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A Thallium Mediated Route to σ-Arylalkynyl Complexes of Bipyridyltricarbonylrhenium(I)

Brendan J. Liddle,[†] Sergey V. Lindeman,[†] Daniel L. Reger,[‡] and James R. Gardinier*[,†]

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53211, and Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

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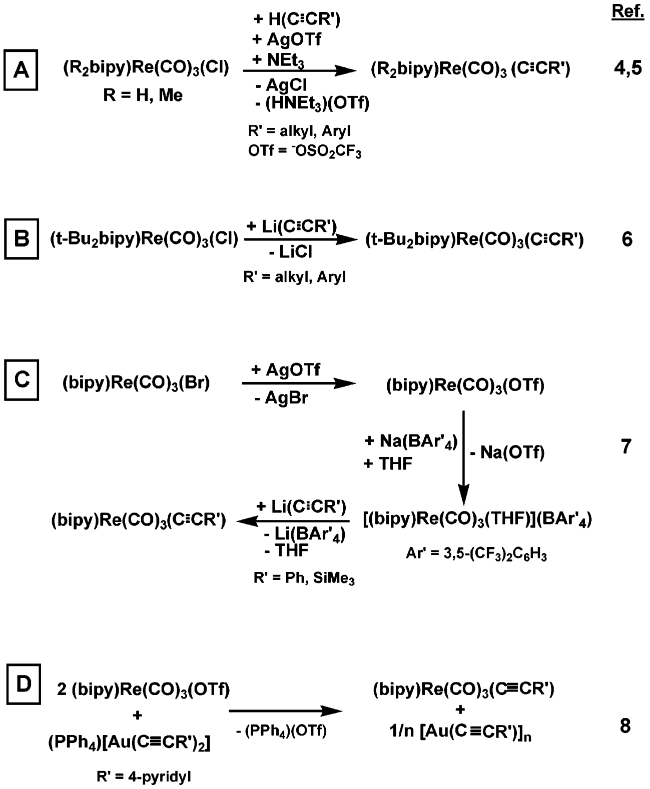
A simple, one-pot preparation of rhenium(I) σ-arylalkynyl complexes is reported using thallium(I) hexafluorophosphate as a halogen abstraction agent. This new route to rhenium σ-alkynyls enjoys higher yields compared to analogous preparations using silver salts by eliminating potential electrochemical degradation pathways.

Scheme 1. Synthetic Routes to σ-Alkynyl Derivatives of (bipy)Re(CO)$_3$



There has been a longstanding interest in complexes of the “(bipy)Re(CO)$_3$” fragment owing to their favorable photo- and electrochemical properties, which hold promise for applications in photocatalysis, solar energy storage, and molecular electronics.[1−3] The attractive solubility and tunable electronic properties of charge-neutral σ-alkynyl derivatives have helped to spur recent research into these compounds.[4−8] Accordingly, there are multiple reported synthetic routes to (bipy)Re(CO)$_3$(alkynyl) complexes, as summarized in Scheme 1. The one-pot route (Scheme 1A) is most favorable in terms of both simplicity and generality.[4,5] The seemingly most straightforward route (Scheme 1B) is surprisingly not general; it is reported to be specific only to 4,4-(^{t}Bu)$_2$bipy derivatives and fails for other bipyridyl derivatives.[6] The route depicted by Scheme 1C[7] is a viable alternative but suffers typical problems associated with multistep syntheses. For instance, in our hands, variable (low) yields of the rhenium triflate intermediate were obtained from the first step (vide infra), and the preparation of the tetraarylborate intermediate adds complications to the procedure. Finally, the route in Scheme 1D[8] suffers from poor yield, employs expensive reagents and a multistep synthetic scheme (to get to the starting materials), and, to our knowledge, has not yet been shown to be general.

During the course of our investigations into preparing rhenium alkynyls as possible components of single-molecule white-light emitters,[9] we initially found the overall yield of the desired products by several of these routes to be capricious, depending on the nature of the bipyridyl, the

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* To whom correspondence should be addressed. E-mail: james.gardinier@marquette.edu.

[†] Marquette University.

[‡] University of South Carolina.

(1) Kalyanasundaram, K. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993.

(2) (a) Meyer, G. J., Ed. Molecular Level Artificial Photosynthetic Materials. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1996; Vol. 44. (b) For a more recent example, see: She, C.; Anderson, N. A.; Guo, J.; Liu, F.; Goh, W.-H.; Chen, D.-T.; Mohler, D. L.; Tian, Z. Q.; Hupp, J. T.; Lian, T. *J. Phys. Chem. B* **2005**, *109*, 19345.

(3) (a) Ward, M. D.; Barigelletti, F. *Coord. Chem. Rev.* **2001**, *216−217*, 127. (b) Sun, S.-S.; Lees, A. J. *Organometallics* **2002**, *21*, 39.

(4) Yam, V.W.-W. *Chem. Commun.* **2001**, 789.

(5) For example, see: Chong, S. H.-F.; Lam, S. C.-F.; Yam, V. W.-W.; Zhu, N.; Cheung, K.-K.; Fathallah, S.; Costuas, K.; Halet, J.-F. *Organometallics* **2004**, *23*, 4924.

(6) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K. K. *Organometallics* **1995**, *14*, 2749.

(7) Hevia, E.; Pérez, J.; Riera, V.; Miguel, D.; Kassel, S.; Rheingold, A. *Inorg. Chem.* **2002**, *41*, 4673.

(8) Ferrer, M.; Rodríguez, L.; Rossell, O.; Lima, J. C.; Gómez-Sal, P.; Martín, A. *Organometallics* **2004**, *23*, 5096.

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Table 1. Summary of the Results Obtained from One-Pot Syntheses of Tricarbonyldipyridylrhenium(I) Arylalkynes Using $Tl(PF_6)$ or $Ag(PF_6)$

			overall yield,[a] %			
entry	rhenium reagent	arylalkyne	$TlPF_6$ (THF, 2 days)	Ag(OTf) (THF, 2 days)	$TlPF_6$, EtN^iPr_2, neat 15 h	$AgPF_6$ EtN^iPr_2, neat 15 h
1	$(bipy)Re(CO)_3Br$	$HC{\equiv}C(C_6H_5)$	60 (54, 1 eq)[b]	29	65	
2	$(4,4'-Me_2bipy)Re(CO)_3Br$	$HC{\equiv}C(C_6H_5)$	79	69	58 (41, 2 h)	
3	$(5,5'-Me_2bipy)Re(CO)_3Br$	$HC{\equiv}C(C_6H_5)$	81	47	81	22
4	$(5,5'-Br_2bipy)Re(CO)_3Br$	$HC{\equiv}C(C_6H_5)$	59	17	59	5
5	$(6,6'-Me_2bipy)Re(CO)_3Br$	$HC{\equiv}C(C_6H_5)$	72 (61, 1 eq)[b]	56	33	20 (2 eq),[b] 13 (1 eq)[b]
6	$(bipy)Re(CO)_3Br$	$HC{\equiv}C[3,5-(pz_3CCH_2OCH_2)_2C_6H_3]$[d]	35	23 (14)[c]		
7	$(4,4'-Me_2bipy)Re(CO)_3Br$	$6-HC{\equiv}C(HpzAn^{Me})$[d]	30	10		

[a] Isolated yields (average of two runs). [b] eq = molar ratio of alkyne/Re. [c] Used Scheme 1C; see text. [d] $HpzAn^{Me}$ = 2-pyrazolyl-4-methylaniline.

terminal alkyne, and on whether silver salts were employed at any point in the synthetic route. In our hands, reactions between $(R_2\text{-bipyridylRe})(CO)_3(Br)$ (R = H, alkyl, halide) and silver salts invariably gave metal as a byproduct *even in the absence of light*, implicating an electrochemical decomposition pathway, although the origin of the decomposition remains unclear. We communicate a significant improvement in the preparation of rhenium σ-arylalkynyls, in terms of the overall yield, that is realized simply by replacing the electrochemically active silver halide abstraction reagent with an equivalent, but electrochemically inert, thallium(I) salt.

The one-pot synthetic route to the bipyridyltricarbonylrhenium(I) arylalkynyls, given in eq 1, is similar to that reported by Yam et al. (Scheme 1A)[4,5] but with the notable modification that $Tl(PF_6)$ replaces Ag(OTf). Table 1 provides

$$\underset{(R = H, Me, Br)}{(R_2bipy)Re(CO)_3(Br)} \xrightarrow[\substack{-TIBr \\ -[HNEt_3][PF_6]}]{\substack{+xs\ H(C{\equiv}C\text{-aryl})\ +TI(PF_6) \\ NEt_3/THF\ \Delta\ 2\text{ days}}} (R_2bipy)Re(CO)_3(C{\equiv}C\text{-aryl}) \tag{1}$$

a comparison of the results obtained from the preparation of a series of different derivatives using either $Tl(PF_6)$, Ag(OTf), or $Ag(PF_6)$ (the different silver salts performed identically) as halide abstraction agents under otherwise identical conditions. Irrespective of all other considerations,[10] the use of Tl^+ in place of Ag^+ clearly afforded higher yields of the desired product (significantly in some cases) and reactions could be performed in air and under exposure to light; no metallic byproducts are observed, as with silver. It is noteworthy that reactions performed according to eq 1 using tetrahydrofuran (THF) as a solvent typically required about 30 h to reach maximum conversion [thin-layer chromatography (TLC) and subsequent workup], while similar reactions performed in CH_3CN gave comparable yields but only after 6 days. Because the starting $(R_2bipy)Re(CO)_3(Br)$ is consumed at comparable rates in either solvent (TLC), $[(R_2bipy)Re(CO)_3(\text{solvent})]^+$ appears to be involved in the rate-limiting step of the reaction. The possibility of using the tertiary amine [NEt_3 and EtN^iPr_2 performed equivalently] both as the solvent and as the alkynyl deprotonating reagent was also explored but with variable success, which could partly be attributed to the differing but generally poor solubilities of the reactants and products in the refluxing amine.

Regardless of the dehalogenation reagent or solvent, optimal yields of rhenium alkynyl were always obtained when an excess (1.5−2 mol equiv) of alkyne was used, in part because partial decomposition of the alkyne occurs. The blue luminescent organic decomposition byproducts are easily removed with the solvent front by column chromatography; the nature of these decomposition products was not further explored owing to the success of the reaction depicted in eq 1. The reaction route in eq 1 also tolerates a variety of functional groups decorating the arylalkyne as noted by entries 6 and 7 in Table 1. The lower yields obtained in the latter two cases are likely due to competitive binding of Lewis donors (pyrazolyls or aniline groups) to the rhenium cation intermediate generated in situ.[11] It should be noted that for Table 1, entry 6, the low overall yields of rhenium alkynyl obtained using the AgOTf/$Na(BAr'_4)$ route[7] (Scheme 1C) could be attributed to two main factors: (i) the poor conversion of $(bipy)Re(CO)_3Br$ to its triflate via AgOTf (averaging 36%), where metal is observed as a side product, and (ii) a competing pyrazolyl deprotonation reaction[12] that occurs with organyllithium reactants during the final step of the reaction sequence (only 45% conversion of the rhenium cation to rhenium alkyne was realized). Finally, as with related rhenium bipyridyl chemistry,[13] there appears to be a weak correlation between the overall yield and the electronic nature of the bipyridyl, where more electron-donating substituents (in the order Me > H ≥ Br) gave higher yields of the desired product.

Each of the rhenium alkynyls has been characterized by NMR, IR, absorption and emission spectroscopy, electrochemistry (see the Supporting Information), and, in some cases, X-ray crystallography. The molecular structures of four arylalkynyl derivatives, (5,5′- and $6,6'-Me_2bipy)Re(CO)_3[C{\equiv}C(C_6H_5)]$, $(4,4'-Me_2bipy)Re(CO)_3[C{\equiv}C(HpzAn^{Me})]$

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(9) For a similar strategy, see: Si, Z.; Li, J.; Li, B.; Zhao, F.; Liu, S.; Li, W. *Inorg. Chem.* **2007**, *46*, 6155.

(10) Of course, proper safety precautions should be employed when using or disposing of toxic thallium compounds.

(11) An ionic species with characteristic bright-yellow luminescence remains adhered to the silica gel. Elution with THF affords $(R_2bipy)Re(CO)_3(PO_2F_2)$, with a coordinating $PO_2F_2^-$ anion produced as a result of PF_6^- hydrolysis on silica gel. See the Supporting Information for an example structure and properties. Complete details will be reported elsewhere.

(12) Katritzky, A. R.; Abdel-Rahman, A. E.; Leahy, D. E.; Schwarz, O. A. *Tetrahedron* **1983**, *39*, 4133.

(13) Hino, J. K.; Ciana, L. D.; Dressick, W. J.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1072.

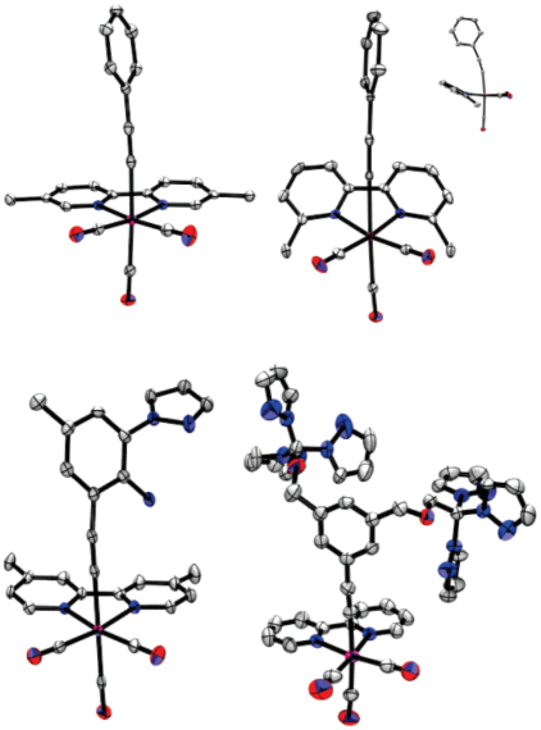

Figure 1. Molecular structures of various rhenium alkynyls. Clockwise from top left: (5,5′-Me_2bipy)$Re(CO)_3[C{\equiv}C(C_6H_5)]$, (6,6′-$Me_2$bipy)$Re(CO)_3$-$[C{\equiv}C(C_6H_5)]$ (the inset emphasizes puckering of the chelate ring), (4,4′-Me_2bipy)$Re(CO)_3[C{\equiv}C(HpzAn^{Me})]$ ($HpzAn^{Me}$ = 2-pyrazolyl-4-methylaniline), and (bipy)$Re(CO)_3[C{\equiv}C(C_6H_3)$-3,5-$(CH_2OCH_2Cpz_3)_2]$. ORTEP diagrams are drawn with 50% probability ellipsoids. Hydrogen atoms have been removed for clarity.

($HpzAn^{Me}$ = 2-pyrazolyl-4methylaniline), and (bipy)$Re(CO)_3[C{\equiv}C(C_6H_3)$-3,5-$(CH_2OCH_2Cpz_3)_2]$, are given in Figure 1, while structures of related rhenium compounds can be found in the Supporting Information. Main features evident from the structures include derivatives with pyrazolyl, and other Lewis base groups decorating the arylalkynyl are indeed bound to rhenium through the alkynyl carbon rather than through the other Lewis donors. Also, derivatives of 6,6′-Me_2bpy contain puckered rhenium chelate rings presumably due to steric interactions between the methyls and equatorial rhenium carbonyls. In cases with 6,6′-Me_2bpy, like that in the top right of Figure 1, the axial carbonyl is directed away from the bipyridyl while the other axial substituent lies above the π cloud of the heterocycle. This puckered geometry results in a slightly more electron-deficient metal center when compared to the other isomers of (dimethylbipyridyl)rhenium(I), as is best indicated by cyclic voltammetry (rhenium-based oxidations) and to a lesser extent by IR spectroscopy (where C−O stretching frequencies vary by only a few wavenumbers). Thus, for (Me_2bipy)$Re(CO)_3$(Br), the 6,6′ isomer is more difficult to oxidize (1.64 V vs Ag/AgCl) and has higher CO stretching frequencies (ν_{CO} 2021, 1906 cm^{-1}, av 1963.5 cm^{-1}) than either the 5,5′ isomer (1.57 V; ν_{CO} 2020 and 1903 cm^{-1}, av 1961.5 cm^{-1}) or the 4,4 isomer (1.50 V; ν_{CO} 2016 and 1907 cm^{-1}, av 1961.5 cm^{-1}). A similar situation holds for the isomers of (Me_2bipy)$Re(CO)_3[C{\equiv}C(C_6H_5)]$, but here the differences between isomers are less pronounced: 6,6′ isomer (1.12 V; ν_{CO} 2008 and 1900 cm^{-1}, av 1954 cm^{-1}); 5,5′ isomer (1.10 V; ν_{CO} 2005 and 1894 cm^{-1}, av 1949.5 cm^{-1}); 4,4′ isomer (1.10 V; ν_{CO} 2006 and 1888 cm^{-1}, av 1947 cm^{-1}).

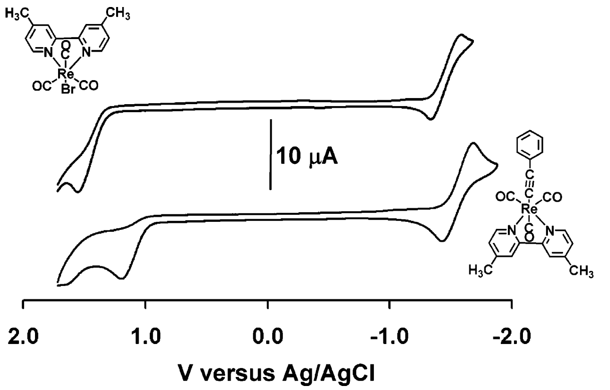

Figure 2. Cyclic voltammograms obtained for THF solutions of (4,4′-Me_2bipy)$Re(CO)_3$(X) [X = Br, top; X = $C{\equiv}C(C_6H_5)$, bottom] measured at a scan rate of 100 mV/s with $(NBu_4)(PF_6)$ as the supporting electrolyte.

Importantly, an examination of the cyclic voltammograms of the rhenium bipyridyls, shown for two derivatives of (4,4′-Me_2bipy)$Re(CO)_3$X (X = Br, C_2Ph) in Figure 2, reveals the typical oxidative instability of charge-neutral rhenium bipyridyl derivatives.[14] As is illustrated in Figure 2, the oxidation of Re^{I} to Re^{II} (around 1.5 V for Br and 1.1 V for C_2Ph derivatives) is clearly irreversible, showing only an anodic wave; the anticipated cathodic wave is absent in each case. Thus, oxidation of either the rhenium starting material or the product provides a potential source for electrochemical degradation (and low yields) in any preparative reaction. Particularly noteworthy is that heating a THF solution containing an equimolar ratio of AgOTf and (5,5′- Me_2bipy)-$Re(CO)_3[C{\equiv}C(C_6H_5)]$ at reflux for 1 day (in the dark and under nitrogen) produced a silver mirror and substantial decomposition of the rhenium alkynyl (only 30% was recovered). On the other hand, the rhenium alkynyl could be fully recovered after a sample of (5,5′-Me_2bipy)$Re(CO)_3$-$[C{\equiv}C(C_6H_5)]$ and $TlPF_6$ were heated in THF. Clearly, the electroactive nature of silver salts and the electrochemical instability of the rhenium compounds are implicated in the lower yields of rhenium alkynyls obtained by the original silver-based preparation.

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Supporting Information Available: Full synthetic details, characterization data, additional structural diagrams, tables of structural data, and crystallographic data in CIF format. This material is available free of charge via the Internet http://pub.acs.org.

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(14) (a) Paolucci, F.; Marcaccio, M.; Paradisi, C.; Roffia, S.; Bignozzi, C. A.; Amatore, C. *J. Phys. Chem. B* **1998**, *102*, 4759. (b) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.