$(bpy)_2Ru^{III}(bpy^{-}\cdot)^{2+*} \rightarrow (bpy)_2Ru^{II}(bpy)^{2+}$, and ligand to ligand electron transfer, $(bpy)_2Ru^{III}(bpy^{-}\cdot)^{2+*} \rightarrow (bpy)(bpy^{-}\cdot)Ru^{III}(bpy)^{2+*}$, are related processes. With nonnegligible vibrational trapping, localization is expected to occur if electronic coupling between ligands is small.

Optical excitation is rapid (10^{-15} s) on the time scale for vibrational equilibration so that the excited states are formed in the solvent and vibrational environments of the symmetrical ground states. In the absorption experiment there is no significant basis for vibrational or solvent trapping of the excited electron, and yet our data show that electron transfer in the initial excitation is confined to a single ligand. This apparent paradox can be resolved if electronic coupling is weak. In the absence of any trapping, the frequency of electron hopping between ligands is given by $\nu \approx 4V/h$,[37] which neglects statistical effects. Even with V = 800 cm^{-1} (0.1V), $\nu \approx 10^{14}$ s^{-1} and electron hopping between ligands would be too slow to couple with electronic excitation. The same conclusions should apply to the excited states in polymeric films, glasses, or crystals. Even in the absence of medium or vibrational trapping, relatively strong electronic coupling between bpy ligands is required for electron hopping to become competitive with the time scale for an individual emission event.

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Os(bpy)_3^{2+}$, 23648-06-8; $Os(bpy)_3(py)_2^{2+}$, 47779-78-2; $Os(bpy)_2(CH_3CN)_2^{2+}$, 75441-70-2; $Os(bpy)_2(dppb)^{2+}$, 80502-63-2.

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Synthetic Routes to Luminescent 2,2′-Bipyridyl Complexes of Rhenium: Preparation and Spectral and Redox Properties of Mono(bipyridyl) Complexes of Rhenium(III) and Rhenium(I)

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New methods of preparing 2,2′-bipyridyl (bpy) complexes of rhenium are described. The procedures involve starting complexes of Re(IV), Re(III), and Re(I) and result in new bpy complexes of the type *fac*-$Re^{III}(bpy)(P)Cl_3$, *trans,cis*-$[Re^{III}(bpy)(P)_2Cl_2]^+$, and *trans,cis*-$[Re(bpy)(P)_2(CO)_2]^+$, where P is a tertiary phosphine. In addition, the complex *cis*-$[Re(bpy)_2(CO)_2]^+$ has been prepared, which is a rare example of a bis(bipyridyl)rhenium species. Aspects of the NMR spectra, electronic spectra, and electrochemistry of the complexes are discussed, and special attention is given to the fact that the Re^I(bpy) complexes luminescence in fluid solution at room temperature. They represent a growing class of potentially exploitable metal-to-ligand charge-transfer (MLCT) excited-state species of Re(I) that have potential interest for use in photochemical energy conversion schemes.

There is now an extensive photochemistry of charge-transfer (CT) excited states based on polypyridyl acceptor ligands such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) and spin-paired d^6 donor metals like Ir(III),[1] Ru(II),[1] Os(II),[1,2-5] Re(I),[5,6,8] W(0), and Mo(0).[5,7] One of our goals is the development of synthetic procedures for the preparation of emitting excited states. Earlier we described the excited-state properties of a series of Os(II)–bpy and –phen complexes[2] of the type $Os(bpy)_2L_2^{2+}$ and $Os(bpy)L_4^{2+}$ (L = py, $^1/_2$bpy, $^1/_2$phen, PR_3, AsR_3, CH_3CN, ...), which have long-lived CT excited states in fluid solution at room temperature.[2b]

In this paper we describe an extension of our synthetic efforts to a new series of luminescent CT excited states based on Re(I) of the type $Re^I(bpy)L_2(CO)_2^+$. An initial example of this type of excited state, *trans,cis*-$[Re^I(phen)(PPh_3)_2(CO)_2]^+$, has been previously reported.[8] Since some of our synthetic routes proceed via the intermediacy of high-valent rhenium precursors, we also report the preparation and spectral and redox properties of mono(bipyridyl) complexes of Re(III) of the type $Re^{III}(bpy)(PR_3)Cl_3$ and $Re^I(bpy)(PR_3)_2Cl_2^+$. The latter complex is particularly valuable as a synthetic entrée to low-valent Re–bpy chemistry.

Experimental Section

Measurements. ^{1}H NMR spectra were all acquired at 250 MHz on a Bruker Cryospec WM250 NMR, and shifts are reported vs. Me_4Si as an internal standard. ^{31}P NMR spectra at 101 MHz were

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proton decoupled, and shifts are reported relative to 0.1 M phosphoric acid as an external standard. Cyclic voltammetry was carried out in acetonitrile with 0.1 M TEAP as supporting electrolyte by using a platinum-bead working electrode. IR spectra in CH_2Cl_2 solution were obtained on a Beckman 4250 IR, and UV-vis spectra in CH_2Cl_2 were obtained on a Bausch & Lomb Spectronic 2000 spectrophotometer.

Materials. All solvents were of reagent grade and were used as received. For emission and electrochemical experiments, high-purity methylene chloride and acetonitrile were obtained from Burdick-Jackson Laboratories and were used without further purification. All ligands were obtained from Aldrich Chemical Co. and were used as received. Rhenium precursors were obtained from Alfa Chemical Co.

Preparations. Re(bpy)Cl_4 was prepared by the same method used for the Os analogue, which has been described previously.[10] In a typical reaction 5 g (1 equiv) of K_2ReCl_6 (Aldrich) was dissolved in a minimum amount of 3 N HCl at 70 °C (~70 mL). While the mixture was stirred, 1.03 equiv (1.68 g) of bpy dissolved in a minimum amount of 3 N HCl was slowly added, causing the precipitation of the bright yellow salt [bpyH_2]-[$ReCl_6$]. Following several hours of cooling at 0 °C, the salt was filtered and washed with cold 3 N HCl, cold H_2O, and finally with ether. Before the salt was pyrolyzed, it was important that it be well dried (typically 2 days in a vacuum oven at 50–70 °C was sufficient). The solid-state pyrolysis of [$ReCl_6$]-[bpyH_2] was carried out under N_2 at 270–300 °C. On a 5-g scale the reaction was complete within 6 h, although the required reaction time is sensitive to a number of factors and it is best to monitor the reaction occasionally by cyclic voltammetry. As the reaction proceeds, HCl is evolved and the bright yellow salt slowly turns mustard yellow. Like Os(bpy)Cl_4, Re(bpy)Cl_4 is extremely insoluble in most solvents. The only purification used was to wash the product with water and ether. The yield is quantitative. Anal. Calcd: C, 24.82; H, 1.67; N, 5.79. Found: C, 24.70; H, 1.80; N, 5.70.

***trans,cis*-[Re(bpy)(PMe_2Ph)$_2Cl_2$](PF_6) from Re(bpy)Cl_4.** The complex was prepared by the reaction between Re(bpy)Cl_4 and excess PMe_2Ph. In a large-scale preparation 480 mg of Re(bpy)Cl_4 and 425 μL of Pme$_2$Ph were heated at reflux in 2-methoxyethanol for 4 h under nitrogen while vigorous magnetic stirring was maintained. The red-purple product was precipitated upon the addition of aqueous NH_4PF_6. Purification was by chromatography (2:1 toluene–acetonitrile, alumina) followed by recrystallization from toluene–MeCN (yield 90%). The product shows a ^1H NMR spectrum that is subject to substantial paramagnetic shifts due to the presence of Re(III), and attempts to obtain the ^{31}P NMR were completely unsuccessful (see Results and Discussion).

The PMe_3 and PPh_2Me analogues may be prepared by the same synthetic route as above, although yields are generally much lower and are irreproducible (20–50%). Purification was by recrystallization from CH_2Cl_2–ether. The complexes were identified by their electrochemistry, which is analogous to that of the PMe_2Ph complex. For PPh_2Me and PMe_3 complexes, respectively, the redox potentials are $Re^{IV/III}$ at 0.99 and 0.85 V, $Re^{III/II}$ at −0.31 and −0.43 V, bpy reduction at −1.62 and −1.68 V. As expected, all of the metal-localized redox couples shift to more negative values upon increasing alkyl substitution of the phosphines. Analytical data were only obtained for the PMe_3 derivative. Anal. Calcd for [Re(bpy)(PMe_3)$_2Cl_2$](PF_6)·CH_2Cl_2: C, 25.69; H, 3.55; N, 3.52. Found: C, 25.97; H, 3.72; N, 3.67.

***trans,cis*-Re(bpy)(PMe_2Ph)$_2Cl_2$ from *mer*-Re(PMe_2Ph)$_3Cl_3$.**[11] To 150 mL of deoxygenated absolute ethanol were added 1.0 g of Re(PMe_2Ph)$_3Cl_3$ and 1.33 g of bpy. The mixture was brought to reflux for 20 h under a N_2 blanket with magnetic stirring. After it was cooled, 100 mL of NH_4PF_6 solution (containing 1 g of NH_4PF_6) was added, the mixture was concentrated to ca. 70 mL, and the red-purple precipitate was then filtered, washed with water followed by ether, and air-dried. Column chromatography on alumina with 2:1 toluene–acetonitrile as eluant as described above yielded 1.03 g of complex (90%).

***fac*-Re(bpy)(L)Cl_3 from Re(bpy)Cl_4 (L = PMe_2Ph, PPh_3, $Ph_2PCH_2PPh_2$).** The general preparation is as follows: The ligand in excess was heated at reflux with Re(bpy)Cl_4 in deoxygenated diglyme solution for 3–12 h; the reaction mixture was then cooled and the crystalline product that deposited was recrystallized from 2:1 CH_2Cl_2–EtOH. Specifically, the following conditions were used: for PPh_3, 200 mg of Re(bpy)Cl_4 and 500 mg of PPh_3, reaction time 12 h, yield 183 mg (65%); for PMe_2Ph, 200 mg of Re(bpy)Cl_4 and 500 μL of PMe_2Ph, 3 h, yield 269 mg (79%); for $Ph_2PCH_2PPh_2$ 0.55 g of Re(bpy)Cl_4 and 1.2 g of $Ph_2PCH_2PPh_2$, 12 h, yield 0.51 g (54%).

***fac*-Re(bpy)(PMe_2Ph)Cl_3 from *mer*-Re(PMe_2P)$_3Cl_3$.** To a deoxygenated solution of diglyme containing 200 mg of Re(PMe_2Ph)$_3Cl_3$ was added 300 mg of bpy. The mixture was brought to reflux for 1 h under a N_2 blanket and cooled and the green crystalline complex collected. Recrystallization from 2:1 CH_2Cl_2–EtOH yielded 130 mg of the complex (78%).

***trans,cis*-[Re(bpy)(PPh_3)$_2$(CO)$_2$](PF_6).** Attempting to prepare this complex by the reported reaction (for the phen derivative) of [Re(bpy)(CO)$_3$(MeCN)](PF_6) with excess PPh_3 in *n*-butyronitrile[8] gave mixtures of the mono- and bis-substituted products in addition to other unidentified impurities; however, the reaction proceeded quantitatively in ethylene glycol. In a typical reaction, 100 mg of [Re(bpy)(CO)$_3$(MeCN)](PF_6) (1 equiv) and 300 mg of PPh_3 (7 equiv) were allowed to react at reflux in 15 mL of ethylene glycol under N_2 for 30 min. The product was precipitated by the addition of aqueous NH_4PF_6, filtered, and washed with ether to remove PPh_3, followed by reprecipitation from 1:1 MeCN–acetone into ether. Column chromatography (1:1 MeCN–toluene, alumina) showed only one product and was probably unnecessary. The bright yellow product luminesces yellow in the solid state and dull orange in solution.

***trans,cis*-[Re(bpy)(PMe_2Ph)$_2$(CO)$_2$](PF_6).** This complex was prepared by the direct carbonylation of *trans,cis*-[Re(bpy)(PMe_2Ph)$_2Cl_2$](PF_6) using formic acid. In a typical preparation 200 mg of [Re(bpy)(PMe_2Ph)$_2Cl_2$](PF_6) was heated at reflux in 25 mL of 88% formic acid for 32 h under a N_2 atmosphere. After the mixture was cooled, solvent was removed, leaving a red oily product. The crude material was dissolved in 1:1:1 ethanol–acetone–water with added NH_4PF_6, and solvent was then slowly removed under vacuum, yielding *trans,cis*-[Re(bpy)(PMe_2Ph)$_2$(CO)$_2$](PF_6) as dark red crystals in 70% yield. The product was further purified by chromatography (1:1 MeCN–toluene, alumina) although this was probably unnecessary. The ^{31}P NMR spectrum in acetone shows a singlet at δ −12.7 consistent with two equivalent phosphines. The ^1H NMR spectrum shows the phosphine methyl protons as a virtually coupled triplet at δ 1.96 supporting a trans phosphine structure (see Results and Discussion).

***cis*-[Re(bpy)$_2$(CO)$_2$](PF_6).** A suspension of 400 mg of Re(bpy)(CO)$_3$Cl[12] and 600 mg of bpy was heated at reflux in 30 mL of ethylene glycol for 2 h. The reaction mixture was cooled to room temperature, and 60 mL of H_2O containing 500 mg of NH_4PF_6 was added with stirring. The dark red complex was filtered, washed with H_2O followed by Et_2O, and then recrystallized *twice* from 2:1 toluene–CH_3CN; yield 78 mg (13%).

Results and Discussion

Two main strategies were used in the attempt to prepare new luminescent bipyridyl complexes of Re(I). The first involved the reaction of a Re(IV) or Re(III) precursor with the appropriate entering ligands followed by reduction to the Re(I) state. The second was suggested by the work of Luong[8] and involves the reaction between the Re(I) mono(bipyridyl) complex and the entering ligands in a high-boiling solvent. Since Re(I) is a highly reducing metal center, it was necessary to employ ancillary ligands that are good π acids in order to obtain complexes for which emission occurs in the visible portion of the spectrum. In this work we used tertiary phosphines and carbon monoxide. Elemental analysis data for the complexes are given in Table I.

Complexes Derived from Re^{IV}(bpy)Cl_4 and *mer*-Re^{III}(PMe_2Ph)$_3Cl_3$. A convenient starting material for mono(bipyridyl) complexes of Re is the complex Re^{IV}(bpy)Cl_4. For convenience, a detailed description of a modified pyrolytic synthesis based on the preparation of Os^{IV}(bpy)Cl_4 is given in in the Experimental Section. Since the chemistry of Re^{IV}(bpy)Cl_4 is relatively unexplored, our first reactions in-

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Table I. Elemental Analysis Data for the Re(I)- and Re(III)-2,2'-Bipyridine Complexes

complex	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
fac-$Re^{III}(bpy)(PMe_2Ph)Cl_3$	36.77	3.23	4.77	36.91	3.47	4.70
fac-$Re^{III}(bpy)(Ph_2PCH_2PPh_2)Cl_3$	50.33	3.59	3.36	50.03	3.41	3.28
fac-$Re^{III}(bpy)(PPh_3)Cl_3$	47.29	3.24	3.94	47.54	3.50	3.91
trans,cis-$[Re^{III}(bpy)(PMe_2Ph)_2Cl_2](PF_6)$	37.43	3.62	3.36	37.39	3.14	3.21
trans,cis-$[Re^{I}(bpy)(PMe_2Ph)_2(CO)_2](PF_6)$	41.06	3.69	3.42	40.71	3.62	3.32
trans,cis-$[Re^{I}(bpy)(PPh_3)_2(CO)_2](PF_6)$	54.00	3.59	2.62	54.18	3.59	2.62
cis-$[Re^{I}(bpy)_2(CO)_2](PF_6)$	37.78	2.29	8.01	37.17	2.38	7.95

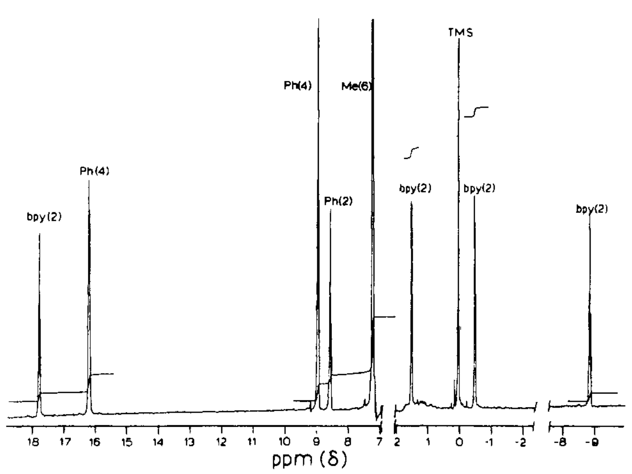


Figure 1. ^1H NMR spectrum of *fac*-$Re(bpy)(PMe_2Ph)Cl_3$ in CD_2Cl_2 solution (Me_4Si as internal standard). Proposed assignments of the proton resonances are shown above the peaks.

volved phosphine ligands where both reduction to Re(III) and halide substitution were expected to occur. Shown in eq 1 is

$$Re^{IV}(bpy)Cl_4 + L \xrightarrow[\Delta]{\text{diglyme}} fac\text{-}Re^{III}(bpy)(L)Cl_3 + Cl^- \quad (1)$$

the reaction of $Re(bpy)Cl_4$ with excess phosphine (L) in a relatively low-polarity, albeit high-boiling solvent, diglyme, to yield the Re^{III} product, *fac*-$Re^{III}(bpy)(L)Cl_3$. The reducing equivalents needed to take Re^{IV} to Re^{III} presumably are supplied by the phosphine both in this and in other reactions to be discussed later. In our experiments the ligand L in eq 1 was PPh_3, PMe_2Ph, or $Ph_2PCH_2Ph_2$, the latter being monodentate under the reaction conditions. An alternate and high-yield procedure that gives *fac*-$Re(bpy)(PMe_2Ph)Cl_3$ involves the phosphine displacement reaction shown in eq 2. It

$$mer\text{-}Re^{III}(PMe_2Ph)_3Cl_3 + bpy \xrightarrow[\Delta]{\text{diglyme}} fac\text{-}Re^{III}(bpy)(PMe_2Ph)Cl_3 + 2PMe_2Ph \quad (2)$$

should be noted that the PPh_3 complex mentioned above is by UV-visible spectral measurements identical with the complex $Re(bpy)(PPh_3)Cl_3$ reported by Rouchias and Wilkinson[13] to which no structure was assigned. Our structural assignment of these complexes as the facial isomer is based on the proton NMR spectrum of *fac*-$Re(bpy)(PMe_2Ph)Cl_3$. Figure 1 shows the NMR spectrum taken in CD_2Cl_2 solution. Although the spectrum exhibits very large paramagnetic shifts, the spectral line widths are exceedingly narrow, display the eight groups of resonances having the expected area ratios, and are thus consistent with the C_{2v} symmetry of the facial isomer. In Figure 1 the proposed assignments for the four bpy resonances, three phenyl resonances, and one methyl resonance are shown.

Although NMR spectral data were not obtained for the PPh_3 and dppm derivatives, the results of cyclic voltammetry and electronic spectral experiments strongly support the same isomeric assignment as the PMe_2Ph complex (vide infra).

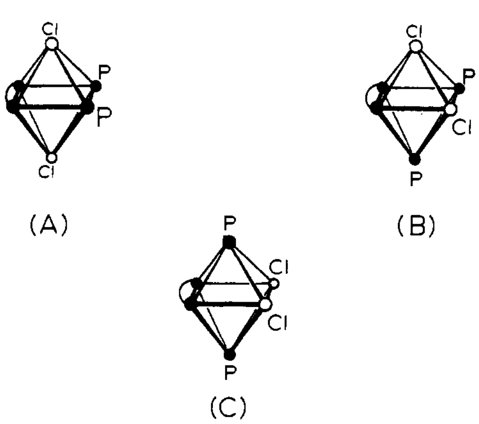


Figure 2. Possible isomers for the complexes $Re^{III}(bpy)P_2Cl_2^+$ (P = phosphine): (A) cis,trans isomer; (B) cis,cis isomer; (C) trans,cis isomer.

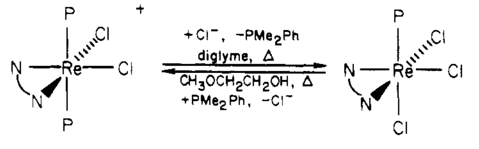
The reactions between $Re(bpy)Cl_4$ and PMe_2Ph or between *mer*-$Re(PMe_2Ph)_3Cl_3$ and bpy, in polar solvents such as EtOH or 2-methoxyethanol, provide high-yield routes to the red-purple cationic Re(III) complex *trans,cis*-$[Re^{III}(bpy)(PMe_2Ph)_2Cl_2](PF_6)$ (eq 3 and 4).

$$Re^{IV}(bpy)Cl_4 + PMe_2Ph\ (\text{excess}) \xrightarrow[\text{EtOH}]{\Delta} Re^{III}(bpy)(PMe_2Ph)_2Cl_2^+ + Cl^- \quad (3)$$

$$Re^{III}(PMe_2Ph)_3Cl_3 + bpy \xrightarrow[\text{MeOCH}_2\text{CH}_2\text{OH}]{\Delta} Re^{III}(bpy)(PMe_2Ph)_2Cl_2^+ + PMe_2Ph \quad (4)$$

The ^1H NMR spectrum of $[Re^{III}(bpy)(PMe_2Ph)_2Cl_2](PF_6)$ in CD_3CN solution (vs. Me_4Si) also exhibits highly shifted resonances, presumably due to temperature-independent paramagnetism. The resonances can be assigned by their first-order splitting and approximate integration in the following manner: methyl resonance, δ 7.25 (singlet, area 6); phenyl resonances, δ 16.18 (ortho protons, doublet, area 4); δ 8.95 (meta protons, triplet, area 4); δ 8.57 (para protons, triplet, area 4); bipyridine resonances, δ 17.78 (triplet, area 2), 1.54 (doublet, area 2), −0.48 (doublet, area 2), −8.84 (triplet, area 2). The NMR spectral data are clearly consistent with planes of magnetic symmetry bisecting and containing the bipyridine ligand.

Of the three isomers shown in Figure 2 only the cis,cis structure can be ruled out by the ^1H NMR spectrum described above. We prefer assigning the product the trans,cis structure but only on the basis of its reactivity. For example, $Re(bpy)(PMe_2Ph)_2Cl_2^+$ can be converted quantitatively into *fac*-$Re(bpy)(PMe_2Ph)Cl_3$ by reaction with tetra-*n*-butylammonium chloride in diglyme (eq 5). As shown in eq 5 the



(5)

reaction can be reversed by heating *fac*-$Re(bpy)(PMe_2Ph)Cl_3$

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Table II. Spectral Properties of the Re(III) and Re(I) Complexes

complex	ν_{CO}, cm^{-1}	$E_{CT}{}^{abs}$, cm^{-1} × 10^3 (ϵ, M^{-1} cm^{-1})	$E_{CT}{}^{EM,c}$, cm^{-1} × 10^3
fac-Re^{III}(bpy)(Ph$_2$PCH$_2$PPh$_2$)Cl$_3$		25.00 (5190),^{a} 15.65 (4030)^a	
fac-Re^{III}(bpy)(PMe$_2$Ph)Cl$_3$		25.51 (5720),^{a} 22.88 (4870),^{a} 15.43 (4950)^a	
fac-Re^{III}(bpy)(PPh$_3$)Cl$_3$		25.00 (69.50),^{a} 15.78 (4060)^a	
trans,cis-[Re^{III}(bpy)(PMe$_2$Ph)$_2$Cl$_2$](PF$_6$)		18.25 (2750),^{b} 19.49 (2580),^{b} 26.25 (3710)^b	
trans,cis-[Re^I(bpy)(PMe$_2$Ph)$_2$(CO)$_2$](PF$_6$)	1961, 1890^a	23.31 (3640)^b	14.92^a
trans,cis-[Re^I(bpy)(PPh$_3$)$_2$(CO)$_2$](PF$_6$)	1966, 1894^a	23.53 (3440)^b	16.13^a
cis-[Re^I(bpy)$_2$(CO)$_2$](PF$_6$)	1922, 1853^a	25.71 (9270), 21.05 (7670)^b	13.95^b

^{a} CH$_2$Cl$_2$ solution. ^{b} CH$_3$CN solution. ^{c} Corrected emission spectrum.

with excess PMe$_2$Ph in 2-methoxyethanol (2-ME). The observed behavior toward substitution is characteristic of the trans labilizing ability of a phosphine ligand, at least at spin-paired d^6 metal centers.[14]

The luminescent dicarbonyl complex *trans,cis*-[Re^I(bpy)(PMe$_2$Ph)$_2$(CO)$_2$]$^+$ can be prepared by reductive carbonylation of Re(bpy)(PMe$_2$Ph)$_2$Cl$_2$$^+$ with formic acid heated at reflux. The cis stereochemistry of the CO groups was established by solution infrared in CH$_2$Cl$_2$ (Table II), which shows two intense absorptions in the carbonyl region, and by the observation of a single ^{31}P NMR resonance at δ −12.7 (vs. H$_3$PO$_4$) which is consistent with the trans disposition of the phosphine ligands.

Luminescent dicarbonyl complexes can also be prepared as products of the reactions between *fac*-Re(bpy)(CO)$_3$Cl or *fac*-[Re(bpy)(CO)$_3$(CH$_3$CN)](PF$_6$) and the appropriate ligand in refluxing ethylene glycol. With PPh$_3$ as the added ligand, the product is *trans,cis*-[Re^I(bpy)(PPh$_3$)$_2$(CO)$_2$]$^+$ as shown in eq 6, while with bpy as the added ligand, the product

$$fac\text{-}[Re(bpy)(CO)_3(CH_3CN)]^+ + 2PPh_3 \xrightarrow[\Delta]{HOCH_2CH_2OH} trans,cis\text{-}[Re(bpy)(PPh_3)_2(CO)_2]^+ + CO + CH_3CN \quad (6)$$

is *cis*-Re(bpy)$_2$(CO)$_2$$^+$ (eq 7). The latter complex is of interest

$$fac\text{-}Re(bpy)(CO)_3Cl + bpy \xrightarrow[\Delta]{HOCH_2CH_2OH} cis\text{-}[Re(bpy)_2(CO)_2]^+ + CO + Cl^- \quad (7)$$

since it appears to be the first well-characterized bis(bipyridyl) complex of low-valent rhenium.[9,15] It is also a new member of an interesting series of isoelectronic and presumably isostructural bipyridyl carbonyls that includes *cis*-M(bpy)$_2$(CO)$_2$ (M = Cr, Mo, W)[16] and *cis*-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$.[17]

The phen analogue of *trans,cis*-[Re(bpy)(PPh$_3$)$_2$(CO)$_2$]$^+$ was first prepared by Wrighton and Luong[8] but was not assigned an unequivocal structure. Our assignment of the stereochemistry is based upon the infrared spectrum, which shows two intense absorptions in the carbonyl region (see Table II), *and* the ^{1}H NMR spectrum, which is consistent with two planes of magnetic symmetry, one of which bisects the bipyridine ligand and one of which contains the planar bpy ligand (see Experimental Section).

The complex *cis*-[Re(bpy)$_2$(CO)$_2$]$^+$ shows the expected first-order pattern of eight doublets and eight triplets between δ 9.45 and δ 7.25 for the proton NMR spectrum in CD$_3$CN solution. The carbonyl absorptions in CH$_2$Cl$_2$ solution appear at 1922 and 1853 cm^{-1}, which is intermediate between *cis*-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$ (2039 and 2029 cm^{-1} in CH$_2$Cl$_2$)[17] and *cis*-Mo(bpy)$_2$(CO)$_2$ (1782 and 1723 cm^{-1} in CH$_3$CN).[16]

Electrochemistry of Bipyridyl Complexes of Re(IV), Re(III), and Re(I). The results of cyclic voltammetry studies on the new Re(I) and Re(III) complexes are summarized in Table III. In addition, data for redox couples of related complexes like Re^{IV}(bpy)Cl$_4$ and analogous complexes of Ir and Os are shown for purposes of comparison. Including the more extended data allows comparisons to be made between redox potentials for a series of isoelectronic and presumably isostructural complexes. The comparisons are of value because they bear directly on the design of redox couples with specific redox potentials, which in turn could have a bearing on the design of catalytic redox reagents.

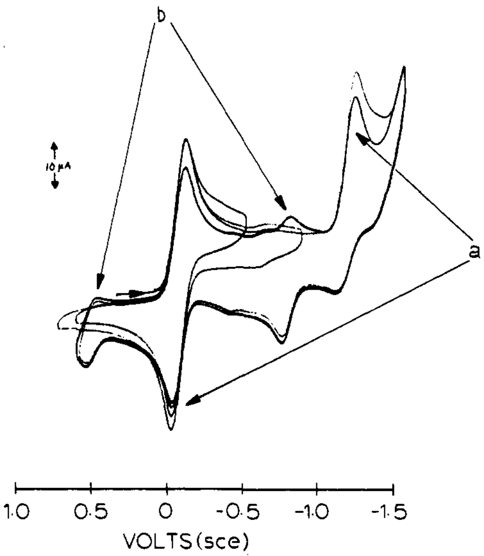

Figure 3. Cyclic voltammogram of Re^{IV}(bpy)Cl$_4$ in 1:1 DMF–CH$_3$CN with tetra-*N*-ethylammonium perchlorate as supporting electrolyte (taken with a Pt-bead electrode at room temperature, 200 mV/s, vs. the saturated calomel electrode (SCE)): (a) most cathodic wave represents Re$^{III/II}$ couple for Re^{IV}(bpy)Cl$_4$ while the anodic wave is the Re$^{IV/III}$ couple; (b) most cathodic wave represents the Re$^{III/II}$ couple for Re^{IV}(bpy)(S)Cl$_4$ while the anodic wave is the Re$^{IV/III}$ couple (S is CH$_3$CN or DMF).

The complexes M^{IV}(bpy)Cl$_4$ (M = Re, Os) show two redox processes in 1:1 CH$_3$CN–DMF solution with 0.1 M TEAP as electrolyte. The most oxidative of the waves corresponds to the reversible reduction process shown in eq 8, which in the

$$M^{IV}(bpy)Cl_4 + e^- \rightleftharpoons M^{III}(bpy)Cl_4^- \quad (8)$$

case of Re corresponds to a change in electron configuration from (dπ)^3 to (dπ)^4 and for Os from a configuration of (dπ)^4 to (dπ)^5. At more negative potentials both complexes exhibit a further one-electron reduction that is coupled to a rapid chemical step. The chemical step appears to involve loss of bound chloride ion and solvolysis to give species of the type M^{II}(bpy)(S)Cl$_3$$^-$ (where S is CH$_3$CN or DMF; see, for example, eq 9 and 10). The products, M^{II}(bpy)(S)Cl$_3$$^-$, exhibit

$$M^{III}(bpy)Cl_4^- + e^- \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} M^{II}(bpy)Cl_4^{2-} \quad (9)$$

$$M^{II}(bpy)Cl_4^{2-} + CH_3CN \rightarrow M^{II}(bpy)(CH_3CN)Cl_3^- + Cl^- \quad (10)$$

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[14] (a) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1037. (b) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Ibid* **1980**, *19*, 1404 and references therein.

[15] See, however: Chakravorti, M. C.; Sen, B. K. *J. Indian Chem. Soc.* **1966**, *43*, 464.

[16] Connor, J. A.; Overton, C. *J. Chem. Soc., Dalton Trans.* **1982**, 2397.

[17] Choudbury, D.; Jones, R. F.; Smith, G.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1143 and references therein.

Table III. $E_{1/2}$ Values from Cyclic Voltammetry Measurements for the Re–Bipyridyl and Related Complexes

complex	$E_{1/2}$-(oxidn),[a] V	$E_{1/2}$-(redn),[a] V
fac-$Re^{III}(bpy)(PMe_2Ph)Cl_3$	+0.47	−0.74
fac-$Re^{III}(bpy)(Ph_2PCH_2PPh_2)Cl_3$	+0.56	−0.69
fac-$Re^{III}(bpy)(PPh_3)Cl_3$	+0.56	−0.70
trans,cis-$[Re^{III}(bpy)(PMe_2Ph)_2Cl_2](PF_6)$	+0.88	−0.39, −1.69
trans,cis-$[Re^{I}(bpy)(PMe_2Ph)_2(CO)_2](PF_6)$	+1.10	−1.42
trans,cis-$[Re^{I}(bpy)(PPh_3)_2(CO)_2](PF_6)$	+1.37[b]	−1.40
cis-$[Re^{I}(bpy)_2(CO)_2](PF_6)$	+0.88	−1.31, −1.51
$Re^{IV}(bpy)Cl_4$[c]		−0.04, −1.26
mer-$Re^{III}(PMe_2Ph)_3Cl_3$	+0.66	−1.01[d]
mer-$Re^{III}(PPh_3)_2(CH_3CN)Cl_3$	+0.66	−0.84
$Os^{IV}(bpy)Cl_4$[c]		+0.51, −0.80[b]
fac-$Os(bpy)(PMe_2Ph)Cl_3$	+0.88	−0.55
$(Ph_4As)[Ir^{III}(bpy)Cl_4]$	+1.04	−1.53

[a] Obtained in CH_3CN solution with 0.1 M $NEt_4(ClO_4)$ as supporting electrolyte unless otherwise noted. All cyclic voltammograms were obtained with a Pt-bead working electrode at a scan rate of 200 mV/s, and the potentials reported are vs. the SCE. All potentials were calculated as $(E_p{}^a + E_p{}^c)/2$ where $E_p{}^a$ and $E_p{}^c$ are the anodic and cathodic peak potentials except where noted. oxidn and redn refer to oxidative and reductive processes, respectively. [b] Irreversible. [c] DMF–CH_3CN. [d] E_p value.

stepwise one-electron oxidations to the M^{III} and M^{IV} oxidation states as shown in eq 11 and 12. Figure 3 shows a cyclic voltammogram of $Re(bpy)Cl_4$ with the electrochemical and chemical steps detailed in eq 8–12 clearly shown.

$$M^{II}(bpy)(S)Cl_3^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{III}(bpy)(S)Cl_3 \qquad (11)$$

$$M^{III}(bpy)(S)Cl_3 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [M^{IV}(bpy)(S)Cl_3]^+ \qquad (12)$$

The cyclic voltammogram of $Ir^{III}(bpy)Cl_4^-$ shows only two redox processes, one a one-electron oxidation involving the $Ir^{IV/III}$ couple and the other a one-electron reduction corresponding to a ligand-localized $bpy^{-}\cdot/bpy$ couple.

Comparison of redox potentials (Table III) for isoelectronic couples shows that, for the $(d\pi)^5/(d\pi)^6$ couples $Ir(bpy)Cl_4{}^{0/-}$ and $Os(bpy)Cl_4{}^{-/2-}$, the *$Os^{III/II}$ couple is shifted 1.84 V to more negative potentials compared to the $Ir^{IV/III}$ couple*. For the $(d\pi)^4/(d\pi)^5$ couples involving Re ($Re(bpy)Cl_4{}^{-/2-}$) and Os ($Os(bpy)Cl_4{}^{0/-}$), *the $Re^{III/II}$ couple is shifted more negatively by 1.77 V compared to the $Os^{IV/III}$ couple*. Although not strictly isoelectronic, the differences in redox properties between metals in isostructural environments is dramatically illustrated by comparison of the $Ir^{IV/III}$ and $Re^{III/II}$ couples, which differ by 3.61 V.

Also, from the redox potential data, potential differences between $(d\pi)^5/(d\pi)^6$ ($M^{III/II}$) and $(d\pi)^4/(d\pi)^5$ ($M^{IV/III}$) couples in the same coordination environment for related Os and Ru bpy couples is ca. 1.6 ± 0.2 V.[2,14b,19] If the same trend were to hold true for Re, it can be estimated from the $E_{1/2}$-(redn) values for the $Re^{III/II}$ couples in Table III that the *$(d\pi)^5/(d\pi)^6$ ($Re^{II/I}$) couple for Re is ca. 5.2 V more reducing than the isoelectronic ($M^{IV/III}$) couple for Ir.* These comparisons are revealing since they put on a more quantitative basis the notion that the early transition metals are more reducing than the group 8 metals.

The complexes $Re^{III}(bpy)(P)Cl_3$ (P = PMe_2, Ph, PPh_3, dppm) show, in general, two metal-based redox processs in CH_3CN solution in our potential window.[18] One of the cyclic voltammetric waves corresponds to oxidation of Re(III) to Re(IV), $(d\pi)^4 \xrightarrow{-e^-} (d\pi)^3$, and the other to reduction of Re(III) to Re(II), $(d\pi)^4 \xrightarrow{+e^-} (d\pi)^5$, as shown in eq 13 and 14. The

$$fac\text{-}[Re^{IV}(bpy)(P)Cl_3]^+ \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} fac\text{-}Re^{III}(bpy)(P)Cl_3 \qquad (13)$$

$$fac\text{-}Re^{III}(bpy)(P)Cl_3 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} fac\text{-}[Re^{II}(bpy)(P)Cl_3]^- \qquad (14)$$

potentials for the couples in eq 13 and 14 occur at ca. +0.6 and −0.7 V, respectively. The values are in the same range as potentials for analogous couples involving the trichlorocomplexes *mer*-$Re(PPh_3)_2(CH_3CN)Cl_3$ and *mer*-$Re(PMe_2Ph)_3Cl_3$[18] (Table III).

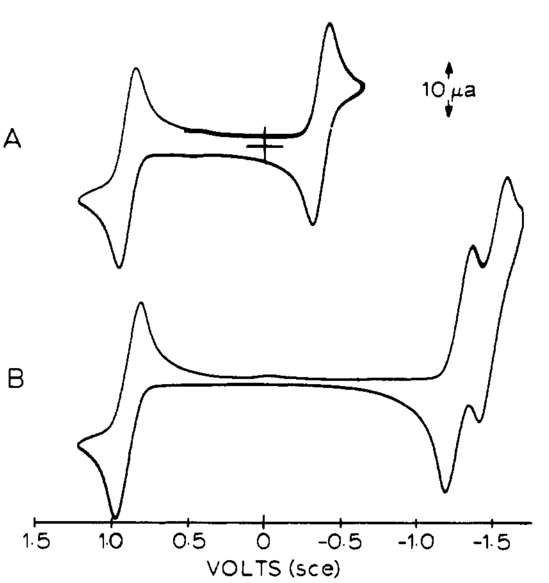

Figure 4. Cyclic voltammograms (CH_3CN solution with 0.1 M tetraethylammonium perchlorate as supporting electrolyte, Pt-bead electrode, scan rate 200 mV/s (see text)): (A) *trans,cis*-$[Re^{III}(bpy)(PMe_2Ph)_2Cl_2]^+$; (B) *cis*-$[Re^{I}(bpy)_2(CO)_2]^+$.

The cyclic voltammogram for $Os^{III}(bpy)(PMe_2Ph)Cl_3$ is similar to the voltammogram for the Re analogue in that waves appear for two reversible one-electron couples (eq 15 and 16).

$$Os^{IV}(bpy)(PMe_2Ph)Cl_3{}^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Os^{III}(bpy)(PMe_2Ph)Cl_3 \qquad E_{1/2} = 0.88\ V \qquad (15)$$

$$Os^{III}(bpy)(PMe_2Ph)Cl_3 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Os^{II}(bpy)(PMe_2Ph)Cl_3^- \qquad E_{1/2} = -0.55\ V \qquad (16)$$

In the coordination environment, $M(bpy)(PMe_2Ph)Cl_3$, redox potentials for the isoelectronic $Os^{IV/III}$ and $Re^{III/II}$ couples show that the Re center is more strongly reducing than Os by 1.89 V, which is very similar to the value found previously for $M(bpy)Cl_4$ complexes.

In the cyclic voltammogram of the complex *trans,cis*-$[Re^{III}(bpy)(PMe_2Ph)_2Cl_2]^+$, waves appear corresponding to a $Re^{IV/III}$ couple at +0.88 V and a $Re^{III/II}$ couple at −0.39 V (see Figure 4). The potentials for the two couples are shifted positively by 300 mV compared to the analogous couples for *fac*-$Re(bpy)(PMe_2Ph)Cl_3$. The observed shift is smaller than the +0.47-V shift observed for the ruthenium complexes

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(18) Other reductive processes occur in the region −1.5 to −2.0 V in CH_3CN solution which result in substitution of Cl^- by the CH_3CN solvent. These are not important in the present work but have been discussed for the prototype molecules *mer*-$M^{III}(PMe_2Ph)_3Cl_3$ (M = Re, Os), see: Calvert, J. M.; Sullivan, B. P.; Meyer, T. J. In "Chemically Modified Surfaces in Catalysis and Electrocatalysis"; Miller, J. S., Ed.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 192.

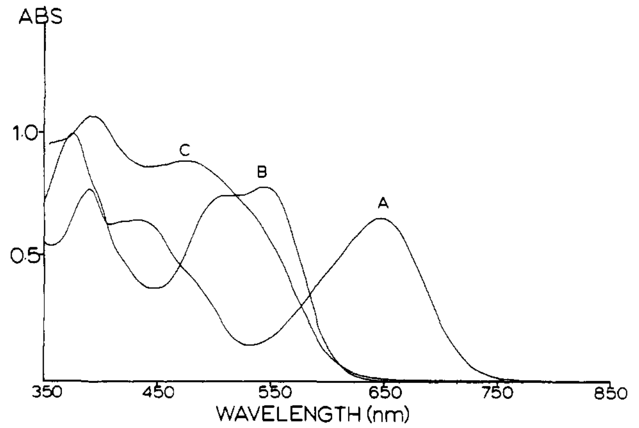

Figure 5. Electronic spectra: (A) *fac*-$Re^{III}(bpy)(PMe_2Ph)Cl_3$ in CH_2Cl_2; (B) *trans,cis*-$[Re^{III}(bpy)(PMe_2Ph)_2Cl_2]PF_6$ in CH_2Cl_2; (C) *cis*-$[Re^{I}(bpy)_2(CO)_2]^+$ in CH_2Cl_2.

cis-$[Ru(bpy)_2(PMe_2P)Cl]^+$ and *cis*-$Ru(bpy)_2Cl_2$.[19]

The Re(I) complexes shown in Table II all show waves in their cyclic voltammograms corresponding to $Re^{II/I}$ couples in the potential region 0.9–1.4 V. For the dicarbonyl complex, $Re(bpy)(PPh_3)_2(CO)_2^+$, the oxidation wave is irreversible while the waves for the other complexes are reversible. The reduction processes of the Re(I) complexes referred to in Table III and in Figure 4 all appear to be bpy localized in nature. For *cis*-$[Re(bpy)_2(CO)_2]^+$, two reversible reductions are observed within the solvent limit (Figure 4), suggesting the existence of sequential, bpy-based reductions as is commonly observed for complexes of the type $M^{II}(bpy)_2L_2^{2+}$ (M = Ru, Os).[2,19]

Electronic Absorption and Emission Spectra of the Re Complexes. Table II summarizes data from absorption spectra for the new Re(III) and Re(I) complexes in CH_2Cl_2 or CH_3CN solution. As shown in Table II and in Figure 5, the Re(III) complexes exhibit intense absorptions in the visible region and thus are highly colored; *fac*-$Re^{III}(bpy)(P)Cl_3$ is forest green and *trans,cis*-$[Re^{IV}(bpy)(PMe_2Ph)_2Cl_2]^+$ is red-purple. The appearance of visible absorption bands is in sharp contrast to the complexes, *mer*-$Re^{III}(PMe_2Ph)_3Cl_3$ and *mer*-$Re^{III}(PPh_3)_2(CH_3CN)Cl_3$, which are relatively transparent in the visible and are yellow in color.[20] Given the similarity in redox potentials for these complexes compared to the series *fac*-$Re^{III}(bpy)(L)Cl_3$, the origin of the visible absorption bands for the bpy complexes is no doubt in $\pi^*(bpy) \leftarrow d\pi(Re^{III})$ metal-to-ligand charge-transfer (MLCT) transitions (eq 17).

$$Re^{III}(bpy)(L)Cl_3 \xrightarrow{h\nu} Re^{IV}(bpy^-\cdot)(L)Cl_3 \qquad (17)$$

For the complex *trans,cis*-$[Re^{III}(bpy)(PMe_2Ph)_2Cl_2]^+$ the absorption maxima of the MLCT bands are shifted to higher energy than for *fac*-$Re^{III}(bpy)(PMe_2Ph)Cl_3$. The shift to higher energy is expected for the latter complex given the higher potential for the $Re^{IV/III}$ couple since it suggests that the $d\pi(Re^{III})$ levels are relatively more stable, which should produce a larger $d\pi(Re)$–$\pi^*(bpy)$ energy gap (see Figure 5).

The Re(I) complexes shown in Table II are all orange to deep red in color. The visible spectra are dominated by intense $\pi^*(bpy) \leftarrow d\pi(Re^{I})$ MLCT transitions; a typical example is the $Re(bpy)_2(CO)_2^+$ spectrum shown in Figure 5. For the series $Re^{I}(bpy)(L)_2(CO)_2^+$, the charge-transfer band maxima shift progressively to lower energies in the order L = PPh_3 > PMe_2Ph > $^1/_2$bpy, which at least qualitatively appears to be the order of decreasing π-acceptor and increasing σ-donor ability of the ligands.

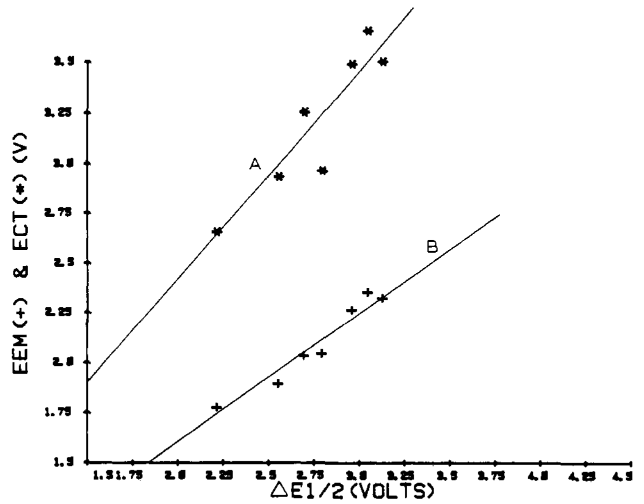

Figure 6. Linear relationship between $\Delta E_{1/2}$, where $\Delta E_{1/2}$ is the difference between the reduction potential for the $Re^{II/I}$ couple and the ligand-based 0/1− reduction, and (A) the lowest energy visible absorption maximum (E_{op}) and (B) the emission maximum (E_{em}) for the series $Re^{I}(bpy)L(L')(CO)_2^+$ (see text).

Further support for the charge-transfer nature of the lowest energy transition (E_{CT}) in the Re(I) complexes comes from the plot of E_{CT} vs. $\Delta E_{1/2}$ in Figure 6 (where $E_{1/2} = E_{1/2}(Re^{II/I}) - E_{1/2}(bpy^{0/-})$). The complexes used for the correlation in Figure 6 are of the type $Re^{I}(bpy)(L)_2(CO)_2^+$, three of which (where L = CO and a tertiary phosphine or nitrogen heterocycle) have been previously discussed. The line drawn in Figure 6 is derived from a linear least-squares analysis of the data and yields for the line a relation of the form[21]

$$E_{op} = 1.05\Delta E_{1/2} + 0.30 \qquad (18)$$

with a correlation coefficient, *r*, of 0.91.

As stated earlier, one of the primary goals of this work was to develop synthetic routes to new luminescent complexes of Re(I) based on CT excited states. The complexes $Re^{I}(bpy)(L)_2(CO)_2^+$ are relatively strong emitters, and, as shown in Table II, the emission energies vary from ca. 13.9 to 16.1 × 10^3 cm^{-1} in CH_3CN or CH_2Cl_2 solution. Like the MLCT absorption band discussed above, the emission maxima of the complexes also track the quantity $\Delta E_{1/2}$ according to eq 19[21] (see Figure 6) with an *r* value of 0.97.

$$E_{em} = 0.66\Delta E_{1/2} + 0.26 \qquad (19)$$

Finally, it should be noted that the photophysical properties of a series of Re^{I} polypyridyl complexes, including an analysis of nonradiative decay constants, has already appeared.[6b]

Acknowledgment is made to the Department of Energy under Grant no. ER-78-S-05-6034 for support of this research.

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(19) See, for example: Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(20) Leigh, G. J.; Mingos, D. M. P. *J. Chem. Soc. A* **1970**, 587.

(21) Correlations of this kind have been discussed in more detail in: Kober, E. M.; Marshall, J. M.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J., submitted for publication.