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Coordination Chemistry of Low-Valent Rhenium Polypyridyl Complexes: Synthesis, Reactivity, and Electrochemistry[†]

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The complex $\mathrm{Re^{III}(benzil)(PPh_3)Cl_3}$ (**2**) is used to synthesize a variety of $\mathrm{Re^{III}}$ and $\mathrm{Re^{II}}$ polypyridyl complexes of the type *cis*-$\mathrm{[Re^{III}(L_2)_2Cl_2]^+}$, $\mathrm{[Re^{II}(L_2)_3]^{2+}}$, $\mathrm{Re^{III}(L_3)Cl_3}$, $\mathrm{[Re^{III}(L_3)_2Cl]^{2+}}$, and $\mathrm{[Re^{III}(L_4)Cl_2]^+}$, where $\mathrm{L_2}$ = bpy (**3** and **6**), tbpy (**4** and **7**), phen (**5** and **8**); $\mathrm{L_3}$ = terpy (**9** and **10**); $\mathrm{L_4}$ = TMPA (**11**). The complex *cis*-$\mathrm{[Re^{III}(bpy)_2Cl_2]^+}$ (**3**) is a useful synthon in the formation of complexes of the type $\mathrm{[Re(bpy)_2L_x]^{n+}}$ that are six- or seven-coordinate $\mathrm{Re^{III}}$ complexes (**13**, **16**, and **18**) or octahedral $\mathrm{Re^{II}}$ or $\mathrm{Re^{I}}$ complexes (**12** and **17**). The $\mathrm{[Re^{III}(terpy)_2Cl]^{2+}}$ (**10**) complex can be reduced to form the $\mathrm{Re^{I}}$ complex, $\mathrm{[Re^{I}(terpy)_2]^+}$ (**21**) and then electrochemically reoxidized to form new complexes of the type $\mathrm{[Re^{III}(terpy)_2L]^{n+}}$. Similar behavior is observed for the $\mathrm{[Re^{II}(bpy)_3]^{2+}}$ (**6**) complex where $\mathrm{[Re^{III}(bpy)_3({}^tBuNC)]^{3+}}$ (**20**) and $\mathrm{[Re^{I}(bpy)_3]^+}$ (**19**) may be formed. The electrochemistry of these complexes is discussed in relation to their reactivity and the observed π-acidity of the polypyridyl ligands. In addition, X-ray crystal structures for *cis*-$\mathrm{[Re^{III}(bpy)_2Cl_2]PF_6}$ (**3**) and $\mathrm{[Re^{I}(bpy)_3]PF_6}$ (**19**) are reported. *cis*-$\mathrm{[Re^{III}(bpy)_2Cl_2]PF_6}$ (**3**, $\mathrm{ReC_{20}H_{16}N_4Cl_2F_6P}$) crystallizes in the monoclinic space group $C2/c$ with $Z = 4$ and lattice parameters $a = 15.043(5)$ Å, $b = 13.261(4)$ Å, $c = 12.440(4)$ Å, and $\beta = 108.86(2)°$ at −100 °C. $\mathrm{[Re^{I}(bpy)_3]PF_6}$ (**19**, $\mathrm{ReC_{30}H_{24}N_6F_6P}$) crystallizes in the rhombohedral space group $R\bar{3}c(h)$ (No. 167) with $Z = 12$ and lattice parameters $a = 13.793(3)$ Å and $c = 51.44(3)$ Å at −100 °C.

Introduction

Transition metal complexes containing polypyridyl ligands continue to receive considerable attention for their potential applications to the fields of photoinitiated energy transfer and redox catalysis.[1−3] Small modifications to the polypyridyl ligand or the metal center can create dramatic differences in the properties of the resulting compounds. Consequently, the spectroscopic, photophysical, photochemical, and electrochemical properties of a large number of polypyridyl complexes have been studied in detail, especially in the case of the d^6 systems of $\mathrm{Ru^{II}}$ [2a,4,5] and $\mathrm{Os^{II}}$.[2b,5,6] A logical extension of these studies would be the investigation of the isoelectronic, $\mathrm{Re^{I}}$ polypyridyl analogues. However, in contrast to the numerous known complexes of Ru and Os, few low-valent rhenium complexes containing bipyridyl or terpyridyl ligands are known.[3,7−11] Of the complexes that have been reported, virtually all contain strong π-acid ligands such as CO or RNC,[12] thus providing substantially different ligand environments compared to ruthenium and osmium.[13] Thus, a synthetic procedure for low-valent rhenium complexes containing only polypyridyl ligands may prove to be of considerable value.

Our interest in low-valent rhenium and osmium compounds as potential π-bases for the activation of unsaturated organic molecules[14] has led to several synthetic approaches to low-valent rhenium amine complexes.[10,15,16] In particular, we have demonstrated that polypyridyl ligands can stabilize the lower

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[†] Abbreviations: ^{t}BuNC = *tert*-butylisonitrile; terpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine; DMA = dimethylacetamide; TBAH = tetrabutylammonium hexafluorophosphate; OTf = trifluoromethanesulfonate (triflate); [PPN]Cl = bis(triphenylphosphoranylidene)ammonium chloride; tbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; phen = 1,10-phenanthroline; DME = 1,2-dimethoxyethane; TMPA = tris(2-pyridylmethyl)amine; py = pyridine.

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(2) For a few recent examples: (a) Coe, B. J.; Thompson, D. W.; Culbertson, C. T.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 3385. (b) Ruminski, R. R.; Serveiss, D.; Jacquez, M. *Inorg. Chem.* **1995**, *34*, 3358. Holmlin, R. E.; Barton, J. K. *Inorg. Chem.* **1995**, *34*, 7. (c) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 2725. Bardwell, D. A.; Barigelletti, F.; Cleary, R. L.; Flamigni, L.; Guardigli, M.; Jeffery, J. C.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 2438.

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(13) Of the few rhenium polypyridyl complexes known, $\mathrm{Re^{I}(bpy)(CO)_3X}$ (X = Cl, Br) and its derivatives are already the focus of a variety of photophysical and electrochemical studies due to its potential to serve as a catalyst for $\mathrm{CO_2}$ reduction and other functions. See ref 3.

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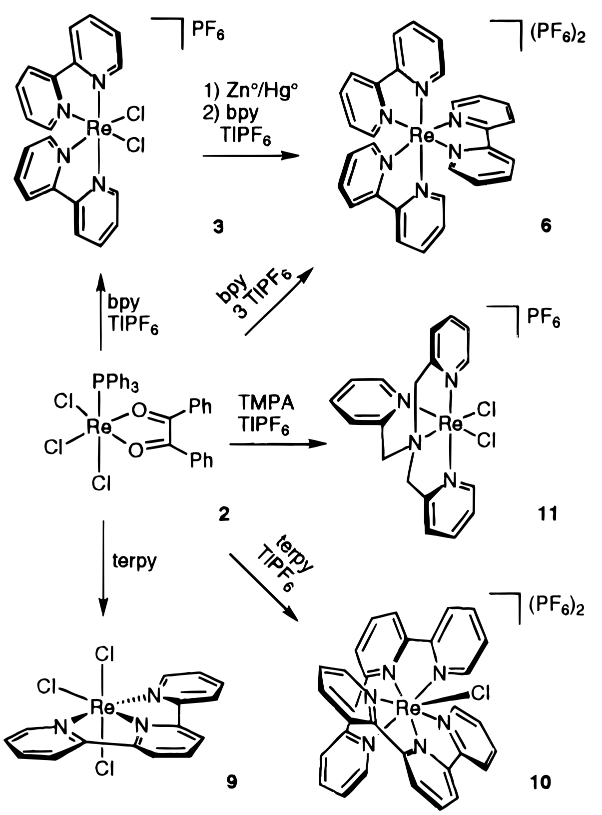

Figure 1. Synthesis of polypyridyl complexes of rhenium (**3**, **6**, **9**−**11**) from $Re^{III}(benzil)(PPh_3)_2Cl_3$ (**2**).

oxidation states of rhenium while still creating a metal center electron-rich enough to bind unsaturated ligands.[10,16]

In the following account, we demonstrate that the complex $Re^{III}(benzil)(PPh_3)Cl_3$ provides access to a novel series of low-valent rhenium complexes containing the ligands bpy, phen, terpy, and TMPA *devoid* of other π-acids. The substitution chemistry and redox properties of the resulting six- and seven-coordinate complexes of Re^{III}, as well as octahedral Re^{II} and Re^{I} complexes, are presented below.

Results and Discussion

Synthesis. The compound $Re^{III}(CH_3CN)(PPh_3)_2Cl_3$ (**1**) has proven to be a useful precursor in the synthesis of other Re^{III} complexes. Rouschias and Wilkinson reported the synthesis of **1** in 1967, along with its reactions with pyridyl ligands that led to the formation of *mer*-$Re^{III}(py)_3Cl_3$, $Re^{III}(py)_2(PPh_3)Cl_3$, and $Re^{III}(bpy)(PPh_3)Cl_3$.[7,17,18] However, we find that the derivative $Re^{III}(benzil)(PPh_3)Cl_3$ (**2**), synthesized from **1**,[7] offers greater synthetic flexibility than its precursor as a synthon for Re^{III} polypyridyl complexes. As shown in Figure 1, complex **2** leads to a variety of Re^{III} or Re^{II} polypyridyl complexes that contain no strong π-acids or phosphines. The reaction of $Re^{III}(benzil)(PPh_3)Cl_3$ (**2**) with the bidentate, polypyridyl ligands bpy, tbpy, or phen and a halide scavanger (e.g. Tl^+) yields different products depending on reaction conditions. At low concentrations of **2** (∼6 mM) and 1 equiv of Tl^+, Re^{III} complexes of the type *cis*-$[Re^{III}(L_2)_2Cl_2]^+$ are obtained, where L_2 = bpy (**3**), tbpy (**4**), or phen (**5**). At high concentrations of **2** (0.045 M) and ∼3.3 equiv of Tl^+, the Re^{II} complexes, $[Re^{II}(L_2)_3]^{2+}$ (L_2 = bpy (**6**), tbpy (**7**), or phen (**8**)), are obtained as major products.[19] The complex *cis*-$[Re^{III}(bpy)_2Cl_2]^+$ (**3**) is also a precursor to the species $[Re^{II}(bpy)_3]^{2+}$ (**6**). The transformation can be done stepwise where **3** is first reduced to *cis*-$Re^{II}(bpy)_2Cl_2$ with Zn^0/Hg^0 in MeOH, and then the chloride ligands are removed with $TlPF_6$ to produce compound **6**.[20] When **3**, bpy, and $TlPF_6$ are refluxed together, none of complex **6** is observed unless free benzil is also added to the reaction mixture. $[Re^{II}(bpy)_3]^{2+}$ (**6**) can also be formed directly from complex **1** using refluxing ethanol as the reducing agent,[21] a reaction analogous to that reported for the formation of $[Tc^{II}(bpy)_3]^{2+}$.[18]

The reaction of $Re^{III}(benzil)(PPh_3)Cl_3$ (**2**) with the tridentate ligand terpy also is sensitive to reaction conditions. When no $TlPF_6$ is used, the expected $Re^{III}(terpy)Cl_3$ (**9**) is formed in 81% yield.[10] However, when 3 equiv of $TlPF_6$ is combined with the benzil complex (**2**) and excess terpy, a seven-coordinate complex, $[Re^{III}(terpy)_2Cl](PF_6)_2$ (**10**), is recovered as the major product.[8,22] $Re^{III}(benzil)(PPh_3)Cl_3$ (**2**) also reacts with the tetradentate ligand TMPA to form a compound similar to the $(bpy)_2$ complex (**3**), $[Re^{III}(TMPA)Cl_2]PF_6$ (**11**).

The cation, *cis*-$[Re^{III}(bpy)_2Cl_2]^+$ (**3**), is a useful synthon to a variety of complexes of the form $[Re(bpy)_2L_x]^{n+}$ (Figure 2). Depending on reaction conditions, addition, reduction, or substitution products may be generated. When an excess of *tert*-butylisonitrile is added to a solution of **3**, a single addition rapidly occurs, resulting in formation of the stable seven-coordinate species $[Re^{III}(bpy)_2(^tBuNC)Cl_2]PF_6$ (**13**). An analogous substitution occurs for complexes **4** and **5**, generating $[Re^{III}(tbpy)_2(^tBuNC)Cl_2]^+$ (**14**) and $[Re^{III}(phen)_2(^tBuNC)Cl_2]^+$ (**15**), respectively.[23] The chlorides on the six-coordinate bpy complex (**3**) or the resulting seven-coordinate complex (**13**) can then be substituted with the addition of excess ^tBuNC and NaOTf to form the $[Re^{III}(bpy)_2(^tBuNC)_3](OTf)_3$ complex (**16**).[24] Complexes **13**−**16** are diamagnetic and show irreversible reduction waves in their cyclic voltammograms, observations that are consistent with a d^4/seven-coordinate system. The ^1H NMR spectrum of $[Re^{III}(bpy)_2(^tBuNC)_3](OTf)_3$ (**16**) has bpy resonances that indicate symmetrical binding, and two signals are observed for the ^tBuNC appearing in a 2:1 ratio. These spectral features suggest a higher symmetry of this complex compared to complexes **13**−**15**, where asymmetrical bpy resonances are observed. The seven-coordinate complex, $[Re^{III}(bpy)_2(^tBuNC)Cl_2]PF_6$ (**13**), can be reduced to Re^I with excess Zn^0/Hg^0 in MeOH (Figure 2). However, the product is not the expected complex, $Re^I(bpy)_2(^tBuNC)Cl$, produced from simple loss of one chloride ligand. Instead, the complex *cis*-$[Re^I(bpy)_2(^tBuNC)_2]PF_6$ (**17**) is obtained in low yield. This

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(15) Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 594.

(16) Orth, S. D.; Barrerra, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1994**, *33*, 3026.

(17) Compound **1** has been utilized as a synthon for other rhenium complexes. Of related interest to this paper is the reaction of **1** with 2-(phenylazo)pyridine (PAP) to form Re^{III} complexes of the type, [*cis*-$Re^{III}(PAP)_2Cl_2]^+$. Ghosh, P.; Pramanik, A.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1883.

(18) The technetium derivative, $Tc^{III}(CH_3CN)(PPh_3)_2Cl_3$ has also been reported to form $[Tc^{II}(bpy)_3]^{2+}$ and $[Tc^{II}(terpy)_2]^{2+}$. Archer, C. M.; Dilworth, J. R.; Thompson, R. M.; McPartlin, M.; Povey, D. C.; Kelly, J. D. *J. Chem. Soc., Dalton Trans.* **1993**, 461.

(19) Compound **6** has been previously reported using a different synthetic route. See ref 11. At the high concentrations of **2**, even if only 1 equiv of Tl^+ is used, $[Re^{II}(bpy)_3]^{2+}$ (**6**) will be obtained as a side product in the formation of **3**.

(20) The chloride ligands on *cis*-$[Re^{III}(bpy)_2Cl_2]^+$ (**3**) cannot be removed by $TlPF_6$, AgOTf, or NaOTf to form $[Re^{III}(bpy)_3]^{3+}$ or another other complex of that type. The reaction from **12** to **6** does not proceed cleanly with Tl^+.

(21) The reaction does not proceed as cleanly or in as high yield as the reaction from the benzil complex (**2**).

(22) When less than 3 equiv of $TlPF_6$ are used, this product is obtained along with an impurity, $[Re^{II}(terpy)(PPh_3)_2Cl]PF_6$.

(23) Complex **15** appears to contain a trace amount of paramagnetic impurities that disrupt the ^1H NMR spectrum.

(24) Substitution using $TlPF_6$ or other ligands such as py or bpy does not proceed cleanly.

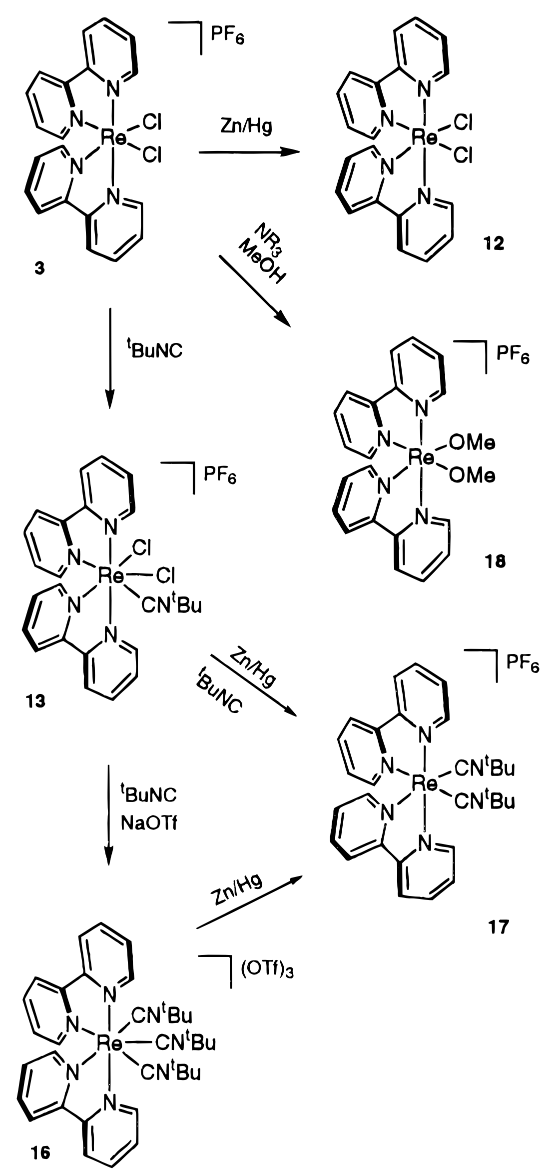

Figure 2. Synthesis of Re^{III}, Re^{II}, and Re^{I} $(bpy)_2$ complexes derived from *cis*-$[Re^{III}(bpy)_2Cl_2]PF_6$ (**3**).

complex can be obtained in ∼50% isolated yield, either by reduction of **13** in the presence of excess ^tBuNC or by direct reduction of complex **16**. The ^1H NMR spectrum of *cis*-$[Re^{I}(bpy)_2(^tBuNC)_2]PF_6$ (**17**) contains asymmetrical bpy resonances and one signal for ^tBuNC, consistent with the assigned symmetry of this complex.

Alternatively, the chloride ligands on *cis*-$[Re^{III}(bpy)_2Cl_2]PF_6$ (**3**) can be substituted by MeO^- ligands (Figure 2); using MeOH in the presence of pyrrolidine, the six-coordinate *cis*-$[Re^{III}(bpy)_2(OMe)_2]PF_6$ complex (**18**) is formed in 76% yield. Judging from ^1H NMR data, the methoxy substituents appear to have a substantial π-donor interaction with the metal center. Presumably, this interaction raises the energy of one of the metal π-orbitals enough to cause the observed diamagnetism of this compound.

Finally, *cis*-$[Re^{III}(bpy)_2Cl_2]PF_6$ (**3**) is readily reduced to the stable neutral complex, *cis*-$Re^{II}(bpy)_2Cl_2$ (**12**), by the action of Zn^0/Hg^0 in MeOH (Figures 2 and S1 (Supporting Information)). Further reduction of the compound with Mg^0 or Na^0/Hg^0 in the presence of a variety of unsaturated ligands such as benzene, pyrrole, naphthalene, acetone, or acetonitrile leads only to intractable mixtures, and a $[Re^{I}(bpy)_2Cl_2]^-$ salt cannot be isolated. The former reactivity is in contrast to the related *cis*-$Os^{II}(bpy)_2Cl_2$ and *cis*-$Ru^{II}(bpy)_2Cl_2$ systems, where one of the chloride ligands is easily substituted under reducing conditions.[25]

The $[Re^{III}(TMPA)Cl_2]PF_6$ (**11**) complex might be expected to have chemical properties similar to the previously reported complex *cis*-$[Re^{III}(ampy)_2Cl_2]^+$ [15] or to *cis*-$[Re^{III}(bpy)_2Cl_2]^+$ (**3**). However, unlike complex **3**, the TMPA analogue (**11**) does not readily undergo an addition reaction in the presence of ^tBuNC; instead, only decomposition is observed. In addition, complex **11** cannot be reduced in $MeOH/Zn^0/Hg^0$ (c.f. $E_{1/2}(III/II) = -0.91$ and -0.20 V vs NHE for compounds **11** and **3**, respectively).[26] Presumably these differences are due to the stronger electron-donating properties of TMPA relative to two bpy ligands and the lesser ability of the former to act as a π-acid.

The Re^{III} bis(chloride) complexes (**3**−**5**) do not appear to behave like their corresponding Os^{III} and Ru^{III} analogues. On Os and Ru, the chlorides can be selectively substituted for a variety of ligands under relatively mild conditions, leading to numerous $(bpy)_2$ complexes.[27] The reluctance of these Re^{III} complexes to release a chloride is also in contrast to an analogous Re^{III} compound with only saturated amines.[15] A chloride of *cis*-$[Re^{III}(en)_2Cl_2]PF_6$ is reversibly substituted by other ligands such as pyridine or isonicotinamide; however, these complexes cannot be reduced to their lower oxidation states due to the lack of π-acids.

The $Re^{III}(benzil)(PPh_3)Cl_3$ (**2**) complex is also an effective synthon for $Re^{III}(terpy)Cl_3$ (**9**) (Figure 1).[28] However, compound **9** apparently does not react like the related $Ru^{III}(terpy)Cl_3$ and $Os^{III}(terpy)Cl_3$ complexes.[5] This compound is insoluble in most conventional solvents and, in our hands, has not led to any useful cationic terpy complexes via the removal of a halide ligand.[29] When the benzil complex (**2**) is combined with an excess of terpy and 3 equiv of $TlPF_6$, $[Re^{III}(terpy)_2Cl](PF_6)_2$ (**10**) is isolated as the major product.[8] Like the other seven-coordinate Re^{III} complexes reported herein, this species exhibits diamagnetic behavior and a chemically irreversible III/II reduction in its cyclic voltammogram (DMA/100 mV/s). The chloride ligand of **10** cannot be removed by Tl^+ or Ag^+ without another ligand present. However, we observe that in the presence of ^tBuNC, the chloride can be abstracted with AgOTf to generate $[Re^{III}(terpy)_2(^tBuNC)]^{3+}$, but this reaction does not proceed cleanly. Finally, we note that when complex **1** and terpy are refluxed in ethanol, under reaction conditions similar to those used to prepare $[Tc(terpy)_2]^{2+}$,[18] the isolated product is $[Re^{II}(terpy)(PPh_3)_2Cl]Cl$.[10]

On the basis of the potentials observed in the cyclic voltammetry of $[Re^{II}(bpy)_3]^{2+}$ (**6**) (Figure 3), this complex should readily undergo either chemical reduction or oxidation to give stable Re^{I} or Re^{III} complexes, respectively. Indeed, both of these oxidation states are accessible using appropriate reagents. As shown in Figure 4, $[Re^{II}(bpy)_3]^{2+}$ (**6**) can be cleanly reduced to $[Re^{I}(bpy)_3]^+$ (**19**) with Zn^0/Hg^0 in MeOH.[30]

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(25) Sullivan, B. P.; Conrad, D.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 3640.

(26) When a stronger reducing agent is used (Mg° in DMA/DME), complex **11** decomposes to an intractable mixture. A chloride ligand on **11** is readily abstracted by $TlPF_6$ as observed by the rapid formation of TlCl; however, no characterizable products could be isolated from this reaction.

(27) As an example, see: ref 6 and references cited therein.

(28) Compound **9** can be produced from other starting materials as well,[10] including a direct reaction of terpy with $Re^{III}(CH_3CN)(PPh_3)_2Cl_3$ (**1**).

(29) Compound **9** does not appear to be an intermediate in the formation of $[Re^{III}(terpy)_2Cl](PF_6)_2$ (**10**) since, when **9** is taken under the same reaction conditions used in the synthesis of **10**, only unreacted starting material is observed.

(30) The $Re^0(bpy)_3$ complex has been reported, but we were not able to isolate that complex from reduction from Re^{II} or Re^{I} even under strongly reducing conditions (Na° in DMA for 3 days). Quirk, J.; Wilkinson, G. *Polyhedron* **1982**, *1*, 209.

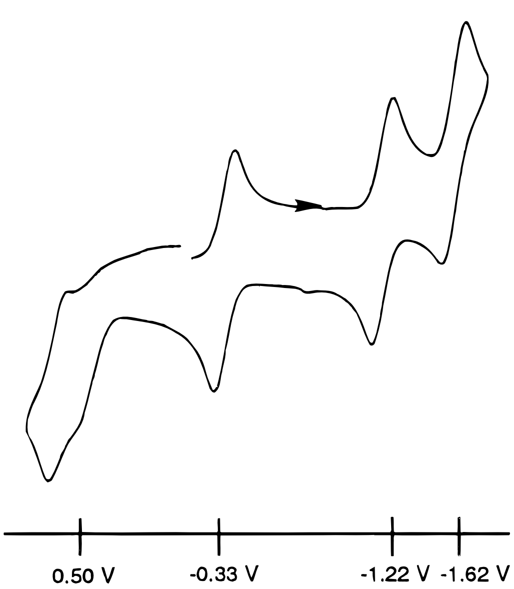

Figure 3. Cyclic voltammogram of [Re^{II}(bpy)$_3$](PF$_6$)$_2$ (**6**) (V vs NHE; [Re] = ~7.5 mM; DMA/TBAH/100 mV/s).

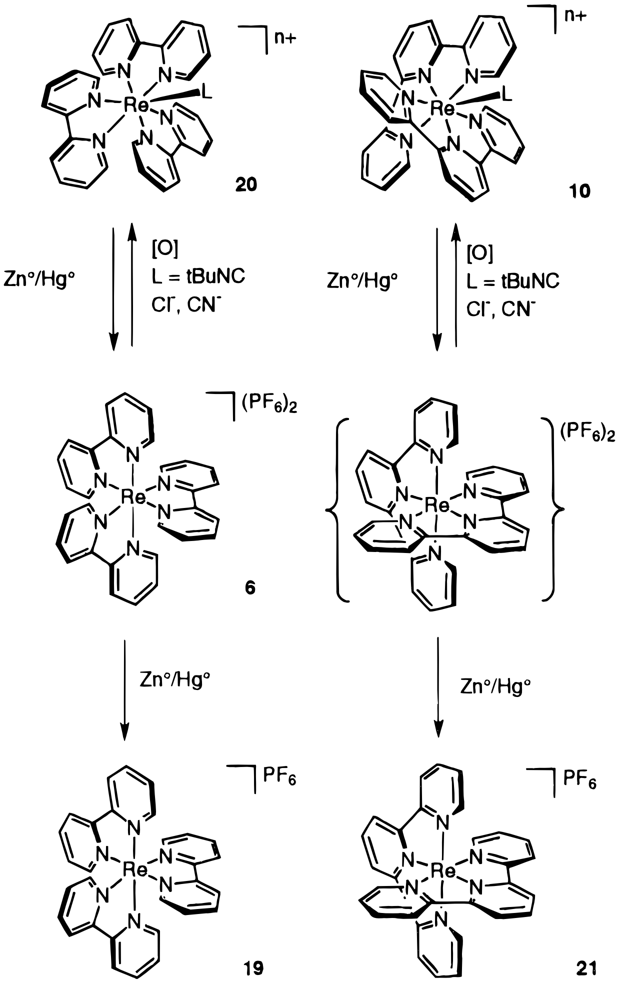

Figure 4. Reversible oxidation and reduction of [Re^{I}(bpy)$_3$]PF$_6$ (**19**) and [Re^{I}(terpy)$_2$]PF$_6$ (**21**) complexes and [Re^{III}(bpy)$_3$L]$^{n+}$ and [Re^{III}(terpy)$_2$L]$^{n+}$ complexes.

This compound (**19**) exhibits a symmetrical, diamagnetic ^{1}H NMR spectrum, closely resembling that of the free ligand. Compound **19** is highly air-sensitive in solution, but in the absence of oxygen it is stable in acetone or CH$_2$Cl$_2$ solution for several days. The III/II oxidation couple is irreversible and occurs at a relatively low potential ($E_{p,a} = +0.61$ V vs NHE).

Table 1. Summary of the Reduction Potentials for Compounds **3**−**21**

complex (no.)	IV/III	III/II	II/I	I/0	0/−I
cis-[Re$^{III/II}$(bpy)$_2$Cl$_2$]$^{n+}$ (**3**/**12**)	0.99^a	−0.20	−1.01		
cis-[Re^{III}(tbpy)$_2$Cl$_2$]$^+$ (**4**)	0.96^a	−0.30	−1.14		
cis-[Re^{III}(phen)$_2$Cl$_2$]$^+$ (**5**)	0.95^a	−0.25	−0.94		
Re^{III}Cl$_3$(terpy) (**9**)	0.52	−0.49	−1.51^b		
[Re^{III}(TMPA)Cl$_2$]$^+$ (**11**)	0.81^a	−0.91	−1.85^b		
cis-[Re^{III}(bpy)$_2$(OMe)$_2$]$^+$ (**18**)	0.53^a	−0.81	−1.34		
[Re^{III}(terpy)$_2$Cl]$^{2+}$ (**10**)	1.37	−0.53^b			
[Re^{III}(bpy)$_2$Cl$_2$(^{t}BuNC)]$^+$ (**13**)	1.12	−0.85^b			
[Re^{III}(tbpy)$_2$Cl$_2$(^{t}BuNC)]$^+$ (**14**)	1.05	−1.06^b			
[Re^{III}(phen)$_2$Cl$_2$(^{t}BuNC)]$^+$ (**15**)	1.10	−0.61^b			
[Re^{III}(bpy)$_2$(^{t}BuNC)$_3$]$^{3+}$ (**16**)		−0.61^b			
[Re^{III}(bpy)$_3$(^{t}BuNC)]$^{3+}$ (**20**)		−0.39^b			
[Re$^{II/I}$(bpy)$_3$]$^{n+}$ (**6**/**19**)		+0.50^a	−0.33	−1.22	−1.62
[Re^{II}(tbpy)$_3$]$^{2+}$ (**7**)		+0.49^a	−0.47	−1.35	−1.75
[Re^{II}(phen)$_3$]$^{2+}$ (**8**)		+0.56^a	−0.31	−1.21	−1.58
cis-[Re^{I}(bpy)$_2$(^{t}BuNC)$_2$]$^+$ (**17**)		1.18^a	0.22	−1.30	−1.62
[Re^{I}(terpy)$_2$]$^+$ (**21**)		0.36^a	0.12	−1.42	−1.76

^{a} Reported values are for $E_{p,a}$. ^{b} Reported values are for $E_{p,c}$.

Consistent with its cyclic voltammetric data, [Re^{III}(bpy)$_3$]$^{3+}$ is not stable in DMA solution and cannot be generated by chemical oxidation.[31] However, in the presence of a small coordinating ligand such as ^{t}BuNC, **19** is easily oxidized with AgOTf to form the seven-coordinate complex [Re^{III}(bpy)$_3$(^{t}BuNC)]$^{3+}$ (**20**). This complex, in turn, can be treated with Zn^0/Hg^0 to obtain the starting material (**19**). According to electrochemical data, the oxidation of **19** to a Re^{III} seven-coordinate complex proceeds by an analogous reaction with Cl$^-$ and CN$^-$ as well (Figure 4).[32] Similar reactivity is observed for the seven-coordinate terpy complex, [Re^{III}(terpy)$_2$Cl](PF$_6$)$_2$ (**10**). Complex **10** can be cleanly reduced in MeOH with excess Zn^0/Hg^0 to form the stable species [Re^{I}(terpy)$_2$]PF$_6$ (**21**) (Figure 4). The ^{1}H NMR spectrum of **21** is also diamagnetic, but it is easily distinguished from **10** due to the higher symmetry of the bpy ligands in this complex. As with its (bpy)$_3$ analogue, complex **21** can also be reoxidized in the presence of small coordinating ligands such as Cl$^-$, CN$^-$, or ^{t}BuNC to form seven-coordinate complexes of the form [Re^{III}(terpy)$_2$L]$^{n+}$ (*vide infra*).[33]

Electrochemistry. The electrochemistry of these compounds provides a convenient measure of the chemical reactivity associated with the redox processes, and corresponding reduction potentials are reported in Table 1. As an example, the III/II couple for [Re^{III}(terpy)$_2$Cl](PF$_6$)$_2$ (**10**) is chemically irreversible (Figure 5). After passing through the reduction wave and reversing the scan, the II/I couple for [Re^{I}(terpy)$_2$]PF$_6$ (**21**) is observed; this process is readily carried out on a synthetic scale. Alternatively, when the cyclic voltammogram of [Re^{I}(terpy)$_2$]PF$_6$ (**21**) is taken in the presence of a free chloride source (e.g., [PPN]Cl), the seven-coordinate complex, [Re^{III}(terpy)$_2$Cl](PF$_6$)$_2$ (**10**), can be observed electrochemically in the return scan upon passing through the III/II potential, and similar findings are observed for other small coordinating ligands, such as CN$^-$ or ^{t}BuNC.[34] This observation suggests that chemical oxidation of [Re^{I}(terpy)$_2$]PF$_6$ (**21**) in the presence of certain ligands would be a viable preparative route to complexes of the type [Re^{III}-

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(31) The [Re^{III}(bpy)$_3$]$^{3+}$ complex is reported in reference 11.

(32) For the electrochemically observed [Re^{III}(bpy)$_3$(Cl)]$^{2+}$ complex, CV (DMA/TBAH/100 mV s^{-1}): $E_{p,c}$ (III/II) = −0.26 V vs NHE.

(33) These complexes were generated electrochemically but not isolated. For the electrochemically observed [Re^{III}(terpy)$_2$(CN)]$^{2+}$ complex, CV (acetone/TBAH/100 mV s^{-1}): $E_{p,c}$ (III/II) = −0.04 V vs NHE and for [Re^{III}(terpy)$_2$(tBuNC)]$^{3+}$ complex, CV (acetone/TBAH/100 mV s^{-1}): $E_{p,c}$ (III/II) = −0.20 V vs NHE.

(34) Similar products are also observed electrochemically when ^{t}BuNC and NaCN are used in the place of [PPN]Cl, these observations suggesting the formation of [Re^{III}(terpy)$_2$(^{t}BuNC)](PF$_6$)$_3$ and [Re^{III}(terpy)$_2$(CN)](PF$_6$)$_2$ complexes, respectively.

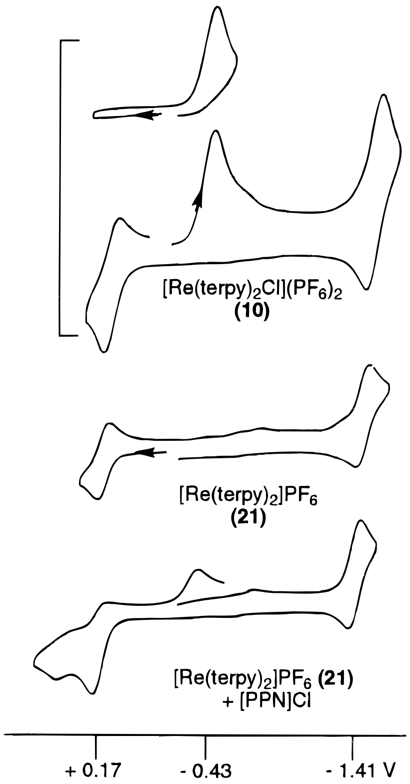

Figure 5. Cyclic voltammograms of [Re^{III}(terpy)$_2$Cl](PF$_6$)$_2$ (**10**) and [Re^{I}(terpy)$_2$]PF$_6$ (**21**) (V vs NHE; [Re] = ~7.5 mM; acetone/TBAH/100 mV/s).

(terpy)$_2$L]$^{n+}$. Behavior similar to that observed for the reduction of seven-coordinate terpy complexes is observed for the bpy analogues, [Re^{III}(bpy)$_3$(^{t}BuNC)]$^{3+}$ (**20**) and [Re^{III}(bpy)$_2$(^{t}BuNC)$_3$](OTf)$_3$ (**16**), as well. In this case, [Re^{I}(bpy)$_3$]PF$_6$ (**19**) and *cis*-[Re^{I}(bpy)$_2$(^{t}BuNC)$_2$]PF$_6$ (**17**), respectively, are observed upon reduction (Figure 4).

A comparison of related compounds provides insight into the π-acidity of the polypyridyl ligand set and, indirectly, the electron density at the metal center. In comparing the III/II potentials of the related *bis*(chloride) complexes, a dramatic shift is seen in their potentials. The III/II potential of the *cis*-[Re^{III}(en)$_2$Cl$_2$]PF$_6$ complex (and the complex [Re^{III}(NH$_3$)$_4$Cl$_2$]PF$_6$)[15] is shifted so far negative that it overlaps with the II/I reduction and only one irreversible, two-electron reduction is observed ($E_{p,a} = -1.88$ V vs NHE).[35] When two of the saturated amine ligands are exchanged for unsaturated, pyridyl groups, as in the *cis*-[Re^{III}(ampy)$_2$Cl$_2$]PF$_6$ case,[15] the III/II reduction can now be observed ($E_{p,a} = -1.15$ V vs NHE) with a shift of >730 mV positive (!). Another 240 mV shift is seen when one more unsaturated group is replaced in the III/II potential of [Re^{III}(TMPA)Cl$_2$]PF$_6$ ($E_{p,a} = -0.91$ V vs NHE). However, when the last saturated group is replaced in the complex [Re^{III}(bpy)$_2$Cl$_2$]$^+$, a 710 mV shift is seen ($E_{p,a} = -0.20$ V vs NHE). Such a large shift would not be expected, except by taking into account the enhanced π-acidic character of the bpy ligands relative to simple unconjugated pyridyl groups. This magnitude of shift is also seen in the comparison of *mer*-Re^{III}(py)$_3$Cl$_3$ and Re^{III}(terpy)Cl$_3$ (see Table 2) where a 620 mV shift positive is observed when a terpy ligand replaces three pyridine rings. The difference in π-acidity between py, bpy, and terpy is also pronounced when the II/I potentials of [Re^{I}(bpy)$_3$]PF$_6$ (**19**) and [Re^{I}(terpy)$_2$]PF$_6$ (**21**) are compared. Here, a 450 mV difference is seen in exchanging three bpy ligands for two terpy ligands; a smaller difference is observed between the III/II couples. These data clearly indicate the profound effect that conjugated polypyridyl ligands have in stabilizing the lower oxidation states of rhenium.

Table 2. Selected Reduction Potentials for Comparison of Related Complexes of Re, Tc, Os, and Ru

compound	d^3/d^4	d^4/d^5	d^5/d^6	d^6/L$_1$	L$_1$/L$_2$	ref
mer-Re^{III}(py)$_3$Cl$_3$^{a}	0.45	−1.11	−1.81			
mer-Tc^{III}(py)$_3$Cl$_3$^{a}	0.79	−0.79	−1.72^b			41
mer-Os^{III}(py)$_3$Cl$_3$^{c}		1.22				42
Re^{III}(terpy)Cl$_3$^{a} (**9**)	0.52	−0.49	−1.51^b			
Tc^{III}(terpy)Cl$_3$^{a}	0.67	−0.34	−1.42^b			41
cis-[Re^{III}(bpy)$_2$Cl$_2$]$^{+\ a}$ (**3**)	1.06	−0.17	−1.01			
cis-[Tc^{III}(dbpy)$_2$Cl$_2$]$^{+\ a}$	1.13	−0.16	−1.11			41
cis-Ru^{II}(bpy)$_2$Cl$_2$^{d}			0.56	−1.85		43
cis-Os^{II}(bpy)$_2$Cl$_2$^{d}		1.15	−0.27	−1.85		44
[Re^{I}(terpy)$_2$]$^{+\ a}$ (**21**)		0.36^e	0.12	−1.42		
[Ru^{II}(terpy)$_2$]$^{2+\ d}$			1.06	−1.53	−1.73	43
[Os^{II}(terpy)$_2$]$^{2+\ d}$			0.73	−1.47	−1.76	
[Re^{II}(bpy)$_3$]$^{2+\ a}$ (**6**)		+0.61^e	−0.33	−1.22	−1.62	
[Tc^{II}(bpy)$_3$]$^{2+\ d}$			−0.58	−1.50	−1.94	18
[Ru^{II}(bpy)$_3$]$^{2+\ d}$			1.00	−1.51	−1.70	45
[Os^{II}(bpy)$_3$]$^{2+\ d}$			0.60	−1.50	−1.70	46
cis-[Re^{I}(bpy)$_2$(^{t}BuNC)$_2$]$^{+\ a}$ (**17**)		1.18^e	0.22	−1.30	−1.62	
cis-[Ru^{II}(bpy)$_2$(^{t}BuNC)$_2$]$^{2+\ d}$			1.64	−1.57		47
cis-[Os^{II}(bpy)$_2$(MeNC)$_2$]$^{2+\ d}$			1.20	−1.51	−1.67	25

[a] In DMA. [b] Values reported for $E_{p,c}$. [c] In CH$_2$Cl. [d] In CH$_3$CN. [e] Values reported for $E_{p,a}$.

In Table 2, the electrochemical potentials for some related compounds of technetium, ruthenium, and osmium are given for comparison with the rhenium compounds presented in this paper. For the d^4/d^5 and d^5/d^6 couples, the values for the rhenium compounds are dramatically shifted negative (typically by about 1 V) to those of the Ru and Os metal centers. In contrast to the differences observed between ruthenium and osmium, the rhenium and technetium compounds show remarkably similar reduction potentials for a given ligand set. For the ligand-centered reduction couples, the II/I and I/0 couples for Ru and Os and I/0 and 0/−I couples for Re and Tc, the first (d^6/L$_1$) and second (L$_1$/L$_2$) couples are largely independent of the metal center as expected.

Lever has demonstrated that the observed reduction potential of a transition metal complex can be estimated by a simple, empirical calculation taking into account individual ligand contributions.[36]

$$E(\text{obs}) = S_M[\sum E_L(L)] + I_M \tag{1}$$

This method provides accurate predictions of reduction potentials in most cases. The compounds reported in this paper, along with some related compounds containing saturated amine ligands,[15] have been compared using this method. The calculated values of E and $\sum E_L$(L) are given in Table S1 (Supporting Information). For the IV/III couples ($S_M = 0.86$; $I_M = 0.51$)[37] and the III/II couples ($S_M = 1.17$; $I_M = -0.88$),[37] the calculated and observed potentials compare very well (the figures are plotted in the Supporting Information, Figures S2 and S3). However, the II/I couples begin to show a deviation from the predicted potentials as the value of $\sum E_L$(L) decreases in the compounds containing a smaller total number of π-acids ($S_M = 0.76$; $I_M = -0.95$; Figure S4 (Supporting Information)).[37] Thus, for the more electron-rich compounds with the saturated amine ligands, the predicted and observed values deviate significantly. In contrast, for the polypyridyl compounds

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(35) A two-electron reduction is predicted according to the Lever analysis. See: refs 36 and 37.

(36) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

(37) Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 1980.

Table 3. UV−Vis Data Collected for Compounds **6-8**, **10**, **12**, **17**, and **19**−**21** and Selected Absorbance Data for Related Ru and Os Complexes

complex	λ (nm)	ϵ (M^{-1} cm^{-1})	color	ref
$[Re^{II}(bpy)_3]^+$ (**6**)	298	43 100	purple	
	398	11 200		
	526	8 290		
	668	8 600		
$[Re^{I}(bpy)_3]^+$ (**19**)	290	30 000	black	
	444	20 300		
	506	17 400		
	823	13 100		
$[Re^{II}(tbpy)_3]^{2+}$ (**7**)	298	47 400	blue	
	428	9 140		
	472	9 270		
	500	8 750		
	680	3 210		
$[Re^{II}(phen)_3]^{2+}$ (**8**)	266	75 600	blue	
	386	7 310		
	532	11 300		
	658	9 520		
	718	6 470		
cis-$[Re^{III}(bpy)_2Cl_2]^+$ (**12**)	296	6 230	brown	
	392	1 090		
	596	868		
cis-$[Re^{I}(bpy)_2(^tBuNC)_2]^+$ (**17**)	244	34 000	black	
	292	36 400		
	298	23 100		
	378	9 460		
	512	7 440		
	612	6 860		
$[Re^{III}(bpy)_3(^tBuNC)]^{3+}$ (**20**)	200	55 200	orange	
	254	22 700		
	298	37 300		
	420	8 260		
	474	5 860		
$[Re^{III}(terpy)_2Cl]^{2+}$ (**10**)	210	58 700	red	
	294	48 600		
	330	34 200		
	498	13 100		
$[Re^{I}(terpy)_2]^+$ (**21**)	206	38 200	brown	
	284	32 800		
	314	31 600		
	438	19 800		
	558	10 900		
$[Ru^{II}(bpy)_3]^{2+}$	185			4
	240			
	285			
	450			
$[Os^{II}(bpy)_3]^{2+}$	290	79 360		46
	328	8 860		
	370	9 130		
	386	8 880		
	446	11 490		
	480	12 110		
	658	2 760		
$[Ru^{II}(terpy)_2]^{2+}$	271	55 900		43
	309	70 200		
	476	17 700		
$[Os^{II}(terpy)_2]^{2+}$	227	37 900		43
	271	38 850		
	312	66 250		
	477	13 750		
	657	3 650		

reported herein, the experimental reduction potentials agree closely with predicted values, even for the II/I couples. Previously, we observed in a series of low-valent rhenium compounds containing terpy a significant deviation from predicted values as the values of $\sum E_L(L)$ decreased.[10]

Spectroscopy. The UV/vis spectra of several of these compounds have been recorded in CH_3CN and are reported in Table 3. All compounds listed exhibit strong absorptions between 200 and 300 nm, assigned to be $\pi-\pi^*$ ligand centered transitions and strong absorptions in the visible region, consistent with their intense colors, assigned for the Re(II) and Re(I) compounds as MLCT bands. The absorption spectra of corresponding osmium and ruthenium compounds are provided in Table 3 for comparison.

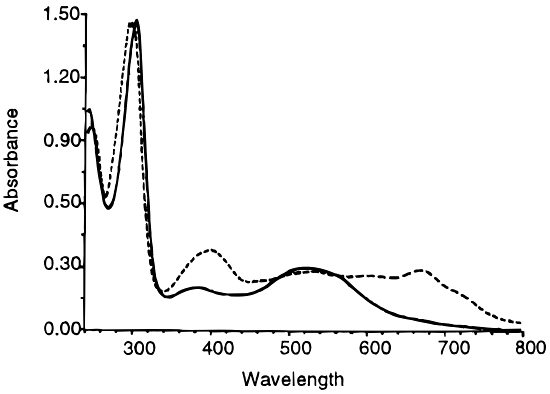

Figure 6. UV−vis spectra of $[Re^{II}(bpy)_3](PF_6)_2$ (**6**) in CH_3CN (dotted line; [Re] = 3.6×10^{-4} M; l = 1 mm) and in CH_3CN and H_2O after exposure to air (solid line).

Table 4. Infrared Stretching Frequencies for the Isocyanide Ligand in Compounds **13**−**17** and **20** and for Related Compounds of Re, Os, and Ru

compound	ν_{NC} (cm^{-1})	ref
$[Re^{III}(bpy)_2Cl_2(^tBuNC)]^+$ (**13**)	2179	
$[Re^{III}(tbpy)_2Cl_2(^tBuNC)]^+$ (**14**)	2131	
$[Re^{III}(phen)_2Cl_2(^tBuNC)]^+$ (**15**)	2185	
$[Re^{III}(bpy)_2(^tBuNC)_3]^{3+}$ (**16**)	2189, 2164	
cis-$[Re^{I}(bpy)_2(^tBuNC)_2]^+$ (**17**)	2094, 2048	
$[Re^{III}(bpy)_3(^tBuNC)]^{3+}$ (**20**)	2153	
cis-$[Re^{II}(bpy)_2(MeNC)_2]^{2+}$	2185, 2205	47
cis-$[Os^{II}(bpy)_2(MeNC)_2]^{2+}$	2150, 2190	25
trans-$Re^{I}Cl(^tBuNC)(dppe)_2$	1920	48
$[Re^{III}(^tBuNC)_3(dppe)Cl_2]^+$	2205, 2160	49
$[Re^{III}(^tBuNC)_6Cl]^{2+}$	2260, 2210	49
trans-$[Re^{I}(MeNC)(^tBuNC)(dppe)_2]Cl$	2114, 2030	50
MeNC	2142	51

The absorbance spectrum of $[Re^{II}(bpy)_3](PF_6)_2$ (**6**) in CH_3CN shows no change when degassed water is added to the solution under nitrogen. However, when the sample is exposed to air and water, the color of the solution changes, and, correspondingly, differences are observed in the absorption spectrum (Figure 6). Most notably, the features at λ_{max} = 398 and 668 nm decrease significantly, while a new absorbance grows in at 526 nm. The "oxidized" spectrum with absorbances at 304 nm (37 400 M^{-1} cm^{-1}), 382 nm (5170 M^{-1} cm^{-1}), and 526 nm (7550 M^{-1} cm^{-1}) closely resembles that previously reported for $[Re^{II}(bpy)_3]^{2+}$ (**6**) in water.[11] For the fully reduced complex $[Re^{I}(bpy)_3]PF_6$ (**19**), the lowest energy MLCT band occurs in the near-IR region (823 nm, 13 100 M^{-1} cm^{-1}; see Figure S5 in the Supporting Information).

The infrared stretching frequencies of the compounds containing isocyanide ligands from this paper are listed in Table 4 along with those of a few related compounds. The frequencies for the seven-coordinate Re^{III} complexes appear relatively close to the frequencies of the free ligand and those of other six- and seven-coordinate Re^{III} complexes. The values for the Re^{I} complex (**17**), however, are substantially lower frequency than that of the free ligand or for the analogous Ru^{II} and Os^{II} systems, indicating an unusually large metal−ligand back-bonding interaction for these compounds.

X-ray Crystallographic Studies. Structure determinations of *cis*-$[Re^{III}(bpy)_2Cl_2]PF_6$ (**3**) and $[Re^{I}(bpy)_3]PF_6$ (**19**) were carried out at low temperature to explore how structural features varied with the oxidation state of the metal. ORTEPs for these

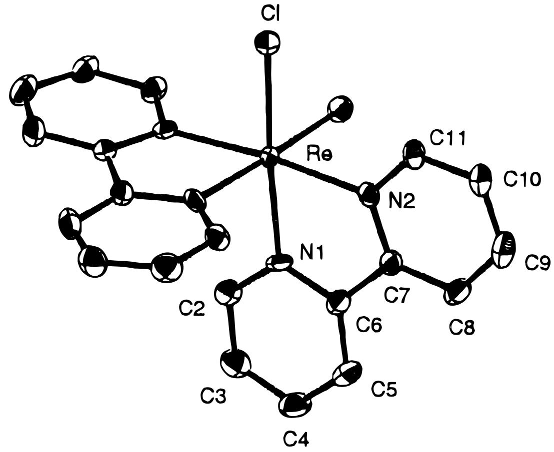

Figure 7. ORTEP drawing of the cation for *cis*-[Re^{III}(bpy)$_2$Cl$_2$]PF$_6$ (**3**).

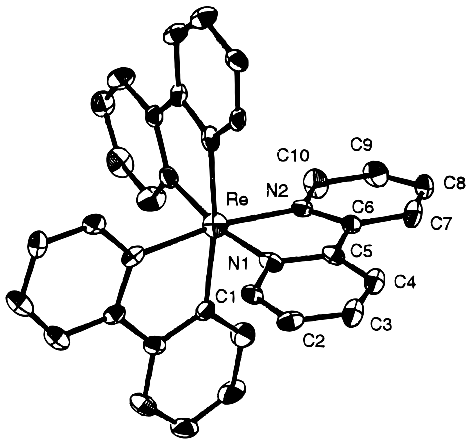

Figure 8. ORTEP drawing of the cation for [Re^{I}(bpy)$_3$]PF$_6$ (**19**).

Table 5. Summary of Crystallographic Data for Compounds **3** and **19**

	cis-[Re^{III}(bpy)$_2$Cl$_2$]PF$_6$ (**3**)	[Re^{I}(bpy)$_3$]PF$_6$ (**19**)
formula	$ReC_{20}H_{16}N_4Cl_2F_6P$	$ReC_{30}H_{24}N_6F_6P$
fw	714.45	799.73
space group	$C2/c$ (No. 15)	$R\bar{3}c(h)$ (No. 167)
a, Å	15.043 (5)	13.793 (3)
b, Å	13.261 (4)	
c, Å	12.440 (4)	51.44 (3)
β, deg	108.86 (2)	
V, Å^3	2348 (2)	8475 (7)
Z	4	12
D_{calc}, g/cm^3	2.021	1.880
μ (Mo Kα), cm^{-1}	56.04	44.85
temp, °C	−100	−100
$2\theta_{max}$, deg	50.0	50.0
λ, Å	0.710 69	0.710 69
R^a	0.033	0.035
$R_w{}^b$	0.042	0.040

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for *cis*-[Re^{III}(bpy)$_2$Cl$_2$]PF$_6$ (**3**) and [Re^{I}(bpy)$_3$]PF$_6$ (**19**)

cis-[Re^{III}(bpy)$_2$Cl$_2$]PF$_6$ (**3**)		[Re^{I}(bpy)$_3$]PF$_6$ (**19**)	
Bond Distances			
Re−C1	2.361(2)	Re−N1	2.05(1)
Re−N1	2.094(5)	Re−N2	2.07(1)
Re−N2	2.096(5)	N1−C1	1.36(2)
N1−C2	1.348(9)	N1−C5	1.37(2)
N1−C6	1.355(9)	N2−C6	1.41(2)
N2−C7	1.359(8)	N2−C10	1.37(1)
N2−C11	1.347(8)	C1−C2	1.38(2)
C2−C3	1.38(1)	C2−C3	1.38(2)
C3−C4	1.37(1)	C3−C4	1.35(2)
C4−C5	1.39(1)	C4−C5	1.42(2)
C5−C6	1.38(1)	C5−C6	1.42(2)
C6−C7	1.48(1)	C6−C7	1.41(2)
C7−C8	1.38(1)	C7−C8	1.39(2)
C8−C9	1.38(1)	C8−C9	1.38(2)
C9−C10	1.39(1)	C9−C10	1.37(2)
C10−C11	1.36(1)		
Bond Angles			
Cl−Re−C1	93.21(8)	N1−Re−N1	97.2(4)
C1−Re−N1	172.3(2)	N1−Re−N2	77.1(4)
C1−Re−N1	90.2(1)	N1−Re−N2	90.8(4)
C1−Re−N2	96.4(1)	N1−Re−N2	170.8(4)
C1−Re−N2	87.8(1)	N2−Re−N2	95.6(4)
N1−Re−N1	87.3(3)		
N1−Re−N2	76.8(2)		
N1−Re−N2	98.7(2)		
N1−Re−N2	98.7(2)		
N2−Re−N2	173.9(3)		

cations are shown in Figures 7 and 8. The pertinent crystallographic parameters and structural features are shown in Tables 5 and 6, respectively; the positional parameters are provided in Tables S3 and S8 in the Supporting Information. As the oxidation state of rhenium is lowered from Re^{III} to Re^{I}, the M−N distances shorten on average from 2.09 to 2.06 Å, consistent with the notion of the greatest M−L back-bonding occurring when the metal is most electron-rich. For comparison, the compound [Re^{III}(terpy)$_2$Cl]$^{2+}$ (**10**) was previously determined to have Re−N distances of 2.10 Å.[8] Of note, these values are significantly shorter than comparable values for saturated amine complexes, where metal-to-ligand π-back-bonding is not possible. For example, in the compound [Re(N$_2$)(ampy)$_2$(PPh$_3$)]PF$_6$, the Re−NH$_2$ distances are 2.21 and 2.22 Å, and for the Re^{I} species [Re(N$_2$)(ampy)(tbpy)(PPh$_3$)]PF$_6$, the corresponding value is 2.193 Å.[16]

Structural evidence for significant π-back-bonding between Re^{I} or Re^{II} and polypyridyl ligands is also manifested in distortions to the heterocycle framework.[38] In Table 7, bond distances for the bpy ligands in complexes **3**, **6**, and **19** are listed along with those for the uncomplexed ligand. The general pattern of bond expansion and contraction is consistent with the significant population of bipyridyl LUMO in the [Re^{I}(bpy)$_3$]PF$_6$ (**19**) structure. Similar findings have been reported for the complex, Mo^{II}(bpy)$_2$(OPr-*i*)$_2$.[39]

Conclusions. The compound Re^{III}(benzil)(PPh$_3$)Cl$_3$ (**2**) has proven to be a versatile precursor to Re^{III}, Re^{II}, and Re^{I} complexes with polypyridyl ligands. Seven-coordinate Re^{III} complexes may be readily reduced with loss of a ligand to form new Re^{I} species, or, conversely, octahedral Re^{I} complexes may be oxidized in the presence of the desired ligand to form new seven-coordinate Re^{III} materials. Electrochemical, structural, and reactivity data confirm that the π-acidic properties of polypyridyl ligands can be substantial with electron-rich metals and are capable of stabilizing the rhenium(I) oxidation state to the point that "classical" coordination complexes of rhenium(I) become accessible.

Experimental Section

This work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox unless otherwise noted. Routine ^{1}H NMR

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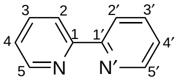
[38] An X-ray determination was also performed for [Re^{II}(bpy)$_3$](PF$_6$)$_2$ (**6**) at low temperature. The compound crystallizes in the trigonal space group $P\bar{3}c1$ (No. 165): $a = 10.687(2)$ Å, $c = 16.136(5)$ Å, $V = 1595(1)$ Å^3, Z =2 at −120 °C. The structure was refined to $R = 0.058$ ($R_w = 0.079$) for 520 reflections with $I > 3\sigma(I)$. However, some disorder observed in the structure prevented a detailed discussion of the geometry.

[39] Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 4945.

Table 7. Summary of Bond Lengths for bpy Ligands in *cis*-[Re^{III}(bpy)$_2$Cl$_2$]PF$_6$ (**3**), [Re^I(bpy)$_3$]PF$_6$ (**19**), and Related Compounds for Comparison of Bond Lengthening and Shortening vs Predicted LUMO Occupation



	M-N M-N′	N-C1 N′-C1′	N-C5 N′-C5′	C1-C2 C1′-C2′	C2-C3 C2′-C3′	C3-C4 C3′-C4′	C4-C5 C4′-C5′	C1-C1′	ref
free ligand		1.346(2)	1.341(2)	1.394(2)	1.385(2)	1.383(3)	1.384(2)	1.490(3)	
[Re^{III}(bpy)$_2$Cl$_2$]PF$_6$ (**3**)	2.094(5)	1.355(9)	1.348(9)	1.38(1)	1.39(1)	1.37(1)	1.38(1)	1.48(1)	
	2.096(5)	1.359(8)	1.347(8)	1.38(1)	1.38(1)	1.39(1)	1.36(1)		
[Re^{II}(bpy)$_3$](ReO$_4$)$_2$	2.094(8)	1.36(1)	1.41(2)	1.36(1)	1.44(2)	1.38(2)	1.36(1)	1.48(2)	
[Re^I(bpy)$_3$]PF$_6$ (**19**)	2.05(1)	1.37(2)	1.36(2)	1.42(2)	1.35(2)	1.38(2)	1.38(2)	1.42(2)	
	2.07(1)	1.41(2)	1.37(1)	1.41(2)	1.39(2)	1.38(2)	1.37(2)		
Mo^{II}(bpy)$_2$(OPr-*i*)$_2$	2.107(2)	1.388(4)	1.375(4)	1.405(4)	1.367(4)	1.418(4)	1.357(4)	1.425(4)	39
	2.123(2)	1.381(4)	1.376(4)	1.414(4)	1.358(4)	1.413(5)	1.359(4)	1.424(4)	
	2.126(2)	1.370(4)	1.373(4)	1.412(4)	1.371(5)	1.417(5)	1.357(4)		
	2.115(2)								
W^{II}(bpy)(PMe$_3$)$_2$Cl$_2$	2.085(6)	1.35(1)	1.38(1)	1.42(1)	1.37(1)	1.39(1)	1.37(1)	1.43(1)	52
	2.071(7)	1.39(1)	1.37(1)	1.40(1)	1.37(1)	1.38(1)	1.37(1)		
Re^I(bpy)(CO)$_3$(PO$_2$F$_2$)	2.14(1)	1.39(2)	1.35(2)	1.37(2)	1.37(2)	1.42(2)	1.42(2)	1.41(2)	53
	2.14(1)	1.37(2)	1.39(2)	1.42(2)	1.44(3)	1.37(3)	1.43(3)		
LUMO		antibond	antibond	antibond	bond	antibond	bond	bond	

(300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a General Electric QE-300 or GN-300 spectrometer at room temperature (23 °C). Chemical shifts are reported in parts per million and are referenced to residual solvent hydrogens (δ(acetone-d_5) = 2.04; δ(DMF-d_6) = 8.03; δ(CH$_3$CN-d_2) = 1.93). Electrochemical experiments were performed under nitrogen using a PAR Model 362 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded (Kipp and Zonen BD90 *XY* recorder) in a standard three-electrode cell from +2.00 to −2.20 V with a glassy carbon working electrode. All potentials are reported vs NHE and were determined in DMA or acetone (0.5 M TBAH) using ferrocene ($E_{1/2}$ = 0.55 V) or cobaltocinium hexafluorophosphate ($E_{1/2}$ = 0.78 V) *in situ* as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 70 and 100 mV for all reversible couples. Infrared spectra were recorded on a Mattson Cygnus 100 FT-IR spectrometer using either a KBr pellet or a glaze on a NaCl salt plate. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer. UV/vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

Solvents. All distillations were performed under nitrogen. All solvents were deoxygenated by purging with nitrogen for at least 20 min; deuterated solvents were deoxygenated by repeated freeze−pump−thaw cycles. Methylene chloride was refluxed for at least 8 h over P$_2$O$_5$ and distilled. Diethyl ether was refluxed for at least 8 h over Na^0/benzophenone and distilled. Methanol was refluxed over Mg(OMe)$_2$, prepared *in situ* from Mg^0 activated by I$_2$, and distilled. Acetonitrile was refluxed over CaH$_2$ and distilled. DMA was dried over CaH$_2$, refluxed for 24 h, and vacuum distilled. Acetone was deoxygenated prior to use. Benzene and hexanes were each refluxed for at least 24 h over Na^0/benzophenone and distilled. DME was refluxed over Na^0 and distilled.

Reagents. Re^{III}(CH$_3$CN)(PPh$_3$)$_2$Cl$_3$ **(1)** and Re^{III}Cl$_3$(benzil)PPh$_3$ **(2)** were prepared according to literature methods.[7] TMPA was prepared according to literature methods.[40] Magnesium powder (Aldrich, 50 mesh) was activated by treatment with iodine in DME under nitrogen, stirring for several hours, and washing with DMA, DME, acetone, and Et$_2$O. Zn^0/Hg^0 was prepared from granulated zinc (30 mesh), HgCl$_2$, and HCl. All of the other reagents were used as purchased.

Synthesis. *cis*-[Re^{III}(bpy)$_2$Cl$_2$]PF$_6$ (3). Re^{III}Cl$_3$(benzil)PPh$_3$ (**2**, 0.757 g, 0.990 mmol) was suspended in DME (150 mL). Bpy (1.019 g, 6.54 mmol) and TlPF$_6$ (0.376 g, 1.08 mmol) were each dissolved in 10 mL of DME and added sequentially. The bright purple reaction mixture was stirred for 2 h and then refluxed for 10.5 h. The reaction was cooled and stirred at room temperature for 2 h. The mixture was filtered through Celite, and the remaining solid was washed with DME (2 × 3 mL). The blue-black filtrate was discarded. The product was dissolved in DMA (4 × 2 mL) and filtered through the Celite. The filtrate was added dropwise to stirring Et$_2$O/CH$_2$Cl$_2$ (110 mL, 10:1). The resulting purple precipitate was filtered, washed with Et$_2$O (2 × 3 mL), and dried *in vacuo*; yield = 0.510 g (0.715 mmol, 72%). X-ray quality crystals were obtained from vapor diffusion of an acetone solution of the complex with Et$_2$O. ^{1}H NMR (acetone-d_6): δ 19.64 (t, 2H), 15.81 (t, 2H), 14.67 (d, 2H), 9.65 (t, 4H), 9.36 (d, 2H), −4.82 (t, 2H), −9.04 (t, 2H). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,a}$(IV/III) = 0.99 V, $E_{1/2}$(III/II) = −0.20 V, $E_{1/2}$(II/I) = −1.01 V vs NHE. UV−vis (DMA; λ, nm (ϵ, M^{-1} cm^{-1})): 296 (6230), 392 (1090), 596 (868). Anal. Calcd for C$_{20}$H$_{16}$N$_4$Cl$_2$F$_6$PRe: C, 33.62; H, 2.24; N, 7.84. Found: C, 33.59; H, 2.22; N, 7.67.

***cis*-[Re^{III}(tbpy)$_2$Cl$_2$]PF$_6$ (4).** Re^{III}Cl$_3$(benzil)PPh$_3$ (**2**, 0.538 g, 0.703 mmol) was suspended in DME (110 mL). Tbpy (0.536 g, 1.99 mmol) and TlPF$_6$ (0.269 g, 0.770 mmol) were each dissolved in 10 mL of DME and added sequentially. The bright purple reaction mixture was stirred at room temperature for 1 h and then refluxed for 4.5 h; a white precipitate formed. After stirring at room temperature for 2 h, the mixture was filtered through Celite, and the solids were washed with DME (2 × 4 mL). The washings and the filtrate were combined, and the volume was reduced to ~40 mL by evaporation. A solution of hexanes/Et$_2$O (70:30) was added slowly until a precipitate was observed (~150 mL). The purple precipitate was filtered, washed with hexanes (2 × 5 mL), and dried *in vacuo*; yield = 0.547 g (0.580 mmol, 83%). ^{1}H NMR (acetone-d_6): δ 19.65 (d, 2H), 15.70 (d, 2H), 14.12 (d, 2H), 8.46 (d, 2H), 9.66 (s, 4H); 2.07 (s, 18H), 1.16 (s, 18H). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,a}$(IV/III) = +0.96 V, $E_{1/2}$(III/II) = −0.30 V, $E_{1/2}$(II/I) = −1.14 V vs NHE. Anal. Calcd for C$_{36}$H$_{48}$N$_4$Cl$_2$F$_6$PRe: C, 45.87; H, 5.10; N, 5.95. Found: C, 46.35; H, 5.20; N, 5.94.

***cis*-[Re^{III}(phen)$_2$Cl$_2$]OTf (5).** Re^{III}Cl$_3$(benzil)PPh$_3$ (**2**, 0.344 g, 0.449 mmol) was suspended in DME (50 mL). Phen (0.218 g, 1.21 mmol)

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and TlOTf (0.161 g, 0.456 mmol) were each dissolved in 5 mL of DME and added sequentially. The bright purple reaction mixture was refluxed for 6 h and then stirred overnight at room temperature. A precipitate formed. The mixture was filtered and the solid washed with DME (2 × 2 mL). The filtrate and washings were discarded. The solid was dissolved in DMA (2 × 2 mL) and filtered through Celite, and then the filtrate was added dropwise to stirring Et_2O/CH_2Cl_2 (70 mL, 80:20). The resulting blue precipitate was filtered, washed with CH_2Cl_2 (3 × 3 mL), Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.190 g (0.249 mmol, 55%). ^{1}H NMR (acetone-d_6): δ 19.40 (t, 2H), 15.05 (t, 2H), 11.78 (d, 2H), 7.25 (d, 2H), 5.68 (d, 2H), 1.91 (d, 2H), −5.34 (d, 2H), −11.04 (d, 2H). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,a}$(IV/III) = +0.95 V, $E_{1/2}$(III/II) = −0.25 V, $E_{1/2}$(II/I) = −0.94 V vs NHE. Anal. Calcd for $C_{25}H_{16}N_4Cl_2F_3O_3ReS$: C, 39.14; H, 2.09; N, 7.31. Found: C, 38.72; H, 2.16; N, 6.76.

$[Re^{II}(bpy)_3](PF_6)_2$ (6).[11] $Re^{III}Cl_3(benzil)PPh_3$ (**2**, 0.451 g, 0.590 mmol) was suspended in 10 mL of DME. Bpy (1.637g, 10.5 mmol) and $TlPF_6$ (0.681 g, 1.95 mmol) were each dissolved in 3 mL of DME and added sequentially. The reaction was stirred at room temperature for 45 min and then refluxed for 15 h. After cooling for 3 h at room temperature, the purple mixture was filtered, and the solid was washed with DME (2 × 5 mL). The filtrate and washings were discarded. The product was dissolved in DMA (3 × 2 mL) and filtered away from the remaining TlCl. The filtrate was added dropwise to stirring Et_2O (100 mL). The resulting purple precipitate was filtered, washed with Et_2O (2 × 4 mL), and dried *in vacuo*; yield = 0.463 g (0.490 mmol, 83%). CV (DMA/TBAH/100 mV/s): $E_{1/2}$(III/II) = 0.61 V, $E_{1/2}$(II/I) = −0.33 V, $E_{1/2}$(I/0) = −1.22 V, $E_{1/2}$(0/−I) = −1.62 V vs NHE. UV−vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})): 298 (43 100), 398 (11 200), 526 (8290), 668 (8600). Anal. Calcd for $C_{30}H_{24}N_6F_{12}P_2Re$: C, 38.14; H, 2.54; N, 8.90. Found: C, 37.99; H, 2.67; N, 8.94.

$[Re^{II}(tbpy)_3](OTf)_2$ (7). $Re^{III}Cl_3(benzil)PPh_3$ (**2**, 0.188 g, 0.246 mmol) was suspended in 5 mL of DME. Tbpy (0.848 g, 3.14 mmol) and TlOTf (1.019 g, 2.88 mmol) were each dissolved in 2 mL of DME and added sequentially. The reaction was refluxed for 10 h, cooled, and then filtered through Celite. The solids were washed with DME (3 × 2 mL). The precipitate was dissolved in DMA (3 mL), filtered, and washed with CH_2Cl_2 (3 mL). The filtrate was evaporated to ∼3 mL and then added dropwise to stirring Et_2O (75 mL). The blue precipitate was filtered, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.191 g (0.148 mmol, 60%). Analytically pure material was obtained from neutral alumina chromatography followed by vapor diffusion of an acetone solution of the complex with CH_2Cl_2/hexanes. CV (DMA/TBAH/100 mV s^{-1}): $E_{1/2}$(III/II) = 0.49 V, $E_{1/2}$(II/I) = −0.47 V, $E_{1/2}$(I/0) = −1.35 V, $E_{1/2}$(0/−I) = −1.75 V vs NHE. UV−vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})): 298 (47 400), 428 (9140), 472 (9270), 500 (8750), 680 (3210). Anal. Calcd for $C_{56}H_{72}N_6F_6O_6ReS_2\cdot{}^3/_2CH_2Cl_2$: C, 48.54; H, 5.28; N, 5.91. Found: C, 48.86; H, 5.40; N, 5.93.

$[Re^{II}(phen)_3](PF_6)_2$ ([8]PF_6). $Re^{III}Cl_3(benzil)PPh_3$ (**2**, 0.390 g, 0.510 mmol) was dissolved in DME (5 mL) and DMA (4 mL). Phen (1.052 g, 5.84 mmol) and $TlPF_6$ (0.667 g, 1.89 mmol) were each dissolved in DME (2 mL) and added sequentially. The reaction was heated in an oil bath (∼85 °C) for 3 h and then cooled overnight at room temperature. The mixture was filtered and the precipitate washed with DME (2 × 2 mL). The filtrate and washings were discarded. The purple solid was dissolved in DMA (3 mL) and filtered, giving a purple filtrate and a white solid. The filtrate was added dropwise to stirring Et_2O/CH_2Cl_2 (120 mL, 90:10). The resulting precipitate was filtered and washed with benzene (3 × 3 mL) and Et_2O (3 × 3 mL). The filter cake was redissolved in CH_2Cl_2 (10 mL) and filtered. The filtrate was added to stirring Et_2O (100 mL). The resulting blue precipitate was filtered, washed with Et_2O (2 × 3 mL), and dried *in vacuo;* yield = 0.476 g (0.468 mmol, 92%). Analytically pure material was obtained from Sephadex (CM C-25, 40−120 μ) chromatography. The solid was loaded on the column with a H_2O/acetone solution and washed with 0.05 M HCl and the purple band eluted with 1 M HCl. A saturated solution of NH_4PF_6 was added to the fraction, and the resulting purple precipitate was filtered, washed with H_2O (2 × 2 mL), and dried *in vacuo*. CV (DMA/TBAH/100 mV s^{-1}): $E_{1/2}$(III/II) = 0.56 V, $E_{1/2}$(II/I) = −0.31 V, $E_{1/2}$(I/0) = −1.21 V, $E_{1/2}$(0/−I) = −1.58 V vs NHE. Anal. Calcd for $C_{36}H_{24}N_6F_{12}P_2Re\cdot H_2O$: C, 41.75; H, 2.51; N, 8.12. Found: C, 41.46; H, 2.13; N, 7.95.

$[Re^{II}(phen)_3](OTf)_2$ ([8]OTf). $Re^{III}Cl_3(benzil)PPh_3$ (**2**, 0.282 g, 0.368 mmol) was dissolved in DMA (3 mL). Phen (0.235 g, 1.30 mmol) and TlOTf (0.145 g, 0.410 mmol) were each dissolved in 1 mL of DMA. The reaction was heated in an oil bath at 92−94 °C for 48 h, cooled for 2 h, and then filtered. The filtrate was added dropwise to stirring Et_2O/CH_2Cl_2 (100 mL, 70:30). The resulting purple precipitate was filtered, washed with benzene (2 × 2 mL) and Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.252 g (0.246 mmol, 67%). Analytically pure material was obtained from neutral alumina chromatography. The solid was loaded on the column with CH_2Cl_2, washed with CH_2Cl_2, and eluted with DME. The electrochemistry is identical to that of the PF_6 salt. UV−vis (CH_3CN, λ, nm (ϵ, M^{-1} cm^{-1})): 266 (75 600), 386 (7310), 532 (11 300), 658 (9520), 718 (6470). Anal. Calcd for $C_{38}H_{24}N_6F_6O_6ReS_2$: C, 44.50; H, 2.34; N, 8.20. Found: C, 44.40; H, 2.47; N, 8.73.

$Re^{III}(terpy)Cl_3$ (9).[10] $Re^{III}Cl_3(CH_3CN)(PPh_3)_2$ (**1**, 1.059 g, 1.78 mmol) was dissolved in DMA (7 mL). Terpy (0.854 g, 3.66 mmol), also dissolved in DMA (1 mL), was added to this orange solution. The solution was heated in an oil bath at 75 °C for 16 h, then cooled, and stirred for 3 h at room temperature. CH_2Cl_2 (4 mL) was added, followed by the slow addition of Et_2O (40 mL). The resulting black precipitate was filtered, washed with Et_2O (3 × 3 mL), and dried *in vacuo*; yield = 0.756 g (1.44 mmol, 81%). ^{1}H NMR (DMF-d_7): δ 23.27 (t, 2H), 6.68 (d, 2H), −0.67 (d, 2H), −11.01 (t, 1H), −15.02 (t, 2H), −24.45 (d, 2H). CV (DMA/TBAH/100 mV s^{-1}): $E_{1/2}$(IV/III) = 0.52 V, $E_{1/2}$(III/II) = −0.49 V, $E_{p,c}$(II/I) = −1.51 V vs NHE. Alternatively, $Re(terpy)Cl_3$ could be prepared from $Re^{III}(benzil)(PPh_3)Cl_3$ (**2**), DMA, and terpy as above with heating to 100 °C for 12 h; yield = 80%. Anal. Calcd for $C_{15}H_{11}N_3Cl_3Re$: C, 34.26; H, 2.11; N, 7.99. Found: C, 34.78; H, 2.16; N, 7.89.

$[Re^{III}(terpy)_2Cl](PF_6)_2$ (10).[8] $Re^{III}(benzil)(PPh_3)Cl_3$ (**2**, 0.219 g, 0.286 mmol) was dissolved in 1.5 mL of DMA and 15 mL of DME, forming a bright purple solution. Terpy (0.259 g, 1.11 mmol) and $TlPF_6$ (0.303 g, 0.867 mmol) were each dissolved in 5 mL of DME and added to the purple solution sequentially. The solution was stirred at room temperature for 30 min and then refluxed for 12 h. A precipitate of TlCl and a dark solid formed. The solids were filtered from the dark purple solution after cooling to room temperature. The dark precipitate was dissolved in 10 mL of acetone and filtered from the remaining TlCl. The filtrate was added to 40 mL of stirring Et_2O. A dark red-purple precipitate formed immediately and was filtered off, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.196 g (0.200 mmol, 70%). ^{1}H NMR (acetone-d_6): δ 9.59 (d, 2H), 9.46 (d, 2H), 9.30 (d, 2H), 8.90 (d, 2H), 8.34 (t, 2H), 8.28 (t, 2H), 8.20, (t, 2H) 8.10 (d, 2H), 7.32 (d, 2H), 7.20 (m, 4H). CV (DMA/TBAH/100 mV s^{-1}): $E_{1/2}$(IV/III) = 1.37 V, $E_{p,c}$(III/II) = −0.53 V vs NHE. CV (acetone/TBAH/100 mV s^{-1}): $E_{1/2}$(IV/III) = 1.43 V, $E_{p,c}$(III/II) = −0.43 V vs NHE. UV−vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})): 210 (58 700), 294 (48 600), 330 (34 200), 498 (13 100). Anal. Calcd for $C_{30}H_{22}N_6ClF_{12}P_2Re$: C, 36.84; H, 2.27; N, 8.60. Found: C, 37.27; H, 2.59; N, 8.22.

$[Re^{III}(TMPA)Cl_2]PF_6$ (11). $Re^{III}(benzil)(PPh_3)Cl_3$ (**2**, 0.100 g, 0.130 mmol) was suspended in 5 mL of benzene. The TMPA (0.041 g, 0.14 mmol) was dissolved in 3 mL of benzene and added to the stirring rhenium suspension. The $TlPF_6$ (0.050 g, 0.14 mmol) was dissolved in 2 mL of DME and added to the reaction mixture. The reaction was refluxed for 72 h and then cooled at room temperature overnight. A dark red precipitate formed with the white TlCl precipitate. The brown solution was filtered off, and the remaining solid was dissolved in 3 mL of acetone and filtered from the TlCl. This bright red filtrate was added to 50 mL of stirring Et_2O. The resulting red precipitate was filtered off, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.059 g (0.085 mmol, 65%). ^{1}H NMR (acetone-d_6): δ 26.63 (t, 2H), 24.80 (d, 2H), 21.36 (t, 1H), 16.07 (d, 2H), 12.14 (d, 1H), 8.63 (d, 2H), 7.84 (t, 2H), 7.39 (d, 1H), 5.00 (t, 1H), −10.11 (d, 2H), −13.99 (s, 2H). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,a}$(IV/III) = 0.81 V, $E_{1/2}$(III/II) = −0.91 V, $E_{p,c}$(II/I) = −1.85 V vs NHE. CV (acetone/TBAH/100 mV s^{-1}): $E_{1/2}$(IV/III) = 0.79 V, $E_{1/2}$(III/II) = −0.75 V, $E_{p,c}$(II/I) = −1.61 V vs NHE. Anal. Calcd for $C_{18}H_{18}N_4Cl_2F_6PRe$: C, 31.22; H, 2.62; N, 8.09. Found: C, 32.44; H, 2.60; N, 7.94.

***cis*-$Re^{II}(bpy)_2Cl_2$ (12).** Excess Zn^0/Hg^0 (2.6 g) was added to a blue suspension of *cis*-$[Re^{III}(bpy)_2Cl_2]PF_6$ (**3**, 0.139 g, 0.195 mmol) in MeOH

(6 mL). The mixture was stirred vigorously for 2 h, changing to dark brown, and then filtered. The solid collected with the zinc amalgam was dissolved in DMA and filtered off of the remaining amalgam. CH_2Cl_2 (2 mL) was added to the filtrate, and this solution was added dropwise to stirring Et_2O (75 mL). The resulting black precipitate was filtered, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.058 g (0.10 mmol, 52%). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,a}$(IV/III) = 0.99 V, $E_{1/2}$(III/II) = −0.20 V, $E_{1/2}$(II/I) = −1.01 V vs NHE. Anal. Calcd for $C_{20}H_{16}N_4Cl_2Re$: C, 42.18; H, 2.83; N, 9.84. Found: C, 41.77; H, 3.03; N, 9.25.

$[Re^{III}(^tBuNC)(bpy)_2Cl_2]PF_6$ (13). Excess *tert*-butylisonitrile (0.5 mL, 300 mg) was added to a blue/black solution of *cis*-$[Re^{III}Cl_2(bpy)_2]PF_6$ (**3**, 0.149 g, 0.208 mmol) in DMA (1 mL) and DME (2 mL), causing an immediate color change. The orange mixture was stirred for 20 min and then filtered. The filtrate was added dropwise to stirring Et_2O (50 mL). The resulting orange precipitate was filtered, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.131 g (0.164 mmol, 79%). ^1H NMR (CD_3CN): δ 9.93 (d, 1H), 9.79 (d, 1H), 8.85 (d, 2H), 8.79 (d, 1H), 8.66 (d, 1H), 8.13 (t, 1H), 8.05 (d, 1H), 7.97 (t, 2H), 7.86 (t, 1H), 7.77 (overlapping t, 2H), 7.08 (t, 1H), 7.02 (t, 1H), 6.83 (d, 1H), 1.23 (s, 9H). CV (DMA/TBAH/100 mV s^{-1}): $E_{1/2}$(IV/III) = 1.12 V, $E_{p,c}$(III/II) = −0.85 V vs NHE. IR (KBr pellet): ν_{NC} = 2153 cm^{-1} (med). Anal. Calcd for $C_{25}H_{25}N_5Cl_2F_6PRe$: C, 37.64; H, 3.14; N, 8.78. Found: C, 37.81; H, 3.63; N, 8.68.

$[Re^{III}(tbpy)_2(^tBuNC)Cl_2]PF_6$ (14). Excess *tert*-butylisonitrile (0.5 mL, 300 mg) was added to a suspension of *cis*-$[Re^{III}Cl_2(tbpy)_2]PF_6$ (**4**, 0.192 g, 0.204 mmol) in DME (2 mL). The red mixture was stirred for 2 h at room temperature and then filtered. An orange solid was filtered from the red filtrate. The solid was washed with DME (2 × 2 mL) and dried *in vacuo*; yield = 0.155 g (0.151 mmol, 74%). ^1H NMR (CD_3CN): δ 9.79 (d, 1H), 9.64 (d, 1H), 8.77 (s, 1H), 8.72 (s, 1H), 8.68 (s, 1H), 8.59 (s, 1H), 7.82 (overlapping d, 2H), 7.35 (d, 1H), 7.09 (td, 2H), 6.64 (d, 1H), 1.54 (s, 9H), 1.53 (s, 9H), 1.40 (s, 9H), 1.37 (s, 9H), 1.22 (s, 9H). CV (DMA/TBAH/100 mV s^{-1}): $E_{1/2}$(IV/III) = 1.05 V, $E_{p,c}$(III/II) = −1.06 V vs NHE. IR (KBr pellet): ν_{NC} = 2131 cm^{-1} (med). Anal. Calcd for $C_{41}H_{57}N_5Cl_2F_6PRe$: C, 48.00; H, 5.56; N, 6.83. Found: C, 48.21; H, 5.76; N, 6.79.

$[Re^{III}(^tBuNC)(phen)_2Cl_2]OTf$ (15). An excess of *tert*-butylisonitrile (0.216 g, 2.60 mmol) was added to a solution of *cis*-$[Re^{III}Cl_2(phen)_2]OTf$ (**5**, 0.146 g, 0.191 mmol) dissolved in DMA (0.5 mL) and DME (1 mL). The red mixture was stirred for 4.5 h. The mixture was filtered and the filtrate added to Et_2O/CH_2Cl_2 (100 mL, 90:10). The resulting orange precipitate was filtered, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.091 mg (0.11 mmol, 56%). The NMR is broadened with ill-defined resonances at 10.6, 9.9, 9.6, 9.0, 8.4, 7.8, 7.7, and 1.6 ppm. CV (DMA/TBAH/100 mV s^{-1}): $E_{1/2}$(IV/III) = 1.10 V, $E_{p,c}$(III/II) = −0.61 V vs NHE. IR (KBr pellet): ν_{NC} = 2185 cm^{-1} (str). Anal. Calcd for $C_{30}H_{25}N_5F_3O_3ReS$: C, 42.35; H, 2.94; N, 8.23. Found: C, 42.08; H, 3.38; N, 8.37.

$[Re^{III}(bpy)_2(^tBuNC)_3](OTf)_3$ (16). $[Re^{III}(bpy)_2(^tBuNC)Cl_2]PF_6$ (**13**, 0.091 g, 0.11 mmol) was dissolved in 5 mL of acetone. Excess ^tBuNC (0.114 g, 1.38 mmol) was added. Excess NaOTf (0.482 g, 2.80 mmol) was dissolved in acetone (3 mL) and added to the stirring orange solution. The reaction was allowed to stir for 2 h with a color change from orange to yellow, and the solution became cloudy. The reaction mixture was filtered, and the clear filtrate was reduced in volume to 1 mL. The solution was precipitated with 50 mL of Et_2O. The pale orange/yellow precipitate was filtered off, washed with Et_2O, and dried *in vacuo*; yield = 0.105 g (0.087 mmol, 80%). ^1H NMR (acetone-d_6): δ 9.02 (d, 4H), 8.81 (d, 4H), 8.52 (t, 4H), 7.92 (t, 4H), 1.62 (s, 9H), 1.48 (s, 18H). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,c}$(III/II) = −0.61 V vs NHE. IR (KBr pellet): ν_{NC} = 2189 and 2164 cm^{-1}. Anal. Calcd for $C_{38}H_{43}N_7F_9O_9ReS_3\cdot{}^3/_2NaCF_3SO_3$: C, 32.74; H, 3.00; N, 6.77. Found: C, 32.55; H, 3.25; N, 6.60. Repeated attempts to remove the excess NaOTf through reprecipitations and chromatography (LH-20 and alumina) failed to completely purify the complex. Reducing the amount of NaOTf used in the reaction or using another reagent like $TlPF_6$ lead to a less pure product. This product can also be directly produced from $[Re^{III}(bpy)_2Cl_2]PF_6$ **(3)** and NaOTf, but the reaction also does not proceed as cleanly as by this method.

***cis*-$[Re^{I}(bpy)_2(^tBuNC)_2]PF_6$ (17).** $[Re^{III}(bpy)_2(^tBuNC)Cl_2]PF_6$ (**13**, 0.124 g, 0.156 mmol) was suspended in 3 mL of MeOH, and excess ^tBuNC (0.146 g) was added followed by excess Zn^0/Hg^0 (0.925 g). The orange suspension was stirred for 3 h, changing to a dark brown solution. The Zn^0/Hg^0 was filtered off, and the solvent volume was reduced to 1 mL. The black solution was added to 25 mL of stirring Et_2O, and the resulting black precipitate was filtered off and discarded. The filtrate was reduced in volume to a black oil. DME (3 mL) was added to the oil followed by 50 mL of Et_2O. Another 25 mL of hexanes was added slowly to prevent oiling, and a black precipitate was filtered off, washed with Et_2O, and dried *in vacuo*; yield = 0.064 g (0.079 mmol, 51%). The remaining inorganic impurities were removed by column chromatography using LH-20 and eluting with CH_2Cl_2. ^1H NMR (acetone-d_6): δ 9.55 (d, 2H), 8.56 (t, 4H), 7.85 (m, 4H), 7.52 (m, 4H), 7.27 (m, 2H), 1.18 (s, 18H). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,a}$(III/II) = 1.18 V, $E_{1/2}$(II/I) = 0.22 V, $E_{1/2}$(I/0) = −1.30 V, $E_{1/2}$(0/−I) = −1.62 V vs NHE. UV−vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})): 244 (34 000), 292 (36 400), 298 (23 100), 378 (9460), 512 (7440), 612 (6860). IR (KBr pellet): ν_{NC} = 2094 and 2048 cm^{-1}. Anal. Calcd for $C_{30}H_{34}N_6F_6PRe$: C, 44.50; H, 4.23; N, 10.38. Found: C, 42.59; H, 4.40; N, 10.10.

***cis*-$[Re^{III}(bpy)_2(OMe)_2]PF_6$ (18).** *cis*-$[Re^{III}Cl_2(bpy)_2]PF_6$ (**3**, 0.077 g, 0.11 mmol) was dissolved in a solution of pyrrolidine (0.342 g, 4.82 mmol) in MeOH (7 mL). The deep green solution was stirred for 3.5 h and then filtered. The volume of the filtrate was reduced to ∼4 mL, and then the solution was added dropwise to a stirring solution of hexanes/Et_2O (35 mL, 90:10). The resulting blue precipitate was filtered, washed with hexanes (2 × 2 mL), and dried *in vacuo*; yield = 0.058 g (0.082 mmol, 76%). ^1H NMR (CD_3CN): δ 8.90 (d, 2H), 8.76 (d, 2H), 8.07 (d, 2H), 7.90 (t, 2H), 7.56 (t, 2H), 7.16 (t, 2H), 6.95 (t, 2H), 6.62 (d, 2H), 3.71 (s, 6H). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,a}$(IV/III) = 0.53 V, $E_{1/2}$(III/II) = −0.81 V, $E_{1/2}$(II/I) = −1.34 V vs NHE. Anal. Calcd for $C_{22}H_{22}N_4F_6O_2PRe$: C, 37.44; H, 3.12; N, 7.94. Found: C, 37.52; H, 2.86; N, 7.86.

$[Re^{I}(bpy)_3]PF_6$ (19). Excess Zn^0/Hg^0 (2.68 g) was added to a suspension of $[Re^{II}(bpy)_3](PF_6)_2$ (**6**, 0.246 g, 0.260 mmol) in MeOH (3 mL). The reaction was stirred vigorously for 1 h and filtered. The solids were washed with MeOH (2 × 2 mL). The filtrate and washings were discarded. The precipitate was dissolved in DMA (3 mL) and filtered from the remaining amalgam. This filtrate was added dropwise to a mixture of stirring Et_2O/CH_2Cl_2 (65 mL, 30:1). The resulting black precipitate was filtered, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.190 g (0.237 mmol, 91%). X-ray quality crystals were obtained from vapor diffusion of an acetone solution of the complex with Et_2O/hexanes. ^1H NMR (acetone-d_6): δ 8.29 (d, 6H), 7.39 (d, 6H), 7.00 (t, 6H), 6.81 (t, 6H). CV (DMA/TBAH/100 mV/s): $E_{p,a}$(III/II) = 0.61 V, $E_{1/2}$(II/I) = −0.33 V, $E_{1/2}$(I/0) = −1.22 V, $E_{1/2}$(0/−I) = −1.62 V vs NHE. UV−vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})): 290 (30 000), 444 (20 300), 506 (17 400), 823 (13 100). Anal. Calcd for $C_{30}H_{24}N_6F_6PRe$: C, 45.06; H, 3.00; N, 10.51. Found: C, 44.47; H, 3.15; N, 10.63.

$[Re^{III}(bpy)_3(^tBuNC)](PF_6)_2OTf$ (20). $[Re^{II}(bpy)_3](PF_6)_2$ (**6**, 0.103 g, 0.109 mmol) was dissolved in 10 mL of acetone, and ^tBuNC (0.058 g, 0.70 mmol) was added. AgOTf (0.032 g, 0.13 mmol) was dissolved in 3 mL of acetone and added to the stirring blue solution. A precipitate began to form immediately, and the solution became green and then yellow. After 2 h, the precipitate was filtered off, and the solvent volume of the filtrate was reduced to 3 mL. The yellow-brown solution was dropped into 40 mL of stirring Et_2O. The orange precipitate was filtered off, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.115 g (0.0982 mmol, 90%). ^1H NMR (acetone-d_6): δ 9.14 (m, 6H), 8.81 (d, 3H), 8.45 (t, 3H), 8.33 (t, 3H), 7.66 (d, 3H), 7.61 (m, 6H), 1.35 (s, 9H). CV (acetone/TBAH/100 mV s^{-1}): $E_{p,c}$(III/II) = −0.39 V vs NHE. UV−vis (CH_3CN; λ, nm (M^{-1} cm^{-1})): 200 (55 200), 218 (39 000), 254 (22 700), 298 (37 300), 322 (s 22 400), 420 (8260), 474 (5860). IR (KBr pellet): ν_{NC} = 2179 cm^{-1} (str). Anal. Calcd for $C_{36}H_{33}N_7F_{15}O_3P_2ReS$: C, 36.74; H, 2.83; N, 8.33. Found: C, 37.44; H, 3.02; N, 8.33.

$[Re^{I}(terpy)_2]PF_6$ (21). Excess Zn^0/Hg^0 (1.02 g) was added to a solution of $[Re^{III}(terpy)_2Cl](PF_6)_2$ (**10**, 0.099 g, 0.10 mmol) in 5 mL of MeOH. The solution rapidly changed from dark red to yellow-brown. The reaction was stirred for 3 h. The Zn^0/Hg^0 was filtered off along with a black precipitate. The filtrate was discarded. The black precipitate was redissolved in 10 mL of acetone and then filtered. The filtrate was reduced to 3 mL of volume and added to 125 mL of stirring Et_2O. A dark brown-green precipitate formed that was filtered off, washed with Et_2O (2 × 2 mL), and dried *in vacuo*; yield = 0.061 g (0.077 mmol, 75%). ^{1}H NMR (acetone-d_6): δ 9.07 (d, 4H), 8.72 (d, 4H), 7.26 (m, 4H), 7.14 (t, 4H), 6.52 (m, 8H). CV (DMA/TBAH/100 mV s^{-1}): $E_{p,a}$(III/II) = 0.36 V, $E_{1/2}$(II/I) = 0.12 V, $E_{1/2}$(I/0) = −1.42 V, $E_{1/2}$(0/−I) = −1.76 V vs NHE. CV (acetone/TBAH/100 mV s^{-1}): $E_{p,a}$(III/II) = 0.42 V, $E_{1/2}$(II/I) = 0.12 V, $E_{1/2}$(I/0) = −1.44 V, $E_{1/2}$(0/−I) = −1.72 V vs NHE. UV−vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})): 206 (38 200), 226 (40 800), 284 (32 800), 314 (31 600), 438 (19 800), 558 (10 900), 706 (9620). Anal. Calcd for $C_{30}H_{22}N_6F_6PRe$: C, 45.17; H, 2.78; N, 10.54. Found: C, 44.50; H, 2.78; N, 10.51.

Crystal Structure of *cis*-[$Re^{III}(bpy)_2Cl_2$]PF_6 (3) and [$Re^{I}(bpy)_3$]PF_6 (19). All X-ray data were collected on a Rigaku AFC6S diffractometer at −100 °C using graphite-monochromated Mo Kα radiation.

Compound 3. A black needle of dimensions 0.24 × 0.18 × 0.45 mm was used for the data collection. Intensities of three standard reflections were monitored, showing neither significant decay nor instrument instability. Empirical absorption corrections were applied by using ψ scans of several reflections. The transmission factors were in the range 0.74−1.00. All calculations were performed on a VAX station 3520 computer with the TEXSAN 5.0 software package. The structure was solved by direct methods (SIR88). Full-matrix least-squares refinement with anisotropic thermal displacement parameters for all non-hydrogen atoms yielded a final R of 0.033 (R_w = 0.042). The final difference Fourier map showed a peak of 1.72 e/Å^3 in the vicinity of the rhenium atom.

Compound 19. A black prismatic crystal of dimensions 0.31 × 0.35 × 0.46 mm was selected for the X-ray experiments. Generally, the diffraction pattern was good, producing sharp, well-defined peaks. No decay nor instrument instability were observed. Empirical absorption corrections with the transmission factors ranging from 0.61 to 1.00 were applied. As for the previous structure, all calculations were done with the TEXSAN 5.0 software and the structure was solved by applying the direct methods program SIR88. Full-matrix least-squares refinement with anisotropic thermal displacement parameters gave a final R of 0.035 (R_w = 0.040). The final difference map had a peak of 1.34 e/Å^3 in the vicinity of the rhenium atom.

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Supporting Information Available: Tables of values for the plots of electrochemical potentials vs the sum of the ligand parameters and experimental details, atomic position parameters, thermal parameters, and bond distances and angles for *cis*-[$Re^{III}(bpy)_2Cl_2$]PF_6 (**3**) and [$Re^{I}(bpy)_3$]PF_6 (**19**), figures of the cyclic voltammagram of **3**, electrochemical potentials vs the sum of ligand parameters for Re couples, near IR spectrum of **19**, and ORTEP drawings for **3** and **19**, and text of least-squares minimization (15 pages). Ordering information is given on any current masthead page.

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