

The line-width increases with increasing pressure are typical in high-pressure Raman spectroscopy. We ascribe the line widths primarily to homogeneous broadening of the Raman transitions due to enhanced intraprotein vibrational dephasing at high pressure. Thus, pressure and temperature effects upon line width tend to cancel one another in these experiments. Indeed, in the 2–8-kbar range, the main effect of elevated pressure is to produce a spectrum which mimics the one observed at ambient rather than cryogenic temperature, including the line-width increases and the coalescence of the two peaks in the 270–280-cm⁻¹ range.^{9,10}

The absence of profound changes in the azurin RR spectrum up to 36 kbar suggests that no substantial changes in the coordination of copper at the active site occur in this pressure range. We have previously suggested^{9,10} that in azurin all four potential ligands (vide supra) form significant bonds to copper, while in plastocyanin the Cu–S(met) bond is effectively nonexistent at room temperature. We may expect that elevated pressure might force significant Cu–S(met) bonding in plastocyanin and that such an effect will be observable in the RR spectrum. In general, we have demonstrated the applicability of this powerful combination of high-pressure, cryogenic, and spectroscopic techniques to metalloproteins. Related investigations are continuing in these laboratories.

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Long-Lived Reactive Excited States of Zero-Valent Phosphine, Phosphite, and Arsine Complexes of Nickel, Palladium, and Platinum

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We wish to report here the first examples of d¹⁰ metal phosphine and phosphite complexes of nickel, palladium, and platinum which possess long-lived emissive excited states at room temperature in fluid solution.¹ In addition we have found that these complexes are photochemically reactive toward organic substrates, an observation that we believe represents an important new consideration in the interpretation of the mechanisms of oxidative addition reactions of this class of compounds. Furthermore in the light of the extensive use of these zero-valent metal complexes in a variety of catalytic and stoichiometric synthetic organic transformations, our observations may lead to a new and general approach to expanding the scope of the reactivity of this class of reagents.

Figure 1 presents the observed absorption and emission spectra of Pd(PPh₃)₄ and Pd₂(dppm)₃ in THF solution. These relatively broad (~3000 cm⁻¹ full width at half-maximum) unstructured room temperature emission spectra are typical of all of the Pd(0) and Pt(0) compounds that we have investigated. Neither Pd₂(dppm)₃ nor Pd(PPh₃)₄ exhibit any additional structure at 77 K. The emission spectra of the Ni(0) complexes show a very poorly resolved shoulder approximately 1000–2000 cm⁻¹ higher in energy than the band maximum. Decay kinetics for the excited states were found to be unaffected by the addition of excess ligand and were cleanly first order as determined by both transient absorption

(1) (a) A brief report of emission from these types of complexes in the solid state has appeared previously.^{1b} (b) Ziolo, R. F.; Lipton, S.; Bori, Z. *J. Chem. Soc., Chem. Commun.* 1970, 1124.

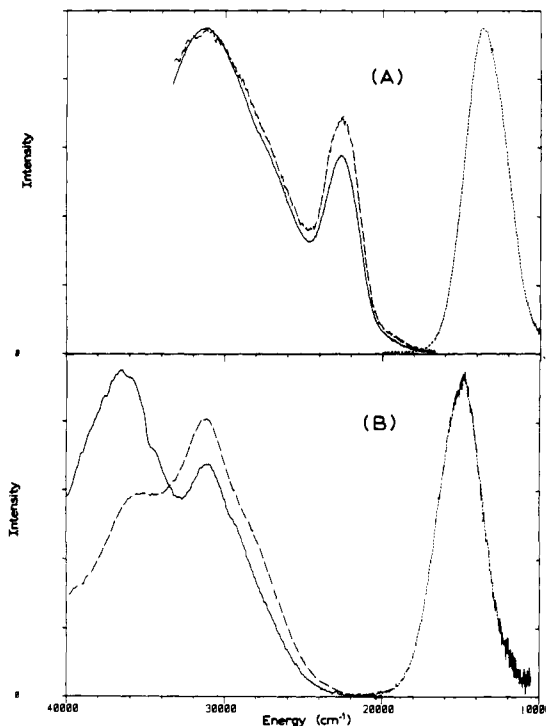


Figure 1. Absorption (—), corrected excitation (---), and corrected emission (···) spectra of Pd₂(dppm)₃ (A) and Pd(PPh₃)₄ (B) at room temperature in tetrahydrofuran solution.

Table I. Spectroscopic and Photophysical Properties of d¹⁰ Metal Phosphine and Phosphite Complexes at 25 °C in Nitrogen-Saturated Tetrahydrofuran Solution

compound ^a	emission max, nm	excited-state lifetime, μs	emission quantum yield, ¹⁴ %	excited-state decay rates	
				radiative, s ⁻¹ × 10 ⁻³	non-radiative, s ⁻¹ × 10 ⁻⁵
Pd(PEt ₃) ₃	646	5.20	1.13	2.17	1.90
Pd(PPh ₃) ₄	660	3.61	1.66	4.60	2.72
Pd(PMe ₂ Ph) ₄	690	1.39			
Pd(PMePh ₂) ₄	675		0.133		
Pd ₂ (dppm) ₃	740	5.38	1.9	3.53	1.82
Pd ₂ (dpam) ₃	710		7.53		
Ni(P(O- <i>o</i> -tol) ₃) ₃	~645 (sh), 745	5.13	0.293	0.57	1.94
Ni(PPh ₃) ₄	~740 (sh), 800				
Pt(PPh ₃) ₄	740	0.70	0.039	0.55	14.2

^aLigand abbreviations: triethylphosphine (PEt₃), triphenylphosphine (PPh₃), diphenylmethylphosphine (PMePh₂), dimethylphenylphosphine (PMe₂Ph), bis(dimethylphosphino)methane (dppm), bis(diphenylarsino)methane (dpam), tri-*o*-tolylphosphite (P(O-*o*-tol)₃).

and fluorescence spectroscopies.² Table I summarizes the observed spectroscopic and photophysical properties of a variety of ML_{*n*} complexes (M = Ni, Pd, Pt; L = tertiary phosphine or phosphite, *n* = 3, 4).³ Also included in the table are the spectroscopic properties of two ligand-bridged dimeric complexes, Pd₂(dppm)₃⁴ and Pd₂(dpam)₃⁵ (see Table I for ligand abbreviations). The dimeric complexes in Table I are expected to have

(2) Sample excitation for transient experiments was carried out at 308 nm using ~10-ns pulses from a XeCl excimer laser. Transient absorption due to the excited-state species was conveniently observed at 650 nm for all of the complexes in Table I.

(3) All complexes were prepared by literature methods. (a) Kuran, W.; Musco, A. *Inorg. Chim. Acta* 1975, 12, 187. (b) Ittel, S. D. *Inorg. Synth.* 1976, 17, 117.

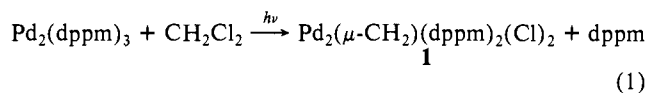
(4) Stern, E. W.; Maples, P. K. *J. Catal.* 1972, 27, 120.

(5) Details of the preparation of this complex from allylpalladium chloride and bis(diphenylarsino)methane will be reported elsewhere.

a planar three-coordinate geometry about each metal center on the basis of the crystal structure of $\text{Pt}_2(\text{dppm})_3$ in which the stereochemistry about each metal is essentially identical with that of monomeric $\text{Pt}(\text{PPh}_3)_3$.⁶ The nature of the emissive species in our experiments is clouded by the fact that the monomeric complexes are known to exist in solution as equilibrium mixtures of ML_n ($n = 2-4$) with the position of the equilibrium depending to a large extent upon the steric bulk of L.⁷ On the basis of a number of lines of evidence we believe that the observed solution luminescence in this class of complexes comes from species that are three-coordinate in both the ground and excited states.⁸

The radiative decay rates for all of the complexes in Table I are slow which suggests that the electronic transitions responsible for the observed emission spectra are only weakly allowed. We have observed that organic triplet quenchers will quench the emissive excited states of $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dppm})_3$, and $\text{Ni}(\text{P}(\text{O}-\text{tol})_3)_3$ with rates that depend systematically upon the organic triplet energy, indicating that emission from the d^{10} complexes originates from low-lying triplet states. The relative insensitivity of the observed emission spectra to the nature of the phosphine, phosphite, or arsine ligands suggests an excited state that is by and large metal localized in character. This is in accord with our extended Hückel molecular orbital calculations⁹ which indicate that the lowest excited state for the planar ML_3 d^{10} complexes should correspond to the promotion of an $(n)d$ electron to a vacant metal localized $(n+1)p_z$ orbital. An analogy exists between the $d^{10} p \leftarrow d$ excited states and the previously investigated¹⁰ $p \leftarrow d$ excited states of square-planar d^8 complexes. In essence the trigonal symmetry of the d^{10} complexes causes the metal d_{xy} and $d_{x^2-y^2}$ orbitals to become degenerate and to lie lower in energy than the $(n+1)p_z$ level. In contrast for d^8 complexes with four-fold symmetry d_{xy} and $d_{x^2-y^2}$ are split and $d_{x^2-y^2}$ lies above $(n+1)p_z$. As a result the lowest energy excited states for both systems become the $p \leftarrow d$ states. The important difference between the d^8 and d^{10} complexes lies in the lifetimes of the $p \leftarrow d$ excited states. For the d^8 complexes the emissive excited states are immeasurably short lived at room temperature in fluid solution,¹¹ which has been a major factor in preventing the investigation of bimolecular photochemistry of these types of complexes.

Given the microsecond excited-state lifetimes of the complexes in Table I in solution it seemed likely to us that bimolecular photochemical reactions of these complexes could be observed. This is indeed the case as shown in eq 1 where low-energy visible



irradiation of $\text{Pd}_2(\text{dppm})_3$ in the presence of CH_2Cl_2 leads cleanly and quantitatively to the formation of the methylene bridged dimer

(6) (a) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1155. (b) Albano, V.; Bellon, P. L.; Scaturin, V. *J. Chem. Soc., Chem. Commun.* **1966**, 507.

(7) (a) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1673. (b) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

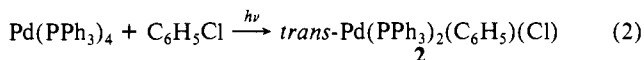
(8) We find that the excited-state lifetimes, emission spectra, and transient absorption spectra of all of the compounds that we have investigated are unaffected by the addition of excess phosphine ligand while quantum efficiencies for emission decrease as the concentration of excess ligand is increased. In addition the emission band shapes are unchanged when the complexes are either imbedded in rigid polymer films or examined as crystalline solids. These results are all consistent with complexes that are three-coordinate in both the ground and excited states. Further details will be presented in the full paper.

(9) Caspar, J. V., unpublished results. For calculational methods, see: (a) Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407. (b) McKinney, R. J.; Pensak, D. A. *Inorg. Chem.* **1979**, *18*, 3413.

(10) (a) Geoffroy, G. L.; Gray, H. B.; Hammond, G. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 3105. (b) Andrews, L. J. *Inorg. Chem.* **1978**, *17*, 3180. (c) Fordyce, W. A.; Crosby, G. A. *Inorg. Chem.* **1982**, *21*, 1455.

(11) (a) This product was previously identified from what was thought to be the slow thermal reaction of $\text{Pd}_2(\text{dppm})_3$ with CH_2Cl_2 .^{11b} We believe that this reaction was in fact proceeding photochemically under room light. After 48 h in the dark we find no detectable thermal reaction between the dimer and methylene chloride. (b) Balch, A. L.; Hunt, C. T.; Lee, C.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

1 in which a formal net four-electron oxidation of the dimer has been effected with one visible photon.¹² The monomeric complexes are also photochemically reactive as shown in eq 2 where



the oxidative addition product 2 can be isolated in 20% yield.^{12a} Significantly 2 has been isolated from the thermal reaction of $\text{Pd}(\text{PPh}_3)_4$ with chlorobenzene at 120 °C^{12b} whereas the photochemical reaction proceeds at room temperature. As a variety of catalytic reactions of d^{10} phosphine and phosphite complexes involve initial activation of halocarbons¹³ via oxidative addition, our photochemical results suggest the possibility of expanding the scope of these catalytic reactions to thermally unreactive substrates. We are also investigating the possibility that some of the previously identified radical reaction pathways in the thermal reactions of halocarbons with d^{10} metals may in fact be photochemically initiated.¹⁴

In summary we have identified a new class of $p \leftarrow d$ excited states general to low-valent metal complexes which have potential applications in photocatalysis. In addition to pursuing the photochemistry we are also expanding our studies of the fundamental photophysics and spectroscopy of these complexes and we are trying to assess the generality of these types of excited states for other metals (e.g., Ag(I), Au(I)) and other coordination environments.

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Synthesis and Characterization of the First Transition-Metal Complex of 1,2:5,6:9,10-Tribenzocyclododeca-1,5,9-triene-3,7,11-triene

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We wish to report the synthesis and structural and partial spectral characterization of a novel Ni(0) complex of a planar dehydroannulene,¹ complex I (Figure 1). The incorporation of a nickel atom into the cavity of the dehydroannulene II leads to novel chemistry when compared to transition-metal complexes of other unsaturated hydrocarbons²⁻⁵ and provides compelling

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