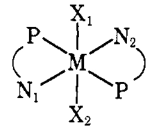
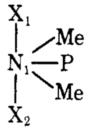
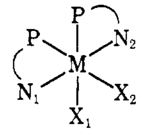
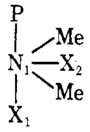
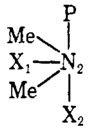
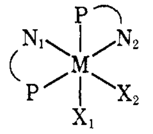
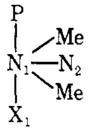
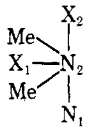
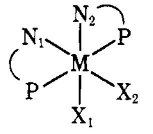
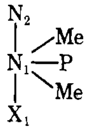
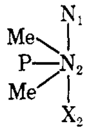
I, 34.7; N, 1.91; P, 4.07. Found: C, 37.4; H, 3.20; I, 33.0; N, 1.84; P, 4.22. Tlc on silica gel using toluene as eluent showed this complex to be identical with isomer B prepared from [Rh(PN)$_2$(CO)$_2$]PF$_6$.

Hydridochloro[bis[*o*-(diphenylphosphino)-*N*,*N*-dimethylaniline]]iridium Hexafluorophosphate [[IrHCl(PN)$_2$]PF$_6$, XVI]. PN (310 mg) and ammonium hexafluorophosphate (100 mg) were suspended in acetonitrile (10 ml) under nitrogen. Ir$_2$Cl$_2$(C$_8$H$_{14}$)$_4$ (250 mg) was added and the slurry stirred for 40 min. The reaction mixture was pale yellow. The solvent was evaporated *in vacuo* and the gelatinous residue triturated with ether. The solid was filtered and washed with ether (10 ml). The off-white residue was dissolved in CH$_2$Cl$_2$. The solution was filtered and the ethanol (10 ml) added to the filtrate. The volume of the solution was reduced to 7 ml on a rotary evaporator, and on cooling the solution to 0° colorless crystals were obtained: yield 480 mg (90%); mp 148°; $\nu_{\text{Ir-H}}$ 2240 cm^{-1}; $\nu_{\text{Ir-D}}$ 1604 cm^{-1}; τ 6.45, 6.51 (NMe$_2$), 32.0 ($J_{\text{P-H}}$ = 8 Hz, Ir-H). *Anal.* Calcd for C$_{40}$H$_{41}$ClF$_6$IrN$_2$P$_3$: C, 48.8; N, 4.16; Cl, 3.53; N, 2.84; P, 8.87. Found: C, 48.9; H, 3.97; Cl, 3.61; N, 2.98; P, 9.45.

Acknowledgment. We wish to thank the National Science Foundation for support of this work under Grant No. GP 38775. This work was also supported in part by the Graduate School Research Fund.

Appendix

One of the attractive features of *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline complexes is the ease with which their stereochemistries can be deduced. The multiplicity of the *N*-methyl resonances in the ^{1}H nmr spectrum can frequently be used to confirm the structure of an individual complex. The chelate ring obtained when both the phosphorus and nitrogen are coordinated is a planar one. The anticipated number of methyl resonances for a given stereochemistry is obtained by viewing down a projection along the N–metal bond. In a number of complexes having two of the chelating ligands, the nitrogens are not identical and a projection is drawn down each N–metal bond.

Stereochemistry	N_1 projection	N_2 projection	No. of resonances
		Same as N_1	$X_1 = X_2$, 1 $X_1 \neq X_2$, 2
			$X_1 = X_2$, 2 $X_1 \neq X_2$, 3
			$X_1 = X_2$, 4 $X_1 \neq X_2$, 4
			$X_1 = X_2$, 2 $X_1 \neq X_2$, 3

Electronic Absorption and Emission Spectral Studies of Square-Planar Rh(I) and Ir(I) Complexes. Evidence for a Charge-Transfer Emitting State

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Received October 3, 1973

Abstract: Absorption and emission spectra for the square-planar complexes [Rh(2-phos)$_2$]Cl, [Rh(2=phos)$_2$]Cl, [Ir(2-phos)$_2$]Cl, and [Ir(2=phos)$_2$]Cl [2-phos is 1,2-bis(diphenylphosphino)ethane; 2=phos is *cis*-1,2-bis(diphenylphosphino)ethylene] have been measured in the solid state and in frozen EPA [ethyl ether–isopentane–ethyl alcohol (5:5:2)] solution at 77°K. Of the four complexes, only [Rh(2-phos)$_2$]Cl fails to luminesce in the solid state at room temperature. At 77°K in EPA the emission maxima fall in the range 16.8–18.4 kcm^{-1}, and the emission lifetimes are between 8.2 and 20.8 μsec; [Ir(2=phos)$_2$]Cl exhibits an unusually sharp, strongly overlapping emission–absorption system, with an emission quantum yield of 0.93 $\pm$ 0.07. It is suggested that in the Ir(I) cases emission occurs from a square-planar d^7 a$_{2u}$ charge-transfer state of E$_u$(^{3}A$_{2u}$) symmetry. The fact that the emission maxima of the two Rh(I) complexes are both red-shifted by about 4000 cm^{-1} from the lowest absorption peak is discussed in terms of an admixture of d–d character in the primarily d^7 a$_{2u}$ emitting state, which could give rise to a distortion of the RhP$_4$ core toward tetrahedral geometry.

There has been very little previous effort devoted to the elucidation of the electronic structures and spectroscopic properties of low-spin d^8 square-planar complexes of Rh(I) and Ir(I). Only ambient tempera-

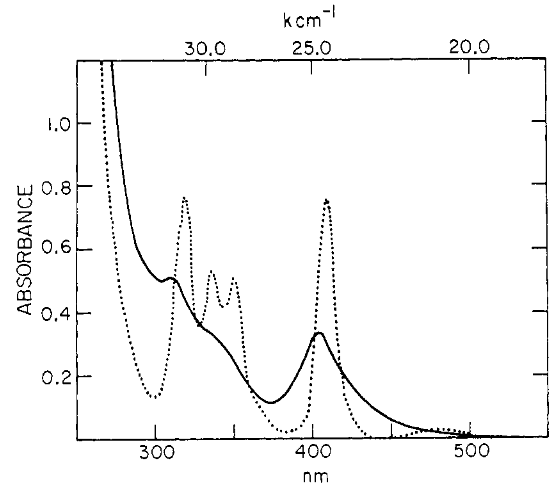

Figure 1. Electronic absorption spectra of [Rh(2=phos)$_2$]Cl in EPA solution at room temperature (—) and 77 °K (· · ·).

ture solution absorption spectra have been measured[1-5] for complexes of the types [MX(CO)L$_2$)], [M(2-phos)$_2$]$^+$, and [M(2=phos)$_2$]$^+$ [M = Rh(I), Ir(I); X = anionic or neutral ligand; L = monodentate, substituted phosphine, or arsine; 2-phos is 1,2-bis(diphenylphosphino)ethane; 2=phos is *cis*-1,2-bis(diphenylphosphino)ethylene], and there have been no published reports at all of successful luminescence experiments.[6]

We have begun a systematic study of both the absorption and emission spectra of the aforementioned Rh(I) and Ir(I) complexes. It is our hope that detailed electronic structural information on the ground and lowest excited states will serve as a useful starting point in attempts to understand the rich oxidative addition chemistry of these species. In this paper we shall be concerned primarily with the assignment of the lowest emission–absorption band systems in [M(2-phos)$_2$]$^+$ and [M(2=phos)$_2$]$^+$ complexes.

Experimental Section

Preparation of Compounds. The chloride salts of [M(2-phos)$_2$]$^+$ and [M(2=phos)$_2$]$^+$ [M = Rh(I), Ir(I)] were prepared by the method of Vaska and Catone.[7] All manipulations with the iridium complexes were conducted using a vacuum line and standard Schlenk techniques or a glove bag filled with argon. The perchlorate salts were prepared by addition of the chlorides to a saturated solution of NaClO$_4$ in methanol. In all cases crystalline products were obtained. *Anal.* Calcd for [Rh(2-phos)$_2$]ClO$_4$: Rh, 10.31; P, 12.42; C, 62.50; H, 4.81. Found: Rh, 9.87; P, 12.39; C, 63.20; H, 4.53. Calcd for [Rh(2=phos)$_2$]ClO$_4$: Rh, 10.35; P, 12.47; C, 62.75; H, 4.42. Found: Rh, 10.31; P, 11.84; C, 62.63; H, 4.93. The electronic absorption spectra of the oxygen-sensitive iridium complexes were found to be in excellent agreement with published data.[1] [Pt(2-phos)$_2$](ClO$_4$)$_2$ and [Pt(2=phos)$_2$](ClO$_4$)$_2$ were prepared by the procedure given by Westland.[8]

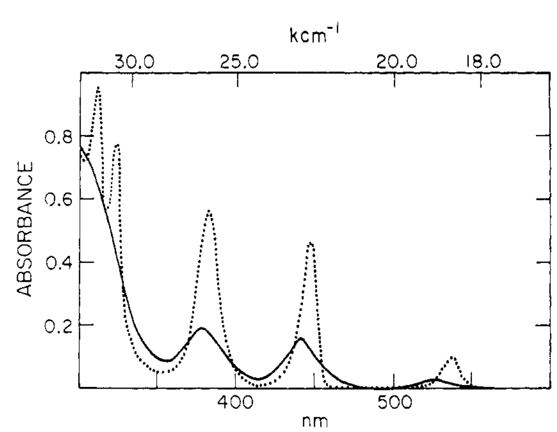

Figure 2. Electronic absorption spectra of [Ir(2=phos)$_2$]Cl in in EPA solution at room temperature (—) and 77 °K (· · ·).

Electronic Absorption Data. Electronic absorption spectra were measured using a Cary 17 spectrophotometer. Spectra at liquid nitrogen temperature were obtained using a low-temperature dewar fitted with Suprasil quartz windows and modified to hold a standard 1.00-cm cell. Measurements were performed in 5:5:2 ethyl ether–isopentane–ethyl alcohol (EPA) solutions and the low-temperature spectra were corrected for solvent contraction.

Emission and Excitation Data. Emission and excitation spectra were obtained using a Perkin-Elmer MPF-3A fluorescence spectrophotometer equipped with a standard accessory which corrects excitation spectra for varying lamp intensity and monochromator efficiency from 200 to 600 nm and corrects emission spectra for varying photomultiplier tube response and monochromator efficiency from 400 to 700 nm. All spectra reported in this paper are corrected. Measurements at 77°K were performed using a specially constructed low-temperature quartz dewar. Emission lifetimes were measured using a TRW decay time fluorometer equipped with a Xenon Corp. nanopulser excitation source. Emission intensities were detected by an RCA 931A PMT and displayed on a Tektronix 454 oscilloscope as a function of time. Plots of log (emission intensity) *vs.* time were linear in all cases. Emission quantum yields were measured relative to the standard [Ru(bipyridine)$_3$]Cl$_2$ (Φ = 0.376 ± 0.036).[9] Care was taken to match the optical density of the sample and the standard under the conditions of the measurement.

Results and Discussion

The room temperature and 77°K absorption spectra of [Rh(2=phos)$_2$]Cl and [Ir(2=phos)$_2$]Cl in EPA solution are shown in Figures 1 and 2. Electronic spectral data for all four [M(2-phos)$_2$]Cl and [M(2=phos)$_2$]Cl [M = Rh(I), Ir(I)] complexes are set out in Table I. Data for the analogous Pt(II) phosphine complexes are given for comparison purposes. Interpretation of the absorption spectra of both the [M(2=phos)$_2$]$^+$ and [M(2-phos)$_2$]$^+$ complexes is facilitated by assuming that the electronic transitions in question originate in a MP$_4$ core of D_{4h} symmetry. Square-planar MP$_4$ core structures for [Rh(2-phos)$_2$]$^+$ and [Ir(2-phos)$_2$]$^+$ have been established by X-ray crystallographic studies of the perchlorate salts.[10] Furthermore, Vaska and coworkers have shown that the spectral, magnetic, and solution conductance properties of the [M(2-phos)$_2$]Cl and [M(2=phos)$_2$]Cl complexes are consistent with an analogous structural formulation.[1,7] In agreement with such a formulation, we have found that the electronic absorption and emission spectra of the perchlorate and respective chloride salts are virtually identical in both solids and in solution.

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(6) L. Vaska and R. Brady have independently observed luminescence from several Rh(I) and Ir(I) complexes containing phosphine and arsine ligands. Their work will be described elsewhere (L. Vaska, private communication).

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Table I. Electronic Absorption Spectral Data

Complex	kcm^{-1} (ϵ_{max}), 300°K	kcm^{-1} (ϵ_{max}), 77°K
[Rh(2-phos)$_2$]Cl^a	21.3 (150)	21.3 (200)
	24.8 (5,150)	24.8 (9,250)
	31.8 (9,300)	31.6 (10,450)
	33.9 (8,400)	34.1 (11,570)
[Rh(2=phos)$_2$]Cl^a	21.1 (200)	20.7 (310)
	24.8 (4,900)	24.3 (12,770)
	29.4 (4,900)	28.4 (7,930)
		29.7 (8,100)
	32.3 (8,400)	31.3 (12,190)
[Ir(2-phos)$_2$]Cl^a	19.0 (800)	19.1 (1,140)
	22.6 (5,300)	22.6 (8,700)
	26.2 (5,650)	26.3 (6,820)
	31.3 (13,100)	31.3 (14,690)
[Ir(2=phos)$_2$]Cl^a	19.0 (700)	18.6 (2,530)
	22.6 (3,900)	22.3 (11,410)
	26.5 (4,350)	26.0 (12,800)
		30.8 (15,300)
	32.1 (7,650)	32.0 (16,230)
[Pt(2-phos)$_2$](ClO$_4$)$_2$^{b}	32.6 sh (~3,000)	
	36.8 sh (30,000)	
	39.5 (44,000)	
[Pt(2=phos)$_2$](ClO$_4$)$_2$^{b}	32.6 sh (3,000)	
	37.0 sh (24,000)	
	42.9 (48,000)	

^{a} EPA solution. ^{b} Ethanol solution.

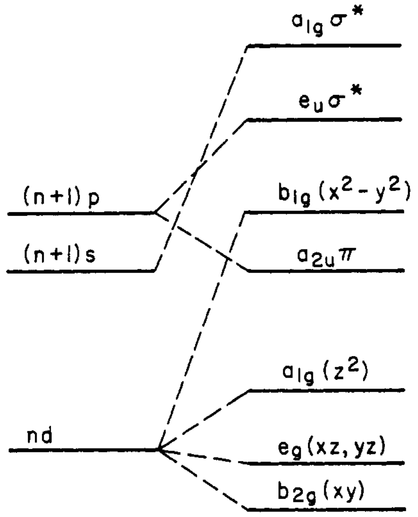

Figure 3. Schematic molecular orbital energy level diagram for a square-planar MP$_4$ complex.

A simplified molecular orbital level scheme for a D_{4h} MP$_4$ core is shown in Figure 3. The level ordering $b_{2g}(xy) < e_g(xz,yz) < a_{1g}(z^2) \ll a_{2u}\pi < b_{1g}(x^2-y^2)$ is based on analogy to Pt(CN)$_4^{2-}$, which has been studied in considerable detail.[11,12] Ignoring spin–orbit coupling, we expect three spin-allowed and three spin-forbidden d–d transitions to be associated with a $^1A_{1g}$ ($b_{2g}^2e_g^4a_{1g}^2$) ground state system. In the series of square-planar MP$_4$ complexes under investigation here, the energy ordering of the lowest d–d transitions should be Rh(I) ≪ Ir(I) $\lessapprox$ Pt(II). The other reasonable candidates for low-energy excitation involve metal-to-ligand charge transfer (MLCT). These transitions, which originate in the metal d orbitals and terminate in the $a_{2u}\pi$ level, would be expected[13] to occur in the energy order Ir(I) < Rh(I) ≪ Pt(II).

The large molar extinction coefficients of the absorption bands for the Rh(I) and Ir(I) complexes and the lack of any intensity decrease upon cooling to 77°K suggest that the bands are due to allowed charge-transfer transitions. The absence of any bands below 32 kcm^{-1} in [Pt(2-phos)$_2$]$^{2+}$ and [Pt(2=phos)$_2$]$^{2+}$ establishes the energy ordering Ir(I) < Rh(I) ≪ Pt(II) and strongly supports an MLCT assignment. Further evidence for the MLCT interpretation may be derived from the room temperature MCD spectra of [Rh(2=phos)$_2$]Cl and [Ir(2=phos)$_2$]Cl in CH$_2$Cl$_2$ solution. Each spectrum clearly shows a positive A term for the lowest band and a B term for the next higher energy transition.[14] This behavior is exactly analogous to that observed in the MCD spectrum of Pt(CN)$_4^{2-}$,[11] for which the two lowest bands have been interpreted[12] successfully in terms of the $d_{z^2} \rightarrow a_{2u}\pi$ transitions $^1A_{1g} \rightarrow E_u(^3A_{2u})$ and $^1A_{1g} \rightarrow A_{2u}(^1A_{2u})$, in order of increasing energy. On the basis of these results we suggest that the two lowest transitions in the Rh(I) and Ir(I) complexes should be assigned analogously.

Electronic Emission Data. Electronic emission data for [M(2=phos)$_2$]Cl and [M(2-phos)$_2$]Cl [M = Rh(I), Ir(I)] are set out in Table II. The absorption, emission, and excitation spectra of [Ir(2=phos)$_2$]Cl in EPA at 77°K are shown in Figure 4. Figure 5 illustrates the degree of overlap of the 77°K absorption and emission spectra of the complexes. All but [Rh(2-phos)$_2$]Cl emit very intensely in the solid state at room temperature, although none of the complexes was found to luminesce in degassed ethanol solution. The solid-state emission intensity increases considerably on cooling and a bright-orange luminescence is observed for [Rh(2-phos)$_2$]Cl at 77°K. All four complexes emit when dissolved in an EPA glass at 77°K, and the excitation spectrum of each complex was found to correspond to the low-temperature absorption spectrum, establishing that internal conversion from the upper excited states to the luminescent state is efficient.

Table II. Electronic Emission Data for Some Rhodium(I) and Iridium(I) Bis(diphosphine) Complexes in EPA at 77°K

Complex	Max, kcm^{-1}	Emission half-width, cm^{-1}	Quantum yield	Emission lifetime, μsec
[Rh(2-phos)$_2$]Cl	16.3	2120	0.052 ± 0.005	20.8
[Rh(2=phos)$_2$]Cl	17.1	2890	0.75 ± 0.07	27.5
	(16.5)^a	(2880)^a		(22.3)^a
[Ir(2-phos)$_2$]Cl	17.1	1610	0.25 ± 0.03	9.8
	(17.7)^a	(1480)^a		(0.4 ± 0.2)^a
[Ir(2=phos)$_2$]Cl	18.4	340	0.93 ± 0.07	8.2
	(18.1)^a	(1720)^a		(1.4 ± 0.2)^a

^{a} Solid sample at room temperature.

Particularly striking is the unusually sharp, strongly overlapping emission–absorption system of [Ir(2=phos)$_2$]Cl (Figure 4). The large emission quantum yield (0.93 ± 0.07) for this complex is also noteworthy.

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(14) G. L. Geoffroy, M. Keil, and H. B. Gray, unpublished results; MCD spectra were measured on a Cary 61 recording spectropolarimeter equipped with a Varian Associates superconducting magnet.

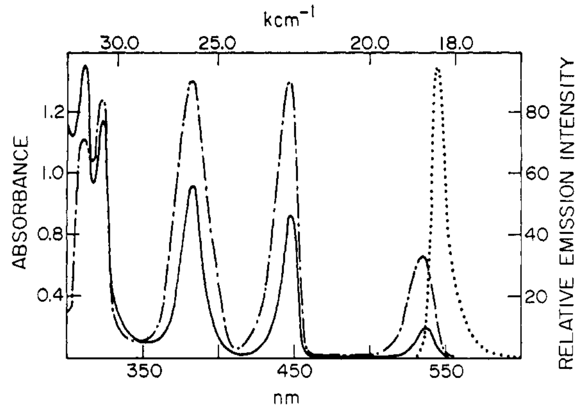

Figure 4. Absorption (——), excitation (------), and emission (····) spectra of [Ir(2=phos)$_2$]Cl in EPA at 77°K.

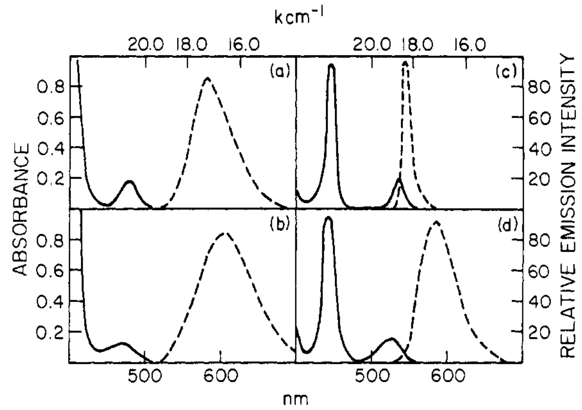

Figure 5. Absorption (——) and emission (- - -) spectra of (a) [Rh(2=phos)$_2$]Cl, (b) [Rh(2-phos)$_2$]Cl, (c) [Ir(2=phos)$_2$]Cl, and (d) [Ir(2-phos)$_2$]Cl in EPA at 77°K.

The observed degree of overlap and the similar widths of the absorption and emission bands of [Ir(2=phos)$_2$]Cl establish that the emitting state possesses an undistorted square-planar structure. These results are entirely consistent with a d^7 a$_{2u}$ excited state as the emitting level. A square planar structure is favored because the a$_{2u}$ MO is π bonding between the metal p$_z$ valence orbital and appropriate 3dπ orbitals of the four phosphorus donor atoms. Thus, it is highly probable that an E$_u$(^{3}A$_{2u}$) excited state is involved in the emission–absorption system. It may also be noted that the observed emission lifetime (Table II) is consistent with the substantial degree of spin-forbidden character of the transition E$_u$(^{3}A$_{2u}$) $\rightarrow$ ^{1}A$_{1g}$.

Although the evidence indicates that the absorption bands are also primarily of the type d $\rightarrow$ a$_{2u}$, the emission spectra of [Rh(2-phos)$_2$]$^+$, [Rh(2=phos)$_2$]$^+$, and [Ir(2-phos)$_2$]$^+$ are significantly broader than that of [Ir(2=phos)$_2$]$^+$. Of greater concern, however, is the observation that the emission maxima of the rhodium complexes are red-shifted by about 4000 cm^{-1} from the lowest absorption peaks (Figure 5). The observed red shifts and half-widths associated with the emission bands of the Rh(I) complexes imply that the MP$_4$ cores in the emitting states are somewhat distorted from the ground state D_{4h} geometry. Such an effect could signal that the emitting state is not purely MLCT in character but possesses a small admixture of one or more of the d–d states which have their potential energy minima on a D_{2d} (distorted tetrahedral) surface.[15] Such MLCT–(d–d) mixing should be much more important in the rhodium complexes than for their iridium counterparts, as the d–d states are expected to be much lower in energy (and therefore in closer proximity to the MLCT states) in the former case.

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