

Spin Trapping of Radicals Formed during the Photolysis of Azidopalladium(II) and Azidoplatinum(II) Complexes

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Although azido complexes of Pd(II) and Pt(II) with phosphine ligands are known to be highly photosensitive, only a few investigations concerning the photochemistry of these complexes have been reported so far [1, 2]; in contrast, the analogous photochemistry of Pt(IV) has been intensively studied [3–5].

In order to elucidate more details of this photo-reaction, e.g. the nature of possible short-lived paramagnetic species involved, we have accomplished photo-ESR studies on Pd(N₃)₂(PPh₃)₂ and Pt(N₃)₂(PPh₃)₂ using the spin trapping technique [6].

Experimental

Pd(N₃)₂(PPh₃)₂ and Pt(N₃)₂(PPh₃)₂ were synthesized according to literature methods [7].

Phenyl-*N*-tert-butyl nitron (PBN), nitrosomethylene (NM), nitrosodurene (ND) and pentamethylnitrosobenzene (PMNB) were used as spin traps [8].

Benzene and dichloromethane solutions, respectively, of the metal complex (0.01 M) and the spin trap (0.01 M) were placed in an H-shaped mixing chamber attached to a quartz flat cell and were purged with purified argon for at least 30 min prior to photolysis.

The samples were photolysed directly in the cavity of the ESR spectrometer (Bruker Model ER 200 tt) using a 100 W Hanovia high pressure mercury lamp. Metal interference and cut-off filters, respectively, were used in order to avoid direct excitation of the spin traps. All experiments were performed at ambient temperature.

Results and Discussion

Pd(N₃)₂(PPh₃)₂

While no reaction was observed when the solution was kept in the dark, irradiation (350–600 nm) of

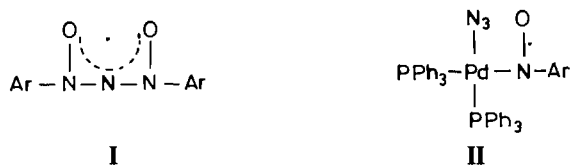
the complex in the presence of PBN in benzene led to intense ESR signals of the ¹N₃ spin adduct ($a_N^1 = 1.389 \pm 0.005$ mT, $a_N^2 = a_H = 0.169 \pm 0.005$ mT).

After several minutes, the intensity of this signal decreased sharply, possibly due to redox reactions occurring between the ¹N₃ spin adduct and the reduced palladium complex and the phosphine ligand. Continuous irradiation led to the generation of additional nitroxides (see Table I). One of these signals exhibits a ³¹P-hyperfine splitting ($a_N = 1.416 \pm 0.005$ mT, $a_H = 0.318 \pm 0.005$ mT, $a_P = 1.852 \pm 0.010$ mT) indicating spin trapping of a P-centered radical.

Although the P-hyperfine splitting falls into the range reported for other PBN spin adducts of P-centered radicals, no assignment could be made.

Upon prolonged irradiation we detected a triplet of doublets ($a_N = 1.429 \pm 0.005$ mT, $a_H = 0.198 \pm 0.005$ mT) which is tentatively assigned to a spin adduct of an O-centered radical for which (PPh₃)₂Pd(N₃)OO[•] is the most likely candidate. A similar nitroxide was detected in the photolysis of the corresponding Pt(II) complex (Table I). Apparently, the solutions contained residual traces of oxygen.

Irradiation (401 nm) of Pd(N₃)₂(PPh₃)₂ in CH₂Cl₂ also gave the spin adduct of ¹N₃ to PBN; in addition, the ESR signal of the ¹CH₂Cl spin adduct ($a_N = 1.429 \pm 0.005$ mT, $a_H = 0.291 \pm 0.005$ mT) was detected. Chlorine abstraction from CH₂Cl₂ by intermediate Pd-centered radicals may serve as a source for ¹CH₂Cl radicals. This postulate is supported by the product analysis where Pd(PPh₃)₂Cl₂ was found in large quantities. Furthermore, irradiation in the presence of different aromatic nitroso spin traps gave rise to characteristic ESR signals of ¹N₃ spin adducts I [9] (see Table I); after ca. 30 s, however, intense signals of spin adducts of a Pd-centered radical were detected with ND and PMNB spin traps (ND: $g = 2.0096 \pm 0.0005$, $a_N = 1.574 \pm 0.008$ mT, $a_P = 0.801 \pm 0.008$ mT, $a_{Pd} = 0.432 \pm 0.010$ mT; PMNB: $g = 2.0094 \pm 0.0005$, $a_N = 1.614 \pm 0.008$ mT, $a_P = 0.807 \pm 0.008$ mT, $a_{Pd} = 0.460 \pm 0.010$ mT).



The detection of the P-hyperfine coupling with only one ³¹P nucleus is explained by assuming *cis*-coordination of the two phosphine ligands in the spin adduct II of the Pd-centered radical with ND and PMNB, respectively.

TABLE I. ESR Parameters of Spin Adducts^a

Complex	Irradiation wavelength ^b	Solvent	Spin trap	Radical	a_N	a_H	a_P	a_X	g	
Pd(N ₃) ₂ (PPh ₃) ₂	401	CH ₂ Cl ₂	ND	*Pd(N ₃)(PPh ₃) ₂	1.574 ^c			0.801 ^c	0.432(1Pd) ^d	2.0096
				*N ₃	0.714(2N)			0.238(1N)		
			PMNB	*Pd(N ₃)(PPh ₃) ₂	1.614 ^c			0.807 ^c	0.460(1Pd) ^d	2.0094
				*N ₃	0.727(2N)			0.235(1N)		
				*N ₃	0.714(2N)			0.238(1N)		
	350–600	C ₆ H ₆	PBN	PBN	*N ₃	1.408	0.181		0.181(1N)	
					*CH ₂ Cl	1.429	0.291			
					*N ₃	1.389	0.169	0.169(1N)		
					*OOPd(PPh ₃) ₂ N ₃	1.429	0.198			
					*N ₃	1.389	0.168	0.168(1N)		
Pt(N ₃) ₂ (PPh ₃) ₂	310	C ₆ H ₆	PBN	*N ₃	1.389	0.168		0.168(1N)		
					*OOPt(PPh ₃) ₂ N ₃	1.429	0.212			

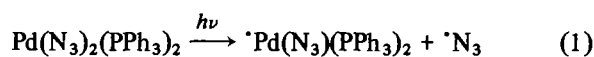
^aAll coupling constants in mT ± 0.005 mT; g values ± 0.0005.

^bIn nm.

^c± 0.008 mT.

^d± 0.010 mT.

The formation of azidyl radicals together with a Pd-centered radical strongly suggests a primary reaction as given in eqn. (1), the quantum yield of which has been determined by ferrioxalate actinometry ($\Phi_{313} = 0.6$, $\Phi_{365} = 0.4$ in CHCl₃).



Pt(N₃)₂(PPh₃)₂

The photoreaction of the platinum complex required irradiation at shorter wavelength ($\lambda \sim 310$ nm). Hence, direct excitation of the spin traps leading to their decomposition could not be completely avoided, and di-tert-butyl nitroxide ($a_N = 1.535 \pm 0.005$ mT, benzene) was detected in the presence of PBN. As mentioned above, an ESR signal of a nitroxide formed by spin trapping of an O-centered radical, possibly (PPh₃)₂(N₃)PtOO^{*}, was recorded in benzene solution (see Table I). In addition, *N₃ spin

adducts were readily observed, pointing toward a reaction analogous to eqn. (1). The quantum yields were found to be 0.85 at 280 nm and 0.1 at 365 nm, respectively.

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