where

$$(\mathrm{Ox,Ox}) + (\mathrm{Red,Red}) \overset{K_{\mathrm{con}}}{\rightleftharpoons} 2(\mathrm{Ox,Red})$$

The $K_{\mathrm{con}}$ values determined for the series from CV values of $\Delta E_{1/2}$ and from the DPP values of the peak separations (Table X) are tabulated in Table XII. Reliable CV values for M = Fe, Mn or DPP values for M = Mn could not be obtained due to distortions brought about by small separations. The ease of measuring peak separations by DPP probably make the $K_{\mathrm{con}}$ values determined by DPP more dependable than those obtained from CV. However, in most cases the differences are not very great, generally within a factor of about 2. The results, in either case, clearly demonstrate that the stability of the mixed U(VI), U(V) species is dependent upon the intervening divalent metal ion and increases in a periodic manner from M = Fe to M = Zn. The structural results do not give any obvious clues to the origin of this periodicity. Except for the usual variation in M–O bond lengths for M = Ni, Co, Fe, Mn, the structures do not exhibit obvious periodic difference especially in the plane of the tetraketonates. Unfortunately, we have not succeeded in preparing and characterizing the binuclear $UO_2^{2+}$ complex with the central position vacant. Similar studies on it could presumably furnish direct information on the importance of an intervening metal ion.

**Acknowledgment.** This work was supported by the National Science Foundation (Grant No. CHE 83-00251).

**Registry No.** $[(UO_2)_2Mn(DBAA)_2(py)_4]\cdot 2py$, 91238-59-4; $[(UO_2)_2Fe(DBAA)_2(py)_4]\cdot 2py$, 91238-61-8; $[(UO_2)_2Co(DBAA)_2(py)_4]\cdot 2py$, 91238-63-0; $[(UO_2)_2Ni(DBAA)_2(py)_4]\cdot 2py$, 81205-64-3; $[(UO_2)_2Cu(DBAA)_2(py)_4]$, 91238-64-1; $[(UO_2)_2Zn(DBAA)_2(py)_4]$, 91238-65-2.

**Supplementary Material Available:** Listings of bond distances and angles, hydrogen atom parameters, thermal parameters, and observed and calculated structure factors (×10) (86 pages). Ordering information is given on any current masthead page.

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# Multiple Luminescence from Borohydridobis(triphenylphosphine)copper(I)

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Low-temperature (77 K) luminescence spectra and lifetimes have been measured for the $Cu(PPh_3)_2BH_4$ ($PPh_3$ is triphenylphosphine) and $Cu(prophos)BH_4$ (prophos is 1,3-bis(diphenylphosphino)propane) complexes. $Cu(PPh_3)_2BH_4$ exhibits multiple emission from $^3\Pi\Pi^*$ and $^3(\sigma\text{-}a_\pi)$ excited states in appropriate solvents, while $Cu(prophos)BH_4$ shows only a single $^3(\sigma\text{-}a_\pi)$ emission in most of the solvents chosen for this study. The electronic transition associated with the $\sigma\text{-}a_\pi$ assignment is analogous to the $l\text{-}a_\pi$ transition for the free phosphine ligand. These unique emission results are discussed in terms of intramolecular and intermolecular (solvent–solute) effects.

## Introduction

The occurrence of multiple-state emission,[1] specifically dual phosphorescence, for transition-metal complexes has two origins that may not be mutually exclusive: (1) spatially isolated (single (chelate)-ring and (2) distinct-orbital emission. The spatially isolated emission is most directly illustrated by the dual phosphorescence exhibited by the $[Rh(bpy)_2phen]^{3+}$ and $[Rh(phen)_2bpy]^{3+}$ complexes.[2] A more subtle but related single-ring emission has been characterized for the $[Ru(bpy)_3]^{2+}$ complex ion with use of excited-state resonance Raman[3] and photoselection[4] spectroscopy. The multiple emissions described here each have the same orbital origin, $\Pi\Pi^*$ for the Rh(III) complexes and $d\Pi^*$ for $[Ru(bpy)_3]^{2+}$ (and a number of its derivatives), and, at present, has only been identified for nominally $d^6$ complexes. In contrast, the second type of multiple emission, distinct orbital, has been observed not only for $d^6$ complexes[5,6] but also for $d^8$ Re(I) complexes[7] and most recently for $d^{10}$ Cu(I) complexes.[8] Here the two phosphorescence emission bands differ in their orbital origin with such combinations as $dd^*\text{–}d\Pi^*$,[5] $dd^*\text{–}\Pi d^*$,[6] and $d\Pi^*\text{–}\Pi\Pi^*$[8] having been observed. In these latter cases emission spectra and lifetimes can be used to identify the multiple-state emission with appropriate extreme precaution taken to ensure purity and identity of the emitting material.

At the inception of this work, the only multiple-state Cu(I) emitters were those reported by McMillin and co-workers[8] for $[Cu(PPh_3)_2L]^+$ ($PPh_3$ is triphenylphosphine) complexes where L is a diimine ligand, e.g., 1,10-phenanthroline. These emissions were assigned as occurring from intraligand ($\Pi\Pi^*$) and metal-to-ligand charge-transfer ($d\Pi^*$) excited states, both of which were associated with the diimine ligand. Recently, Kutal and co-workers determined[9] that Cu(I) complexes such

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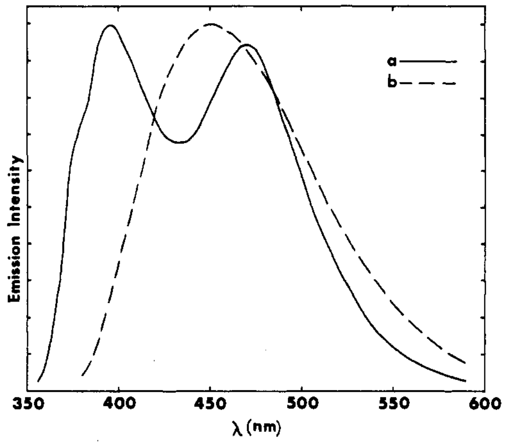

**Figure 1.** Low-temperature (77 K) emission spectra in glassy toluene (313-nm excitation): (a) $Cu(PPh_3)_2BH_4$; (b) $PPh_3$.

as $Cu(PPh_3)_2BH_4$ and $Cu(prophos)BH_4$ (prophos is 1,3-bis(diphenylphosphino)propane) are efficient photosensitizers of the valence isomerization of norbornadiene to quadricyclene, while $Cu(diphos)BH_4$ (diphos is 1,2-bis(diphenylphosphino)ethane) is not an efficient sensitizer. Room-temperature absorption and emission data were included in these studies to identify and locate the state responsible for sensitization. The emitting excited state was characterized as $\sigma$-$a_\pi$, analogous to the l-$a_\pi$ designation of Kasha and Rawls,[10] which appears to be the most appropriate assignment for the corresponding free-ligand emission. Here, additional luminescence data are reported for the $Cu(PPh_3)_2BH_4$ and $Cu(prophos)BH_4$ complexes to corroborate and supplement the previous emission assignments. Preliminary data for the triphenylphosphine complex did evidence an unusual emission band shape at low temperature. Therefore, special attention has been focused upon these complexes to determine if they are additional examples of multiple-state emitters.

## Experimental Section

The preparation of $Cu(PPh_3)_2BH_4$ and $Cu(prophos)BH_4$ has been previously described.[9]

Spectral-grade solvents were used for all luminescence measurements. Solvents obtained from different commercial sources had no effect on the observed complex and free-ligand luminescence; moreover, blank-solvent emission spectra were measured to verify that the solvents could safely be used as received. All emission spectra reported herein were measured immediately following solution preparation even though the solutions yielded reproducible spectra for at least several hours (with one exception noted in the next section). Solutions of the complexes in many of the solvents are stable for periods of days to weeks, depending upon the preparation and storage conditions. Fresh-solution spectra are also independent of concentration (i.e., exhibit a constant bandshape) in the experimentally usable concentration range ($\sim 10^{-4}$–$10^{-2}$ M).

Low-temperature (77 K) emission spectra were obtained with an Aminco-Bowman spectrophotofluorometer (SPF). The excitation source used for the emission measurements was a Hanovia 200-W Hg–Xe lamp, and a Hamamatsu R955 photomultiplier tube (PMT) was used for detection. Emission spectra were not corrected for PMT or monochromator response.

Emission decay curves for the complexes (measured at appropriate emission wavelengths) were recorded, and lifetimes were calculated as described elsewhere.[11] The decay curves for $PPh_3$ and prophos were photographed from oscilloscope displays with use of an Aminco-Bowman phosphoroscope or a simple guillotine-shutter method with the SPF. Lifetimes for the free ligands were calculated as indicated for the complexes.

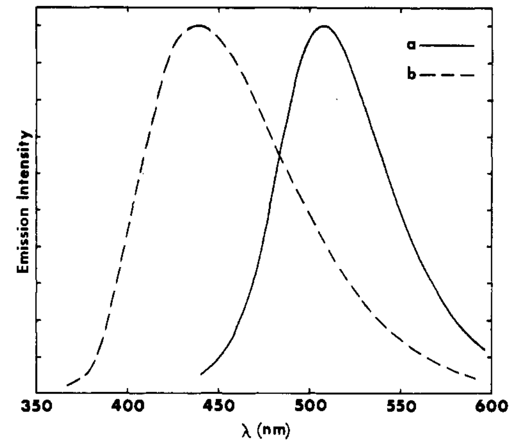

**Figure 2.** Low-temperature (77 K) emission spectra in glassy toluene (313-nm excitation): (a) $Cu(prophos)BH_4$; (b) prophos.

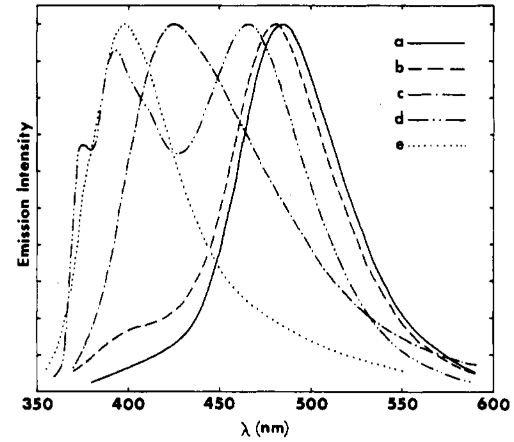

**Figure 3.** Low-temperature (77 K) emission spectra of $Cu(PPh_3)_2BH_4$ (313-nm excitation) in (a) cyclohexane, (b) benzene, (c) chloroform, (d) EPA glass, and (e) 1:1 toluene–chloroform.

Table I. Low-Temperature (77 K) Lifetimes in Glassy Toluene

| species | λ, nm | lifetime, ms | species | λ, nm | lifetime, ms |
|---|---|---|---|---|---|
| $PPh_3$ | 450[a] | 20[b] | prophos | 439[a] | 25[b] |
| $Cu(PPh_3)_2BH_4$ | 390[c] | 2.1 | $Cu(prophos)BH_4$ | 508[a] | 0.7 |
| | 490[c] | 0.8 | | | |

[a] Emission maximum. [b] Long-lived emission component. [c] Not equal to emission maximum (see text).

## Results and Discussion

**A. Low-Temperature (77 K) Luminescence Data.** Emission spectra of $Cu(PPh_3)_2BH_4$, $Cu(prophos)BH_4$, $PPh_3$, and prophos in glassy toluene[12] are presented in Figures 1 and 2. $PPh_3$ and prophos exhibit broad, structureless emissions of similar energy and lifetime (Table I). The luminescence spectrum of $Cu(PPh_3)_2BH_4$ consists of two bands, the maxima of which occur at 395 and 470 nm. The relative intensities of these two bands exhibit a significant dependence upon the excitation wavelength, but the ratio of the two peak intensities varies only a few percent between samples for a given excitation energy. A shoulder can also be observed on the high-energy side of the 395-nm band. In contrast, the emission of $Cu(prophos)BH_4$ shows only a single, structureless emission band at 508 nm. Lifetime data for the two phosphine–Cu(I) borohydride complexes are given in Table I. Decay curves for $Cu(prophos)BH_4$ were recorded at the emission maximum

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(10) M. Kasha and H. R. Rawls, *Photochem. Photobiol.*, **7**, 561 (1968).

(11) W. L. Huang, D. P. Segers, and M. K. DeArmond, *J. Phys. Chem.*, **85**, 2080 (1981).

(12) Toluene forms a slightly opaque (foggy) glass at low temperature.

while the emission wavelengths for $Cu(PPh_3)_2BH_4$ were chosen such that single-exponential decays were measured.

The curious low-temperature luminescence of $Cu(PPh_3)_2BH_4$ in toluene initiated an investigation of the complex emission in several solvents. Emission spectra of $Cu(PPh_3)_2BH_4$ in cyclohexane, benzene, chloroform, EPA (5:5:2 diethyl ether–isopentane–ethanol), and 1:1 toluene–chloroform are shown in Figure 3. Spectra were also measured in frozen dichloromethane (spectrum similar to that in cyclohexane) and in a 1:1 toluene–ethanol glass (spectrum nearly identical with that in EPA).

Cu(prophos)$BH_4$ exhibits a single-band emission similar to that in toluene in cyclohexane, benzene, 1:1 toluene–chloroform, and dichloromethane but is insufficiently soluble in EPA and 1:1 toluene–ethanol. Cu(prophos)$BH_4$ does show an overlapping two-band emission spectrum in chloroform, which appears to be composed of a broad, structureless emission at ~430 nm (similar to that observed for $Cu(PPh_3)_2BH_4$ in chloroform) and an emission analogous to the ~510-nm emission in the other solvents. Emission spectra recorded for Cu(prophos)$BH_4$ in chloroform vary in appearance from one sample to the next, differing in the relative intensities of the two bands.

**B. Solution Behavior and Stability.** A priori, the origin of the unique luminescence of $Cu(PPh_3)_2BH_4$ and Cu(prophos)$BH_4$, notably the multiple features in some of the emission spectra, must be considered in terms of the stability of the complexes in solution. $Cu(PPh_3)_2BH_4$ is readily soluble in chloroform, dichloromethane, benzene, and toluene and is moderately soluble in cyclohexane, EPA, and 1:1 toluene–ethanol. Cu(prophos)$BH_4$ is somewhat less soluble in most of these solvents but is relatively insoluble in EPA and 1:1 toluene–ethanol. Reported[9a,b,13] to be undissociated in benzene and chloroform, $Cu(PPh_3)_2BH_4$ appears to also be undissociated in dichloromethane, toluene, and cyclohexane, and is likely undissociated *initially* in EPA and 1:1 toluene–ethanol (vide infra). The two bands in the emission spectrum of $Cu(PPh_3)_2BH_4$ in toluene do not result from dissociation of a $PPh_3$ ligand since neither band corresponds to the free-ligand emission in this solvent; likewise, $PPh_3$ dissociation cannot account for the spectra measured in the other solvents. Analogously, Cu(prophos)$BH_4$ is believed to be undissociated in those solvents in which the complex is soluble.

Although colorless solutions of $Cu(PPh_3)_2BH_4$ and Cu(prophos)$BH_4$ in the various solvents initially exhibit the emissions described above, visual and spectral observations indicate that *slow* thermal and/or photochemical decomposition of the complexes in solution does occur, typically over a period of several days to several weeks.

Even though the products and the mechanistic details of any subsequent decomposition have not been characterized, the emission spectrum recorded for $Cu(PPh_3)_2BH_4$ in toluene does not appear to result from decomposition. Fresh solutions of concentration $1.0 \times 10^{-4}$–$5.0 \times 10^{-3}$ M, solutions prepared at 0 °C and immediately cooled to 77 K, deoxygenated (purged with $N_2$) as well as air-saturated solutions, solutions prepared with spectral-grade toluene from various commercial sources, solutions prepared with toluene previously dried with appropriate molecular sieves, and solutions extracted with water all exhibit the same emission. Fresh solutions of varying concentration in cyclohexane, dichloromethane, benzene, and chloroform also yield reproducible spectra, suggesting that the integrity of $Cu(PPh_3)_2BH_4$ is also initially maintained in these solvents. Qualitative studies of the behavior of $Cu(PPh_3)_2BH_4$ in EPA and 1:1 toluene-ethanol indicate that, although an emission similar to the higher energy band observed in the emission spectra may result from dissociation of $BH_4^-$ (which subsequently undergoes solvolysis by ethanol), dissociation of the borohydride ligand does not account for the presence of the higher energy band in *fresh-solution* spectra. Dissociation of the $BH_4^-$ ligand in toluene, cyclohexane, and dichloromethane is also not evident and, as previously noted, has been shown not to occur in chloroform or benzene.

Cu(prophos)$BH_4$ is qualitatively more stable than $Cu(PPh_3)_2BH_4$ in the solvents discussed above (EPA and 1:1 toluene-ethanol excluded) but does undergo some decomposition analogous to that of $Cu(PPh_3)_2BH_4$ (with the relative stability of $Cu(PPh_3)_2BH_4$ and Cu(prophos)$BH_4$ likely relating to differences in the lability of the phosphine ligands); however, the emission of this complex in these solvents, including chloroform, is believed to be characteristic of the unreacted complex. Solutions of Cu(prophos)$BH_4$ in chloroform do not exhibit any visual or obvious spectral decomposition for at least several days. Even though the relative intensity of the two bands in the emission spectrum varies with the sample, or for one sample that is thawed and refrozen, low-temperature spectra measured for a given sample after each of several thaw-freeze cycles do not evidence systematic changes.

Thus, the unusual low-temperature luminescence of $Cu(PPh_3)_2BH_4$ and Cu(prophos)$BH_4$, including the multiple bands observed in some of the spectra, must result from intramolecular properties which are perturbed by the solvent environments that the complexes experience. These unique solvent effects will be discussed in conjunction with the characterization of the emitting excited state(s) for the two complexes.

**C. Emission Assignments. Free Ligands.** The low-temperature emission of $PPh_3$ and prophos in many solvents consists of a short-lived fluorescence and a long-lived delayed fluorescence of E type;[14,15] also, the orbital character of the emitting excited state is most appropriately designated as l-$a_\pi$ type.[10] In contrast, the emission of these arylphosphines in acidic alcohol solution[16] consists of a phosphorescence (~395 nm) and a higher energy fluorescence (~300 nm), both of which can be associated with a phenyl-ring-localized $\pi^* \rightarrow \pi$ transition. The occurrence of a $\Pi\Pi^*$ rather than an l-$a_\pi$ emission in acidic solution likely results from protonation of the lone-pair electrons. This $\Pi\Pi^*$ assignment is supported by the similarity of this emission and that of $Ph_3PO$,[14] for which no lone pair on phosphorus exists.

The nature of the prominent long-wavelength band in the absorption spectra of aromatic phosphines has been the subject of many papers, and the assignments of the corresponding transition range from $\pi \rightarrow \pi^*$ to $n \rightarrow \pi^*$.[17] Presently, the l-$a_\pi$ designation appears to be generally accepted even though the extent of p–π conjugation between the l-orbital electrons and π system of the attached aromatic groups remains a matter of dispute.[18]

The l-$a_\pi$ absorption band in the electronic spectrum of an arylphosphine may undergo a bathochromic shift upon the introduction of substituents into the molecule. The different explanations suggested in the literature to account for this effect include the following:[17,18] (1) intensification of p–π conjugation with an increase in the C–P–C valence angle(s), (2) stabilization of the l-$a_\pi$ excited state with a change in the

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(13) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, 7, 1051 (1968).

(14) N. A. Rozanel'skaya, A. I. Bokanov, B. M. Uzhinov, and B. I. Stepanov, *J. Gen. Chem. USSR* (*Engl. Transl.*), **45**, 263 (1975).

(15) Our data show that the longer lived emission may occur at slightly lower energy in some solvents, indicative of some triplet character in the emission. Free-ligand spectral data presented herein were measured by utilizing the phosphorescence setup of the luminescence spectrometer.

(16) D. P. Segers and M. K. DeArmond, unpublished data.

(17) G. V. Ratovskii, A. M. Panov, O. A. Yakutina, Yu. I. Sukhorukov, and E. N. Tsvetkov, *J. Gen. Chem. USSR* (*Engl. Transl.*), **48**, 1394 (1978).

(18) I. Bokanov and B. I. Stepanov, *J. Gen. Chem. USSR* (*Engl. Transl.*), **49**, 1036 (1979) and references therein.

Table II. Room-Temperature Emission Data[9]

| species | solvent | $\lambda_{max}$, nm | lifetime | emission yield |
|---|---|---|---|---|
| $PPh_3$ | benzene | 474–476 | <10 ns | $3.3 \times 10^{-3}$ |
| $Cu(PPh_3)_2BH_4$ | benzene | 474–476 | <10 ns | $3.4 \times 10^{-4}$ |
| $Cu(prophos)BH_4$ | cyclohexane | $510^a$ | 4.2 μs | |

$^a$ Corrected.

twist angle between the axis of the phosphorus l orbital and the adjacent carbon $2p_\pi$-orbital axis, and (3) a change in orbital energies as a result of steric strain of the bonds. Regardless of which explanation is the most appropriate, a lowering of the l-$a_\pi$ transition energy is apparent for arylphosphines as intramolecular steric hindrance increases. This fact is significant to the understanding of the luminescence of the complexes.

**Complexes.** Room-temperature emission data previously reported for $PPh_3$, $Cu(PPh_3)_2BH_4$, and $Cu(prophos)BH_4$ are included in Table II (with appropriate references) for comparison with the low-temperature results. The emitting state for each of the complexes at room temperature can be assigned as a $\sigma$-$a_\pi$[9b] charge-transfer excited state analogous to the l-$a_\pi$ assignment for the corresponding free ligand. The possibility exists that the emission for each complex occurs from a d$\Pi^*$ (or d-$a_\pi$[10]) excited state ($\pi^* \rightarrow$ d transition), but the $\sigma$–$a_\pi$ assignment is supported by the ligand-localized nature of the observed luminescence.

The room-temperature emission spectra of $Cu(PPh_3)_2BH_4$ and $PPh_3$ in benzene indicate that the emitting levels of $PPh_3$ and the complex are nearly isoenergetic and suggest that the electronic states of $PPh_3$ are not significantly perturbed upon coordination. In contrast, the electronic states of diphos are strongly affected by coordination of this ligand to copper in $Cu(diphos)BH_4$ (537-nm emission vs. the 500-nm emission of free diphos) possibly due to the steric constraint imposed by the formation of a five-membered chelate ring.[9a,b] A similar result is apparent for $Cu(prophos)BH_4$, but the ligand states are less perturbed likely because a less sterically hindered (six-membered) chelate ring is formed. Alkyl substitution at the ortho positions of the phenyl groups relative to the phosphorus atom in arylphosphines results in a lowering of the l-$a_\pi$ transition energy.[17,18] Moreover, an increase in the splitting of the l-$a_\pi$ singlet and triplet excited states may occur.[14] This effect and the effect of coordination of diphos or prophos to Cu(I) are parallel; therefore, the importance of steric factors to the photophysical properties of arylphosphine–Cu(I) complexes is apparent. The $\pi$ system of the ligands may also be perturbed in the complexes by interaction with metal d orbitals. The mixing of empty phosphorus d orbitals with metal d orbitals has been described,[19] and evidence also exists that the phosphorus d orbitals may mix with the $\pi^*$ orbitals of the phenyl groups,[20] resulting in a lower energy emitting excited state.

Although the room-temperature emission of $PPh_3$ is characterized as fluorescence, the spin character of the $Cu(PPh_3)_2BH_4$ emitting excited state in fluid solution (benzene or toluene) is not obvious. The similar emission band shapes, energies, and short lifetimes (presently indistinguishable) of $Cu(PPh_3)_2BH_4$ and $PPh_3$ suggest that the complex emission is also a fluorescence. In that case the lower emission quantum yield of $Cu(PPh_3)_2BH_4$ compared to that of $PPh_3$ may be qualitatively explained by a more efficient quenching of fluorescence as a result of increased intersystem crossing to a nonluminescent triplet state. Alternatively, complete intersystem crossing (allowing for $S_1 \rightarrow S_0$ internal conversion) and the occurrence of phosphorescence in solution are still possibilities. Even though an unambiguous assignment of the spin nature of the $Cu(PPh_3)_2BH_4$ $\sigma$-$a_\pi$ emission at room temperature cannot be made because the lowest singlet and triplet excited states are so close in energy, the microsecond lifetime of the $Cu(prophos)BH_4$ $\sigma$-$a_\pi$ emission in fluid solution allows assignment of this latter emission as spin forbidden.

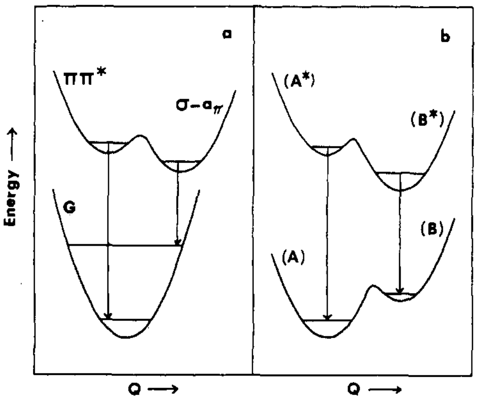

**Figure 4.** (a) Multiple-state emission for $Cu(PPh_3)_2BH_4$ resulting from a pseudo-Jahn–Teller excited-state potential surface (G ≡ ground state, Q ≡ distortion coordinate). (b) Multiple emission resulting from double-minimum ground- and excited-state potential surfaces where A and B represent different chemical species or possibly two geometric forms of the same molecule (Q ≡ reaction coordinate).

In frozen solution, the luminescence of $Cu(PPh_3)_2BH_4$ and $Cu(prophos)BH_4$ is complicated by additional solvent effects. The room-temperature emission spectra of $Cu(PPh_3)_2BH_4$ and $PPh_3$ in toluene are similar to those in benzene in that a single emission band (~475 nm) is observed for each species,[16] but at low temperature the emission of the complex and the free ligand are distinctly different (Figure 1). The dependence of the overall band shape on excitation wavelength, the variation of lifetime (Table I) across the emission spectrum, and the difference in energy of the emission maxima show that different origins exist for the two prominent bands in the spectrum of $Cu(PPh_3)_2BH_4$ in toluene. Analogous dual emissions occur for $Cu(PPh_3)_2BH_4$ in benzene, EPA, and 1:1 toluene–ethanol at 77 K.[21]

The occurrence of multiple emission in a rigid matrix may be rationalized by one (or a combination) of the following phenomena:[5b] (1) differences in orbital parentage (including distinct-orbital and spatially isolated types[1]), (2) microenvironmental heterogeneity, or (3) double-minimum potentials for the ground and emitting excited states.

The multiple emission observed for $Cu(PPh_3)_2BH_4$ likely does not result from a solvent heterogeneity or "red-edge" effect as reported[22] for some chromium complexes because (1) a two-band emission occurs for a large range of solvent polarities and (2) emissions with significantly different structures and energies are observed.

Differences in orbital parentage can most reasonably account for the dual luminescence of $Cu(PPh_3)_2BH_4$ in toluene at low temperature. The higher energy band in the $Cu(PPh_3)_2BH_4$ spectrum is similar in energy and band shape to the protonated free-ligand $\Pi\Pi^*$ phosphorescence, indicating that this band arises from a triplet $\Pi\Pi^*$ excited state. The

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(19) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley, New York, 1972, pp 719–21.

(20) N. P. Borisova and L. N. Petrov, *J. Struct. Chem.* (*Engl. Transl.*), **13**, 648 (1972).

(21) Although lifetimes were not measured for the complex in these particular solvents, emission spectra obtained by utilizing the SPF phosphoroscope (rotating chopper) indicate that dual lifetimes do exist for these multiple emissions and are similar in magnitude to those measured in toluene. Dependence of the emission band shape on the excitation wavelength is also observed.

(22) (a) F. Castelli and L. S. Forster, *J. Am. Chem. Soc.*, **95**, 7223 (1973); (b) F. Castelli and L. S. forster, *ibid.*, **97**, 6307 (1975).

lower energy emission of millisecond lifetime must arise from a spin-forbidden $\sigma$-$a_\pi$ state. The interaction of these two states can be described by a pseudo-Jahn-Teller potential[23] as depicted in Figure 4a. Such a multiple emission can be assigned as distinct-orbital type. The variation of lifetime across the emission band and the band shape dependence on excitation wavelength respectively show that the two states are not thermally equilibrated at 77 K and that population of the two states may occur through different relaxation pathways. The observation of only $\sigma$-$a_\pi$ emission at room temperature suggests that the two states could be thermally equilibrated at higher temperatures (with the $\Pi\Pi^*$ state at sufficiently higher energy) and/or that efficient nonradiative relaxation of the $\Pi\Pi^*$ state occurs.

The dual luminescence observed for $Cu(PPh_3)_2BH_4$ in glassy EPA and 1:1 toluene–ethanol and in frozen benzene is also assigned as a distinct-orbital multiple emission from $\Pi\Pi^*$ and $\sigma$-$a_\pi$ excited states. The variation in the relative intensities of the two emissions from solvent to solvent is likely determined by the interaction of the solvent(s) with the excited molecule but may indicate that the geometry of the complex is different in the various crystalline and glassy matrices. A difference in geometry as manifested by changes in the intramolecular coordinates, e.g., the C–P–C valence angle(s) and/or the P–C twist angle(s), could affect the relative energies of the ground and excited states.

$Cu(prophos)BH_4$ does not exhibit a distinct-orbital multiple emission from $\Pi\Pi^*$ and $\sigma$-$a_\pi$ states; this apparently results from the fact that the $\sigma$-$a_\pi$ state is considerably lower in energy, presumably for steric reasons, than the localized $\Pi\Pi^*$ state of the phenyl ring(s).[8b] An analogous argument accounts for the single $\sigma$-$a_\pi$ emission of $Cu(PPh_3)_2BH_4$ in frozen cyclohexane and dichloromethane, where the solvent likely imposes a particular geometry on the molecule.

In chloroform at 77 K the $Cu(PPh_3)_2BH_4$ complex exhibits a single emission at an energy intermediate to the $\Pi\Pi^*$ and $\sigma$-$a_\pi$ emission energies measured in the solvents discussed above. In addition, no room-temperature emission is observed for $Cu(PPh_3)_2BH_4$ in chloroform,[16] and in 1:1 toluene–chloroform at 77 K only the $\Pi\Pi^*$ emission is observed. These results suggest that chloroform (1) destabilizes the $\sigma$-$a_\pi$ excited state and/or (2) affects the ground-state (and excited-state) geometry of the complex and, consequently, the extent of any p–$\pi$ conjugation; therefore, the low-temperature emission of $Cu(PPh_3)_2BH_4$ in chloroform as compared to the luminescence of the complex in the other solvents may evidence a lowering of the $\Pi\Pi^*$ state in addition to a destabilization of the $\sigma$-$a_\pi$ state or could indicate that a unique potential surface exists for the emitting excited state as a result of a change in the coupling (mixing) of the $\Pi\Pi^*$ and $\sigma$-$a_\pi$ states. Granted, additional studies are needed to clarify the origin of the $Cu(PPh_3)_2BH_4$ emission in $CHCl_3$.

$Cu(prophos)BH_4$ in chloroform shows an emission analogous to that of $Cu(PPh_3)_2BH_4$ in chloroform as well as a lower energy emission from a $\sigma$-$a_\pi$ state. The curious dual emission of $Cu(prophos)BH_4$ in chloroform may result from nonequivalent phenyl groups attached to the phosphorus atoms[9b] in a given molecule leading to a spatially isolated multiple emission or may indicate an equilibrium between two distinct conformers in the ground state (double-minimum ground- and excited-state potential surfaces, Figure 4b). In either case, the fact that the spectra measured for $Cu(prophos)BH_4$ in $CHCl_3$ are not reproducible makes any present conclusion suspect; however, the variation in the relative intensities of the two bands from sample to sample suggests that (1) different solvent-site environments exist, some of which perturb the solute geometry to such an extent that the emission is altered, and (2) the distribution of sites varies from one frozen sample to another.

A ground-state double-minimum potential (and a corresponding excited-state potential) could possibly be envisaged to account for any of the observed multiple emissions of the complexes as suggested in Figure 4b, but the occurrence of simultaneous $\Pi\Pi^*$ and $\sigma$-$a_\pi$ emissions for $Cu(PPh_3)_2BH_4$ in several solvent systems, the steric factors favoring a single *equilibrium* ground-state geometry for the coordinated ligands, and the apparent absence of rapid photochemical processes lead us to believe that this dual emission is a true intramolecular multiple-state emission of distinct-orbital type. The origin(s) of the multiple emission of $Cu(prophos)BH_4$ in chloroform is considerably less certain.

## Conclusions

The lifetimes and emission spectra at room and liquid-nitrogen temperatures in various solvents for the free phosphine ligands and the $Cu(PPh_3)_2BH_4$ and $Cu(prophos)BH_4$ complexes enable the following assignments of orbital and spin origin for the various emissions: (1) Both complexes exhibit a room-temperature emission having a $\sigma$-$a_\pi$ origin with the $Cu(prophos)BH_4$ emission assigned as a phosphorescence. (2) $Cu(PPh_3)_2BH_4$ at low temperature exhibits a multiple-state emission from $^3\Pi\Pi^*$ and $^3(\sigma$-$a_\pi)$ excited states in appropriate solvents. (3) $Cu(prophos)BH_4$ luminescence in frozen solution normally can be assigned as $^3(\sigma$-$a_\pi)$ emission. (4) $Cu(prophos)BH_4$ in chloroform exhibits an anomalous dual emission at 77 K.

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**Registry No.** $Cu(PPh_3)_2BH_4$, 16903-61-0; $Cu(prophos)BH_4$, 81432-70-4.

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(23) (a) B. Dellinger and M. Kasha, *Chem. Phys. Lett.*, **36**, 410 (1975); (b) B. Dellinger and M. Kasha, *ibid.*, **38**, 9 (1976).