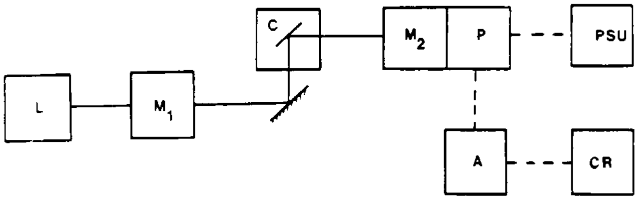

Figure 3. Block diagram of emission spectrometer used in this study. The light path is shown as a continuous line and the electrical connections as dotted lines. Details of the components are as follows: L = 450-W Xe arc lamp; M$_1$ = Bausch and Lomb high-intensity monochromator; C = cryostat head with cold LiF window; M$_2$ = Spex Minimate; P = RCA 1P28 photomultiplier tube; PSU = Brandenburg 476R regulated power supply unit; A = Keithley 414S picoammeter; CR = Tekman TE200 chart recorder.

spectra, and thus fluorescence would not have been detected. The lack of detectable phosphorescence at 12 K leads us to suggest that the previously reported emission at about 530 nm is not due to the phosphorus donor complex but to possible photolysis or decomposition products.

The lack of detectable phosphorescence from $W(CO)_5PMe_3$ and $W(CO)_5PCl_3$ can be interpreted as showing that the lowest triplet state is not appreciably populated and therefore that the photochemistry of $W(CO)_5L$ complexes proceeds primarily via the lowest singlet state. This indicates that internal heavy-atom induced spin–orbit coupling is not important in the case of tungsten P-donor complexes and that differences in photochemical yields for unique ligand ejection and CO exchange in $M(CO)_5L$ complexes (M = Cr, Mo, W) are due to differences in the rates of internal conversion between the $d_{x^2-y^2}$ and d_{z^2} σ^* orbitals.[7] Further work is in progress to determine emission lifetimes and quantum yields in order to calculate photophysical and photochemical rate constants for such systems.

Experimental Section

All $M(CO)_5L$ complexes were prepared with use of standard literature methods, with only slight modifications, as published earlier.[1-10,14-16] The purity of the complex was checked by infrared spectroscopy and by elemental analysis. The vacuum system and the equipment used to achieve cryogenic temperatures have been described extensively together with the gas deposition system.[15] Matrix gases with a purity of BOC grade X were used. Initial experiments were carried out, with use of infrared spectroscopy (Grubb-Parsons Spectromajor infrared spectrometer) in order to determine spray-on conditions to obtain well-isolated species. Typically, matrix to sample ratios of about 2000:1 were used. Deposition temperatures varied between -5 °C for $W(CO)_5PMe_3$ and 70 °C for $W(CO)_5$(3-Br-py) and spray-on times varied from 60 to 200 min, in order to obtain an absorbance of 0.2 to 1.0 for the lowest-lying d → d transition. UV-visible absorption spectra were recorded on a Pye Unicam SP 1800 spectrometer. Emission and excitation spectra were recorded on a homemade spectrometer, the details of which are given in Figure 3. The emission monochromator was regularly calibrated with use of a medium pressure mercury lamp. Reproducibility of the results was checked by measuring the spectra of each complex several times. The following precautions were taken to ensure that the detected luminescence came from the complex. (a) Photolysis of the sample by the excitation wavelength was reduced by blocking off the radiation between measurements with different exciting wavelength. The extent of any photolysis was monitored by running infrared spectra before and after the luminescence measurements. (b) Experiments with matrix gases alone or with possible photolysis products, e.g., $M(CO)_4$py, showed no detectable emission. (c) No emission was detectable upon exciting at wavelengths outside the observed absorption bands of the $M(CO)_5L$ complexes. The phosphorescence lifetime of $W(CO)_5$py in an argon matrix at 12 K was measured with use of the time-correlated single-photon-counting technique.[35,36]

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Registry No. $Mo(CO)_5$py, 14324-76-6; $W(CO)_5$py, 14586-49-3; $W(CO)_2$(3-Br-py), 17000-12-3; $W(CO)_5$pyr, 65761-20-8; $W(CO)_5$pip, 31082-68-5; $W(CO)_5PMe_3$, 26555-11-3; $W(CO)_5PCl_3$, 21223-85-8.

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New Luminescent Quantum Counter Systems Based on a Transition-Metal Complex

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New luminescent quantum counter systems based on tris(2,2′-bipyridine)ruthenium(II) chloride dispersed in either poly(vinyl alcohol) (PVA) or poly(vinylpyrrolidone) (PVP) solid films are described. While these new systems have a somewhat more limited wavelength range (≤540 nm) than the ever-popular Rhodamine B quantum counters (≤600 nm), their sensitivity is double that of the standard Rhodamine B counter and their response vs. wavelength can be flatter. The films have only been calibrated to 360 nm, but solution work indicates that they should be useful to ~280 nm. Further, the films are easier to handle than the dye solutions.

Introduction

The term "quantum counter" was originally used by Bowen in 1936[1] to describe an optically dense fluorescent screen placed before a detector. With selection of a luminescent material having an emission spectrum and photon yield which were independent of excitation wavelength, the response of the composite system was quantum flat (i.e., equal phototube current for the same flux in photons per second) within the absorbing range of the dye. Bowen originally found crystalline uranyl ammonium sulfate in paraffin (252–436 nm) and aqueous aesculin (252–367 nm) to be quantum flat within the accuracy of his measurements.

Luminescent quantum counters did not acquire popularity until after 1955 when Melhuish[2] introduced optically dense solutions of the dye Rhodamine B (RhB). This dye is now known to be nearly quantum flat in response for the range 250–600 nm.[3-5] Luminescent quantum counters are now

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widely used in emission spectrometer calibrations, the measurement of chemiluminescence efficiencies, photon yield determinations, and the correction of excitation spectra.[6,7] As has been shown by Taylor and Demas, however, Rhodamine B is not an ideal material.[4,5] The wavelength dependence of its response varies slightly with wavelength, solvent, and concentration. Further, its large degree of self-absorption at quantum-counting concentrations makes it less sensitive for applications not requiring the deep red penetration of Rhodamine B.

We wish to report the first utilization of a transition-metal complex as a quantum counter. We find that $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) dissolved in plastic matrices has exemplary properties as a quantum counter, and it can replace Rhodamine B counters in a variety of applications. We have also begun to examine the photophysical properties of this complex in polymer films.

Experimental Section

Complex. $[Ru(bpy)_3]Cl_2\cdot6H_2O$, purchased from G. Frederick Smith Chemical Co., was recrystallized four times from water to yield bright red plates. The complex as supplied is dark red, clearly impure, and unsatisfactory. The recrystallized material had absorption and emission spectra and lifetimes which agreed well with that given in the literature.

Polymer Films. The poly(vinyl alcohol), 99–100% hydrolyzed, (PVA) from Cellomer Associates and the type NP-K90 poly(vinylpyrrolidine) (PVP) from GAF Corp. were used without further purification. Both polymers and the complex were highly soluble in water, and films were prepared by evaporating aqueous solutions onto 4.5-cm diameter quartz plates. After drying at 40 °C in a convection oven, the films were inspected carefully for evidence of inhomogeneity or crystallization.

Spectral Calibration and Measurements. A microcomputerized luminescent quantum counter comparator[8] was used to measure the relative quantum yield vs. excitation wavelength of the films. A manual version of this instrument has been described elsewhere.[5] The reference material was Rhodamine B (5 g/L) in methanol, and the data were corrected for the known spectral response of this dye system.[5] A Corning CS 2-62 filter was placed over the RCA C7164R extended red response photomultiplier to restrict the viewing region to >600 nm and thus eliminate stray excitation light. The working excitation range of our instrument was limited to >360–590 nm by the severe attenuation of the light output by the system's Pyrex optics and the copper sulfate filter used to eliminate red stray light.

Emission spectra were taken on a microcomputerized SLM Model 8000 spectrofluorimeter. A back viewing arrangement was used for the films so as to simulate the viewing conditions used in the quantum counter arrangment; however, self-absorption is small in the region of the sample emission maxima. Emission spectra were corrected for the spectral response of the emission detection system by means of a standard lamp.[7]

Luminescence lifetimes were measured at room temperature by exciting the sample with a Molectron UV-14 pulsed nitrogen laser. The 10-ns duration pulse was sufficiently short in these experiments to permit it to be considered a δ function. Data were recorded on a Hewlett-Packard Model 181A storage oscilloscope equipped with a Model 1810A sampling plug-in with a 50-Ω input impedance. Stored oscilloscope traces were photographed onto Polaroid Type 46L transparency film, projected onto graph paper, traced, digitized manually, and reduced on a calculator.

Results

$[Ru(bpy)_3]^{2+}$ was appreciably more soluble in the PVA films, and there was no sign of precipitation at concentrations of 14.0 wt % in PVA while some crystallization was observed at 57 wt %. In PVP, it was necessary to go to 3.8 wt % to prevent recrystallization. As both polymers appear essentially transparent to <260 nm, the need for thick quantum-counting layers to achieve total absorption was acceptable. Both polymers formed clear but not optically perfect films. Some rippling and distortion were seen when an object was viewed through the films, although the surface in contact with the quartz was smooth and uniform. The PVA films could be peeled off the quartz or, if not handled carefully, would begin to peel at the edges. The PVP films were exceptionally tenacious and could only be removed by dissolving them.

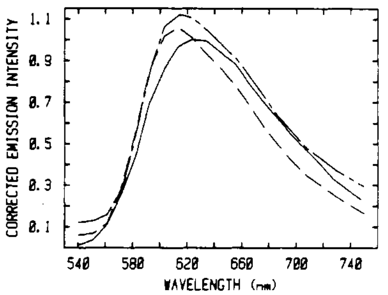

Figure 1. Emission spectra of $[Ru(bpy)_3]^{2+}$ in water (—), in a PVA film (– – –) and in a PVP film (---). The spectra in PVA and in PVP have been displaced vertically by 0.06 and 0.12, respectively, to enhance viewing.

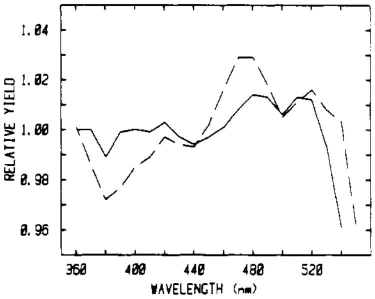

Figure 2. Relative photon responses of $[Ru(bpy)_3]^{2+}$ in PVA (—) and in PVP (– – –) films. The falloff in response at 540 and 550 nm for the PVA and PVP films, respectively, is due to sample transmission. The amount of $[Ru(bpy)_3]Cl_2\cdot6H_2O$ in both films was 2.1 mg/cm^2 of film. The concentration of $[Ru(bpy)_3]Cl_2\cdot6H_2O$ was 14.0 wt % in the PVA film and 3.8 wt % in the PVP film.

The emission spectra of $[Ru(bpy)_3]^{2+}$ in water solutions and in PVA and PVP films are shown in Figure 1. The emission maxima are 623 (water), 613 (PVA), and 615 nm (PVP). The small spectral shifts are similar to those observed for $[Ru(bpy)_3]^{2+}$ dissolved in different solvents. For example, λ_{max} in methanol is 615 nm. The apparent slight sharpening of the spectra in the films is probably real.

Figure 2 shows the spectral response of $[Ru(bpy)_3]^{2+}$ quantum counters in PVA and in PVP films. The sharp falloff in response at ~540 and 550 nm for the films arises from the onset of severe sample transmission which is not accounted for by the data reduction technique.

The spectral flatness of quantum counters can be quantitated with use of the maximum spread in sensitivity, D_{max}, and the relative standard deviation, F, about the mean sensitivity over the operating range of the counter. These terms are defined in eq 1 and 2, where the S_i's are the relative photon

$$D_{max} = 200\%(S_{max} - S_{min})/(S_{max} + S_{min}) \qquad (1)$$

$$F = \sum_{i=1}^{N} [(S_i - \bar{S})^2/(N-1)]^{1/2}/\bar{S} \qquad (2a)$$

$$\bar{S} = (1/N)\sum_{i=1}^{N} S_i \qquad (2b)$$

yields of the sample at different wavelengths, S_{max} and S_{min} denote the maximum and minimum sensitivities of the counter,

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Table I. Comparison of $[Ru(bpy)_3]^{2+}$ Polymer Films and the Rhodamine B Solution Quantum Counters

counter system	rel sensitivity	recommended wavelength range, nm	D_{max},[b] %	*F*,[c] %
RhB-methanol[a]	1	<360-600	4.0[d]	1.1[d]
$[Ru(bpy)_3]^{2+}$-PVA	2	<360–530	2.5	0.7
$[Ru(bpy)_3]^{2+}$-PVP	2	<360–540	5.7	1.6

[a] 5 g/L. [b] Maximum deviation. [c] Spectral flatness. [d] Evaluated for the 360–540-nm range to permit a direct comparison with the $[Ru(bpy)_3]^{2+}$ films over this region.

N is the total number of data points, and $\bar{S}$ is the average sensitivity. All sums and values are taken only in the operating range of the counter. In Table I, D_{max} and *F* are given for both film counters along with the recommended operating range. For comparison, the Rhodamine B solution quantum counter (5 g/L in methanol) recommended by Taylor and Demas[4,5] is also included.

Lifetime measurements were made on PVA films at three different concentrations of $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$: 57.0, 14.0, and 4.9 wt %. The most dilute sample had an essentially exponential decay curve and exhibited a lifetime of 1.65 μs. The intermediate concentration which was one used in the quantum-counting experiment exhibited a major long-lived component with a lifetime of 1.50 μs and a small component of a short-lived emission which accounted for <5% of the total emission and had a lifetime of 0.2 μs. The highest concentration sample which exhibited some crystallization had appreciably more (ca. 20%) of a short-lived component (0.2 μs) and exhibited a long-lived component with a lifetime of 0.97 μs.

Discussion

Quantum Counter Implications. The $[Ru(bpy)_3]^{2+}$ counter in PVA is flatter than the previously recommended RhB counter over the range studied. The $[Ru(bpy)_3]^{2+}$-PVP system is only somewhat poorer in spectral flatness as compared with the RhB counter. The $[Ru(bpy)_3]^{2+}$ systems are both twice as bright as the standard RhB counters (5 g/L in methanol) recommended by Taylor and Demas and three times brighter than the widely used 8 g/L of Rhodamine B in ethylene glycol.[5] The emissions seen by the phototube in a quantum counter arrangement are similar for the $[Ru(bpy)_3]^{2+}$ and the RhB counters; thus, the phototube sensitivty is probably not the dominant factor in the differences in sensitivity. The effective yield of RhB is probably less under the quantum counter conditions used than that of the $[Ru(bpy)_3]^{2+}$.

In addition to improved spectral flatness and sensitivity, the polymer films are easier to handle and less messy than the dye solutions which can leak and contaminate a system with highly fluorescent material. Further, the films can be suspended in any orientation without concern for leakage or filling bubbles blocking the optical paths.

The more restrictive wavelength of $[Ru(bpy)_3]^{2+}$ counters than RhB counters is frequently not a disadvantage as many researchers work below 530–540 nm. For example, workers examining the relative intensities of the different lines from an ionized argon laser would typically only be concerned with wavelengths as long as 514.5 nm or occasionally with the weak 528.7-nm laser transition; all of these lines fall within the operating range of the $[Ru(bpy)_3]^{2+}$ counters. In this case the increased sensitivity, reduced sample handling problems, and excellent spectral flatness of $[Ru(bpy)_3]^{2+}$ films can more than make up for the unfamiliarity of working with a metal complex rather than an organic dye.

For comparison we have also prepared RhB polymer-film quantum counters. We find, however, that spectrially these films are not as flat in response and are ~2–9 times less sensitive than the RhB counter (5 g/L in methanol).[9] Thus, the ruthenium complex is far superior to RhB polymer-film counters.

We add that the response of $[Ru(bpy)_3]^{2+}$ film counters can probably be extended ~30–40 nm to the red. Demas and Taylor[10] have shown that optically dense solutions of $[Ru(bpy)_3]^{3+}$ in water and in methanol are quantum flat to better than ±2% to at least 570–580 nm. While these solutions are less satisfactory quantum counters because of their appreciably lower proton yields (~4–8 times) than the films, the results show that by increasing the thickness of the counter film to reduce transmission in the red, appreciably enhanced red sensitivity beyond that reported here is possible.

Below 360 nm, we do not have data on the spectral response of the film counters, but in methanol the photon yield of $[Ru(bpy)_3]^{2+}$ is known to be flat (±2%) to at least ~280 nm.[11] We infer that the films have similar properties since there is no competitive absorption from the polymers.

We have not examined the stability of the films under irradiation, but we assume they will be excellent. In pure water $[Ru(bpy)_3]^{2+}$ has a decomposition yield[12] of $<10^{-5}$, which rivals that of the best laser dyes. PVA films are known to stabilize RhB to bleaching[13] and similar results may well prevail for $[Ru(bpy)_3]^{2+}$. This is especially true since the primary mode of photodecomposition of $[Ru(bpy)_3]^{2+}$ appears to be solvation[14] which should be greatly hindered or eliminated in the exceptionally high-viscosity polymer films.

We now discuss the choice of PVA or PVP as the polymer matrix for a $[Ru(bpy)_3]^{2+}$ quantum counter. The PVA film is noticeably flatter in response and, thus, is a more accurate quantum counter. Indeed, this system is the flattest quantum counter that we have ever examined. The PVA films, however, lack mechanical integrity and have a tendency to pull away from the glass with a loss of optical quality. Although the support-free films can be used as counters, they are mechanically fragile (like cellophane) and hard to support, and the reflectance of the air–polymer interface is probably not as good a match for the quartz–air interface of the samples with which they will normally by used. The PVP film, while less spectrally flat, is mechanically so sound that the quartz-plate-supported films could certainly be used in mobile equipment without fear of film separation.

We conclude by pointing out that $[Ru(bpy)_3]^{2+}$ may not be the best Ru(II) complex for quantum counting. On the basis of its observed lifetime, τ, of 1.5 μs and the known intrinsic lifetime, τ_0, of 14 μs,[11] we estimate its yield, in the film, at ~10% ($\phi = \tau/\tau_0$). The tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) complex, however, has a yield of 30% in deoxygenated ethanol or ethanol–water, which compares with ~4% for $[Ru(bpy)_3]^{2+}$ under similar conditions.[15] Further, this complex has appreciably deeper red absorption than $[Ru(bpy)_3]^{2+}$. Thus, we would expect it to be superior to $[Ru(bpy)_3]^{2+}$ in both sensitivity and wavelength ranges, although it is not commercially available and would need to calibrated.

Spectral Results. The absorption spectrum of $[Ru(bpy)_3]^{2+}$ in PVA at least in the region of the CT absorption is not noticeably affected by being in the polymer solvent rather than in water or methanol. This result is not surprising because of the known insensitivity of the absorption spectrum of

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$[Ru(bpy)_3]^{2+}$ to variations in solvent. Except for some sharpening, the emission is nearly unaffected. This emission sharpening can probably be attributed to the increased rigidity of the environment similar to the sharpening observed when the complex is measured in a rigid glass at 77 K.

The shortening of the lifetime in PVA with increasing concentration can probably be attributed to concentration quenching. On the basis of an assumed density of the matrix equal to that of bulk PVA, we can calculate a Stern–Volmer self-quenching constant, K_{SV}, from eq 3, where τ_0 is the un-

$$K_{SV} = [(\tau_0/\tau) - 1]/[[Ru(bpy)_3]^{2+}] \qquad (3)$$

quenched lifetime (taken as the value in the most dilute matrix) and τ is the quenched lifetime. For the quantum counter sample in PVA, we obtain $K_{SV} = 0.4\ M^{-1}$. The onset of nonexponentiality in the decay curves at high concentrations can probably be attributed to one of two sources. As the concentration rises, the complex molecules may be crowded together into adjacent occupancy sites in the polymer, giving rise to an increase in nearest-neighbor quenching. Alternatively, we may just be observing the onset of crystallization in microscopic domains. This latter possibility seems most probable for the following reasons. The nonexponentiality becomes most severe after the visual appearance of crystals and the lifetime of the fast component are the same for the crystallized sample and the quantum counter where no discernible crystallization is apparent.

We suggest that the somewhat poorer spectral flatness of the PVP film may be correlated with the much lower solubility of $[Ru(bpy)_3]^{2+}$ in this matrix. Even at the low but near saturated concentration used in the PVP counter, we may still be observing the presence of some microdomain crystallization.

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Registry No. $[Ru(bpy)_3]Cl_2$, 14323-06-9; PVA, 9002-89-5; PVP, 9003-43-4.

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Metal-to-Ligand Charge-Transfer Spectra of Some *cis*- and *trans*-$[Pt(PEt_3)_2(X)(Y)]$ Complexes

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Solution electronic absorption and magnetic circular dichroism (MCD) spectral data at 298 K are reported for *cis*-$[Pt(PEt_3)_2X_2]$, *cis*-$[Pt(PEt_3)_2(Me)X]$ (X = Cl, Br), *cis*-$[Pt(PEt_3)_2(R)_2]$ (R = Me, Et), *trans*-$[Pt(PEt_3)_2X_2]$ (X = Cl, Br, I), *trans*-$[Pt(PEt_3)_2(H)X]$, *trans*-$[Pt(PEt_3)_2(Me)X]$, and *trans*-$[Pt(PEt_3)_2(Et)X]$ (X = Cl, Br). Electronic absorption spectra obtained at 77 K in glassy solution (7/4 methylcyclohexane/pentane) are also reported for *cis*-$[Pt(PEt_3)_2Me_2]$, *cis*-$[Pt(PEt_3)_2(Me)Cl]$, *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = Me, Et), and *trans*-$[Pt(PEt_3)_2Br_2]$. All of these complexes exhibit intense absorptions in the UV spectral region which are assigned as metal-to-ligand charge transfer (MLCT) transitions from occupied Pt 5d orbitals to empty phosphorus 3d orbitals of the PEt_3 ligands. Some of the halide complexes also exhibit ligand field (LF) and ligand-to-metal charge-transfer (LMCT) bands in addition to the MLCT transitions. Detailed spectral assignments are given, and the relative energies of the MLCT transitions as a function of the X and Y ligands are discussed. For the cis complexes, the ordering $Et_2 < Me_2 < MeX < X_2$ (X = Cl, Br) is found whereas for the trans complexes the ordering $HX < EtX < MeX < X_2$ (X = Cl, Br) obtains. Since the positioning of the MLCT transitions is a sensitive function of the Pt oxidation state, the above orderings imply that the metal ion becomes less oxidized upon descending the series X > Me > Et > H.

Introduction

Square-planar complexes of metals with the d^8 electronic configuration which possess π-acceptor ligands generally show intense metal-to-ligand charge-transfer (MLCT) bands in their electronic absorption spectra.[2-8] These result from electronic excitation from occupied MO's, mainly of metal *n*d character, to empty ligand-based orbitals. Excitation of this type may be viewed as an incipient oxidation of the metal ion and the energetics of excitation reflect metal orbital stability and are related to the redox properties of the metal ion in the complex. Thus the MLCT excited states, which are often the lowest energy-allowed excited states, are of considerable interest not only from the standpoint of electronic structure but also in formulating electronic models for reaction pathways involving metal oxidation.

Hydride and alkyl ligands play a pivotal role in organometallic chemistry and are invoked as key intermediates in numerous transition metal catalyzed or mediated organic reactions. Yet, surprisingly few studies have been conducted which have examined the electronic structures of complexes of these ligands, and no single comparative study is available for a series of complexes in which these and accompanying ligands are systematically varied. In order to partly fill this void, we have measured the electronic absorption and magnetic circular dichroism (MCD) spectra of a series of planar *cis*- and *trans*-$[Pt(PEt_3)_2(X)(Y)]$ complexes in which X and Y include hydride, alkyl, and halide ligands. This data has allowed us to assess the relative oxidation state of the metal ion in these complexes and to correlate the oxidation state with

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