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Electrochemistry, electron spin resonance, optical spectroscopy, and reactivity of organometallic platinum(II) complexes containing strongly π-accepting aromatic α-diimine ligands

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Abstract

Low-lying metal-to-ligand charge transfer (MLCT) transitions of the new complexes $LPtPh_2$ (L = 3,3′-bipyridazine (bpdz), 4,4′-bipyrimidine (bpm), 2,2′-bipyrazine (bpz) and 1,4,7,10-tetraazaphenanthrene (tap)) have been studied by emission and solvent-dependent absorption spectroscopy. The complex (bpm) $PtPh_2$ is strongly solvatochromic, and exhibits five absorption bands in toluene solution, but does not show luminescence. The other complexes emit visible light on excitation in the solid or in acetonitrile solution (bpdz complex). The one- and two-electron-reduced states were generated electrochemically; the ESR spectra of the paramagnetic intermediates, including $[(bpy)PtPh_2]^{-\cdot}$, are consistent with the formulation $Pt^{II}/(L^{-\cdot})$. The rate of oxidative addition of iodomethane to $Ph_2Pt(L)$ correlates with the basicity of L.

Introduction

Relatively few types of electron-rich d^8 organometal centers with their rather special coordination geometries have been studied spectroscopically in the case of complexes containing π-accepting α-diimine ligands [1–5]. Among the earliest examples were diorganoplatinum complexes of 2,2′-bipyridine, which exhibit solvent-dependent colours from MLCT transitions in the visible [1]. In particular, diarylplatinum complexes were found to be more sensitive to solvent changes than their dialkyl analogues [1,2].

We describe here four new complexes of diphenylplatinum(II) containing the well-characterized [5–7] heteroaromatic α-diimine ligands 3,3′-bipyridazine (bpdz), 4,4′-bipyrimidine (bpm), 2,2′-bipyrazine (bpz) and 1,4,7,10-tetraazaphenanthrene (tap) (Fig. 1).

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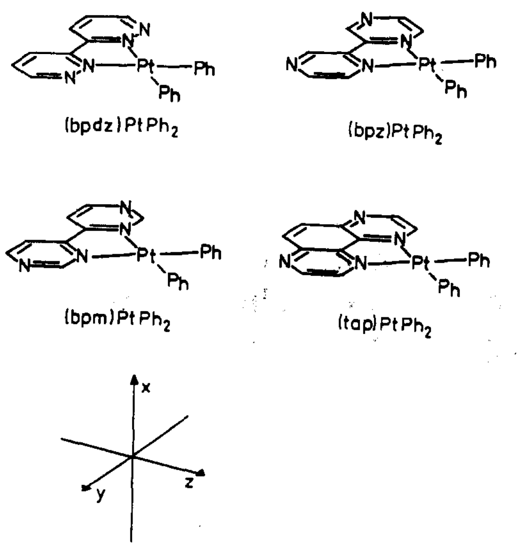


Fig. 1. New complexes described in this work.

These four ligands have (i) rather low-lying π^* orbitals, as indicated by their reduction potentials E_{red}; (ii) moderately basic N lone pairs, as indicated by positive pK_{BH^+} values; and (iii) varying degrees of π-acceptor capability, as evident from ESR coupling constants $a(^{14}N)$ of the coordinating nitrogen centers in the corresponding anion radicals (Table 1). When compared with results for R_2Pt complexes containing 2,2'-bipyridine (bpy) and 2,2'-bipyrimidine (bpym) [1,2,8], the data for the new complexes should provide further understanding of the spectroscopic behaviour, the electronic structure, and reactivity of such coordinatively unsaturated compounds, recently recognized to have potential in catalysis [9], selective protein or DNA labeling [10], and photophysics [11]. Presented are ^1H NMR data for the neutral compounds and ESR data for the singly reduced forms, along with absorption spectra and their solvent dependence, emission maxima, electrochemical reduction potentials, and rates of oxidative addition of iodomethane.

Table 1

Characteristics of α-diimine ligands

Ligand	E_{red} [a]	pK_{BH^+} [b]	$a(^{14}N)$ [c]
bpy	−2.66	4.4	0.241
bpdz	−2.33	3.37	0.42
bpm	−1.87	1.5	0.158
bpz	−2.08	0.45	0.370
tap	−2.00	[d]	0.340
bpym [e]	−2.30	≈ 2.5	0.143

[a] Potentials in V *vs.* ferrocene/ferrocenium pair, measurements in acetonitrile/0.1 *M* $Bu_4N^+PF_6^-$ (from refs. 5 and 7b). [b] Dissociation constants of conjugated acids (from ref. 5). [c] ESR coupling constants in mT of α-diimine nitrogen centers in ligand anion radicals (from refs. 6b and 7b). [d] Not available. [e] 2,2'-Bipyrimidine.

Experimental

Syntheses

The ligands bpdz and bpm [6], the precursor complex (COD)$PtPh_2$ [12], and the reference compound (bpy)$PtPh_2$ [1] were prepared by published procedures.

α-Diimine complexes: A solution of 0.5 mmol of the α-diimine and 0.5 mmol of the platinum precursor in 50 ml of benzene or toluene was heated under reflux for 2 to 3 h. The precipitates formed after cooling to 5°C were washed with n-hexane, separated from insoluble materials by dissolution in 1,2-dichloroethane, and isolated in 70–80% yield by evaporation of the solvent.

Found: C, 44.50; H, 2.96; N, 12.07 (bpdz complex); C, 45.94; H, 3.12; N, 10.73 (bpm complex); C, 46.38; H, 3.26; N, 10.72 (bpz complex). $C_{20}H_{16}N_4Pt$ (507.37; bidiazine isomers) calc.: C, 47.34; H, 3.18; N, 11.04%.

Instrumentation

^1H NMR: Bruker AM-200. ESR: Bruker ESP-300. The g factors were determined by use of an NMR gaussmeter Bruker ER 035 M and a microwave counter HP 5350 B, or by the double cavity technique with the perylene anion radical in DME as reference ($g = 2.002656$) [6b,13]. UV/VIS absorption spectroscopy: Bruins Instruments spectrometer Omega 10. Emission spectra: Perkin–Elmer LS-3B (no correction applied). Cyclic voltammetry: PAR potentiostat 273/175; three electrode configuration with glassy carbon working electrode, Pt counter electrode and Ag/AgCl or SCE as reference; ferrocene/ferrocenium pilot system. Dry acetonitrile/0.1 *M* Bu_4NPF_6 was used as electrolyte.

Generation of anion radicals

Anion radical complexes $[(\alpha\text{-diimine})PtPh_2]^{-\cdot}$ were produced for *intra muros* ESR measurements in dry THF/0.1 *M* Bu_4NClO_4 by use of the previously described two-electrode capillary cell with platinum electrodes [13]. The potential was slowly increased until EPR signals were detectable.

Kinetic measurements

The rates of reactions of the α-diimine complexes $LPtPh_2$ (L = bpy, bpdz, bpm and bpz) with iodomethane in acetonitrile were measured under pseudo-first order conditions ($[CH_3I] \gg 10 \cdot [Pt]_T$) at 20°C. The kinetics mode of the Shimadzu UV-160 spectrophotometer was used at the appropriate absorption maximum. The data were fitted to an exponential expression by use of a SIMPLEX program [14] on an EPSON PC. All reactions were of first order in $[LPtPh_2]$ for at least four half-lives, and conformed to the rate expression $-d[LPtPh_2]/dt = k_{obsd} \cdot [LPtPh_2]$.

Results and discussion

^1H NMR

The ^1H NMR spectra show the expected [6a] coupling patterns for the ABX spin systems of the diimine ligands; the chemical shifts in acetone-d_6 solution (Table 2) are only slightly changed compared with those for the free ligands [6a]. The *ortho*-protons of the diimine and of the phenyl groups show ^{195}Pt isotope

Table 2
^1H NMR data for complexes (α-diimine)$PtPh_2$ in acetone-d_6

Complex	α-diimine		phenyl	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz) (Pt-H2,6)
(bpdz)$PtPh_2$	9.27, dd(H6)	5.00(H5-H6)	7.29, m(H2,6)	74.4
	8.88, dd(H4)	8.55(H4-H5)	6.80, m(H3,5)	
	8.38, dd(H5)	1.72(H4-H6)	6.69, m(H4)	
(bpm)$PtPh_2$	9.28, d(H5)	5.26(H5-H6)	7.41, m(H2,6)	71.5
	9.01, d(H2)	1.28(H2-H6)	6.97, m(H3,5)	
	8.34, dd(H6)	12.9(Pt-H2)	6.83, m(H4)	
(bpz)$PtPh_2$	9.97, d(H3)	1.31(H3-H6)	7.36, m(H2,6)	70.8
	8.97, d(H5)	2.97(H5-H6)	6.93, m(H3,5)	
	8.52, dd(H6)	21.1(Pt-H6)	6.78, m(H4)	
(tap)$PtPh_2$	9.46, d(H3,8)	2.58(H2-H3)	7.44, m(H2,6)	72.0
	8.86, d(H2,9)	2.58(H8-H9)	6.98, m(H3,5)	
	8.57, s(H5,6)	20.6(Pt-H2,9)	6.78, m(H4)	

coupling ($I = 1/2$, 33.8% natural abundance). This coupling is rather small for the H-2 atom in (bpm)$PtPh_2$, which is situated between two nitrogen centers.

Cyclic voltammetry

Electrochemical studies of the new complexes were carried out in acetonitrile/0.1 *M* $Bu_4N^+PF_6^-$ in order to minimize interactions of the coordinatively unsaturated species with the electrolyte. Figure 2 illustrates a typical cyclic voltammogram with two reversible one-electron waves in the reductive scan. For bpy and bpdz complexes, the second reduction is fully reversible only at rapid scan rates > 1000 mV/s. Anodic oxidation gave highly irreversible waves with strongly solvent-dependent peak potentials, suggesting a rapid attack on, or Pt–C homolysis [15] of, the resulting Pt^{III} (d^7) species. The electrochemical data are summarized in Table 3.

For the one-electron reductive processes there is the alternative of α-diimine reduction to an anion radical and dianion ligand or a metal reduction to Pt^1 [15]

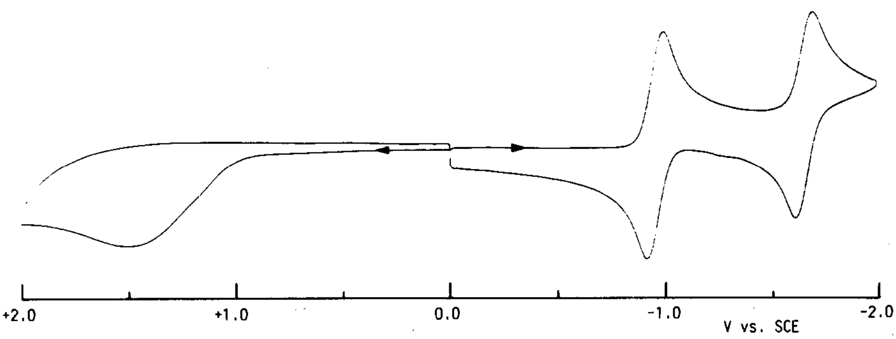


Fig. 2. Cyclic voltammograms of (tap)$PtPh_2$ in CH_3CN/0.1 *M* Bu_4NPF_6 at 200 mV/s (separate oxidation and reduction scans).

Table 3

Electrochemical data for complexes (α-diimine)$PtPh_2$ from cyclic voltammetry at 200 mV/s in acetonitrile/0.1 *M* Bu_4NPF_6 [a]

Complex	$E_{red1}(\Delta E_{pp})$	$E_{red2}(\Delta E_{pp})$	E_{ox}(pa) [b]
(bpy)$PtPh_2$	−1.98(60)	−2.66(irr)	[c]
(bpdz)$PtPh_2$	−1.54(60)	−2.31(130) [d]	+0.64
(bpm)$PtPh_2$	−1.32(70)	−1.99(80)	+0.96
(bpz)$PtPh_2$	−1.46(70)	−2.18(90)	+0.95
(tap)$PtPh_2$	−1.44(60)	−2.12(60)	+0.67

[a] Potentials E in V *vs.* ferrocene/ferrocenium pair; peak potential differences ΔE_{pp} in mV. [b] Anodic peak potential for irreversible oxidation. [c] Not determined. [d] At 5000 mV/s, irreversible wave at lower scan rates.

(d^9) and Pt^0 (d^{10}), the latter with an 18 valence electron configuration. Not only the ESR and UV/VIS absorption spectra of these and similar complexes [8c] but also the data from Table 3 confirm the α-diimine ligand as predominant site of the electron addition. First, the differences between first and second reduction potentials of about 0.7 V are typical for aromatic α-diimines [6a]; in addition, the potentials of the complexes follow closely the sequence bpy < bpdz < bpz < bpm observed for the free ligands (Table 1). The potentials for the tap complex are very similar to those of the bpz analogue, suggesting the similarity of the redox orbitals despite the presence of two close lying unoccupied MOs in tap [7a]. It is noteworthy that the ability of $PtPh_2$ to facilitate the reduction of the α-diimine ligands is lower than that of $Mo(CO)_4$ [6a], $[Ru(bpy)_2]^{2+}$ [16] or $Re(CO)_3Cl$ [17] fragments, indicating a higher degree of orbital mixing [5].

Electron spin resonance

In THF, 1,2-dimethoxyethane [8c] or 1,2-dichloroethane solution, the electrochemically [13] one-electron-reduced complexes $[(\alpha\text{-diimine})PtPh_2]^{-\cdot}$ show ESR spectra with little (bpym [8c]) or no resolved hyperfine structure (Fig. 3). Isotropic ^{195}Pt isotope splittings ($I = 1/2$, 33.8% natural abundance) are not observed, and must be < 4 mT. An anisotropic spectrum of the $bpdz^{-\cdot}$ complex in frozen dichloroethane (there is slow decomposition in THF) shows a typical [8c] rhombic pattern with one rather low g_1 component at 1.925 and two high g components $g_{2,3}$ at 2.0062 and 2.0390 (Fig. 3); the central feature is accompanied by two ^{195}Pt isotope satellites ($A_2 = 3.5$ mT).

The isotropic g value is invariably smaller than g (electron) L = 2.0023, the values being 1.9933 (bpy complex), 1.9908 (bpdz complex), 1.9952 (bpm complex) and 1.9933 (bpz complex, all in THF solution), indicating the presence of close-lying excited states such as spin-orbit admixed quartet states [8c]. In agreement with results for corresponding radical complexes of $[Ru(bpy)_2]^{2+}$ [13], the value of g is highest for the $bpm^{-\cdot}$ system and low for $bpz^{-\cdot}$ and $bpdz^{-\cdot}$ isomers. Despite the predominantly ligand-based spin, the anisotropy of g is relatively large, *e.g.* in the case of bpym [8c] or bpdz complexes (Fig. 3), because of the very large spin–orbit coupling constant of approximately 5000 cm^{-1} for platinum(II) [18]. In addition to $d\pi$, *i.e.* the $5d_{xz}$ orbital (axes shown in Fig. 1), there is a close-lying $6p_x$ orbital of platinum that can interact with the ligand π^* MO [11f,g].

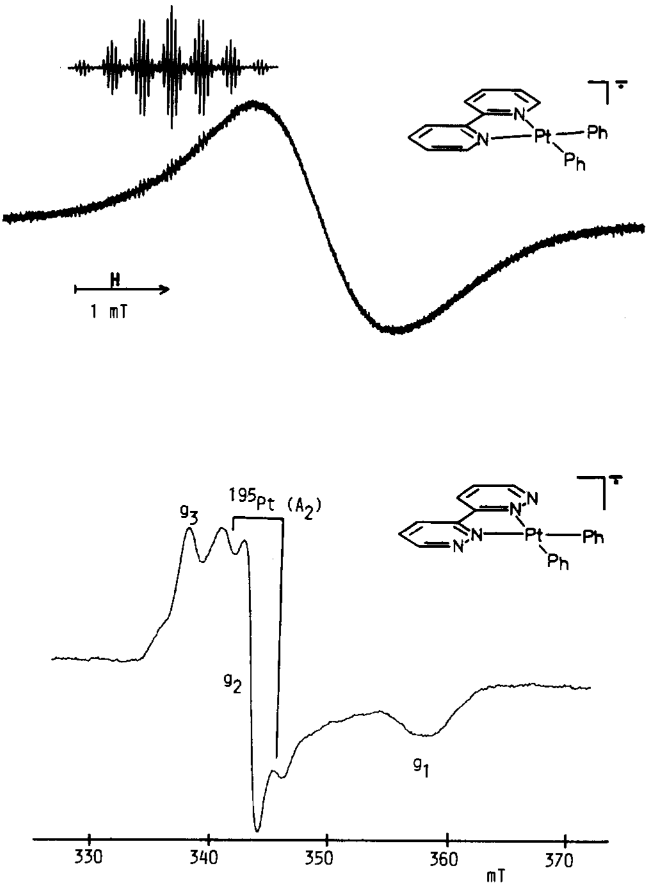


Fig. 3. ESR spectra of $[(bpy)PtPh_2]^{-\cdot}$, generated electrochemically at 300 K in THF/0.1 *M* Bu_4NPF_6 (top, with perylene anion-radical spectrum as reference for *g*) and of $[(bpdz)PtPh_2]^{-\cdot}$ at 150 K in 1,2-dichloroethane/0.1 *M* Bu_4NClO_4 (bottom).

UV/VIS absorption spectra and solvatochromism

Complexes containing electron-rich metal centers and π acceptor ligands such as the α-diimines exhibit low-energy metal-to-ligand charge transfer (MLCT) absorptions that can be solvent dependent (solvatochromism) [1a,6a,19–21]. Absorption maxima in THF solution are listed in Table 4; the bpdz and bpm complexes were also studied in several other solvents (Tables 4–6).

In contrast to, *e.g.*, $Mo(CO)_4$ complexes of the α-diimines, with their two main absorption features to the b_1 and a_2 π^* molecular orbitals [6a], the $PtPh_2$ complexes often exhibit several intense absorption maxima, expecially in non-polar solvents such as toluene (Fig. 4).

The large number of easily observable low-lying transitions is attributable not only to the presence of eight occupied *d* orbitals and the availability and admixture of 6*s* and 6*p* orbitals but also to the increased probability of triplet absorptions because of heavy metal-induced spin–orbit coupling. Single crystal polarized spectra at low temperatures for the related $(bpym)Pt(CN)_2$ reveal the high com-

Table 4

Long-wavelength absorption and emission maxima of complexes (α-diimine)$PtPh_2$

Complex	λ_{abs}(nm) (ϵ[M^{-1} cm^{-1}]) [a]	λ_{em} (nm)
(bpy)$PtPh_2$	455 (2880), 379	525 [b]
(bpdz)$PtPh_2$	526, 363	628 [b]
	490 (1580), 345 [c,d]	570 [c,e]
		520 [c,f]
		460 [c,g]
(bpm)$PtPh_2$	533 (2250), 477sh	[h]
	586, 550sh, 496, 460sh, 432sh [i,k]	
(bpz)$PtPh_2$	508 (3065), 410	595 [b]
(tap)$PtPh_2$	508, 416	620 [b]

[a] In THF solution. [b] *For the solid (uncorrected maxima).* [c] In acetonitrile. [d] For solvent dependence, see Table 5. [e] Excitation between 488 and 540 nm. [f] Excitation below 470 nm. [g] Excitation below 420 nm. [h] No emission observed. [i] In toluene solution. [k] For solvent dependence, see Table 6.

plexity in such systems [11f,g]. Nevertheless, the most intense, negatively solvatochromic long-wavelength band is attributed to an allowed transition a_2 (π, $5d_{xy}$) $\rightarrow b_1$ (π^*, $6p_x$) of approximate MLCT character [1a,11g]. (Note that the molecular plane is yz, Fig. 1.)

Comparison of the spectra of the complexes (α-diimine)$PtPh_2$ in THF solution reveals a familiar [6a,16,17] pattern in that the bpm and bpdz complexes absorb at rather low energies; the former because of the low lying π^* (bpm) MO and the latter because of the comparatively high basicity of bpdz (Table 1), which causes a destabilization of occupied d levels. On the other hand, bpz is a very weak base and bpy has a high lying π^* level (Table 1).

The extinction coefficients for the long-wavelength bands (Table 4) are relatively small for an MLCT transition [6a,16,17], indicating rather poor metal/ligand overlap. Because of the large number of allowed transitions, an assignment of transitions to the second lowest unoccupied α-diimine MO a_2 cannot be made; the well known b_1/a_2 energy differences [6a] cannot be used in view of the large and possibly variable ligand field splitting of platinum d-orbitals.

Quantitative analysis of the negative solvatochromism of the long-wavelength absorption band was performed for bpdz and bpm complexes along the lines described previously [19–21]. Correlations of the energies at the absorption maxima with empirical solvent parameters E^*_{MLCT}, as derived by Manuta and Lees [21] and used by several groups [19,20,22], were successful (Fig. 5), the correlation

Table 5

Solvatochromism of the long-wavelength absorption of (bpdz)$PtPh_2$

Solvent	E^*_{MLCT} [a]	λ_{max} (nm)	$\tilde{\nu}_{max}$ (cm^{-1})
DMSO	1.00	483	20700
acetonitrile	0.98	490	20420
acetone	0.82	502	19920
THF	0.59	526	19010
toluene	0.30	549sh	18230sh

[a] Solvent parameter from ref. 21.

Table 6

Solvatochromism of the long-wavelength absorption of (bpm)PtPh$_2$

Solvent	E^*_{MLCT} [a]	$\lambda_{\max}$ (nm)	$\tilde{\nu}_{\max}$ (cm^{-1})
acetonitrile	0.98	501	19940
DMF	0.95	503	19880
acetone	0.82	507	19750
THF	0.59	533	18780
benzene	0.34	584	17120
toluene	0.30	586	17070

[a] Solvent parameter from ref. 21.

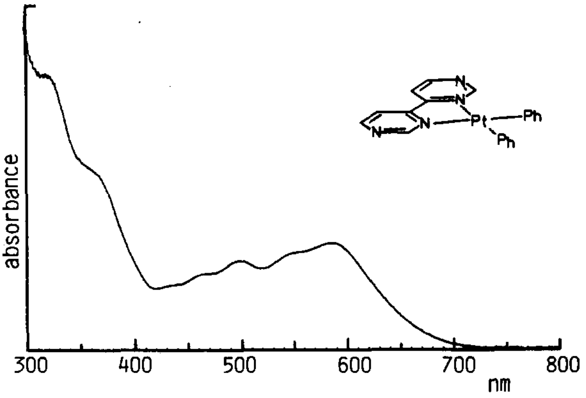


Fig. 4. UV/VIS absorption spectrum of (bpm)PtPh$_2$ in toluene solution.

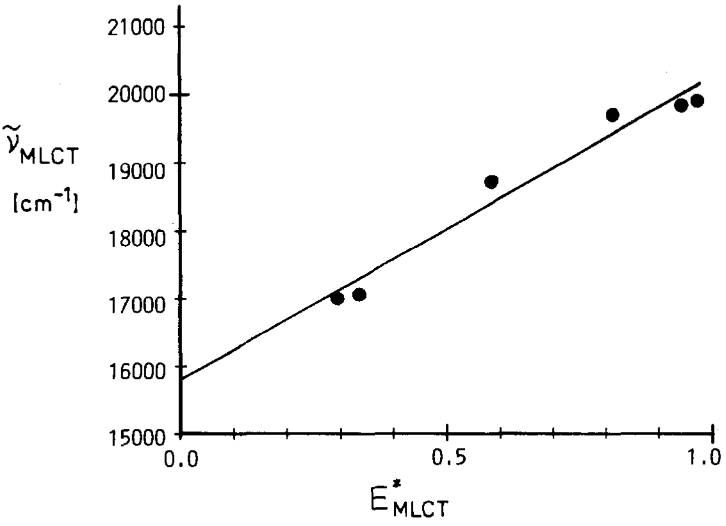


Fig. 5. Correlation between long-wavelength absorption maxima of (bpm)PtPh$_2$ in different solvents and the solvent parameters E^*_{MLCT} (Table 6).

equations are $\tilde{\nu} = 15810\ \mathrm{cm}^{-1} + 4440\ \mathrm{cm}^{-1} \cdot E^{*}_{\mathrm{MLCT}}$ ($r = 0.982$, bpm complex), and $\tilde{\nu} = 16970\ \mathrm{cm}^{-1} + 3600\ \mathrm{cm}^{-1} \cdot E^{*}_{\mathrm{MLCT}}$ ($r = 0.995$, bpdz complex).

The presumably near-planar $\mathrm{Pt^{II}}$ complexes [11g] do not exhibit the "special" solvatochromism, including the unusual response to aromatics, that was recently established for compounds $\mathrm{(TCNE)M(CO)_5}$ with their strongly π-accepting planar TCNE ligand [23]. The solvatochromism of the complexes (α-diimine)$\mathrm{PtPh_2}$ is comparatively strong and quite obvious from colour changes between yellow-orange and purple; the negative sign indicates that the transition dipole moment (M → L) is directed antiparallel to the ground state dipole moment (L → M). The particularly large solvatochromic response of bpm complexes was noted previously [19], and we now interpret it as a consequence of a large ground state dipole moment due to relatively little back donation and a not-too-extensive amount of charge transfer in the MLCT excited state (small $a(^{14}\mathrm{N})$ in Table 1 [20]).

Emission spectra

Several recent publications have dealt with luminescent $\mathrm{Pt^{II}}$ dihalide or bis(pseudohalide) complexes containing α-diimine ligands [11]. Emission was found to occur in the solid state and in solution, from ^{3}IL (intraligand), ^{3}LF (ligand field) or ^{3}MLCT excited states [11]. An assignment for the diorganoplatinum(II) complexes described here has to take into account the differences in the occurrence of detectable emission. The observed ligand dependence is familiar from photophysical studies of corresponding complexes with $\mathrm{[Ru(bpy)_2]^{2+}}$ [16], $\mathrm{Re(CO)_3Hal}$ [17] and $\mathrm{[Cu(PPh_3)_2]^{+}}$ [7b]. In particular, the bpm complex does not emit, even in the solid state, because of efficient non-radiative processes at the 1,1′-nitrogen centers [24]; the bpy, bpz, tap and bpdz complexes do show luminescence in the solid (Table 4), and the latter also emits in acetonitrile solution (Fig. 6).

The broadness of the emission bands, and the Stokes shifts of about 3000 cm^{-1} are compatible [11k] with a luminescence from a ^{3}MLCT excited state; the alternatives, an emission from LF or IL excited states, seem less likely because of

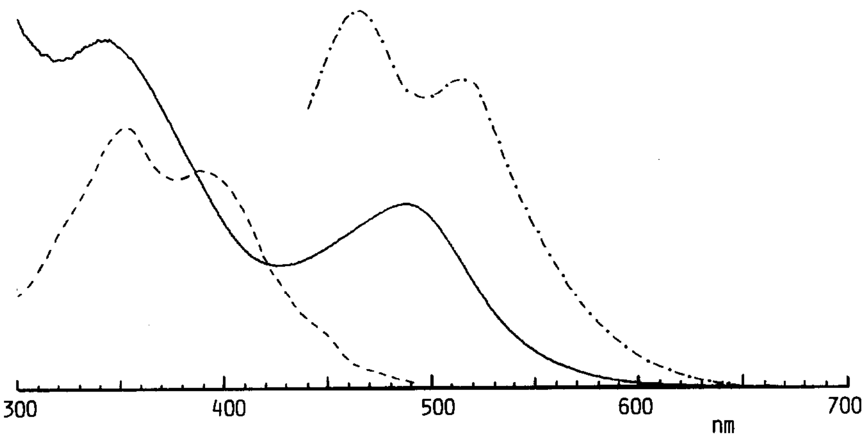


Fig. 6. Absorption spectrum (———), emission spectrum after excitation at 410 nm (·–·–·–·), and excitation spectrum (- - - - -), monitored at 520 nm, with maxima at 450sh, 390 and 350 nm of (bpdz)$\mathrm{PtPh_2}$ in acetonitrile at room temperature. Intensity scale different for each spectrum.

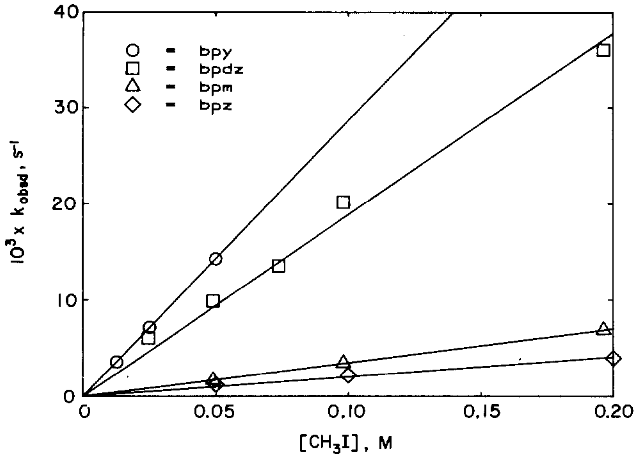
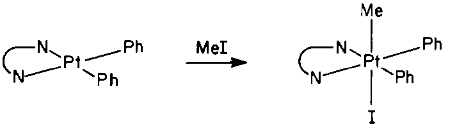


Fig. 7. Dependence of the pseudo-first order rate constants k_{obsd} on iodomethane concentration for the oxidative addition to $LPtPh_2$.

the large ligand field splitting exerted by two phenyl substituents and bpy or bpdz [25] ligands and because of the low energies of the emission maxima. More detailed photophysical investigations on diorganoplatinum(II) complexes are in progress [26].

Kinetics of oxidative addition

A typical reaction of tetracoordinate platinum(II) complexes is oxidative addition, *e.g.* of iodomethane, which generally leads to hexacoordinate Pt^{IV} systems without low-energy MLCT features [1] and which can be of catalytic relevance [9].



(2)

Oxidative addition $Pt^{II} \rightarrow Pt^{IV}$ can occur in the ground state or in a photoassisted process (POA) [27]. We used the four complexes $LPtPh_2$ with the well characterized (Table 1) ligands L = bpy, bpdz, bpm and bpz in order to compare and interpret the rates of thermal (20°C) oxidative addition of CH_3I in acetonitrile. The variation in such rates with the aryl ligands has been reported previously

Table 7

Second-order rate constants for oxidative addition of iodomethane to platinum(II) complexes

Pt^{II} complex	k (M^{-1} s^{-1})	log k	pK_{BH^+}(ligand)
$(bpy)PtPh_2$	0.2865(6)	−0.543	4.4
$(bpdz)PtPh_2$	0.189(5)	−0.723	3.37
$(bpm)PtPh_2$	0.0353(3)	−1.452	1.5
$(bpz)PtPh_2$	0.0206(8)	−1.686	0.45

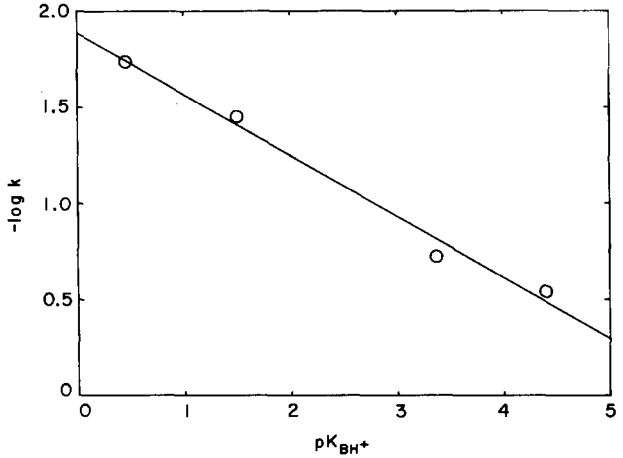


Fig. 8. Correlation between log k for oxidative addition of iodomethane to $LPtPh_2$ and the pK_{BH^+} values of the ligands (Table 7): $\log k = 0.32 \cdot pK_{BH^+} - 1.89$ ($r = 0.993$).

[1]. Slow formation of iodine in THF solution prevented relevant rate studies in that solvent.

The plots (Fig. 7) of the pseudo first-order rate constants k_{obsd} *versus* the iodomethane concentration, which passed through the origin, gave the second-order rate constants, k, listed in Table 7 ($k_{obsd} = k \cdot [CH_3I]$).

The linear correlation of log k with the pK_{BH^+} values of the ligands (Fig. 8) indicates the ground state character of the transition state in that reaction; obviously, the effects of back donation to the α-diimine on the rate are negligible [1].

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