

Note

Spectrophotometric studies of the photolysis of diazido-bis(phosphine)-metal(II) complexes

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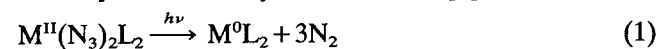
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Abstract

The photolysis of mixed ligand complexes of the type $ML_n(N_3)_2$ ($M = Ni, Pd, Pt$; $L =$ phosphane and diphosphane ligands, respectively; $n = 1, 2$) was monitored by electronic spectroscopy in absorption, emission and excitation. Initial quantum yields of these complexes were measured in CH_2Cl_2 and EtOH in dependence on the irradiation wavelength. Photochemically formed M^0I_n fragments of Pd and Pt are distinguished by an intensive emission detected at 77 K. No emission was observed with respect to the appropriate Ni^0 fragments. An initial emission at 615 nm detected by irradiating $Pd(PPh_3)_2(N_3)_2$ at 77 K is explained by assuming a photochemical *cis/trans* isomerization. Quenching experiments have been performed by using $Ru(bpy)_3Cl_2$, $Os(bpy)_3Cl_2$, $Re(CO)_3(phen)Cl$ and $Cr(bpy)_3(ClO_4)_3$ as sensitizers and the mixed-ligand complexes under discussion as quenchers.

Electron-rich metal complex fragments of low-valent platinum, palladium and nickel with phosphine as stabilizing ligands are of considerable catalytic interest, particularly when the activation of small molecules is regarded. Such metal(0) fragments may be generated photochemically (eqn. (1)) and can be used as catalysts [1] in particular with respect to the catalytic activation of acetylene and alkyne derivatives [2].



The general photochemical behaviour of mixed-ligand azido complexes of nickel(II), palladium(II) and plat-

inum(II) has been summarized very recently [3]. A few results are published on the photochemistry of the starting $M(N_3)_2L_2$ complexes [4–7] and only little is known regarding the luminescence spectroscopic properties of the corresponding metal(0) fragments.

Thus, it has been shown that $Pt(PPh_3)_2$ exhibits a blue emission at 77 K [4, 9]. Within the framework of our investigations in photocatalysis [8] we were interested in further details of the photolysis of mixed-ligand complexes of the sort $M(N_3)_2L_2$ [10] and in particular in the spectroscopic properties of their metal(0) fragments ML_2 ($M = Pt, Pd, Ni$; $L_2 = dppe, dppp$; $L = PPh_3$ where $dppe = 1,2$ -bis(diphenylphosphino)ethane, $dppp = 1,3$ -bis(diphenylphosphino)propane). In addition to our earlier results [2, 4–7] we want to report on the stationary photolysis of $M(N_3)_2L_2$ complexes at room temperature as a function of the irradiation wavelength, the emission and excitation spectra of the photochemically generated and catalytically active metal(0) fragments ML_2 and the evaluation of the photolysis of $Pd(N_3)_2(PPh_3)_2$ at 77 K by emission end excitation spectroscopy. Finally, some preliminary results of the quenching of $Ru(bpy)_3Cl_2$ and other sensitizers in the presence of $M(N_3)_2L_2$ mixed-ligand complexes will be reported.

The $M(N_3)_2L_2$ mixed-ligand complexes were prepared according to the literature [11–14]. Solutions in CH_2Cl_2 , THF, 2-MeTHF or ethanol were used for the photolysis experiments. The solvents were distilled and dried according to standard procedures. All solutions were purged with argon before using. Luminescence spectra were obtained by using a Perkin-Elmer LS50 spectrophotometer with a 10 μs pulsed 200 W xenon lamp. The low temperature studies were performed in a quartz tube cuvette in a cryostat adapted to the LS50 and cooled by liquid nitrogen. A 200 Hg-Xe lamp model LTi02-A102S (AMKO LTI, wissenschaftlich-technische Instrumente GmbH) in vertical position was used as irradiation source for irradiation of samples within the quartz tube cuvette positioned in the cryostat.

The absorption spectra of the mixed-ligand azido complexes can be divided into areas distinguished by d–d transitions (> 350 nm), azide-to-metal (250–330 nm) and metal-to-phosphine (< 250 nm) charge-transfer transitions. The following results were obtained with respect to the stationary photolysis as a function of the irradiation wavelength. Table 1 summarizes the initial photolysis quantum yields in dependence on the irradiation wavelength when using CH_2Cl_2 as solvent.

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TABLE 1. Initial photolysis quantum yields in dependence on the irradiation wavelength in CH_2Cl_2 at room temperature

	254 nm (LMCT)	313 nm (LMCT)	365 nm (d-d)
$\text{Pt}(\text{PPh}_3)_2(\text{N}_3)_2$	0.007 ± 0.01	0.10 ± 0.01	0.095 ± 0.01
$\text{Pd}(\text{PPh}_3)_2(\text{N}_3)_2$		0.06 ± 0.005	0.022 ± 0.005
$\text{Ni}(\text{dppp})(\text{N}_3)_2$		0.7 ± 0.005	0.014 ± 0.005

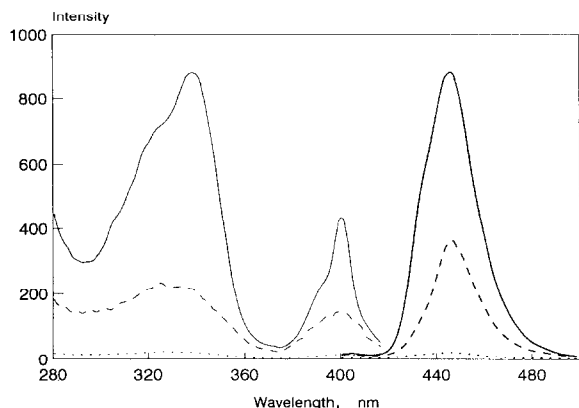


Fig. 1. Luminescence spectra of $\text{Pt}(\text{PPh}_3)_2$ (—), $\text{Pt}(\text{dppp})$ (---) and $\text{Pt}(\text{dppe})$ (····) in ethanol at 77 K after photolysis of $\text{Pt}(\text{N}_3)_2\text{L}_2$ ($\text{L} = \text{PPh}_3$, $\text{L}_2 = \text{dppp}$ and dppe ; emission bold, excitation thin).

The quantum yields of nickel and palladium complexes decrease with increasing irradiation wavelength. However, no significant dependence was observed in the case of the platinum complexes. Upon irradiation with visible light ($\lambda_{\text{irr}} < 350$ nm) the LMCT band disappears due to the oxidation of the azide ligands. Coupling of d-d and LMCT excited states seems to be responsible for that behaviour which is assumed to play no role in the case of palladium and nickel complexes. That conclusion is in agreement with the increasing ligand field splitting with increasing atomic number within a transition-metal group.

Upon irradiation of the platinum(II) and palladium(II) mixed-ligand complexes in ethanol ($c \leq 10^{-3}$ mol l^{-1} , $\lambda_{\text{irr}} \geq 250$ nm) at 77 K, emission has been observed that originates unambiguously from the corresponding M^0L_2 fragments. Figure 1 shows the uncorrected electronic emission and excitation spectra of Pt^0L_2 . The emission spectra are distinguished by a band maximum at 445 nm and the excitation spectra exhibit two bands around 330 and 400 nm, each of them with a shoulder at the high energy side. An usual band separation procedure applied to the spectra of $\text{Pt}(\text{PPh}_3)_2$ yields band maxima at 322, 340, 392 and 400 nm. The excitation spectrum of $\text{Pt}(\text{PPh}_3)_2$ at 77 K in ethanol is in excellent agreement with the difference absorption spectrum in benzene at room temperature after laser

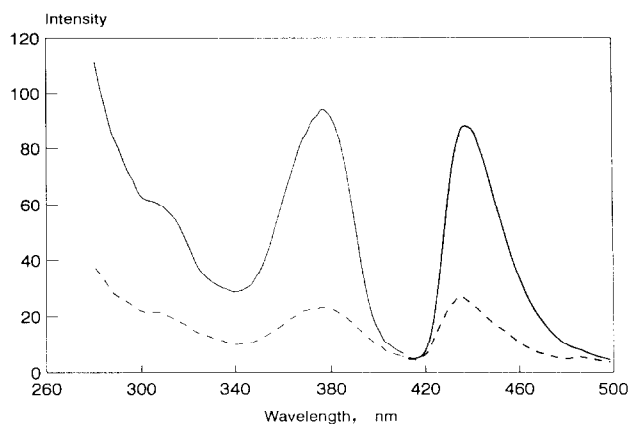


Fig. 2. Luminescence spectra of $\text{Pd}(\text{PPh}_3)_2$ (—) and $\text{Pd}(\text{dppp})$ (---) in ethanol after photolysis of $\text{Pd}(\text{N}_3)_2(\text{PPh}_3)_2$ and $\text{Pd}(\text{N}_3)_2(\text{dppp})$ at 77 K (emission bold, excitation thin).

flash photolysis of $\text{Pt}(\text{O}_2)(\text{PPh}_3)_2$. In this case the photolysis led also to the formation of $\text{Pt}(\text{PPh}_3)_2$ [9].

Interestingly, there are no significant differences in the luminescence spectra of di- or monodendately coordinated phosphine ligands as shown in Fig. 1, whereas the luminescence intensity is decreased in the order $\text{Pt}(\text{PPh}_3)_2 > \text{Pt}(\text{dppp}) > \text{Pt}(\text{dppe})$.

After irradiation of $\text{Pd}(\text{N}_3)_2(\text{PPh}_3)_2$ and $\text{Pd}(\text{N}_3)_2(\text{dppp})$ in ethanol at 77 K with wavelengths $\lambda_{\text{irr}} \geq 260$ nm an emission band at 437 nm was observed. The excitation spectra show a maximum at 375 nm and a shoulder around 300 nm (Fig. 2). We assign these spectra to $\text{Pd}(\text{PPh}_3)_2$ and $\text{Pd}(\text{dppp})$, respectively.

The emission disappears upon warming up to room temperature where formation of the dimer $\text{M}_2(\text{L}_2)_2$ species is expected. Contrary to the platinum and palladium mixed-ligand complexes no luminescence was observed during the photolysis of $\text{Ni}(\text{N}_3)_2(\text{dppe})$ and $\text{Ni}(\text{N}_3)_2(\text{dppp})$ at 77 K. This is in agreement with the decreasing of the luminescence intensities of PdL_2 when compared with PtL_2 .

In ethanol, MeTHF or in the solid state the starting complex $\text{Pd}(\text{N}_3)_2(\text{PPh}_3)_2$ exhibits at low temperature (77 K) an intense red emission at 615 nm (Fig. 3). A luminescence lifetime of 74 ± 1.5 μs has been estimated. The excitation spectrum shows bands around 400 nm. The relatively long lifetime and the weak absorption bands at 400 and 470 nm ($\epsilon < 1$) in ethanol refer to a spin-forbidden phosphorescence transition.

The emission at 615 nm disappears upon excitation of the complex at 400 nm leading to the expected emission of $\text{Pd}(\text{PPh}_3)_2$ at 437 nm as shown in Fig. 4. It can be clearly seen from Fig. 4 that there is a fast decrease of the emission of $\text{Pd}(\text{N}_3)_2(\text{PPh}_3)_2$ (615 nm) and a delayed appearance of the luminescence of $\text{Pd}(\text{PPh}_3)_2$ (437 nm) indicating a non-luminescence species obviously due to the formation of an intermediate isomerization product [7, 15].

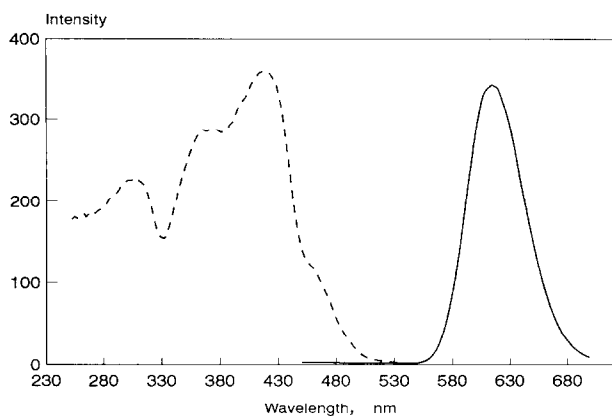


Fig. 3. Luminescence spectra of $\text{Pd}(\text{N}_3)_2(\text{PPh}_3)_2$ in 2-MeTHF at 77 K (---, excitation; —, emission).

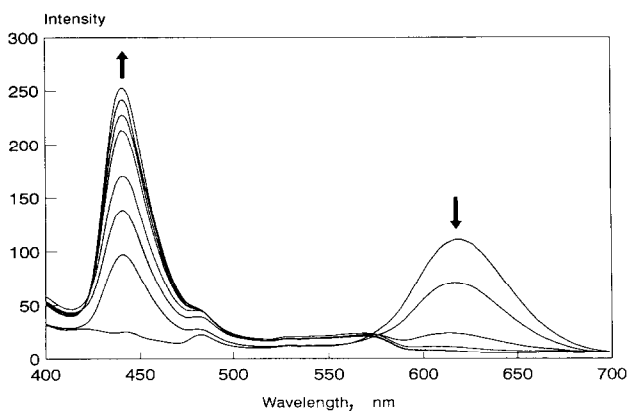
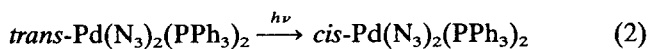


Fig. 4. Change of the luminescence spectra upon irradiation of $\text{Pd}(\text{N}_3)_2(\text{PPh}_3)_2$ in 2-MeTHF at 77 K (starting with the spectrometer light source at $\lambda_{\text{exc}} = 400$ nm and continuing with $\lambda_{\text{exc}} \geq 300$ nm of an Hg-lamp to accomplish the formation of $\text{Pd}(\text{PPh}_3)_2$ emitting at 437 nm).

Because the bidentate ligands dppe and dppp necessarily form *cis*- $\text{Pd}(\text{N}_3)_2\text{L}_2$ complexes and do not show any emission around 600 nm, we assign the emission band of $\text{Pd}(\text{N}_3)_2(\text{PPh}_3)_2$ at 615 nm to the *trans*-isomer. The following two separate primary photolysis steps can therefore be assumed (eqns. (2) and (3)).



Preliminary experiments have shown that the emission of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ at 600 nm is quenched by the mixed-ligand azido complexes under discussion in CH_2Cl_2 solution at room temperature.

The quenching rate constants determined by means of Stern-Volmer plots and their dependence on different phosphine ligands can be explained by assuming a diffusion controlled luminescence quenching (Table 2). With the increasing size of the phosphine ligands the rate constants decrease. Further, we have been able

TABLE 2. Rate constants for the luminescence quenching of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in CH_2Cl_2 , k (10^9 M s^{-1}) ($\lambda_{\text{excitation}} = 460$ nm, $\lambda_{\text{emission}} = 615$ nm; the relative ratio between luminescence intensities (I_0/I_m) was corrected with respect to the inner filter effect [16])

	$\text{L} = \text{PPh}_3$	$\text{L}_2 = \text{dppp}$	$\text{L}_2 = \text{dppe}$
$\text{PtL}_2(\text{N}_3)_2$	3.1 ± 0.3	5.1 ± 0.1	10.8 ± 0.5
$\text{PdL}_2(\text{N}_3)_2$	26.1 ± 1	29.4 ± 2	90 ± 5
$\text{NiL}_2(\text{N}_3)_2$		11.8 ± 0.1	19.3 ± 0.8

to show that the triplet emission of $\text{Os}(\text{bpy})_3\text{Cl}_2$ [17] and $\text{Re}(\text{CO})_3(\text{phen})\text{Cl}$ [18, 19] is also quenched by the mixed-ligand azido complexes within the diffusion controlled limit. However, the doublet emission of $\text{Cr}(\text{bipy})_3(\text{ClO}_4)_3$ [20] was not quenched. This result suggests that triplet acceptor orbitals might be involved in those complexes which are efficiently quenched.

The palladium complexes exhibit larger quenching rate constants as compared with the corresponding platinum or nickel complexes. However, it cannot yet be decided whether electron transfer or energy transfer quenching is operative. This question is currently under investigation.

Acknowledgement

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