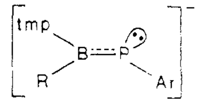
resulted in novel phosphide anions, **8a,b**. The identities of these



8a, R = Me
b, R = *t*-Bu

anions were proved by, e.g., reaction with H^+ to form (tmp)(R)BP(Ar)(H) (R = Me, *t*-Bu) which have been prepared by an independent route. The ^{31}P NMR chemical shifts are unusual (**8a** (THF) δ + 72; **8b** (THF) δ +85, +87). Normally, phosphide anions exhibit negative ^{31}P chemical shifts (e.g., δ −148 for $[ArP(SiMe_3)]^-$).[5] We attribute the substantial deshielding in the case of **8a,b** to partial donation of a phosphorus lone pair into a vacant boron orbital. In turn, the development of phosphorus-boron multiple-bond character, together with the increased steric bulk, explains the observation of two ^{31}P chemical shifts for **8b** (tmp group syn and anti to the phosphorus lone pair).

Studies of the reactivity and coordination chemistry of **1** are in progress. Indeed, very recently we have found that **1** (but not **2**) will react with $Fe_2(CO)_9$.

Acknowledgment. We are grateful to the Texas Advanced Technology Research Program for financial support.

Note Added in Proof. Professor Philip P. Power has informed us that his group has obtained X-ray crystallographic data on the following phosphinideneborate species: $[Li(Et_2O)_2PRB(mesityl)_2]$ ($R = C_6H_{11}$, mesityl) and $[Li(12\text{-crown-}4)_2][(mesityl)PB(mesityl)_2]\cdot THF$. The P–B bond lengths fall in the range 1.823 (7)–1.835 (13) Å and are thus consistent with phosphorus–boron multiple bonding. Moreover, the boron and phosphorus centers are planar in all three compounds. We are most grateful to Prof. Power for sending a preprint of his manuscript.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for **2** (6 pages). Ordering information is given on any current masthead page.

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[9] ^{31}P NMR data for **7** (32.38 MHz, THF): s, δ −96, $^1J_{PH}$ = 225 Hz. MS (70 eV): *m/e* 463 (12%, M^+), 277 (100%, $[ArPH]^+$), 186 (49%, $[(tmp)BCl]^+$.

Photochemical Preparation of Luminescent Platinum(IV) Complexes via Oxidative Addition on Luminescent Platinum(II) Complexes

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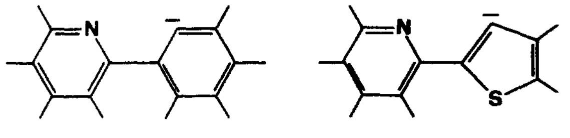
We have recently reported[4,5] the preparation and characterization (including absorption spectra, emission spectra, and excited state lifetimes) of the orthometalated Pt(II) complexes $Pt(Phpy)_2$ and $Pt(Thpy)_2$, which contain the ligands shown in Figure 1 ($Phpy^-$ and $Thpy^-$ are the C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine). We have now found that such complexes are photosensitive in several organic solvents, giving rise to oxidative addition reactions which lead to the formation of new luminescent orthometalated Pt(IV) complexes.



$Phpy^-$ $Thpy^-$

Figure 1. Structural formulas of the ligands.

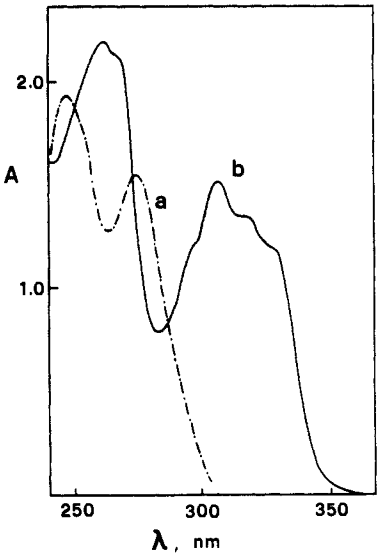


Figure 2. Absorption spectra of PhpyH 1.1×10^{-4} M (a) and $Pt(Phpy)_2(CH_2Cl)Cl$ 9.6×10^{-5} M (b) in CH_2Cl_2 at room temperature.

In a typical experiment, a 2.0×10^{-4} M solution of $Pt(Thpy)_2$ in deaerated CH_2Cl_2 was irradiated with light of a medium-pressure Hg lamp ($\lambda > 400$ nm). Irradiation caused the disappearance of the metal-to-ligand charge-transfer band of $Pt(Thpy)_2$ with λ_{max} = 420 nm[4,5] and other spectral changes, with clean isosbestic points.[6] At the end of the photoreaction, NMR analysis of the solution showed that only one species was present.[6] Evaporation of the solution yielded a light yellow powder that was recrystallized from CH_2Cl_2. Elemental analysis and NMR spectroscopy showed that this product corresponds to the formula $Pt(Thpy)_2(CH_2Cl)Cl$, indicating that the observed photochemical reaction is a simple photooxidative addition:

$$Pt(Thpy)_2 + CH_2Cl_2 \xrightarrow{h\nu} Pt(Thpy)_2(CH_2Cl)Cl$$

Similar reactions have been recently reported[7-9] for other Pt(II) complexes. A completely analogous photochemical reaction takes place with $Pt(Thpy)_2$ in $CHCl_3$ and with $Pt(Phpy)_2$ in CH_2Cl_2 or $CHCl_3$, as shown by the characterization of the reaction products. $Pt(Thpy)_2$ and $Pt(Phpy)_2$, as well other orthometalated Pt(II) complexes recently prepared in our laboratory, are photosensitive in several solvents, suggesting that photochemical oxidative addition might be a convenient route to prepare a variety of orthometalated Pt(IV) complexes. Detailed photochemical results and a discussion of the photochemical mechanism will be reported elsewhere.

The Pt(IV) complexes obtained via the photochemical oxidative addition reaction described above have a cis configuration, as shown by NMR spectra.[6] Their electronic absorption spectra (Table I; Figure 2) show intense bands in the near-UV spectral

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[4] Chassot, L.; Muller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249.
[5] Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Joliet, P.; von Zelewsky, A. *Chem. Phys. Lett.* **1985**, *122*, 375.
[6] Chassot, L.; von Zelewsky, A., submitted for publication.
[7] Hill, R. H.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1218.
[8] Vogler, A.; Kunkely, H. *Inorg. Chem.* **1982**, *21*, 1172; *Angew. Chem.* **1982**, *94*, 217.
[9] Roundhill, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 4354.

0002-7863/86/1508-6084$01.50/0

Table I. Absorption and Emission Properties of Orthometalated Pt(IV) Complexes

	absorption[a]		emission				
			293 K[a]			77 K[b]	
complex	λ_{max}, nm	ϵ	λ_{max},[c] nm	τ,[d] μs	Φ[e]	λ_{max},[c] nm	τ,[d] μs
$Pt(Phpy)_2(CH_2Cl)Cl$	260 306	23 000 15 000	447	150	0.15	444	300
$Pt(Phpy)_2(CHCl_2)Cl$	261 307	26 000 15 000	446	100	0.10	444	360
$Pt(Thpy)_2(CH_2Cl)Cl$	287 344	22 000 17 000	513	200	0.05	507	340
$Pt(Thpy)_2(CHCl_2)Cl$	287 344	22 000 16 000	513	270	0.05	507	430

[a] In CH_2Cl_2. [b] In propionitrile–butyronitrile 4:5 v/v mixture. [c] λ of the high-energy feature of the phosphorescence emission. [d] Emission lifetime in deaerated solution; estimated error ±10%. [e] Luminescence quantum yield, based on the value 0.028 reported in water at room temperature for $Ru(bpy)_3^{2+}$ (Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697); estimated error ±20%.

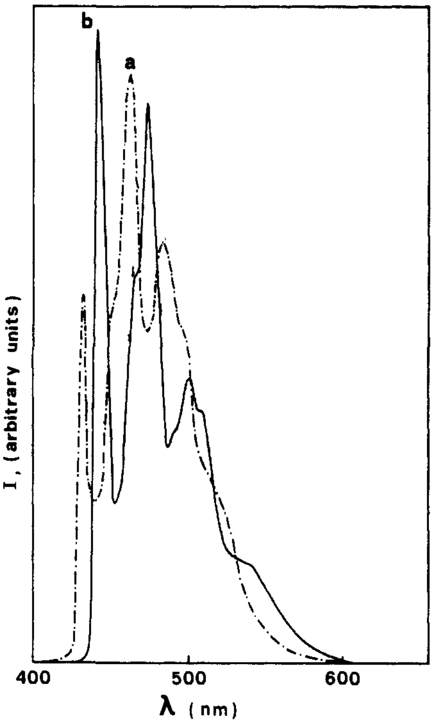

Figure 3. Emission spectra of PhpyH (a) and $Pt(Phpy)_2(CH_2Cl)Cl$ (b) in propionitrile–butyronitrile 4:5 v/v mixture at 77 K.

region, red-shifted with respect to those of the "protonated" ligand.

A quite interesting property of these Pt(IV) complexes is their ability to give a strong and long-lived luminescence. The previously reported[7-9] oxidative addition products of Pt(II) complexes apparently do not exhibit this property and, to our knowledge, the Pt(IV) complexes discussed in this paper constitute the first example of luminescent Pt(IV) organometallic complexes. In rigid nitrile matrix at 77 K the emission spectra have structures similar to those of the phosphorescenee spectra of the free protonated ligands, with a small red shift (see, e.g., Figure 3). This suggests that the emitting excited state is the lowest triplet ligand centered excited state, perturbed by metalation. The relatively long emission lifetimes (Table I) are consistent with this assignment. It should also be noted that metal-to-ligand charge-transfer excited states (which are responsible for the emission of the starting Pt(II) complexes)[5] are expected to lie at very high energies in Pt(IV) complexes and that emission from metal centered (and likely also from ligand-to-metal charge transfer) excited states would give rise to broad and unstructured luminescence bands.[10,11]

Strong luminescence and long emission lifetime are also observed at room temperature in deaerated solution (Table I), which makes these Pt(IV) complexes interesting as potential photosensitizers. Another important point of interest of the reaction described in this paper is the following. One can envisage the addition, to the orthometalated Pt(II) complexes, of $Cl-(CH_2)_n-X$ species, where X is an appropriate luminescent moiety. This would lead to the preparation of a new class of bichromophoric complexes suitable for the study of intramolecular energy- and electron-transfer processes.

In conclusion, we have shown that new, strongly luminescent orthometalated Pt(IV) complexes can be easily prepared by a photochemical oxidative addition on the corresponding orthometalated Pt(II) complexes. The reported reaction, which represent the quite unusual case of a photochemical process that converts a luminescent complex into another luminescent complex, offers a promising route for the synthesis of complexes containing distinct emitting units.

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(10) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970.

(11) Crosby, G. A. *J. Chem. Educ.* **1983**, *60*, 791.

Tight, Oriented Binding of an Aliphatic Guest by a New Class of Water-Soluble Molecules with Hydrophobic Binding Sites

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There is much current interest in the design and synthesis of water-soluble organic molecules with hydrophobic binding sites.[2] A variety of interesting artificial receptors (hosts) based on cyclophane skeletons has been prepared and shown to bind flat, aromatic guests very efficiently.[3-6] In contrast, efforts to bind

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(1) (a) Fellow of the W. R. Grace Foundation, 1985. (b) Fellow of the Atlantic Richfield Foundation, 1984. (c) Camille and Henry Dreyfus Teacher Scholar, 1984–1989.

(2) Tabushi, I.; Yamamura, K. *Top. Curr. Chem.* **1983**, *113*, 145–183.

(3) (a) Diederich, F.; Dick, K. *J. Am. Chem. Soc.* **1984**, *106*, 8024–8036. (b) Diederich, F.; Griebel, D. *J. Am. Chem. Soc.* **1984**, *106*, 8037–8046. (c) Diederich, F.; Dick, K. *Chem. Ber.* **1985**, *118*, 3817–3829. (d) Diederich, F.; Dick, K.; Griebel, D. *Chem. Ber.* **1985**, *118*, 3588–3619.

(4) (a) Odashima, K.; Itai, A.; Iitaka, Y.; Koga, K. *J. Am. Chem. Soc.* **1980**, *102*, 2504–2505. (b) Soga, T.; Odashima, K.; Koga, K. *Tetrahedron Lett.* **1980**, *21*, 4351–4354. (c) Odashima, K.; Soga, T.; Koga, K. *Tetrahedron Lett.* **1981**, *22*, 5311–5314.

(5) (a) Jarvi, E. T.; Whitlock, H. W. *J. Am. Chem. Soc.* **1982**, *104*, 7196–7204. (b) Miller, S. P.; Whitlock, H. W. *J. Am. Chem. Soc.* **1984**, *106*, 1492–1494.

(6) (a) Tabushi, I.; Yasuhisa, K.; Yoshio, K. *Tetrahedron Lett.* **1976**, *37*, 3327–3330. (b) Tabushi, I.; Kimura, Y.; Yamamura, K. *J. Am. Chem. Soc.* **1978**, *100*, 1304–1306. (c) Tabushi, I.; Kimura, Y.; Yamamura, K. *J. Am. Chem. Soc.* **1981**, *103*, 6486–6492.