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A New Class of Luminescent Polypyridine Complexes of Rhenium(I) Containing *cis*-Carbonyl Ligands

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The preparation and characterization of new luminescent metal complexes, especially those exhibiting metal-to-ligand charge transfer excited states,[1] has contributed to the understanding of the fundamental principles of excited state decay. As this field has matured, applications of luminescent MLCT excited states, in particular Re(I)−polypyridine complexes containing carbonyl ligands,[2] have been found in such diverse areas as solar energy conversion,[3] biological labeling,[4] and sensor development.[5] Of specific interest to us is the discovery of new excited states which are capable of probing their immediate physical environment, for example by reporting on changes in pressure, temperature, or effective dielectric properties.[6] In this Communication we report several different, high-yield routes to a new class of long-lived luminescent complexes of the type *cis*-Re(CO)$_2$(N-N)(P-P)$^+$ (where N-N is a chelate polypyridine ligand and P-P is a chelate phosphine). Also, the synthetic procedures reported here provide a new, but general, entry route to the known *cis-trans*-Re(CO)$_2$(P)$_2$(N-N)$^+$ complexes, several of which have been prepared by other methods.[7] All the new Re excited states are of extraordinary stability, exhibit spectral responses well to the red of similar tricarbonyl complexes of Re(I), and apparently do not conform to the same energy gap law as *fac*-Re(bpy)(CO)$_3$L$^{(+/0)}$ complexes (L is a variety of neutral and anionic ligands).[8]

As shown in Scheme 1, three methods were used to prepare the complexes. These are route 1, reaction of *fac*-Re(P-P)(CO)$_3$Cl with stoichiometric N-N and TlPF$_6$ in *o*-dichlorobenzene (ODB);[9] route 2, reaction of *fac*-Re(N-N)(CO)$_3$Cl with stoichiometric P-P and TlPF$_6$ in ODB;[10] and route 3, reaction of *fac*-Re(N-N)(CO)$_3$-OTf with stoichiometric P-P in ODB.[11] Route 4 in Scheme 1 is the direct preparation of complexes of the type *cis-trans*-Re(CO)$_2$(P)$_2$(N-N)$^+$ where P can be PPh$_3$, or even bidentate phosphines like *trans*-Ph(H)C═C(H)Ph that can serve as the basis for linear oligomeric chromophores.[12] In all cases, reaction times for ODB heated at reflux were between 5 and 18 h, and yields after purification ranged from 60 to 80%. For all the routes, the intermediate *fac*-Re(bpy)(CO)$_3$(phosphine)$^+$ appears early in the reaction, which implies that the success of the chemistry relies on the ability of phosphine ligands to labilize a carbonyl ligand in the coordination sphere under the extreme temperature conditions. Characterization of the complexes was achieved by a combination of elemental analysis and IR and ^{31}P NMR spectroscopies (see Table 1). As is shown in Table 1, two intense

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(10) Preparation of [*cis*-Re(CO)$_2$(dppm)(bpy)]PF$_6$ from *fac*-Re(bpy)(CO)$_3$-Cl: *fac*-Re(bpy)(CO)$_3$Cl (100 mg), 76 mg of TlPF$_6$, and 91 mg (10% excess) of dppm were combined in a 50 mL round bottom flask which was covered with aluminum foil. Approximately 7.5 mL of *o*-dichlorobenzene was added, and N$_2$ was bubbled through the solution for 5 min, which was then placed under a N$_2$ blanket and refluxed for 5 h. During this time the solution changed from white to orange-red. The reaction workup was exactly the same as that for *cis*-[Re(CO)$_2$(c-dppene)(phen)]PF$_6$. Anal. Calcd: C, 47.90; N, 3.02; H, 3.26 Found: C, 48.02; N, 3.09; H, 3.31.

(11) Preparation of [*cis*-Re(CO)$_2$(dppm)(bpy)](OTf) from *fac*-Re(bpy)(CO)$_3$-OTf: Re(bpy)(CO)$_3$(OTf) (155 mg, 0.27 mmol) and dppm (104 mg, 0.27 mmol) were placed in a 50 mL round bottom flask containing 10 mL of *o*-dichlorobenzene. The reaction mixture was purged with nitrogen for 30 min and refluxed for 5 h, after which time 40 mL of diethyl ether was added, following cooling. The yellow-orange solid which precipitated was collected and washed with ether, resulting in an orange oil. This oil was dissolved in dichloromethane and dropped into stirring ether, giving the yellow-orange product, which was collected, washed with ether, and air-dried (188 mg, 73% yield).

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Scheme 1. New Preparative Reactions (Routes 1−4; See Text) for the *cis*-Carbonyl Complexes

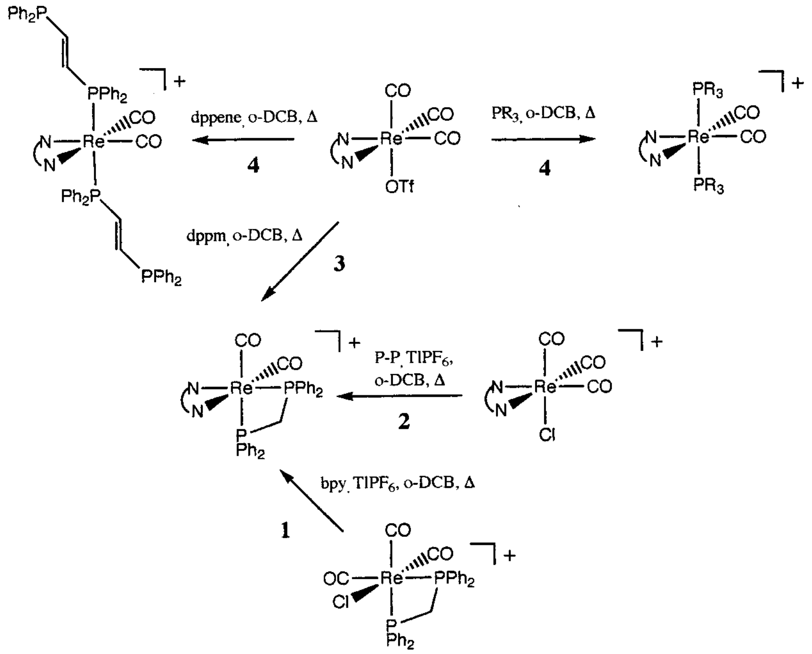

Table 1. Spectral and Photophysical Data for the Complexes[a,b]

no.	complex	^{31}P NMR shifts (ppm)[c]	IR freq (cm^{-1})	E_{op} (nm)[d]	E_{em} (nm)[d]	τ (ns)[e]	ϕ[f]
1	*cis*-Re(CO)$_2$(dppm)(bpy)$^+$	−30.7, −18.7	1950, 1884	439 (3.53)	642	768	0.020
2	*cis*-Re(CO)$_2$(c-dppene)(bpy)$^+$	+40.0, +49.9	1956, 1886	389 (3.56)	612	378	0.033
3	*cis*-Re(CO)$_2$(c-dppene)(phen)$^+$	+41.1, +51.3	1960, 1890	390 (3.70)	603	3840	0.123
4	*cis*−*trans*-Re(CO)$_2$(t-dppene)$_2$(bpy)$^+$	+16.6, −5.7	1942, 1873	420 (3.38)	637	191	0.014
5	*cis*−*trans*-Re(CO)$_2$(dppm)$_2$(bpy)$^+$	−28.6, +14.5	1940, 1869	428 (3.45)	634	199	0.014
6	*cis*−*trans*-Re(CO)$_2$(PPh$_3$)$_2$(bpy)$^+$	+24.6	1938, 1868	425 (3.54)	620	775[g]	0.039[g]

[a] All complexes are triflate salts in CH_2Cl_2 except complex **3**. [b] Abbreviations: dppm is bis(diphenylphosphino)methane, c-dppene is *cis*-(bis(diphenylphosphino))ethylene, t-dppene is *trans*-(bis(diphenylphosphino))ethylene, bpy is 2,2′-bipyridine, and phen is 1,10-phenanthroline. [c] In CH_3CN with an 85% phosphoric acid external standard. [d] E_{op} and E_{em} are respectively the absorption and emission spectral maxima corresponding to the lowest energy MLCT excited state (log ϵ_{max} is reported). [e] Measured by the phase shift demodulation method with a glycogen scattering standard. Errors are ±5%. [f] Measured against an air-saturated sample of *fac*-[Re(bpy)(CO)$_3$py]OTf in water ($\phi = 0.012$). [g] Reported value of 801 ns as a PF_6^- salt in CH_2Cl_2 (Caspar, J. V. Ph.D. Dissertation, 1982).

CO vibrational modes in the region of ca. 1870−1890 and 1940−1960 cm^{-1} and the appropriate number of ^{31}P NMR spectral peaks are consistent with the structural assignments of the complexes.

All complexes exhibit a yellow to red-orange coloration in the solid and in solution that is due to MLCT transitions in the 390−440 nm region. The corresponding luminescence occurs in the ca. 600−640 nm range (see Table 1). Of special interest from a photochemical perspective are the complexes *cis*-[Re(CO)$_2$(dppm)(bpy)]OTf (**1**) and *cis*-[Re(CO)$_2$(c-dppene)(phen)]PF$_6$ (**3**) (dppm is bis(diphenylphosphino)methane and c-dppene is *cis*-1,2-(bis(diphenylphosphino))ethylene). Complex **1** possesses spectral and photophysical parameters similar to those of Ru(bpy)$_3^{2+}$; for example, compare the energy maxima for absorption and emission and the lifetimes and quantum yields of the lowest MLCT excited state for **1** (440 nm, 642 nm, 768 ns, 0.029; CH_2Cl_2) and Ru(bpy)$_3^{2+}$ (449 nm, 607 nm, 490 ns, 0.024; CH_2Cl_2).[7a] Complex **3** exhibits a lifetime of 3.84 μs and a quantum efficiency of emission of 12.3% (CH_2Cl_2), both of which are extraordinary in the photochemistry of MLCT excited state chromophores.

The new complexes exhibit surprisingly long lifetimes relative to the *fac*-Re(bpy)(CO)$_3$L^{n+} series (L is Cl$^-$ ($n = 0$) or L is a neutral nitrogen or phosphorus donor ($n = 1$)). For example, complex **1** and *cis*-[Re(CO)$_2$(c-dppene)(bpy)]OTf (**2**) exhibit lifetimes of 768 and 378 ns, respectively. This difference is primarily due to a smaller than expected nonradiative rate constant, k_{nr}.[13] In the energy gap law analysis published by Caspar and Meyer for *fac*-Re(bpy)(CO)$_3$L^{n+} the linear relationship $\ln k_{nr} = 40.155 - 1.458E_{em}$ was found.[8] On the basis of this finding, the calculated k_{nr} values for **1** and **2** are 1.13×10^7 and 3.80×10^7 s^{-1} versus the observed values of 1.27×10^6 and 2.56×10^6 s^{-1}. Given the relatively constant value of k_r (ca. 10^5 s^{-1}) characteristic of the *fac*-Re(bpy)(CO)$_3$L^{n+} series, the calculated k_{nr} values predict lifetimes of 26 and 85 ns for **1** and **2**. Several explanations are possible for this behavior. One is the presence of higher-lying states that can be thermally populated, leading to either longer lifetimes for the dicarbonyls or shorter ones for the tricarbonyls depending on the identity of the state (e.g., ligand-localized versus d−d).[14] Another is an inherent difference in Franck−Condon factors. Since some studies have shown that medium-frequency bpy modes, in addition to higher CO modes, act as energy acceptors,[2b] one possible cause of the dramatically increased relative lifetimes is the removal of a critical high-energy mode that participates in energy disposal and its replacement with fewer modes of smaller quantum spacing. Our future work will be aimed at resolving this issue. An important point to remember, however, is that regardless of origin, the room temperature energy gap law behavior is an empirical yardstick by which MLCT excited states may be judged for their utility in numerous applications.

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[14] A meaningful comparison of k_{nr} values can be made only if the potential temperature dependence of this rate constant is taken into account. Studies of the temperature variation of k_{nr} for both the tricabonyls and dicarbonyls must be done before any conclusion concerning the origin of the lifetime differences can be drawn.