

Enhanced Excited-State Basicities of Coordinated Bridging Bis(diimines) (BL) in Ru(bpy)₂(BL)²⁺ (bpy = 2,2'-Bipyridine)

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Monomeric complexes of the type Ru(2,2'-bipyridine)₂(BL)²⁺, where BL = 2,3-bis(2-pyridyl)pyrazine (dpp) or [4,7]-phenanthroline[5,6-*b*]pyrazine (ppz, a planar fused analogue of dpp), emit in the 650–700-nm region in neutral aqueous solution. When the pH is lowered below pH 1, the emission is completely quenched for both. No changes are observed in the UV-visible absorption spectra from pH = 7 to pH = 0. Titrations in concentrated sulfuric acid show that protonation of the free pyrazyl nitrogen occurs for the ground states of these complexes in very acidic media: $H_0 = -4.9$ for the dpp monomer; $H_0 = -6.8$ for the ppz monomer. The absence of emission from the protonated complexes precludes determination of the excited-state pK_a 's from fluorescence titrations. Bimolecular quenching rate constants, k_q , for quenching by H⁺ indicate that the process is diffusion limited for each complex. The apparent pK 's from fluorescence titration curves are consistent with diffusion-limited quenching dominated by the lifetime of the deprotonated complex. Since this would require a favorable proton-transfer reaction, a lower limit for the excited-state pK_a 's would be -1.75 , the value for H₃O⁺.

Introduction

Study of the excited-state properties of tris(diimine) complexes of ruthenium(II) has been an active area of research¹⁻³ because of the unusual excited-state redox properties of Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) and related complex ions, which have been utilized in a number of light-conversion and storage schemes.

One area of interest¹⁻³ involves the mechanism of quenching of excited states of such complexes by various ions and molecules and the implications of the results for electron transfer to or from the excited state. In cases where one of the ligands has one (or more) protonatable sites (e.g. on carboxyl or imino groups), the quenching may be observed⁴⁻⁸ as a function of pH. Several such systems have been studied, with a common type of ligand involved in such proton-dependent quenching being bis(diimines) such as bipyrazine and bipyrimidine. In a number of cases the excited state has been observed⁵⁻⁹ to be a much stronger base than the ground state. In some cases, the coordinated ligand has been reported¹⁰ to exhibit enhanced basicity in the ground state as well, while in other cases its ground-state basicity has been interpreted as lower.⁵ As we discuss below, the case rests on which free ligand pK_a is used for comparison.

We have prepared and studied^{11,12} monomeric complexes of the type Ru(bpy)₂(BL)²⁺, where BL = 2,3-bis(2-pyridyl)pyrazine (dpp) or [4,7]phenanthroline[5,6-*b*]pyrazine (ppz, a planar fused analogue of dpp) as well as their dimeric analogues. We have observed that the monomeric complexes, which emit in neutral solution, are completely quenched below pH 1. The emissions of the dimeric complexes, as expected, are not affected by the same pH conditions. We report here more extensive characterization

of the pH effects on the ground- and excited-state properties of these complexes, including ground-state pK_a 's and an estimate of the increase in excited-state basicity.

Experimental Section

Materials. The monomeric dpp and ppz complexes were prepared and purified as previously reported.^{11,12} Fisher technical grade sulfuric acid (96%) was used in pH titrations. Above pH 1, pH was determined by using an Orion 501 pH meter with a combination pH electrode. Below this range, H_0 was determined by correlation to the literature values^{13,14} from the concentration of H₂SO₄, as standardized following dilution and NaOH titration using phenolphthalein as indicator.

Physical Measurements. Absorption spectra were recorded on a Cary 14 or a Perkin-Elmer Lambda 3 UV-visible spectrophotometer. Emission spectra were recorded on a Perkin-Elmer Hitachi MPF-2A emission spectrophotometer. Lifetimes were measured by using a Quanta-Ray DCR-2A Nd:YAG laser as excitation source and a Bausch & Lomb 33-86-76 monochromator to disperse the 90° emitted light. Detection was accomplished with an RCA C31034A PMT connected to a Tectronix 7834 oscilloscope.

Results

Absorption Spectra. Figure 1 shows the visible absorption spectra of the dpp (top) and ppz (bottom) monomeric complexes in the range 350–650 nm at pH 7 (solid lines). The corresponding spectra of the complexes in concentrated (>10 M) perchloric acid are also presented (dashed lines). As Figure 1 shows, in perchloric acid the two metal-to-ligand charge-transfer peaks of the dpp monomer are lost and replaced by a single peak with a maximum absorbance at 575 nm. This is accompanied by a color change from yellow-orange to deep purple, a color strikingly similar to that of the dimeric complex, which exhibits a similar longer wavelength charge-transfer band at 525 nm. A similar change is observed for the ppz monomeric complex, which exhibits a charge-transfer band centered at 600 nm in concentrated perchloric acid. In this case the color is a deep blue, again similar to that of the binuclear complex, which shows a maximum at 573 nm. The spectra at pH 7 in aqueous solution and in perchloric acid (Figure 1) are not for identical concentrations of complex. In concentrated perchloric acid, both complexes are bleached after several hours, probably due to oxidation processes. Concentrated sulfuric acid solutions were used therefore to quantitate the pH conditions under which these spectral changes occur.

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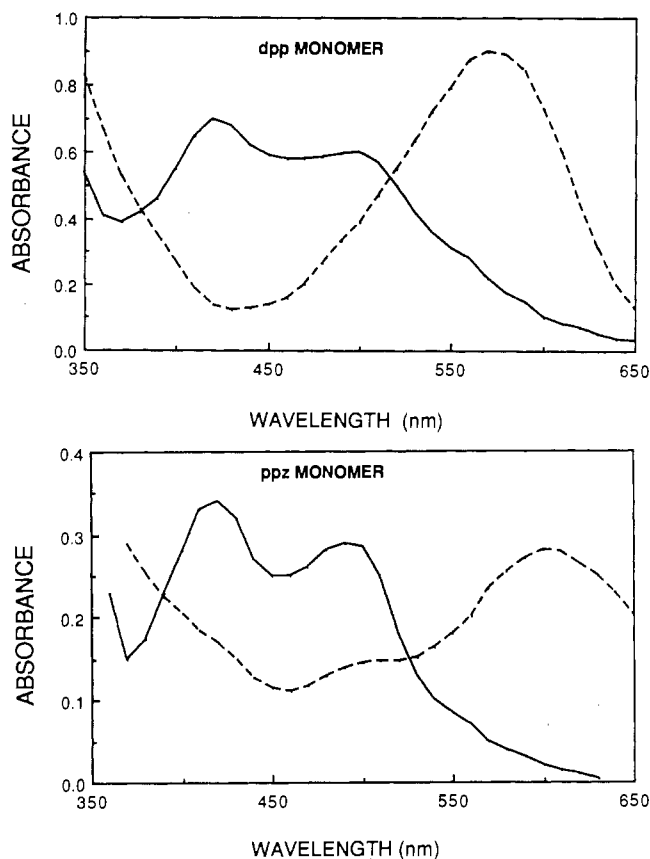


Figure 1. Absorption spectra of dpp (top) and ppz (bottom) monomeric complexes in water at pH 7 (—) and in concentrated perchloric acid (---).

Titrations for both the dpp and ppz monomeric complexes were reversible in sulfuric acid solutions. A single isosbestic point was observed at 511 nm for the dpp complex and at 530 nm for the ppz complex. When the rise in absorbance at the long-wavelength maxima was plotted versus the Hammett acidity function ($-H_0$) for the sulfuric acid solutions, the following pK_a 's for protonation of the complexed ligands were obtained: dpp, $H_0 = -4.9$; ppz, $H_0 = -6.8$. We associate these with the protonation of the imino nitrogen opposite the coordinated ruthenium(II) on the pyrazyl portion of each ligand. A careful study of the spectra in the visible and ultraviolet regions from pH 7 to the acidity where the above transitions were observed revealed no other pH-linked absorbance changes. The anticipated protonation of the free pyridyl imino nitrogen at a pH significantly higher (pH \approx 1–3) is not observed.

Our study of the free dpp ligand showed that a spectral shift from 282 to 293 nm takes place with a half-maximal change for pH 2.0. No further changes were observed in the UV spectrum, even in 96% sulfuric acid. The hydrochloride of dpp titrates for two protons (i.e. it is the dihydrochloride), confirming the existence of the two pyridyl protonations with approximately the same (unresolvable) pK_a 's. On statistical grounds,¹⁹ the macro- pK_a 's for two independent groups with identical micro- pK_a 's must vary by 0.6 pK unit. Thus, approximate values for the unresolved pK_a 's for the pyridyl groups would be ~ 1.7 and ~ 2.3 .

Emission Measurements. The emission of both complexes is completely quenched below 0.1 M acid. Fluorescence titration curves for both complexes are presented in Figure 2. Emission was monitored at 675 nm for the dpp monomeric complex and at 690 nm for the ppz complex. The ionic strength was less than $\mu = 0.05$ in all cases, since dilute sulfuric acid was used to adjust solution pH values. In neither case were we able to observe any residual emission in the 550–830-nm range, despite careful investigation with an instrument usually used for Raman spectroscopy equipped with a red-sensitive phototube (RCA C31034A)

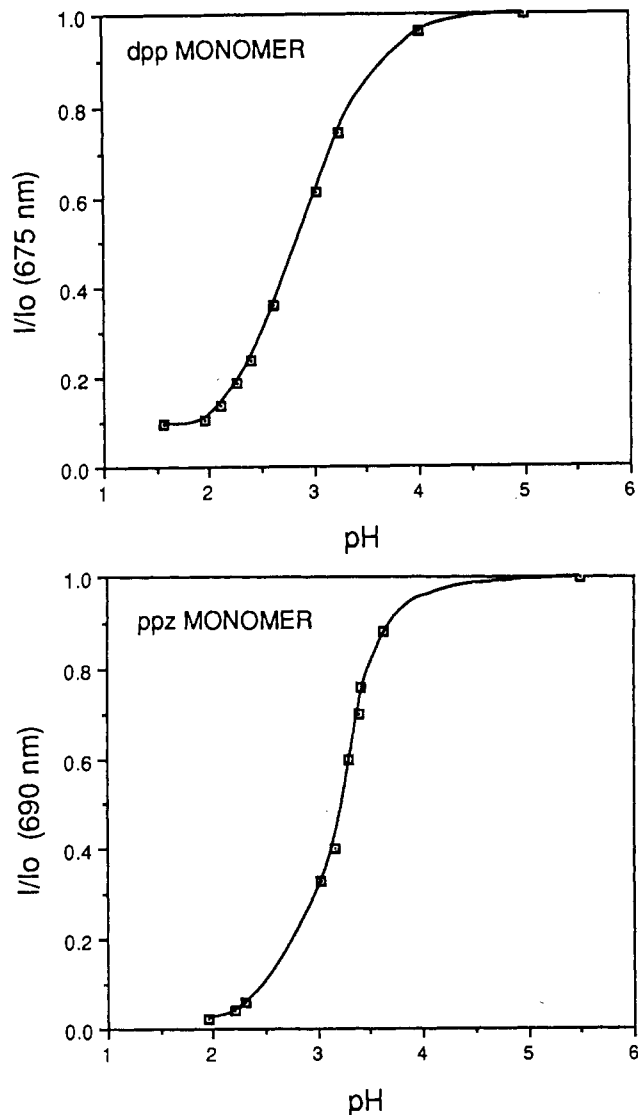


Figure 2. Relative emission (wavelength as indicated) versus pH for the dpp (top) and ppz (bottom) monomeric complexes.

and argon laser excitation. Likewise, no emission was observed from solutions of H_0 sufficiently low to establish a 100% protonated ground state.

Lifetime measurements for the dpp complex show the pH = 7 lifetime of 120 ns dropping to 91 ns at pH 2.89. The lower pH limit is a result of the weakening of the emission intensity (see Figure 1) as the pH is lowered to a level where reliable lifetime determinations are not possible with our equipment. Although the lifetime appears to be dropping, the error in these measurements (~ 10 – 20% at lowest pH) allows no firm conclusions to be drawn.

Discussion

Interpretation of Fluorescence Titration Curves. The ground-state pK 's for both complexes establish that, in the pH range where emission intensity diminishes (~ 1 – 4), only the unprotonated form is excited. Because the protonated form of each complex does not emit, fluorescence titration curves cannot be used²⁰ to establish excited-state pK values. The Stern–Volmer plots in Figure 3 yield bimolecular quenching rate constants (k_q) of 5.5×10^9 for the dpp complex and 1.6×10^{10} for the ppz complex, establishing that the proton encounter reaction is diffusion limited in each case. Indeed, if one assumes a protonation rate of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and uses the lifetimes of the complexes to generate quenching data, the resulting fluorescence titration curves show apparent pK_a 's of 3.1 (dpp) and 3.3 (ppz). The magnitude of k_q indicates^{21,22} that proton

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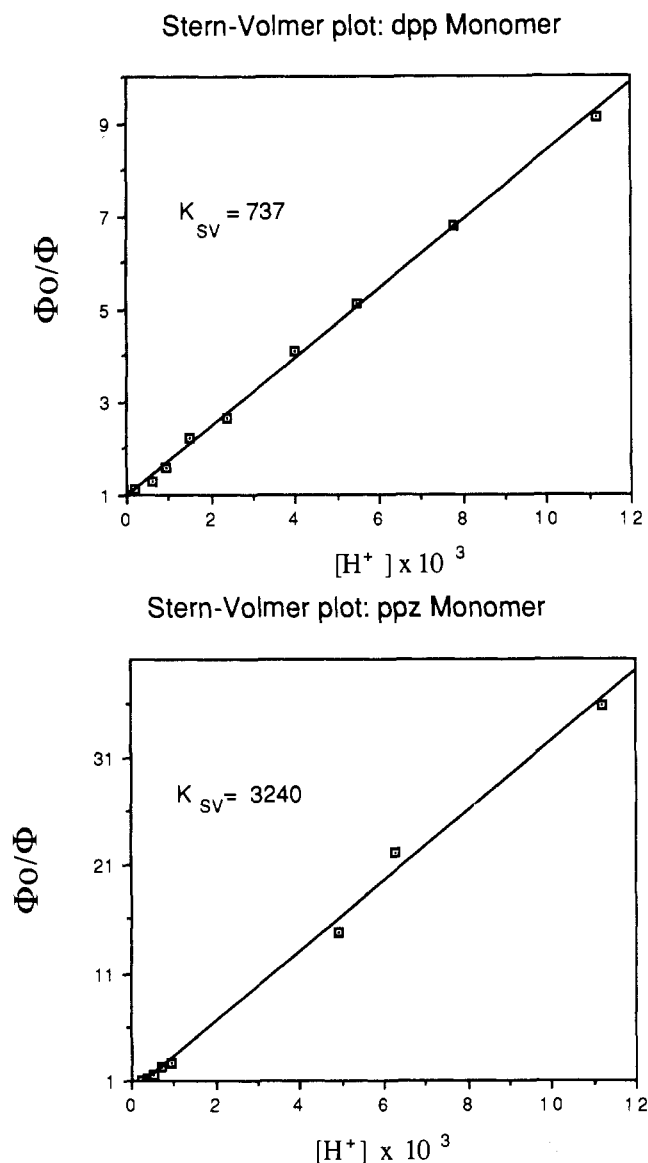


Figure 3. Stern-Volmer plots of data in Figure 2.

encounter is most probably site-specific protonation of the excited base, which is thermodynamically favored in each case. Since the pK_a of H_3O^+ is -1.75 , this would establish a lower limit for the excited-state pK_a of each complex. If the excited-state pK values were lower, one could not observe such effects in aqueous solution.

Acid Dissociation Constants of Diimines and Ru(II)-Complexed Diimines. The pK_a for protonation of pyridine is 5.23 (Figure 4), while for pyrazine¹⁶ it is only 0.80, indicating the reduced basicity of pyrazine due to the para imino nitrogen. The second protonation for pyrazine is at -6.25 , now even less basic because of the first para protonation. When pentaammineruthenium(II) is coordinated to pyrazine¹⁰ (Figure 5), the pK_a is 2.5. Thus, the imino nitrogen in the complex has been considered more basic than pyrazine itself by about 2 orders of magnitude. However, if one considers the comparison to the pyrazinium ion (single H^+ rather than pentaammineruthenium(2+)), it may be fair to say that coordination of the ruthenium(II) really *increases* the basicity by much more than 2 orders of magnitude (cf. -6.25 and 2.5). Part of this effect can be attributed to the back-bonding from ruthenium(II) to pyrazine.

For 2,2'-bipyridine¹⁷ (bpy) and 2,2'-bipyrazine⁵ (bpz) interpretation of the protonations is further complicated by electrostatic

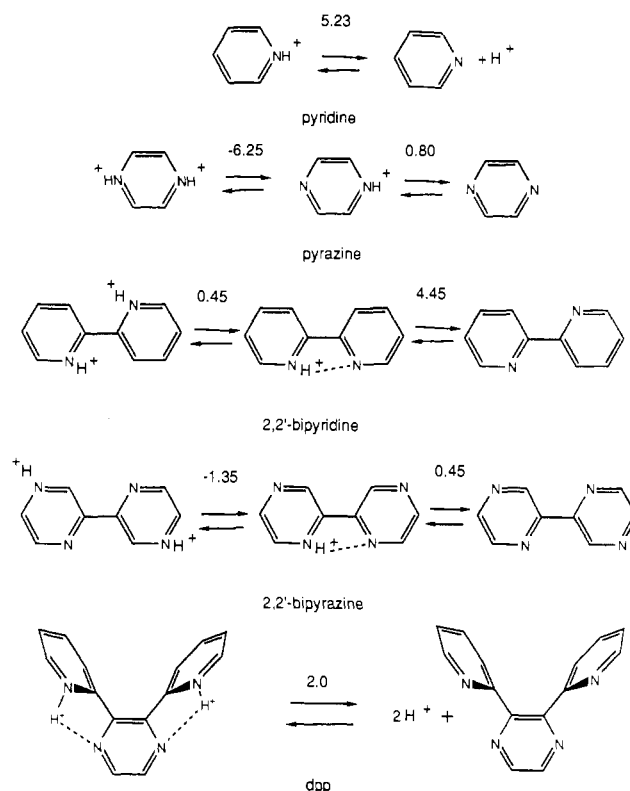


Figure 4. Structures and pK_a 's for diimine and bis(diimine) ligands (references in text.)

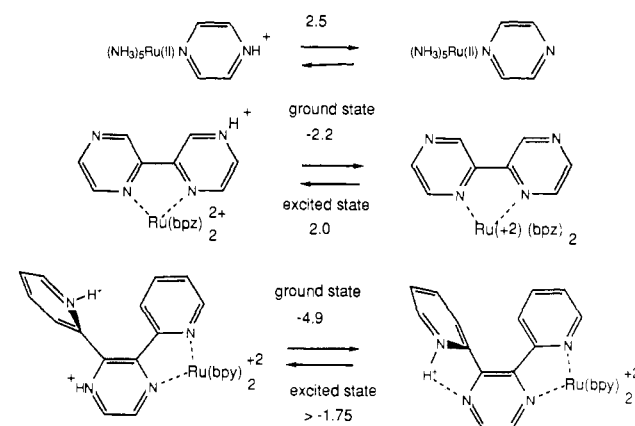


Figure 5. Structures and pK_a 's for diimines coordinated to ruthenium(II) (references in text.)

interactions, primarily a large repulsion for the diprotonated forms and an attraction of the 2-imino nitrogen on the ring next to the protonated nitrogen in the monoprotated form. Thus, the first pK_a 's for bpy and bpz are a bit lower than those of pyridine and pyrazine, respectively, but the second pK_a is much lower (0.45) for bpy but only slightly lower (-1.35) for bpz. The difference is due to the alternate protonation scheme for bpz in which the 3,3'-nitrogens are protonated, rather than both 2,2'-nitrogens, in the diprotonated form. The third protonation, which would be sterically similar to the coordinated bpz protonation, has been reported⁵ at about $H_0 = -10$. Figure 5 shows that the coordinated bpz in the tris complex protonates below $pH = -2.2$ and is thus much more basic than bpz (again compare the -10 figure). The excited state shows an increase in pK_a to 2.0, consistent with the increased electron density on the bpz ligand in the metal-to-ligand excited state. This was measured⁵ by emission quenching as a function of pH.

For the ligand dpp, our pK_a for protonation (Figure 4) of the pyridyl nitrogens of 2.0 (or individual values of 1.7 and 2.3) is reasonable, since 2,2'-bpy is 2-pyridylpyridine, and in dipyridylpyrazine the first two protonations involve isolated pyridyl

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functionalities. As indicated in Figure 4, the pyridyl rings for unprotonated dpp are probably rotated out of the pyrazyl plane due to steric hindrance. This is inferred¹⁷ from the ultraviolet spectrum, which shows a single strong band at 282 nm and only a weak band at 240 nm. For the diprotonated form only a single band at 293 nm is seen, indicating an even more nonplanar conformation. Nevertheless, in Figure 4 we indicate some electrostatic attraction of the pyrazyl nitrogens for the protons at the pyridyl nitrogens.

For the complexed dpp we were unable to detect the protonation of the single pyridyl nitrogen using absorption spectroscopy. But because it is somewhat remote from the Ru(bpy)₂²⁺ chelation site, we would assume its pK_a is close to that of the free-ligand value, or perhaps somewhat more basic (pK_a > 2.0). The spectrally detected protonation with H₀ = -4.9 in concentrated sulfuric acid is therefore assigned as protonation of the pyrazyl nitrogen para to the ruthenium(II) and is probably hindered by the attraction of this site to the previously protonated pyridyl group. Once protonation takes place, electrostatic repulsion would force rotation of the positive charge away from the pyrazyl plane, as illustrated. The marked color change and shifts in charge-transfer spectra also argue for the correctness of this assignment by analogy to the dimeric complexes. The extremely low pK_a value for protonation of the pyrazyl nitrogens in the complexed dpp, which may be considerably more basic than the uncomplexed ligand sites, would lead to the conclusion that these protonations might not be observable for the free ligand. In fact, the ultraviolet spectrum of dpp shows no further changes from below 1 M acid to 96% sulfuric acid.

For the ppz monomeric complex as well as the ligand, one would expect the protonation at the pyrazyl sites to be even more difficult than that for dpp, since the fused aromatic ring system will not allow any alleviation of the steric repulsion of two adjacent positive charges and in addition increases electron-withdrawal effects. The measured value of H₀ = -6.8 is consistent with this. (Note: the successive pK_a's for 1,10-phenanthroline¹⁸ are 4.9 and -0.2.)

Increased Basicity of Coordinated Diimines in Excited States.

For the excited-state complexes involving coordinated dpp and ppz, the lower limit of pK is -1.75. Thus, in the MLCT excited states, the coordinated ligands are better bases, with pK values at least 3 (dpp) and 5 (ppz) units higher than those of the ground states. Resonance-enhanced Raman spectra have confirmed^{11,12} that the lowest energy charge-transfer state for both the dpp and ppz monomeric complexes involves transfer of electron density to these ligands and not bpy. Further interpretation of the nature of the most enhanced normal modes in these spectra suggests that the pyrazyl ring is the site of more electron density in the excited state and that charge is not transferred symmetrically, as would be the case for bpy or bpz. This would be consistent with increased basicity of the imino nitrogen para to the ruthenium(II). Also, consider that for the radical anion of 2,2'-bipyridine, which is analogous to the charge-transfer excited state, the reported¹⁸ pK_a's are ~24 and 8 (cf. neutral bpy values of 4.45 and 0.45).

The juxtaposition of an already protonated pyridyl nitrogen with a pK_a near 2.0 suggests that, in the excited state, protonation of the now much more basic pyrazyl nitrogen is perhaps unusually facile because it can be accomplished by simply rearranging the proton between two already electrostatically attracted (and favorably oriented) sites that transiently possess imino nitrogens with similar pK_a's. This should occur at an unusually fast (picoseconds) rate and may explain why no emission is detected from the protonated form, since this kind of high-speed dynamic process may provide an especially favorable route to nonradiative deexcitation, if one considers the additional involvement of solvent water in such an H-bonding network.

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Reduction of CO₂ and Other Substrates Using Photochemical Reactions of the W₂(CO)₁₀²⁻ Complex

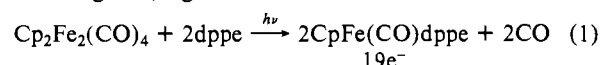
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The photochemistry of the W₂(CO)₁₀²⁻ complex was investigated with the goal of determining if irradiation of this dimer generates a powerful reducing agent, presumably a 19-electron species. In general, the photochemistry of the W₂(CO)₁₀²⁻ complex is comparable to that of other metal-metal-bonded carbonyl dimers. Irradiation into the low-energy tail of the dπ → σ* electronic transition of the W₂(CO)₁₀²⁻ complex led to W-W bond homolysis. The resulting 17-electron W(CO)₅ radicals could be trapped with suitable ligands such as 4-cyanopyridine to give "19-electron adducts". (See ref 3 for an important definition of the phrase "19-electron adduct".) Evidence is presented that the ligands PPh₃ and PBU₃ also react with photogenerated W(CO)₅⁻ to form adducts: W(CO)₅⁻ + PR₃ → W(CO)₅PR₃⁻. These adducts are powerful reducing agents, and they were used to reduce CO₂ to formate and CO. The only organometallic product formed in the reaction was W(CO)₅PPh₃, the oxidized form of the 19-electron complex. In a similar manner, Mn₂(CO)₁₀ was reduced to Mn(CO)₅⁻, Cp₂Co⁺ to Cp₂Co, benzophenone to the radical anion, and methylviologen (MV²⁺) to MV⁺. Alternative reduction mechanisms involving the W(CO)₅⁻ radical, W(CO)₅²⁻, or HW₂(CO)₁₀⁻ as reductants were shown not to be operating. Nineteen-electron complexes generated by irradiation of Cp₂Mo₂(CO)₆ proved incapable of reducing CO₂.

In several recent papers, we demonstrated that 19-electron organometallic complexes³ can be used as photogenerated reducing agents.⁴⁻⁶ Nineteen-electron complexes form transiently when

metal-metal-bonded carbonyl dimers are irradiated in the presence of selected ligands, e.g.⁵⁻⁸



dppe = 1,2-bis(diphenylphosphino)ethane

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(3) The phrase "19-electron complex" or "19-electron adduct" is used to describe the adducts that form when 17-electron radicals react with 2-electron ligands. No implication of geometric or electronic structure is implied by this definition. A more complete discussion of the electronic and geometric structures of the 19-electron complexes is found in: Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215-245.

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