support for this proposal and accounts for the fact that the insertion into a metal–alkyl bond occurs through a different mechanism.

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Photophysical Investigation of Palladium(II) Ortho-Metalated Complexes

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Syntheses and structural characterizations of four complexes of Pd(II) with ortho-metalated 2-phenylpyridinate (ppy⁻) are reported. These complexes include a parent dimer, [Pd(ppy)Cl]$_2$, and three derivative monomers, [Pd(ppy)(bpy)]Cl, [Pd(ppy)(en)]Cl, and [Pd(ppy)(CO)Cl], where bpy = 2,2′-bipyridine and en = ethylenediamine. Photophysical characterizations of these species indicate low-energy absorption bands (~360 nm) and emission bands at 77 K (~460 nm) that are assigned to transitions localized on the ppy⁻ ligand. Some evidence for low-energy charge-transfer states is found in trends in luminescence lifetimes.

Introduction

Ortho-metalated complexes of palladium(II) have long been recognized in the literature,[1-8] yet there is an apparent lack of photochemical and photophysical data reported for these complexes.[9] We have prepared four palladium(II) complexes, each of which contains the ortho-metalating ligand 2-phenylpyridinate (ppy⁻). Ortho-metalates of palladium were chosen for our investigation in order to explore the effects of metal–carbon σ bonds on the low-energy excited states of Pd(II) complexes. Investigations of these Pd(II) complexes are being carried out in order to establish whether or not low-energy charge-transfer excited states are present and to evaluate their potential use in photoinduced electron- and energy-transfer schemes.

Photophysical descriptions of several palladium(II) ortho-metalated azobenzene complexes[10] indicate that the photophysics of these systems is predominantly ligand-localized in character. Luminescence lifetimes of these complexes are short in room-temperature fluid solutions (<1 ns) and are characterized as singlet intraligand fluorescence emissions. Photophysical characterizations of rhodium(III), iridium(III), and platinum(II) compounds containing the ortho-metalating ligand ppy⁻ have been reported previously.[11-14] [Rh(ppy)$_2$Cl]$_2$ has a low-energy charge-transfer feature in the absorption spectrum (395 nm); however, low-temperature emission and luminescence lifetime data indicate that the emission originates from a ligand-localized excited state. The analogous [Ir(ppy)$_2$Cl]$_2$ dimer also exhibits a low-energy charge-transfer absorption (435 nm), and in this case the emission has been assigned as metal-to-ligand charge-transfer (MLCT) emission. Photophysical results for platinum(II) complexes that contain ppy⁻ as a ligand indicate that the emitting state is

MLCT.[13-14] Since Pd(II), like Rh(III), is difficult to oxidize, one might expect to observe MLCT transitions in the absorption spectra of palladium–ppy⁻ complexes while the emission may originate from ligand-localized states. On the other hand, palladium(II) being a d^8 transition metal may alter the ground-state energies enough that new MLCT states would be observed. Current results indicate that coordination to iridium(III) and rhodium(III) by the anionic carbon of an ortho-metalating ligand enhances the electron density about the metal center.[11] This suggests that ortho-metalating ligands coordinated to Pd(II) may promote metal-to-ligand charge-transfer transitions via σ donation of electron density to the palladium metal center.

We have prepared four palladium-centered complexes. Common to each species is the anionic 2-phenylpyridinate ligand. In the work presented here we report on our initial investigation of the photophysical properties of these ortho-metalated Pd(II) complexes (bpy = 2,2′-bipyridine, en = ethylenediamine): [Pd(ppy)Cl]$_2$ (I); [Pd(ppy)(bpy)]Cl (II); [Pd(ppy)(en)]Cl (III); [Pd(ppy)(CO)Cl] (IV).

Experimental Section

A. Syntheses. Bis(2-phenylpyridinato-C^2,N)bis(μ-chloro)di-palladium(II). Li$_2$PdCl$_4$ (0.670 g, Aldrich) was dissolved in methanol, and to this solution was added 420 μL of C-protonated 2-phenylpyridine (ppy). The brown solution immediately lightened upon addition of ppy, and after 24 h a yellow-green solid was collected on a glass frit. This material was washed with dichloromethane. The solid was then dissolved in *N,N*-dimethylformamide and the solution filtered. Evaporation of the DMF produced the bright yellow [Pd(ppy)Cl]$_2$ powder (0.5026 g, 66% yield). This yield correlates well with previously reported values for the synthesis of this compound.[6] Recrystallization of the [Pd(ppy)Cl]$_2$ powder from dichloromethane and hexanes provided material suitable for elemental analysis.

Anal. Calcd for Pd$_2$C$_{22}$H$_{16}$N$_2$Cl$_2$: C, 44.63; H, 2.72; N, 4.73. Found: C, 44.42; H, 2.72; N, 4.84.

(2-Phenylpyridinato-C^2,N)(2,2′-bipyridine)palladium(II) Chloride. 2,2′-Bipyridine (0.1075 g, Aldrich) was added to a dichloromethane solution of [Pd(ppy)Cl]$_2$ (0.0610 g, 400 mL) and stirred at ambient temperature for 48 h. The yellow precipitate was removed and washed with diethyl ether. The remaining solid was dissolved in 300 mL of hot methanol and the solution filtered. Isobutyl alcohol (100 mL) was added, and the solvents were allowed to evaporate slowly. The yellow microcrystals of [Pd(ppy)(bpy)]Cl were collected, dried in vacuo, and weighed (0.0708 g, 76% yield).

Anal. Calcd for PdC$_{21}$H$_{16}$N$_3$Cl·CH$_2$Cl$_2$: C, 49.19; H, 3.37; N, 7.82. Found: C, 49.94; H, 3.20; N, 7.93.

(2-Phenylpyridinato-C^2,N)(ethylenediamine)palladium(II) Chloride. Ethylenediamine (64.5 μL, Aldrich) was added to a dichloromethane solution of [Pd(ppy)Cl]$_2$ (0.0720 g, 500 mL). The yellow solution lightened and formed a white precipitate within several minutes. This reaction mixture was stirred at room temperature for 4 h. The white flocculent product was collected on a glass frit and washed with di-

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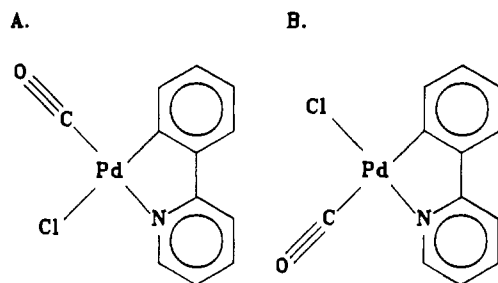A.   B.

Figure 1. Possible conformations of complex IV. Isomer A has CO trans to the nitrogen, and isomer B has CO trans to the carbon of the coordinated 2-phenylpyridinate ligand.

chloromethane and diethyl ether. This material was then dissolved in methanol, the solution was filtered, and the methanol was removed by rotoevaporation. The remaining white solid, [Pd(ppy)(en)]Cl, was weighed after vacuum-drying (0.0714 g, 82%). This compound can be recrystallized from water/acetone (1:1 by volume) in the presence of large excesses of sodium tetrafluoroborate to afford the [Pd(ppy)(en)]BF$_4$ complex.

Anal. Calcd for PdC$_{13}$H$_{16}$N$_3$BF$_4$·^{1}/$_3$C$_3$H$_6$O: C, 38.39; H, 4.25; N, 9.85. Found: C, 38.98; H, 3.67; N, 9.37.

(2-Phenylpyridinato-C^2,N')carbonylchloropalladium(II). Carbon monoxide was bubbled through a dichloromethane slurry of [Pd(ppy)Cl]$_2$ (0.0536 g, 30 mL). The solution immediately lightened, and the undissolved [Pd(ppy)Cl]$_2$ rapidly went into solution. Treatment with 1 atm of CO was continued until all of the dichloromethane solvent had completely evaporated. The white solid formed was then dissolved in chloroform, the solution filtered, and the solvent again evaporated under a CO atmosphere. This yielded the white [Pd(ppy)(CO)Cl] product (0.0497 g, 85% yield).

Anal. Calcd for PdC$_{12}$H$_8$NOCl: C, 44.47; H, 2.49; N, 4.32. Found: C, 44.35; H, 2.33; N, 4.60.

B. Measurements. Emission spectra were obtained with a Spex Fluorolog 2 emission spectrofluorometer. The samples were excited with a 150-W xenon lamp. Luminescence was detected perpendicular to incident radiation with a Hamamatsu R928 photomultiplier tube (thermostatically cooled), which was configured for photon counting. A Spex Datamate computer digitized and displayed the data. Absorption measurements were performed with a Cary 15 or HP 8452A photodiode array spectrometer. The ^{1}H NMR spectra were obtained on a Nicolet NT-300 or GN-500 FT NMR spectrometer. Luminescence lifetimes were determined by using the following apparatus. The laser, optics, and detection and analysis techniques used for measurements of luminescence lifetimes of [Pd(ppy)Cl]$_2$ are described elsewhere.[12] Lifetime measurements for the three monomeric materials were performed with excitation from an Avco-Everett nitrogen laser (337 nm). Emission wavelengths were selected with a Fastie-Ebert monochromator. The dc signal from an RCA 8852 photomultiplier was digitized and displayed by using a PAR Model 4420 boxcar averager equipped with a PAR Model 4422 gated integrator and a Model 4402 signal processor. Infrared spectra were obtained with a Digilab FTS-60 FT-IR spectrophotometer.

Results and Discussion

Infrared spectroscopy was used to identify the coordinated carbonyl for [Pd(ppy)(CO)Cl]. Stretching frequencies of 2132 cm^{-1} in dichloromethane solution and 2118 cm^{-1} for the solid in KBr were observed. The carbonyl ligand has two possible coordination positions, trans to the nitrogen or trans to the carbonyl of the ppy$^-$ ligand (see Figure 1). We feel that the correct structure has CO coordinated trans to nitrogen (structure A, Figure 1). The similarity of the CO stretching frequency for complex IV (2118 cm^{-1} in KBr) to the CO stretching frequency reported for [Pd(NC$_9$H$_6$CH$_2$)(CO)Cl] (2108 cm^{-1} in KBr)[15] suggests similar CO environments. For [Pd(NC$_9$H$_6$CH$_2$)(CO)Cl] the carbonyl ligand has been shown to exist trans to nitrogen. Additionally, ^{1}H NMR spectral data suggest that the CO ligand for IV is trans to the pyridyl ring (vide infra). Upon standing for prolonged periods (days), a dichloromethane solution of [Pd(ppy)(CO)Cl] changes from a clear to a yellow solution, eventually precipitating a yellow solid, which was analyzed as the

Table I. Absorption Data for Palladium Phenylpyridinate Complexes I–IV and the Ligands 2-Phenylpyridine and 2,2'-Bipyridine

compd	wavelength, nm	extincn coeff, 10^3 M^{-1} cm^{-1}
[Pd(ppy)Cl]$_2$ (I)^a	254	30.7
	265 (sh)	28.7
	305 (sh)	10.7
	315	11.2
	360	4.2
[Pd(ppy)(bpy)]Cl (II)^b	248	9.3
	305	6.2
	360	1.1
[Pd(ppy)(en)]Cl (III)^b	248 (sh)	7.5
	263	9.8
	304 (sh)	2.5
	315	2.6
	340	2.2
[Pd(ppy)(CO)Cl] (IV)^a	255	13.1
	265	12.9
	305 (sh)	5.2
	315	5.2
	360	2.0
Hppy^c	247	12.1
	274	9.8
bpy^d	235	12.7
	243	10.5
	283	16.3

^{a}Solvent dichloromethane. ^{b}Solvent methanol. ^{c}Reference 14. ^{d}Reference 21.

dimer, [Pd(ppy)Cl]$_2$. As a solid, the [Pd(ppy)(CO)Cl] complex slowly decomposes, yielding a gray solid.

The ^{1}H NMR spectrum of [Pd(ppy)Cl]$_2$ is of marginal quality due to low solubility. Low solubility has been reported for similar palladium arylpyridinato dichloro-bridged dimers.[16] There are seven resolvable resonances for complex I extending from 7.1 to 8.8 ppm in CD$_2$Cl$_2$. Four triplet signals are apparent that correspond to four predicted triplets for an ortho-metalated 2-phenylpyridinate ligand. Four doublet resonances are also expected; however, only one clearly resolved doublet is seen at 7.65 ppm. Two partially resolved doublets appear around 7.43 ppm, and a broad singlet is observed downfield at 8.8 ppm. The integration for this aromatic region equals 8; this is correct for a metalated 2-phenylpyridinate ligand where the carbon atom ortho to the bridging carbon has lost a proton as a result of metal–carbon bond formation. The simplicity of this ^{1}H NMR spectrum indicates that the environments of the ppy$^-$ ligands in this dichloro-bridged dimer are equivalent.

[Pd(ppy)(en)]BF$_4$ ^{1}H NMR spectrum was obtained in CD$_3$OD and acetone-d_6. Solving the integration of the aromatic region indicates eight aromatic protons. Two symmetric multiplets are seen in the aliphatic region of the NMR spectrum centered at 2.70 and 2.78 ppm in deuteriated acetone. These multiplets integrate for a total of eight protons. The high-field chemical shifts are not equivalent to the reported values for free ethylenediamine of 1.19 and 2.60 ppm.[17] We take this to confirm the existence of chelated ethylenediamine.

The [Pd(ppy)(CO)Cl] ^{1}H NMR spectrum is shown in Figure 2. Again, the integration confirms ortho-metalated ppy$^-$. There is a large downfield shift of one doublet that comes as a result of replacing chloride from [Pd(ppy)Cl]$_2$ with CO. ^{1}H NMR assignments for similar arylpyridinate complexes confirm that the low-field doublet for these square-planar Pd(II) complexes is due to the proton adjacent to the coordinated nitrogen.[16] Comparing the ^{1}H NMR spectra for I and IV allows assignment of the doublet that has shifted downfield in complex IV to the proton adjacent to the coordinated pyridyl nitrogen. Replacement of a weakly π-back-bonding chloride anion by carbon monoxide, which com-

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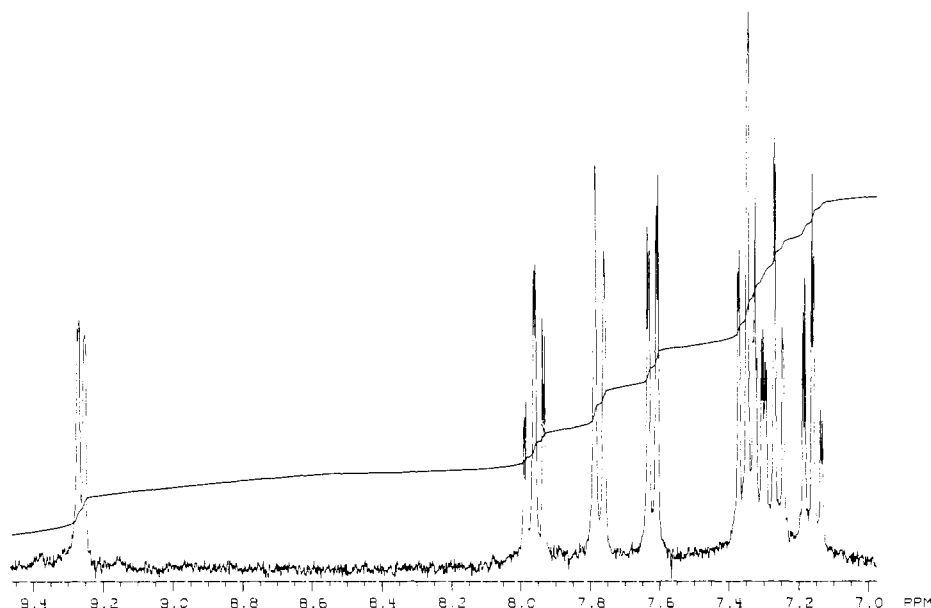
Figure 2. ¹H NMR spectrum of [Pd(ppy)(CO)Cl] in CD₂Cl₂.

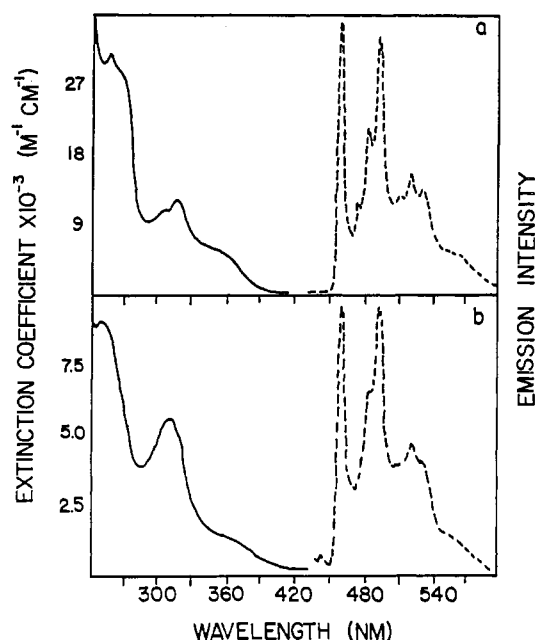**Figure 3.** (a) (—) Absorption and (- - -) 77 K emission spectra of [Pd-(ppy)Cl]₂ (I) and (b) (—) absorption and (- - -) 77 K emission spectra of [Pd(ppy)(bpy)]Cl (II).

Figure 4. Room-temperature absorption spectra of (—) Hppy and (- - -) HppyH⁺.

petes for π-electron density from the pyridine moiety, results in deshielding of the adjacent (HP-6) proton. Consequently, a significant downfield shift of this proton resonance is observed.

Absorption and emission data for the parent dimer [Pd(ppy)Cl]₂ and the [Pd(ppy)(bpy)]Cl complex are shown in Figure 3. Table I contains a list of absorption features, wavelengths, and corresponding extinction coefficients for all three of the monomeric compounds (II–IV), the parent dimer complex (I), and the ligands Hppy and bpy.

Phenylpyridine upon protonation of the external nitrogen shows a very distinct red shift in the absorption maxima. The N-protonated (HppyH⁺) and neutral (Hppy) 2-phenylpyridine absorption spectra are shown in Figure 4. The high-energy features observed (<330 nm) in the absorption spectra for the palladium complexes appear to correspond to red-shifted π–π* absorptions of 2-phenylpyridine similar to the red shift observed as a result of N-protonation. Where ppy⁻ and bpy are both present in compound II, superimposed π–π* transitions of the chelated bpy and metalated ppy⁻ ligands are responsible for broadening the high-energy features of the spectrum.
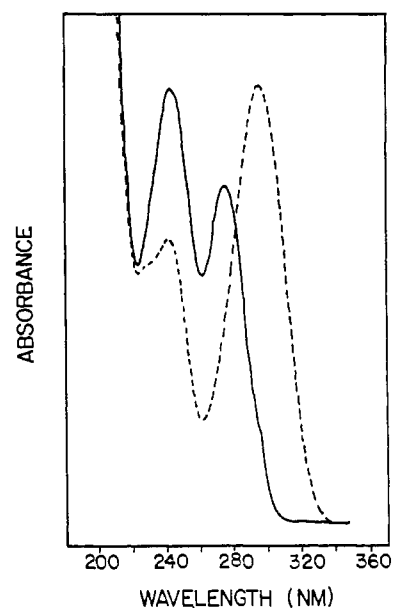
Each of the palladium phenylpyridinate complexes (I–IV) displays a broad structureless absorption band in the lower energy portion of the absorption spectrum (>330 nm) that does not correspond to any feature of the neutral or N-protonated forms of 2-phenylpyridine or 2,2′-bipyridine. Absorption data indicate that these low-energy absorption features are only slightly influenced by changing the ligands trans to the ortho-metalated 2-phenylpyridinate ligand (see Figure 5). Varying the ligands on the palladium phenylpyridinate complex is expected to directly affect electron density on the metal center by means of σ-donor and π-acceptor abilities of the bpy, en, and CO ligands. If this low-energy feature corresponded to a metal-to-ppy⁻ charge-transfer transition, we would expect the energy of this band to be sensitive to the changing ligands. Assignment of the low-energy transitions as MLCT would suggest that the σ-donor ligand ethylenediamine should facilitate charge transfer from the metal to the ppy⁻ ligand, whereas the π-accepting ligand bpy might introduce a lower energy metal-to-bpy charge-transfer transition and raise the energy of the metal-to-ppy charge transfer. Neither of these effects is obvious from the absorption data. Due to limited solubility of these compounds, measurement of effects on the energy of the transition by changing solvents was precluded. Complexes of
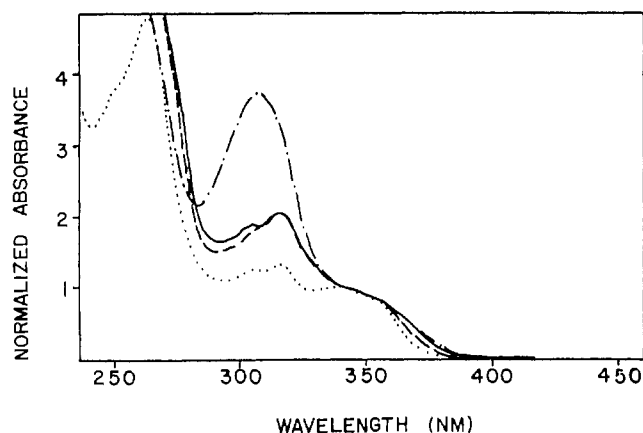
Figure 5. Normalized absorption spectra of (—) [Pd(ppy)Cl]$_2$ (I), (—·—) [Pd(ppy)(bpy)]Cl (II), (···) [Pd(ppy)(en)]Cl (III), and (- - -) [Pd-(ppy)(CO)Cl] (IV).

platinum containing ppy$^-$ exhibit electronic transitions in the visible region of the spectrum[13,14] that correspond to MLCT transitions. There are no corresponding transitions for any of the palladium phenylpyridinate complexes (I–IV). From these data we conclude that the low-energy features observed for these complexes are not MLCT transitions. Previous studies on the electronic transitions of d^8 palladium complexes[18,19] indicate that, in addition to lig-and-centered transitions, ligand-to-metal charge-transfer transitions also occur within the energy range of our unassigned feature (27 800 cm^{-1}), and we must therefore consider this possible contribution to the absorption spectrum. In the region 24 000–28 000 cm^{-1} for other Pd(II) and Ni(II) complexes, reports[18,19] generally suggest that these bands arise from LMCT transitions. We would once again expect that changing the electron density about the metal center by varying the σ- and π-donor and -acceptor strengths of the substituted ligands would affect the energy of a LMCT transition. We therefore rule out LMCT assignment of the low-energy portion of the absorption spectra for complexes I–IV.

Extinction coefficients at 360 nm for complexes I–IV are larger than expected for a d–d transition, and by virtue of this we eliminate ligand-field transitions as an explanation for these bands.

The final possibility for this electronic transition assignment is a perturbed ligand-localized transition. Interaction induced by restraining the phenyl and pyridyl ring to a planar conformation would create lower energy orbitals from interaction of π^* orbitals on the phenyl and pyridyl rings which are now oriented in such a position to enhance electronic interaction. This would also create higher energy ligand π orbitals from the increased phenyl–pyridyl π-orbital interaction. The energy of the electronic transition for this configuration-induced state would thus be lower than the π–π electronic transitions for ppy$^-$.[20] Additionally, the energy of the resulting electronic transition would not be expected to be affected, as the ligands trans to ppy$^-$ are substituted if ppy$^-$ is held rigid for each complex.

Extinction coefficients for the dimer complex are substantially larger than for the monomeric derivatives. Monomers III–IV would be expected to have ϵ values of approximately half of the ϵ values for the dimer due to the number of chromophores per mole of complex. Although we find no well-defined trend for the monomer complexes, the extinction coefficients do range from one-half to one-quarter of the ϵ values found for I.

The Pd(II) complexes we report here do not luminesce at room temperature, but each has a very structured emission at liquid-nitrogen temperature. Values of the 0–0 emission maxima and

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Table II. 77 K Luminescence Data for Ortho-Metalated Pd(II) Complexes

complex	0–0 energy, mm	luminescence lifetime, μs
[Pd(ppy)Cl]$_2$ (I)^a	460	116
[Pd(ppy)(bpy)]Cl (II)^b	460	190
[Pd(ppy)(en)]Cl (III)^b	460	419
[Pd(ppy)(CO)Cl] (IV)^a	458	488

^{a}Measured in ethanol/methanol/dichloromethane 4:1:1 glass. ^{b}Measured in ethanol/methanol 4:1 glass. ^{c}Estimated experimental error for lifetime measurements is ±5%.

luminescence lifetimes are listed in Table II. The emission 0–0 energies are very similar for the four palladium complexes. The lack of influence that the ligand trans to the ortho-metalated ligand has upon the energy of the emitting state parallels the room-temperature absorption results, supporting assignment of the emissions from localized, ligand-centered excited states for these systems. Similar emission spectra have been reported for C-protonated 2-phenylpyridine[14] and for [Rh(ppy)$_2$Cl]$_2$[12] at 77 K. These are very characteristic triplet, ligand-centered emissions.

Unlike the emission energies, the 77 K emission lifetimes of these complexes are sensitive to the identity of the ligand trans to 2-phenylpyridinate. The most noticeable change in the lifetime occurs as a result of going from a dimer to a monomer complex. Phosphine and phosphite derivatives of [Rh(ppy)$_2$Cl]$_2$ were also reported to show an increase in lifetime relative to that of the parent dimer.[12] This was explained to be a result of reduction in the amount of charge transfer to the ppy$^-$ ligand, as a result of increased π-back-bonding to the phosphine and phosphite ligands. More contribution to the lifetime would then come from the ligand-localized triplet transition, thus increasing the lifetime. The palladium results also conform to this trend. First, the order of the lifetimes follows what would be expected if π-back-bonding were competing with charge transfer to ppy$^-$ for electron density. On that basis the CO derivative would have the longest lifetime, the ethylenediamine derivative would have a shorter lifetime, and the dichloro-bridged dimer would have the shortest lifetime. The bpy derivative is a more complex case due to the likelihood that the Pd-to-bpy charge transfer would supplant the Pd-to-ppy$^-$ charge transfer as the lowest energy charge-transfer excited state. Lifetime data compiled in Table I indicate that the dimer and the en and CO derivatives do follow the anticipated pattern associated with π-back-bonding effects. The bpy derivative does not fit this simple pattern.

Conclusions

Absorption and low-temperature emission data for these four palladium ortho-metalates indicate large contributions to the excited states from transitions localized on the 2-phenylpyridinate ligand. The higher energy absorption transitions (240–340 nm) are intraligand π–π^* transitions localized on the 2-phenylpyridinate ligand. The low-energy features observed in the absorption spectra are also assigned as ligand-localized π–π^* transitions of the 2-phenylpyridinate ligand. These are new states that may result from interaction between the π orbitals of the heterocyclic and aryl rings induced by the coplanarity imposed by ortho-metalation.

The luminescence lifetime trend for complexes I–IV supports some MLCT contribution to the excited state, yet it is apparent from the 77 K emission spectra and the magnitude of the luminescent lifetimes of these complexes that the emitting state is principally a triplet state that corresponds in structure to the triplet emission of 2-phenylpyridine at low temperature. Comparison of these photophysical results to absorption and emission data for Pt(ppy)$_2$[14] also suggests that the four palladium complexes have ligand-centered excited states rather than the MLCT excited states observed in Pt(ppy)$_2$. The lifetimes of the palladium complexes relative to those of the platinum species coupled with the increased structure and energy of the emissions indicate a large contribution to the excited state from metal-perturbed ligand-centered states. It is also apparent that the ligands substituted trans to ppy$^-$ have little effect upon the energy of this excited state.

Photophysical properties of cyclopalladates must be recognized in order to realize application of such systems in photoconversion roles. We have reported here initial photophysical studies of several ortho-metalated palladium compounds. Drawing from these results, we are actively modeling and studying additional palladium compounds that may be useful in the processes of energy or electron transfer.

Remarkable Structures of Dialane(4), Al2H4

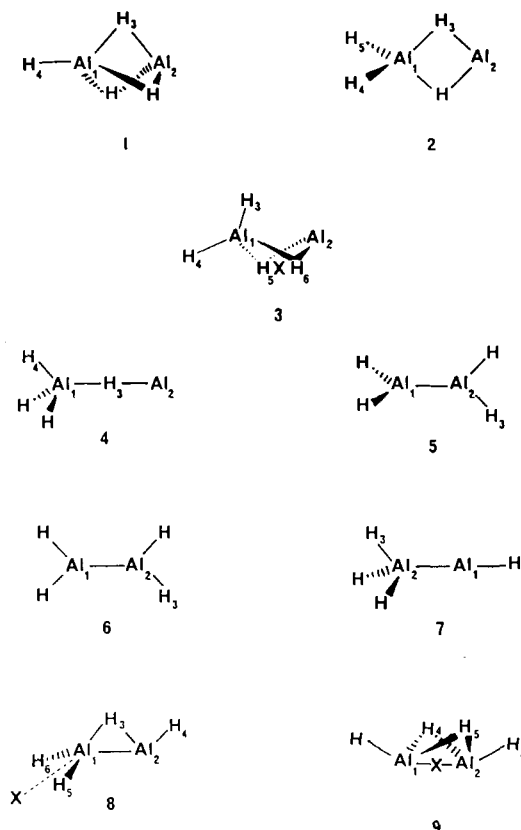Koop Lammertsma,*,† Osman F. Güner,† R. Michelle Drewes,† Alan E. Reed,‡ and Paul von Rague Schleyer‡

The potential energy surface of dialane(4), Al2H4, has been studied by ab initio molecular orbital theory at the MP4(SDTQ)/6-31G**//HF/6-31G* + ZPE level. Five minima (**1, 2, 5, 7,** and **8**) and three transition structures (**3, 6,** and **9**) were determined at the HF/6-31G* level. The most stable isomers are salt-like structures: i.e., **1** (C_{3v}), being the face complex of Al$^+$ with tetrahedral AlH4$^-$, and the 1.0 kcal/mol less stable **2** (C_{2v}), where Al$^+$ complexes to an AlH4$^-$ edge. Structure **5** (D_{2d}) is 10.7 kcal/mol less stable than **1**, with a barrier for Al–Al bond rotation of only 1.8 kcal/mol (**6**), and has an energy difference with **7** (H3AlAlH) of 11.3 kcal/mol; the μ-hydrido structure **8** is of intermediate energy. The doubly hydrogen-bridged isomer **9** is the energetically least favored (transition) structure, in strong contrast to B2H4, where it represents a minimum with nearly the same energy as the D_{2d} isomer.

Introduction

Diverse structures can be exhibited by Al2H4 molecules with 10 valence electrons. The qualitative prediction, based on Walsh diagrams, that perpendicular H2A–AH2 geometries (D_{2d}) should be favored over planar arrangements (D_{2h}) has been verified by various theoretical calculations on B2H4.[1] Since experimentally known B2X4 (X = F, Cl, Br) molecules[2] prefer such classical geometries,[3] other structural possibilities have only been considered more recently. Initial examinations suggested B2H4 isomers with single and double hydrogen bridges as well with C_{3v} geometries not to be favorable. The same conclusion was reached in our study of the C2H4^{2+} potential energy surface, where the usual D_{2d} H2C–CH2^{2+} form was the global minimum.[4] However, CH3–B–H$^+$ (C_{3v}) was the most stable CBH4$^+$ isomer.[5] Moreover, very recent MINDO/3 calculations on C2H4^{2+} [6a] and ab initio results at correlated levels (MP2/6-31G**) for both C2H4^{2+} [6b] and B2H4[1a] showed doubly bridged geometries to be quite low in energy. Similar hydrogen-bridged (e.g., in B2H7$^-$,[7] Al2H7$^-$,[8] and C2H$_n$$^+$ [9]) and multiple-hydrogen-bridged arrangements (e.g., in Si2H2[10] but not in P2H2[11] or Si2H4[10b]) are now being found commonly.

Pertinent to the present work, Zakzhevskii and Charkin[12] included the salt-like structures M$^+$[MCl4],$^-$ which are known for Ga2Cl4 and In2Cl4,[13] in their investigation of various M2X4 molecules (M = B, Al; X = H, F). With two different double ζ basis sets, they found Al2H4 to be quite unlike B2H4, which favors largely covalent structures. The salt-like Al$^+$[AlH4]$^-$ isomer of the former was the most stable, although the H2Al–AlH2 (D_{2d} and D_{2h}) forms were close in energy.[12] These Al$^+$[AlH4]$^+$ species are related to more conventional ionic molecules such as M$^+$-[AlH4]$^-$ and M$^+$[BH4]$^-$ (M = Li,Na)[14] and Li$^+$[CH4],[15] and to species with "inverted" geometries,[16,17] e.g., [SiH3]$^-$Li$^+$ [16] and [AlH2]$^-$Li$^+$ [16] as well as carbon-based systems. The potential

Chart I

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existence of Al2H4[18] and its relevance in Friedel–Crafts chemistry has been noted.[19]