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Coordination Compounds as Building Blocks: Single-Step Synthesis of Heteronuclear Multimetallic Complexes Containing Ru^{II} and Os^{II}

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Introduction

Covalently linked multimetallic complexes are of great interest for the fundamental study of photoinduced energy and electron transfer, as well as for the construction of photochemical molecular devices.[1] In particular, heterometallic arrays containing Ru^{II}− and Os^{II}−polypyridine chromophores have received a great deal of attention because of their outstanding redox and spectroscopic properties.[2] These multi-heteronuclear complexes have been predominantly constructed by the synthesis of multitopic ligands followed by a stepwise metal complexation.[2,3] This approach, although productive, is elaborate and does not always provide full control over the final structure and composition of the assembly.

We report herein on a convergent and powerful approach for the fabrication of heteronuclear complexes containing Ru^{II} and Os^{II} metal centers. In this strategy, functionalized Ru^{II} and Os^{II} coordination complexes are utilized as building blocks and synthetic organic chemistry is performed on the periphery of the octahedral complexes. Thus, palladium-catalyzed cross-coupling reactions between $[(bpy)_2M_1(L1)]^{2+}$ and $[(bpy)_2M_2(L2)]^{2+}$ (where L1 and L2 are bromo- and ethynyl-functionalized 1,10-phenanthroline ligands) provide heteronuclear complexes *in a single synthetic step*. No ligand displacement occurs, and full control over the structure and composition of the assembly is achieved.

Experimental Section

Physical Measurements. ^1H NMR spectra were recorded on a Varian Unity 500 spectrometer. All spectra were taken in CD_3CN and were referenced to the residual proton signals of the solvent. Chemical shifts are reported as δ values in ppm downfield of 0.0. UV−vis spectra were recorded on a HP 8452A diode-array spectrometer using acetonitrile as a solvent. ESI mass spectra were measured at the Mass Spectrometry Facility, University of California, Riverside, CA.

Electrochemistry. Electrochemical experiments were performed with a Bioanalytical Systems Model BAS-CV50W voltammetric analyzer. Cyclic voltammograms were measured in 1 mM degassed acetonitrile solutions containing 0.1 M Bu_4NPF_6, using a $Ag/AgNO_3/CH_3CN$ reference electrode and Pt working and auxiliary electrodes at a 100 mV/s scan rate. Peak potentials were obtained from the square-wave voltammograms taken with the same solutions and setup. A 1 mM solution of ferrocene (Fc) in acetonitrile containing 0.1 M Bu_4NPF_6 was used as a standard. Under these conditions, $E_{1/2} = 0.084$ V for Fc/Fc^+.

Materials. $(bpy)_2RuCl_2$ was purchased from Johnson & Matthey, and $(bpy)_2OsCl_2$ was synthesized according to a reported procedure.[4] Anhydrous solvents were purchased from Fluka. Other standard reagents and solvents were of analytical grade and were used as received.

Synthesis. 3-Bromo-1,10-phenanthroline and 3,8-dibromo-1,10-phenanthroline were synthesized by a modification of our published procedure,[5] as described below. Representative procedures for the preparation of Os^{II}-containing building blocks are described. The Ru^{II}-containing building blocks have been made using similar procedures.[6,7] All cross-coupling reactions were carried out under Ar atmosphere. [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) [$(dppf)PdCl_2$] has been found to be more effective than, for example, $(Ph_3P)_2PdCl_2$ in these cross-coupling reactions. Table 1 summarizes the yields and mass, spectral, and electrochemical data for all compounds.

3-Bromo-1,10-phenanthroline and 3,8-Dibromo-1,10-phenanthroline. 1,10-Phenanthroline hydrochloride monohydrate (3.0 g, 13 mmol) is added to bromobenzene (200 mL) in a round-bottom two-neck flask, and the mixture is sonicated for 20 min. A reflux condenser and an addition funnel are connected, and the reaction mixture is heated to 135 °C. Once the temperature is maintained, bromine (2 mL, 39 mmol), dissolved in bromobenzene (100 mL), is added dropwise over a period of 10 h. (*CAUTION: Bromine is toxic and corrosive! This operation must be performed in a well-ventilated fume hood. Appropriate gloves should be used.*) The reaction mixture is kept at 135 °C for an additional 36 h and then cooled to room temperature. Concentrated ammonium hydroxide (100 mL) is added, the mixture is sonicated, and the phases are separated in a separatory funnel. The organic phase is washed with ammonium hydroxide (3 × 100 mL) and brine (3 × 100 mL), and the combined aqueous phase is back-extracted with dichloromethane (3 × 100 mL). The combined organic phase is dried and evaporated to dryness. Careful flash chromatography on Silicagel 60 separates the products. 3,8-Dibromo-1,10-phenanthroline is eluted with 0.1−0.3% methanol/dichloromethane. Increasing the polarity to 1% methanol/dichloromethane elutes the 3-bromo-1,-10-phenanthroline. The reaction is sensitive to changes in temperature, concentration, and rate of addition; therefore, yields may vary. In a typical reaction, 25% yield of the monobrominated product and 25% yield of the dibrominated product are obtained. 3-Bromo-1,10-phenanthroline can be recrystallized from boiling water (0.5 g/250 mL). See ref 5 for physical data. Other brominated phenanthrolines are isolated in small amounts (3,6-dibromo-1,10-phenanthroline, mp 220 °C, and 3,5,8-tribromo-1,10-phenanthroline, mp 290 °C).

$[(bpy)_2Os(3\text{-bromo-}1,10\text{-phenanthroline})]^{2+}(PF_6^-)_2$ (3). 3-Bromo-1,10-phenanthroline (0.12 g, 0.47 mmol) and $(bpy)_2OsCl_2{\cdot}2H_2O$ (0.27 g, 0.48 mmol) were refluxed in deoxygenated methoxyethanol (15 mL) for 24 h, in the dark. The crude reaction mixture was evaporated to

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Table 1. Preparation and Selected Spectral Data for the Reported Complexes

complex	yield[a]	MS[b]	UV−vis[c]	$E_{1/2}$[d] Os$^{3+/2+}$	$E_{1/2}$[d] Ru$^{3+/2+}$
1	90	819 (M^+), 336 (M^{2+})	236 (4.2), 272 (6.0), 284 (5.8), 448 (1.2)		1.020
2	76	763 (M^+), 309 (M^{2+})	238 (4.5), 276 (7.2), 286 (7.1), 450 (1.4)		1.004
3	84	907 (M^+), 381 (M^{2+})	236 (5.2), 276 (6.4), 288 (6.6), 430 (1.3), 478 (1.3)	0.580	
4	89	853.3 (M^+), 354.1 (M^{2+})	238 (5.5), 290 (6.6), 386 (1.0), 434 (1.1), 474 (1.1)	0.564	
5	80	897 (M^+), 376 (M^{2+})	244 (5.2), 280 (8.1), 324 (1.4), 444 (1.4)		1.064
6	73	787 (M^+), 321 (M^{2+})	244 (5.3), 280 (8.5), 326 (1.6), 440 (1.5)		1.064
7	76	985 (M^+), 420 (M^{2+})	244 (4.9), 282 (7.6), 320 (1.8), 430 (1.3), 478 (1.4)	0.616	
8	74	877.2 (M^+), 366.1 (M^{2+})	246 (3.8), 288 (6.5), 328 (1.7), 432 (1.1), 474 (1.0)	0.552	
9	65	750.2 (M^{2+}), 451.4 (M^{3+})	246 (7.0), 286 (15.0), 346 (5.4), 360 (4.8), 440 (2.5)		1.020
10	78	794.2 (M^{2+}), 481.8 (M^{3+})	242 (7.5), 288 (14.1), 344 (5.1), 362 (4.5), 440 (2.5)[e]	0.576	1.024
11	64	839.3 (M^{2+}), 511.1 (M^{3+})	246 (7.2), 290 (15.3), 346 (5.6), 362 (5.0), 440 (2.6), 484 (2.4)	0.568	
12	53	1248.5 (M^{2+}), 783.2 (M^{3+})	244 (14.1), 288 (28.2), 370 (11.2), 442 (5.3), 472 (4.0)	0.620	1.024
13	47	1292.3 (M^{2+}), 813.1 (M^{3+})	244 (14.3), 288 (29.4), 368 (12.1), 440 (5.6) 474 (2.9)	0.568	1.056

[a] Isolated yields of chromatographed complexes as their PF_6^- salts (%). **1**-**8**: yields for direct complexation of $(bpy)_2MCl_2$ with the corresponding 1,10-phenanthroline, except for **2** and **6** (overall yield for a two step synthesis from **1** and **5**, respectively). **9**−**13**: yields for cross-coupling reactions. [b] Electrospray ionization MS (*m/z*). The observed peaks correspond to $[M - nPF_6^-]^{n+}$. [c] In acetonitrile. Absorption maxima are given in nm and extinction coefficients ($10^{-4}\epsilon$) in M^{-1} cm^{-1}. [d] Electrochemical potentials in V as measured in acetonitrile vs Ag/Ag$^+$. See Experimental Section. [e] Broad absorption tailing to >600 nm.

dryness. Flash chromatography on Silica 60 using saturated aqueous $KNO_3/H_2O/CH_3CN$ (0.2/19.8/80 to 0.6/19.4/80 v/v) and anion exchange with aqueous NH_4PF_6 afforded an olive green solid after precipitation from acetonitrile/water. ^{1}H NMR: δ 8.61 (d, 1H), 8.54−8.47 (m, 4H), 8.42 (dd, 1H), 8.27 (d, 1H), 8.17 (d, 1H), 8.05 (d, 1H), 8.01 (dd, 1H), 7.94−7.90 (m, 2H), 7.86−7.81 (m, 2H), 7.77 (d, 1H), 7.71−7.69 (m, 2H), 7.51 (d, 1H), 7.39−7.37 (m, 3H), 7.17−7.14 (m, 2H). ^{13}C NMR: δ 160.39, 160.26, 160.20, 159.94, 153.78, 153.58, 152.73, 152.62, 152.47, 152.17, 150.86, 149.93, 139.55, 138.65, 138.61, 138.55, 138.46, 137.93, 132.82, 132.64, 130.57, 129.23, 129.18, 129.07, 128.98, 128.63, 127.61, 125.74, 125.68, 125.61, 125.56, 122.19.

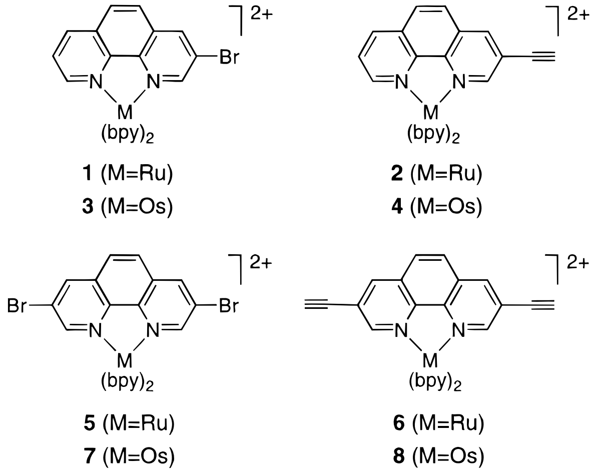
[(bpy)$_2$Os(3-ethynyl-1,10-phenanthroline)]$^{2+}$(PF$_6^-$)$_2$ (4) was prepared from 3-ethynyl-1,10-phenanthroline and $(bpy)_2OsCl_2{\cdot}2H_2O$ in ethanol using a procedure similar to the preparation of **3**. Flash chromatography on Silica 60 using saturated aqueous $KNO_3/H_2O/CH_3CN$ (0.2/19.8/80 to 0.8/19.2/80 v/v) and anion exchange with aqueous NH_4PF_6 afforded an olive green solid after precipitation from acetonitrile/water. ^{1}H NMR: δ 8.53−8.46 (m, 5H), 8.41 (d, 1H), 8.27 (d, 1H), 8.20 (d, 1H), 8.03 (d, 1H), 8.01 (d, 1H), 7.93−7.89 (m, 2H), 7.84−7.79 (m, 2H), 7.76 (d, 1H), 7.71−7.67 (m, 2H), 7.49 (d, 1H), 7.39−7.35 (m, 3H), 7.13 (m, 2H), 3.76 (s, 1H). ^{13}C NMR: δ 160.37, 160.34, 160.18, 160.01, 154.90, 153.51, 152.69, 152.54, 152.38, 152.20, 150.68, 150.53, 140.67, 138.56, 138.55, 138.43, 138.38, 137.81, 133.05, 131.57, 130.25, 129.19, 129.17, 129.08, 129.04, 128.97, 127.73, 125.70, 125.67, 125.58, 125.53, 122.38, 85.79, 79.28.

Dinuclear Complex 11. A representative Pd-mediated cross-coupling procedure is as follows: A mixture of **3** (53 mg, 50 μmol), CuI (0.6 mg, 3.1 μmol), and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (3.0 mg, 3.6 μmol) in degassed DMF (1.5 mL) and triethylamine (0.5 mL) was heated to 80 °C under Ar. A degassed solution of **4** (50 mg, 50 μmol) in DMF (1 mL) and triethylamine (0.5 mL) was cannulated in under Ar over 30 min. After an additional 30 min, the reaction mixture was cooled to room temperature and evaporated to dryness. Flash chromatography on Silica 60 using saturated aqueous $KNO_3/H_2O/CH_3CN$ (1/19/80 to 2/18/80 v/v) and anion exchange with aqueous NH_4PF_6 afforded an olive green solid after precipitation from acetonitrile/water. ^{1}H NMR: δ 8.57−8.47 (m, 10H), 8.42 (d, 2H), 8.29 (d, 2H), 8.23 (d, 2H), 8.18 (d, 2H), 8.02 (d, 2H), 7.99−7.95 (m, 2H), 7.94−7.90 (m, 2H), 7.86−7.80 (m, 4H), 7.75 (d, 2H), 7.71−7.68 (m, 4H), 7.50−7.48 (m, 2H), 7.40−7.36 (m, 6H), 7.15−7.11 (m, 4H). ^{13}C NMR: δ 160.33, 160.26, 160.14, 160.03, 154.29, 153.69, 152.53, 152.42, 152.39, 152.18, 150.90, 150.65, 140.45, 138.68, 138.65, 138.55, 138.50, 137.85, 133.29, 131.58, 130.39, 129.27 (2C), 129.11, 129.05, 127.87, 125.68, 125.63 (2C), 125.62 (2C), 122.05, 90.90.

Results and Discussion

The building blocks shown in Chart 1 can be prepared via two major routes (Table 1). Complexation of 3-bromo-1,10-phenanthroline[5] with $(bpy)_2MCl_2$ (M = Ru, Os) provides **1** and **3**. The functionalized complexes **1** and **3** can be cross-coupled to (trimethylsilyl)acetylene, followed by desilylation to give **2** and **4**, respectively.[6,7] Alternatively, 3-Bromo-1,10-phenanthroline can be cross-coupled to (trimethylsilyl)acetylene, followed by desilylation to provide 3-ethynyl-1,10-phenanthroline.[8] Complexation with $(bpy)_2MCl_2$ provides **2** and **4**. The difunctional complexes **5**−**8** are similarly synthesized from 3,8-dibromo-1,10-phenanthroline.[5]

Chart 1. Ru^{II} and Os^{II} Building Blocks



Palladium-mediated cross-coupling reactions between the bromo-containing complexes and the ethynyl-containing mononuclear complexes gave the bimetallic complexes **9**−**11** in good yields (Scheme 1). Thus, a DMF solution of **1** and **2** reacts smoothly in the presence of [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II), CuI, and Et_3N at 70 °C to afford the homodinuclear complex **9** (Table 1). Similarly, cross-coupling **3** and **4** under identical reaction conditions affords the di-Os^{II} complex **11**. The heterodinuclear complex **10** is obtained by a cross-coupling reaction between the bromo-containing Ru^{II} complex **1** and the ethynyl-containing Os^{II} complex **4** or by reacting the ethynyl-containing Ru^{II} complex **2** and the bromo-containing Os^{II} complex **3** under the same reaction conditions.

Complexes of higher nuclearity can be made from difunctional building blocks. Thus, cross-coupling **7** with 2 equiv of

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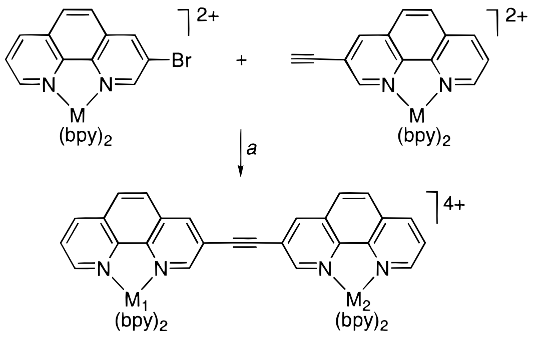
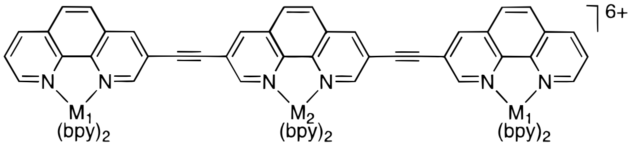
Scheme 1[a]



9 (M$_1$ = Ru, M$_2$ = Ru)
10 (M$_1$ = Ru, M$_2$ = Os)
11 (M$_1$ = Os, M$_2$ = Os)

[a] Reagents and conditions: (dppf)PdCl$_2$, CuI, DMF, Et$_3$N; 70 °C.

Chart 2. Ru^{II}- and Os^{II}-Containing Trinuclear Complexes



12 (M$_1$ = Ru, M$_2$ = Os)
13 (M$_1$ = Os, M$_2$ = Ru)

2 using the same general procedure gave the trinuclear complex **12** (Chart 2) containing a central Os^{II} complex covalently attached to two Ru^{II} centers. Similarly, cross-coupling **6** with 2 equiv of **3** gave the trinuclear complex **13** containing a central Ru^{II} complex covalently linked to two Os^{II} centers. Such "Os$_2$-Ru" and "Ru$_2$Os" trinuclear complexes would be extremely difficult to synthesize by a stepwise or "statistical" complexation of the metal precursors with the corresponding ligand.

The absorption spectra of the mononuclear building blocks show intense bands in the UV region due to the overlapping $\pi-\pi^*$ transitions of the bipyridine and phenanthroline ligands and typical metal to ligand charge transfer (MLCT) bands in the visible region (Table 1). Extending the conjugation of the phenanthroline moieties results in the appearance of lower energy bands between 340 and 360 nm in the dinuclear complexes **9**−**11**.[6,8] The MLCT bands of the homodinuclear complexes **9** and **11** closely resemble their mononuclear precursors.[6−8] As expected, the heterodinuclear complex **10** shows a broad absorption tailing up to >600 nm due to the overlapping MLCT transitions of the Ru^{II} and Os^{II} centers. The trinuclear complexes **12** and **13** show similar spectral patterns, i.e., an intense absorption at 370 nm due to the conjugated phenanthroline ligands and a broad visible absorption due to the overlapping MLCT bands.

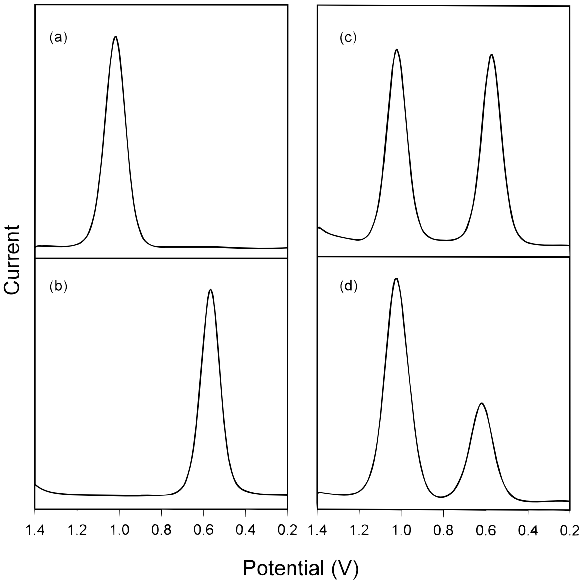


Figure 1. Square-wave voltammograms of (a) **9**, (b) **11**, (c) **10**, and (d) **12** in acetonitrile as measured vs Ag/Ag$^+$.

Cyclic and square-wave voltammetry illustrate the composition of the multinuclear complexes (Figure 1). The di-Ru^{II} complex **9** shows a reversible wave at $E_{1/2} = +1.02$ V vs Ag/Ag$^+$ for the Ru$^{II/III}$ couple. The di-Os^{II} complex **11** shows a reversible redox couple at $E_{1/2} = +0.57$ V. As expected, the heterodinuclear complex **10** shows two redox processes at $E_{1/2} = +1.02$ and $+0.58$ V corresponding to the Ru$^{II/III}$ and Os$^{II/III}$ couples, respectively. The composition of the Ru$_2$Os trinuclear complex **12** is beautifully illustrated by the square-wave voltammogram showing two peaks at $E_{1/2} = +1.02$ and $+0.62$ V with a 2:1 ratio, respectively (Figure 1). When compared to the dinuclear complexes, the Ru$^{II/III}$ redox couple remains essentially unchanged, while the Os$^{II/III}$ couple is shifted to a more positive potential ($\Delta E_{1/2} = +50$ mV). This shift may be due to the two "external" Ru^{II} centers that electrostatically destabilize the oxidized form and make the Os^{II} center more difficult to oxidize.

Conclusions. We have demonstrated that monofunctionalized, as well as difunctionalized, coordination compounds containing Ru^{II} and Os^{II} can be used as synthetic building blocks and cross-coupled to one another to give conjugated heteronuclear complexes. Such new building blocks will facilitate the fabrication of multimetallic arrays with unique architectures, as well as metal-containing oligomeric and polymeric materials that are practically inaccessible by alternative approaches.

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