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Modular Synthesis of Alkyne-Substituted Ruthenium Polypyridyl Complexes Suitable for "Click" Coupling

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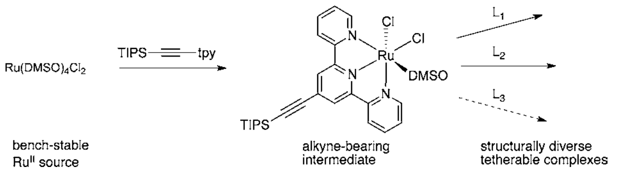
Supporting Information

ABSTRACT: A modular synthetic method has been developed for the preparation of Ru polypyridyl complexes bearing a terminal alkyne. This method proceeds through a readily accessible intermediate with a silyl-protected alkyne and allows access to a variety of five- and six-coordinate Ru complexes. These complexes can be easily attached to azide-functionalized electrode surfaces with only slight perturbation of the redox properties of the parent complex.

Ruthenium polypyridyl complexes can access multiple oxidation states at reasonable potentials and have been widely studied as (photo)electrochemical redox mediators and electrocatalysts.[1−3] A number of recent studies have targeted covalent functionalization of electrode surfaces with these molecules.[3b,4] In this context, we have employed Cu-catalyzed azide−alkyne cycloaddition (i.e., "click" coupling[5]) to tether $\mathrm{Ru^{II}(tpy)_2}$ (tpy = 2,2′;6′,2″-terpyridine) to boron-doped diamond and tin oxide electrodes and investigated the electrochemical and photochemical properties of these conjugates.[6] These reactions involve coupling of a surface-bound azide with a terminal alkyne appended to the molecular Ru complex (Scheme 1). Several methods have been identified for functionalizing surfaces with azide groups, including the direct introduction of a surface-bound azide[7] or attachment of an azide tethered to the surface via an alkyl chain.[8] The preparation of Ru polypyridyl complexes bearing a terminal alkyne, however, has proven to be synthetically challenging because many routes to coordination complexes of this type use $\mathrm{RuCl_3}$,[1b,3c,9] which is chemically incompatible with alkynes. Here, we describe an efficient synthetic route to alkyne-derivatized Ru polypyridyl complexes, originating from a readily accessible $\mathrm{Ru^{II}}$ source (Scheme 2). By proceeding through a common alkyne-functionalized intermediate, this route allows for late-stage installation of bidentate or tridentate ligands to produce electronically modified Ru complexes suitable for use in "click" coupling. In this manner, the problem of attaching *m* complexes to *n* surfaces would require *m* + *n* syntheses rather than *m*·*n*.[10]

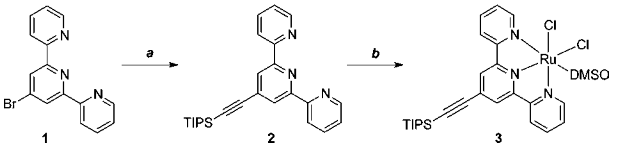
Scheme 1. Attachment of an Alkyne-Substituted Catalyst to an Azide-Modified Electrode

Scheme 2. Modular Synthesis of Alkyne-Functionalized Ruthenium Polypyridyl Complexes



Initial efforts to prepare the target compounds sought to ligate alkyne-functionalized tpy ligands to $\mathrm{RuCl_3}$; however, these efforts were unsuccessful.[11] As an alternative, we identified a synthetic route originating from the $\mathrm{Ru^{II}}$ precursor, *cis*-$\mathrm{Ru(DMSO)_4Cl_2}$ (DMSO = dimethyl sulfoxide; Scheme 3).[12]

Scheme 3. Synthesis of Common Intermediate 3[a]



[a]Conditions: (a) triisopropylsilyl acetylene, $\mathrm{Pd(PPh_3)_2Cl_2}$, CuI, $i\mathrm{Pr_2NH}$, benzene; (b) *cis*-$\mathrm{Ru(DMSO)_4Cl_2}$, $\mathrm{CH_2Cl_2}$; see the SI for synthetic details.

The reaction of 4′-bromo-2,2′:6′,2″-terpyridine (**1**) with triisopropylsilyl (TIPS) acetylene under Sonogashira conditions (Pd, Cu catalysts; see the Supporting Information, SI) affords the protected alkyne-substituted tpy ligand (**2**). The reaction of **2** with *cis*-$\mathrm{Ru(DMSO)_4Cl_2}$ affords the ligated $\mathrm{Ru^{II}}$ *cis*-dichloride complex **3**. Although **3** is a bench-stable solid, UV−visible spectroscopy reveals that it undergoes photoisomerization in solution to the more stable and less-reactive *trans*-dichloro isomer (Figure 1).[13]

Complex **3** is a common intermediate for further synthetic elaboration.[14] To demonstrate the versatility of complex **3** as a synthetic intermediate, we sought complexes of **3** with a bidentate bipyrimidine (bpm) ligand and a tridentate unsubstituted tpy ligand. The bpm complex represents a substituted analogue of a molecular water oxidation catalyst reported by Meyer et al.[3b] Dehalogenation of **3** by $\mathrm{AgNO_3}$, followed by treatment with the appropriate bidentate or tridentate ligand,

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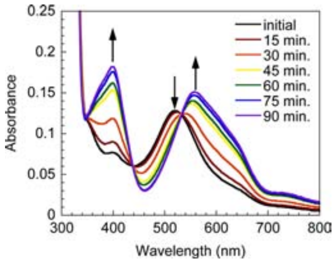
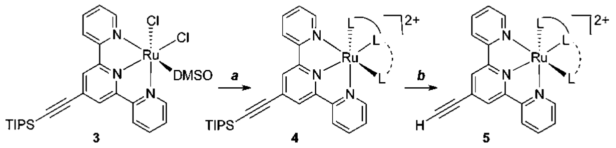


Figure 1. UV−visible spectra revealing the cis-to-trans isomerization of **3** in solution by ambient-light illumination on the benchtop (33 μM, CH_3CN; cf. NMR spectra in Figure S12 in the SI).

affords **4bpm** and **4tpy** (Scheme 4, step a).[15,13] Removal of the TIPS group proved challenging because standard silyl deprotection reagents are ineffective against this robust protecting group.[16] After screening various conditions (Table S1 in the SI), including ones reported in the literature to be effective on similar complexes, we found that AgF effects the desilylation in high yield to afford **5bpm** and **5tpy** (Scheme 4, step b).[17] Spectroscopic and crystallographic characterization of **5bpm** and **5tpy** confirms the presence of the deprotected alkyne (Figure 2).

Scheme 4. Synthesis and Elaboration of Alkynyl Complex 4[a]



[a]Conditions: (a) $AgNO_3$ and then addition of a ligand; (b) AgF and then $HClO_4$; see the SI for synthetic details.

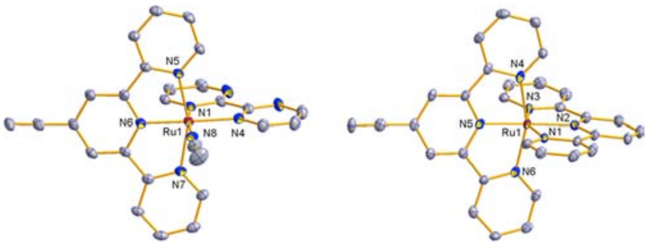
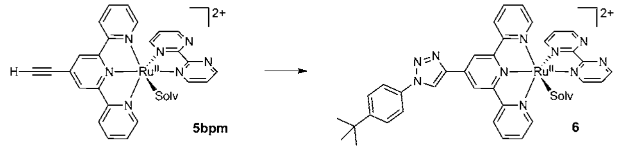


Figure 2. ORTEP plots of (ellipsoid at 40% probability) X-ray crystal structures of **5bpm** with a coordinated MeCN solvent molecule (left) and **5tpy** (right). Counterions and hydrogen atoms not shown.

With the deprotected alkyne-functionalized complexes in hand, we explored their reactivity with azide coupling partners in click reactions in order to probe the electrochemical properties and robustness of the linkage. Of specific interest in this study was the degree to which triazole attachment affects the redox properties of the parent complex and whether the presence of the labile solvent ligand in **5bpm** would interfere with the “click” reaction.

The reaction of **5bpm** with 4-*tert*-butylphenyl azide under click conditions affords the molecular aryltriazole complex **6** (Scheme 5). Cyclic voltammograms (CVs) of **6** in 0.1 M aqueous HNO_3 display redox features that closely match those of the $[Ru(tpy)(bpm)(OH_2)]^{2+}$ parent complex (Figure 3). These results indicate that the triazole linker does not significantly perturb the redox properties of parent molecules.

Scheme 5. Click Coupling of 5bpm to an Aryl Azide[a]



[a]Conditions: *p*-*tert*-butylphenyl azide, $[Cu^{II}(TBTA)]SO_4$, sodium ascorbate, DMSO; see the SI for full synthetic details.

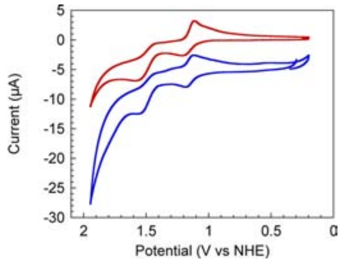


Figure 3. CVs of $[Ru(tpy)(bpm)(OH_2)]^{2+}$ (red, $E_{1/2} = 1.17$ and 1.51 V) and triazole-modified complex **6** (blue, offset by −5 μA, $E_{1/2} = 1.15$ and 1.50 V) (10 mV/s scan rate, 50 mM in 0.1 M HNO_3).

Having confirmed that triazole attachment to **5bpm** is possible, we investigated attachment of the modified water oxidation catalyst **5bpm** to a diamond surface bearing azides tethered to the surface via an alkyl chain (Scheme S3 in the SI). CVs obtained from the **5bpm**-treated surfaces display a reversible oxidation centered at 1.18 V vs NHE (Figure 4A). The disappearance of the broad, quasi-reversible feature seen at higher potential in Figure 3 may reflect the higher scan rate necessary to observe significant current from the surface-bound complex. Peak currents display a linear scan rate dependence, consistent with a surface-attached species (Figure 4B). Additionally, X-ray photoelectron spectroscopy (XPS) confirms the presence of Ru on the functionalized surfaces (Figure S3A in the SI).[18]

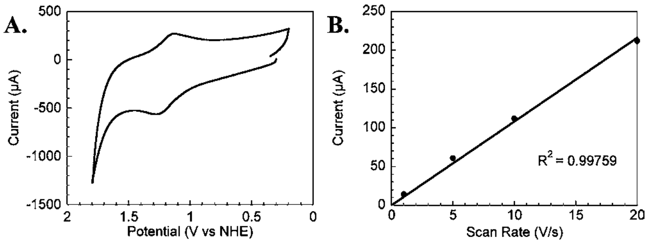


Figure 4. Electrochemical data from **5bpm**-functionalized diamond electrodes in 0.1 M aqueous HNO_3: (A) CV, 20 V/s scan rate ($E_{1/2}$ = 1.18 V); (B) anodic peak current versus scan rate.

Preliminary studies suggest that the **5bpm**-functionalized diamond surface is not sufficiently stable to withstand sustained electrolysis at potentials needed for electrocatalytic water oxidation.[19−21] Nevertheless, the synthetic protocol elaborated herein provides a valuable foundation for the use of click-coupling methods to attach Ru polypyridyl derivatives to diverse molecules and materials and to explore the photo- and electrocatalytic chemistry of such conjugates. Specifically, the reactions outlined in Schemes 3 and 4 allow rapid access to alkyne-functionalized Ru complexes with a variety of redox properties, and the triazole linkage arising from the click-coupling reaction has a minimal effect on the redox properties of complexes to which it is attached.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, alternate synthetic routes, experimental procedures and details, crystallographic data, and further characterization of derivatized surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Many reviews on Ru polypyridyl complexes have been published. For examples, see: (a) Campagna, S.; Puntoriero, F.; Nastasi, F.; Bergamini, G.; Balzani, V. *Top. Curr. Chem.* **2007**, *280*, 117–214. (b) Lancaster, K. M.; Gerken, J. B.; Durrell, A. C.; Palmer, J. H.; Gray, H. B. *Coord. Chem. Rev.* **2010**, *254*, 1803–1811. (c) Marcêlis, L.; Ghesquière, J.; Garnir, K.; Kirsch-De Mesmaeker, A.; Moucheron, C. *Coord. Chem. Rev.* **2012**, *256*, 1569–1582.

(2) For applications in dye-sensitized solar cells, see: (a) Grätzel, M. *J. Photochem. Photobiol., C* **2003**, *4*, 145–153. (b) Ardo, S.; Meyer, G. J. *Chem. Soc. Rev.* **2009**, *38*, 115–164. (c) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595–6663.

(3) A particular electrocatalysis showcase has been water oxidation: (a) Sala, X.; Romero, I.; Rodríguez, M.; Escriche, L.; Llobet, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2842–2852. (b) Concepcion, J. J.; Jurss, J. W.; Brennaman, M. K.; Hoertz, P. G.; Patrocinio, A. O. T.; Iha, N. Y. M.; Templeton, J. L.; Meyer, T. J. *Acc. Chem. Res.* **2009**, *42*, 1954–1965. (c) Wasylenko, D. J.; Ganesamoorthy, C.; Henderson, M. A.; Koivisto, B. D.; Osthoff, H. D.; Berlinguette, C. P. *J. Am. Chem. Soc.* **2010**, *132*, 16094–16106.

(4) (a) Geneste, F.; Moinet, C.; Jezequel, G. *New J. Chem.* **2002**, *26*, 1539–1541. (b) Gagliardi, C. J.; Jurss, J. W.; Thorp, H. H.; Meyer, T. J. *Inorg. Chem.* **2011**, *50*, 2076–2078. (c) Adeloye, A. O.; Olomola, T. O.; Adebayo, A. I.; Ajibade, P. A. *Int. J. Mol. Sci.* **2012**, *13*, 3511–3526.

(5) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.

(6) (a) Ruther, R. E.; Rigsby, M. L.; Gerken, J. B.; Hogendoorn, S. R.; Landis, E. C.; Stahl, S. S.; Hamers, R. J. *J. Am. Chem. Soc.* **2011**, *133*, 5692–5694. (b) Benson, M. C.; Ruther, R. E.; Gerken, J. B.; Rigsby, M. L.; Bishop, L. M.; Tan, Y.; Stahl, S. S.; Hamers, R. J. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3110–3119.

(7) (a) Devadoss, A.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2007**, *129*, 5370–5371. (b) McCrory, C. C. L.; Devadoss, A.; Ottenwaelder, X.; Lowe, R. D.; Stack, T. D. P.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2011**, *133*, 3696–3699. (c) Landis, E. C.; Hamers, R. J. *Chem. Mater.* **2009**, *21*, 724–730.

(8) (a) Strother, T.; Knickerbocker, T.; Russell, J. N., Jr.; Butler, J. E.; Smith, L. M.; Hamers, R. J. *Langmuir* **2002**, *18*, 968–971. (b) Collman, J. P.; Devaraj, N. K.; Chidsey, C. E. D. *Langmuir* **2004**, *20*, 1051–1053. (c) Lummerstorfer, T.; Hoffmann, H. *J. Phys. Chem. B* **2004**, *108*, 3963–3966. (d) Wang, M.; Das, M. R.; Li, M.; Boukherroub, R.; Szunerits, S. *J. Phys. Chem. C* **2009**, *113*, 17082–17086. (e) Wang, X. Y.; Landis, E. C.; Franking, R.; Hamers, R. J. *Acc. Chem. Res.* **2010**, *43*, 1205–1215. (f) Nakazawa, J.; Smith, B. J.; Stack, T. D. P. *J. Am. Chem. Soc.* **2012**, *134*, 2750–2759. (g) Yao, S. A.; Ruther, R. E.; Zhang, L.; Franking, R. A.; Hamers, R. J.; Berry, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 15632–15635.

(9) Exceptions include syntheses of Ru(bpy)$_2$L$_2$ complexes that proceed via Ru(bpy)$_2$Cl$_2$, which is ill-suited for the preparation of Ru(tpy) complexes. (a) Wang, H.-X.; Zhou, K.-G.; Xie, Y.-L.; Zeng, J.; Chai, N.-N.; Li, J.; Zhang, H.-L. *Chem. Commun.* **2011**, *47*, 5747–5749. (b) Baron, A.; Herrero, C.; Quaranta, A.; Charlot, M.-F.; Leibl, W.; Vauzeilles, B.; Aukauloo, A. *Inorg. Chem.* **2012**, *51*, 5985–5987.

(10) Diverse strategies exist for functionalizing electrodes with electroactive molecules; see refs 2, 3b, 4, and 6–9 and the SI for a partial bibliography. Most of these approaches are specific to the electrode surface that is employed, while an ideal linkage would allow attachment of any desired catalyst to any surface.

(11) The initial route developed for preparation of the desired compounds employs RuCl$_3$ as a starting material, and the Ru center is reduced to Ru^{II} prior to incorporating the alkyne. This route proved to be less effective than the route reported in the main text. This alternate route is elaborated on in the SI (see Scheme S2 and associated text).

(12) James, B. R.; Ochiai, E.; Rempel, G. L. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 781–784.

(13) The relative stability and reactivities of *cis*- and *trans*-dichloro Ru(tpy)(DMSO)Cl$_2$ have been studied by Ziessel et al.: Ziessel, R.; Grosshenny, V.; Hissler, M.; Stroh, C. *Inorg. Chem.* **2004**, *43*, 4262–4271.

(14) Generally, DMSO complexes of divalent iron-group dihalides are versatile intermediates for further elaboration. These compounds have been reviewed in: Alessio, E. *Chem. Rev.* **2004**, *104*, 4203–4242.

(15) Preliminary investigations involved the production of Ziessel's (tpy)(DMSO)RuCl$_2$ complex^{13} and testing of the reaction conditions to bind bpm to it to generate (tpy)(bpm)RuX, where X is either DMSO or chloride. The alternate attachment of the bidentate ligand first is facile with bipyridine, but attempting this approach with bpm yielded an intractable, possibly coordination-polymeric, material rather than the desired analogue to Ru(bpy)(DMSO)$_2$Cl$_2$.

(16) Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1965**, *4*, 217–228.

(17) (a) Kim, S.; Kim, B.; In, J. *Synthesis* **2009**, 1963–1968. (b) Escamilla, I. V.; Ramos, L. F. R.; Escalera, J. S.; Hernández, A. Á. *J. Mex. Chem. Soc.* **2011**, *55*, 133–136.

(18) In addition to diamond substrates, complex **5bpm** was exposed to azide-functionalized vertically aligned carbon nanofiber (VACNF) substrates.^{7c} XPS shows evidence of Ru incorporation on the surfaces (Figure S5 in the SI), but the substrates proved unstable under oxidizing conditions, precluding electrochemical studies. Similar e-chem results to diamond were obtained on graphitic surfaces, e.g., pyrolized photoresist.

(19) CVs obtained from **5bpm**-treated diamond surfaces following a 5-min electrolysis at 1600 mV (vs NHE) do not display the reversible redox feature observed in the preelectrolysis surfaces (Figure S4 in the SI), and an XPS spectrum of the same postelectrolysis sample shows no evidence of Ru (Figure S3B in the SI). These observations presumably reflect destructive oxidation of the tether or diamond substrate.

(20) Similar grafting of a different Ru catalyst has recently been reported; however, no postelectrolysis characterization data were presented: Tong, L.; Göthelid, M.; Sun, L. *Chem. Commun.* **2012**, *48*, 10025–10027.

(21) Martin, H. B.; Argoitia, A.; Landau, U.; Anderson, A. B.; Angus, J. C. *J. Electrochem. Soc.* **1996**, *143*, L133–L136.