Inorganica Chimica Acta, *178* (1990) 71–76

Spectroscopic studies on the mechanism of photolysis of $Pt(N_3)_2(P(C_6H_5)_3)_2$

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(Received May 2, 1990; revised July 18, 1990)

Abstract

$Pt(N_3)_2(P(C_6H_5)_3)_2$ has been irradiated in different media between r.t. and 10 K mainly with the 351, 364 nm lines of an argon ion laser. The photoreactions taking place have been studied by following the changes of the $\nu_{as}(N_3)$ IR band. The intensity decrease of this band indicates that a photoredox reaction between the metal and azide ligands has occurred partly via d–d band absorption. An azide containing intermediate was detected, which was stable in the dark but also disappeared upon further irradiation. It has been assigned to the *trans* form of the parent complex. A different intermediate, $PtN_3(P(C_6H_5)_3)_2$, was detected by laser flash photolysis with 308 nm, having $\lambda_{max} = 460$ nm and a lifetime of $(75 \pm 25)10^{-6}$ s in CH_2Cl_2, and $(210 \pm 60)10^{-6}$ s in 2-MeTHF, respectively. The azide free photoproduct $Pt^0P(C_6H_5)_3)_2(2\text{-MeTHF})_n$ was stabilized in 2-MeTHF at 133 K showing an absorption band with $\lambda_{max} = 409$ nm.

Introduction

Azido–metal(II) complexes are possible starting compounds in the formation of electron rich complex fragments with free coordination sites at low-valent metal centres. By coordination at these free sites small molecules may be activated for chemical reactions [1]. Within our extensive studies on photocatalytic reactions [2] such azide complexes are therefore of interest. Contrary to platinum(IV)–azide complexes the photolysis of Pt(II)–azide compounds has hardly been investigated [3]. Very recently, we reported the results of stationary photolysis, ESR spin-trapping, and microsecond flash photolysis experiments with $M(N_3)_2L_2$ complexes ($M = Pt$, Pd; $L =$ phosphine and diimine, respectively). From the experimental results a mechanism of the photoredox reaction was derived [4, 5]. An essential feature of the mechanism is a two-step reduction of the metal in reactions (1) and (2).

$$M^{II}(N_3)_2((P(C_6H_5)_3)_2 \xrightarrow{h\nu} {\bullet}M^IN_3((P(C_6H_5)_3)_2 + {\bullet}N_3 \qquad (1)$$

$${\bullet}M^I(N_3)(P(C_6H_5)_3)_2 \longrightarrow M^0(P(C_6H_5)_3)_2 + {\bullet}N_3 \qquad (2)$$

The present study has been carried out in order to obtain additional evidence for this two-step mechanism and for further side-reactions. For this purpose we followed the changes of the $\nu_{as}(N_3)$ IR band and the UV–Vis spectra during irradiation of the title complex (I). Both low temperature (IR and UV–Vis detection) and laser flash (UV–Vis detection) photolysis were used to detect and identify intermediates of these photoredox reactions.

Experimental

Materials and preparations

$Pt(N_3)_2(P(C_6H_5)_3)_2$ (I) was prepared according to the literature [6]. CH_2Cl_2, 2-MeTHF and THF were dried, distilled and stored under nitrogen according to standard procedures. Satisfying concentrations for IR experiments could be obtained only with CH_2Cl_2 as a solvent. In 2-MeTHF and CH_3CN the solubility of the complex is only about 10^{-3} M. All samples were handled by means of the Schlenk technique. The samples of the azide complex in polymer film

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matrices have been prepared according to literature procedures [7]. About 8 mg of the complex together with 600 mg of Corvic D60/11 (ICI) PVC-powder were dissolved in THF and kept in a Petri dish of 9 cm in diameter in a desiccator overnight. The desiccator was flushed with a slow stream of nitrogen to remove the solvent.

Spectra

Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV–Vis spectrophotometer equipped with a model 3600 data station. IR spectra were recorded on a Nicolet 7199B FT-IR interferometer with a liquid-nitrogen cooled MCT detector. Low temperature studies were performed with IR or UV cells in an Oxford type cryostat cooled by liquid nitrogen. The PVC films with the azide complexes were clamped between two CaF_2 windows at the cryotip of a Displex apparatus (Air Products and Chemical Inc.) and irradiated at r.t. and 10 K under vacuum. IR intermediate spectra in the region of the $\nu_{as}(N_3)$ stretching vibration around 2000 cm^{-1} were obtained by subtraction of the initial spectrum recorded before irradiation multiplied by a factor f between zero and one from the spectrum of the irradiated sample. This factor f has been found by fitting to a reasonable zero-line in the difference IR spectrum. It gives the degree of conversion of the starting complex by the photochemical reaction as $(1-f)$.

Photochemistry

For the photochemical reactions an SP model 2020 argon ion laser or a 100 W Hg-lamp were used as irradiation sources. The flash photolysis set-up consisted of a Lambda Physik/EMG-101 excimer laser filled with XeCl thus providing 308 nm pulses of 10 ns duration. An OMA-III detection system of EG&G was used.

Results

Spectroscopic properties

Figure 1 presents the electronic absorption spectrum of **I** in CH_2Cl_2. We assign the band at 269 nm ($\epsilon \approx 2\times10^4\ M^{-1}\ cm^{-1}$) to a charge-transfer transition from the azide ligand to the metal (LMCT), as this band disappears with the decomposition of the azide ligand upon irradiation. The laser irradiation wavelengths used are also indicated in the spectrum, which shows weak d–d transitions at the low energy side of the LMCT band.

Figure 2 shows the IR $\nu_{as}(N_3)$ band of **I** (see also Table 1), which is asymmetric or even split, in agreement with literature data [8–10]. $As(C_6H_5)_4{}^+N_3{}^-$ (**II**) with an azide anion has been included for comparison.

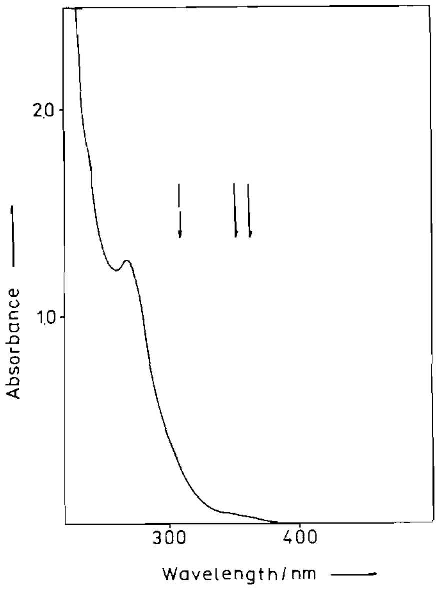

Fig. 1. UV–Vis absorption spectrum of **I** in CH_2Cl_2 (0.2 mm IR cell, 2.5×10^{-3} M, λ_{max} 269 nm). The irradiation wavelengths of the argon ion laser (351, 364 nm) and the excimer laser (308 nm) are indicated.

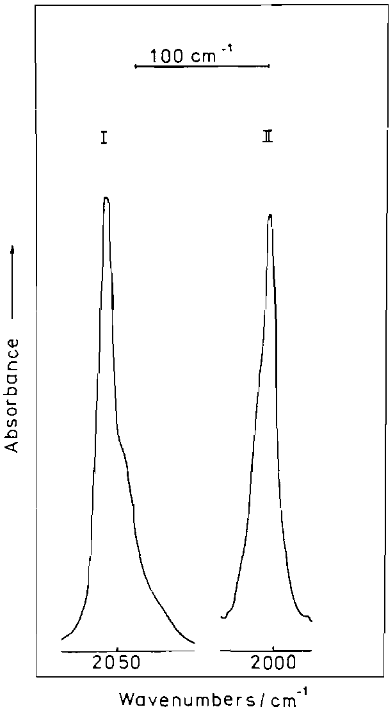

Fig. 2. $\nu_{as}(N_3)$ stretching bands of **I** and **II** in CH_2Cl_2 at r.t.

According to the literature, **I** exists in the *cis*-planar form in CH_2Cl_2. For such a conformation

TABLE 1. $\nu_{as}(N_3)$ stretching frequencies (cm^{-1}) of $Pt(N_3)_2(P(C_6H_5)_3)_2$ and of intermediates on irradiation [a]

Medium	Temperature (K)	Complex	Intermediates
2MeTHF	r.t.	2044	
			2048
		2057	
	133	2059	2052
CH_2Cl_2	r.t	2043	
			2051
		2059	
	183	2061	2053
			2053[b]
			2054[c]
PVC	r.t.	2057	2046[e]
	10	2059	2043[d]
			2046[e]

[a] Irradiation with 351, 364 nm argon ion laser lines, if not otherwise stated. $\nu_{as}(N_3)$ stretching band of $As(C_6H_5)_4{}^+N_3{}^-$ in CH_2Cl_2 (r.t.) at 2005 cm^{-1}. [b] Unfiltered Hg lamp. [c] Solvent saturated with O_2. [d] Irradiation with 313 nm, Hg lamp. [e] Irradiation with 366 nm, Hg lamp.

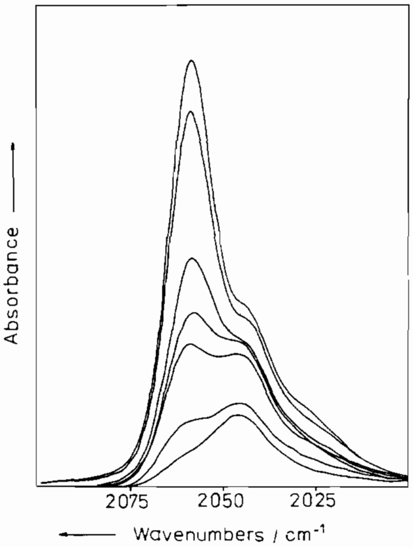

Fig. 3. Decreasing absorbance in the $\nu_{as}(N_3)$ stretching region during photolysis of I in a PVC polymer matrix at 10 K. $\lambda_{irr}=366$ nm.

two $\nu(N_3)$ vibrations are expected in the IR, giving rise to a split band, whereas the *trans* isomer has only one IR allowed $\nu_{as}(N_3)$ vibration [10]. The splitting of this band of I depends on the medium, the temperature and the concentration.

Photochemistry

Irradiation of I caused an intensity decrease of the $\nu_{as}(N_3)$ IR band with a concomitant change of shape (Fig. 3). Finally this band disappeared completely. This proves that the azide group has decomposed at least partly via formation of an azide containing intermediate. This intermediate, having its $\nu_{as}(N_3)$ vibration as a fairly symmetric band (Fig. 4) in between the two band maxima of the starting complex, was also formed in an oxygen saturated CH_2Cl_2 solution, and upon irradiation with the unfiltered Hg lamp, see Table 1.

From Fig. 5 it follows that the IR absorbances of the intermediate around 30% conversion are about 1:5:10 for the initial concentrations of 10^{-3}, 5×10^{-3} and 10^{-2} M, respectively. This supports the con-

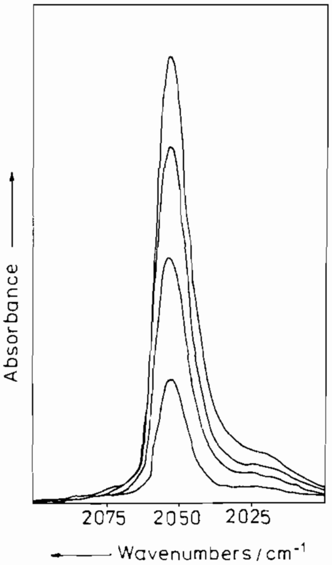

Fig. 4. Increasing IR band of the intermediate during photolysis of I in CH_2Cl_2 at 183 K (unfiltered Hg lamp).

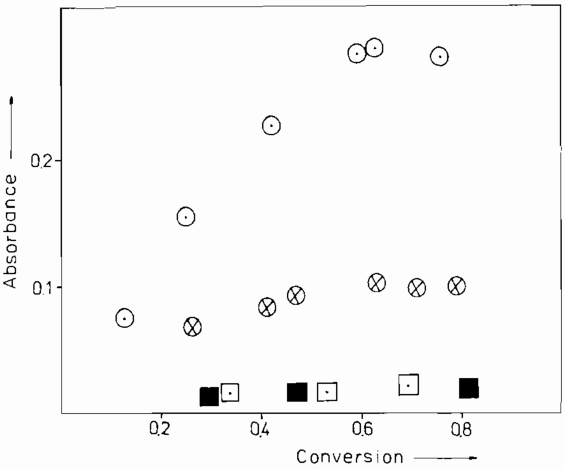

Fig. 5. IR absorbance of the intermediate in dependence of conversion at different initial concentrations of I (at 2053 cm^{-1} in CH_2Cl_2, 183 K, $\lambda_{irr}=351$, 364 nm, absorbance of I at $\lambda_{irr}\leqslant 0.2$). ⊙ 10^{-2} M, ⊗ 5×10^{-3} M, ⊡ 10^{-3} M, ■ $A_{2052\ cm^{-1}}$, saturated solution in 2-MeTHF at 133 K.

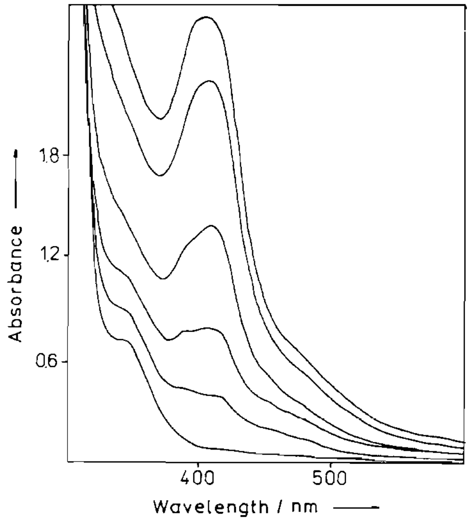

Fig. 6. UV–Vis spectral changes upon irradiation of I (5×10^{-4} M in 2-MeTHF at 133 K) with 351, 364 nm.

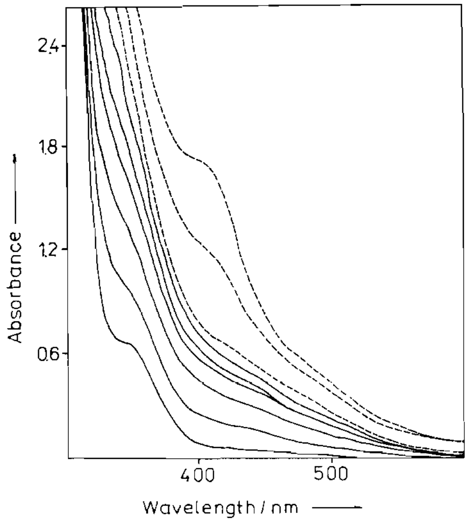

Fig. 7. UV–Vis spectral changes upon irradiation of I (5×10^{-4} M in 2-MeTHF) with 350, 364 nm. ——, 183 K; – – –, after cooling to 133 K and continued irradiation.

clusion that the intermediate is not formed in a bimolecular reaction of the starting complex and/or species derived from it. The reaction mixture was thermally stable in the dark during the period of an experiment at the reaction temperature, so that the occurrence of a maximum or plateau in the absorbance/conversion curves of Fig. 5 was caused by photochemical conversion of the intermediate.

We also searched for the azide radical which is formed in reactions (1) and (2) and which had been detected by ESR spin-trapping experiments [4, 5]. Very recently, its asymmetric stretching vibration was detected at the wavenumbers of 1645 [11] and 1658 [12] cm^{-1}, respectively. No indication of this radical could, however, be found in this wavenumber region

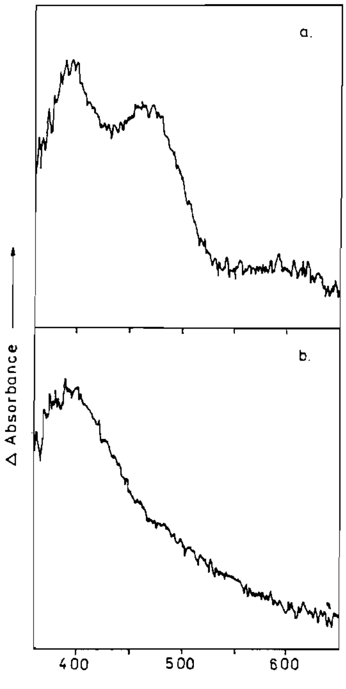

Fig. 8. UV–Vis difference spectra obtained after 308 nm laser flash photolysis of I (1.5×10^{-3} M in CH_2Cl_2 at r.t.): a, 20 ns after the flash; b, 1 ms after the flash.

when I was irradiated in a PVC-polymer film matrix at 10 K, where its detection would have been most probable under our conditions. Obviously the PVC film is not an appropriate matrix to the stabilization and detection of the azide radical. Just as in the solvents an azide containing intermediate shows up in the PVC matrix, although with a band maximum (2043, 2046 cm^{-1}) at significantly lower wavenumber than in fluid solution (2051, 2053 cm^{-1}), independent of the temperature (r.t. or 10 K).

The photoreactions have also been followed with UV–Vis spectroscopy. In both CH_3CN and CH_2Cl_2 no significant changes could be observed in the UV–Vis spectra when the photoproducts of I, obtained at low temperature, were warmed up to r.t. This means that no reactive intermediates could be stabilized.

The UV–Vis spectrum of the product mixture in 2-MeTHF at r.t. or even 183 K, is significantly different from the one obtained at 133 K, at which temperature a strong band shows up at 409 nm, Fig. 6. It is remarkable, that this band cannot be observed at 183 K, which in most cases is a sufficiently low temperature for 2-MeTHF to act as a coordinating solvent. When a partly photolyzed solution was cooled down to 133 K, the intermediate in question was formed from the remaining unreacted I, Fig. 7.

Nanosecond absorption spectroscopy at r.t. in CH_3CN, CH_2Cl_2 and 2-MeTHF in the time range up to 1 ms after the flash showed a difference spectrum with two clear maxima (380–390 and 460 nm) immediately after the flash, Fig. 8. The low energy band decreases with a lifetime of about 25 μs in CH_3CN. Because of this, it had not been detected in the microsecond flash photolysis experiments [5]. In CH_2Cl_2 this band decayed according to a first-order rate law with a lifetime of $(75 \pm 25) 10^{-6}$ s, and in 2-MeTHF with $(210 \pm 60)10^{-6}$ s. The second band remained almost unchanged within the observable time range in accordance with earlier observations [5]. Another band at 590 nm in Fig. 8 was too weak to be evaluated for its time behaviour.

As we could not detect hydrazine after irradiation of **I** in methanol containing ammonia according to ref. 13, it seems that nitrene intermediates were not formed in our photolysis mixture.

Discussion

The 351, 364 nm laser lines used for most of the experiments excite almost exclusively into the low lying d–d bands. Photosubstitution reactions, e.g. by solvent molecules, are expected from these excited states. The IR band of the azide containing intermediate in solution is, however, not due to the formation of a complex like $PtN_3(solv)(P(C_6H_5)_3)_2{}^+N_3{}^-$ with ionic $N_3{}^-$, which would show an IR band at smaller wavenumbers as for **II**, see Table 1.

The disappearance of the azide group upon irradiation points to a photoredox reaction between Pt^{II} and the azide ligands. This is in agreement with previous spin-trapping experiments on Pt^{II} and Pd^{II} azide complexes, which showed the formation of radicals also upon irradiation with $\lambda > 350$ nm [4, 5]. Obviously internal conversion or intersystem crossing between a LF-state and a lower lying LMCT state occurs before the metal is reduced.

In order to explain the changes in the IR spectra upon irradiation with respect to the appearance of an azide containing intermediate the following possibilities have to be taken into consideration.

(i) The intermediate is $\cdot Pt^IN_3(P(C_6H_5)_3)_2$ (**III**) as detected by means of spin-traps [4, 5]. The chance for its detection should increase with decreasing temperature.

(ii) The intermediate is $Pt^{II}N_3Cl(P(C_6H_5)_3)_2$ formed in reaction (3). It is taken into consideration because of previous observations of photoinduced oxidative addition of chlorine from chlorinated solvents to Pt- and Pd-metal centres [14, 15].

$$\cdot Pt^IN_3(P(C_6H_5)_3)_2 + CH_2Cl_2 \longrightarrow Pt^{II}N_3Cl(P(C_6H_5)_3)_2 + \cdot CH_2Cl \tag{3}$$

Reaction (3) is assumed to be followed by the sequence

$$Pt^{II}N_3Cl(P(C_6H_5)_3)_2 \xrightarrow{h\nu} \cdot Pt^ICl(P(C_6H_5)_3)_2 + \cdot N_3 \tag{4}$$

$$Pt^ICl(P(C_6H_5)_3)_2 + CH_2Cl_2 \longrightarrow Pt^{II}Cl_2(P(C_6H_5)_3)_2 + \cdot CH_2Cl \tag{5}$$

(iii) Another azide containing complex is formed by photosubstitution of a phosphine ligand by a solvent molecule according to reaction (6).

$$Pt^{II}(N_3)_2(P(C_6H_5)_3)_2 \xrightarrow[\text{solvent}]{h\nu} Pt^{II}(N_3)_2(solv)P(C_6H_5)_3 + P(C_6H_5)_3 \tag{6}$$

(iv) Apart from the photoredox reaction a *cis–trans* photoisomerization occurs. As a result the ratio of the isomers will change during irradiation.

In the following the experimental IR results (Table 1) and other spectroscopic data are discussed in the light of these possibilities. Since the excitation wavelength of the excimer laser (308 nm) and the μs-flash (270–380 nm) [5] are close in energy to the stationary light sources, the conditions were the same and similar reactions are expected.

Taking into account an uncertainty of the wavenumber of $\nu_{as}(N_3)$ of 1 cm^{-1} and the general trend of slightly increasing wavenumbers upon going to lower temperatures, no significant differences were observed between the IR bands of the intermediates obtained in CH_2Cl_2, 2-MeTHF or the PVC-matrix at r.t. and at 183, 133 and 10 K, respectively. The thermal stability of the intermediate detected in the IR spectra at r.t. does not support the idea that the intermediate is **III**.

Moreover in the microsecond flash photolysis study we found a fast reaction of oxygen with **III** within the time of the μs-flash [5]. The IR intermediate band in an oxygen saturated CH_2Cl_2 solution at 183 K does not differ significantly from oxygen free solutions. This result supports our conclusion that the intermediate detected in the IR spectrum of oxygen free solutions is not **III**, which should exhibit a change of the IR spectrum after reaction with O_2. Case (i) is therefore ruled out.

The band at 460 nm in the difference spectra from ns-flash photolysis (Fig. 8) showed up in an absorbance free region of the starting complex and can unambiguously be assigned to a thermally labile intermediate. Its formation within the ns-flash and decay with a lifetime $\leqslant 210$ μs depending on the solvent, is strong evidence for this intermediate to be **III**, which reacts to the azide free coordinatively unsaturated $Pt^0(P(C_6H_5)_3)_2$ (**IV**) according to reaction (2).

The difference spectrum at 1 ms after the ns-flash with a band maximum at 380–390 nm has to be assigned to **IV**, which is assumed to react mainly in reaction (7)

$$2Pt^0(P(C_6H_5)_3)_2 \longrightarrow Pt_2(P(C_6H_5)_3)_4 \qquad (7)$$

The intermediate which has been detected in the UV–Vis spectrum after stationary photolysis in 2-MeTHF at 133 K cannot be the same as the one observed in the IR spectrum which contains an azide group. The latter intermediate is not stable upon continued irradiation, contrary to the one detected by UV–Vis spectroscopy. We therefore assign this UV–Vis band at 409 nm to $Pt^0(P(C_6H_5)_3)_2(2\text{-}MeTHF)_n$ which was formed from **IV**.

Cases (ii), (iii) and (iv) still remain as possible alternatives for the assignment of the IR intermediate band. Neglecting the small shifts due to solvent effects, the product bands after irradiation in CH_2Cl_2 and 2-MeTHF at r.t. coincide, but case (ii) cannot apply for the latter solvent. Photosubstitution of one phosphine ligand by *p*-nitroso-*N*,*N*′-dimethylaniline had been observed for $Pd(N_3)_2(P(C_6H_5)_3)_2$, but not in the case of I [5]. At least in the non-coordinating solvent CH_2Cl_2 case (iii) is less probable. Therefore we favour case (iv). The azide species observed as an intermediate in the IR spectrum after irradiation in solution should then be the *trans* isomer of I, formed in reaction (8)

$$cis\text{-}Pt^{II}(N_3)_2(P(C_6H_5)_3)_2 \xrightarrow{h\nu} trans\text{-}Pt^{II}(N_3)_2(P(C_6H_5)_3)_2 \qquad (8)$$

Photochemically induced *cis–trans* and *trans–cis* isomerization with $Pt^{II}Cl_2(P(C_6H_5)_3)_2$ has been reported [16, 17].

Reaction (8) obviously also occurs at 10 K in the solid solution of the PVC film. Similar photoisomerizations in matrices are rather common, see for example refs. 18 and 19. The complete disappearance of the $\nu_{as}(N_3)$ stretching band also shows that *trans*-I finally decomposes by photochemical reduction of Pt(II). It cannot be decided from our experiments if the *trans* form of I isomerizes to the *cis* form in a photo-stationary state before photoreduction of Pt^{II} or not.

Conclusions

It can be concluded that the major photoprocess upon irradiation of I is the photoreduction of Pt^{II} by the azide ligands. Following the $\nu_{as}(N_3)$ band *cis–trans* photoisomerization of **I** has been observed as a minor photoreaction between r.t. and 10 K in different media. The photoreduction occurs in two steps as proved by ns-flash photolysis where $^{\bullet}Pt^IN_3(P(C_6H_5)_3)_2$ was detected. This intermediate could not be stabilized at low temperature, but instead its product, the azide free $Pt^0(P(C_6H_5)_3)_2(2\text{-}MeTHF)_n$, could be detected at 133 K in 2-MeTHF.

Acknowledgements

We wish to thank Professor Dr A. Oskam for his helpful discussions, A. Terpstra for his assistance during the flash-photolysis experiments, and G. C. Schoemaker for his assistance during PVC film experiments. Professor Dr J. W. Verhoeven is thanked for putting at our disposal the laser flash photolysis equipment.

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