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Electronic Spectroscopy of Diphosphine- and Diarsine-Bridged Rhodium(I) Dimers

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Abstract: Fluorescence at room temperature and 77 K and phosphorescence at 77 K have been observed from the complexes $[Rh_2(t\text{-}BuNC)_4(dpm)_2](PF_6)_2$, $[Rh_2(n\text{-}BuNC)_4(dpm)_2](BPh_4)_2$, $[Rh_2(PhNC)_4(dpm)_2](PF_6)_2$, and $[Rh_2(n\text{-}BuNC)_4(dam)_2](BPh_4)_2$ [dpm = bis(diphenylphosphino)methane, dam = bis(diphenylarsino)methane]. The terms assigned to these emissions, $^1B_{1u}$ and $^3B_{1u}$, respectively, were also observed in the absorption and/or excitation spectra. $[Rh_2(PhNC)_4(dpm)_2](PF_6)_2$ was unique, exhibiting a relatively intense phosphorescence at 10 500 cm^{-1} at room temperature in the solid state. Low-temperature phosphorescence lifetime data indicate an unusually small spin–orbit splitting of the $^3B_{1u}$ term into two levels separated by ~7 cm^{-1}. On the basis of the invariance of the splitting upon substitution of dam for dpm, we conclude that the electronic transition is $\sigma^*(4d_{z^2}) \rightarrow \sigma(5p_z)$. These results are compared with those of other dimers studied recently and with those of related Rh(I) monomers.

Numerous studies of the chemistry of binuclear complexes of Rh(I) containing the bridging ligands bis(diphenylphosphino)methane (dpm) and bis(diphenylarsino)methane (dam) have been reported.[1-5] Recent interest has focused on those complexes having an "A-frame" geometry.[5-10] In contrast, the electronic spectra of these species have remained relatively unexplored with the exception of reports containing room-temperature absorption measurements.[1,3-5] Therefore we have undertaken a spectroscopic study of $[Rh_2(RNC)_4(dpm)_2]^{2+}$ (R = *tert*-butyl, *n*-butyl)[1] and $[Rh_2(n\text{-}BuNC)_4(dam)_2]^{2+}$,[4] first prepared and examined by Balch and co-workers, and a new member of the series, $[Rh_2(PhNC)_4(dpm)_2]^{2+}$. These complexes are related in structure (face-to-face square planes) and are isoelectronic with $[Rh_2(bridge)_4]^{2+}$ (bridge = 1,3-diisocyanopropane), studied by Gray and co-workers,[11-13] and $[Pt_2(pop)_4]^{4-}$ [pop = (HO)OP–O–PO(OH)$^{2-}$], examined in our laboratory.[14] We were particularly interested to compare the spectroscopic results from these related dimers and from Rh(I) monomers containing chelating diphosphine and diarsine ligands[15,16] with results from the dpm and dam bridged Rh(I) dimers. We report here the absorption, emission, emission lifetime, and emission excitation spectroscopy of these complexes at room temperature and low temperature (1.8–77 K).

Experimental Section

Preparation of Compounds. Bis(diphenylphosphino)methane (dpm), bis(diphenylarsino)methane (dam), and *tert*-butyl isocyanide were obtained from Strem Chemicals, Inc. The *n*-butyl isocyanide was obtained from Aldrich Chemical Co. Phenyl isocyanide was prepared by the reported procedure.[17] $[Rh_2(t\text{-}BuNC)_4(dpm)_2](PF_6)_2$ and $[Rh_2(n\text{-}BuNC)_4(dpm)_2](BPh_4)_2$ were prepared by the method of Balch.[1] $[Rh_2(PhNC)_4(dpm)_2](PF_6)_2$ was prepared analogously except that isolation of the product was accomplished by boiling off solvent at atmospheric pressure rather than by rotary evaporation under reduced pressure. $[Rh(n\text{-}BuNC)_4(dam)_2](BPh_4)_2$ was prepared by the method of Balch et al.[4] Satisfactory C, H, and N analyses (±0.4%) were obtained for all the complexes.

Spectroscopic Measurements. The solvents used in the spectroscopic measurements were spectroscopic grade or distilled before use. Absorption spectra were obtained in acetonitrile solution at room temperature on a Cary 14 spectrophotometer. Glasses for low-temperature spectral measurements were prepared by first dissolving the complex in one part dichloromethane and then adding ~20 parts of 4:1 ethanol–methanol. Emission spectra were recorded with a red-sensitive spectrophotometer constructed in this laboratory and described earlier,[18] except that the lock-in detection system was replaced by dc detection and computer averaging. All emission spectra were corrected for monochromator and photomultiplier efficiency. Emission excitation spectra were obtained by irradiating the sample with the output from a 1000 W tungsten–iodide lamp passed through a Spex Doublemate monochromator. Variations in emission intensity were monitored by a detection system consisting of a Spex Minimate monochromator and a RCA 7102 photomultiplier cooled by a dry ice–ethanol slurry. Owing to the lack of a well characterized quantum counter for this spectral region we were unable to correct the excitation spectra for wavelength sensitivity. A weak feature at 13 500 cm^{-1} occurring in our spectra was identified as scattered light, since it possessed characteristics previously seen in excitation correction curves for this particular monochromator.

Emission lifetimes were obtained by exciting the samples in glassy solution with 337-nm radiation from a Molectron UV-22 nitrogen laser. The emitted light was filtered through a KNO_2 solution, detected with a RCA 7102 photomultiplier wired for fast response,[19] and displayed on a Tektronix 549 oscilloscope. Lifetimes were determined by a linear least-squares fit of ln intensity versus time. At all temperatures no deviations from exponential behavior were detected over a range of at least two lifetimes. Sample temperature (other than 77 K) was controlled in an Andonian Model 0-24/7 M-H dewar described previously.[20]

Data acquisition and computations were accomplished with a Digital 11/34 system. Spectra were plotted on a Tektronix 4662 digital plotter.

Results

Summarized in Table I are absorption (room temperature)[21] and emission (77 K) spectral data. Shown in Figure 1 are the absorption and emission spectra also at room temperature. No room-temperature emission was observed from $[Rh_2(t\text{-}BuNC)_4(dpm)_2]^{2+}$. Diplayed in Figure 2 are the emission spectra at 77

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(21) The extinction coefficients we report for the lowest energy absorption bands of $[Rh_2(t\text{-}BuNC)_4(dpm)_2]^{2+}$ and $[Rh_2(n\text{-}BuNC)_4(dpm)_2]^{2+}$ are substantially less than those reported by Balch (ref 1). Solutions of the complexes were found to decompose after several hours; consequently, spectra were run immediately after preparation of solutions. We are unable to explain the discrepancy.

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Table I. Spectral Data

complex	absorption[a] (room temperature)	emission[b] (77 K)	
	ν_{max}, cm^{-1} × 10^{-3} (ϵ_{max}, M^{-1} cm^{-1})	ν_{max}, cm^{-1} × 10^{-3}	lifetime, μs
$[Rh_2(t\text{-}BuNC)_4(dpm)_2](PF_6)_2$	19.2 (16 800), 29.8 (10 400),[c] 31.1 (14 600), 36.3 (10 800)[c]	16.1, 13.0	21.2
$[Rh_2(n\text{-}BuNC)_4(dpm)_2](BPh_4)_2$	17.9 (12 600), 29.5 (6420),[c] 31.3 (16 900), 36.5 (13 300)[c]	14.9, 11.7	10.4
$[Rh_2(PhNC)_4(dpm)_2](PF_6)_2$	16.5 (12 300), 28.1 (28 700), 28.9 (30 100), 34.0 (18 300)[c]	13.3, 10.5	2.5
$[Rh_2(n\text{-}BuNC)_4(dam)_2](BPh_4)_2$	17.5 (11 900), –, 30.8 (17 300), 36.5 (15 000),[c] 37.7 (20 600)[c]	14.4, 11.3, 10.9[c]	6.8

[a] Acetonitrile solution. [b] 16:4:1 ethanol–methanol–dichloromethane glass. [c] Shoulder.

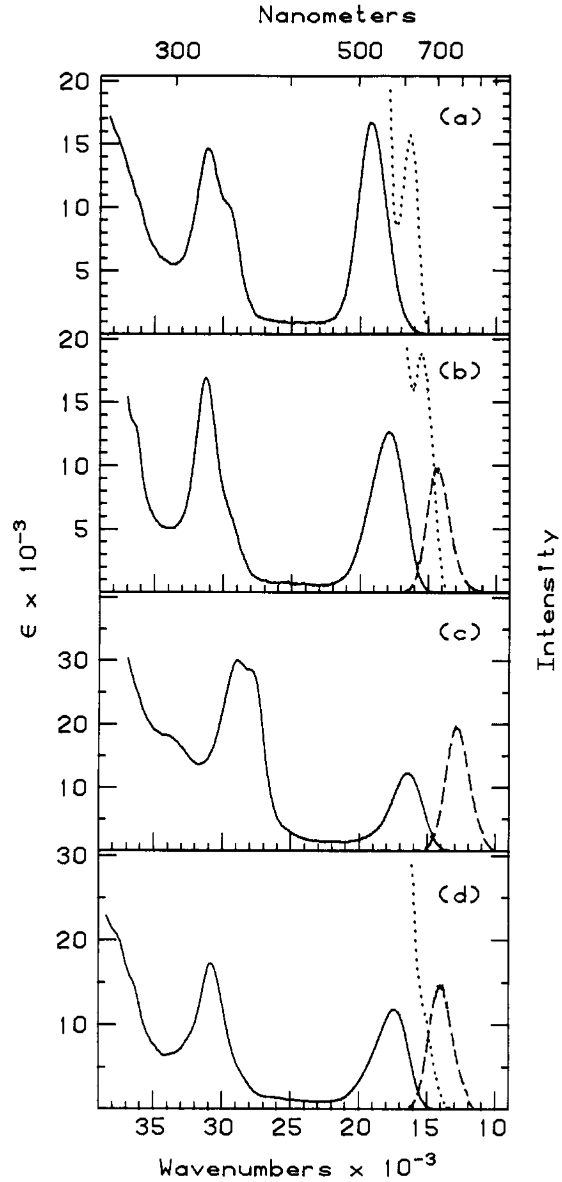

Figure 1. Room-temperature absorption spectra in acetonitrile (—), 77 K phosphorescence excitation spectra of solid samples (•••), and room-temperature emission spectra in 16:4:1 ethanol–methanol–dichloromethane (- - -) of (a) $[Rh_2(t\text{-}BuNC)_4(dpm)_2](PF_6)_2$, (b) $[Rh_2(n\text{-}BuNC)_4(dpm)_2](BPh_4)_2$, (c) $[Rh_2(PhNC)_4(dpm)_2](PF_6)_2$, and (d) $[Rh_2(n\text{-}BuNC)_4(dam)_2](BPh_4)_2$.

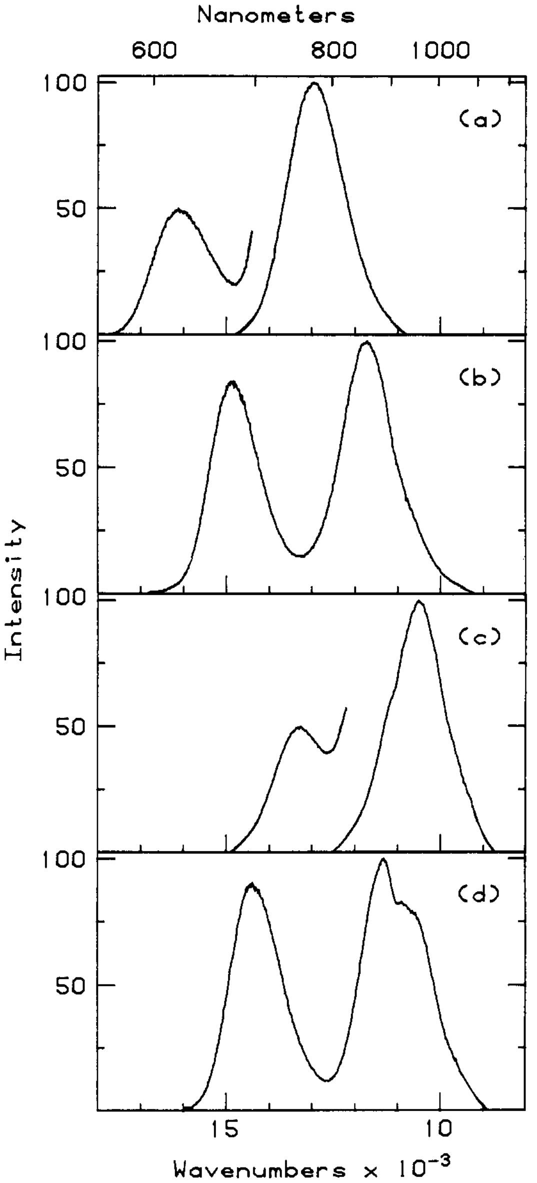

Figure 2. Emission spectra at 77 K in 16:4:1 ethanol–methanol–dichloromethane of (a) $[Rh_2(t\text{-}BuNC)_4(dpm)_2](PF_6)_2$, (b) $[Rh_2(n\text{-}BuNC)_4(dpm)_2](BPh_4)_2$, (c) $[Rh_2(PhNC)_4(dpm)_2](PF_6)_2$, and (d) $[Rh_2(n\text{-}BuNC)_4(dam)_2](BPh_4)_2$.

K. $[Rh_2(n\text{-}BuNC)_4(dpm)_2]^{2+}$ and $[Rh_2(n\text{-}BuNC)_4(dam)_2]^{2+}$ show two emissions of approximately equal intensity. Unlike the others the lower energy emission from $[Rh_2(n\text{-}BuNC)_4(dam)_2]^{2+}$ displayed a shoulder at 10 000 cm^{-1}. The higher energy emissions (fluorescence) from $[Rh_2(t\text{-}BuNC)_4(dpm)_2]^{2+}$ and $[Rh_2(PhNC)_4(dpm)_2]^{2+}$ were considerably less intense than the lower energy bands (phosphorescence) yet clearly discernable at higher instrument sensitivity. The fluorescence maxima were blue shifted ~400 cm^{-1} from the corresponding room-temperature peaks. Emissions from solid samples of all the complexes except $[Rh_2(PhNC)_4(dpm)_2]^{2+}$ displayed predominantly fluorescence at room temperature but mostly phosphorescence at 77 K. This is shown in Figure 3 for $[Rh_2(n\text{-}BuNC)_4(dam)_2]^{2+}$. Generally, emission maxima from solid samples were blue shifted ~400 cm^{-1} from the corresponding maxima of spectra taken in glassy solution under the same conditions. In the solid state $[Rh_2(PhNC)_4(dpm)_2]^{2+}$ showed unique behavior, displaying an intense phosphorescence both at room temperature and at 77 K.

Fluorescence and phosphorescence excitation spectra of all the samples at 77 K revealed the low-energy band observed in the room-temperature absorption spectra although some narrowing of the band and a slight red shift (~400 cm^{-1}) of the maximum occurred. Phosphorescence excitation spectra of solid samples

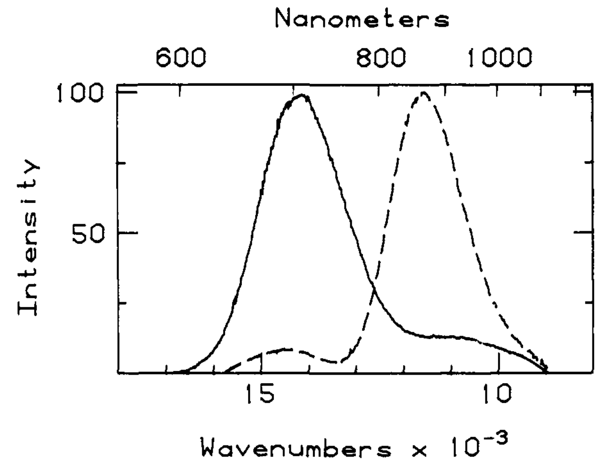

Figure 3. Emission spectra of solid samples of $[Rh_2(\textit{n}\text{-}BuNC)_4(dam)_2](BPh_4)_2$ at room temperature (—) and 77 K(- - -).

at 77 K revealed a new lower energy absorption band shown in Figure 1. This band was apparently obscured for $[Rh_2(PhNC)_4(dpm)_2]^{2+}$ due to a grating artifact (vide supra).

The emission lifetimes of the complexes in glassy solution at 77 K are listed in Table I. Only for the case of $[Rh_2(\textit{n}\text{-}BuNC)_4(dpm)_2]^{2+}$ were the fluorescence and phosphorescence separated experimentally with the aid of an emission monochromator. The fluorescence lifetime proved to be well below our detection limit (<0.5 μs) whereas the phosphorescence lifetime was identical with that obtained from monitoring the decay of the entire emission band envelope without use of the monochromator. We infer that all the lifetimes reported in Table I are those of the phosphorescence bands.

Variable (Low) Temperature Experiments. The phosphorescence spectra both of glasses and of solid samples of $[Rh_2(\textit{t}\text{-}BuNC)_4(dpm)_2]^{2+}$ and $[Rh_2(PhNC)_4(dpm)_2]^{2+}$ did not vary significantly as the temperature was lowered below 77 K. For the emission spectra of $[Rh_2(\textit{n}\text{-}BuNC)_4(dpm)_2]^{2+}$ and $[Rh_2(\textit{n}\text{-}BuNC)_4(dam)_2]^{2+}$ in glasses, however, a decrease in the intensity of the phosphorescence relative to the fluorescence was observed for temperatures below 5 K. The phosphorescence lifetimes of all the samples increased dramatically below 5 K, as shown in Figure 4. Our method of analysis of the temperature dependence of the observed lifetimes, which is based on two emitting levels in Boltzmann equilibrium, is identical with that described previously.[15,16] The computer-generated fits and resultant level schemes are also shown in Figure 4. The degeneracy factor of two for the higher level in the emitting manifold is not derivable from the experimental data but is consistent with the proposed term assignments (vide infra). We point out that the τ value of the higher level represents the lifetime of the entire level and not just that of a single component state.

Discussion

The absorption spectra of these complexes are typified by an intense low-energy band well separated from the higher energy transitions. Balch and Tulyathan[3] designated these bands as "proximity shifted" absorptions since their unusually low energy relative to the low-energy bands of the related monomers appeared to be associated with the close approach of the two metal centers. The orbitals (D_{2h} symmetry) pertinent to a discussion of the low-energy transitions in these bridged species are assumed to be $1a_g(4d_{z^2}) < 1b_{1u}(4d_{z^2}) < 2a_g(5p_z) < 2b_{1u}(5p_z)$. This scheme, modified for D_{2h} symmetry, is the same as that diagrammed by Mann et al.[22] The $1a_g$ and $1b_{1u}$ orbitals are both occupied in the ground state. Although in the ground state the bond order is formally zero, interaction of the a_g and b_{1u} orbital pairs, respectively, could produce weak Rh–Rh bonding. A formal bond order of 1.0 exists in the lowest predicted excited state obtained from ${}^1A_g \rightarrow {}^1B_{1u}$ ($1b_{1u} \rightarrow 2a_g$) excitation. We assign the intense low-energy absorption band in all the complexes to this allowed transition and the higher energy emission observed both at room temperature and at 77 K to the corresponding fluorescence. Although unusual for most transition-metal complexes, fluorescence has been observed from all d^8 square-planar face-to-face dimers studied spectroscopically.[11,14] The weak absorption observed in the 77 K excitation spectra of the solid samples is assigned to the ${}^1A_g \rightarrow {}^3B_{1u}$ ($1b_{1u} \rightarrow 2a_g$) transition and the lower energy emission at 77 K to the corresponding phosphorescence.

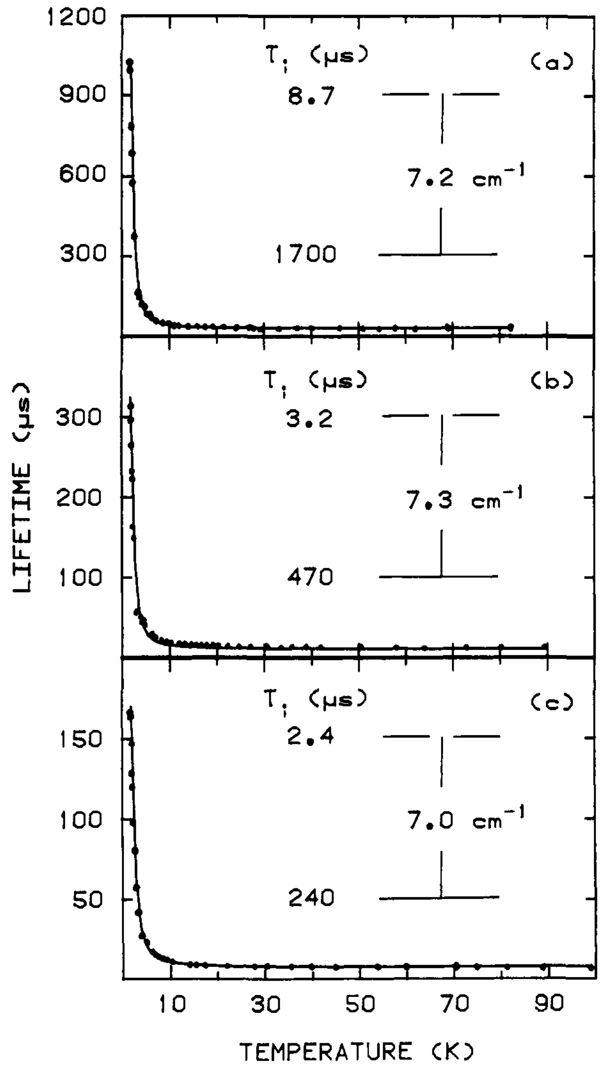

Figure 4. Temperature dependence of the lifetimes and computer-generated fits with resultant level schemes for (a) $[Rh_2(\textit{t}\text{-}BuNC)_4(dpm)_2](PF_6)_2$, (b) $[Rh_2(\textit{n}\text{-}BuNC)_4(dpm)_2](BPh_4)_2$, and (c) $[Rh_2(\textit{n}\text{-}BuNC)_4(dam)_2](BPh_4)_2$ in 16:4:1 ethanol–methanol–dichloromethane; •, experimental values; –, "best-fit" computer-generated curves.

It is interesting to note that the absorption and emission maxima of $[Rh_2(PhNC)_4(dpm)_2]^{2+}$ are lower in energy than those of any other Rh(I) dimers that we are aware of. Balch[1] has found that the energy of the low-energy absorptions correlates with the size of the alkyl group on the isocyanide. Smaller groups allow closer approach of the Rh(I) centers increasing the orbital interaction and decreasing the absorption energy. Apparently in $[Rh_2(PhNC)_4(dpm)_2]^{2+}$ the planar phenyl groups twist such that groups on opposing Rh(I) centers are parallel to one another and allow a close approach of opposing ligands. Dispersion forces between facing rings could then contribute to ground-state stabilization. Thus, Rh–Rh distance in this complex may be determined primarily by the dpm bridging groups and the electrostatic interactions between Rh(I) centers. Another unusual feature of this complex is the relatively intense near-IR (10 500 cm^{-1}) emission of the solid that occurs at room temperature.

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The singlet–triplet splitting in these complexes, measured from the fluorescence and phosphorescence maxima at 77 K, is 3000 (±200) cm^{-1}, a value that is slightly less than the 3500-cm^{-1} splitting observed in Rh(I) monomers with chelating diphosphine ligands.[16,23] The Stokes shift, measured between the room-temperature absorption and fluorescence maxima, is 3600 (±100) cm^{-1}, a value approximately the same as that found from the triplet absorption and phosphorescence maxima of Rh(I) monomers.[16,23]

The phosphorescence lifetime versus temperature results indicate that emission from the higher level is partially allowed whereas emission from the lower level is forbidden. The decrease in emission intensity that occurs as the temperature is lowered suggests that the difference in the radiative rates of the levels is considerably greater than that indicated by the measured lifetimes. This is identical with the situation observed for the Rh(I) and Ir(I) monomers[15,16] and also for $[Pt_2(pop)_4]^{4-}$.[14] In consonance with this previous work we assign the phosphorescence manifold to a spin–orbit-split $^3B_{1u}$ term in D_{2h}. The accidentally degenerate higher level is assigned to B_{2u} and B_{3u} components (both dipole allowed) and the lower level to the A_u (dipole forbidden) state. Within the precision of our procedures, we find no evidence for splitting of the higher levels. The absence of any temperature effect (4.2–77 K) on the intensity of the shoulder relative to the main phosphorescence band in $[Rh_2(n\text{-}BuNC)_4(dam)_2]^{2+}$ indicates that this shoulder is vibrational and not electronic in origin.

The most unusual feature of the parameters obtained from the decay data is the small energy gap ($\Delta\epsilon$) between the spin–orbit-split levels, a factor of 5 less than the splitting obtained for Rh(I) monomers.[15,16] The inferred weak spin–orbit coupling is manifested also in the weak triplet absorption intensity (vide infra) and the observation of fluorescence; both are characteristic traits of organic molecules for which the splitting of triplet levels is on the order of tenths of wavenumbers.[24] These same manifestations of weak spin–orbit interaction have been observed in other metal dimers as well.[11,14]

Comparison of the $\Delta\epsilon$ values of the complexes yields information about the nature of the orbitals involved in the emitting manifold.[25] No significant change in $\Delta\epsilon$ was observed upon switching the bridging ligand from dpm to dam. In contrast, $\Delta\epsilon$ of Rh(I) monomers increased significantly upon substitution of arsine for phosphine ligands, presumably due to the greater spin–orbit coupling constant of arsenic ($\Delta\epsilon$ for $[Rh(Ph_2PCHCHPPh_2)_2]^+$, $[Rh(Ph_2AsCH_2CH_2PPh_2)_2]^+$, and $[Rh(Ph_2AsCHCHAsPh_2)_2]^+$ is 37.8, 44.8, and 57.6 cm^{-1}, respectively[16]). This effect corroborated the charge-transfer nature of the excited state of the Rh(I) monomers. The lack of any such dependence for these Rh(I) dimers leads us to conclude that the low-energy excited states are primarily metal centered, $\sigma^*(4d_{z^2}) \rightarrow \sigma(5p_z)$. This conclusion is in agreement with the results obtained for $[Rh_2(bridge)_4]^{2+}$ [12] and $[Pt_2(pop)_4]^{4-}$ in which a vibration superimposed on low-temperature triplet absorption[12,14] and phosphorescence[14] spectra could be identified as a metal–metal stretch.

Previous workers[1,3-5] have assigned the low-energy absorptions of Rh(I) dpm and dam bridged dimers to metal-to-ligand charge-transfer transitions. These assignments were, in part, based on the "shift" of the ~25 000-cm^{-1} band observed in Rh(I) monomers to much lower energy in the dimers.[1] The band present in monomers had been assigned earlier to a charge-transfer transition.[23] In light of the new metal-centered assignment of the dimer absorptions, the lack of an absorption band at ~25 000 cm^{-1} in the dimers indicates considerable $5p_z$ orbital character in the acceptor orbital of Rh(I) monomers.

Application of the Strickler–Berg formula[26] to the intense low-energy absorption bands of these dimers leads to predicted fluorescence radiative lifetimes within the range 15–35 ns. From the phosphorescence lifetimes, application of the formula predicts an upper limit of ~150 M^{-1} cm^{-1} for the extinction coefficients of the triplet absorptions.

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Registry No. $[Rh_2(t\text{-}BuNC)_4(dpm)_2](PF_6)_2$, 80533-10-4; $[Rh_2(n\text{-}BuNC)_4(dpm)_2](BPh_4)_2$, 80533-12-6; $[Rh_2(PhNC)_4(dpm)_2](PF_6)_2$, 80533-14-8; $[Rh_2(n\text{-}BuNC)_4(dam)_2](BPh_4)_2$, 80533-16-0.

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(25) Although we did not directly observe emission from the lower level in these complexes, indicated by a leveling off of the lifetime curve at low temperature, our confidence in the fit values was increased by checking the fit values of truncated data sets from Rh(I) and Ir(I) monomers in which the lower level lifetime was observed.[15] Truncation of the data sets down to a point at which the lifetime was one-half that of the lifetime of the lower level in the manifold resulted in only ±5% deviations of the $\Delta\epsilon$ values.

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Synthesis, Microwave Spectrum, Electric Dipole Moment, Molecular Structure, and Anomeric Effect in Fluoroethylene Ozonide[1]

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Abstract: Twelve isotopic species of fluoroethylene ozonide (vinyl fluoride ozonide or 3-fluoro-1,2,4-trioxolane) were synthesized including the parent and all eight possible singly substituted D, ^{18}O, and ^{13}C species. The ground state microwave spectra of these were assigned as well as two excited vibrational states of the parent. The isotopic syntheses were consistent with the Criegee mechanism of ozonolysis. The dipole moment of the parent was found to be 2.317 (21) D, with principal axis components $|\mu_a| = 1.456$ (7), $|\mu_b| = 1.346$ (34), $|\mu_c| = 1.199$ (13). The ring conformation is a distorted twisted half-chair with the fluorine occupying an axial site, and with a long C–F bond length of 1.375 (5) Å and short adjacent C_F–O bonds, both of 1.382 (10) Å. The structure is rationalized in terms of the anomeric effect.

The ozonolysis of alkenes in solvents has been known for over 70 years.[2] The ozonides produced in this reaction were first explained by the mechanism proposed by Criegee (Scheme I)[3,4] and revised to include stereochemical effects.[5,6] Efforts to further

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