. A mixture of benzene-1,3-diboronic ester derivative **3**, two equivalents of **5** and palladium(0) tetrakis-triphenylphosphine (10% mol) in biphasic solution (1,2-dimethoxyethane, EtOH, aq Na₂CO₃ 2M) was refluxed under argon for 20 h. Work-up and column chromatography (SiO₂; CH₃CN-aqueous NaBF₄ as eluent) afforded **1** in 35 % yield. A typical experimental procedure is given in reference¹¹. The same procedure applied to the diester of the terphenyl diboronic acid **4** gave **3** in 18 % yield. These compounds were characterized by ¹H NMR, FAB-MS and UV-Vis spectroscopy¹¹.



Scheme 1

The diboronic derivatives **3** and **4** have been obtained following classical methods, i.e. bromination of the aromatic spacer (in the case of terphenyl), preparation of the dilithio or Grignard derivatives, reaction with trimethyl borate, hydrolysis of the diboronic acid and the esterification with 2,2-dimethyl-1,3-propane diol. The cyclometallated ruthenium(II) complex **5** was prepared from Ru(tpy)Cl₃⁸ (tpy = 4'-p-tolyl-2,2':6',2''-terpyridine) and 1-bromo-3,5-dipyridyl benzene¹² as previously reported for the analogous non-brominated ruthenium complex⁸.

This new methodology should be applicable to a wide range of metal complexes and organic synthons, also using other mild cross coupling reactions involving organometallic derivative of tin, zinc, magnesium, copper, etc... It can be also useful to functionalize directly the metal complex by a reactive function. In this area, we have found the cyclometallated ruthenium complex **6** could be converted selectively to the nitro derivative **7**, (Menke conditions¹³), and subsequently to the amino derivative **8**¹⁴ (Scheme 2).



Scheme 2

The use of kinetically inert metal (Ru(II), Os(II), Rh(III), Ir(III), Pd(II), Pt(IV)) complexes as building blocks for constructing multicomponent molecular systems becomes possible by the way of some classical organic reactions. In future work, we will try to develop and to generalize this new approach.

References

- Balzani, V.; Scandola, F. *Supramolecular Photochemistry* Horwood : Chichester, **1991**.
- Miller, J.R. *Nouv. J. Chim.* **1987**, *11*, 83.
- Gust, D.; Moore, T.A. *Science* **1989**, *244* 35.
- Tecilla, P.; Dixon, R.P.; Slobodkin, G.; Alavi, D.S.; Valdeck, D.H.; Hamilton, A.D. *J. Am. Chem. Soc.* **1990**, *112*, 9408.
- Harriman, A.; Kubo, Y.; Sessler, J.L. *J. Am. Chem. Soc.* **1992**, *114*, 388.
- Brun, A.M.; Atherton, S.J.; Harriman, A.; Heitz, V.; Sauvage, J.P. *J. Am. Chem. Soc.* **1992**, *114*, 4632.
- Denti, G.; Serroni, S.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Perspectives in Coordination Chemistry*, Williams, A.F.; Floriani, C.; Merbach, A.E. Eds., HCAV and VCH, Basel and Weinheim, **1992**.
- Beley, M.; Collin, J.-P.; Louis, R.; Metz, B.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8521 ; Constable, E.C.; Cargill Thompson, A.M.W.; Greulich, S. *J. Chem. Soc. Chem. Comm.* **1993**, 1444.
- Constable, E.C.; Cargill Thompson, A.M.W.; Harverson, P.; Macko, L.; Zehnder, M. *Chem. Eur. J.* **1995**, *1*, 360.
- Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Comm.* **1981**, *11*, 513.
- Pd(P(C₆H₅)₃)₄ (16 mg, 10 μmol) was added, under argon, to a suspension of **5** (176 mg, 200 μmol) in freshly distilled DME (20 mL). Then, an aqueous solution of Na₂CO₃ 2M (20mL) and the diboronic derivative **3** (30 mg, 100 μmol) in EtOH (5 mL) were added via canula. The purple reaction mixture was refluxed for 20 h. After cooling, the solvents were removed and the residue was dissolved in CH₃CN (25 mL). The precipitate obtained by addition of an aqueous solution of KPF₆ (0.2 g in 50 mL of water) was washed successively with water (50 mL) and ether (50 mL). The product was purified by silica gel column

chromatography. Elution with NaBF₄ in a CH₃CN-water mixture (95:5, NaBF₄ 0.04 M) and anion exchange procedure gave **1** as a deep red solid (68 mg, 35 %).

1 : ¹H NMR : δH (CD₃CN) 9.03 (s, 4H) ; 8.81 (s, 4H) ; 8.67 (d, 1H, 0.25 Hz) ; 8.6 (d, 4H, 7.9 Hz) ; 8.41 (d, 4H, 7.9 Hz) ; 8.12 (d, 4H, 8.2 Hz) ; 8.09 (dd, 2H, 7.5 and 1.7 Hz) ; 7.85 (t, 1H, 7.6 Hz) ; 7.74 (dd, 4H, 8.36 and 1.5 Hz) ; 7.68 (dd, 4H, 8.2 and 1.5 Hz) ; 7.56 (d, 4H, 7.8 Hz) ; 7.23 (d, 4H, 4.8 Hz) ; 7.17 (d, 4H, 5.0 Hz) ; 7.00 (dd, 4H, 7.0 and 1.2 Hz) ; 6.71 (dd, 4H, 7.3 and 1.3 Hz) ; 2.33 (s, 6H). FAB-MS (nitrobenzyl alcohol matrix) : (m-PF₆⁻) : 1531.3 C₈₂H₅₈N₁₀RuPF₆ requires 1531. UV-Vis (CH₃CN) λ_{max} (ε [M⁻¹cm⁻¹]) : 552 (36400), 512 (40000), 288 (183000), 242 (128000).

2 : ¹H NMR : δH (CD₃CN) 9.02 (s, 4H) ; 8.67 (s, 4H) ; 8.59 (d, 4H, 7.8 Hz) ; 8.35 (d, 4H, 7.9 Hz) ; 8.15 (m, 8H) ; 8.02 (m, 4H) ; 7.98 (s, 4H) ; 7.72 (m, 8H) ; 7.59 (d, 4H, 8.2 Hz) ; 7.16 (m, 8H) ; 7.01 (m, 4H) ; 6.75 (m, 4H) ; 2.25 (s, 6H). FAB-MS (nitrobenzyl alcohol matrix) : (m-PF₆⁻) : 1683.2 C₉₄H₆₆N₁₀Ru₂PF₆ requires 1683. UV-Vis (CH₃CN) λ_{max} (ε [M⁻¹cm⁻¹]) : 544 (33000), 511 (37000), 375 (72000), 287 (137000), 242 (82000), 229 (80000).

12. Beley, M. ; Chodorowski, S. ; Collin, J.-P. ; Sauvage, J.-P. *Tetrahedron Lett.* **1993**, *34*, 2933.
13. Clark, G.R. ; Headford, C.E.L. ; Roper, W.R. ; Wright, L.J. ; Yap, V.P.D. *Inorg. Chim. Acta.* **1994**, *220*, 261.
14. **7** : ¹H NMR : δH (CD₃CN) 9.08 (s, 2H) ; 9.00 (s, 2H) ; 8.57 (d, 2H, 8Hz) ; 8.36 (d, 2H, 8Hz) ; 8.10 (d, 2H, 8Hz) ; 7.72 (m, 4H) ; 7.56 (d, 2H, 8Hz) ; 7.27 (d, 2H, 6Hz) ; 7.07 (d, 2H, 6Hz) ; 6.92 (ddd, 2H, 7.5, 5.7 and 1.4 Hz) ; 6.81 (ddd, 2H, 7.5, 5.6 and 1.4 Hz) ; 2.52 (s, 3H). FAB-MS (nitrobenzyl alcohol matrix) : (m-PF₆⁻) = 701.1 C₃₈H₂₇N₆O₂Ru requires 701. UV-Vis (CH₃CN) λ_{max} (ε [M⁻¹cm⁻¹]) : 532 (18700), 374 (9500), 285 (50600), 233 (34550).
- 8** : ¹H NMR : δH (CD₃CN) 9.22 (s, 2H) ; 8.79 (d, 2H, 8Hz) ; 8.14 (m, 4H) ; 7.91 (s, 2H) ; 7.72 (td, 2H, 8 and 1.5 Hz) ; 7.58 (td, 2H, 8 and 1.4 Hz) ; 7.42 (d, 2H, 7.9 Hz) ; 7.18 (m, 4H) ; 6.98 (td, 2H, 6 and 1.4 Hz) ; 6.65 (td, 2H, 6 and 1.4 Hz) ; 2.38 (s, 3H). ES MS m/z = 670.77 C₃₈H₂₉N₆Ru requires 671. UV-Vis (CH₃CN) λ_{max} (ε [M⁻¹cm⁻¹]) : 552 (17100), 320sh (15500), 378 (14280), 293 (55900), 235 (40800).

(Received in France 14 December 1996; accepted 7 March 1996)