lecular structure of the W compounds. The X-ray powder diffractograms have been obtained by courtesy of the Department of Geological Sciences of this University.

Supplementary Material Available: Tables SI–SV, containing crystal data for **3b**, complete angles and distances, X-ray powder diffraction data, anisotropic thermal parameters for non-hydrogen atoms, and the derived hydrogen positions (7 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

Notes

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Luminescence Spectroscopy of Dinuclear Platinum Complexes Containing Bridging Alkenylidene Ligands

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There has been a long-standing interest in luminescent Pt complexes. Until recently, most of the attention has focused on mononuclear complexes. However, the discovery of the tetrakis(μ-pyrophosphito)diplatinum anion $Pt_2(P_2O_5H_2)_4^{4-}$ ($Pt_2(POP)_4^{4-}$) has led to the development of a group of remarkably efficient luminescent materials based on binuclear Pt complexes.[2] Thus far, to our knowledge, these materials have been restricted to systems where the central core remains two stacked square-planar Pt(II) centers held together by four POP ligands.

Earlier, we reported on the first example of a luminescent binuclear Pt(II) complex (**1** of Figure 1) where the two Pt atoms are nonequivalent and did not involve the Pt^{II}POP basic structural unit. Further, this complex is an organometallic complex with a bridging phenylethenylidene ligand, phenyl-substituted vinylidene, which possesses considerable π-bonding character. Despite the disparate structures of the two classes of compounds, similar photochemistry is observed. Theoretical calculations predict similarity between the electronic structures of complex **1** and the well-studied $Pt_2(POP)_4^{4-}$, and although the geometries of the two complexes are quite different, complex **1** exhibits photochemical reactivity similar to that observed for $Pt_2(POP)_4^{4-}$.[3]

Because of the paucity of examples of luminescent dinuclear Pt(II) complexes, we were encouraged to explore this type of complex in greater depth. We report here the results of this study and present a number of new, interesting examples of luminescent complexes involving a basic planar $Pt_2C{=}C$ chromophore unit. Further, our studies have provided some insight into the structural features that govern the photophysical processes of these complexes. We present some guidelines that could serve as the basis for further work to enhance the luminescence properties of these compounds.

Experimental Section

Synthesis. All reactions were performed under dry, prepurified nitrogen. Solvent purification procedures, spectroscopic methods, microanalytical services, and reagent preparation have been published previously.[4-6] References to the syntheses of the complexes are noted in Table I. All of the complexes except **2** are unresolved isomer pairs depending on the position of the phenyl group.

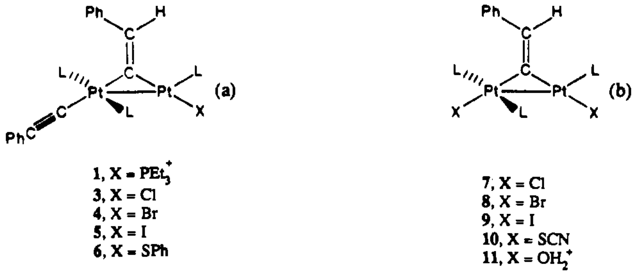

Figure 1. Structural representation of complexes (a) **1** and **3–6** and (b) **7–11**.

The structures of the complexes studied are shown in Figure 1. Except for **11** and **12**, the complexes reported here were prepared from $[Pt_2(\mu\text{-}C{=}CHY)(C{\equiv}CY)(PEt_3)_4]BF_4$ (Y = Ph (**1**) or H (**2**)) by nucleophilic substitution using procedures described previously.[3]

$[Pt_2(C{=}CHPh)(PEt_3)_3(OH_2)_2](BF_4)_2$ (**11**) was prepared by addition of 0.25 mmol of $AgBF_4$ to a stirred solution of 0.1 mmol of $Pt_2(C{\equiv}CHPh)(C{\equiv}CPh)(PEt_3)_3Br_2$ in 10 mL of CH_2Cl_2. The solution was stirred at 25 °C for 30 min and underwent a color change from orange to deep red. The solution was filtered through Celite, and the solvent was removed at reduced pressure. The complex was isolated as a red-brown solid (76%) that became an oil upon exposure to air: mp 67–69 °C; ^1H NMR ($CDCl_3$) δ 1.23 (m, 27, CH_3), 2.05 (m, 18, CH_2), 5.8 (s, 1, CHPh), 7.30 (m, 3, para Ph, meta Ph) 8.00 (d, 2, ortho Ph, J = 8.7 Hz); $^{31}P\{^1H\}$ NMR (5% $CDCl_3/CHCl_3$) δ 21.5 (broad s, 3, PEt_3, $^1J_{PtP}$ = 2130.984 Hz). Anal. Calcd for $C_{26}H_{51}O_2P_3Pt_2(H_2O)_2$: C, 29.56; H, 5.24; P, 8.79. Found: C, 29.59; H, 5.46; P, 8.94.

Photophysical Studies. Room-temperature absorption spectra were recorded by using a Hewlett-Packard 8452A diode-array spectrophotometer. Emission and excitation spectra were recorded on a Spex Fluorolog 2 spectrofluorometer. Emission spectra were corrected for solvent background and instrument response. Low-temperature (77 K) spectra were recorded from 4:1 ethanol–methanol glass matrices by using an optical Dewar sample holder.

Luminescence quantum yields, Φ, were measured at low temperature by the Parker-Rees method[7,8] using $[Ru(bpy)_3]Cl_2$ (bpy = 2,2′-bipyridine) [Φ 0.376][9] as a standard. The quantum yields are the averages of at least two sets of seven measurements with the sample being removed and replaced in the sample holder for every other measurement. Room-temperature absorption spectra were used for sample optical densities, which leads to an estimated ±30% uncertainty on the low-temperature yields.

Excited-state lifetimes (τ) were measured by using a pulsed N_2 laser (337 nm) nanosecond decay system, and software described elsewhere.[10] The same optical Dewar used for emission spectra was used as the sample holder for the lifetime measurements. The nonexponential decays were fit by nonlinear least-squares[11] methods to the sum of two exponentials (eq 1), where $I(t)$ is the luminescence intensity at time t and the K's and

$$I(t) = K_s \exp(-t/\tau_s) + K_l \exp(-t/\tau_l) \qquad (1)$$

τ's are the preexponential weighting factors and the excited-state life-

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[1] (a) University of Virginia. (b) Vanderbilt University. (c) James Madison University.

[2] Zipp, Arden P. *Coord. Chem. Rev.* **1988**, *84*, 47.

[3] Baralt, E.; Boudreaux, E. A.; Demas, J. N.; Lenhert, P. G.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R.; Myers, J. B., Jr.; Sacksteder, L.; True, W. R. *Organometallics* **1989**, *8*, 2417–2430.

[4] Afzal, D.; Lenhart, P. G.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 3050–3052.

[5] Lukehart, C. M.; True, W. R. *Organometallics* **1988**, *7*, 2387–2393.

[6] Afzal, D.; Lukehart, C. M. *Organometallics* **1987**, *6*, 546–550.

[7] Parker, C. A.; Rees, W. T. *Analyst (London)* **1962**, *87*, 83.

[8] Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

[9] Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841.

[10] (a) Turley, T. J. M.S. Thesis, University of Virginia, 1980. (b) Turley, T. J.; Demas, J. N. *Anal. Chim. Acta* **1987**, *197*, 121. (c) Sacksteder, LouAnn; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1989**, 1787.

[11] (a) Demas, J. M. *Excited State Lifetime Measurements*; Academic: New York, 1983. (b) Demas, J. N.; Demas, S. E. *Interfacing and Scientific Computing on Personal Computers*; Allyn & Bacon: New York, 1990.

[12] Baralt, E.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R. *Organometallics* **1991**, *10*, 516.

0020-1669/91/1330-3955$02.50/0

Table I. Photophysical Properties of Diplatinum Alkenylidene Complexes

no.	complex	λ_{max}, nm abs	λ_{max}, nm em	Φ	τ, μs	$k_r \times 10^{-3}$, s^{-1}	$k_{nr} \times 10^{-5}$, s^{-1}	τ_r, μs	ref
1	$[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4](BF_4)$	408							4
2	$[Pt_2(\mu\text{-}C{=}CH_2)(C{\equiv}CH)(PEt_3)_4](PF_6)$	388	516	0.036 (5)	12.0	3.0	0.8	330	6
3	$[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3Cl]$	390	696	0.010 (2)	1.7	5.9	5.8	170	3
4	$[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3Br]$	388	688	0.006 (1)	0.8	7.5	11.0	130	3
5	$[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3I]$	412	710	<0.0001					3
6	$[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3SPh]$	494							3
7	$[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3Cl_2]$	370	634	0.005 (1)	1.7	3.0	5.7	330	3
8	$[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3Br_2]$	376	634	0.003 (1)	0.5	6.4	19.4	160	3
9	$[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3I_2]$	388	650	0.007 (2)	0.6	12.4	17.8	81	3
10	$[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3(SCN)_2]$	384	638	0.076 (12)	2.9	26.2	3.2	38	3
11	$[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3(OH_2)_2](BF_4)_2$	422							text
12	$[Pt_2(\mu\text{-}\eta^1,\eta^3\text{-}1,2,4\text{-}Ph_3butadienediyl)(PEt_3)_4](BF_4)$	404	690	0.004 (1)	6.2	0.6	1.6	1740	12

times, respectively. The subscripts s and l refer to the short and long-lived components respectively.

Radiative, k_r, and nonradiative, k_{nr}, decay constants and the radiative or intrinsic lifetimes, τ_r, were calculated from

$$k_r = \Phi/\tau \qquad (2a)$$

$$k_{nr} = (1 - \Phi)/\tau \qquad (2b)$$

$$\tau_r = 1/k_r \qquad (2c)$$

where Φ is the absolute quantum yield and τ is the observed lifetime under the same conditions. τ_r is the lifetime that would be observed if there were no radiationless deactivation of the excited state. These expressions assume that the intersystem crossing efficiency is unity. For a series of platinum metal complexes (Ru(II) and Os(II) with α-diimine ligands) this has been shown to be true.[9] Further, it is clear that the intersystem crossing yield for $Pt_2(POP)_4^{4-}$ is very high since the fluorescence is a minor contribution to the total emission.[2] Therefore, in the current systems, a unit intersystem crossing yield is a reasonable assumption.

Results and Discussion

The photophysical data collected from the series of dinuclear Pt complexes are summarized in Table I.

Absorption Data. The absorption spectra of complexes **4**–**6** in CH_2Cl_2 solution are similar to those we previously reported for complexes **1** and **3** having strong absorbances in the 230–340-nm region.[3] A less intense, lower-energy absorption band shifts over a range of ~5500 cm^{-1} as the phosphine ligand of complex **1** is replaced by halides and thiophenolate anion.

Complex **2** is an analogue of **1** in which the phenyl groups have been replaced with hydrogen atoms. The main features of the spectra of the two complexes are the same, although the 280–330-nm region of the spectrum of **2** lacks the well-defined bands present in the spectrum of **1** (Figure 2A). The lowest energy absorption maximum is blue-shifted relative to that of the complex containing the aromatic ligand.

The absorption spectrum of **10** is shown in Figure 2B. This type of spectrum is representative of complexes **7**–**10**, which all have a halide or a pseudohalide replacing the phenylacetylide ligand of complexes **3**–**5**. Two intense absorptions are observed in the 240–330-nm region, and a lower intensity band is seen between 370 and 390 nm.

The spectrum of **11** was broad and relatively featureless. Complex **12**, which has a structure different from the other complexes of the series, shows a very simple spectrum with an intense band at 272 nm. Slight shoulders occur at 350, 366, and 404 nm (Figure 2C).

None of the spectra showed significant change between CH_2Cl_2 and a 4:1 ethanol–methanol solution.

Emission Data. Those complexes with the lowest energy absorption band lying at high energy (<405 nm) emit at 77 K while no emission can be detected from those with lower energy absorptions. The emission bands for all the complexes are broad and unstructured. The maxima are reported in Table I. Typically, the emission spectra show large Stokes shifts (~11 000 cm^{-1}) and emit with quantum efficiencies of less than 0.01. Exceptions are **2** with a Stokes shift of 6400 cm^{-1} and a quantum yield of 0.036 and **10**, which as a Φ of >7 times those for the other halide-substituted complexes. The emission spectra of **2**, **10**, and **12** are shown in Figure 2. None of the complexes studied appear to emit at room temperature.

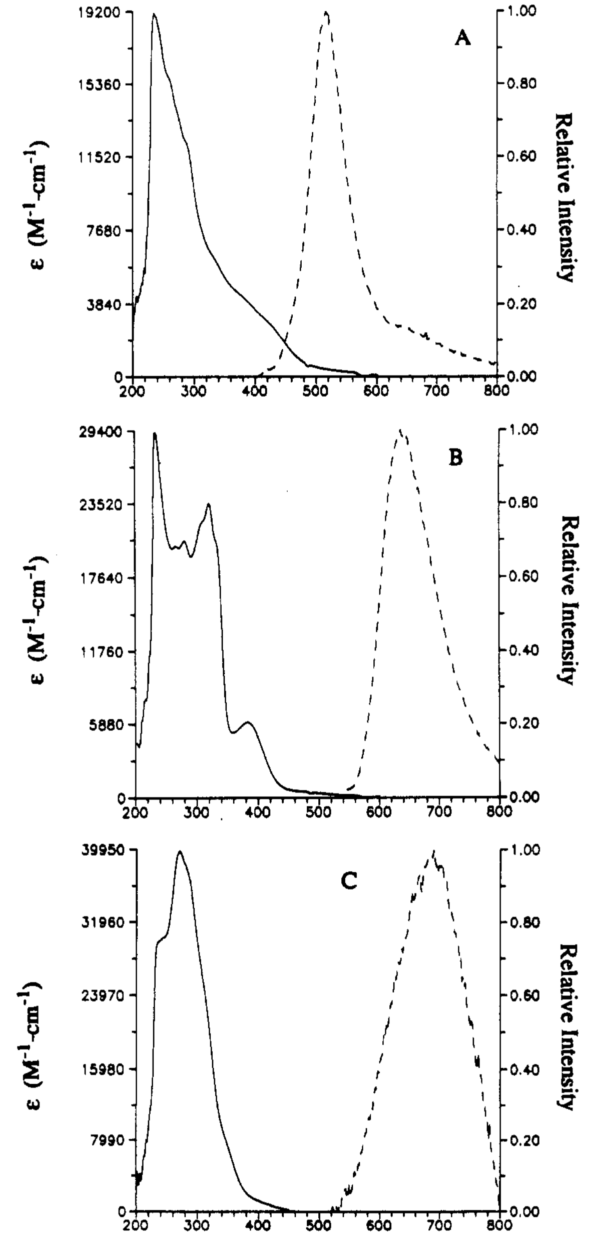

Figure 2. Absorption (solid line) and 77 K emission (dashed line) spectra of (A) **2**, (B) **10**, and (C) **12**. Absorption spectra were recorded from CH_2Cl_2 solution; normalized emission spectra were measured from 4:1 ethanol–methanol glasses.

The emission decays are nonexponential and can be fit with a sum of two exponentials (typically τ_l was less than a factor of 2-5 longer than τ_s). The weighted averages of the lifetimes are reported in Table I. From the average τ values, radiative and nonradiative rate constants were calculated. Radiative lifetimes are on the order of hundreds of microseconds. The two apparent lifetimes may arise from cis-trans isomer pairs. However, the need for a double exponential fit for **2**, which has only a single isomer, suggests a different explanation. These complexes exist in a variety of different conformations, each with a potentially different lifetime. We suggest that the nonexponentiality arises from site heterogeneity. We have seen heterogeneity effects in mononuclear Pt complexes.[13]

In the presence of heterogeneity, the decomposition of the luminescence decays into their components is not meaningful. Further, since we do not know the number of or the quantum yields for the different conformers, there is no reason to use anything other than an average lifetime in our estimation of the radiative and nonradiative rate constants.

X-ray crystallographic structure determinations have been performed for complexes **1**, **3**, **5**, **8**, and **12**.[3,12] Figure 1 diagrams the skeletal geometry of the dinuclear platinum complexes with bridging alkenylidene ligands. The principal coordination planes of the two platinum centers are nearly orthogonal to one another, but the two Pt atoms and the alkenylidene ligand are essentially coplanar.

The geometrical complexity and the low symmetry of these complexes results in a large number of possible electronic transitions. Phenylacetylene absorbs below 250 nm, and for those complexes with the phenylacetylide ligand, the absorption spectrum in this region must involve at least some contribution from ligand-localized transitions involving this species. PEt_3 absorbs at 230 and 325 nm, but these absorptions are far too weak to give rise to the bands observed in the dinuclear platinum spectra. We conclude that the bands at longer wavelengths than 250 nm must be charge-transfer or metal-centered transitions.

We now consider in detail the nature of the chromophoric group and the direction of charge movement in the lowest energy excited state. In view of the similarity of the lowest absorption and the emission of **1** and **2**, these transitions must involve the acetylide, the Pt—Pt group, and the C=C moiety. Since removing the acetylide does not affect the nature of the lowest state (compare **3**-**5** with **7**-**9**), the chromophoric group must be the $Pt_2C{=}C$ portion. As we will now show, the lowest state must arise from a Pt_2 to C=C charge-transfer transition.

The spectrum of **2** is similar to the spectra of the phenyl-substituted complexes, although the <280-nm region is less intense, suggesting that this region is dominated by CT transitions. The lowest energy band is blue-shifted relative to the analogous band of **1**. We attribute this band to a Pt_2-to-alkenylidene charge-transfer transition (MLCT) and explain the dependence of the band position on the identity of the substituent in terms of the ability of a Ph group to stabilize the negative charge relative to a H atom. This band is present in complexes **1**-**11**, which all have bridging alkenylidene ligands, and is absent from the spectrum of **12**, which does not have this structural feature (see Figure 2C).

The position of the low-energy band is also dependent upon the substitution on the Pt_2 in a manner that supports our assignment. As more electronegative groups are substituted for the PEt_3 and phenylacetylide ligands, the low-energy band shifts to higher energy. The electronegative groups drain electron density from the platinum atoms, making transfer of charge away from the metals a more energetic process. This trend is echoed in the shortening of the Pt-Pt bond lengths as ligands of increasing electronegativity and number are substituted on the complex: **1**, 2.750 (2) Å; **3**, 2.721 (1) Å; **5**, 2.711 (1) Å; and **8**, 2.685 (1) Å. The interatomic repulsion between the two formally negative Pt atoms is alleviated as the charge is decreased by the electron-withdrawing substituents. This argument holds, whether or not one accepts the antibonding Pt-Pt interactions of the molecular orbital calculations.[3]

The emissions of these complexes track the MLCT absorption bands, having a nearly constant energy separation of ~11 000 cm^{-1} for all the alkenylidene complexes with phenyl substituents. The radiative lifetimes, τ_r, which are all in the 10-330-μs range, indicate that the process is not a fluorescence, and we attribute the emission to the spin-forbidden Pt_2-to-alkenylidene CT transition. The large Stokes shift implies a significant distortion of the geometry of the complexes upon excitation. This effect may be a manifestation of the decreased Pt-Pt repulsion when an electron is promoted from the dinuclear fragment.

Complexes **1**, **6**, and **11** do not emit. If these complexes have the same energy separation between the low-energy absorption band and the emission band as do the other complexes in the series, the emission bands would occur at 725, 1051, and 771 nm, respectively. The energy gap law predicts that the nonradiative decay rates for these complexes would be larger than those for complexes with higher energy emissions. Also, the sensitivity of our phototube is poor this far to the red, and so, we would not expect to be able to detect even the 725-nm emission easily.

Our results suggest ways to design molecules with enhanced luminescence efficiency. The low quantum efficiency of most of the complexes can be largely ascribed to the low emission energy and to efficient radiationless deactivations. Increasing the emission energies will result in increased emission efficiency. Complex **2** has a hydrogen atom substituted for the phenyl substituent of the phenylethenylidene ligand, and the emission energy is the highest of all the complexes studied. The phenyl analogue (**1**) does not emit all, presumably due to a very low energy of the emitting state. Thus, building a series of complexes analogous to **3**-**11** with hydrogen atoms replacing the phenyl groups should raise the MLCT state energy, reduce radiationless deactivation, and enhance the luminescence efficiencies.

Clearly, there is a spectator ligand effect on both the lifetimes and quantum yields. The SCN is singular in its impact, having a profound effect on the luminescent efficiency. The origin of this remarkable change is not obvious as neither the ligand field strength nor the π-bonding capability of this ligand is exceptional when compared to Et_3P. At this point we can only note that this and similar ligands are clearly worth additional attention.

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[13] Sacksteder, L.; Baralt, E.; DeGraff, B. A.; Lukehart, C. M.; Demas, J. N. *Inorg. Chem.* **1991**, *30*, 2468.

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Small-Carborane-Stabilized Iron-Indole and Iron-Thiophene π-Complexes[1,2]

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The scope of organometallic transition-metal sandwich chemistry has been substantially broadened by the introduction of cyclic $R_2C_2B_3H_3^{4-}$ and pyramidal $R_2C_2B_4H_4^{2-}$ ligands in combination with aromatic hydrocarbons.[3] The carborane ligands not only

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(1) Organotransition-Metal Metallacarboranes. 22. (a) Part 21: Chase, K. J.; Bryan, R. F.; Woode, M. K.; Grimes, R. N. *Organometallics*, in press. (b) Part 20: Benvenuto, M. A.; Grimes, R. N. *Inorg. Chem.* **1991**, *30*, 2836.

(2) Based in part on the Ph.D. thesis of K.J.C., University of Virginia, 1990.