

Synthesis of Bis-cyclometallating N-C-N Hexadentate Ligands via C-C Aromatic Couplings and their Dinuclear Ruthenium(II) Complexes

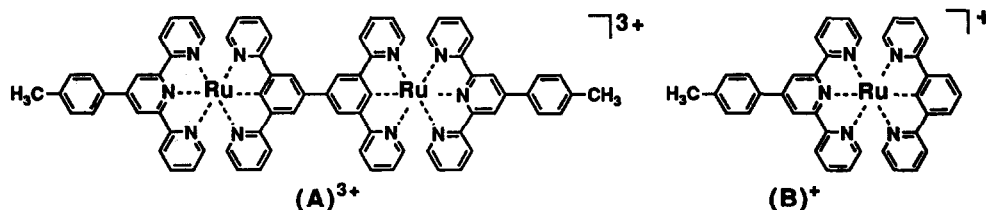
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Abstract. By combining palladium catalyzed C-C coupling procedures either based on aromatic stannanes or utilizing boronic acids or esters (Suzuki's reaction), various bis-cyclometallating N-C-N ligands could be prepared. Their di-ruthenium(II) complexes have also been synthesized.

Mild and efficient aromatic cross coupling reactions catalyzed by various transition metal complexes have recently been developed.¹⁻³ Besides natural products synthesis, construction of large organic receptors in host-guest chemistry,⁴ or elaboration of dendrimers⁵ or one-dimensional polymers,⁶ aromatic couplings can be used to build multi-site ligands able to incorporate two or several transition metals. By varying the length and the nature of the aromatic spacers bridging the metal centres, it will be possible to exert a strict control over the degree of communication between the metals and to better understand the factors which contribute to electronic interactions within multi-metallic complexes.⁷

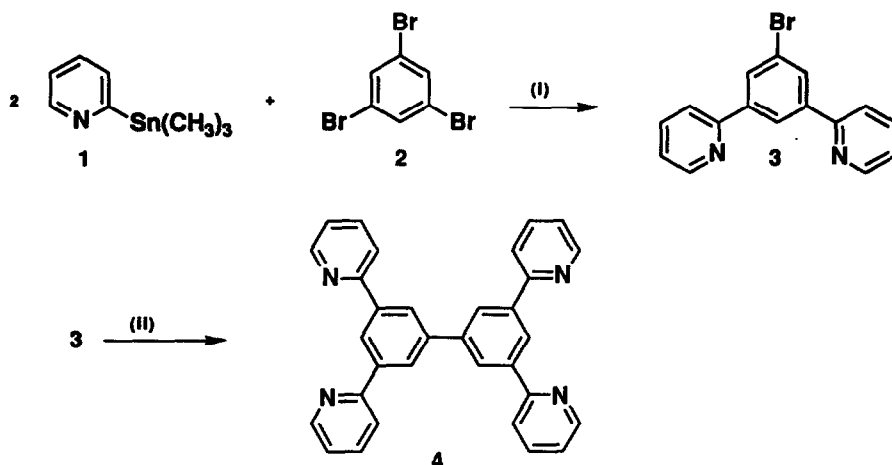
We recently found that a bis-cyclometallating ligand (deprotonated form of 4, Figure 1)



Scheme 1

leads to exceptional electronic coupling in dinuclear ruthenium complexes,⁸ with in particular a stable and delocalized Ru^{II} Ru^{III} mixed valence state (Scheme 1)

The diruthenium complex (A)²⁺ was obtained by oxidative coupling of the corresponding mononuclear compound⁸ (B⁺) and it was not possible to demetalate this complex in order to liberate the protonated free ligand **4**. A specific synthesis of **4** and related molecules was thus developed, the universal precursor being the functionalized N-CH-N potentially terdentate chelating species **3** of Figure 1.



(i) THF under argon, reflux 23h / Pd(P(C₆H₅)₃)₂Cl₂ (5%).

(ii) DMF at 50°C for 21h / Ni(P(C₆H₅)₃)₂Cl₂ (5%) / Zn.

Figure 1.

2-Trimethylstannyl-pyridine **1**⁹ was reacted with 1,3,5-tri-bromo-benzene **2** under conditions previously used by Bailey for preparing 4-(2'-pyridyl)-methyl benzoate.¹⁰ **3** was obtained in 35% yield as a white solid.¹¹ It was coupled using nickel(0) to afford a 70% yield of **4**.¹²

In order to modulate the length of the aromatic ligand bridging the two metal centres, we investigated the possibility of building two-site ligands by heterocoupling of **3** with various disubstituted aromatic nuclei, to be incorporated as spacers in the bridging ligand (BL) structure. Compounds **6** and **8** of Figure 2 were thus prepared using Suzuki's cross-coupling procedure.²

A mixture of benzene-1,4-diboronic acid,¹³ two equivalents of **3** and palladium tetrakis-triphenylphosphine (5% mol) in biphasic solution (toluene, EtOH, aq. Na₂CO₃ (2M) (15 : 15 : 1 v/v)) was refluxed under argon for 16 h. Work-up and column chromatography (SiO₂ ; CH₂Cl₂ - CH₃OH as eluent) afforded **6** in 78% yield.¹⁴ The same procedure applied to the ethyleneglycol diester of 4,4'-biphenylene diboronic acid^{6,13b} gave **8** in 30% yield.¹⁴

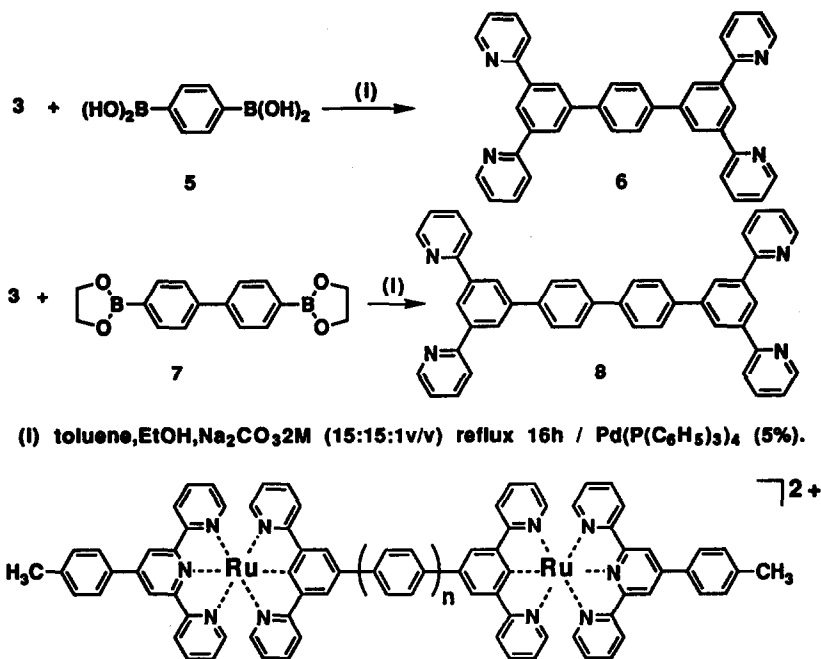


Figure 2.

The two dinuclear complexes **9** and **10** were prepared from Ru(tterpy)Cl₃⁸ (2 equivalents ; tterpy : 4'-p-tolyl-2,2',6',2'' terpyridine) by first replacing the chloride ligands by solvent molecules using AgBF₄ (6 equivalents) as a dechlorinating agent (reflux of acetone for 2 h.) followed by addition (1 equivalent) of bridging ligand **6** or **8**. The mixture was refluxed under argon in 1-butanol for 6 h.

The hexafluorophosphate salts were obtained after chromatographic purification (silica, acetone - aqueous KNO₃ as eluent) and addition of a saturated aqueous KPF₆ solution.

The two products **9** and **10** were obtained in 77% and 56% yield respectively. Their ¹H-NMR and FAB-MS spectra are in agreement with their structures.¹⁵

References

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11. All new compounds were characterized by ¹H-NMR and FAB-MS spectroscopy.
12. **4** : ¹H NMR: δH (CD₂Cl₂) 8.76 (dd, 4H, 4.8 and 1.8 Hz) ; 8.72 (t, 2H, 1.6 Hz) ; 8.48 (d, 4H, 1.6 Hz) ; 7.98 (d, 4H, 8.0 Hz) ; 7.84 (td, 4H, 7.5 and 1.8 Hz) ; 7.31 (ddd, 4H, 7.4, 4.8 and 1.2 Hz) ; MS : m/z = 462 (C₃₂H₂₂N₄ requires 462, 18). Anal. Calcd for C₃₂H₂₂N₄. H₂O : C, 79.90 ; H, 5.03 ; N, 11.60. Found : C, 80.00 ; H, 4.90 ; N, 11.60. Fp : 193-196°C.
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14. **6** : ¹H NMR: δH (CD₂Cl₂) 8.75 (d, 4H, 4.7 Hz) ; 8.70 (t, 2H, 1.6 Hz) ; 8.41 (d, 4H, 1.6 Hz) ; 7.97 (m, 4H) ; 7.94 (s, 4H) ; 7.84 (td, 4H, 7.4 and 1.7 Hz) ; 7.31 (ddd, 4H, 7.1, 4.8 and 1.1 Hz) ; MS : m/z = 538 (C₃₈H₂₆N₄ requires 538.65). Anal. Calcd for C₃₈H₂₆N₄. H₂O : C, 81.92 ; H, 5.07 ; N, 10.06. Found : C, 81.00 ; H, 4.80 ; N, 9.84. Fp : 269-271°C.
- 8** : ¹H NMR: δH (CD₂Cl₂) 8.75 (d, 4H, 4.1 Hz) ; 8.70 (t, 2H, 1.6 Hz) ; 8.40 (d, 4H, 1.6 Hz) ; 7.94 (d, 4H, 8.0 Hz) ; 7.9 (s, 8H) ; 7.84 (m, 4H) ; 7.31 (ddd, 4H, 7.3, 4.7 and 1.1 Hz). FAB MS (nitrobenzyl alcohol matrix) : m/z : 615.2 C₄₄H₃₀N₄ + H requires 615.24. Anal. Calcd for C₄₄H₃₀N₄. 1/2 H₂O : C, 84.73 ; H, 5.01 ; N, 8.98. Found : C, 84.40 ; H, 5.20 ; N, 8.40. Fp > 280°C.
15. **9** : ¹H NMR: δH (CD₃CN) 9.04 (s, 4H) ; 8.71 (s, 4H) ; 8.62 (d, 4H, 7.7 Hz) ; 8.37 (d, 4H, 8.1 Hz) ; 8.26 (s, 4H) ; 8.12 (d, 4H, 8.2) ; 7.75 (m, 4H) ; 7.68 (m, 4H) ; 7.54 (d, 4H, 8.0 Hz) ; 7.23 (d, 4H, 4.6) ; 7.15 (d, 4H, 4.9) ; 7.02 (m, 4H) ; 6.71 (m, 4H) ; 2.51 (s, 6H). FAB MS (nitrobenzyl alcohol matrix) : (m-PF₆⁻) : 1530.3 C₈₂H₅₈N₁₀Ru₂PF₆ requires 1530.54 ; (m-2PF₆⁻) : 1385.4 ; C₈₂H₅₈N₁₀Ru₂ requires 1385.58 ; m/z : 693.2. C₈₂H₅₈N₁₀Ru₂/2 requires 693.14.
- 10** : ¹H NMR: δH (CD₃CN) 9.00 (s, 4H) ; 8.64 (s, 4H) ; 8.57 (dd, 4H, 7.9 and 1.4 Hz) ; 8.32 (d, 4H, 8.0 Hz) ; 8.16 (d, 4H, 8.6 Hz) ; 8.08 (d, 4H, 8.1 Hz) ; 8.00 (d, 4H, 8.1 Hz) ; 7.83 (m, 8H) ; 7.63 (d, 4H, 7.9 Hz) ; 7.29 (m, 8H) ; 6.96 (t, 4H, 7.0 Hz) ; 6.69 (t, 4H, 7.1 Hz). FAB MS (nitrobenzyl alcohol matrix) : (m-PF₆⁻) : 1606.6 C₈₈H₆₂N₁₀Ru₂PF₆ requires 1606.64 ; (m - 2PF₆⁻) : 1461.78 C₈₈H₆₂N₁₀Ru₂ requires 1461.68 ; m/z : 730.9. C₈₈H₆₂N₁₀Ru₂/2 requires 730.84.

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