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Creating New Binding Sites in Ligands and Metal Complexes Using the Negishi Cross-Coupling Reaction

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The Negishi cross-coupling reaction creates a new binding site in a ruthenium complex with high efficiency as exemplified by the synthesis of a heterodimetallic ruthenium–osmium complex.

Advances in inorganic photochemistry over the past two decades have driven the diversification of model systems under investigation.[1] As interest in energy and electron transfer studies in mono- and polymetallic complexes grew, so did the synthetic approaches to obtain these complexes. *Homodimetallic* complexes are readily synthesized by first preparing symmetric dinucleating ligands followed by the direct synthesis of their dimetallic complexes. However, more elaborate energy and electron transfer studies require the preparation of the synthetically more challenging *heterodimetallic* complexes.

Most synthetic approaches to heterodimetallic complexes make use of symmetric dinucleating ligands.[2] The monometallic complexes of dinucleating ligands are usually obtained in moderate yield as a statistical mixture from the reaction of the ligand with 1 equiv of metal ion, followed by the introduction of the second metal ion. Protection−deprotection methodology has also been developed to build up polymetallic complexes, whereby one metal-binding site is protected by methylation, followed by metal ion complexation, deprotection, and subsequent heterometal ion binding.[3] More recently, the “chemistry-on-the-complex” approach, in which classic organic and organometallic reactions are performed directly on metal complexes, has shown significant versatility and promise.[4] Typically, this approach simplifies the purification of products, increases the overall yields, and, in some cases, proves to be the only method to obtain the desired products.

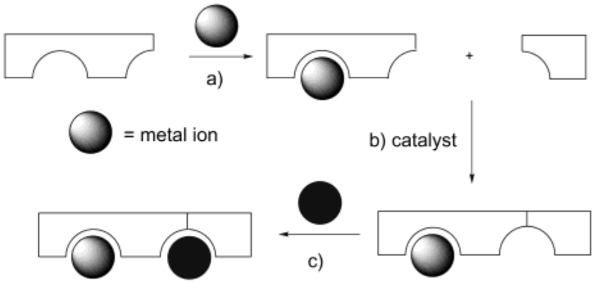

Figure 1. Strategy for the synthesis of heterodimetallic complexes: (a) the first metal ion binds to a complete chelating site; (b) a new binding site is created in a reaction on the metal complex; (c) the second metal ion is then introduced giving a heterodimetallic complex.

The “chemistry-on-the-complex” approach is even more powerful when a new binding site is created in the complex, which allows further metal ion complexation (Figure 1).[5] The first metal ion binds selectively to a complete chelating site as opposed to an incomplete binding site (Figure 1a). A catalytic reaction, in this case the Negishi reaction, creates a new binding site in the metal complex (Figure 1b). A second and different metal ion is introduced into the newly created binding site, thus allowing the straightforward synthesis of heterodimetallic complexes.

Herein, we describe the use of 2-pyridylzinc bromide to create a new bidentate coordination site in both ligands and

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(1) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Denti, G.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, U.K., 1991.

(2) Recent work with asymmetric ligands allows heterodimetallic complexes to be formed selectively: Ward, M. D.; Barigelletti, F. *Coord. Chem. Rev.* **2001**, *216−217*, 127. Encinas, S.; Barigelletti, F.; Barthram, A. M.; Ward, M. D.; Campagna, S. *Chem. Commun.* **2001**, 277.

(3) Denti, G.; Serroni, S.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Perspect. Coord. Chem.* **1992**, 153. Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 4750.

(4) (a) Aspley, C. J.; Gareth Williams, J. A. *New J. Chem.* **2001**, *25*, 1136. (b) Griffiths, P. M.; Loiseau, F.; Puntoriero, F.; Serroni, S.; Campagna, S. *Chem. Commun.* **2000**, 2297. (c) Fanni, S.; Di Pietro, C.; Serroni, S.; Campagna, S.; Vos, J. G. *Inorg. Chem. Commun.* **2000**, *3*, 42. (d) Pabst, G. R.; Pfuller, O. C.; Sauer, J. *Tetrahedron*, **1999**, *55*, 8045. (e) Dunne, S. J.; Constable, E. C. *Inorg. Chem. Commun.* **1998**, *1*, 167. (f) Patoux, C.; Launay, J.-P.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; James, S.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1998**, *120*, 3717. (g) Constable, E. C.; Cargill Thompson, A. M. W.; Greulich, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1444. (h) Beley, M.; Collin, J. P.; Louis, R.; Metz, B.; Sauvage, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 8521.

(5) Johansson, K. O.; Lotoski, J. A.; Tong, C. C.; Hanan, G. S. *Chem. Commun.* **2000**, 819. Other examples of this methodology: Tomohiro, Y.; Satake, A.; Kobuke, Y. *J. Org. Chem.* **2001**, *66*, 8442.

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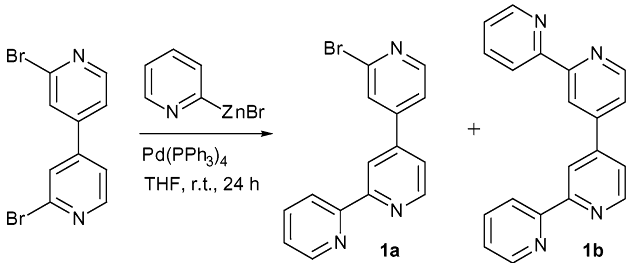
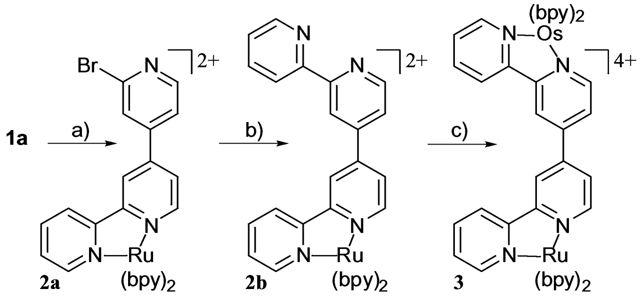
Scheme 1. Synthesis of Polypyridyl Ligands **1a**,**b**[a]



[a] The precipitation of the zinc bromide salt of **1a** leads to the enhanced yield (76%) of monobrominated product even with an excess of 2-pyridylzinc bromide.

Scheme 2. Preparation of Heterodimetallic Ruthenium−Osmium Complex **3a**[a]



[a] Reaction conditions: (a) $Ru(bpy)_2Cl_2$, $AgNO_3$, EtOH, 93% yield; (b) 2-pyridylzinc bromide, $Pd(PPh_3)_4$, DMF, r.t., 97% yield; (c) $Os(bpy)_2Cl_2$, $HOCH_2CH_2OH$, 43% yield.

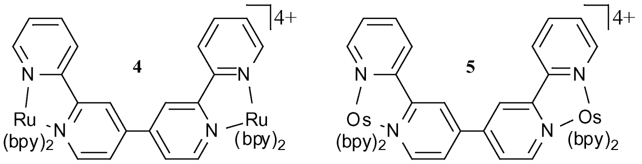
metal complexes by way of the Pd-catalyzed Negishi reaction. As an example of a heterodimetallic complex, a mixed Ru−Os dimetallic complex has been made in high overall yield using this methodology, and its physical properties have been examined.

The Negishi reaction affords a facile method to prepare new binding sites in ligands. 2,2′-Dibromo-4,4′-bipyridine[6] (0.75 mmol) readily reacts with 2-pyridylzinc bromide (1.5 mmol) at r.t. (room temperature) in THF with $Pd(PPh_3)_4$ (0.025 mmol, 3%) [$Pd(PPh_3)_4$ = tetrakis(triphenylphosphine)-palladium(0)] as catalyst to afford a mixture of terpyridine **1a** and quaterpyridine **1b** (Scheme 1). It is noteworthy that, even with an excess of 2-pyridylzinc bromide, **1a** forms selectively because of its precipitation from the reaction mixture, which disfavors the formation of dinucleating ligand **1b**. The monohalogenated ligand is obtained in high yield by avoiding reactions that generate statistical mixtures of products.

Allowing ligand **1a** to react with an equimolar amount of $Ru(bpy)_2Cl_2$ (bpy = 2,2′-bipyridine) in EtOH at reflux in the presence of $AgNO_3$ gives monometallic complex **2a** in 93% yield (Scheme 2a). The $Ru(bpy)_2^{2+}$ moiety binds much more effectively to the bpy-like site in **1a** as opposed to the monodentate 2-bromopyridyl site because of the chelate effect. In addition, the bromine atom hinders the pyridyl nitrogen's ability to bind to the metal ion.

The 2-bromopyridyl site in **2a** is readily converted into a chelating bpy-like site using the Negishi reaction (Scheme 2b). The reaction of **2a** (0.10 mmol) with an excess of 2-pyridylzinc bromide (0.50 mmol) under mild Negishi cross-coupling conditions, stirring at room temperature in DMF with $Pd(PPh_3)_4$ as catalyst (20 mol % based on **2a**), affords **2b** in 97% yield. Thus, the conversion of 2,2′-dibromo-4,4′-bipyridine to **2b** occurs in 69% overall yield. Because of the hydration of **2a**, excess organozinc reagent (5 equiv) is required for the Negishi reaction to proceed. The crude product is purified by sequestering excess zinc halides formed in the transmetalation step with EDTA, followed by column chromatography on silica gel. These cross-coupling conditions are considerably milder than those required for cross-coupling stannyl or borane reagents with metal complexes.[7] The newly formed ligand **1b** in complex **2b** is not isolated in its metal-free state. Indeed, the reaction of the metal-free ligand **1b** with $Ru(bpy)_2Cl_2$ would require difficult purification steps as both bpy sites could react with $Ru(bpy)_2Cl_2$. The newly created bpy site in **2b** is then allowed to react with *cis*-$(bpy)_2OsCl_2$ in ethylene glycol to yield the heterodimetallic complex **3** in 43% yield (Scheme 2c). The lower yield in the last step is typical for the synthesis of osmium bpy complexes.

Chart 1. Homodimetallic Complexes **4** and **5**



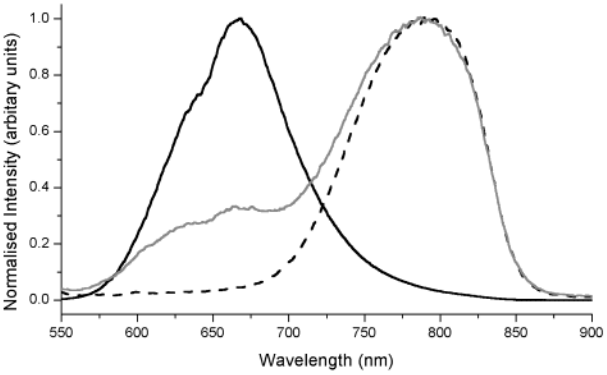


Figure 2. Luminescence data for the dimetallic complexes **3** (gray line), **4** (black line), and **5** (dashed line) on excitation at their isoabsorption wavelengths (500, 490, and 510 nm, respectively).

To interpret the emission spectrum of **3**, the homodimetallic complexes of ruthenium (**4**) and osmium (**5**) were required (Chart 1). Allowing excess $Ru(bpy)_2Cl_2$ and $Os(bpy)_2Cl_2$ to reflux in ethylene glycol with **1b** afforded **4**[8] and **5**, respectively.

Preliminary luminescence studies of heterodimetallic complex **3** indicate that energy transfer is occurring from the $Ru(bpy)_3$-like site to the $Os(bpy)_3$-like site (Figure 2). Upon irradiation of monoruthenium complex **2b** and diruthenium complex **4** at an isoabsorption point (490 nm), their

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[6] Kelly, T. R.; Lee, Y.-J.; Mears, R. J. *J. Org. Chem.* **1997**, *62*, 2774.

[7] Stille and Suzuki reactions on metal complexes have previously been described; however, no new binding sites were created. See refs 4a, 4d−f.

[8] Downard, J.; Honey, G. E.; Phillips, L. F.; Steel, P. J. *Inorg. Chem.* **1991**, *30*, 2259.

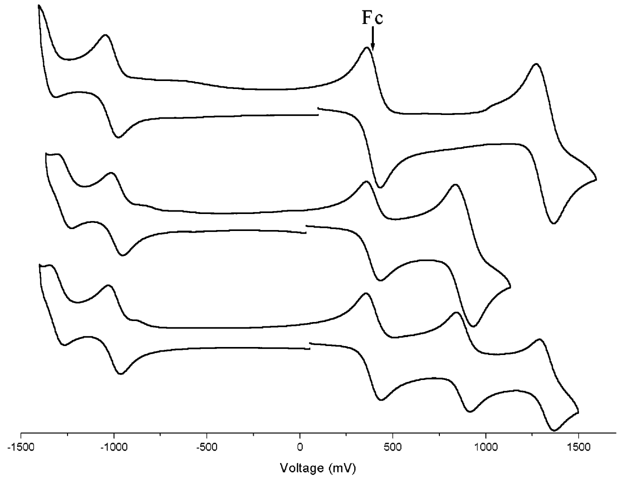

Figure 3. Oxidation and reduction potentials for homodimetallic complexes **4** (top) and **5** (middle) and heterodimetallic complex **3** (bottom). Values reported in the text are referenced to internal ferrocene (Fc).

emission bands are observed at 667 nm and are of equal intensity. Diosmium complex **5** exhibits a single emission at 790 nm on irradiation at either 510 nm (^{1}MLCT absorption) or 620 nm (^{3}MLCT absorption). Irradiation of complex **3** at 500 nm shows a strong quenching of the ruthenium emission with an emission band occurring at 788 nm instead. This implies that partial energy transfer from the ^{3}MLCT excited-state of ruthenium to the ^{3}MLCT excited-state of osmium occurs in **3**.

The electrochemistry of complexes **3**, **4**, and **5** indicates that limited communication exists between the metal centers (Figure 3). The oxidation potentials of the metal centers in homodimetallic complexes **4** (+1.31 V) and **5** (+0.87 V) have a separation between the cathodic and anodic peak of 98 and 92 mV, respectively. The peak separation in **4** has previously been reported as an indication of weak communication between the metal centers.[8] Likewise, we ascribe the oxidation in **5** to two coincidental one-electron processes. In heterodimetallic complex **3**, the oxidation of the osmium metal center (+0.87 V, (74 mV)) does not alter the oxidation potential of the ruthenium metal center (+1.31 V, (70 mV)), indicating weak metal−metal interaction in these complexes.

We have shown that organozinc reagents undergo the Negishi reaction with metal complexes in high yield. The lower toxicity of organozinc reagents compared to stannyl reagents, the mild reaction conditions, and the commercial availability of a wide range of heterocyclic zinc reagents make this the method of choice for creating new binding sites in metal complexes. The coordination of different metal ions in the newly created binding site can lead to heterodimetallic complexes, one of which exhibits Ru-to-Os energy transfer. The extension of this work to the synthesis of polymetallic complexes is currently under investigation.

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Supporting Information Available: Experimental procedures for ligands **1a**,**b** and complexes **2a**,**b**, **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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